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PLENARY

NAGORE ORTIZ-VITORIANO[1,2]

E. García-Gaitán[1], M.F. Palermo[1], U. Urruela[1]

Naturally-derived Biopolymer-based Electrolytes for Electrically Rechargeable Zn-air Batteries

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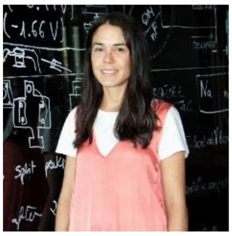
[2]Ikerbasque, Basque Foundation for Science, María Díaz de Haro 3, 48013 Bilbao, Spain

Electrochemical energy storage technologies play a crucial role in reducing dependency on fossil fuels and minimizing greenhouse gas emissions. They enable the storage of renewable energy, facilitate grid integration, and drive the global energy transition. While lithium-ion batteries dominate the market—powering applications from portable devices to electric vehicles and stationary systems—they face challenges such as high raw material costs, limited cycle life, and reliance on critical raw materials. These limitations underscore the need for competitive, cost-effective alternatives, particularly for stationary energy storage. Electrically Rechargeable Zinc-air batteries (ERZABs) emerge as a promising alternative, although their advancement requires industrially scalable breakthroughs.

Currently, primary zinc-air batteries, used in low-power, long-term applications such as hearing aids, railway signalling and electric fences, are the only commercially available metal-air systems. These batteries offer significant environmental benefits, including inherent lack of runaway safety concerns, non-toxicity due to aqueous electrolytes, and reliance on abundant, recyclable zinc instead of costly metals. However, transitioning to larger-scale, electrically rechargeable systems is hindered by challenges including anode durability and issues with liquid electrolytes prone to leakage and evaporation. Naturally derived, biodegradable solid electrolytes hold significant potential in addressing these challenges.

This presentation will provide a comprehensive overview of biopolymer-based electrolytes for Zn-air batteries, focusing on the development of novel solid electrolytes derived from a natural, and biodegradable polymer such as agarose. In this study, their manufacture and characterization will be discussed, as well as their electrochemical performance. The proposed electrolyte demonstrates a conductivity that is comparable to the widely used 8M KOH liquid electrolyte (6.1×10^{-1} $S\cdot cm^{-1}$). However, challenges remain in the dimensional stability and electrolyte retention of the membrane during electrochemical testing.

BIOGRAPHY



Nagore Ortiz-Vitoriano is a Senior Researcher and Ikerbasque Research Associate Professor, currently leading the Transport and Interfaces team at CIC energiGUNE (Spain). She earned her PhD in 2011 from the University of the Basque Country (UPV/EHU) for her work on solid oxide fuel cells, receiving the Doctoral Special Prize for her work. Dr. Ortiz-Vitoriano has held prestigious fellowships, including a Marie Curie International Outgoing Fellowship at MIT (USA), Ikerbasque and Ramón y Cajal Fellowships. Her research focuses on metal-air batteries, biopolymer-based electrolytes, and sustainable energy storage materials, combining fundamental studies and practical applications. She has authored over 60 publications, delivered 25 invited talks, and raised over €3M in public and private funding in recent years, leading to significant research outputs, including a patent application for a Zn-air battery electrolyte.

PLENARY

MARIA-EUGENIA SANIN

Driving the Green Shift: Carbon Taxes, Subsidies, and the Road to Inclusive, Sustainable Private Transport

Université d´Evry Val d´Essonne, Université Paris-Saclay, France

This keynote addresses the intersection of transport decarbonization and social equity, focusing on car-fuel poverty and electric vehicle (EV) accessibility. We first introduce the concept of car-fuel poverty, bridging energy and transport poverty research by adapting and extending fuel poverty metrics to car-fuel expenditures. Using novel indicators—including the Low-Income High Transport Costs (LIHTC) and measures capturing both overburdened and under-consuming households—we quantify car-fuel poverty in France and identify key socio-economic risk factors. The findings highlight the limitations of untargeted fossil-fuel subsidies and propose alternative compensation mechanisms that enhance efficiency while protecting vulnerable households.

Building on this, we assess the role of policies and market mechanisms in accelerating EV adoption among low- and middle-income households. Analyzing the French car market between 2016 and 2019, we evaluate the welfare and distributive impacts of interventions implemented between 2019 and 2024. The results reveal that taxing new polluting vehicles is crucial for fleet decarbonization but also emphasize the importance of targeting used EVs to enhance affordability. Contrary to conventional approaches, income-based subsidies often fail to reach the poorest households, while interventions that reduce the value of polluting vehicles in the fleet prove more effective.

Finally, we extend these empirical insights with a theoretical framework that reconsiders the role of subsidies in transport decarbonization. By incorporating both vintage- and fuel-type differentiation, we show that subsidies cannot replicate Pigouvian taxes on their own and demonstrate the need for a dual-subsidy policy targeting both new and used EVs. Empirical estimates confirm that a sole subsidy for new EVs distorts the market, hindering used EV adoption and limiting overall fleet electrification. In contrast, complementing new EV subsidies with substantial support for used EVs increases welfare gains by 75%, underscoring the critical role of the second-hand market in the energy transition.

Together, these findings highlight the need for a holistic, evidence-based approach to transport decarbonization—one that balances economic efficiency with social equity, ensuring that the transition to cleaner mobility is both inclusive and effective.

BIOGRAPHY

Maria-Eugenia Sanin is an Associate Professor in Economics at Paris-Saclay University at Université Val d’Essonne. She is an applied economist interested in public policy evaluation and design. In 2010 she was a post-doctoral researcher at the Ecole Polytechnique and obtained her PhD in Economics at CORE, Université Catholique de Louvain, in November 2009. Maria-Eugenia also worked at the World Bank (2008-2009) on issues relating to energy security in Latin America. Her most recent research projects focus on environmental and energy economics, green finance, development & climate justice and industrial organization.

PLENARY

NICOLAS PINNA

Novel Materials Chemistry for Energy and Environmental Applications

Department of Chemistry, Humboldt University of Berlin, Brook-Taylor-Str. 2, 12489 Berlin, Germany

The current trend in various energy applications, ranging from batteries to electrolizers, lays in the control of structural, physicochemical and morphological properties of materials and their interfaces. During this presentation, recent scalable strategies for nanostructured materials synthesis, targeting energy and environmental applications will be discussed. Especially, we will focus on one-pot strategies for the fabrication of hybrid and complex nanomaterials focusing on the importance of the organic-inorganic and inorganic-inorganic interfaces. Among the examples presented, we will discuss the synthesis of complex nanostructures and the stabilization of metastable phases for applications in energy storage and conversion. We will see that nowadays the available strategies allow a control in terms of composition, crystalline structure, morphology and nanostructuration that would have been unimaginable just few years ago. Finally, the open challenges the field is currently facing and possible further developments which are needed to meet the always growing demand for high performing materials will be also discussed.

BIOGRAPHY

Nicola Pinna received his Ph.D. in physical chemistry from the Université Pierre et Marie Curie (Paris) in 2001. He has since worked at the Fritz Haber Institute of the Max Planck Society (Berlin), the Max Planck Institute of Colloids and Interfaces (Potsdam), the Martin Luther University of Halle-Wittenberg, the University of Aveiro (Portugal), and the Seoul National University (Korea). In July 2012 he joined the Department of Chemistry of the Humboldt University of Berlin as professor of inorganic chemistry. From July 2016 to April 2021, he was also head of the Department. His research activity focuses on the development of novel materials chemistry routes to nanostructured materials for energy and environmental applications.

PLENARY

PIERRE MILLET[1,2]

Polymer Electrolyte water electrolysis : from functional materials to industrial developments

[1] Elogen Co., 8 avenue du Parana, 91940 Les Ulis, France
[2] Paris-Saclay University, ICMMO, 17 avenue des Sciences, H. Moissan, 91400 Orsay, France

The concept of Polymer Electrolyte Membrane (PEM) water electrolysis was developed in the 1970s once proton-conducting ionomers became commercially available1. The purpose of this talk is to described the main features of the technology and to present examples of recent industrial achievements. Figure 1 shows a cross-section of the unit cell which is delimited on each side by two metallic bipolar plates (5-5'). The polymer membrane (1) placed at the center is coated by two catalyst layers (2-2') where half-cell reactions take place during electrolysis. Flow disruptors (4-4') and porous transport layers (3-3') are used to adjust mass transport and collect hydrogen and oxygen.

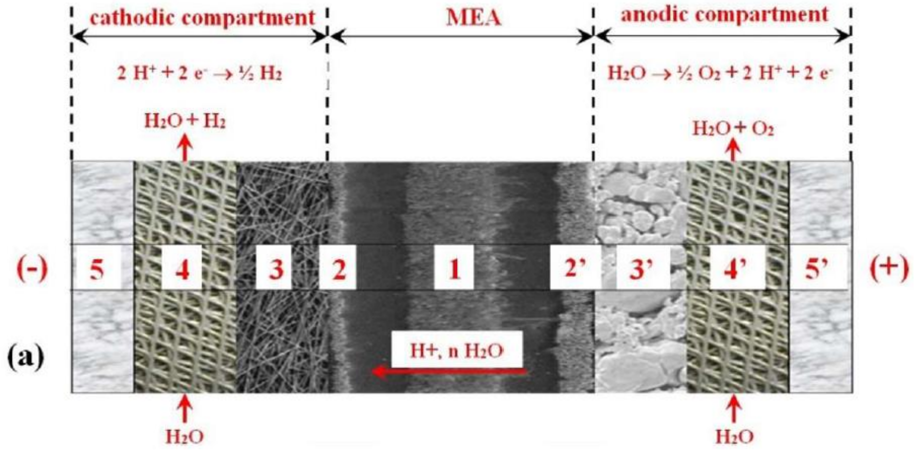


Figure 1 : cross section of the unit PEM water electrolysis cell showing the different functional layers.

Figure 2 shows a photograph of a 1.2 MW containerized PEM water electrolyzer suitable for on-demand production of pressurized hydrogen. This technology is energy efficient and very compact. It can be directly powered by renewable energy sources and operated with transient input power. Examples will be presented.

Figure 2 : 1.2 MW conteneurized PEM water electrolyzer (courtesy: Elogen Co.).

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[1] D. Bessarabov, P. Millet, in « PEM water Electrolysis" (Vol.1 et Vol.2), "Hydrogen and Fuel Cells Primers", B.G. Pollet Editor, 1st Edition, Elsevier Ltd. (2018).

BIOGRAPHY

Pierre Millet is an electrochemical engineer, University Professor in materials science and physical-chemistry. He graduated in 1986 from the French "Ecole Nationale Supérieure d'Electrochimie et d'Electrométallurgie de Grenoble" (ENSEEG) at the "Institut National Polytechnique de Grenoble" (INPG). He completed his PhD thesis on PEM water electrolysis in 1989, at the French "Centre d'Etudes Nucléaires de Grenoble" (CEA-CENG). He then worked at Electricité de France on alkaline water electrolysis and then spent most of his career as Professor of physical-chemistry at the French University of Paris-Saclay where he directed the "Laboratory of Research and Innovation in Electrochemistry for Energy applications", at the "Institute of Molecular Chemistry and Material Science" (https://www.icmmo.universite-paris-saclay.fr/en/teams/eriee/). His research activities focus on the development of innovative materials, nanostructures and electrochemical reactors, mainly for water electrolysis, water photo-dissociation, carbon dioxide electro- and photoreduction. He is also active in the field of hydrogen storage using hydride-forming materials, hydrogen compression and hydrogen permeation across metallic membranes. He has developed several industrial collaborations and is working as Scientific Director at Elogen, the French manufacturer of PEM water electrolyzers (https://elogenh2.com/en/).

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PLENARY

CHRISTEL LABERTY-ROBERT

Composite Electrolyte for All Solid State Batteries

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Solid-state batteries are attracting significant interest in the electric vehicle industry due to their high energy density and safety levels, making them a promising solution for the future. However, despite the attention and ongoing research, their full potential still needs to be confirmed to determine if they truly represent a technological revolution.

The main technological challenges hindering the development of solid-state batteries are centered around managing interfaces and ensuring their stability during both assembly and operation. Variations in the composition of cathode particles, for example, cause mechanical issues at the contact points between electrode particles (which expand or contract) and the solid electrolyte. On the anode side, the deposition of metallic lithium creates significant stress at the interface with the solid electrolyte, leading to deposition not only at the electrode-electrolyte interface but also within the solid electrolyte itself, including its pores and grain boundaries. This confined lithium deposition generates regions of extremely high "hydrostatic" stress, which can lead to fractures in the electrolyte, ultimately compromising the battery's performance and lifespan.

The integration of composite materials in solid-state batteries offers a promising solution to address the key challenges of managing solid/solid interfaces during cycling. However, implementing these composites presents significant challenges, as they often involve complex, multi-step manufacturing processes that are not well-suited for large-scale production and carry a notable environmental impact. Additionally, variations in the composition of cathode particles cause mechanical issues at the interface with the solid electrolyte, while metallic lithium deposition at the anode generates high stress at the electrode-electrolyte interface. This results in deposition within the electrolyte itself, including its pores and grain boundaries, creating regions of intense "hydrostatic" stress that can lead to fractures in the electrolyte. These factors severely compromise the performance, stability, and lifespan of the batteries, making it crucial to develop more efficient manufacturing methods and better materials to overcome these limitations.

References

R. Chometon, M. Deschamps, R. Dugas, E. Quemin, B. Hennequart; M. Deschamps, J.M.T. Tarascon, **C. Laberty-Robert**, *ACS Appl. Mater. Interfaces*,15, 58794-58805, 2023

A Naboulsi, R Chometon, F Ribot, G Nguyen, O Fichet, **C Laberty-Robert**, *ACS Appl. Mater. Interfaces*, 16, 13869–13881, 2024.

A. Naboulsi, S. Franger, G. Nguyen, O. Fichet, **C. Laberty-Robert**, *J. Electrochem. Soc*. 171 020523, 2024.

J. Richard, N. Solati, A. Singh, V. Meunier, Y. Toda, A. Grimaud, A. Perez, **C. Laberty-Robert**, *ACS Applied Energy and Materials*, 7, 4335–4346, 2024.

BIOGRAPHY

Christel Laberty-Robert is a professor at Sorbonne University and a specialist in composite materials for energy devices. She focuses particularly on all-solid-state batteries and is interested in the connection between electrochemistry, chemistry, and mechanical properties. France 2030, the ANR, and bilateral contracts fund her research. She has also supervised several PhD and postdoctoral students. Additionally, she was involved for about 10 years in coordinating the Materials specialty at Polytech Sorbonne. She is the recipient of the 2024 Joannides Prize from the Academy of Sciences, and since January 2025, she has been appointed as scientific director of the RS2E network.

PLENARY

ALDO DI CARLO

See-through Photovoltaics

CNR-ISM Istituto di Struttura della Materia del CNR, Rome (Italy)
CHOSE-University of Rome Tor Vergata, Rome(Italy)

See-through photovoltaics (STPV) based on metal halide perovskites represent a transformative technology in the field of renewable energy, offering unprecedented opportunities for applications such as building-integrated photovoltaics (BIPV) and agrivoltaics. Metal halide perovskites are distinguished by their tunable bandgaps, cost-effectiveness, and superior optoelectronic properties, making them ideal for transparent photovoltaic applications. Their ability to precisely adjust bandgaps across a wide spectral range enables the development of semi-transparent solar cells and modules that maintain high power conversion efficiency (PCE) while providing significant visible light transmission. This is particularly relevant for BIPV, where photovoltaic windows can generate electricity from near-infrared (NIR) and/or near-ultraviolet (NUV) light while preserving aesthetic appeal. The integration of see-through perovskite photovoltaics in urban environments addresses the challenge of limited rooftop space by utilizing windows and facades as active solar surfaces. Additionally, in agrivoltaic applications, semi-transparent perovskite modules can optimize light distribution to crops while simultaneously harvesting solar energy, thereby enhancing land use efficiency.

To further enhance the performance of see-through perovskite solar cells, advanced tandem configurations have been explored. These configurations combine perovskite top cells with NIR organic bottom cells, leveraging bandgap optimization to boost efficiency without compromising average visual transmittance (AVT). Light management techniques, including the integration of photonic crystals and engineered materials, have demonstrated the potential to achieve up to 15% PCE with 50% AVT, significantly improving the light utilization efficiency (LUE) of the system.

Within the EU CITYSOLAR consortium we actively addressing the challenges related to material optimization, light management, and innovative characterization approaches to surpass the current state of the art in STPV. Recent advancements include large area PSC with LUE > 5.7 [1], the development of scalable fabrication techniques, such as low-temperature blade-coating methods for producing semi-transparent FAPbBr3-based perovskite modules on large substrates (300 cm²). Moreover, novel coupling approaches between top perovskite modules and bottom organic modules have been demonstrated, showcasing the potential of see-through perovskite photovoltaics to redefine energy harvesting in both urban and agricultural contexts.

This presentation highlights the latest progress made within the consortium, offering insights into fabrication processes ranging from solution methods to physical deposition techniques, with the goal of maximizing both energy efficiency and aesthetic integration in modern architectural and agricultural settings.

[1] D. Di Girolamo et al. Adv. En. Mat 14, 2400663 (2024)

BIOGRAPHY

Aldo Di Carlo is a Full Professor at the Department of Electronic Engineering of the University of Rome Tor Vergata (Italy). Since September 2019, he has held the position of Director of the Structure of Matter Institute of the National Research Council of Italy (CNR-ISM), and since 1st January 2021, he has also been the president of the CNR Research Area of Rome – RM2, which includes over 10 research institutes. From 2007 to 2019, Di Carlo served as Director of the

Organic Solar Pole of the Lazio Region, where he supervised the research and development of organic and hybrid organic/inorganic solar cells. Additionally, he served as Chairman of the Scientific Council of the Dyepower consortium for the development of Dye Solar Cells (DSC) from 2009 to 2015. Di Carlo's research interests encompass the study, design, and optimization of electronic and optoelectronic devices. In recent years, his research has focused on the development and scaling-up of emerging photovoltaic cells, with particular emphasis on Dye Solar Cells (DSC) and Perovskite Solar Cells, for industrial applications. He has authored/co-authored over 600 international scientific publications and holds 13 international patents. Furthermore, he has acted as a general coordinator/partner coordinator for more than 25 large European Projects.

KEYNOTES

SYLVIE MATELLY

Boosting European Innovation: A Complex Challenge?

Institut Jacques Delors, Paris, France

The European Union was the first region in the world to commit to carbon neutrality, with the ambition of also becoming the most innovative in this field. A few years later, however—and in what seems like a recurring story—it appears to be significantly outpaced by China and even the United States, while the decline of the European economy has been accelerating since COVID. In his recent report, Mario Draghi estimated that at least €800 billion would need to be invested over the next decade to catch up, stop the decline, and ensure both the green and digital transitions. Why does such a prosperous continent struggle so much to become a leader in innovation? This is the question I will seek to answer.

BIOGRAPHY

Sylvie Matelly has been Director of the Institut Jacques Delors since 2023. She was previously deputy director of the Institut de Relations Internationales et Stratégiques (IRIS) between 2016 and 2023. She joined IRIS in 2001 as a researcher in international and defence economics, and is an expert in geopolitics and economics, particularly defence industries and policies, export controls and corruption. Between 2009 and 2016, she was a professor at the Ecole de Management Léonard de Vinci (Paris-La Défense), where she headed the Department of Economics, Finance, Law and International Relations. Sylvie has a doctorate in international economics. She wrote a thesis on the economic determinants of military spending, which she defended at the Université Pierre Mendès France in Grenoble in September 2000.

KEYNOTES

WOJCIECH MACYK

Taymaz Tabari, Marcin Kobielusz

Profiting from merging photocatalysis with catalysis

Faculty of Chemistry, Jagiellonian University, Gronostajowa 2, 30-387 Kraków, Poland

There is a fundamental difference between the photocatalytic oxidation of pollutants and the photocatalytic production of solar fuels. Similarly to combustion, the oxidation of pollutants is an exergonic process, while water splitting or carbon dioxide reduction are endergonic reactions. In energy downhill processes absorbed light is utilized to overcome the activation energy of elemental steps, e.g., activation of oxygen or C-H bond. The role of photons is, therefore, to "ignite" the energy downhill reaction. Production of hydrogen from water or methanol from CO_2 is, however, a highly endergonic reaction. Photocatalytic production of solar fuels is a process of solar quantum energy conversion to the energy of chemical bonds. In such processes, photons can be considered as reagents. This differentiation is crucial to understanding the theoretical limit of quantum efficiencies available in these types of processes. In the energy uphill reactions, the energy gain (the energy of chemical bonds) originates from the energy of photons. One absorbed photon can generate one e^-/h^+ pair which can be used in single elemental reduction/oxidation reactions. Therefore, the limit of the overall quantum efficiency, defined as the number of e^-/h^+ redox steps divided by the number of absorbed photons, amounts to 1. In the energy downhill reaction, the energy evolved in the process can be dissipated as heat (and lost) or can be used to accelerate the next elemental, catalytic steps. Taking this into account one can expect the overall quantum efficiency might exceed the unity. To facilitate it appropriate catalytic and redox conditions should be provided. The possibility of such reactions, including the design of appropriate catalytic/photocatalytic materials, will be illustrated and discussed.

Acknowledgements: This work was supported by the National Science Centre (Poland) within the Opus program (grant number 2022/45/B/ST5/04087).

BIOGRAPHY

Wojciech Macyk – graduated from the Jagiellonian University in Kraków (Poland), completed his PhD degree at the University of Erlangen-Nürnberg (Germany). He was the head of the Department of Inorganic Chemistry at JU (2013-2021), vice-dean (2016-2020) and the dean (2020-2024) of the Faculty of Chemistry at JU. Since 2024, he has been the vice-rector for research. In 2014 and 2015, he was a visiting professor at the Catalysis Research Center, Hokkaido University, Sapporo, and at the School of Computing, Engineering and Mathematics, Western Sydney University. His research interests include mechanisms of photocatalytic processes, photocatalytic detoxification and disinfection, photocatalytic carbon dioxide fixation, photo(electro)catalytic water splitting, organic synthesis, photoelectrochemistry and spectroelectrochemistry of semiconductors. He is the author of >160 papers and book chapters (cited ca. 11 200 times, h = 45), several patents and patent applications. W. Macyk is a co-founder of InPhoCat – Innovative Photocatalytic Solutions Sp. z o.o. More info: www.photocatalysis.eu

KEYNOTES

PIERRE HENNEAUX

Multi-energy networks: ensuring the security of supply

Université Libre de Bruxelles, Belgique

Coupling energy systems can help to tackle the energy trilemma. Indeed, by providing flexibility, they can help to integrate renewable energy sources at the lowest cost while keeping the security of supply at the desired level. Nevertheless, the ongoing energy transition leads to new challenges to ensure the security of supply. The massive integration of renewable energy sources increases the variability and the unpredictability on the supply side. The trend is the same on the demand side, with the electrification of several uses, among which in the transportation sector (electric vehicles). This presentation will thus explore the use of advanced probabilistic approaches to assess and to ensure optimally the security of supply of multi-energy networks, with a focus on electric power systems.

BIOGRAPHY

Pierre Henneaux holds a MSc degree in Engineering Physics (2009) and a PhD in Applied Sciences (2013), both from the Université libre de Bruxelles (ULB, Belgium). Since 2018, he is an associate professor (chargé de cours) with ULB in the field of electric energy systems. Before that, we worked a few years as Energy System Planning & Economics Expert with Tractebel (Engie group). His research activities deal mainly with power system reliability, probabilistic methods applied to power systems, electricity markets and the optimization of energy systems under uncertainty.

INNOVATION SESSION

PRAKASH C. GHOSH

Green Hydrogen: Paving the Way for Clean Cooking in Rural Areas

ZestClean Power Private Limited

director@zestcleanpower.com

The increasing reliance on traditional cooking methods, such as open fires and inefficient stoves, especially in developing regions like India, presents both significant environmental and health challenges. These practices, often fueled by kerosene, biomass, and coal, lead to substantial household air pollution. This not only endangers the health of millions, particularly women and children, but also contributes to deforestation and escalates carbon emissions, worsening climate change.

A promising solution to these pressing issues is the use of solar photovoltaic based green hydrogen. This renewable energy-derived hydrogen offers a clean, sustainable alternative to conventional cooking fuels. Green hydrogen derived from solar photovoltaic being a modular and scalable technology, making it an ideal option for off-grid or remote communities.

Zest Clean Power Pvt. Ltd., in collaboration with IIT Bombay, has made remarkable progress in this area and have successfully demonstrated an indigenous, clean cooking system powered by green hydrogen. The system comprises an electrolyzer that generates hydrogen and a hydrogen burner designed specifically for cooking with pure hydrogen. This innovative system offers several advantages: it reduces indoor air pollution, addresses health risks associated with traditional cooking fuels, and decreases the overall carbon footprint.

BIOGRAPHY

Dr.-Ing Prakash C. Ghosh is a Professor at IIT Bombay and the Founding Director of Zest Clean Power Pvt. Ltd., specializing in fuel cells, green hydrogen, and energy storage. Holding a PhD from RWTH Aachen, Germany, he has held prestigious research positions in Germany and India. Dr. Ghosh has authored 100+ journal papers, holds multiple international patents, and has secured 5 million euro in research funding. His contributions to national and international energy projects include electrifying an army base at 17,000 ft. Currently, he is actively working on providing clean cooking solutions to underserved communities, aiming to improve the health of women and children in last-mile regions.

INNOVATION SESSION

DANIEL LINCOT, DAMIEN GAMET, JEAN MICHEL LOURTIOZ*

Light weigth high efficiency flexible CIGS modules for building integrated photovoltaic removable systems

Soleil-sur-Yvette Photovoltaïque, Plate-forme SOLCIS-CNRS-UPS, Université Paris Saclay

Daniel.lincot@soypv.fr, Jean-michel.lourtioz@soypv.fr, Damien.gamet@soypv.fr

SOY PV* aims to fabricate ultra-light, high-efficiency (> 15%) solar cells deposited on flexible substrates, metal foil or polymer, while simultaneously exploring new applications. The technology used is CIGS (alloy of copper, indium, gallium, selenium or sulfur) and unlike its competitors, the company develops electrolytic processes at atmospheric pressure to deposit thin layers on flexible substrates.

The demonstration that SOY PV has just proposed the fall of 2024 in the frame of the Metropolitan Innovation Districts of Paris Metropole, in the city of Aulnay-sous-Bois, illustrates the full benefits of light, flexible photovoltaic solar panels in an urban environment. This is a removable photovoltaic system, integrated into a net, on the facade of a building (Fig.1). The system can be easily moved from one place to another, from one building to another, and in a given place, it is characterized by the possibility of being unfolded and folded at will, allowing simplified installation and maintenance. The unfolded system can be seen as a real photovoltaic veil or as a giant blind, because the deployed surface could reach several tens of square meters without any particular limitation, due to the reduced weight of the panels. The veil installed in Aulnay-sous-Bois had a surface area of 12 m², and the installed power was 1.25 kW. It uses commercial CIGS modules already available on the market. To our knowledge, the demonstration carried out is a first in itself. It opens the prospect of covering very large building surfaces, temporarily or permanently, today on the facade and tomorrow on the roof as well.

We can also imagine the application of vertical removable photovoltaic systems to evolving spaces, construction sites, parks, sites set up for temporary events, and even in agricultural environments. These prospects will be enhanced in the near future by the use of so-called tandem cells, with two thin photovoltaic layers (CIGS-perovskite), whose conversion efficiencies in the laboratory already reach 25%. SOY PV is also now committed to the race for these very high conversion efficiencies in collaboration with CNRS-IPVF, CNRS in Nantes and Solar Cloth in the frame of a France 2030 project.

Fig.1 : On the left, photovoltaic veil made by SOYPV in the CNRS-UPS platform at the Universtity Paris Saclay; on the right, deployment of the veil on the facade of a building in Aulnay-sous-Bois

BIOGRAPHY

Daniel LINCOT graduated from École Supérieure de Physique et de Chimie Industrielles. From 1980 to 2021, he has been a scientist at the Centre National de la Recherche Scientifique (CNRS). Since 2022, he is emeritus research director at CNRS at Institut Photovoltaïque d'Île-de-France (IPVF). In 2021, he funded the start-up Soleil-sur-Yvette Photovoltaïque (SOY PV) with Jean-Michel Lourtioz. Daniel Lincot is recognized as a specialist in the fields of photovoltaic solar energy and electrochemistry. In 2021-2022, he held the chair for industrial innovation at the Collège de France on the topic of « Photovoltaic solar energy and energy transition ». In 2024, he received the Vittorio de Nora Prize from The Electrochemical Society, the Alexandre Edmond Becquerel Award for photovolaics and joined the Academie of technologies.

Jean-Michel LOURTIOZ graduated from École Centrale de Paris. From 1976 to 2016, he has been a scientist at the Centre National de la Recherche Scientifique (CNRS). Since 2016, he is emeritus research director at CNRS and is working with the Center for Nanoscience and Nanotechnology (C2N). He is also honorary Vice President of Paris-Sud (Paris-Saclay) University. In 2021, he co-funded the startup SOYPV with Daniel Lincot. Jean-Michel Lourtioz is recognized as a specialist in Photonics and Optoelectronics. He directed the "Fast circuits and quantum optoelectronics" group at the Institute for Fundamental Electronics (IEF) from 1990 to 2000. He led the French CNRS research group on Microcavities and Photonic Crystals from 1996 to 2000. He was the head of IEF from 2000 to 2010. He co-initiated the C2N Lab which was created in 2016. From 2017 to 2023, he has succcessively coordinated the French MOOC “understanding nanosciences” and the SPOC “challenges of the green transition”.

Damien GAMET graduated from Institut National Polytechnique de Grenoble in 2000. From 2000 to 2003, he has worked on thin layer deposition for MEMS (Micro Electro-Mechanical Systems) at CEA-LETI, and received the PhD degree in material sciences from the University of Grenoble in 2003. From 2003 to 2020, he worked in different hi-tech R&D companies or institutions, respectively Polymage (from 2004 to 2007), CEA LETI in Grenoble (from 2007 to 2009), Stantum (from 2010 to 2012), Hologram Industries (from 2013 to 2018) and Toppan Photomasks (from 2019 to 2020). He joined SOYPV and the SOLCIS platform in 2022 as a research engineer in the field of electrochemical deposition.

INNOVATION SESSION

ISSAM BAGHDADI, ABOUZEDE MONDOHA*

Smarter Batteries, Faster

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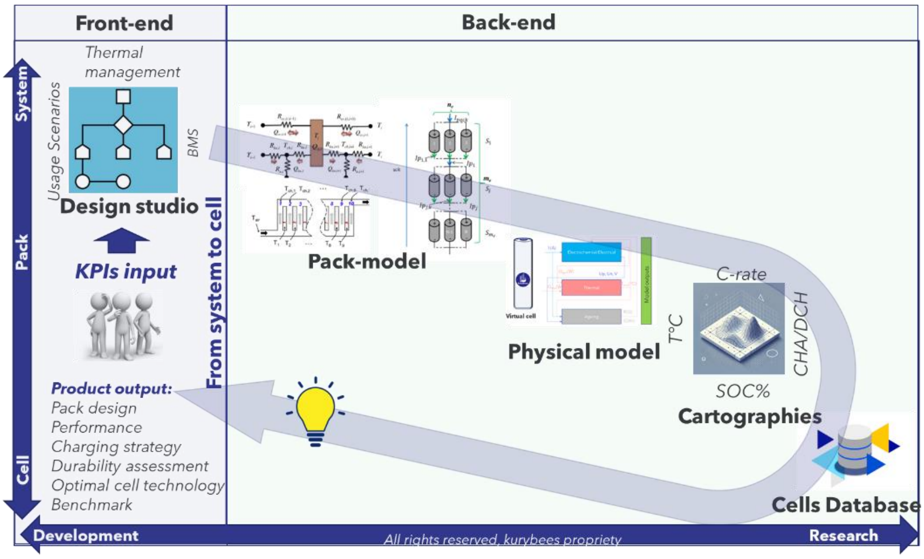
Kurybees accelerates battery innovation by helping companies select the optimal cell technology 4× faster using advanced testing data and intelligent digital modeling tools. Founded by battery experts with deep R&D and industrial experience, Kurybees combines a high-tech lab with a powerful software suite to deliver reliable battery pack designs, performance simulations, and life predictions. Trusted by clients across mobility, energy storage, and electronics, Kurybees is reshaping battery development with precision, speed, and insight — from cell to system.



BIOGRAPHY

Issam Baghdadi, PhD – CEO & Co-founder. Battery expert with 10+ years of R&D and OEM experience. Former battery innovation lead at Stellantis, he holds 7 patents and a PhD in battery modeling. Issam founded Kurybees to make advanced battery design faster and more accessible.

Abouzede Mondoha, PhD – CTO & Co-founder. Specialist in battery modeling and testing with a PhD in battery energy management. Abouzede leads Kurybees' simulation tools and lab operations, bringing deep technical expertise to every project.

The hydrogen perfume

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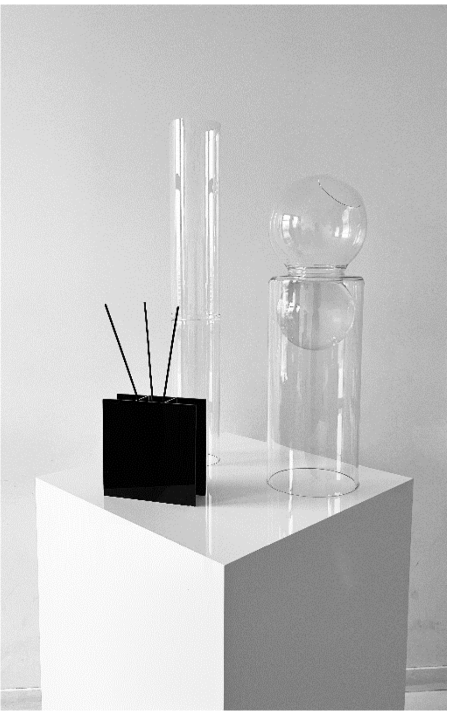

Water electrolysis is considered as the most promising green technology for the production of Hydrogen, a very energetic molecule considered as the fuel of the future. During this process, water reacts in the membrane-electrode assembly (MEA), the heart of the electrolysis device, and is transformed into dioxygen and into the dihydrogen molecule. Inspired by the power of processes, the nature and origin of materials used, and the potential impact of such a method, Jennifer Peron, Professor at Université Paris Cité working on hydrogen production by electrolysis partnered with Clémence Besse, Perfumer, to design an installation that transforms the process of hydrogen production through water electrolysis into an olfactory poetry experience. This is conveyed through three fragrances: one for water, one for the MEA, and one for the Hydrogen.

The objective of this project is to introduce the general public to a clean and powerful energy carrier, Hydrogen, and its production technology through electrolysis but also to engage and raise awareness among scientists about an innovative and sensory-based form of science communication. Finally, by interacting with the installation, audience will be invited, through an olfactory poetry, to share passion for science, technology, sensoriality and creativity.

ABSTRACTS OF THE ORAL PRESENTATIONS

ORAL #1

Insights on the role of the covalent Ni-O bonds in $LiNiO_2$ positive electrodes: a comprehensive hard X-ray spectroscopy study

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Understanding the local atomic and electronic structures of Ni-rich layered oxide cathode materials is crucial for optimizing their electrochemical properties, particularly for high-energy density applications in electric vehicles. Despite extensive studies, the intricate interplay between the Ni-O bond framework and the charge compensation mechanism in $LiNiO_2$ (LNO) remains unresolved due to its complex electronic and structural behavior. This work integrates complementary spectroscopic techniques to provide deeper insights into these relationships. Using pristine and electrochemically cycled LNO electrodes as a model system, the study examines both average and local structural evolution during lithium ion extraction through ex situ X-ray diffraction (XRD) and extended X-ray absorption fine structure (EXAFS). Additionally, X-ray absorption near-edge structure (XANES) at the Ni K-edge and non-resonant X-ray emission spectroscopy (XES) at the Ni $K\beta$-edge are employed to probe Ni's electronic environment, where the high covalency of Ni-O bonds obscures traditional spectroscopic signatures. Advanced methods such as X-ray Raman scattering (XRS) at the Ni L,-edges and O K-edge provide bulk sensitive insights into the charge compensation process, revealing oxygen's critical role due to the covalent nature of Ni-O interactions.

This comprehensive spectroscopic analysis underscores the importance of correlative workflows to unravel the complex structural-electrochemical interplay in Ni-rich cathode materials. By advancing our understanding of Ni-O covalency and oxygen's role in charge compensation, this work provides valuable insights into the electronic and structural dynamics of LNO, with broader implications for improving Ni-rich positive electrode materials.

On the path to developing MOF-based materials for sustainable (energy-related) processes

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Metal–organic frameworks (MOFs), also known as crystalline porous coordination polymers, have been proven to be excellent contenders for bridging the gap between zeolites and mesoporous silica. MOFs are formed by metal ions/clusters and organic linkers and have captured widespread interest, achieving an explosive development over the past two decades. The crystalline nature, structural diversity, and tuneability, as well as ultrahigh surface area make MOFs find their potential applications in diverse areas, such as gas sorption and separation, chemical sensing, proton conductivity, biomedicine, and catalysis. However, in numerous MOFs the structural stability and performance limits their practical applications, relatively to other porous materials. Consequently, distinct strategies have been used to prepare MOF based materials and overcome these drawbacks. (1,2)

The modification and derivation of MOF materials, and their utilization as platform, template or subtract opens an avenue to the preparation of diversified porous MOF-based materials with unique advantages in comparison to traditional pristine materials. Following our interest in the development and application of functional MOFs towards sustainable energy-related processes an overview of interesting MOF-based materials prepared and investigated in our research group is reported.

Funding

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Acknowledgements

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References

(1) L. Jiao, Y. Wang, H.-L. Jiang and Q. Xu, Adv. Mater. 30 (2018) 1260.
(2) Y.-Z. Chen, R. Zhang, L. Jiao and H.L. Jiang, Coord. Chem. Rev. 362 (2018) 1.

Interface Engineering for Stable Perovskite Solar Cells

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Hybrid organic inorganic metal halide perovskites (MHPs) denote a family of compound semiconductors, which established a novel class of optoelectronics, most prominently known for the perovskite solar cell. While the power conversion efficiency of these photovoltaic devices saw a steep rise in the past decade, tailoring the interfaces between the MHP film and charge transport layer became the major control lever to enhance performance and stability.[1] The goal of my talk is to give general insights into the interface and interlayer design of perovskite solar cells (PSC), and an overview of our analytical approach to derive design guidelines for the cell architecture.

The use of classical interface characterization tools, i.e. photoemission spectroscopy to analyze the chemical and electronic properties of these interfaces, has been challenging due to many possible chemical reactions at the buried interfaces.[2,3] For instance, it has been well documented that the optoelectronic properties of the MHP can be altered by the substrate (or selective contact) underneath.[4] We hence fabricated a functional lateral heterojunction device, which consists of a substrate with two laterally arranged selective contacts, onto which we deposited MHP films. We then used a series of photoemission measurements along with complementary experiments such as X-ray absorption spectroscopy, Kelvin probe force microscopy, and hyperspectral imaging, to measure how substrate selectivity is affecting the optoelectronic properties at the perovskite surface. We find evidence suggesting that the contact selectivity is inducing a carrier concentration gradient in the perovskite layer across the junction connected to the functionality of the lateral device opening an avenue for fundamental materials studies in *operando* approaches but also new device architectures including buried cells terminals.[5,6]

Furthermore, I will present hard X-ray photoelectron spectroscopy (HAXPES) experiments to address the chemistry of MHPs and oxide overlayers grown by atomic layer deposition on top. We find evidence for the formation of new chemical species (PbO, N and halide-containing compounds) and changes in the energy level alignment at the MHP/oxide interface.[7]

Eventually, I will give a general account on precautions that should be considered for the presented measurement methodology along with our experience on data acquisition. This approach also enables the assessment of transient chemistry in MHP films as well as the observation of potentially defect-tolerant properties or self-healing capabilities.[8,9]

REFERENCES

1. J. Christians, P. Schulz et al. *Nature Energy* **2018**, *3*, 68
2. S. Béchu, M. Ralaiarisoa, A. Etcheberry, P. Schulz, *Adv. Energy Mater.* **2020**, 201904007
3. P. Schulz, D. Cahen, A. Kahn, *Chem. Rev.* **2019**, *119*, 3349
4. P. Schulz, L.L. Whittaker-Brooks, B. A. MacLeod, D. C. Olson, Y.-L. Loo, A. Kahn. *Adv. Mater. Interfaces* **2015**, *2*, 1400532
5. S. Dunfield, A. Bojar, et al., *Cell Rep. Phys. Sci.*.**2021**, *2*, 100520
6. D. Regaldo, A. Bojar, et al., *Prog. Photovolt.: Res. Appl.* **2021**, *30*, 994
7. N. Mallik et al., *Nano Energy* **2024,** *126*, 109582
8. M. Ralaiarisoa et al., *Small Methods* **2023,** 2300458
9. V. Milotti et al., *Small Methods* **2023,** 2300222

Status of hydrogen storage in LOHCs

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Among the various methods of storing hydrogen, either for transport, mobility or intermittent use, liquid organic hydrogen carriers is a very promising option. Catalytic hydrogenation and dehydrogenation cycles are the basis of the concept. Several LOHC couples have been studied for more than 40 years but the most popular ones, having reached a mature development are methylcyclohexane/toluene (MCH/TOL), perhydro-N-ethyl-carbazole/N-ethylcarbazole (H12-NEC/NEC), perhydrobenzyltoluene/benzyl-toluene (H12-BT/BT) and perhydrodibenzyltoluene/dibenzyltoluene (H18-DBT/DBT). Recently, new biosourced LOHC pairs have emerged. This contribution provides an update on recent developments at IRCELYON in the use of LOHC.

The main drawbacks to LOHC deployment are 1) the use of noble metal catalysts, 2) the need to carry out the dehydrogenation reaction at high temperature and 3) the use of LOHC coming from the oil industry. In the various LOHC systems we are studying, our research attempts to overcome at least one of these obstacles.

We have explored the transfer hydrogenation of acetone using H18-DBT, to produce isopropanol which can feed a direct isopropanol fuel cell. Compared to the dehydrogenation of H18-DBT, transfer hydrogenation can be carried out at much lower temperature, because the reaction is almost athermal[1]. It still uses a platinum catalyst but our efforts are focused on its replacement.

Concerning H12-BT, new Pt/TiO_2 catalysts have been synthesized and compared with a standard Pt/Al_2O_3 during dehydrogenation at 260 °C. Much less methylfluorene (MF), an undesired by-product, was obtained using Pt/rutile, which was also twice more active than Pt/Al_2O_3 to release hydrogen, allowing platinum saving. In-depth characterizations (acidity measurements, CO-IR spectroscopy) were carried out to propose explanations for the performance benefits obtained.

Now considering biosourced LOHC, some experiments were carried out using 1,2-propanediol (PDO), producing pyruvaldehyde (Pyr.). Even if the hydrogen storage capacity of PDO is rather modest for this system (< 5.3 wt%), many advantages make it relevant: 1) its possible biosourcing, 2) the reference catalyst is copper-based (no PGM), 3) the dehydrogenation can be achieved at a temperature below 200 ◦C thanks to the equilibrium shifting[2]. The tests carried out at 175 °C with a CuO/ZnO/MgO/Al_2O_3 catalyst showed a hydrogen productivity per gram of catalyst similar to that of H12-BT dehydrogenation at 260 °C with 0.5 wt% Pt/Al_2O_3. Considering the price difference between the 2 catalysts and the energy saved when working at lower temperature, further research on vicinal diol systems is essential.

The objectives of the presentation will be to summarize the existing works and to highlight all the challenges that remain, to make hydrogen storage through LOHC a viable and competitive option compared to other hydrogen storage means (compressed, liquefied...).

References

(1) Sievi, G. et al, Energy & Environmental Science, **2019**, 12, 2305-2314
(2) Alagy, J.; Trambouze, P. J. L. Patent, **2020**, WO, 2020141282A1

Proton-Conducting Solid Oxides for Hydrogen Technologies

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Solid oxide cells (SOCs) are a promising technology for the efficient and reversible conversion of the chemical energy of a fuel into electricity (fuel cell mode, SOFC) and vice versa (electrolysis mode, SOEC). In particular, producing green hydrogen using renewable energy through hightemperature electrolysis is emerging as a potential solution to decarbonize the steel industry first and then the energy transportation and storage sectors. The recent substitution of electrolytes transporting oxide anions with proton-conducting solid oxides promoted the development of protonic ceramic cells (PCCs), which can work at lower temperatures (500-600 °C), maintaining the elevated efficiencies typical of SOCs. Additionally, PCC electrolyzers possess the advantage of producing dry H_2. However, researching efficient and innovative proton-conducting materials requires the characterization of countless compositions.

A high-throughput approach was chosen to accelerate the material research and identify the best-performing electrolytes inside the ternary system $BaCe_{0.8-x-y}Sn_xZr_yY_{0.1}Yb_{0.1}O_{3-\delta}$ (BCSZYY). We developed a combinatorial procedure by producing large samples containing hundreds of compositions and measuring their functional properties using accelerated routines (1).

Thin-film combinatorial libraries were produced by pulsed laser deposition (PLD) on top of Si(100) single crystal substrates with 100 mm diameter. The composition gradient is obtained through alternate depositions of $BaCe_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BCYY), $BaSn_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BSYY), and $BaZr_{0.8}Y_{0.1}Yb_{0.1}O_{3-\delta}$ (BZYY) centered on the edges of the substrate. Adding a Pt interlayer between the substrate and the combinatorial thin film allowed the control of the deposition orientation and the introduction of an internal reference for high-temperature measurements.

The thickness of the combinatorial deposition was characterized by XY-resolved spectroscopic.

The deposition centers correspond to the maximum values, i.e., 220 nm for BCYY and BSYY and 200 nm for BZYY. XY-resolved X-ray diffraction (XRD) was performed to study the deposition structure at both room and operating temperatures (up to 1000 °C). A Matlab code was developed to analyze all the XRD patterns and calculate the cell parameters of the combinatorial thin film using a pseudocubic structure. At room temperature, the *a* cell parameters range from 4.176 Å for the BSYY center, to 4.251 Å for BZYY, and up to 4.418 Å for BCYY, in good accordance with the values obtained by Rietveld refinement for reference powders of single materials. A custom-made furnace was specifically developed to perform the high-temperature XRD measurements in dry and wet conditions to measure the effect of proton incorporation on unit cell expansion. This *in situ* characterization was performed at the DiffAbs beamline of the Soleil synchrotron through the simultaneous acquisition of XRD and XRF signals. XRF allowed the evaluation of the BCSZYY elemental distribution at room temperature. For high-temperature XRD measurements, Pt was employed as an internal probe of the surface temperature because of the radial thermal losses of the large hotplate. The BCSZYY sample was measured in dry and wet N_2 to calculate the thermal expansion curves and extract information about hydration thermodynamics for the entire BCSZYY ternary system. A custom-made setup for electrochemical impedance spectroscopy is under development to measure the electrochemical performance.

References

(1) C. Bozal-Ginesta et al., Adv. Mater., 2407372 (2024).

ORAL #6

Study of 2,5 Polybenzimidazole-ZrO_2 Nanocomposite Membrane Towards Cost-effective Alkaline Water Electrolyzer

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Green hydrogen holds significant promise as a sustainable energy solution for the future. However, its widespread adoption is heavily reliant on reducing the capital costs of key components, particularly the electrolyzer. Among the various types of electrolyzers, the alkaline electrolyzer (AWE) stands out due to its relatively lower capital cost, but the high expense of the Zirfon® membrane, commonly used in these systems, remains a substantial challenge. This membrane is based on expensive materials, which hinders the overall cost-effectiveness of the technology.

To address this issue, the present work focuses on developing a low-cost, zirconium oxide (ZrO)based nanocomposite membrane for use in alkaline electrolyzers. ZrO_2 nanomaterials are synthesized using a hydrothermal method, with ZrOCl·8HO and KOH as the precursors. The synthesized ZrO_2 is extensively characterized using techniques such as powder X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission gun scanning electron microscopy (FEG-SEM), and transmission electron microscopy (TEM) to understand its structure and morphology.

The ZrO_2 nanomaterial is then incorporated into a composite membrane prepared from 2,5polybenzimidazole (ABPBI) polymer, which is well-known for its thermal and chemical stability and mechanical properties. The resulting nanocomposite membrane is subjected to a variety of characterizations, including mechanical stability testing, XRD analysis, contact angle measurements, electrochemical impedance spectroscopy (EIS), and FEG-SEM imaging. These tests aim to evaluate the mechanical properties, ionic conductivity, and overall performance of the membrane as a separator in the alkaline water electrolyzer.

The results show that the incorporation of ZrO_2 nanoparticles into the ABPBI polymer matrix leads to significant improvements in mechanical stability, robustness, and comparable ionic conductivity. These enhancements contribute to a membrane that exhibits better performance in the AWE system compared to conventional membranes. The nanocomposite membrane demonstrates greater structural integrity and ionic conductivity, which is essential for efficient electrolysis. As a result, this novel membrane reduces material costs without sacrificing the performance of the alkaline electrolyzer, advancing the potential for green hydrogen production.

This research represents a step forward in making alkaline electrolyzers more economically viable and sustainable by providing an alternative to the costly commercial separators, offering a pathway for more affordable and efficient for green hydrogen production.

Anti-corrosion thin films by Atomic Layer Deposition for low-cost Porous Transport Layers and Bipolar Plates in Proton Exchange Membrane electrolyzers

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Proton Exchange Membrane (PEM) electrolysis is a promising technology for the production of decarbonized hydrogen from water molecules, operating at low temperatures (< 100 °C). This technology offers several advantages, including higher energy efficiency, high gas purity, and the ability to directly couple with renewable energy sources (solar, wind), despite their frequent and unpredictable power fluctuations. However, one of the main limitations in terms of cost and performance lies in the porous transport layers (PTL) and bipolar plates (BPP). These components are often made of titanium due to its excellent corrosion resistance under electrolyzer operating conditions (1,2). Nevertheless, the highly oxidative environment at the anode leads to the formation of a thick, resistive titanium oxide layer, which increases contact resistance between the anodic compartment components and reduces the overall efficiency of electrolysis. Furthermore, these components account for over 60% of the total electrolyzer cost (3,4). Our study proposes an innovative and multidisciplinary approach to replace expensive titanium with more cost-effective 316L stainless steel for BPP and PTL components. These substrates are coated with protective and conductive Sn-based thin films, free of platinum group metals, deposited via Atomic Layer Deposition (ALD) (5,6). Initial results on the optimization of different films deposited on 316L stainless steel and titanium substrates are presented. A comprehensive micro- and nanostructural characterization of the coatings has been performed using techniques such as ellipsometry, X-ray diffraction, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), etc. The anti-corrosion properties of the coatings were evaluated ex-situ through stability and corrosion tests in an acidic medium simulating PEM cell operating conditions. Preliminary in situ results obtained from PEM electrolyzer testing will also be discussed.

References

(1) S. Lædre et al., Int. J. Hydrogen Energy. 42 (2017) : 2713–2723.
(2) S. Stiber et al., Energy Environ. Sci. 15 (2022) : 109.
(3) U. Babic et al., J. Electrochem. Soc. 164 (2017): F387-F399
(4) M.Prestat, Journal of Power Sources. 556 (2023): 232469.
(5) M. Bechelany et al., Chem. Mater. 30 (2018): 7368–7390.
L.Santinacci, Curr. Opin. In. 63 (2023): 101674.

ORAL #8

Designing Eco-Friendly and Durable MOF-based Proton Exchange Membranes for Fuel Cells

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Proton Exchange Membrane Fuel Cells (PEMFCs) are promising clean energy solutions efficiently converting hydrogen into electricity. However, their reliance on Nafion, a perfluoroalkyl substance (PFAS)-based polymer, raises significant environmental and sustainability concerns. PFAS are persistent in the environment, contributing to long-term ecological and health risks, while Nafion's production involves high costs and energy demands. Replacing PFAS-based membranes with eco-friendly alternatives is crucial for the development of greener PEMFC technologies.[1]

To address this issue, we developed sustainable composite materials combining water-stable, high-proton-conductive Metal-Organic Frameworks (MOFs) with bio-sourced, water-soluble polymers such as polyvinyl alcohol, and chitosan. These composite membranes leverage the customizable structures and exceptional proton conductivity of MOFs alongside the biodegradability, renewability, and environmental compatibility of natural polymers.

Using eco-friendly synthesis methods, nano-MOFs[2] were synthesized and incorporated into the polymer matrices resulting in smooth proton exchange membranes. The composites were characterized using X-ray diffraction, thermogravimetric analysis, scanning electron microscopy, and electrochemical impedance spectroscopy. The membranes demonstrated excellent structural stability and enhanced proton conductivity compared to pure polymer membranes. These improvements were attributed to synergistic interactions between MOFs and polymers, optimizing proton transport pathways while maintaining membrane uniformity and integrity.

By eliminating the need for PFAS-based materials, these bio-sourced MOF-polymer membranes offer a viable, sustainable alternative to Nafion, addressing both environmental concerns and performance demands. This work highlights the potential of eco-friendly MMMs to transform PEMFC technology, aligning clean energy generation with sustainable material practices.

Keywords : Proton Exchange Membranes, MOFs, Composites, Fuel Cells

References

(1) Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C. A Review of Polymer Electrolyte Membrane Fuel Cells: Technology, Applications, and Needs on Fundamental Research. *Applied Energy* **2011**, *88* (4), 981–1007. https://doi.org/10.1016/j.apenergy.2010.09.030.

(2) Lim, D.-W.; Kitagawa, H. Rational Strategies for Proton-Conductive Metal–Organic Frameworks. *Chem. Soc. Rev.* **2021**, *50* (11), 6349–6368. https://doi.org/10.1039/D1CS00004G.

Assessment of Ni-Mo-Fe based catalysts for PV-hydrogen production

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Alkaline water electrolysis presents a promising avenue for green hydrogen production, circumventing the reliance on noble metals as catalysts. Combining alkaline electrolyzers with solar photovoltaic can efficiently convert solar energy into clean hydrogen, offering a versatile means of energy storage and contributing to decarbonization efforts. However, the efficiency and durability of these systems depend highly on the optimization of the catalysts. Through meticulous catalyst design, we can maximize the performance of these configurations to advance the integration of photovoltaic systems in H_2 production. Commonly employed catalysts for alkaline electrolyzer include Ni, Mo, Fe, and their alloys. Despite their abundance, these catalysts often exhibit inferior performance compared to their proton exchange membrane counterparts in terms of activity and stability. In this study, we address this limitation by developing stable and efficient NiMoFe-based catalysts using a sputtering deposition technique. The deposition technique is compatible with multiple substrate types. We evaluated the performance of the thin-film catalysts in an original PV-alkaline electrolyzer system operating at 10 mA/cm^2 for both HER and OER. The relationship between the chemical composition of the thin-film catalysts and their catalytic activity and stability has been conducted by combining in-situ Raman spectroscopy, X-ray absorption spectroscopy, and ex-situ XPS analysis. These results highlight the influence of the oxides and hydroxides formed under catalytic conditions on the electrode's activity and stability. Our results underscore the potential of our catalysts in enabling sustainable and efficient hydrogen production through solar-driven electrolysis.

Nitride and oxide-based anticorrosion thin films characterized by conductive Atomic Force Microscopy for their integration in PEM water electrolyzers

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In the context of the transition to green energy sources, hydrogen is proposed as an alternative energy vector due to its high energy density and potential use for zero CO_2 emissions; this is done to ensure the European Union's objective of achieving zero net emissions in 2050 (1). One of the technologies used to produce hydrogen is the so-called Proton Exchange Membrane (PEM) water electrolysis. These electrolyzers consist of a stack composed of Bipolar Plates (BPP), Porous Transport Layer (PTL), and a polymeric membrane coated with anodic and cathodic catalyst layers. 51% of the cost of the stack comes from the BPP made of titanium (2). One solution to make this technology more affordable is using cheaper metals such as stainless steel. However, the operating conditions (applied potential, pH, temperature) on the anodic compartment of the PEM electrolyzer lead to the growth of a thick passivating and insulating oxide layer, whether titanium or steel, is used. Other corrosion phenomena are observed also observed (3). To maintain the performance of the PEM cell and avoid damage to these components, anti-corrosion thin films can be deposited as protective coatings. The conditions for high-performance thin films includes high surface coverage, with good adhesion and low resistivity in the order of a few (4). In this study, conductive nitride and oxide layers have been prepared by physical vapor deposition (PVD) and atomic layer deposition (ALD), optimizing the deposition parameters on various substrates, including Ti and stainless steel. The resulting films have been subsequently characterized by Atomic Force Microscopy (AFM), Quantitative Nanomechanical Microscopy, and conductive atomic force microscopy (C-AFM) to investigate the role of micro and nanostructures in the coating's adhesion and conductivity (5).

References

1. IEA, *The Future of Hydrogen*. 2019: IEA.
2. Babic, U., et al., *Critical Review-Identifying Critical Gaps for Polymer Electrolyte Water Electrolysis Development.* Journal of The Electrochemical Society, 2017. **164**(4): p. F387-F399.
3. Butler, G. and E.G. Stroud, *The influence of movement and temperature on the corrosion of mild steel. II. High purity water.* Journal of Applied Chemistry, 1965. **15**(7): p. 325-338.
4. Abdulagatov, A.I., et al., *Al2O3 and TiO2 atomic layer deposition on copper for water corrosion resistance.* ACS Appl Mater Interfaces, 2011. **3**(12): p. 4593-601.
5. Lanza, M., *Conductive Atomic Force Microscopy*. 2017.

ORAL #11

Advanced Diagnostic Tools for Early Detection of Degradation Mechanisms

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The increasing prevalence of electric vehicles has intensified the demand for efficient and reliable lithium-ion batteries (LIBs), exposing critical challenges in battery performance under demanding conditions. Among these challenges, the formation of lithium plating on graphite anodes at low temperatures represents a significant safety and performance risk, as it accelerates degradation and shortens the lifespan of LIBs (1).

To address these issues, this study investigates the use of Electrochemical Impedance Spectroscopy (EIS) as a diagnostic tool for evaluating the state of health (SoH) of LIBs and identifying safety critical conditions. By integrating advanced analytical techniques, such as Differential Capacity Analysis (dQ/dV) (2) and Distribution of Relaxation Times (DRT) (3), the research enhances the interpretation of impedance data, offering detailed insight into key degradation mechanisms.

The methodology involved an antemortem characterization of the cell's baseline state, followed by controlled aging under low-temperature conditions (-10 °C) designed to promote lithium plating. The aging process was terminated once the cell reached 80% SoH. Diagnostic evaluations were conducted periodically throughout cycling, using dQ/dV to analyze capacity-based changes and DRT to deconvolute impedance data into contributions from charge transfer and diffusive processes. A postmortem analysis was performed to validate these findings and confirm the physical presence of lithium plating on the anode, along with structural damage such as particle cracking in the NMC cathode.

This study demonstrates the efficacy of combining dQ/dV and DRT analyses with postmortem validation to track and understand degradation mechanisms in lithium-ion cells. By enabling the early detection of lithium plating and other critical degradation phenomena, this approach offers valuable insights into battery aging and safety risks. These findings pave the way for the development of enhanced diagnostic tools and monitoring strategies aimed at improving the reliability and safety of LIBs in real-world applications.

KEYWORDS: Antemortem analysis, degradation mechanism, lithium plating, diagnosis tools, dQ/dV, EIS, DRT, Post mortem analysis.

REFERENCES

(1) Brown, D. E., McShane, E. J., Konz, Z. M., Knudsen, K. B., & McCloskey, B. D. (2021). Detecting onset of lithium plating during fast charging of Li-ion batteries using operando electrochemical impedance spectroscopy. *Cell Reports Physical Science*, *2*(10).
(2) Spitthoff, L., Vie, P. J., Wahl, M. S., Wind, J., & Burheim, O. S. (2023). Incremental capacity analysis (dQ/dV) as a tool for analysing the effect of ambient temperature and mechanical clamping on degradation. *Journal of Electroanalytical Chemistry*, *944*, 117627.
(3) Iurilli, P., Brivio, C., & Wood, V. (2022). Detection of Lithium-Ion Cells' Degradation through Deconvolution of Electrochemical Impedance Spectroscopy with Distribution of Relaxation Time. Energy Technology, 10(10), 2200547.

How can we ensure the reliable characterization of electrode materials during their operation using operando XAS? By using Full-Field Hyperspectral Imaging!

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The hyperspectral imaging technique available on the ROCK beamline combines the temporal resolution of a few hundred milliseconds, achievable with Quick-XAS, with the spatial resolution of a CCD camera on the order of a few microns. Since the 1990s, XAS has been utilized as a chemical probe to characterize electrode materials, initially in ex situ experiments to determine the local structure and oxidation state of the involved cation. Subsequently, in situ approaches were developed to mitigate issues arising from the removal of electrodes from electrochemical cells. Approximately twenty years later, operando measurements became feasible, particularly with the advent of 3rd and 4th generation synchrotrons, which provide more intense photon fluxes on beamlines, enabling faster detection modes and improved signal-to-noise ratio. Electrochemical cell designs have also significantly evolved, now offering more reliable cells with electrochemical performance closely resembling that of coin cells. However, scientific literature increasingly reports concern about the effects of X-rays on battery materials during their characterization on beamlines. In this research field Operando Quick-EXAFS Full-field Hyperspectral Imaging appears to be a promising approach especially when coupled with chemometrics analysis. We propose to present recent results obtained on $LiNiO_2$ and $LiFePO_4$ using this technique, highlighting how it enables the acquisition of reliable data consistent with simultaneously measured electrochemistry. Additionally, we will demonstrate how this method can mitigate beam-induced effects as well as issues arising from imperfect electrochemical cells or electrodes.

ORAL #13

Optimizing cell finishing processes: Study of the impact of process parameters on EEI formation using ex situ and operando nuclear microprobe characterizations

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In 2022, domestic transport, primarily from private cars, accounted for 32 % of France’s greenhouse gas emissions(1). Electrifying vehicles is therefore one of the chosen levers to reduce the emissions of the transportation sector in the coming decades. Despite the availability of electric vehicles on the market, improvements in battery lifespan, cost, energy density, and safety are still needed. Optimizing the cell finishing process could be a key point for the improvement of these parameters, impacting significantly both the production cost and performance of the cells.

Cell finishing, the final phase of battery production following electrode manufacturing and assembly, is time-consuming (up to three weeks) and cost intensive due to specific equipment and duration required for the process. This phase includes three main steps called pre-treatment (or wetting), formation, and quality testing (or aging)(2). The role of the pre-treatment step is to ensure an optimum electrolyte wetting in the electrodes prior to formation using parameters like compression, temperature, or current. Following the wetting, a formation protocol – typically one to three cycles at a low C-rate – is performed. This step is crucial for forming protective layers known as EEI (Electrode Electrolyte Interface) at the electrode-electrolyte interface. These layers, made of decomposition products coming from the electrolyte and the electrode, should be stable and homogeneous to protect the electrodes from further degradations, EEI growth and capacity fade during cycling.

Currently, while various formation and wetting protocols exist, knowledge of the underlying mechanisms of cell finishing remains limited and poorly understood. The EEI, being very thin (from 3 to 100 nm) and fragile, poses challenges for observation and characterization(3). Therefore, one needs to use adapted characterization techniques like ion beam analysis (IBA) on a nuclear microprobe. IBA is a family of spectroscopy techniques based on the use of an energetic ion beam enabling the quantification and visualization of many elements including light elements like lithium.

This work focuses on *ex situ* characterizations of graphite and NMC ($LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$) electrodes from pouch cells cycled under a range of compression values at different steps of the cell finishing process. Cell compression is a crucial parameter that enhances electrical contact within the electrodes, thereby improving performance when optimized (4). During the formation step, applying external pressure seems to enhance the cells capacity, however the mechanisms behind the effects of varying pressure values on performance remain poorly understood. IBA characterizations revealed significant heterogeneity in graphite negative electrodes at low compression values, particularly due to the presence of lithium plating areas that emerge from the initial formation cycle. These results highlight the need for further investigation into the effects of compression on battery cells during formation.

References

(1) Hervé Huyghues Despointes et al., ‘Chiffres Clés Des Transports - Edition 2024, March 2024, https://www.statistiques.developpement-durable.gouv.fr/edition-numerique/chiffres-clestransports-2024/pdf/chiffres-cles-des-transports-2024.pdf.
(2) https://doi.org/10.3390/wevj14040096.
(3) https://doi.org/10.1016/j.carbon.2016.04.008.
(4) https://doi.org/10.1016/j.est.2023.109883.

Engineering electrode surface for Lithium Battery application by Atomic Force Microscopy

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The increased demand for electricity and energy has led to the necessary development of efficient storage systems. In this context, battery technology has come into the picture. During the last decades, battery technologies have improved significantly to meet the challenges of practical electric vehicles and circumvent the issue of intermittent and variability of renewable energy sources. Lithium-ion batteries (LIBs) are currently considered the most suitable energy storage device for powering electronic devices owing to their attractive properties, including high energy efficiency, lack of memory effect, long cycle life, high energy density, and high power density. These advantages allow them to be smaller and lighter than conventional rechargeable batteries. During the initial stages of LiB operation, the so-called Solid Electrolyte Interphases (SEI) start to grow at the electrodes' surface. It corresponds to an interfacial layer resulting from the electrochemical reduction of the solvent, salts, and impurities. This SEI layer plays a crucial role in the long-term performance of LIBs. Thus, SEI formation and electrochemical stability over long-term operation should be a primary topic of future investigation in LIB development (1). Atomic Force Microscopy (AFM) is considered one of the most demanding techniques to get maximum information about the various surface properties of the LiB electrodes, such as topography, mechanical, electrical, electrochemical, and surface potential (2). To follow up the different properties, AFM delivers different modes such as Quantitative Nanomechanical Microscopy, Kelvin Probe Force Microscopy (surface potential), Scanning Electrochemical Microscopy (electrochemistry), and TUNA conductivity (electrical properties). By using AFM and its different modes, a depth analysis of the surface properties and interfaces of the electrode is possible. To understand deeply we need to study all the parameters involved in this study. Graphite is one of the most used electrode materials with different studies being done to understand the surfaces (3). This work includes the mechanical and electrical properties at different scan rates to analysis the center and the edges of the graphite surfaces (4). Because the formation of the SEI layer is different at the center and the edge of the sample. The results show that the scan rate plays a definite role in the electrical properties, while in the case of mechanical, it doesn't show up with a huge difference. Once the parametric study is finished, we will continue this designed study with some advanced electrode materials such as $LiNiMnCoO_2$ (NMC).

References

1 School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel, 164 (7) A1703-A1719 (2017).
2 Agrawal, D. H., et al. "A Portable Experimental set-up for AFM to work at cryogenic temperature." National Conference on Recent Trends in Engineering & Technology. 2011.
3 Jeong, S.-K., Inaba, M., Iriyama, Y., Abe, T., & Ogumi, Z. (2003). AFM study of surface film formation on a composite graphite electrode in lithium-ion batteries. Journal of Power Sources, 119, 555-560.
4 Deng, X., Liu, X., Yan, H., Wang, D., & Wan, L. (2013). Morphology and modulus evolution of graphite anode in lithium-ion battery: An in situ AFM investigation. Science China Chemistry, 57(1), 178-183.

ORAL #15

Study of Charge Transport Limitations in Lithium-ion Battery Electrodes

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There is an increasing demand for advanced energy storage systems to reduce carbon emissions and aid the energy transition in the transportation sector. Rechargeable Lithium-ion batteries are currently the most efficient in this regard.(1) However, there are still challenges for improving their energy and power densities, due to limitations in their electronic and ionic conduction mechanisms.(2) In this study, we employed broadband dielectric spectroscopy (BDS), from low to microwave frequencies, to simultaneously characterize the electronic and ionic motions and their corresponding limitations arising in the composite positive electrode.(3)

We used the scale-dependent polarization response of the processes, spanning from 50 to 1010 Hz, to investigate the influences of the chemical composition of the active materials, the ratio of both non-active polymeric binder and conductive additive, the particle size distribution/morphology, and finally the electrode porosity, on the multiscale charge transport mechanisms of the hierarchical composite electrodes. We utilized electric vehicle-grade NMC with varying elemental compositions, including NMC333 ($LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$), NMC532 ($LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$), and NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$), and performed dielectric measurements under different conditions, such as: on dry electrodes, on electrodes wetted with commercial liquid electrolyte, and on full half-cell configuration at different states of charge. The permittivity and conductivity, and their relative evolution, provided meaningful data on the charge transport properties, at the multiple interfaces of the electrodes.(3) The conductivities of NMC811 are one order of magnitude higher than those of NMC532. The presence of liquid electrolyte also leads to a 25% increase in cluster conductivity, which further increased by 20% after the first charge delithiation. These investigations will be correlated with the overall performance of the electrodes and advantageously used to optimize the electrode formulation.

References

(1). J. B. Goodenough, A. Manthiram, A perspective on electrical energy storage. MRS Communications 4, 135–142 (2014).
(2). A. Agrawal, O. Dubrunfaut, L. Assaud, S. Franger, B. Lestriez, J.-C. Badot, Influence of a Liquid Electrolyte on Electronic and Ionic Transfers in a $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ /Poly(vinylidene Fluoride-co-hexafluoropropylene)-Based Composite Material. J. Phys. Chem. C 125, 17629–17646 (2021).
(3). J.-C. Badot, B. Lestriez, O. Dubrunfaut, Interest in broadband dielectric spectroscopy to study the electronic transport in materials for lithium batteries. Materials Science and Engineering: B 213, 190–198 (2016).

Characterization of Electronic Conductivity by Broadband Dielectric Spectroscopy of Positive Electrode Materials of Spinelle-Type Li-ion Batteries

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Despite $LiMn_{2-x}Ni_xO_4$ *(i.e. LMNO)* spinel positive electrodes' high theoretical specific capacity (147 mAh*g^{-1}), high operation voltage (~4.7 V), and absence of Co, a critical raw material, in their composition compared with conventional NMC positive electrodes. They were not commercialized as batteries in the electrical vehicles sector. This is due to a partial understanding of the correlation between their structure and their electrochemical performance. Here in this study, we investigate the electronic conductivity and its mechanism in a crystalline structurally ordered LMNO series with Ni_x content of 0.50, 0.45, 0.40, and 0.35. Combining analysis of DFT calculations, galvanostatic, and broadband dielectric spectroscopy *(i.e. BDS from 10 Hz to 10 GHz)* measurements. From the 10th galvanostatic measurement done on coin cell of two electrode system, we found increase of two populations in the range of 3.8 – 4.4 V vs Li^+/Li when decreasing the Ni content. From lower to higher voltage, the first one is due to the oxidation/reduction of pure Mn3+, and the other is due to oxidation of Mn3.83+. Suggesting the presence of unlocalized electrons clusters, in which electrons hop in the cationic tetrahedral unit of the spinel. The number of electrons increases with increasing the local disorder arising from the substitution of Ni2+ with Mn3+ when deviation from the ideal stoichiometry (Ni = 0.5). Furthermore, the conductivity of the grain increases with the number of unlocalized electrons as evident from the BDS measurements of sintered 3mm pellets. Finally, it is speculated that the clusters form a percolation network within the grain in between Ni content of 0.45 and 0.40.

Platinum Carbonyl Chini Clusters as Catalysts for Photocatalytic H_2 Generation: Theory and Experiment

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The so called "Chini clusters" of a general formula $(Pt_3(CO)_6)_n^{2-}$ (where usually n = 1-10) display attractive properties as precursors of catalysts and nanostructures like nanoparticles and nanowires. They can be used as coatings for photocatalytic TiO_2 particles or fluorescent quantum dots, because they display characteristic UV–visible absorption spectra with two bands in the visible range and a remarkable dependence on the nuclearity number *n*.

In the current contribution, the electronic, photochemical, and charge transport properties of the platinum Chini clusters are studied with the Density Functional theory (PBE and CAMB3LYP/6-31G(d, p) + LANL2DZ) as a function of their nuclearity n.

The geometries of the systems were determined: the Pt-Pt distance within one unit is equal to 2.75 Å while the separation between Pt_3 triangle units is ca. 3.15 Å, in agreement with the XRD data. The theoretical spectra show the intensive absorption bands whose intensity and positions vary depending on the nuclearity *n*. The analysis of the clusters' orbitals allowed to determine the character of the excitations. To understand the charge transport properties of the clusters, we calculated the molecular reorganisation energies accompanying electron and hole transport, indicating that systems under study would exhibit better hole than electron transport rates.

Next, the interaction of the Chini clusters with atomic and molecular hydrogen was studied. Hydrogen binds to Pt atoms forming stable Pt-H bonds of ca. 1.68 Å. The generation of H_2 is thermodynamically favourable in all studied complexes.

Our theoretical predictions are followed by experimental proof of concept, in which synthesized Chini clusters are deposited as cocatalysts on TiO_2 for photocatalytic hydrogen generation from water-methanol mixture. We demonstrate that the smaller clusters (n = 4) are more effective than the larger ones (n = 7-8) and that the composites having lower Pt content perform better.

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Evaluation of the ability of hematite and titanium dioxide heterojunctions to photo(electro)chemically generate H_2

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Hydrogen production is considered a promising solution to meet future energy demands in a sustainable way (1). Among the most studied methods to achieve this goal, photocatalytic production stands out (1). TiO_2 and α-Fe_2O_3 are two of the most widely investigated materials for the development of efficient photocatalysts due to their abundance, chemical stability, low cost, and non-toxicity (2, 3). However, TiO_2, has a band gap of 3.2 eV and is only sensitive to ultraviolet radiation, which limits its application in sunlight (2). On the other hand, α-Fe_2O_3, which has a band gap energy of 2.2 eV, absorbs visible light but has a conduction band potential unsuitable for efficient hydrogen production under open circuit conditions (3). In addition, both oxides have high photogenerated electron and hole recombination rates, which impairs their performance (2, 3). In this work, the formation of heterojunctions between TiO_2 and α- Fe_2O_3 was proposed as a strategy to overcome these limitations. The approach is not new but has been limited by the formation of an unsuitable oxide at the heterojunction's interface. Here, we used a microwave-assisted route to produce the heterojunction, which offers the advantage of the generation of hot spots at the surface of the oxides nanoparticles, leading to the production of different intermediates oxides at the interface of the heterojunction, when compared to conventional methods. Structural and morphological characterizations confirmed the crystalline phases of TiO_2 anatase and α-Fe_2O_3 hematite. XPS binding energy shifts confirm the heterojunction formation. The comparison of the properties of heterojunction prepared under conventional and microwave methods showed that the mixed oxides formed at the heterojunction interface contributed to better charge separation, which was corroborated by subsequent photochemical application. Evaluation of the efficiency of the materials prepared under microwave conditions for hydrogen production showed promising results, with a significant improvement in performance compared to materials obtained by conventional methods. The microwave-assisted route proved to be an efficient approach for the synthesis of TiO_2 and α-Fe_2O_3 heterojunctions, resulting in photocatalysts with optimized properties for hydrogen generation using solar energy.

References

1. Farooq, U., et al., *Review on Metals and Metal Oxides in Sustainable Energy Production: Progress and Perspectives.* Energy & Fuels, 2023. **37**(3): p. 1577-1632.
2. Sari, Y., et al., *A review of TiO2 photocatalyst for organic degradation and sustainable hydrogen energy production.* International Journal of Hydrogen Energy, 2024. **55**: p. 984-996.
3. Mishra, M. and D.-M. Chun, *α-Fe2O3 as a photocatalytic material: A review.* Applied Catalysis A: General, 2015. **498**: p. 126-141.

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Inverse Opal Titania Modified with Gold for Visible-light Photocatalytic Activity

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Photonic crystals, particularly inverse opals, have been applied in optical fields for decades (1). More recently, many studies have focused on their application in photocatalysis due to high photocatalytic activity, achieved by a unique feature of slow photon effect (2,3). Additionally, visible-light photoactivity is recognized as an important path for the development of photocatalysis. Therefore, this study aims to obtain visible-light activity based on titanium(IV) oxide (TiO_2, titania) inverse opal (IOT). In this regard, noble metals, such as gold nanoparticles (Au NPs), have been incorporated in IOT structure to utilize visible-light activity arising from the localized surface plasmon resonance (LSPR) effect (4).

The procedure of this study includes the fabrication of Au-IOT films, their characterization, and the evaluation of resultant photocatalytic activity. The initial step involves fixing IOT on a substrate - a basic platform for further processes. Although, the synthesis of IOT involves usually at least three steps, i.e., (i) opal template formation, (ii) inverse opal formation, and (iii) crystallization, here two first steps have been combined by a co-assembly method. Titania infiltration proceeds simultaneously with the formation of polystyrene (PS) opal. Accordingly, fast formation of IOT with high quality and without extra cracks (caused by capillary force during infiltration) has been succeeded. Moreover, the second step, i.e., the removal of PS opal template combined with TiO_2 crystallization, eliminates additional heat treatment. Furthermore, to obtain gold-modified IOT, a novel three-phase co-assembly method has been developed to combine PS opal template, TiO_2 infiltration, and Au NPs' deposition. Properties of obtained materials have been investigated by various methods, including DRS, XRD, SEM, and TEM. The photocatalytic activity has been evaluated under UV and visible-light irradiation for different reaction systems, including hydroxyl radicals' formation.

Surprisingly, continuous and well-ordered IOT films can reach millimeter (mm) scale under the optimized conditions. As a result, the color reflected due to the photonic bandgap (PBG) of inverse opal film can be directly observed even by human eyes. Moreover, gold-modified IOT samples have been successfully prepared, in which two kinds of structures (gold embedded in or deposited on the inner wall of IOT) allows also the discussion on the property-governed activity.

Concluding, the co-assembly as well as three-phase co-assembly methods provide rapid and efficient approaches for the preparation of high-quality IOT and Au-modified IOT films with significant enhancement of photocatalytic activity. The further discussion on the key factors of activity and mechanism will be presented during the meeting.

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References

(1) Cersonsky, R.K.; Antonaglia, J.; Dice, B.D.; Glotzer, S.C. *Nature Communications* **2021**, *12.*
(2) Chen, J.I.L.; von Freymann, G.; Choi, S.Y.; Kitaev, V.; Ozin, G.A. *Journal of Materials Chemistry* **2008**, *18*, 369-373.
(3) Raja-Mogan, T.; Ohtani, B.; Kowalska, E. *Catalysts* **2020**, *10.*
(4) Kowalska, E.; Mahaney, O.O.P.; Abe, R.; Ohtani, B. *Physical Chemistry Chemical Physics* **2010**, *12*, 2344-2355.

Photocatalytic Hydrogen Production: Insights into Titanium-Based MOFs MIP-177(Ti) and MIP-209(Ti)

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Since the seminal discovery by Fujishima and Honda in 1972, titanium dioxide (TiO_2) has become a cornerstone of heterogeneous photocatalysis1, inspiring decades of renewable energy research. Building on this legacy, titanium oxide-based Metal-Organic Frameworks (MOFs)2 represent a new frontier in photocatalysis, offering structural and functional tunability for applications ranging from hydrogen production (from water or organic resources) to environmental remediation (charge conductivity, volatile organic compound (VOC) degradation...). This study focuses on the photocatalytic potential of two specific titanium-based MOFs MIP177(Ti)3,4 and MIP-209(Ti)5 (MIP stands for Materials from Institute of Porous Materials of Paris), both of which are built up from an identical $Ti_{12}O_{15}$ cluster but from very distinct organic likers, namely nitroterephthalate, and a tetra-carboxylate 3,3,5,5-tetracarboxydiphenylmethane (mdip), respectively (Figure 1). Interestingly, these two MOFs are among the very scarce examples of Ti-MOFs sharing similar inorganic building units, showcasing the potential versatility of titanium-based MOFs.

In this communication, we will highlight the molecular imprinted strategy we deployed with MIP-177(Ti)-LT (LT: low-temperature structure) which allowed to demonstrate its exceptional ability to selectively dehydrogenate formic acid, achieving a significantly high hydrogen release rate of approximately **700 μmol H_2/gcat/h**. This performance surpasses benchmark photocatalysts such as MIL-125(Ti) and UiO-66(Zr) by an order of magnitude and is over 30 times more efficient than TiO_2-P25. Furthermore, it achieves an apparent quantum yield of 22% in the UV region, emphasizing its efficiency.

On the other hand, MIP-209(Ti) exchanged with chromium (˜5% at versus Ti), exhibits enhanced stability in water compared to the unmodified MOF. This improvement enables one of the highest reported hydrogen evolution rates (HER) for water splitting under simulated solar light irradiation, achieving **5812 μmol H_2/g_{cat}/h**, significantly outperforming the benchmark Ti-MOF, IEF-116, which produced **1391 μmol H_2/g_{cat}/h** under similar conditions. Notably, without the use of any noble metal co-catalyst, MIP-209(Ti) also exhibited a sixfold enhancement in overall water-splitting (OWS) performance, generating **681 μmol H_2/gcat/h** and **325 μmol O_2/g_{cat}/h**, compared to **94 μmol H_2/g_{cat}/h** and **53 μmol O_2/g_{cat}/h**, respectively, for IEF-11.

Interestingly, the HER performances obtained for MIP-209(Ti) are of the same order of magnitude as those achieved by the unmodified MIP-177(Ti).

These findings underscore the high potential of these two Ti12-based MOFs prompting them as benchmarks noble metal-free MOF photocatalysts for hydrogen production. Together, they illustrate the adaptability and promise of Ti-based MOFs in addressing diverse challenges in renewable energy.

Synergistic Integration of Persistent Luminescent Materials and Black TiO_2 for Enhanced Green Hydrogen Production

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Converting renewable solar energy into clean, carbon-neutral fuels is a promising strategy to address current energy and environmental crises. Hydrogen is considered a clean, renewable energy carrier and an attractive alternative to fossil fuels. However, its production predominantly relies on steam reforming, a process dependent on fossil fuels and associated with CO_2 emissions. In this context, photocatalysis offers a sustainable, renewable, and effective route for hydrogen production, using solar energy to split water into hydrogen. Among photocatalysts, anatasephase TiO_2 is widely employed due to its low cost, chemical stability over a broad pH range, and robustness under UV illumination. However, its high bandgap energy (3.2 eV) restricts excitation to UV light, while rapid recombination of photogenerated electron-hole pairs (e^-/h^+) limits its photon-to-charge conversion efficiency. Black TiO_2–x, modified with oxygen vacancies, addresses these limitations by lowering the bandgap to approximately 1.2–1.7 eV, enabling visible light absorption and enhancing photocatalytic activity. Persistent luminescent (PeL) materials, also known as energy storage phosphors, provide an innovative addition to this system. These materials can emit light for minutes to hours after the excitation source is removed, a phenomenon attributed to charge carrier traps forming long-lived states. The performance of PeL materials is governed by the interaction between the host lattice, optically active ions, and structural defects. Combining PeL materials with photocatalysts can yield multifunctional heterostructures, opening new possibilities for clean energy applications. In this work, we synthesized TiO and black TiO_2 using ascorbic acid as a reducing agent, and coupled them with PeL $ZnGa_2O_4$:Cr^{3+} for green hydrogen production. XRD confirmed the anatase phase for TiO_2 and black TiO_2, while PeL exhibited a $ZnGa_2O_4$ structure. UV-vis diffuse reflectance spectroscopy (DRS) showed significant enhancement in visible light absorption up to 800 nm for black TiO_2. Electron paramagnetic resonance (EPR) confirmed an increase in oxygen vacancies, while photoluminescence measurements indicated reduced charge recombination for black TiO_2. PeL materials displayed excitation peaks at 280, 440, and 560 nm and emitted at 700 nm, consistent with the black TiO_2 absorption, alongside great persistence after excitation at 280 nm. The PeL was incorporated into TiO_2 via two approaches: (i) integration during TiO synthesis and (ii) physical mixing for 24 h. Both methods preserved the anatase TiO_2 and $ZnGa_2O_4$ phases. Preliminary hydrogen production results demonstrated that the PeL material generated 0.6 μmol g^1 of H after 4 h of reaction under simulated solar irradiation, increasing to nearly 2.0 μmol g^1 after 2 h under no irradiation. Using an Hg lamp, H generation reached only ˜0.2 μmol g^1 and no continue H_2 production was observed after ceasing the irradiation. Composite materials showed significant enhancement in hydrogen production under both irradiation sources. Finally, these findings highlight the synergistic potential of combining PeL and black TiO_2 for efficient green hydrogen production.

Dry Spray-Coated Graphite/PVdF Electrodes for EV Lithium-Ion Batteries

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Lithium-ion batteries (LIBs) have emerged as the main energy storage solution for consumer electronics and electric vehicles (EVs). Traditional LIB electrodes are prepared through a wet process, which involves coating solvent-based mixtures onto metallic current collectors. These mixtures, often referred to as slurries, typically contain at least one electrochemically active material, a conductive carbon, a polymer binder, and a solvent for binder dissolution. Recently, there has been a surge in interest in developing new manufacturing processes for electrodes that prioritize environmental sustainability and remain economically viable. One such approach involves fabricating electrodes without the use of solvents, directly depositing active materials onto current collectors, and eliminating the need for a drying step.

In this work, our objective was to manufacture graphite negative electrodes using PVdF as a binder through an electrostatic dry-spraying coating process. In this process, a high voltage is applied to a previously dry-mixed electrode powder, which then gets electrically charged, forming a cloud of charged particles. The charged particles are then accelerated towards the grounded current collector, where they form a uniform and continuous coating layer, which is then hot calendered to thermally activate the binder and control the coating thickness and density. This change in the manufacturing process can affect the electrode characteristics such as homogeneity of binder distribution, porosity, adhesion, and cohesion between active material and carbon black (CB) conducting agent particles and the current collector, electrical properties, and therefore the battery performance.

Using the electrostatic spraying method, we were able to manufacture graphite/PVdF and graphite/PVdF/CB negative electrodes with high mass loadings, suitable for electric vehicle applications. We studied two different PVdF binders with different physicochemical properties such as primary particle size, crystallinity, melting temperature and viscosity, and varied the PVdF concentration in the electrode. The influence of the mixing times of the dry electrode components and of the calendering pressure were also studied.

After optimization we have obtained well performing graphite electrodes of 5 mAh cm^{-2} surface capacity (density 1.5 g cm^{-3}), showing a capacity retention of 97% at the 100th cycle as NMC811/Graphite full cells in pouch-cell format. Our findings therefore indicate that this dry fabrication technique offer viable alternative, yielding high-quality electrodes with short production time, good electrochemical and mechanical properties, comparable to those produced through conventional wet-slurry based methods.

At a more fundamental level, this work opens up a deeper understanding of the binder influence. Indeed, very interestingly, the PVdF distribution in the dry mixed electrode powder, which also determe the PVdF distribution in the calendered electrode, could be visualized and precisely quantified. This one exists as discrete nanometric particles at the surface of the graphite particles and as micrometric agglomerates. The quantification of both fractions, as a function of the PVdF grade, concentration, and of the mixing times of the dry electrode powder, allowed to establish quantitative and novel relationships between the PVdF distribution and the electrode properties, which are likely also valid for wet-processed electrodes.

Elucidating new synthesis procedures for Na_3PS_4 sodium solid electrolyte

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This study explores the synthesis and optimization of Na_3PS_4 (NPS) thiophosphate solid electrolytes, critical components for next-generation sodium solid-state batteries. Focusing on the tetragonal and cubic polymorphs of NPS, the research investigates the effects of mechanochemical synthesis methods and heat treatment (HT) conditions on the purity, crystallinity, and ionic conductivity of the material.

Two synthesis techniques were employed: low-energy ball milling and hand milling, both conducted under controlled Ar atmospheres. Ball-milled samples (bm-NPS) and hand-milled samples (hm-NPS) underwent HTs at various temperatures to crystallize specific NPS phases. Ionic conductivity was assessed using electrochemical impedance spectroscopy in stainless-steel cells. The study highlighted significant differences in structural and conductive properties due to synthesis and HT processes.

The findings revealed that bm-NPS samples calcined at intermediate temperatures exhibited high ionic conductivity, with bm-NPS heat treated at 350 °C and followed by additional HT at 500 °C reaching a conductivity of 0.39×10^{-3} $S\cdot cm^{-1}$, the highest in the study. This outcome, linked to the tetragonal phase, contrasts with the conventional view that cubic NPS is more conductive. Conversely, bm-NPS treated at 600 °C reverted to a predominantly cubic structure, with conductivity declining to 0.21×10^{-3} $S\cdot cm^{-1}$. These variations were attributed to sulfur loss during HT, affecting grain boundary chemistry and creating vacancies that temporarily enhance Na conductivity but eventually reduce it under prolonged exposure to high temperatures.

Hand-milled samples demonstrated similar trends. Direct HT of hm-NPS at 550 °C produced tetragonal phases with 0.31×10^{-3} $S\cdot cm^{-1}$ conductivity, which decreased upon further treatment at 600 °C. Notably, the cubic phase predominated at both low and high temperatures, while the tetragonal phase emerged at intermediate conditions, displaying unexpected conductivity advantages.

This study underscores the critical role of HT conditions in optimizing the structural and conductive properties of NPS electrolytes. Results challenge the prevailing assumption that the cubic phase always offers superior conductivity. Instead, achieving optimal ionic conductivity involves precise control of HT temperatures, with intermediate conditions favoring the tetragonal phase. Furthermore, synthesis methods appeared less critical than HT conditions, as both milling techniques yielded materials with comparable properties under optimized treatment protocols.

These insights provide valuable guidance for refining synthesis protocols for NPS solid electrolytes in sodium battery applications. The findings suggest future efforts should focus on replicating the synthesis and electrochemical testing to reduce uncertainty and establish confidence intervals for ionic conductivity values.

Exploring the massive electron storage in the polyoxometalates

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Keywords: Polyoxometalates, Electrochemistry, Spectroscopy

Polyoxometalates (POMs) represent one class of fascinating inorganic molecules built from transition metals in their highest oxidation states. One of the most striking properties of POMs is their ability to exchange massively electrons in aqueous solution. Understanding this storage capacity is a pivotal question that carries substantial implications for energy storage and conversion.To address this issue, we examined the super-reduction of the most prevalent elementary constituent element in POMs, the trimetallic unit. Previous results shew Keggintype(1) and pseudo-Dawson-type(2) POMs were able to store 6 electrons on one metal triad, while Cronin's team demonstrated that the Wells-Dawson anion $(P_2W_{18}O_{62})^{6-}$ can accept up to 18 electrons, which allows it to act as a high-performance redox flow battery electrolyte (giving a practical discharged energy density of 225 $Wh.l^{-1}$).(3)(4) Nobody tried however to totally uncover its electron storage capacity, by understanding the localization of the electrons added.

We unveiled thus the super-reduction process of Dawson-type POMs $(P_2W_{15}Mo_3O_{62})^{6-}$, containing a trimolybdic unit $\{Mo_3O_{13}\}$ sustained by a polyoxotungstate core. Using the combination of *in-situ* measurements (XANES/EXAFS) and *ex-situ* techniques (X-ray diffraction, UVvis spectroscopy, voltammetry and multinuclear NMR), we reveal that: (i) the super-reduction of Dawson-type POMs can lead to the formation of metal-metal bonds between Mo centers, and out of the blue, (ii) the molybdic centers can be reduced to their trivalent state, having thus the possibility to reach a total of four oxidation states, which had never been demonstrated in the field of POMs.

References

(1) C. Falaise and al. *Inorg. Chem.* **2023**, *62*, 2494
(2) G. Mpacko Priso and al. *Angew. Chem. Int. Ed.* **2023**, e202312457
(3) L. Cronin, and al. *Nature Chem* **2018**, *10*, 1042
(4) L. Cronin, and al. *J. Am. Chem. Soc.* **2022**, *144*, 8951

Revisiting the electrochemical activity of alpha-V_2O_5 electrode for aqueous ammonium ion batteries

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Sustainable rechargeable batteries have attracted attention as energetic transition vectors pushing circular economies. Among them, aqueous rechargeable batteries (ARB) constitute ecofriendly solutions for stationary uses. In addition, devices using a low content of metals in the cell manufacturing show environmental and cost advantages, specially when the charge carrier is not metallic. This is the case of H^+, H_3O^+, OH^- and NH_4^+-based ARB that are currently expanding its importance worldwide. Considering the ammonium ion rechargeable batteries (AIRB) (1,2), the proposed positive electrodes range in three main categories: Prussian-blue derivatives with caged structure, layered transition metal oxides and open organic polymers. Because of the well-known capacity of vanadium oxides to host several mono- and multi-valent cations, bi-layered V_2O_5 was examined in a full AIRB by Song et al. (3) finding a reversible capacity of 90 mAh.g^{-1} between 0 and 1.5V at 0.1 A.g^{-1}. alpha-V_2O_5 polymorph can be obtained by heating such oxide at 400 °C, and showed faster capacity fading upon cycling, which was attributed to the rigidity of the orthorhombic structure (3). However, evidence for this was not given. Thus, we decided to re-examine alpha-V_2O_5 electrochemical properties in AIRB. We found that alpha-V_2O_5 turns partially into a NH_4^+-containing xerogel with enlarged structure, upon contacting with the electrolyte, even at open cell potential. Therefore, ammonium ions and charge storage are due to two different electroactive materials that also show distinct stability against dissolution. Finally, a three-electrodes cell based on alpha-V_2O_5 provided more than 180 mAh.g^{-1} of capacity in the voltage range of -0.5V-1.0V vs Ag/AgCl at regimes as fast as 10C (1.5 A.g^{-1}) with cycling efficiency of 100%. These features fully justify the interest in revisiting this AIRB electrode.

References

(1) A. Kulkarni, C. Padwal, J. MacLeod, P. Sonar, T. Kim, D. Dubal. Toward Safe and Reliable Aqueous Ammonium Ion Energy Storage Systems. *Advanced Energy Materials* 14, 2400702 (2024).
(2) Q. Chen, W. Liang, Z. Tang, J. Jin, J. zhang, G. Hou, L. Mai, Y. Tang. Aqueous ammonium ion storage materials : A structure perspective. *Materials Today* 72, 359 (2024).
(3) S. Dong, W. Shin, H. Jiang, X. Wu, Z. Li, J. Holoubek, W. F. Stickle, B. Key, C. Liu, J. Lu, P. Alex Greaney, X. Zhang, X. D. Ji. Ultra-fast NH4+ Storage: Strong H Bonding between NH4+ and Bi-layered V2O5. *Chem.* 5, 1537 (2019).

Electrochemical Functionalization of Porous Materials for Supercapacitor Applications

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Aqueous supercapacitors are essential for meeting sustainable energy storage needs, offering enhanced safety, low cost, and high power performance. However, their low energy density limits their competitiveness against batteries, driving the need for research to extend their voltage range. This limitation arises from the interaction between the aqueous electrolyte and the carbon electrode, which triggers parasitic reactions such as water oxidation, water reduction, and carbon oxidation. These reactions currently limit the voltage range to 1.2 V.

Parasitic reactions result from electron transfer between the electrode and the electrolyte. One potential solution to increase the voltage range is to form a passivating layer at the electrodeelectrolyte interface, which permits ion transport while maintaining capacitance. To achieve this, diazonium salts are electrochemically grafted onto the electrode surface[2]. Fluorinated diazonium salts, in particular, are selected due to their ability to create hydrophobic surfaces, preventing water molecule interactions with the surface of the electrode.

The initial study aims to understand how the geometry of the diazonium molecules-such as the position or length of substituents-affects the thickness and properties of the grafted films[3]. Various characterizations, including electrochemical analysis, XPS, and contact angle measurements, were performed.

The grafting process was applied to porous carbon electrodes. A self-supporting electrode without Teflon, combining nanotubes and activated carbon was fabricated, exhibiting high electronic conductivity and capacitance. Then, the capacitance and the rated voltage of electrografted electrodes was tested in 0.5 MLi_2SO_4.

[1] Renewable and Sustainable Energy Reviews. 2018 Jan;81:1868–78.
[2] J Phys Chem B. 2005 Dec 1;109(51):24401–10.
[3] Langmuir. 2009 Jan 6;25(1):286–93.

ORAL #27

In-situ Multimodal Analysis of Metal Halide Perovskite Film Formation and Degradation for Stable Perovskite Solar Cells

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The recent developments in the metal halide perovskite solar cells were able to achieve power conversion efficiencies comparable to silicon solar cells. Perovskite materials have emerged as promising contenders in the field of photovoltaic technology, offering a cost-effective and energyefficient alternative to traditional silicon-based solar cells. Their low-temperature fabrication processes and earth-abundant precursor materials position them as highly attractive for scalable solar energy solutions (1). Despite achieving an impressive performance, perovskite solar cells still face significant challenges for outdoor implementation due to limited reliability. Although there are many external factors at play such as humidity, temperature and even the prolonged sun exposure, the interfaces between the halide perovskite absorber layer and adjacent charge transport films play a big part in the inherent stability of the cell component (2).

Here, we studied the effect of external stressors such as the exposure to air and humidity on double cation, $Cs_{0.3}FA_{0.7}Pb(Br_{0.2}I_{0.8})_3$ and triple cation, $Cs_{0.05}(MA_{0.17}FA_{0.83})0.95Pb(Br_{0.2}I_{0.8})_3$ perovskites, where MA and FA stand for methylammonium (CH_3NH_3) and formamidinium ($(CH_2(NH_2))_2$) as well as perovskite crystallisation by in-situ Grazing Incidence Grazing Incidence Wide Angle X-ray Scattering (GIWAXS) and photoluminescence (PL) spectroscopy measurements (3). We carried out GIWAXS measurements whilst depositing perovskite on different substrates (e.g. SnO_2 and NiO) to study perovskite crystallisation, where we were able to detect differences in perovskite crystallisation. Furthermore, to advance our understanding of degradation, we carried out real-time GIWAXS and concomitant PL measurements as the perovskite degrades under different conditions where it was possible to detect different perovskite crystal structures, present heterogeneously, diminish with time as the PbI_2 concentration increased at the interface. We observed that different conditions triggered unique defect routes with different reaction kinetics. In air, we observed phase instabilities such as the breakdown of both double and triple cation perovskites into non-perovskite organic iodide species ($CH3NH_2I$) as well as cesium iodide, CsI. These phase instabilities were not present under 100% humidity without oxygen. Whilst the phase instabilities were present in air for both double cation and triple cation, we observed no intrinsic phase instabilities when 2D interlayer (4-FPEAI) was deposited on top of the perovskite. For 100% humidity, we observed partially reversible electron transfer from I^- to Pb^{2+} leading to irreversible Pb^0 formation for double and triple cation perovskite cells.

References

Liu, S.; Biju, V. P.; Qi, Y.; Chen, W.; Liu, Z. Recent Progress in the Development of HighEfficiency Inverted Perovskite Solar Cells. NPG Asia Mater. 2023, 15 (1), 27.
Schulz, P.; Cahen, D.; Kahn, A. Halide Perovskites: Is It All about the Interfaces? Chem. Rev. 2019, 119 (5), 3349–3417.
Reus, M. A.; Reb, L. K.; Weinzierl, A. F.; Weindl, C. L.; Guo, R.; Xiao, T.; Müller-Buschbaum, P. Time-Resolved Orientation and Phase Analysis of Lead Halide Perovskite Film Annealing Probed by In Situ GIWAXS. Adv. Opt. Mater.2022, 10 (14), 2102722.

Development of Hole Transporting Molecules for Perovskite Solar Cells

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In this talk, we present our recent advances in development of small molecule hole transporting materials (HTMs) for halide perovskite solar cells (PSCs). We report the design and synthesis of different series of conjugated molecules for use as charge transporting materials in PSCs. The thermal, morphological, optical and electrochemical properties of all prepared compounds have been investigated in detail and a comparative discussion has been presented. Their characteristics have suggested that these molecules could be suitable for use as HTM in perovskite photovoltaic devices. The preliminary photovoltaic application have given devices with power conversion efficiency (PCE) around 17 %. Selected molecules have been subjected for further device optimization and in deep interface engineering (between the perovskite and hole transport layers) improving PCE to higher than 23 % and this champion PCE is even higher than that of the Spiro-OMeTAD-based device. Thermal stability test at 85 °C for over 1000 h showed that the PSC employed novel HTM retains 86% of initial PCE, while the SpiroMeOTAD-based PSC degrades unrecoverably. Time-of-flight secondary ion mass spectrometry studies combined with Fourier transformed infrared spectroscopy reveal that novel HTM shows much lower lithium ion diffusivity than spiro-MeOTAD due to a strong complexation of the lithium ion with HTM, which is responsible for the higher degree of thermal stability. Under optimized condition, the perovskite solar cells employed additive-free HTM gave a PCE of ca. 16%. This work delivers an important message that capturing mobile Li^+ in hole transporting layer is critical in designing novel HTM for improving thermal stability of PSCs. In addition, it also highlights the importance of interfacial engineering on the non-conventional HTM.

Recent related publications:

Nanographene Coupled with Interfacial Pyrene Derivative for Thermally Stable Perovskite Solar Cells. S.-G. Kim, T. de Monfreid, J.-H. Kim, F. Goubard, J. J. Berry, K. Zhu, **T.-T. Bui**, N.-G. Park, *ACS Energy Letters* **2023***, 8, 5, 2267–2275*.
Tetraphenylpyrrolo(3,2-*b*)pyrroles: Synthesis, Thermal, Optical, Electrochemical Properties and Photovoltaic Applications. T.-T. Dang, M. Spence, S. K. Thomas, M. Carnie, **T.-T. Bui**, *Journal of Materials Science: Materials in Electronics* **2022**, *33*, 17773 – 17779.

Capturing Mobile Lithium Ion in Molecular Hole Transporter Enhances Thermal Stability of Perovskite Solar Cells. S.-G. Kim, T. H. Le, T. de Monfreid, F. Goubard, **T.-T. Bui,** N.-G. Park, *Advanced Materials* **2021**, *33,* 2007431.

Narrow Interconnection in Inverted Perovskite Solar Modules Using a Single Nanosecond UV Laser

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Perovskite solar cells (PSCs) have experienced remarkable advancements over recent decades, achieving power conversion efficiencies that now exceed those of traditional silicon-based cells. However, critical challenges remain for the widespread commercialization of PSCs, including long-term stability and maintaining high-efficiency during large-scale manufacturing.(1) A key obstacle in scaling-up is the efficiency loss that accompanies an increase in the active area of the device. This decrease in efficiency primarily stems from the increased series resistance of the transparent conductive oxide (TCO) electrodes, which lowers the fill factor.

To mitigate this issue, the P1-P2-P3 scribing method is commonly used, as it allows a set of cells to be connected in series on the same substrate, increasing the potential difference and maintaining the cell current at a lower current. This scribing method can be executed by masking or by mechanical or laser scribing, with the choice of method depending on the deposition techniques used in device fabrication. Among these, laser ablation is particularly advantageous due to its versatility, precision, and ability to produce smooth, well-organized modules.(2)

The laser ablation process for the P1-P2-P3 scribing method involves a sequence of scribes, each tailored to establish the necessary electrical connections between solar cell subunits. In the P1 scribe, the TCO layer on the substrate is selectively removed to create an insulating barrier between sub-cells. During the P2 scribe, the hole transport layer, perovskite layer, and electron transport layer are ablated to define individual sub-cells. Lastly, the P3 scribe eliminates all layers except the TCO bottom electrode, ensuring electrical isolation of the back contacts between adjacent cells. The module's design is characterized by the geometric fill factor (GFF), a parameter that represents the proportion of the active area relative to the total area, including both active and inactive (dead) regions.(3) Optimizing GFF is essential for maximizing energy output and ensuring the economic viability of PSC technology.

In this work, the interconnection width (dead area) was minimized to achieve high GFFs in inverted perovskite solar modules (PSMs) with the structure glass/FTO/PTAA/F-PEIA/Cs0.05(FA0.85MA0.15)0 PEIA/PCBM/BCP/Ag. The sizes and numbers of cells were varied in the PSM. The laser ablation system employed was a UV laser setup featuring a 355 nm UV laser source with a power output of 5 W, a pulse frequency range of 20–200 kHz, and a minimum pulse width of 15 ns. To evaluate the performance of the PSM, *I-V* curves were used, while SEM and EDX were employed to analyze and verify the scribe residues. Using this approach, an interconnection width of 135 *μ*m was achieved, resulting in a GFF of 99%.

References

1. Príncipe, J., et al. Energy Technology, 2022. **10**(4): p. 2100952.
2. Jamaatisomarin, F., et al. 2023. **7**, 94 DOI: 10.3390/jmmp7030094.
3. Di Giacomo, F., et al., Micromachines, 2020. **11**(12): p. 1127.

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ORAL #30

Innovative Synthesis and Characterization of Non-Toxic Gold-Based Double Perovskites

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Renewable energy sources are increasingly recognized as the most viable solution for lowcarbon electricity production across various sectors, including industry, transportation, and buildings, while significantly reducing dependence on fossil fuels (1). Among these, photovoltaic energy, harnessing the sun as an inexhaustible resource, plays a pivotal role in accelerating the global energy transition. Within the diverse solar technologies, halide perovskites semiconductors stand out as particularly promising. Since their emergence in 2009 (2), these materials have demonstrated exceptional advantages, including remarkable optoelectronic properties (power conversion efficiency exceeding 25%, excellent charge carrier mobility, and low defect density) and cost-effective, energy-efficient fabrication processes (low-temperature synthesis), surpassing traditional silicon-based technologies in several aspects. However, perovskites face two major challenges: environmental instability and toxicity due to the presence of lead, which limit their widespread industrial adoption.

To address the issue of toxicity, numerous lead substitution strategies are being explored. In this work, we focus on Gold-based double perovskites, *Cs2Au(I) Au(III)X6* (*X = Cl, Br, I*), a promising non-toxic alternative to the conventional *APb(II)X3* composition . These new materials exhibit bandgaps in the range of 1–1.6 eV, which are highly suitable to maximize photovoltaic efficiencies.

We present an innovative synthesis method for these materials and provide comprehensive data on their structural (XRD, SEM, EDX, XPS) and optical (photoluminescence, Raman, absorption spectroscopy) characterization. These characterizations not only confirm the successful formation of the target phase but also unveil the intricate interactions between charge carriers and lattice vibrations, which could directly limit charge mobility while enhancing heat dissipation processes. Our analysis offers valuable insights into the potential of these semiconductor materials for applications such as photovoltaics, as well as photocatalysis, which is less dependent on charge carrier diffusion length.

(1) *International Energy Agency, 'Net Zero by 2050 – A Roadmap for the global sector'.*
(2) *Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. J. Am. Soc. 2009, 131, 6050-6051.* https://doiorg/10.1021/ja809598r.

Photon Catchers and Electron Keepers: The Potential of Hybrid Polyoxometalates in Solar Energy Conversion

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One of the primary goals of artificial photosynthesis is to harness solar energy for driving the transfer of electrons and protons from water to carbon dioxide, producing renewable fuels. Achieving this requires systems capable of long-lived charge separation and charge accumulation to facilitate multi-electron catalysis in water splitting and CO_2 reduction.

Polyoxometalates (POMs), renowned for their exceptional electron-storage capacity and redox stability, have attracted significant attention in artificial photosynthesis as redox mediators, electron shuttles, and electron/proton reservoirs. These molecular metal oxides have also been shown to exhibit photocatalysis, though their photoactivity is limited only in the ultraviolet region. To overcome this limitation, our group has developed hybrid POMs functionalized with photosensitizers, forming photoactive donor-acceptor dyads that mimic key aspects of natural photosynthesis.

We have synthesized and investigated hybrid systems featuring organic dyes, such as BODIPY and push-pull dyes, covalently linked to Keggin- and Dawson-type polyoxotungstates. These hybrids generate charge-separated states through rapid photoinduced electron transfer from the photosensitizer to the POM (1). Transient spectroscopy studies of POM-BODIPY hybrids reveal that charge separation kinetics are influenced by the redox potentials of the dye-POM pair, solvent environment, and counter-ion effects (2).

More recently, we have extensively studied the photoinduced charge accumulation in Dawsontype POM-BODIPY hybrids. Under steady-state illumination with triethylamine as a sacrificial electron donor, these hybrids store only one electron. However, introducing an organic acid (e.g., trifluoroacetic acid or acetic acid) promotes proton-assisted two-electron storage, achieving near-quantitative photoconversion within minutes. In the dark, the reduced POM can then activate oxygen and oxidize an organic substrate, as well as transfer an electron to a reversible acceptor such as benzoquinone.

As an alternative approach to a molecular system, we have also explored the integration of these hybrids into photocathode assemblies (3). A generation of POM-BODIPY and POMpush-pull dye hybrids with anchoring groups have been grafted onto mesoporous NiO electrodes showing promising photophysical and electrochemical behavior suitable for dye-sensitized photoelectrochemical cells. Future work will focus on coupling these systems with catalysts for hydrogen production and CO reduction.

In this communication, we highlight advancements in POM-dye hybrid systems, emphasizing strategies for optimizing charge separation and accumulation through structural design, redox potential tuning, and the choice of sacrificial electron donors.

References

(1) Black, F. A.; Jacquart, A.; Toupalas, G.; Alves, S.; Proust, A.; Clark, I. P.; Gibson, E. A.; Izzet, G. Chem. Sci. **2018**, 9 (25), 5578–5584.
(2) Toupalas, G.; Karlsson, J.; Black, F. A.; Masip-S´anchez, A.; Lòpez, X.; Ben M'Barek, Y.; Blanchard, S.; Proust, A.; Alves, S.; Chabera, P.; Clark, I. P.; Pullerits, T.; Poblet, J. M.; Gibson, E. A.; Izzet, G. Angew. Chem. Int. Ed. **2021**, 60 (12), 6518–6525.
(3) Benazzi, E.; Karlsson, J.; Ben M'Barek, Y.; Chabera, P.; Blanchard, S.; Alves, S.; Proust, A.; Pullerits, T.; Izzet, G.; Gibson, E. A. Inorg. Chem. Front. **2021**, 8 (6), 1610–1618.

ORAL #32

Loadflow method for long-term planning and the valorization of new levers

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The production of renewable energy plants on the network (renewable energies), and the diversification of electrical uses (private solar panels, electric vehicles, storage) create a change in the distribution of loads on the medium voltage network leading to the appearance of high voltage constraints.

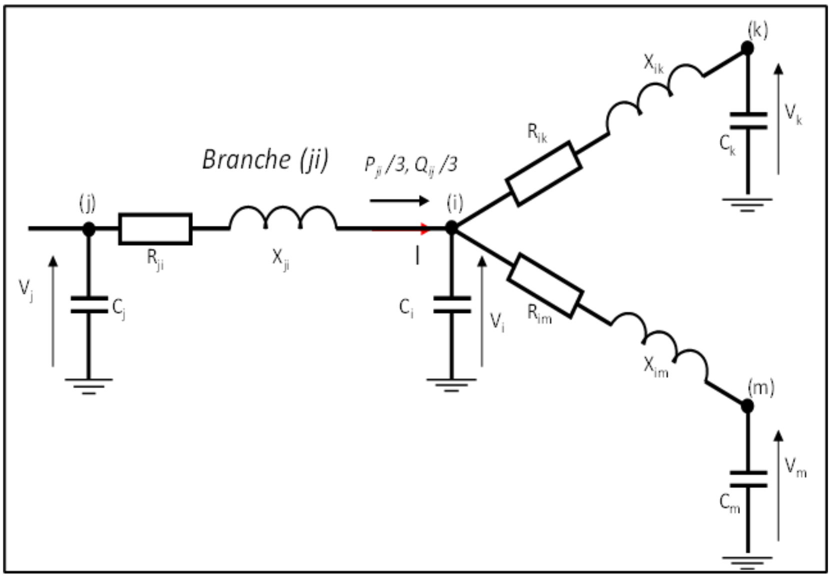
This new context forces distribution system operators (DSOs) to carry out long-term planning studies, which are characterized by a high calculation (1) cost, to maintain a time step of an hour.

In addition, DSOs have many levers to resolve the appearance of constraints, these can take different forms such as reinforcement, operation, or flexibility levers.

To assess the relevance of each solution in a long-term planning framework, it is essential to have a fast and precise calculation model.

The loadflow model developed in this article is based on the linearization of the voltage equations and on the principle of load additivity, to achieve a low calculation cost.

With the assumption of voltages close to the set voltage of the source substation, the accuracy error of the calculations is only a few percent. However, since the appearance of high voltage constraints is defined by a 2% increase in voltage along a feeder, this condition is mostly met on French networks.



Generic PI model on a radial structure

Thus, the linearization of the voltage equations developed in this article allows the matrix writing U = M P* P + M Q*Q , where:

- U the column vector of the voltages at the nodes.
- P,Q the column vectors of the active and reactive powers at each node.
- M P, M _Q : the sensitivity matrices of the node voltages as a function of the powers at the network nodes

But also, the writing U = M _R*R+ M X*X where :

- U the column vector of the voltages at the nodes.
- R,X the column vectors of the resistances and reactance of the lines connecting the nodes.
- M R,M _X the sensitivity matrices of the node voltages as a function of the electrical characteristics of the lines.

This equation allows us to extract the network sensitivity matrices and thus analytically obtain several parameters:

- The capacity to accommodate production and consumption at a node k, without creating any constraint at a node i.
- The costs of the levers (line replacement, coil installation, capping in production, etc.) in (€/V), i.e. the cost to invest for the number of volts by which we wish to lower the voltage.

In conclusion, we manage to obtain a fast and precise loadflow allowing to carry out long-term planning studies with a time step of the order of an hour.

A long-term study in planning medium-voltage networks will be carried out subsequently to grasp all the benefits of this approach combined with the advantages provided by flexibilities.

(1) O. R. a. J. Bartels, Evaluation of Temporal Complexity Reduction Techniques Applied to Storage Expansion Planning in Power System Models, DLR–Institut für Vernetzte Energiesysteme e.V., Carl-von-Ossietzky-Str. 15, 26129 Oldenburg, Germany; 2020.

Energy-optimal placement of storage systems in the power grid network

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Energy storage systems (ESS) are a critical technological solution to induce the transition towards net-zero emission energy mixes. While a lot of research has been conducted on positioning strategies for storage deployment (Zhang 2022 for a review), most of these efforts focus on limited distribution network samples. The high voltage transmission part remains understudied, although some field tests have been experimented such as the Ringo project of RTE. Looking for optimal positions on the whole power grid should provide additional energy savings. Coupling previous graph theory-based methodology (Korjani 2018, Emery 2025) with Energy Return on Energy Invested considerations, we investigate the consequences of storage configurations on the overall power flow. We distinguish three fundamental dynamics in power flow analysis: production to consumption, production to storage and storage to consumption. By integrating this three-layer network analysis with energy investment considerations, this work explores new approaches for developing forecasting tools to support the energy transition.

References

- Zhang, Shafiullah, Das, and Wong, A systematic review of optimal planning and deployment of distributed generation and energy storage systems in power networks (2022) - Korjani, Facchini, Mureddu, Caldarelli, and Damiano, Optimal positioning of storage systems in microgrids based on complex networks centrality measures, Scientific Reports, (2018)
- Emery, Bercegol, Jonqueres and Aumaître, Complex Network Analysis of Transmission Networks Preparing for the Energy Transition: Application to the Current French Power Grid, The European Physical Journal B (2025)

Energy Arbitrage Potential of Bidirectional Electric Vehicles Considering Virtual Mileage Impact on Vehicle Residual Value

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Vehicle-to-grid (V2G) technology knows an increasing interest with the rapid uptake of electric vehicles (EVs). This technology allows the EVs to leverage the periods it sits idle (i.e. not driving), which represents 97% of the time. When a bidirectional vehicle is plugged, it can either provide services to the grid (for example: frequency regulation, voltage support) or arbitrate its electricity consumption (for example: behind-the-meter energy optimisation, or trading energy on the market by using the EV battery as storage). We focus on the second use case since we observe a saturation of the most profitable markets such as primary frequency reserves by stationary batteries. In this work, we present a new approach as to how to assess vehicle economic degradation caused by additional cycles on the battery due to V2G operations. In most studies, this economic impact is represented by a fraction of the battery price depending on the storage capacity loss of the battery. However, this approach lacks realism as this cost is never actually paid by any actor. Upcoming standards and regulations will force EVs to account and display so-called ”virtual mileage”, which is an image of the energy discharged by the battery when performing V2G services. One virtual kilometre (*vkm*) is meant to represent the same vehicle degradation as a real (driving) kilometre. If virtual mileage is interpreted as such by the consumers, V2G will have a considerable impact on the vehicle retail value, also called ”residual value”. This devaluation depends on the age and accumulated mileage of the vehicle but is on average 1.09 c€/vkm and can go up to 4.07 c€/vkm according to our data. This translates as 0.054 € per discharged kilowatt-hour, which constitute a substantial hinderance to V2G profitability. We analysed the economic potential of V2G with EVs simulated to participate to the day-ahead electricity market for the French bidding zone and the year 2019, considering devaluation induced by virtual mileage. Our results show that the average economic benefits to V2G are much lower than the figures found in the literature, with an average of 8.54 €/EV over the simulated year. In an alternative scenario in which we do not account for devaluation, all things being equal, we reach a potential value of 39.7 €/EV. Virtual mileage could therefore become one of the largest inhibitors to V2G whereas a virtual kilometre is not as damaging to the vehicle as a real kilometre: the tires, the powertrain, and other equipment used while driving are not used when the EV is performing V2G. Moreover, virtual mileage only accounts for additional cycling ageing of the battery, which is only a component of the full battery degradation, so that, for instance, an EV with a high virtual odometer may retain a higher residual battery capacity than an EV with a low virtual odometer but stored fully charged for a long time. This paper hence highlights the limits to the concept of virtual mileage and proposes to favour alternative indicators for vehicle degradation.

Sustainable management of energy storage and transfer in electric vehicles involved in a green smart city environment

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The daily well-being of modern civilization is closely linked to the use of various devices operating by means of various sources related to the conversion, transfer and storage of energy. The exercise of these tools displays projected results, which are regularly concomitant with unsolicited side effects. A laudable management objective is to reinforce the desired results and reduce the unwanted effects. Electric vehicles are increasingly used for green transportation in smart urban mobility, thus protecting environmental biodiversity and ecosystem. Energy storage by electric vehicle batteries is a critical point of such ecologically aware transportation. This storage is strongly linked not only to the type of internal composition of the battery, but also to the different external managements related to its capacity state. Such managements concern the interconnection of the storage to energy resources, the battery charging strategies, the complexity of charging infrastructure and the charging strategy impacts on environmental biodiversity and the ecosystem. In an elegant urban context such as smart cities, charging strategies would use connected wireless devices. These may involve complex infrastructures and unwanted electromagnetic field interferences. A sustainable management of connected wireless devices and battery state conditions allows for optimized operation and minimized adverse effects. Such management includes the sustainable design of the devices as well as the monitoring of the complex connected procedures. The present contribution aims to analyze and illustrate such management and to highlight the mathematical routines enabling the design and control tasks involved. The involved investigations are closely related to the approaches of, responsible attitude, One Health, and supervising digital twins. The paper make it possible to highlight these notions, allowing a deeper awareness of the themes linked to their crucial role in the management concerned. Thus, the analysis and fusion of these themes are at the heart of this contribution. This management concerns not only the designers and manufacturers of devices but also the users involved in biodiversity and having decision-making faculty relating to the rules of use, namely public authorities. Precautions should therefore be taken by monitoring spaces involving electromagnetic radiations or by establishing restricted areas without radiation sources. The paper sections are related to: an overview of electric vehicle embedded battery and charging device and their integration in smart mobility, sustainable design and control, effects of electromagnetic exposures, governing physical phenomena and their mathematical representation, charging routines analysis in smart environment context, protection against adverse effects, supervision of complex connected vehicle – smart environment – grid. Moreover, case studies support the demonstration of the approaches used in the contribution. For example, the case of the role of responsible attitude and One Health approaches for the battery charging mode of an urban bus, and the case of the biological effects of electromagnetic exposure in a human body near an electric vehicle. The investigations followed in the paper are assisted by instances from the literature.

Keywords

Electric vehicles, energy transfer and storage, Responsible Attitude, One Health, Digital Twins, urban ecology, wireless battery charging, electromagnetic noise, biological effects.

Titania modified with copper species for photocatalytic activity enhancement

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Titania is well-known photocatalyst due to its high activity, stability and abundance, but inactivity under vis irradiation and charge carriers' recombination should be overcome for broad applications. Modification of titania with noble metals (NMs) for both purposes have been extensively investigated, because NMs work as an electron scavenger and might activate titania towards vis response due to plasmonic properties (1-2). Gold, platinum, silver and copper have been mainly examined as titania modifiers, and obtained results have been prospective. However, gold and platinum are expensive, but silver and copper are not enough stable, which results in their surface oxidation during storage under aerobic conditions. Therefore, mixed-oxidation states of copper/silver are usually present in the respective photocatalysts (even those prepared under highly reductive conditions) (3-7). Accordingly, it is difficult to find the main reason of high photocatalytic activity of these photocatalysts, e.g., NM as an electron pool, S-scheme mechanism (e.g., TiO_2/Cu_xO; TiO_2/Ag_xO), and/or plasmonic photocatalysis. Moreover, the mechanism of photocatalytic activity for these materials has not been fully clarified yet (8-10). The present study has focused on titania modification with copper species, i.e., both zero-valent copper and copper oxides. It has been found that some modifications have resulted in highly improved performance under broad irradiation ranges (UV and vis). Interestingly, based on XPS analysis, it has been found that Z-scheme mechanism is the most probable for the core(Cu_xO)shell(TiO_2) structure under UV irradiation (11-12). At present, the study on stabilization of zero-valent copper is in progress. The property-governed activity, and the discussion on photocatalytic mechanism will be presented during this talk.

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References

(1) E. Kowalska, R. Abe, B. Ohtani, *Chem. Commun.*, 2009, 2, 241-243.
(2) E. Kowalska, et al. *Appl. Catal. B: Environ* 178 (2015) 133-143.
(3) Z. Wei, et al. *Appl. Catal. B: Environ*. 2017, 206, 393-405.
(4) Z. Wei, et al. *Chem. Eng. J.* 318 (2017) 121-134.
(5) Z. Wei, et al. *Appl. Catal. B: Environ.* 237 (2018) 574-587.
(6) E. Kowalska, et al. *Catal. Today*, 2015, 252, 136-142.
(7) M. Janczarek, et al. *J. Photon. Energy* 2017, 7(1), 012008, 1-16;
(8) Z. Wei, et al. *Catalysts* 2020, 10, 1070.
(9) M. Janczarek and E. Kowalska, *Catalysts*, 2017, 7, 317;
(10) M. Janczarek, et al. *Materials*, 2018, 11(11), 2069.
(11) K. Wang, et al. *J. Mat. Chem. A* 2021, 9, 10135-10145.
(12) M. Endo-Kimura, et al. *Surf. Interfaces* 2022, 32, 102125.

Photocatalytic Tandems Based on Polyoxothiometalates and Metallic Clusters for the Production of Dihydrogen

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The photocatalytic hydrogen evolution reaction (HER) involves cascade reactions starting with light excitation of a photosensitizer to transfer an electron to a proton reduction catalyst and ending with regeneration of the photocatalytic system through a sacrificial electron acceptor/donor agent, as illustrated in Figure. The most effective molecular photosensitizers known for homogeneous catalysis are noble metal complexes. In this study, we investigate the potential of luminescent octahedral metal clusters and thio-polyoxometalates (ThioPOMs) as Nobel metal-free photocatalytic tandem in homogeneous HER. The ThioPOMs,(1-3) which combine a lacunary polyoxometalate and the aquo cluster $(Mo_3S_4(H_2O)_9)^{4+}$, are known to be efficient catalysts for proton reduction.(4) Our ambition is therefore to use ThioPOMs in conjunction with octahedral molybdenum clusters of the $M_6X_8L_6$ variety to act as photosensitizers(4) to replace the more expensive iridium or ruthenium-based photosensitizers. Here, we report the synthesis and multinuclear NMR characterization of ThioPOMs as well as HER photocatalytic activity in organic solutions and organic-water mixtures using different clusters. The results are compared with previous work on equivalent systems and discussed in terms of the hydrolytic stability effects of the clusters and ThioPOM catalysts in the media studied. Finally, the crystal structures of new CLUSPOM compounds, salts of cationic octahedral metal clusters and anionic POMs, are also obtained and can serve as models(5) for cluster-ThioPOM catalyst tandems.

1. E. Cadot, M. N. Sokolov, V. P. Fedin, C. Simonnet-Jegat, et al. *Chem. Soc. Rev.*, **2012**, *41*, 7335.
2. A. Müller, V. P. Fedin, C. Kuhlmann, H. Bögge, B. Hauptfleisch, et al. *Chem. Commun.*, **1999**, 1189.
3. M. N. Sokolov, I. V. Kalinina, E. V. Peresypkina, et al. *Angew. Chem. Int. Ed.*, **2008**, *47*, 1465.
4. Y. Smortsova, C. Falaise, A. Fatima, M.-H. Ha-Thi, et al. *Chem.-Eur. J.*, **2021**, *27*, 17094.
5. A. Fatima, Y. Smortsova, C. Falaise, N. Leclerc, et al. *Chem. Commun.*, **2023**, *59*, 10988.

ORAL #38

High-entropy Tungsten-Based Oxide as Electrocatalyst and Potential Photo-electro-catalyst for H_2 Evolution

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High-entropy oxides (HEO_x) have emerged as a novel class of materials in the last decade. They display unique properties and can incorporate multiple cations into a single crystalline structure, resulting in high configurational entropy(ΔSconfig). This high entropy, combined with the presence of oxygen vacancies, can significantly enhance the mobility of charge carriers, leading to improved catalytic performance. Moreover, these materials exhibit exceptional thermal, chemical, and structural stability, making them highly suitable for a variety of catalytic and functional applications (1) (2). Despite their potential, HEOx materials have been relatively unexplored, especially in the field of photoelectrocatalysis. This work aims to address this gap by investigating the photoelectrocatalytic behavior of these HEOx materials and optimizing their properties.

In this study, $\mathbf{(Co_{0.2}Ni_{0.2}Fe_{0.2}Cu_{0.2}Zn_{0.2})WO_4}$ was synthesized using a top-down approach and characterized using various techniques to investigate its structural and optical properties. X-ray diffraction (XRD) confirmed the formation of a single-phase monoclinic structure. UV-visible spectroscopy revealed a band gap in the visible light region, making the material suitable for photoelectrocatalytic applications. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was also performed to study its morphological features and elemental distribution.

The electrocatalytic activity for the oxygen evolution reaction (OER) was assessed for the material using electrochemical techniques. Cyclic Voltammetry (CV) revealed a reversible redox reaction comparable to Cobalt and nickel based OER catalysts. Linear Sweep Voltammetry (LSV) demonstrated high catalytic activity, a current density of 10 $mA \cdot cm^2$ with an overpotential of 420 mV. Electrochemical Impedance Spectroscopy (EIS) was also employed to measure charge transfer resistance. These results were also compared with the individual metal tungstate (MWO_4), synthesized using the same process as HEO_x. The photoactivity was confirmed by observing photocurrent generation when the material was deposited on glassy carbon and illuminated with light at an intensity of 1.3 $W \cdot cm^2$. In addition to this photoactivity, the band gap of HEO_x material situated in the visible region of the solar spectrum can enable efficient solar energy conversion to hydrogen.

References

(1) B. L. Musicó *et al.*, "The emergent field of high entropy oxides: Design, prospects, challenges, and opportunities for tailoring material properties," *APL Mater.*, vol. 8, no. 4, Apr. 2020, doi: 10.1063/5.0003149.
(2) Y. Sun and S. Dai, "High-entropy materials for catalysis: A new frontier," *Sci. Adv.*, vol. 7, no. 20, May 2021, doi: 10.1126/sciadv.abg1600.

HKUST-1/TiO_2 chitosan beads as photocatalyst for green hydrogen generation by photocatalysis

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To address the issues of energy shortage and environmental pollution caused by the fossil fuels consumption, the use of carbon-free energy sources receives increasing attention. In this context, the conversion of renewable solar energy into hydrogen (H_2) via photocatalysis received significant attention due to its low cost and easy implementation, making it an attractive alternative for producing green fuels with net-zero emissions.

H_2 generation by photocatalysis relies on the activation of a photocatalyst by light, resulting in the formation of electron/hole pairs in the conduction and valence bands, respectively. Subsequently, the photo-induced electrons react with H^+ ions from water to produce H_2, while the photo-induced holes react with a scavenger, typically a hydrogen donor like an alcohol, added to the water to prevent water oxidation and to reduce the recombination rate.

A key factor in achieving high-performance H_2 production is the development of new efficient photocatalyst through the design of photocatalytic hybrid systems able to absorb visible light and having fast charge carrier separation and transfer. To address this issue, high photoactive composite based on HKUST-1 (copper Metal Organic Framework)/TiO_2 proved a high H_2 production efficiency of 5.11 mmol/g/h after 4h under a Xenon lamp (300W). However, the form of the photocatalyst, such as free powder or supported materials, is also a challenge to facilitate its use over several cycles. Therefore, the aim of this work was to develop supported materials to facilitate the reuse and the collection of the HKUST-1/TiO_2.

In this study, millimeter-sized HKUST-1/TiO_2 chitosan (CS) were synthesized via a three-step process. The HKUST-1/TiO_2 CS beads have good spherical appearances and uniform size with a diameter of 3.8 ± 0.1 mm for hydrated beads and 1.3 ± 0.1 mm for dried beads. No modification of beads size was recorded with the variation of the amount of the composite (from 0.25mg to 0.5 mg of catalyst / bead). Diffuse reflectance and Fourier-transform infrared spectroscopies assert that HKUST-1/TiO_2 is not altered by the synthesis process. Time resolved microwave conductivity characterization proves that the charge carrier dynamic has remained. Photocatalytic hydrogen production was then tested in a water/methanol mixture (1:3) with a 150 W mercury lamp as a function of the hydration and photocatalyst loading of the beads. The number of beads and their reuse were also investigated. Results demonstrated that hydrated beads are more sustainable for H_2 generation with a significantly higher hydrogen generation (459 μmol/g/h) compared to the one in dried beads (45 μmol/g/h) according to better water and hydrogen diffusion in the hydrated beads. Nevertheless, this system appears insufficient to permit the efficient diffusion of H_2 from the interior of the beads to the reaction medium, resulting in the H_2 storage within the composite beads and their floatability. The results also demonstrated that the optimum concentration of composite per bead was 0.36 mg. The highest production rate reaches 854 μmol/g/h with 4 HKUST-1/TiO_2 CS beads loaded with 0.36 mg of photocatalyst per bead. Recyclability tests reveal good durability without significant loss of efficiency.

Design of Chiral Porous bio-hybrid materials as catalysts for CO_2 conversion

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MOFs are porous crystalline hybrid materials constructed through the assembly of metal ions and organic polydentate ligands. They are highly attractive for applications including gas storage/separation, catalysis, biomedicine etc...(1) Particular attention has been paid to limit their environmental impact by privileging biocompatible MOFs. Biomolecules such as peptides are attractive building blocks to design bioMOFs which still represent only a marginal fraction of 3D MOFs discovered so far. (2) In this communication, we will present our recent results concerning the design of bioMOFs by combining inorganic nanoclusters and peptides. BioMOFs based nanocomposites are also prepared following different strategies in solution, involving the assembly of MOFs nanoparticles with a series of functionalized peptides. The structure of these materials is characterized by combining powder X-ray diffraction, solid state NMR, N_2 porosimetry, FT-IR and thermogravimetric analysis. Their chemical/thermal stability, homochirality, Lewis/ Brønsted acid-base properties, and CO_2 adsorption properties are also characterized by coupling multiple advanced characterization techniques. The catalytic performance of these materials is also currently evaluated for the CO_2 cycloaddition to epoxides. Our objective is to develop a series of bioMOFs based heterogeneous catalysts with a high chemical stability that are able to operate under ambient (room temperature (RT) and 1 bar) and eco-compatible solvent-free conditions.

(1) Ali Saad, Subharanjan Biswas, Effrosyni Gkaniatsou, Clémence Sicard, Eddy Dumas, Nicolas Menguy, and Nathalie Steunou *Chem. Mater.*, **2021**, 33, 15, 5825–5849.

(2) Effrosyni Gkaniatsou, Clémence Sicard, Rémy Ricoux, Jean-Pierre Mahy, Nathalie Steunou, Christian Serre, *Mater. Horiz.*, **2017**,4, 55-63

Development of hybrid ZnO nanostructured layers electrodeposited on high-efficiency ACIGS solar cells for enhanced photoelectrochemical CO_2 reduction

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Industrialization and economic growth have disrupted the natural carbon cycle, causing a sharp increase in atmospheric CO levels from approximately 340 ppm in the 1980s to over 425 ppm today. This alarming trend has intensified global challenges such as energy crises and climate change, underscoring the urgent need for effective CO emission reduction strategies. Photoelectrochemical (PEC) systems, inspired by natural photosynthesis, present a sustainable solution by utilizing solar energy to convert CO into valuable fuels and chemicals.This study aims to enhance PEC efficiency by integrating molecular catalysts into photovoltaic (PV) systems. Photovoltaic materials, by capturing light in the visible spectrum, can significantly enhance photocurrents, making them excellent candidates for driving PEC reactions. Building on previous work, this research focuses on embedding earth-abundant molecular catalysts into the window layers of high-efficiency $Cu(In,Ga)Se_2$ solar cells, addressing challenges to electron and proton transfer kinetics and improve selectivity of photo-CO_2 reduction reaction (photo-CO_2RR).

The approach focuses on developing hybrid ZnO nanostructured layer combined with watersoluble molecular catalysts based on metal phthalocyanine (MePcTA). These ZnO layers were fabricated using a one-step electrodeposition method, ensuring uniform catalyst distribution inside the oxide layer, while maintaining catalytic activity. Different types of ZnO-based nanostructured window layers were explored such as nanoporous sponge-like structures or ZnO nanorods (ZNR). Structural and chemical characterization such as scanning electron microscopy (SEM) combined with EDX and Raman spectroscopy confirmed the effective incorporation of cobaltsubstituted phthalocyanine (CoPcTA) into the ZnO nanostructures.

The hybrid ZnO/catalyst layers were integrated into ZnO:Al window layers of CIGS-based solar cells via a simple photoelectrochemical deposition process. The effects of layer composition, thickness, and morphology on PEC performance were systematically evaluated using linear sweep voltammetry (LSV) under AM 1.5G illumination (1 Sun) in CO-saturated organic electrolytes. Results demonstrated that hybrid ZnO structures significantly enhance PEC performance even with minimal catalyst loading. Optimized ZnO-based nanostructures enabled remarkable PEC efficiency, with the modified CIGS solar cells achieving a CO-to-CO conversion at a Faradaic efficiency of 98% and a CO selectivity of 95%. The system maintained high current densities of up to 10 mA/cm^2 at an applied potential of -1.3 V versus the saturated calomel electrode (SCE). These findings underscore the potential of hybrid ZnO layers as efficient platforms for integrating molecular catalysts into PEC systems, offering a promising pathway toward scalable and sustainable CO conversion technologies.

ORAL #42

Efficient CO_2 Electroreduction to CO Using Nanostructured Silver-based Catalysts

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The electrochemical reduction of CO_2 into value-added products presents a viable pathway to address global warming and reduce atmospheric CO_2 levels. Carbon monoxide (CO), a vital component of syngas, is a key target product with extensive industrial applications.1,2 This study investigates the performance of silver nanowires (AgNWs) as catalysts for the selective reduction of CO_2 to CO, considering their excellent electrical conductivity and interconnected nanowire network structure. AgNWs were employed in gas diffusion electrodes (GDEs) and tested in two electrochemical systems: a three-electrode flow cell and a zero-gap electrolyzer. Catalyst performance was evaluated under varying applied potentials, current densities, and CO_2 flow rates. AgNWs demonstrated CO selectivity exceeding 90% in both the flow cell (at high overpotentials -1.7V to -1.8V vs Ag/AgCl) and the zero-gap electrolyzer (at -3.2V). Stability tests revealed structural alteration at higher current densities, underscoring the need to optimize conditions for sustained catalyst integrity. The effect of CO flow rates was investigated to simulate conditions relevant to using CO from diluted sources. Results revealed that higher flow rates limited conversion efficiency, while lower flow rates enhanced conversion efficiency but reduced CO selectivity. These findings highlight the potential of AgNWs as efficient and selective catalysts for CO_2 electroreduction.

New selective PET based nanoporous membranes functionalized with MOFs for diffusion-osmotic mixing for blue energy optimization

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Blue energy is a promising renewable energy generated by harnessing the energy from the osmotic pressure difference between seawater and fresh water. This can be realized through nanoporous membranes to separate the salt ions in the water and generate electrical energy. Up to now, their major limitations in this field are the low energy efficiency of the systems and the cost and fouling of the membranes.(1)So the development of new materials and techniques is fundamental.(2)

Prospective candidates to add new physicochemical properties to the nanoporous membranes for blue energy are Metal Organic Frameworks (MOFs).(3),(4) MOFs can enhance the efficiency of the membranes by changing their surface properties. Here, we propose a reproducible way to realize model poly-ethylene terephthalate (PET) based selective single- and multi-pore membranes and functionalized with MOFs. Linkers with different moieties to enhance ionic selectivity are explored. The ultimate goal is to change parameters such as the size of the patterns and their nature (surface charge or conductivity), to lower the resistance trough the convective transport of ions and increase the efficiency in terms of power density of the system.

(1) Nijmeijer, K. et al, Sustain. Sci. Eng., **2**, 95–139 (2010)
(2) Juan Pelta et al., *Nano Res.* **15**, 9906–9920 (2022)
(3) Su et al. *Chem. Eng. Journal* **476**, 146649 (2023)
(4) Pan S et al . *Ang. Chem.*, **62**, 19 (2023)

Green Hydrogen: Paving the Way for Clean Cooking in Rural Areas

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The increasing reliance on traditional cooking methods, such as open fires and inefficient stoves, especially in developing regions like India, presents both significant environmental and health challenges. These practices, often fueled by kerosene, biomass, and coal, lead to substantial household air pollution. This not only endangers the health of millions, particularly women and children, but also contributes to deforestation and escalates carbon emissions, worsening climate change.

A promising solution to these pressing issues is the use of solar photovoltaic (PV)-based green hydrogen. This renewable energy-derived hydrogen offers a clean, sustainable alternative to conventional cooking fuels. Green hydrogen is not only a modular and scalable technology, making it an ideal option for off-grid or remote communities, but it also provides a reliable, efficient cooking solution. The hydrogen can be stored and transported with ease, ensuring that even regions lacking stable infrastructure can benefit from a consistent energy source.

Zest Clean Power Pvt. Ltd., in collaboration with IIT Bombay, has made remarkable progress in this area and have successfully demonstrated an indigenous, clean cooking system powered by green hydrogen. The system comprises an electrolyzer that generates hydrogen and a hydrogen burner designed specifically for cooking with pure hydrogen. This innovative system offers several advantages: it reduces indoor air pollution, addresses health risks associated with traditional cooking fuels, and decreases the overall carbon footprint.

The system's ability to reduce health hazards related to indoor pollution, alongside its potential to mitigate environmental damage, makes it a highly viable alternative for households. By presenting this cutting-edge technology, the talk highlights the transformative potential of green hydrogen in revolutionizing the cooking sector. It emphasizes the role that such innovations could play in creating a cleaner, healthier, and more sustainable future for communities in both developing and underdeveloped nations.

ORAL #45

Thermogalvanic Effects in Ionic Liquids: Study of New Cu(II)/Cu(I) Redox Systems

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The search for alternative energy sources accelerates as the world's needs increase. A potential source that is often wasted is low-grade heat, typically at temperatures below 150 °C, which is regularly released from industrial processes, geothermal sources, engines, and more. Thermoelectrochemical cells which work on the principle of temperature dependency of redox reactions are a possible way to recycle this heat (1). Combined with ionic liquids as electrolytes, stable systems operating in large ranges of temperatures with simple designs and high thermoelectric coefficients can be constructed (2). One major challenge in this field is to find abundant and cheap materials to increase the economic feasibility.

In this work, we propose and explore copper(I) and copper(II) complexes as promising redox species in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMIM.TFSI) ionic liquid through experiments and density functional theory (DFT) calculations. Various ligands were tested as complexation agents for increased stability of the copper ions, and the obtained solutions were studied by spectral and electrochemical methods.

With commercial Cu(I)(dmp)2 and Cu(II)(dmp)2 complexes in pure EMIM.TFSI, Propylene Carbonate (PC) and their mixtures, the Seebeck coefficients (Se) in the range of -0.7 to -1 mV/K, and maximum non-convective power densities in the range of 1.05 - 4.4610^{-2} μW/cm^2 were measured. In the presence of sulfobetaine-copper(I and II) complexes in EMIM.TFSI, Se in the ranges of -1.5 to -1.8 mV/K and maximum non-convective power densities in the ranges of 1.3 - 1.710^{-4} μW/cm^2 were obtained. It was also found that water addition had a significant effect on this system, with the preliminary results showing Se ˜ -3.5 mV/K and a maximum non-convective power density of 3.1010^{-4} μW/cm^2 in hydrated EMIM.TFSI. DFT calculations provided insight into the complexation of Cu(I and II) ions with sulfobetaine species and water, highlighting mechanisms behind the favored ligands for different oxidation states. In light of these findings, Cu(I and II) complexes were identified as a cost-effective redox species with significant potential for thermoelectrochemical applications.

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References

(1) Kristine Laws, Mark A. Buckingham, Matthew Farleigh, Michelle Ma, and Leigh Aldous,”High Seebeck coefficient thermogalvanic cells via the solvent-sensitive charge additivity of cobalt 1,8-diaminosarcophagine”, Chem. Commun., 2023, 59, 2323, DOI: 10.1039/d2cc05413b
(2) Wellington D. G. Gon¸calves, Cintia Caspers, Jairton Dupont, and Pedro Migowski, ”Ionicliquids for thermoelectrochemical energy generation,” Current Opinion in Green and Sustainable Chemistry 2020, 26:100404, doi.org/10.1016/j.cogsc.2020.100404

Thermogalvanic energy conversion improvement in ionic liquids: redox solvation and coordination chemistry

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Thermogalvanic cells (or thermocells) utilize a temperature difference across the electrodes immersed in an electrolyte solution to drive the electrochemical (redox) reactions that generate an electric potential and current. Solid thermoelectric devices, on the other hand, function as thermodynamic engines to directly convert heat into electricity or vice versa. For both systems, the first indicator of the thermal-to-electric energy conversion capacity is the materials' Seebeck coefficient; i.e., the ratio between the applied thermal energy (DT) and the extracted electric energy (DV).

Among different types of thermocells, those made with room temperature ionic liquids not only have high Seebeck coefficient but also present technologically and environmentally desirable properties: e.g., a wide electrochemical range of stability, thermal stability (> 200 °C), low toxicity and volatility, making this class of devices greener and more sustainable. It has been shown that the primary factor affecting the reaction potential in ionic liquids resides in the close vicinity of the redox pair near the electrode surfaces, more so than the liquid medium itself. In the present study we take a closer look at the effect of solvated water molecules in on a bare ion redox pair of europium ($Eu^{3+/2+}$) and a strongly complexed cobalt, $(Co(2,2'\text{-bipyridine})3)^{3+/2+}$ in 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMI-TFSI) in the range of H_2O content between < 500 and 16000 ppm. It is found that depending on the redox species, water molecules can coordinate with the metal ions, leading to marked changes in their structural and electrochemical behavior of the complexes. In the long term, exploring how to utilise the solvation and coordination chemistry of redox species will help advance our understanding of the fundamentals of the thermogalvanic effect in complex media, and simultaneously, enable the fine-tuning of the thermocell efficiency toward their industrial exploitations.

ORAL #47

HER as a major vulnerability of TiO_2-based aqueous batteries. Could this system be an asset for electrocatalysis?

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Although the current market is dominated by Li-ion technology, aqueous batteries remain widely studied in the hope of addressing issues related to organic electrolytes(1). While promising, the aqueous approach brings new challenges, the most significant being water electrolysis(1). Indeed, the insertion/adsorption reactions are limited by the **hydrogen evolution reaction** (**HER**), which constrains the electrode's capacity and stability(2). Furthermore, **insertion reactions can alter the material** in terms of crystalline structure, electronic properties, and proton adsorption capacity. These changes may enhance **the catalytic activity for HER**(3– 5). The objective is therefore to study the **water/electrode interface to determine the impact of cation insertion on the electrode's HER activity and its stability**. This information will be valuable in the field of batteries, to better understand how to inhibit HER, as well as in the field of electrolyzers, to explore new catalytic pathways for HER without noble metals.

This fundamental work focuses on nanosized anatase TiO_2 electrode, originally studied as a negative electrode candidate in aqueous batteries(6,7). A sol-gel process combined with hybrid self-assembly via dip-coating deposition of a nanostructured TiO_2 film(8) enables the production of an additive-free thin-film sample, suitable for high-precision in situ techniques such as **spectroscopic ellipsometry** or **Quartz Crystal Microbalance**.

Modulating the selected electrolyte initially demonstrated the relationship between insertion reactions in TiO_2 ($xC^+ + xe^- + TiO_2 \rightarrow C_xTiO_2$) and HER ($2AH + 2e^- \rightarrow H_2 + 2A^-$). Adding an XCl^-type salt (X = Li, Na, K) to a pH 9 buffer solution ($C_4H_{11}NO_3H^+/C_4H_{11}NO_3$, 1M) enables the variation of proton transport at the interface, activating both reactions (TiO_2: -2.18 V at 10mA/cm^2 **vs** $H_{0.3}TiO_2$: -1.71 V at 10mA/cm^2). Studying the H^+/Li^+ insertion competition further revealed that the nature of the inserted cation influences HER ($H_{0.3}TiO_2$: -1.71 V at 10mA/cm^2 **vs** $Li_{0.2}TiO_2$: -1.53 mV at 10mA/cm^2). The role and accessibility of protons appear to be the key factors in the observed phenomenon.

Currently, an *in situ* study **EQCM/ac-EQCM** is underway to better understand the electrode/electrolyte dynamics associated with insertion mechanisms and HER processes. *In situ* ICP is being considered to investigate electrode degradation during cycling. Finally, the evolution of the local pH within the porosity will be mapped using **correlative spectroscopy**.

References

(1) Ahn, H. *Commun Mater* **2023**, *4* (1), 1–19
(2) Makivic, N. Thèse de Doctorat d'Electrochimie Moléculaire, University of Paris
(3) Li, G. *J. Am. Chem. Soc.* **2017**, *139* (45), 16194–16200
(4) Spencer, M. A. *The Journal of Chemical Physics* **2022**, *156* (6), 064704
(5) Shokhen, V. *FlatChem* **2019**, *14*, 100086
(6) Makivic, N. Cho, *J.-Y. Chem. Mater.* **2021**, 33 (9), 3436–3448.
(7) Kim, Y.-S. Kriegel, S. *J. Phys. Chem. C* **2017**, 121 (19), 10325–10335.
(8) Bass, J. D. *J. Am. Chem. Soc.* **2008**, 130 (25), 7882–7897

ORAL #48

Non-linear Optical Studies of Water Structure in the Electrical Double Layer at the Electrode-Electrolyte Interface

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Water molecules are a key factor in determining the efficiency and kinetics of sustainable green energy storage and conversion systems (hydrogen-oxygen fuel cells and electrolyzers). The molecular details of the electrochemical interface are governed by the formation of the electrical double layer (EDL) in the presence of ions and aqueous solvent molecules. Deciphering the mechanism of water and its aqueous adsorbates' interplay in this dynamic electrode-electrolyte junction under potential-controlled conditions could not only sharpen the comprehension of water's structures and orientations in different electrolyte systems but also advance the performance of relevant electrocatalytic events (hydrogen evolution reaction HER and oxygen evolution reaction OER) (1). With the symmetry breaking of the molecular arrangement at the electrodeelectrolyte interface, second harmonic generation (SHG) spectroscopy is a molecular-specific and inherently interface-sensitive non-linear optical spectroscopy evinced to be specifically wellsuited for *in situ* coupling to an electrochemical cell elucidating the electronic properties of electrodes. In particular, the SHG signal could reveal the surface direct current field strength (2).

In this study, we successfully designed and fabricated a novel external thin-layer spectroelectrochemical cell for *in situ* coupling to optical spectroscopic setups. The potential dependence of non-linear optical spectroscopies from platinum (Pt) electrodes was examined for aqueous electrolyte solutions ranging from acidic to basic media. Some key parameters, such as pH and electrolyte composition, were investigated to understand their influence on the behavior of water at the Pt/charged water interface. The results show that the SHG signal from the polycrystalline Pt surface in both acidic and basic media exhibits a drastic increase during the electrochemical deposition of hydrogen. This phenomenon is attributed to the charge transfer resulting from the chemisorption of the hydrogen species (Pt + H^+ + e^- Pt-H*ad*). Besides, an increasing pattern of the SHG signal in H_2SO_4 solutions over the potentials corresponding to the double-layer charging layer (EDL) was also observed and ascribed to the specific adsorption of (bi)sulfate ions before experiencing a decreasing tendency due to the formation of PtO_x monolayer of the Pt surface. These findings are in line with previous results (3). Our ultimate objective is to differentiate the interfacial information of water molecules in the two sublayers of the EDL (the Stern and the diffuse layer) thanks to the usage of sum-frequency generation (SFG). The SFG vibrational spectra could allow us to differentiate the spectral fingerprint of hydrogen-bonded water molecules (3200-3400 cm^{-1}) and free-OH surface groups (3670 cm^{-1}), and study their behavior as a function of the potential applied to the Pt electrodes.

References

(1) Pham, B-L.; Ranjbari, A., Tadjeddine, A.; Dalstein, L.; Humbert, C. *Symmetry* **2024** (submitted)
(2) Dalstein, L.; Chiang, K-Y.; Wen, Y-C. *J. Phys. Chem. Lett.* **2019**, *10*, 5200-5205.
(3) J. Campbell, D.; M. Corn, R. *J. Phys. Chem.* **1988**, *20, 92*, 5796-5800

ORAL #49

Design of alloy-type nickel-copper nanoparticles by organometallic approach for the electrocatalytic hydrogen evolution reaction

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The hydrogen evolution reaction (HER) is one of the most widely studied reactions in electrochemistry, electrocatalysis and/or photoelectrocatalysis (1). For electrochemical devices, electrode materials containing nickel and copper are the most attractive in the transition metal series (2), due to their accessibility and their electronic and chemical properties.

Given our expertise in the synthesis of metal nanoparticles (NPs) by the organometallic approach (3), we have investigated NiCu NPs synthesized by this approach as cathode material for anion exchange membrane water electrolysis application. Optimizing the synthesis conditions allowed us to achieve alloy-type NiCu NPs with an average size of *ca*. 4.2±0.5 nm as indicated by TEM analysis (figure 1). Other state-of-the-art techniques (ICP, IR-FT, HRTEM-EDX, XPS, XRD, XANES, EXAFS) permitted to have a precise overview of the other structural properties of these NiCu NPs. Then, they were deposited onto a carbon support (Ketjentblack) for evaluation in the electroproduction of hydrogen by a range of electrochemical methods. This novel NiCu electrocatalyst exhibited a good catalytic activity in alkaline environment, displaying an overpotential of 273 mV at the current density of -10 mA cm^{-2} and a good stability within 24 h as well.

References

(1) J. Zhu, L. S. Hu, P. X. Zhao, L. Y. S. Lee, K. Y. Wong, *Chem. Rev*. **2020**, 120, 851– 918.
(2) C. Wei, Y. Sun, G. G. Scherer, A. C. Fisher, M. Sherburne, J. W. Ager, Z. J. Xu. *J. Am. Chem. Soc*. **2020**, 142, 7765– 7775.
(3) C. Amiens, D. Ciuculescu-Pradines, K. Philippot, Coord. *Chem. Rev.*, **2016**, 308, 409–432.
(4) T. Straistari, N. Romero, J. Esvan, M. Gil-Sepulcre, C. Amiens, O. Rüdiger, S. DeBeer, D. Jones, J. Rozière, S. Cavaliere, K. Philippot, *manuscript in preparation*.

New {Mo_3S_x}-based electrocatalysts for Hydrogen Evolution Reaction

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Releasing new ”green” energy sources with low carbon footprint is the actual driving force for

numerous studies. Besides renewables, hydrogen is a clean energy vector that can be obtained through different processes. Water Electrolysis, namely Proton Exchange Membrane Water Electrolysis (PEMWE), is the most efficient technique for green hydrogen production since it can be easily coupled to renewable source of electricity. However, using expensive and scarce Platinum Group Metals (PGMs)-based electrocatalysts represents an important drawback (1-3). In this communication, we will reveal a new class of PGM-free electrocatalyst for Hydrogen Evolution Reaction (HER). These electrocatalysts were obtained through two different approaches while maintaining the main principle: coupling the molecular catalyst {Mo_3S_x} to polyoxometalates (POM), leading to WO_n-Mo_3S_x materials. This is considered a successful extrapolation of molecular approaches developing high performing POM-{Mo_3S_4} electrocatalysts (4,5). In addition to their synthesis and thorough physicochemical

characterizations, these electrocatalysts were studied in a three-electrode cell

through Linear Sweep Voltammetry, Cyclic Voltammetry and Electrochemical Impedance Spectroscopy. Further investigations at the active site scale through Atomic Force Microscopy (AFM) or AFM coupled to Scanning Electrochemical Microscopy were conducted. Implementing the best performing catalysts in real operating conditions PEM cell is the final aim of this study.

(1) M. Chatenet et al., Chem. Soc. Rev., 2022, 51, 4583.
(2) J. Al Cheikh et al., Mater. Adv., 2020, 1, 430.
(3) A. Pineiro Garcia et al., ACS Sustain. Chem. Eng., 2023, 11, 7641.
(4) J. Tourneur et al., J. Am. Chem. Soc., 2019, 141, 11954.
(5) Y. Smortsova et al., Chem. – A Eur. J., 2021, 27, 17094.

Photo-thermo catalysis: a strategy for boosting catalytic performances

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The sun is an ideal renewable energy source to be integrated into catalytic processes to make them more sustainable and cost-effective. Cooperative effects between thermal and photonic excitations in catalysis emerged in the last decade for a span of reactions, driven by the need of accelerating reaction rates (shorter processing times and higher yields), enhancing selectivity and catalyst stability and/or reaching same yields at milder temperature/pressure conditions (1).

We aim at showing the benefit that accrues from a dual photonic/thermal excitation of semiconductor catalysts using several reactions of interest, namely the gas phase dehydrogenation of formic acid (FA) to H_2, the synthesis of NH_3 from N_2 and H_2, the hydrogenation of CO_2 to CH_4, and the CO preferential oxidation (CO-PROX) in H_2-rich streams. The photo-thermo catalytic tests were realized in a continuous-flow gas-phase reactor (Harrick Sci. HVC-MRA 5 reaction chamber), with control of the photonic excitation at 365 nm or 450 nm (0-365 mW/cm^2) and the temperature (< 350 °C).

Applying a dual photonic/thermal excitation to Ru/TiO_2 catalysts boosted the FA dehydrogenation to H_2, and the higher the UV-A irradiance, the stronger the H_2 production. The dual excitation not only drives the reaction at milder temperature while keeping similar H_2 productions to those in the dark, but also enhances the H_2 selectivity *vs.* CO, the effect being irradiance-dependent. The change in conversion and selectivity suggested the implication of light-excited electrons in the non-plasmonic Ru nanoparticles through an alternative low-energy transition state with reduced apparent energy activation (as derived from Arrhenius plots), rather than thermalization with localized-heat delivery.

A span of semi-conductor and isolating supports for Ru nanoparticles was used to get deeper understanding on the catalytic behavior under dual photonic/thermal excitation. In particular, $Ru/g\text{-}C_3N_4$ was shown to be a remarkable photo-thermo catalyst that outperforms the Ru/TiO_2 in terms of H_2 production, and with the ability to produce selectively larger CO-free flows of H_2. A strong irradiance-dependent photo-enhancement was achieved in the 50-150 °C temperature range. Key-factors were identified, *ie.* the Ru particle size and the beneficial surface chemistry of the $g\text{-}C_3N_4$ support, that inhibits completely the CO formation.

Similarly, a dual UV-A photonic/thermal excitation also boosted the NH_3 synthesis rates from N_2 and H_2 on both Ru- and Fe-based TiO_2 catalysts, and allowed to drive the NH_3 synthesis at a lower temperature compared to dark catalysis. The photo-enhancement was related to a decrease in the apparent activation energy for Ru/TiO_2, while it remained constant for $Fe\text{-}TiO_2$. Different reaction mechanisms were therefore proposed for each catalytic system, *via* the formation of light-excited (hot) electrons in metallic Ru (electron-driven mechanism), and *via* a light-induced localized heat-delivery mechanism in $Fe\text{-}TiO_2$. Additionally, while Ru/TiO_2 deactivated on-stream, stable rates were achieved on $Fe\text{-}TiO_2$ composites.

To summarize, using also the CO_2 hydrogenation to CH_4 and the CO preferential oxidation (CO-PROX) in H_2-rich streams, we aim at highlighting the high-prospect strategy of a dual photonic/thermal excitation in heterogeneous catalysis.

(1) N. Keller, J. Ivanez, J. Highfield, A.M. Ruppert, Appl. Catal. B: Environ. 2021, 296, 120320.

ORAL #52

Electrochemical oxidation of ammonia from wastewater treatment plant sludges

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Electrolysis of water with renewable electricity is a preferable solution for hydrogen production than hydrocarbon reforming, because it emits much less CO_2. An alternative electrochemical process that requires less energy is ammonia electrolysis, i.e. water reduction coupled with ammonia oxidation.

Ammonia is a waste product derived from human urine and is present in significant quantities in sewage collected by wastewater treatment plants (WWTPs). It is converted to gaseous nitrogen (N_2) through a two-step biological treatment: aerobic nitrification to convert ammonium to nitrate, followed by anoxic denitrification to reduce nitrate to N_2. This biological treatment of nitrogen is the main source of energy consumption in WWTPs (due to the forced aeration required during the first stage). In addition, it has an efficiency of 70% and results in the emission of N_2O (~5%), a potent greenhouse gas (240 times more than CO_2). An alternative that could convert ammonia to N_2 in a single step would reduce energy and chemical costs, as well as the environmentally harmful intermediates in the nitrogen cycle (nitrates, nitrites, nitrous oxide).

Our aim is to study the feasibility of electrochemical oxidation of ammonia contained in an ammonia-rich sludge from a WWTP, while producing H_2. This sludge comes from SIAAP, the largest operator of wastewater treatment plants in the Paris region. It contains ~60 mmol L^{-1} of ammonia. Platinum was chosen because it is a very efficient catalyst for the electrooxidation of ammonia. However, this catalytic reaction must take place at high pH (> 13), which implies alkalinization of the sludge.

Cyclic voltammetry was performed with model ammonia solutions and the alkalinized sludge at a platinized platinum electrode and compared with water oxidation under the same conditions. Alkalinization of the sludge causes discoloration and sedimentation of suspended solids. However, the electrochemical response is comparable to that of model ammonia solutions. Water reduction and ammonia oxidation (on a Pt mesh) need a cell potential of 0.64 V (at 10 mA cm^{-2}), much lower than for water oxidation (1.79 V). Analysis of the gas evolved at the anode during electrolysis showed that faradic efficiencies of ~80% for the formation of N_2 can be easily achieved. These results are encouraging and could be improved by using modified Pt catalysts to further enhance N_2 production.

ORAL #53

Innovative transition metal-based catalysts for the dehydrogenation of a LOHC

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My work focuses on designing a catalyst capable of promoting both the hydrogenation and the dehydrogenation reactions for a Liquid Organic Hydrogen Carrier. A LOHC is a system composed of a hydrogen-rich organic molecule and a lean-hydrogen molecule, linked together by catalytic de-hydrogenation reactions. LOHC systems allow a safer storage and transportation of H_2 using less energy than current methods (Liquified H_2, H_2 pressurized tanks) in the general context of the hydrogen economy. They are also safer as they are liquid at room temperature, ensuring better storage and transportation conditions.

Beyond that, most of the LOHC currently under development or next to the market are (poly)cyclic aromatic molecules coming from petroleum, some being expensive and toxic. While they present a very high hydrogen loading and properties similar to the current fuels used for transportation, they also have issues concerning the thermodynamic of hydrogenation or dehydrogenation and these reactions lead to variety of products (lack of selectivity).

That is why we propose here, as an alternative, circular compounds, which may be biosourced as possible organic hydrogen carriers. One of the best examples is formic acid with, admittedly, a lower hydrogen loading (4.4 wt%) but much more favorable thermodynamics. Moreover, formic acid is part of the CO_2 circular economy.

The development of an efficient catalyst is essential to ensure the development of this kind of LOHC. While molecular catalysts have shown great activity, they suffer from deactivation (degradation) issues and are difficult to recover. A solution to these issues is the use of heterogeneous solid catalysts, with metals supported on a carbon or oxide support. Unfortunately, most of these catalysts either use rare noble metals (Ir, Ru, Au...) or are not very efficient. Lately, the arrival of new class of catalysts, namely Single-Atom Catalysts (SACs), have pushed the limits of heterogeneous catalysis with a metal efficiency capable of reaching 100% and with a much lower metal content than the previous catalysts. These catalysts are often described to be the frontier between homogeneous molecular catalysts and heterogeneous solid catalysts. The literature has taken an interest in cobalt SACs, showing promising activity. We propose to explore the development of manganese catalysts as an alternative to cobalt, using the Zeolite Imidazole Framework decomposition technique. This technique consists in synthesizing ZIF Metal Organic Frameworks (MOF) that are then pyrolyzed at high temperature (800 – 1000 °C), creating isolated metal atoms anchored in a carbon support through nitrogen atoms. This type of material present a real versatility in term of synthesis, allowing tuning the activity. A comparison of the Mn and Co catalysts will be presented for the dehydrogenation of formic acid, along with some relevant characterizations allowing understanding the reactivity of the catalysts. A focus will be made on the formic acid / CO_2 + H_2 system.

Experimental and Numerical Investigation of Dual-Fuel Hydrogen/Diesel Combustion: Effects of Diesel Mass, Injection Timing Strategies, and Engine Speed on Performance and NO_x Emissions in a Single-Cylinder Engine

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This study investigates the combustion processes of hydrogen-diesel dual-fuel (DF) operation in a single-cylinder research engine, integrating findings from two complementary research efforts. A combination of experimental and numerical analyses was used to examine the effects of fuel injection strategies, hydrogen enrichment, and exhaust gas recirculation (EGR) on engine performance and emissions. The engine was tested at two speeds (1500 and 2000 RPM) and a constant brake mean effective pressure (BMEP) of 5 bar, with and without EGR. Hydrogen was introduced via port fuel injection (PFI), while diesel was directly injected into the cylinder through single and dual injection strategies.

The numerical simulations were conducted using a calibrated GT-SUITE model, validated through the Three Pressure Analysis (TPA) method and experimental data. Key performance metrics, including in-cylinder pressure traces, ignition delays, heat release rates, and NO_x emissions, were predicted with high accuracy. Parametric studies were performed to evaluate the influence of diesel injection mass distribution and timing strategies on combustion behavior.

In the first phase, results indicated that the distribution of diesel fuel between pilot and main injections did not significantly impact ignition delay times but strongly influenced combustion duration and NO_x emissions. Increasing the diesel pilot injection proportion raised NO_x emissions, while the inclusion of EGR effectively reduced NO_x levels without compromising overall engine efficiency. This highlighted the potential for controlling emissions through careful manipulation of injection parameters and EGR rates.

In the second phase, a reduction in diesel mass injection to 0.82 mg (a 50% reduction) proved to be an effective strategy for enhancing combustion performance in hydrogen-enriched systems.

This reduction increased the laminar flame speed, minimized unburned hydrogen fuel, and improved combustion efficiency. Advancing diesel injection timing further enhanced indicated mean effective pressure (IMEP) and efficiency, whereas retarding the injection timing reduced NO_x emissions at the expense of performance. A balance was achieved through optimized injection timing and EGR integration, which significantly curtailed NO_x emissions while maintaining engine efficiency.

Overall, the findings reveal the critical interplay between injection strategies, hydrogen enrichment, and EGR in optimizing dual-fuel engine operation. Reducing diesel mass injection, coupled with appropriate injection timing and EGR strategies, enables cleaner and more efficient combustion. This research underscores the potential of hydrogen-diesel DF systems in supporting the energy transition by reducing reliance on fossil fuels and lowering harmful emissions. Future work should focus on refining injection parameters and ensuring safety in hydrogenenriched environments to maximize the sustainability and performance of dual-fuel engines.

Prospects for hydrogen-powered internal combustion engines to reduce emissions in the transport sector: what are the main challenges in terms of multi-level energy governance?

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As cities, towns and local actors in the *Ile-de-France* upgrade their policies to tackle the urgent threat of climate change by accelerating their energy transitions, investments in transport systems are increasingly being determined by the choice of technologies used to operate vehicles. While the NESMO project examined a diversity of energy sources for municipal vehicles, it focused on thermal hydrogen engines which, from a Life Cycle Analysis point of view (emissions produced by battery manufacturing and during vehicle use), constitute a promising alternative to fossil fuels. In order for hydrogen vehicles to be understood and then adopted by municipalities as an integral part of their municipal vehicle fleet, an interdisciplinary approach has been necessary. This research project brought together the scientific modeling of a new type of hydrogen engine with the social sciences' understanding of the functioning of municipal policy-making within the context of multilevel energy governance in the *Ile-de-France* region. At a time when the impacts of climate change are accelerating around the world and the window of opportunity to contain its worst effects is rapidly closing, science cannot be confined to the laboratory. The social sciences dimension of the NESMO project has endeavored to translate complex new technologies, such as the thermal hydrogen engine, into terms that are familiar to the law-maker and elected officials.

From the social sciences perspective, NESMO has involved an in-depth sampling of municipal governance in the *Ile-de-France* region, with a geographical focus on the *plateau de Saclay*, located in the north of *Essonne* and the south-east of *Yvelines*. The objective has been be to determine: (i) how energy policies are selected and implemented according to variations in administrative structures/hierarchies and access to resources, (ii) how different administrative/budgetary structures may work together to influence best practices on a local scale, and (iii) what are the optimal policy tools for implementing a new technology, such as hydrogen thermal engines, across sample cities, taking into account differences in administrative capacities and resources. One purpose of the sample selection has been to determine the capacity of municipalities to work together to achieve environmentally friendly transportation solutions. Sample municipalities were selected according to criteria such as population size, budgetary capacity, and commitment to diversifying carbon-neutral transportation solutions. The twenty municipalities that were selected were also representative of the different types of administrative structures/hierarchies in place within the region. The capital city, Paris, served as a point of policy comparison to the other municipalities and towns in the sample given its stated commitment to a diversified, carbon-neutral transportation system.

Investigating the Potential of Renewable Energy Deployment for Energy Security and Resilience in Times of Climate and Geopolitical Instability

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In the context of geopolitical conflicts, the energy systems of affected countries can be subject to numerous destabilizations. Disruptions in the import and export of energy commodities, caused by economic sanctions in the countries concerned, can have severe economic consequences and jeopardize the energy security of importing countries. More broadly, these events can also lead to destabilizations and price fluctuations on the energy markets and those that are strongly interconnected to them. Consequently, the energy security of the concerned countries, as well as that of countries reliant on their electricity supply, is often compromised. These conditions may affect consumption patterns, underscoring the need to explore how consumers are impacted and can adjust to these disruptions, potentially reshaping their energy practices in response to ongoing uncertainties and instabilities. Faced with these challenges, this article explores the relationship between renewable energy deployment and energy security in the context of geopolitical disruption. Our research then examines how the integration of renewable energies could modulate the economic consequences of these disruptions in terms of electricity prices. The aim is to assess whether these technologies can effectively strengthen the resilience and recovery of electricity prices and ensure improved continuity of electricity supply. To study the relationships between production and price variables, our methodology employs time series analysis alongside a regression model and econometric tools, using electricity production data from renewables, fossil, and nuclear sources, spot prices (day-ahead) of electricity, gas prices, and CO_2 emissions rates. It is applied to the cases of Germany and France, in the context of the RussiaUkraine War. The aim is to compare two different kinds of electricity mix in Europe, facing a gas disruption in the context of this geopolitical shock. This modeling enables us to track how geopolitical shocks spread through energy systems and markets and to examine the resulting dynamics. The objective is to investigate the link between renewable energy deployment and energy security in affected countries. This method is then intended to be applied to other crisis and uncertainty events, with different timeframes (such as extreme weather events), in order to assess the dynamics of electricity prices Ultimately, this research allows us to outline potential resilience strategies based on our findings, contributing to a deeper understanding of effective responses to these global challenges.

Structural Factors and Demand: Levers for Accelerating the Energy Transition

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Accelerating the energy transition is crucial for Small Island Developing States (SIDS), whose dependence on hydrocarbons, energy price volatility, and ecological vulnerability require a rapid and sustainable transformation of their energy systems. This research analyzes the dynamics influencing this process and proposes recommendations for energy policies adapted to local specificities and the economic and social objectives of these territories. With its high potential for renewable energy and robust economic growth, the Dominican Republic serves as a relevant case study.

This research combines quantitative and qualitative analyses to assess the viability of Dominican energy scenarios for 2036 (also extrapolated to 2050) and their impacts on the key challenges faced by SIDS: economic stability, sustainable development, and energy security. Using the “Regional Energy Planning Model”, it estimates the feasibility of introducing renewable technologies and identifies the factors influencing their adoption, through economic, historical, and sociological analysis. This approach highlights the links between energy resource allocation and multidimensional challenges, offering recommendations tailored to the Dominican context for a fair and effective energy transition.

The study shows that the Dominican energy strategy, based on supply-oriented tools -insufficient to capture local specificities-, hinders the country’s ability to achieve its transition and development goals. Integrating structural factors and demand-sided ones into energy policies could promote a just energy transition and accelerate its progress, particularly through the optimization of resources by creating synergies between energy and development. However, although these factors are emphasized in the literature, each academic discipline tends to analyze them separately, leading to fragmented knowledge and preventing an integrated view of their systemic impact. Further research is needed to structure and quantify these relationships to better guide energy strategies toward greater efficiency and resilience.

This study thus demonstrates the importance of an integrated approach to accelerating the energy transition in SIDS while considering local specificities. It proposes adapted solutions and paves the way for a quantitative extension to measure the dynamics of the energy system and its relationship with economic, social, and ecological spheres.

ORAL #58

Rare Earth Elements in Africa

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The African continent is not rich in rare earth elements. The African reserves of rare earths are estimated to be less than 3% of global reserves. This is relatively small compared to resourcerich nations like China, Vietnam and Brazil, which comprise 75 % of the world's reserves. The misbelief that rare earths are largely present in African soil stems from confusion between rare earths and rare metals. Rare metals refer to metals with a low average abundance in the Earth's crust, like antimony or cobalt, while rare earth elements are a group of seventeen elements with similar chemical and physical properties. These unique properties make rare earth elements (REEs) essential raw minerals for high technologies. Four of them (neodymium, praseodymium, dysprosium and terbium) are core components of permanent magnets. Small permanent magnets can be found in consumer electronics, while larger magnets are used in wind turbine generators and electric vehicle motors. The use of REEs in low-carbon technology is driving the global demand for these minerals in the context of energy transition. Nonetheless, the production of REEs is highly concentrated in China, mainly in the processing industry and further on the supply chain for the manufacturing of magnets. In 2010, a rare earth crisis erupted after a diplomatic incident between China and Japan. The crisis caused a global shortage of rare earths and skyrocketing prices. Since this episode, China has been accused of manipulating the market in order to keep its dominant position. Resulting in global concern about supply chain vulnerability for dependent industries, notably in Western countries and Japan. Parallelly, countries with smaller reserves but with mining histories have intensified the extracted volumes to keep up with growing demand and a new supply chain is developing outside China. For the past decade, the literature has been analysing the market dynamics, from China's policy influence to global demand for the energy transition. Yet, the African continent remains a blind spot in the study of rare earth elements, even though several projects are reaching a mature stage. This paper aims to fill this gap by describing ongoing rare earth projects in Africa. We then draw on this description to develop an analysis of the potential benefit for African countries in entering the market and press challenges regarding the environmental and social impact of rare earth extraction.

ABSTRACTS OF THE POSTER PRESENTATIONS

A Comparison of Direct Water Injection with Membrane Humidifier for Proton Exchange Membrane Fuel Cells Humification

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Effective water management is essential for optimal performance of fuel cells. For this reason, many vehicle systems use a membrane humidifier, a passive device that humidifies the air before the cathode inlet. Although they offer good performance, humidifiers are voluminous, costly and fragile, hence the desire to find an alternative. Direct water injection could be an option, although this method lacks maturity. It consists in injecting liquid water as a spray in the dry heated air coming out from the compressor. Preliminary studies have been published on the humidification capacity of this alternative without offering any clear comparison with state-of-the-art methods. This work focuses on the evaluation of direct water injection and its performance compared to membrane humidifier selected as a reference.

Two architectures were experimentally tested to humidify an industrial 2 kW short stack made up of 20 cells of 150 cm^2 each. For the reference architecture, the inlet air is humidified with a commercial membrane humidifier. For the direct water injection architecture, a pneumatic nozzle was selected to generate a fine spray in the air flow with a Sauter mean diameter of about 20 μm. Initial performance were compared over the entire range of current based on polarisation curves. Then, the influence of various parameters impacting water management was studied, such as the temperature, the gas stoichiometry and the water injection flow rate.

The experimental results obtained confirm the feasibility of humidifying the fuel cell using direct water injection. The difference in performance compared with the use of a membrane humidifier depends on the operating conditions. Larger in demanding humidification conditions, the voltage drop was limited to 4% (30 mV per cell) at 1 A/cm2 (1,8 bara, 80 °C). The heat of compression used to evaporate the injected liquid water in the case of DWI being limited, a mix of liquid and vapour water enters the fuel cell whereas only vapour is present when a humidifier is used. Our experiments showed moreover that the evaporation process is slowed down by the agglomeration of droplets, which reduces the exchange surface area, resulting in less effective membrane humidification.

Our work highlights the potential of this promising method considering the potential gains in cost, space, and durability. Opportunities for optimisation have been identified that should offset the slight performance decrease when compared to conventional membrane humidifiers, known to be fragile, cumbersome and expensive.

Abundant electrocatalysts for H_2 generation using water electrolyzers

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The use of renewable energy sources such as solar and wind is a crucial step towards a sustainable future. These renewable energy sources offer a cost-effective and environmentally friendly alternative to fossil fuels. However, their intermittency and the high cost and scarcity of materials used in technologies like Proton Exchange Membrane (PEM) Water Electrolyzers to produce green H_2 remain a significant challenge.. The use of noble metal-based electro-catalysts, such as platinum and iridium, poses a challenge for the large-scale deployment of PEM electrolyzers for the generation of green hydrogen. To address this challenge, we propose to develop Hydrogen Evolution Reaction (HER), and Oxygen Evolution Reaction (OER) electro-catalysts based on abundant elements, specifically using oxo-metalate matrices doped with catalytically active units, such as cobalt ions for OER and $\{Mo_3S_4\}$ units for HER. This approach should allow us to exploit the high stability of oxo-metalate matrices in acidic environments as well as their electrochemical properties. The thesis project is based on three objectives: i) develop fundamental knowledge on the formation of doped oxo-metalate matrices, ii) continue the development of HER catalysts and evaluate the best candidates in semi-pilot PEM electrolyzers, and iii) develop and evaluate the performance of the OER catalysts obtained from doping oxometalate matrices. In this communication, we will present the preliminary results concerning the development of OER electrocatalyst based on oxo-metalate matrices.

References

(1) Chatenet, M. et al Chem. Soc. Rev. 2022, 51 (11), 4583–4762.
(2) An, L. et al Advanced Materials 2021, 33 (20), 2006328.

POSTER #3

Anti-corrosion thin films by Atomic Layer Deposition for low-cost Porous Transport Layers and Bipolar Plates in Proton Exchange Membrane electrolyzers

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Proton Exchange Membrane (PEM) electrolysis is a promising technology for the production of decarbonized hydrogen from water molecules, operating at low temperatures (< 100 °C). This technology offers several advantages, including higher energy efficiency, high gas purity, and the ability to directly couple with renewable energy sources (solar, wind), despite their frequent and unpredictable power fluctuations. However, one of the main limitations in terms of cost and performance lies in the porous transport layers (PTL) and bipolar plates (BPP). These components are often made of titanium due to its excellent corrosion resistance under electrolyzer operating conditions (1,2). Nevertheless, the highly oxidative environment at the anode leads to the formation of a thick, resistive titanium oxide layer, which increases contact resistance between the anodic compartment components and reduces the overall efficiency of electrolysis. Furthermore, these components account for over 60% of the total electrolyzer cost (3,4). Our study proposes an innovative and multidisciplinary approach to replace expensive titanium with more cost-effective 316L stainless steel for BPP and PTL components. These substrates are coated with protective and conductive Sn-based thin films, free of platinum group metals, deposited via Atomic Layer Deposition (ALD) (5,6). Initial results on the optimization of different films deposited on 316L stainless steel and titanium substrates are presented. A comprehensive micro- and nanostructural characterization of the coatings has been performed using techniques such as ellipsometry, X-ray diffraction, scanning electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS), high-resolution transmission electron microscopy (HRTEM), electron energy loss spectroscopy (EELS), etc. The anti-corrosion properties of the coatings were evaluated ex-situ through stability and corrosion tests in an acidic medium simulating PEM cell operating conditions. Preliminary in situ results obtained from PEM electrolyzer testing will also be discussed.

References

(6) S. Lædre et al., Int. J. Hydrogen Energy. 42 (2017) : 2713–2723.
(7) S. Stiber et al., Energy Environ. Sci. 15 (2022) : 109.
(8) U. Babic et al., J. Electrochem. Soc. 164 (2017): F387-F399
(9) M.Prestat, Journal of Power Sources. 556 (2023): 232469.
(10) M. Bechelany et al., Chem. Mater. 30 (2018): 7368–7390.
L.Santinacci, Curr. Opin. In. 63 (2023): 101674.

Chemical Passivation of GaN Nanowires for the Development of Innovative Photocatalysts

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Green dihydrogen (H_2) produced from water through photocatalysis represents a promising solution for achieving a sustainable energy transition by 2050. Innovative photocatalysts based on GaN nanowires (bandgap ˜3.4 eV) or GaN/Ga_2O_3 are developped, which are epitaxially grown on silicon substrates and functionalized with metallic nanoparticles (Pt, Cu, Ni) generated on the nanowire surface via radiolysis. The interdisciplinary approach spans the synthesis of these materials, their characterization, and the study of charge carrier dynamics (such as photocurrent, cyclic voltammetry, time-resolved microwave conductivity), all aimed at enhancing H_2 production efficiency.

Cu-based MOF/TiO_2 Composite Nanomaterials for Photocatalytic Hydrogen Generation and the Role of Copper

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Hydrogen (H_2) is a promising solution to reduce our dependence on fossil resources, as it is a clean energy vector that could mitigate problems related to energy use and environmental pollution. However, it can be produced from green resources! Photocatalysis is a promising way to produce green H_2 from water considering the possibility of coupling this technique to a renewable energy source such as sunlight[1].

Herein, we develop composite nanomaterials based on TiO_2 coupled with HKUST-1, a copper metal-organic framework, for its application in hydrogen generation by photocatalysis using water and methanol as sacrificial agents. To design a highly active composite, we study and optimize the mass ratios between HKUST-1 and TiO_2. The photoactive composite materials are characterized by TEM, UV-Vis spectroscopy, FTIR, XRD, XPS, and photoelectrochemical studies. We also study the charge carrier dynamics, a key factor in photocatalysis, by Time Resolved Microwave Conductivity (TRMC). Moreover, we examine the oxidation states and the role of copper in HKUST/TiO_2 before, during, and after the photocatalytic cycles by electron paramagnetic resonance spectroscopy. Finally, we optimize the composition of the water-methanol solution for hydrogen evolution to avoid the use of excessive sacrificial agents

The photocatalytic activity for hydrogen generation of the MOF-composite nanomaterials were compared with those of TiO_2 surface-modified with metal nanoparticles (Pt and Cu) induced by radiolysis. The findings reveal a very high hydrogen evolution rate of HKUST-1/TiO_2 (5.11 mmol g^{-1} h^{-1} for the first cycle with the mass ratio (1:20), which increases as a function of the irradiation time until surpassing the performance of the 1%Pt (TiO_2) material, used as a benchmark and known as a reference in terms of photocatalytic hydrogen production, after six photocatalytic cycles (13.24 mmol g^{-1} h^{-1}).

Reduction of Cu and formation of very small clusters of copper (0) are expected to be responsible for this increased photocatalytic activity. DFT calculations were also conducted to understand the photocatalytic mechanism and the role of copper in H_2 generation. It is expected that our results will help the development of very active and sustainable materials for photocatalytic solar fuels' generation.

A proposed mechanism can explain how the synergy of HKUST-1 and TiO_2 may inhibit electronhole recombination. This synergy favors transfer of electrons from TiO_2 to the HKUST-1 after photoexcitation and generating Cu^+/Cu^0 reversible species, which is useful for improved hydrogen production.[1] Copper also plays the role of cocatalyst in H^+ reduction and formation of H_2.

(1) Martínez, F. M.; Albiter, E.; Alfaro, S.; Luna, A. L.; Colbeau-Justin, C.; Barrera-Andrade, J. M.; Remita, H.; Valenzuela, M. A. Hydrogen Production from Glycerol Photoreforming on TiO_2/HKUST-1 Composites: Effect of Preparation Method. *Catalysts* **2019**, *9* (4), 338. https://doi.org/10.3390/catal9040338.

POSTER #6

Engineering electrode surface for Lithium Battery application by Atomic Force Microscopy

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The increased demand for electricity and energy has led to the necessary development of efficient storage systems. In this context, battery technology has come into the picture. During the last decades, battery technologies have improved significantly to meet the challenges of practical electric vehicles and circumvent the issue of intermittent and variability of renewable energy sources. Lithium-ion batteries (LIBs) are currently considered the most suitable energy storage device for powering electronic devices owing to their attractive properties, including high energy efficiency, lack of memory effect, long cycle life, high energy density, and high power density. These advantages allow them to be smaller and lighter than conventional rechargeable batteries. During the initial stages of LiB operation, the so-called Solid Electrolyte Interphases (SEI) start to grow at the electrodes' surface. It corresponds to an interfacial layer resulting from the electrochemical reduction of the solvent, salts, and impurities. This SEI layer plays a crucial role in the long-term performance of LIBs. Thus, SEI formation and electrochemical stability over long-term operation should be a primary topic of future investigation in LIB development (1). Atomic Force Microscopy (AFM) is considered one of the most demanding techniques to get maximum information about the various surface properties of the LiB electrodes, such as topography, mechanical, electrical, electrochemical, and surface potential (2). To follow up the different properties, AFM delivers different modes such as Quantitative Nanomechanical Microscopy, Kelvin Probe Force Microscopy (surface potential), Scanning Electrochemical Microscopy (electrochemistry), and TUNA conductivity (electrical properties). By using AFM and its different modes, a depth analysis of the surface properties and interfaces of the electrode is possible. To understand deeply we need to study all the parameters involved in this study. Graphite is one of the most used electrode materials with different studies being done to understand the surfaces (3). This work includes the mechanical and electrical properties at different scan rates to analysis the center and the edges of the graphite surfaces (4). Because the formation of the SEI layer is different at the center and the edge of the sample. The results show that the scan rate plays a definite role in the electrical properties, while in the case of mechanical, it doesn't show up with a huge difference. Once the parametric study is finished, we will continue this designed study with some advanced electrode materials such as $LiNiMnCoO_2$ (NMC).

References

[1] School of Chemistry, Tel Aviv University, Tel Aviv 69978, Israel, 164 (7) A1703-A1719 (2017).
[2] Agrawal, D. H., et al. "A Portable Experimental set-up for AFM to work at cryogenic temperature." National Conference on Recent Trends in Engineering & Technology. 2011.
[3] Jeong, S.-K., Inaba, M., Iriyama, Y., Abe, T., & Ogumi, Z. (2003). AFM study of surface film formation on a composite graphite electrode in lithium-ion batteries. Journal of Power Sources, 119, 555-560.
[4] Deng, X., Liu, X., Yan, H., Wang, D., & Wan, L. (2013). Morphology and modulus evolution of graphite anode in lithium-ion battery: An in situ AFM investigation. Science China Chemistry, 57(1), 178-183.

Enhancing Light Harvesting and Photocatalytic Performance of Graphdiyne through Structural Engineering

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Graphdiyne (GDY), a two-dimensional carbon allotrope composed of sp and sp2 hybridized carbon atoms, making it a regular, highly conjugated and porous structure (1). GDY, with its unique electronic properties and inherent bandgap (0.4 to 1.7 eV), has emerged as a promising candidate for light harvesting and photocatalytic applications (2). However, its intrinsic structural limitations, such as low processability, thickness of the film and narrow band energy often restrict its full potential in energy conversion processes. To address these challenges, heteroatom doping, defect engineering, functionalization and hybridization of GDY with organic and inorganic active materials are straightforward solutions (3, 4).

Here we showed the strategies to modify the GDY framework, aiming to optimize its photophysical properties for light harvesting and photocatalytic applications. In a very straightforward approach pristine GDY was oxidized to create oxygen defects, followed by size reduction to produce quantum dots (QDs). The engineered GDY-QDs showed enhanced light capturing ability and high processability. Alternatively, nitrogen doping was employed by adopting bottom up approach to adjust the bandgap and enhance the optical properties of GDY. The structural features of GDY, both pre- and post-modification, were analyzed using high-resolution transmission electron microscopy, Raman spectroscopy, and X-ray photoelectron spectroscopy. Experimental and theoretical analyses revealed that oxygen defects and heteroatom doping significantly influenced the electronic and optical behavior of GDY. The structurally engineered GDY materials exhibited outstanding photosensitization capabilities when combined with commercial TiO-P25 for photocatalytic hydrogen production. Notably, a hybrid material containing 1 wt% defect-rich GDY-QDs achieved a hydrogen evolution rate of 1322 μmol g^1 h^1, which is five times greater than that of TiO-P25 alone.

References

(1) M. Wang, J. Pu, Y. Hu, Y. Zi, Z.-G. Wu, W. Huang, *Adv Funct Mater* **2024**, *34*, 2308601.

(2) J. Li, A. Slassi, X. Han, D. Cornil, M. Ha-Thi, T. Pino, D.P. Debecker, C. Colbeau-Justin, J. Arbiol, J. Cornil, M.N. Ghazzal, *Adv Funct Mater* **2021**, *31*, 2100994.

(3) Y. Zhao, J. Wan, H. Yao, L. Zhang, K. Lin, L. Wang, N. Yang, D. Liu, L. Song, J. Zhu, L. Gu, L. Liu, H. Zhao, Y. Li, D. Wang, *Nat Chem* **2018**, *10*, 924.

(4) C. Xie, X. Hu, Z. Guan, X. Li, F. Zhao, Y. Song, Y. Li, X. Li, N. Wang, C. Huang, *Angewandte Chemie - International Edition* **2020**, *59*, 13542.

POSTER #8

High-entropy Tungsten-Based Oxide as Electrocatalyst and Potential Photo-electro-catalyst for H_2 Evolution

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High-entropy oxides (HEO_x) have emerged as a novel class of materials in the last decade. They display unique properties and can incorporate multiple cations into a single crystalline structure, resulting in high configurational entropy(ΔSconfig). This high entropy, combined with the presence of oxygen vacancies, can significantly enhance the mobility of charge carriers, leading to improved catalytic performance. Moreover, these materials exhibit exceptional thermal, chemical, and structural stability, making them highly suitable for a variety of catalytic and functional applications (1) (2). Despite their potential, HEOx materials have been relatively unexplored, especially in the field of photoelectrocatalysis. This work aims to address this gap by investigating the photoelectrocatalytic behavior of these HEOx materials and optimizing their properties.

In this study, $\mathbf{(Co_{0.2}Ni_{0.2}Fe_{0.2}Cu_{0.2}Zn_{0.2})WO_4}$ was synthesized using a top-down approach and characterized using various techniques to investigate its structural and optical properties. X-ray diffraction (XRD) confirmed the formation of a single-phase monoclinic structure. UV-visible spectroscopy revealed a band gap in the visible light region, making the material suitable for photoelectrocatalytic applications. Scanning electron microscopy (SEM) combined with energy-dispersive X-ray spectroscopy (EDX) was also performed to study its morphological features and elemental distribution.

The electrocatalytic activity for the oxygen evolution reaction (OER) was assessed for the material using electrochemical techniques. Cyclic Voltammetry (CV) revealed a reversible redox reaction comparable to Cobalt and nickel based OER catalysts. Linear Sweep Voltammetry (LSV) demonstrated high catalytic activity, a current density of 10 $mA{\cdot}cm^2$ with an overpotential of 420 mV. Electrochemical Impedance Spectroscopy (EIS) was also employed to measure charge transfer resistance. These results were also compared with the individual metal tungstate (MWO_4), synthesized using the same process as HEO_x. The photoactivity was confirmed by observing photocurrent generation when the material was deposited on glassy carbon and illuminated with light at an intensity of 1.3 $W{\cdot}cm^2$. In addition to this photoactivity, the band gap of HEO_x material situated in the visible region of the solar spectrum can enable efficient solar energy conversion to hydrogen.

References

(1) B. L. Musicó *et al.*, "The emergent field of high entropy oxides: Design, prospects, challenges, and opportunities for tailoring material properties," *APL Mater.*, vol. 8, no. 4, Apr. 2020, doi: 10.1063/5.0003149.
(2) Y. Sun and S. Dai, "High-entropy materials for catalysis: A new frontier," *Sci. Adv.*, vol. 7, no. 20, May 2021, doi: 10.1126/sciadv.abg1600.

Investigation of a hybrid system based on chiral metal nanoparticles and TiO_2 nanotubes

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The increasing energy demand in industrial and domestic sectors drives the growing consumption of fossil fuels, producing toxic waste that harms human health and the environment while intensifying the greenhouse effect. This has led to a search for clean, economically viable energy sources, such as H_2 production. However, typical methods like steam reforming and coal gasification emit greenhouse gases and yield low-purity H_2.

Photocatalytic water disproportionation using semiconductor metal oxides, particularly TiO_2, has gained attention. However, TiO_2's high bandgap limits visible-light absorption, and charge recombination reduces efficiency. Doping TiO_2 with plasmonic metal nanoparticles (NPs), such as Au and Pd, enables visible-light absorption via localized surface plasmon resonance (LSPR) and improves UV photocatalytic activity by trapping electrons and preventing recombination. Bimetallic NPs of these metals show promising results. Additionally, hybrid materials combining chiral plasmonic NPs with semiconductor oxides offer multifunctionality by tailoring optical, electrical, and mechanical properties. These materials enhance H_2 production, attributed to electron spin effects influenced by nanoparticle chirality.

In this project, titanate nanotubes were produced through the alkaline hydrothermal treatment of TiO_2, followed by a calcination process to generate anatase TiO_2 nanotubes (TiNT). Nanoparticles of 2 nm of Au, Pd, and AuPd (9:1) were prepared by rapidly reducing the respective metal salt with NaBH4. The TiNTs were decorated with 1% of the pre-prepared seeds. The resulting hybrid materials were immersed in a solution containing the metal salt precursor, L-ascorbic acid as a reducing agent, and a chirality inducer (L/D-cysteine), promoting the growth of supposedly chiral nanoparticles. The final materials were named D/L-AuTiNT, D/LPdTiNT, and D/L-AuPdTiNT.

The resulting materials were evaluated for photocatalytic hydrogen generation using triethanolamine as a hole scavenger under UV and visible light irradiation. The chiral materials demonstrated higher photocatalytic efficiency compared to their non-chiral counterparts. The photocatalytic activity followed the trend: D/L-PdTiNT < D/L-AuTiNT < D/L-AuPdTiNT. These findings highlight the potential of hybrid chiral metal nanoparticle–metal oxide systems for enhanced hydrogen production.

Effects of Yb Doping on $LaFeO_3$ Nanoparticles: Experimental and DFT Studies

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This work aims to prepare nanoparticles of $LaFeO_3$ (LFO) with different proportions of Ytterbium by co-precipitation method. X-Ray Diffraction analyses show that all samples crystallize in the orthorhombic perovskite phase, with nanoscale crystallite sizes ranging between 40 and 110 nm. Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (EDX) was employed to observe the morphology of the synthesized nanoparticles and to identify the presence and proportion of various constituents, including dopants. The Fourier-transform infrared spectroscopy (FTIR) spectra exhibited peaks related to the Fe-O vibration. A comparative investigation of the structural and electronic properties of $La_{1-x}Yb_xFeO_3$ nanoparticles (x = 0.00 and 0.04) is also performed in this manuscript. The optical bandgap energies were determined based on the DFT calculations and found to be 2.301 eV and 2.064 eV following (100) and (001) directions, respectively. Afterward, this parameter reduced to 2.14 eV and 2.06 eV (along (100) and (001) directions, respectively) by adding 4% of Yb at La sites. LFO compounds exhibit indirect bandgap energies with p-type semiconductor behaviour. The unique properties of the synthesized LFO nanoparticles, attributed to their nanoscale size and specific crystal structure, suggest their potential application in photoelectrochemical water splitting, catalysis, gas sensing, and energy conversion devices.

Mass spectrometry for electrocatalysis analysis

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Mass spectrometry is a potent tool to unveil the chemistry of complex system. Though association to a electrochemical cell is a difficult task due to the complex conditions present in a eletrochemical reaction cell, salt loading and pH mainly, that prevents easy ionization of the species. Despite the challenge, a few attempts to associate a chemical cell to a mass spectrometer presented some very interesting new results, mainly on CO_2 reduction analysis. In this work, we present the first step of this integration. We studied by mass spectrometry two different systems : one for CO_2 reduction and the other for biomass-issued molecules electroreduction. First project intents is to study individuals steps of CO_2 reduction by metal-porphyrin by high resolution mass spectrometry (HR-MS). We determined the working conditions to identify the redox state of the insered metal in a iron-porphyrin catalytic system. HR-MS allowed to test the hypothesis of CO_2 addition at the Fe(I) state.

The second project aims at developing an interface between an flow-cell and a mass spectrometer. Working conditions studied in a APCI sources for furfural reduction to 2-HMF. Low pH and high salt loading, conditions that can be detrimental to the mass spectrometer source, were bypassed by diluting in the proper solvent the solutions. A system using a spray was tested for direct connection to the MS.

Finally, we will present the recent results obtained by these systems and validation of the concepts that we are currently developing on already known reactions. This work aims at demosntrating the use of mass spectrometry in electrochemistry.

MOF based composites as Li-ion solid conductors

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Li metal has the lowest electrochemical potential (−3.04 V vs. standard hydrogen electrode) and high theoretical specific capacity (3860 mAh g^{-1}), making it a suitable anode for high-energy batteries.(1) However, conventional Li-metal batteries face safety issues since liquid electrolytes are prone to leakage, combustion, and Li dendrite growth during the battery cycle. Solid-state electrolytes appear as promising alternatives to solve the above challenges due to their high safety since they do not contain organic solvents and display a high mechanical strength, inhibiting Li dendrites' growth. However, existing solid-state electrolytes still face problems, such as poor electrochemical stability and ionic conductivity. Hence, designing solid-state electrolytes with electrochemical stability and high ionic conductivity remains challenging.

Metal-Organic Frameworks (MOFs) have emerged as good candidates for energy applications in the quest for new ionic conductors. MOFs are porous materials resulting from the assembly of metal ions/clusters and organic ligands. Their versatile compositions, ordered channels, and tunable porosity offer the required structural features for potential applications in ion batteries. In Li metal batteries, MOF-based ionic conductors can be classified into two types: MOF-incorporated polymer hybrids and liquid electrolyte-laden MOF hybrids. The structure of MOF will affect Li+ diffusion, but the current mechanism remains unclear. Hence, establishing a structure-property link and clarifying the ionic diffusion properties with MOF structures is significant.

In this work, a new type of MOF-incorporated polymer hybrid is introduced, and the effect of the functional group of MOF into Li^+ migration is demonstrated. MIP-207 and its structural analogue MIP-207-SO_3H, have been selected, due to their 2D structure, composed of Ti_8O_8 oxo-clusters and 1,3,5-tricarboxylic acid (BTC) and 5-sulfoisophthalic acid linkers (MIP refers to Materials of the Institute of Porous Materials from Paris).(2) The structure of both MOFs was characterized by X-ray diffraction (XRD), Fourier Transform infrared spectroscopy (FTIR), N_2 adsorption, thermogravimetric analysis (TGA), and scanning electron microscope (SEM). MOF-incorporated polymer hybrids, composed of MOF nanoparticles, PVDF-HFP, and LiTFSI, were prepared using a solution casting method. The electrochemical properties of the electrolyte were tested in 2032-type coin cells. The connection between the function group of MOF and Li^+ migration was established by analyzing the bulk impedance of electrolyte, charge transfer impedance, exchange current density, and Li^+ transference number. Li symmetric and LFP full cells were assembled to investigate their stability and practicality. The results show that compared with MIP-207, MIP-207-SO_3H displays a higher conductivity, promoting Li^+ migration, accelerating charge transfer, and ultimately improving the electrochemical performance of the electrolyte. Moreover, the symmetrical and full batteries have very good cycle stability.

References

(1) J. M. Tarascon, M. Armand, Nature 2001, 414, 359–367.

(2) a) S. J. Wang, H. Reinsch, N. Heymans, M. Wahiduzzaman, C. Martineau-Corcos, G. Weireld, G. Maurin, and C. Serre, Matter, 2020, 2, 440-450. b) S. Nandi, S. J. Wang, M. Wahiduzzaman, V. Yadav, K. Taksande, G. Maurin, C. Serre, and S. Devautour-Vinot, ACS Appl. Mater. Interfaces 2021, 13, 20194–20200.

Nanodiamonds: an alternative for photocatalysis under solar light?

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Among nanoscale semiconductors (SC), nanodiamond (ND) has been rarely considered for photocatalytic reactions. This originates from the confusion with ideal monocrystalline diamond behaving a wide bandgap (5.5 eV) that requires deep UV illumination to initiate photoreactivity. At nanoscale, diamond particles enclose native defects that create energetic states decreasing the light energy needed to initiate charge separation. This is supported by experimental results and DFT calculations that involved our group (1, 2). The presence of sp2 carbon in hydrogenated detonation ND allows the emission of solvated electrons in water under visible light (400 nm) according to ultrafast transient absorption spectroscopy (2). In addition, like bulk diamond, the electronic structure of ND can be strongly modified tuning its surface terminations (oxidized vs hydrogenated) as shown by Miliaieva et al. (3). With these assets, ND becomes competitive to other SC toward photoreactions.

In the present study, we reveal for the first time that oxidized detonation nanodiamonds (OxDND) can produce hydrogen under solar illumination without addition of co-catalyst or formation of heterojunction with another SC (4). This hydrogen production was investigated using two sacrificial reagents and compared to the one of hydrogenated DND. The effect of the OxDND and sacrificial reagent concentrations on the hydrogen production was also studied. At its maximum, a H_2 production yield of 32 μmol.h-1 was obtained for an Ox-DND concentration of 12.5 μg/mL (using only 1 vol.% of TEOA as a sacrificial reagent). This yield is similar to the one of TiO_2 nanoparticles tested at the same concentration in the same illumination conditions.

References

(1) R. Su, Z. Liu, H. Abbasi, J. Wei, H. Wang, Materials. **2020**, 13, 4468.
(2) F. Buchner et al., Nanoscale. **2022**, 14, 17188.
(3) D. Miliaieva et al., Nanoscale Advances, **2023**, 5**,** 4402
C. Marchal et al., Advanced Energy and Sustainability Research, **2024**, 5, 2300260

New aerogel-based materials for the production of green hydrogen in low temperature water electrolyzers (PEMWE)

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Hydrogen is set to play a crucial role in the energy transition and can be produced though a range of technologies. Although proton exchange membrane water electrolysis (PEMWE) proves to be beneficial, it heavily relies on scarce iridium oxide (IrO_2) acting as a catalyst in the OER reaction, creating scalability challenge (1). As IrO_2 is only active on the surface during the process, its surface-to-volume ratio must be increased so as to optimize its mass activity (2). Aerogels, with their highly porous texture, offer a solution to reduce IrO_2 loading in PEM electrolyzers. They can act as support structures (3), prompting the investigation of aerogelsupported IrO_2 thin films.

In this work, TiO_2 aerogel-supported IrO_2 thin films catalysts have been elaborated in two steps: aerogel support synthesis and film deposition. Selecting stable support materials like TiO_2 is crucial in the corrosive anodic environment of PEMWE. TiO_2 aerogels with high specific surface areas (˜600 m^2/g) were obtained by sol-gel method followed by CO_2 supercritical drying (4). Films were deposited via two different methods: chemical bath deposition (5) and hydrothermal deposition (6). Physical characterizations by SEM, N-sorption, HR-TEM and XRD were carried out to adjust the morphology of the aerogel supports and analyze the dispersion and size of the IrO_2 nanoparticles constituting the thin films. Spectroscopic analysis such as XPS gave information about the oxidation state of the investigated element. The OER activity and durability of such low-loaded iridium catalysts were evaluated in rotating disk electrode (RDE) and showing a promising five-times higher mass activity compared to state-of-the-art reference IrO_2 catalyst. These results are encouraging for proposing low-loaded iridium catalysts highly active for OER.

(1) C. Minke et al., *Int. J. Hydrogen Energy*, **2021**, 46, 23581-23590.
(2) C. Daiana Ferreira da Silva, *ACS Catal.*, **2021**, 11, 4107-4116.
(3) L. Solà-Hernàndez, *Int. J. Hydrogen Energy*, **2019**, 44(45), 24331-24341.
(4) D. D'Elia, *Int. J. Hydrogen Energy*, **2011**, 36(22), 14360-14373.
(5) W. Huang, *Surf. Coat. Technol.*, **2022**, 435, 128271.
(6) K. Zhang, *Int. J. Hydrogen Energy*, **2024**, 69, 1105-1112.

POSTER #15

$NiFe_2O_4$-PVDF Nanocomposites: Synthesis, Characterization, and Applications

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Experimental realization of flexible thin films with a significant room temperature magnetoelectric coupling is highly desirable for the wearable electronic devices, magnetic field sensors, actuators, energy harvesting and memory devices. Here a flexible miltiferroic composite was fabricated using ferromagnetic nickel ferrite ($NiFe_2O_4$) nanoparticles (NPs) as filler with varying concentration (2.5,10,20, and 30) wt%) in the ferroelectric polyvinylidene fluoride (PVDF) matrix. X-ray diffraction (XRD) confirmed the crystalline phases, while Fourier-transform infrared spectroscopy (FTIR) highlighted interactions between PVDF and $NiFe_2O_4$. Scanning electron microscopy (SEM) revealed a uniform distribution of nanoparticles in the PVDF matrix. Tensile tests showed enhanced mechanical properties with increasing filler content. Vibrating sample magnetometry (VSM) demonstrated tunable magnetic behavior, making these composites suitable for multifunctional applications.

Persistent luminescent photocatalysts based on SrMgSiO:Eu^{2+},Dy^{3+} and WO/BiVO for tetracycline degradation and hydrogen generation

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Water and energy are indispensable resources for human life. Beyond their essential roles in consumption, they are also critical for agriculture, industry, and various everyday applications. However, rapid population growth and industrial expansion have led to their uncontrolled use and the contamination of water bodies crucial to the global water supply. Additionally, these trends are accelerating the depletion of fossil fuel resources currently relied upon for energy production (1,2). In this context, semiconducting metal oxides offer promising solutions for the photocatalytic degradation of contaminants and the production of hydrogen (H) (3). In this study, the SrMgSiO:Eu^{2+},Dy^{3+} (SMSO)/WO/BiVO heterojunction was synthesized using microwave-assisted methods: solvothermal synthesis for WO, reflux synthesis for BiVO, and solid-state synthesis for SMSO. Structural analysis via X-ray diffraction (XRD) confirmed the formation of crystalline materials, with BiVO exhibiting a monoclinic phase and WO and SMSO displaying tetragonal phases-recognized as the most active phases for photocatalytic applications. For tetracycline (TC) degradation, 3 mg of the photocatalyst was dispersed in 10 mL of a 0.01 mg/mL TC solution and stirred magnetically for 4 hours to minimize adsorption effects. Experiments were conducted using a solar simulator, with the suspensions irradiated under simulated sunlight for 60 minutes. To evaluate the persistent photoluminescent activity of SMSO, the system was subsequently kept in the dark for an additional 60 minutes, with aliquots collected at 15-minute intervals throughout both phases. The system was also evaluated for hydrogen photogeneration using triethanolamine as a hole scavenger under visible light irradiation for 4 hours. To further assess the capacity of SMSO photoluminescence to promote charge separation and sustain hydrogen production, the system was monitored for an additional 4 hours in the dark. The photocatalytic degradation of TC achieved approximately 80% efficiency, while hydrogen generation exhibited promising results, with activity persisting even after light irradiation ceased. These findings highlight the potential of the SMSO/WO/BiVO heterojunction for applications in organic pollutant degradation and sustainable energy production.

(1) Jones, E. R. et al. Current wastewater treatment targets need to be increased to protect surface water quality. Commun Earth Environ 3, 1–8 (2022)
(2) Jain, I. P. Hydrogen the fuel for 21st century. Int. J. Hydrogen Energy 34, 7368–7378 (2009).
Fujishima, A. & Honda, K. Electrochemical Photolysis of Water at a Semiconductor Electrode. Nature 238, 37–38 (1972)

Photoanodes based on heterojunctions of TiO_2, graphene oxide and α-Fe_2O_3 for application in hydrogen gas production

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Photoelectrochemical water splitting into H_2 and O_2 using semiconductor materials as photoelectrodes is promising for obtaining hydrogen gas (H_2). TiO_2 and α-Fe_2O_3 are oxides widely investigated for use as photoanodes due to their natural abundance, chemical stability, nontoxicity, high resistance to photocorrosion and low production cost. Despite being promising materials, these oxides have some drawbacks. TiO_2 presents limitations such as low electrical conductivity, limited time in the excited state, and small diffusion distance, furthermore, it has a high band-gap energy (3.2 eV), making it sensitive only to UV radiation. On the other hand, the conduction band of hematite does not have the appropriate potential to reduce H^+ to H_2, preventing the reaction from occurring at an open-circuit potential, and requiring the application of an external potential for the reaction to occur. To overcome these disadvantages, an attractive strategy is to prepare heterojunctions of these materials, which improves the charge separation and efficiency. Also, incorporating graphene oxide into TiO_2 increases the photoelectrochemical activity of the resulting material, attributed to the favorable band alignment of the semiconductors and the properties of graphene that facilitate charge separation. Using microwave radiation to synthesize these heterojunctions is very attractive since it reduces time and energy consumption and, at the same time, allows the obtention of interfaces with unique characteristics.

Here, we report how the unique interactions of microwaves with the reactional media can produce TiO_2-graphene-Fe_2O_3 composites with enhanced properties. The method of synthesis used was adapted from previously reported conventional synthesis, with adaptations for microwave conditions. Ammonium sulfate was added as a capping agent to orientate the TiO_2 growth. The results obtained through the Raman spectroscopy, X-ray diffraction and Fourier-transform infrared spectroscopy show that it was possible to form TiO_2 in the anatase phase under the synthesis conditions investigated. The scanning electron microscope images show a cluster of TiO_2 on graphene oxide. The measurements of potential zeta were similar to the values in the literature, where the particle's surface was negatively charged.

Considering the characteristics of the heterojunction produced is possible to apply this material as a photoanode in the water splitting process to obtain hydrogen gas in an environmentally friendly way.

POSTER #18

Reverse water-gas shift reaction at low temperatures over palladium- and ruthenium-based catalysts

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Climate change represents one of the highest threats of our era. It is mainly due to the increase in greenhouse gas (GHG) emissions, which trap the heat in the earth's atmosphere. CO_2 emissions are responsible for *ca.* 68% of the global GHG emissions. Consequently, Carbon Capture and Utilization (CCU) represents a strategic approach to meet the global energy and climate goals(1). Syngas production from captured CO_2 is a promising path for CCU, as syngas can be used to make various fuels(2). To produce syngas, CO_2 is combined with H_2 *via* the reverse water-gas shift (RWGS). The RWGS produces CO and H_2O through the hydrogenation of CO_2 (Equation 1), CO can further react with H_2 in order to produce fuel *via* the Fisher-Tropsh synthesis (FTS) (Equation 2). As the RWGS is slightly endothermic, CO_2 conversion to CO is limited by the temperatures required for the FTS process. The sum of Equation 1 and Equation 2, leads to a new process called the CO_2-FTS, which allows obtaining long-chain hydrocarbons from CO_2 and H_2.

Equation 1: RWGS: $CO_2(g) + H_2(g) \rightarrow CO(g)+H_2O(g)$ $\Delta H^{\circ}298 = 41.2$ kJ mol^{-1}

Equation 2: FTS: $nCO+(2n+1)H_2 \rightarrow CnH_2n+2+ nH_2O$ ΔH° $298 = -165$ kJ mol^{-1}

Metallic cobalt is well-adapted for producing synthetic hydrocarbons using the traditional FTS process at low temperature(3). However, when using cobalt catalysts for CO_2-FTS, the weak adsorption of CO_2 and the thermodynamic limitations of the RWGS under conventional conditions of FTS reaction leads to low ratio of CO to H species adsorbed on catalyst surface and low CO coverage. This results in the preferential production of methane and short-chain hydrocarbons(4). Various parameters can be optimized to enhance the selectivity of C5+ products on cobalt-based catalysts such as the choice of cobalt active phase and support, the metal-support interfaces, and the addition of promoters(5). Beyond these parameters, the development of a specific catalyst tailored to low-temperature RWGS could be explored, thereby mitigating the thermodynamic constraints of this reaction(6). Obtaining a performing RWGS catalyst at low temperature (e.g. 200-250 °C) will offer the possibility to design a one-step CO2-FTS, where CO_2 can be directly hydrogenated in a single reactor at one temperature and one pressure into long-chain hydrocarbons. This constitutes the main objective of the present work, focusing on ruthenium- and palladium-based catalysts for low-temperature RWGS reaction.

(1) Lim, X.; *Nature.* **2015**, *526* (7575), 628–630
(2) Mihet, M.; Dan, M.; Lazar, M.D. ; *Molecules.* **2022**, *27*, 3367
(3) Lin,T.; An, Y.; Yu, F.; Gong, K.; Yu, H.; Wang, C.; Sun, Y.; Zhong, L.; *ACS Catal.* **2022**, 2, 12092–12112
(4) Bredy, P.; Farrusseng, D.; Scuurman, y.; Meunier, F.C.; *J. Catal*, **2022**, 411, 93-96
(5) Scarfiello, C.; Pham Minh, D.; Serp, P.; Soulantica, K.; *Adv. Mater. Interf.* **2023**, 10, 2202516
(6) Torres-Sempere, G.; Gonzalez-Arias, j.; Penkova, A. ; Santos-Munoz, J.L. ; Bobadilla, L.F. ; Odriozola, J.a.; Pastor-Perez, L.; Reina, T.R.; *Sci. Total Environ.*, **2023**, 857 (3), 159394

Semiconducting conjugated oligomers for photo-driven water oxidation

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Conjugated polymer (CP) nanostructures appear as a new class of photocatalytic nanomaterials very active under visible light for water treatment and water splitting. In this study, a monomer 1,2-bis(pyridyl)butadiyne (BPB) was synthesized and we develop different nanostructures of **poly- bis(pyridyl)butadiyne (PBPB)**. The photocatalytic activity for H_2O_2 generation under visible light of these nanostructures was studied. Measurement of hydrogen peroxide (H_2O_2) was evaluated by iodometry method. H_2O_2 produced reacted with excess KI to form I_3^- ion, which showed yellow colour and can be quantified by following absorption spectra at 350 nm.

Different experimental conditions for H_2O_2 tests were conducted to study the reaction mechanism. As shown in Figure 1, the amount of H_2O_2 detected under O_2 bubbling was more than that in air, suggesting the boosting effect of oxygen for peroxide generation. In presence of parabenzoquinone (p-BQ) (under air) as the scavenger of oxygen radical O_2•-, H_2O_2 concentration reduced drastically, meaning that this O_2•- specie is crucial for peroxide formation. On the other hand, when using isopropanol as the scavenger of hole (h^+) and OH•, the generation of H_2O_2 stays almost the same, meaning that H_2O_2 is not generated via 1 electron water oxidation to form OH•. Under argon atmosphere, only a small amount of H_2O_2 could be detected. The HOMO and LUMO for nano-PBPB were estimated to be 1.06 V and -0.64 V vs RHE, proposing the reduction of oxygen and oxidation of water are thermodynamically possible. Photocatalytic tests were also performed with nano-PBPB deposited on glass slides. The production of H_2O_2 was accelerated with deposited PBPB nanostructures on substrate, but recyclability test showed a decline of H_2O_2 production overtime. Throughout each cycle, there was a decrease of absorption of the substrate in visible range, pointing out the diminishing conjugation of the polymer chain and instability. No O_2 was detected with Clark electrode, signaling PBPB is not capable of doing O_2 evolution. Iodometry was also conducted for bulk PBPB, however the maximum absorbance detected was 344 nm instead of 350 nm. Therefore, iodometry is not precise for quantification of H_2O_2 generated from bulk sample.

In conclusion, a monomer 1,2-bis(pyridyl)butadiyne (BPB), bulk and nanostructured PBPB were synthesized with and without using soft template. The photocatalytic H_2O_2 production of the conjugated nanostructures PBPB was investigated using iodometry. The nano-PBPB synthesized in mesophase by γ-radiolysis generates H_2O_2 with a good rate. H_2O_2 production was studied in different conditions and mechanistic insight of the photocatalytic process was investigated.

References

(1) Ghosh, S.; et al., New J. Chem. 39 (2015), 8311.
(2) Geetarani, S., et al., Chem. Mater. 17 (2005), 1505-1514
(3) Ghosh, S.; et al., Nat. Mater. 14 (2015), 505-11.
(4) Patel, J.; et al., Chem. Sci. 11 (2020), 7324-7328

SOLEIL Substainable Energy Science Section: State of the art beamlines for ex situ and operando energy-relevant materials characterization

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In operation since 2017, SOLEIL is the French Synchrotron Radiation facility located on the Saclay Plateau nearby the research laboratories of the Paris-Saclay University. Over the 29 beamlines in operation, 24 beamlines can be used for in depth characterization of energy-relevant materials in static and/or dynamic conditions. The full wide spectral bandwidth of the electromagnetic spectrum provided by SOLEIL, ranging from the far-infrared to the hard X-rays, is exploited to this purpose. Synchrotron-based X-ray spectroscopy (EXAFS, XPS...) techniques are unique for providing element specific information about the atomic local structure. Thus, *in situ* real time monitoring oxidation state transformation occurring when materials are in operation (e.g. during charge/discharge for a battery materials) becomes possible. Synchrotron-based X-ray scattering (SAXS, WAXS, XRD, GISAXS, XRR) techniques offer a comprehensive understanding of the medium or long-range ordered structures encompassing interface, morphology and crystalline properties (size, strain, faults...) descriptions. Synchrotron based X-ray imaging techniques (scanning micro- and nanoprobes, tomography) can be used for direct visualization of the energy-relevant materials at the various multiple length scales (e.g. from a few nanometers to several micrometers) explaining the macroscale properties of materials. A large portfolio of sample environments is available at, or can be shared between, beamlines (electrochemical cells, photochemical reactors, ...) for the study of the energy-relevant materials in operation and shed into the light the well-known structure-property relationships mandatory for improving the performance of existing materials for energy generation, storage, and conversion and accelerating the design of new materials.

The poster session will be an opportunity to meet SOLEIL's scientists and discuss with them to the potential of their beamlines for obtaining multi-faceted information about all aspects of the synthesis, operating, and/or degradation of energy-relevant materials that you may have.

List of the SOLEIL's beamlines involved strongly in the field:

CRISTAL, GALAXIES, TEMPO, SAMBA, HERMES, SWING, ANTARES, ROCK, ANATOMIX, DIFFABS, SIXS, SIRIUS, LUCIA, ODE, AILES, MARS, PSICHE...

Synthesis of Mesoporous Nitrogen-Enriched and Graphitized Carbon Supports for Proton Exchange Membrane Fuel Cells

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Proton Exchange Membrane Fuel Cells (PEMFCs) are green and sustainable energy conversion devices that are attracting significant attention in the context of the energy transition. They are widely considered as one of the most promising energy sources for electric vehicles.

PEMFCs offer several advantages, including high power density, superior energy conversion efficiency, low operating temperature, and fast startup.

One of the key materials for the optimal functioning of these fuel cells is the **catalyst**, which significantly impacts cost, energy conversion efficiency, and the cell's lifespan. However, the large-scale deployment of PEMFCs is hindered by the high cost of platinum and its limited stability.

Indeed, using platinum as a catalyst leads to stability issues with nanoparticles (NPs) on the support materials. Over time, these nanoparticles can degrade, reducing the overall efficiency of the fuel cell. This degradation can result in phenomena such as platinum dissolution, nanoparticle aggregation, and other degradation mechanisms (Figure 1).

My research aims to address these stability issues by developing carbon supports for platinum with specific properties :

- **Nitrogen enrichment**: The support must be enriched with nitrogen to stabilize platinum NPs and prevent Ostwald ripening or nanoparticle agglomeration.
- **Mesoporosity**: The material should be mesoporous to confine platinum NPs, preventing detachment and loss of catalytic activity.
- **Graphitization**: Enhancing the graphitization of the carbon structure improves thermal stability and electrical conductivity.

Thus, carbon supports play a crucial role in PEMFCs, significantly impacting their performance and durability.

My research is part of the **PEMFC95 project** within the **PEPR-H2 program**, which aims to develop PEMFCs capable of operating at a stabilized temperature of 95°C (compared to the current 80°C). My specific contribution to this project involves selecting a noble-metal-free carbon-based catalyst support that meets the above-mentioned properties.

POSTER #22

Cancelled

Synthesis and Characterization of Siloxene and Siloxene/BP Composite as Anode Material for Lithium-Ion Batteries

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Two-dimensional siloxene demonstrated significant potential as an anode material for Liion batteries due to its high gravimetric capacity and superior mechanical properties during lithiation/delithiation compared to bulk Silicon. In this study, siloxene nanosheets material were synthesized by removing bulk Si contaminants and probe their electrochemical behavior as anode material. The siloxene-based anodes, containing 50 %, 60 %, and 70 % of siloxene delivers a capacity of 356.69, 859.44, and 393.94 at 0.2 C after 10 cycles with a coulombic efficiency of 96.16, 95.69, and 97.02 %. However, the siloxene-based anodes demonstrated excellent stability and superior retention capacity after 10 cycles. Interestingly, the insertion of Black Phosphorus (BP) into the siloxene matrix improves its electrochemical performance. The siloxene/BP anode delivers a remarkably high capacity of about 1224.38 mAh g^{-1} and a superior coulombic efficiency of 98.38 %.

Towards In situ Magic Angle Spinning Nuclear Magnetic Resonance Spectroscopy for Batteries

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Various techniques are used to characterize phenomena and reactions occurring inside batteries. One powerful technique is solid state Nuclear Magnetic Resonance Spectroscopy (ssNMR). ssNMR is a valuable tool to decipher electrochemical mechanisms such as phase transition, electrolyte degradation, metal-plating or dendrite formation in an operating battery.(1) However, the full potential of this technique cannot be reached *in situ* or *operando* due to the broad NMR signals acquired from sample-static conditions. An additional experiment is needed to interpret the obtained spectral data, the *ex situ* Magic-Angle Spinning (MAS) NMR spectroscopy. This sample-spinning MAS technique reduces the signal linewidth and enables comprehensive characterizations. Unfortunately, the *ex situ* nature of this technique implies dismantling the battery cell that causes introduction of unwanted artifacts.(2) Thus, it does not always represent the real electrochemistry of the cell.

Combining the strengths of *in situ* and MAS for battery studying is highly desirable. In situ MAS NMR spectroscopy would allow for high spectral resolution data of the whole battery cell. Such experimental development is unprecedented due to the challenge of spinning an operational battery cell. Indeed, it raises many issues such as spinning a cell with metals under a strong magnetic field, stabilizing the cell components under the centrifuge force, heating impact on the electrolytes or airtightness and electrical contacts of the cell. Those challenges show that in situ MAS NMR is extremely challenging.

Currently, only one spinning MAS cell is reported in the literature as a cylindrical jellyroll design composed of $LiCoO_2$ and graphite electrodes connected with Ti-metal wires current collectors.(3) The results obtained in this study give an idea of the in situ MAS NMR spectroscopy potential for batteries, but, the complexity of the cell design and the possibility of heating due to the presence of metals limit its application and representativeness.

The aim in this work is to develop a novel metal-free spinning carbon-based battery cell design to perform *in situ* MAS NMR spectroscopy and acquire high spectral resolution data. A new method of *in situ localized* MAS NMR spectroscopy is also considered to monitor spatially and temporally reactions and phenomena inside a battery cell. We will present our preliminary results, both on electrochemical and spinning, towards the development of the new cell.

(1) J. Z. Hu, N. R. Jaegers, M. Y. Hu, et K. T. Mueller, ” In situ and ex situ NMR for battery research ”, *J. Phys. Condens. Matter*, vol. 30, no 46, p. 463001, oct. 2018, doi: 10.1088/1361-648X/aae5b8.

(2) B. Key, R. Bhattacharyya, M. Morcrette, V. Sezn´ec, J.-M. Tarascon, et C. P. Grey, ” RealTime NMR Investigations of Structural Changes in Silicon Electrodes for Lithium-Ion Batteries ”, *J. Am. Chem. Soc.*, vol. 131, no 26, p. 9239-9249, juill. 2009, doi: 10.1021/ja8086278.

(3) A. I. Freytag, A. D. Pauric, S. A. Krachkovskiy, et G. R. Goward, ” In Situ Magic-Angle Spinning 7Li NMR Analysis of a Full Electrochemical Lithium-Ion Battery Using a Jelly Roll Cell Design ”, *J. Am. Chem.Soc.*, vol.141, no 35, p.13758-13761, sept.2019, doi:10.1021/jacs.9b06885.

POSTER #25

Decreasing the cost of H_2 production by using ultra-low PGM based catalysts for the HER in alkaline media

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As we navigate through the energy transition, there is a pressing need to reduce greenhouse gas emissions and achieve sustainability goals. Hydrogen is a clean energy carrier that serves as an important role in this global energy transition, with green hydrogen offering a near carbonneutral production from renewable sources. Among electrolysis technologies, Anion Exchange Membrane Water Electrolyzer (AEMWE) is an emerging technology, that leverages advantages from different approaches, promising an increase in electrolysis efficiency as well as hydrogen production. Despite its potential, challenges remain in achieving high and stable AEMWE performance, particularly regarding HER catalysts.[1] To address this, a new concept of heterofunctional catalysts has been proposed to enhance HER kinetics in alkaline medium.[2] In this work, we present the synthesis of Ni-based heterofunctional electrocatalysts with ultra-low noble metal content, that exhibit a significantly low overpotential, highly comparable to the one of the state-of-the-art catalyst Platinum. Using the polyol synthesis method, we achieved highly crystalline materials with controlled particle size, shape, and distribution.[3] Advanced characterization techniques including XRD, XPS, XRF, SEM, and TEM confirmed the successful synthesis of Ni-based heterofunctional catalysts. These analyses revealed the presence of ultra-small noble metal nanoparticles decorating the surface of Ni platelets. Additionally, X-ray absorption spectroscopy (XAS) was employed under both ex-situ and in operando conditions to provide detailed insights into the material composition and atomic distribution, further elucidating the structural and electronic properties responsible for the higher catalytic performance. Performance evaluation in a membrane electrode assembly (MEA) configuration revealed that these electrocatalysts reached 1.85 V at a current density of 1 A cm^2. These findings demonstrate the potential of heterofunctional catalysts to enhance AEMWE efficiency, offering a sustainable pathway for scalable hydrogen production with reduced reliance on critical noble metals.

POSTER #26

Electrochemical study of iron-containing sandwich-type polyoxometalate as catalysts for hydrogen peroxide reduction

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Among the diverse fuel cell configurations, Direct Peroxide Peroxide Fuel Cells (DPPFCs) have emerged as a promising technology due to their inherent advantages. Unlike conventional fuel cells that utilize oxygen (O) and hydrogen (H) as oxidant and fuel, respectively, DPPFCs employ hydrogen peroxide (HO) for both functions. This single-compartment design eliminates the need for a proton exchange membrane (PEM), resulting in a simpler and more compact cell system. Additionally, DPPFCs operate with liquid oxidant and fuel, circumventing the humidification challenges encountered in PEM fuel cells (PEMFCs). Given these advantages, the exploration of efficient and durable cathodic materials for DPPFCs remains an active area of research.

Iron-containing polyoxometalates (POMs) have garnered significant interest as potential cathodic catalysts for HO reduction in acidic media. (1-2) This study investigated a series of sandwich-type POMs (STPs) featuring variations on the number and/or nature of elements ”sandwiched” with FeIII element in the metal cluster. Cyclic voltammetry was employed to characterize the electrochemical behavior of these iron-containing STPs and their electrocatalytic activity toward HO reduction. Our findings suggest that the location, nature, and number of d-metal centers within the POM framework can significantly impact the interactions between redox-active sites, thereby modulating the catalytic performance.

(1) B. Keita, I. M. Mbomekalle, Y. W. Lu, L. Nadjo, P. Berthet, T. M. Anderson, C. L. Hill, *Eur. J. Inorg. Chem.* **2004**, *2004*, 3462-3475.

(2) F. Doungmene, C.S Ayingone Mezui, P. de Oliveira, A.-L. Teillout, I. M. Mbomekall´e, *Current Inorganic Chemistry*, **2017**, 7, 28-38.

Towards a better knowledge of alkylcarbazoles as LOHC

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Hydrogen storage and transport in LOHC through a cycle of catalytic hydrogenationdehydrogenation of H_2-poor and H_2-rich organic compounds is a major challenge towards renewable energy management. In recent research, many reviews focused on promising molecule pairs in terms of thermodynamics and catalytic activities, but few focused on suitable reactors and processes. The ANR RID-LOHC project aims to propose efficient reactors capable of managing the huge heat release or demand and the significant gas flow involved in the reactions. For this purpose, compounds from the carbazole family (N-ethylcarbazole (NEC) and N-propylcarbazole (NPC)) were chosen as LOHC because of their low dehydrogenation temperature and reaction enthalpy. Although NEC has been widely studied, we pointed out some discrepancies and inaccuracies to be first clarified.

Both NEC and NPC are solid at room temperature. The existence of an eutectic mixture has been demonstrated in the literature (1), claiming 33 °C as the lowest temperature for liquid state for a mixture of 30%NEC+70%NPC. However, blends of 30% to 60%NEC have not been assessed. Narrowing the range, we found the lowest temperature at about 23◦C for an almost equimolar mixture (48%NEC). The corresponding dynamic viscosity is relatively high at 25 °C (270.96 mPa.s), but decreases sharply with temperature (7.3 mPa.s at 80◦C) and the hydrogen solubility is only around 25% lower than that for toluene (2-3).

Hydrogenation experiments were carried out with the eutectic mixture diluted in isododecane (1:4 by weight) at 20 bar between 100◦C and 170 °C, in a basket semi-batch reactor filled with industrial catalyst pellets. Kinetic modelling showed that NEC and its hydrogenated compounds Hx-NEC (x/2 = 2, 4 and 6 for the hydrogenated bonds) behaved similarly to NPC and Hx-NPC and can be lumped together as Hx. The reaction scheme appears to follow direct pathways (H0 → H4 → H8 → H12), except for two H12 isomers which seem to be formed directly from H2-lean compounds.

Finally, based on published results (4-7) concerning pure H12-NEC dehydrogenation experiments, performed in similar reactors with 5wt.% Pd/Al_2O_3 catalysts at 1 bar between 160 and 200 °C, we developed probable kinetic models. Surprisingly, a unique reaction scheme with direct pathways could not match the four data sets: H12-NEC → H4-NEC had to be added for two of them, while for another, H12-NEC → NEC had to be added. This suggests that different proportions of isomers were present in H12-NEC batches, as the latter are not commercial and were produced by various authors, and precise compositions of LOHC are needed for process development.

References:

(1) Stark et al., J. Chem. Eng. Data 2016, 46, 15660–15670
(2) Aslam et al., J. Chem. Eng. Data 2016, 61, 643–649
(3) Brunner, J. Chem. Eng. Data 1985, 30, 269-273
(4) Yang et al., Int. J. Hydrog Energy 2014, 39, 18976–18983
(5) Feng et al., Environ. Sci. Pollut. Res. 2020, 27, 36172–36185
(6) Kiermaier et al., Int. J. Hydrog. Energy 2021, 46, 15660–15670
Wang et al., Int. J. Hydrog. Energy 2018, 43, 7317–7325

POSTER #28

Active Photonic Glass for Hydrogen Generation

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Improving the efficiency of photogeneration and extending the lifetime of charge carriers, both linked to light harvesting, are critical challenges in advancing materials for photocatalysis. The integration of photonic crystals (PCs) into the design of a photocatalyst has the potential to significantly enhance its light-harvesting capability. The confinement of light within a PC structure can reduce the time propagation of light through the material due to multiple light-scattering phenomena and the slow photon effect, resulting in enhanced light harvesting. However, the fabrication of photonic photoactive glasses with chiral nematic structures (CN) as photocatalysts has not yet been reported. This work proposes a straightforward one-pot method to fabricate bioinspired PC glasses of TiO_2/SiO_2 (CNST) containing a replica of CN, as photocatalysts with improved light harvesting. The fabrication method combines sol-gel chemistry with Evaporation-Induced Self-assembly (EISA) of bio-template nanomaterials, specifically cellulose nanocrystals (CNCs). The resulting glasses exhibit iridescent colors with a controllable Bragg peak, achieved by adjusting the sol formulation without manipulating the incident light angle. Tuneable Bragg peak position offers the opportunity to access the region of slow photon phenomena, particularly the blue edge. The photocatalytic activity for H_2 generation was assessed under Mercury lamp illumination. The results indicated that CNST exhibits higher photocatalytic activities compared to TiO_2-P25. The successful transformation of CN into TiO_2 glass increases the light scattering within the nanostructure and, thus, the absorption factor of TiO_2. Furthermore, the study demonstrated that adjusting the blue edge of the Bragg peak position directly influences the photocatalytic performance of the photocatalyst, exploiting the slow photon effect. This unique structure was employed for depositing gold nanoparticles (AuNPs) inside the mesopores formed during the calcination of the biotemplate. The AuNPs serve as cocatalysts, effectively utilizing highly photogenerated charge carriers to facilitate the production of H_2. This study not only expands our understanding of photonic crystal properties but also highlights the potential for tailored design to optimize photocatalytic performance.

AuNPs embedded in SiO_2@TiO_2 core-shells to boost H_2 production: Optical and structural characterizations

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The conversion of solar energy to chemical fuels, such as hydrogen (H_2), as clean energy to replace

the use of fossil fuels has gained significant attention. H_2 is recognized as a green energy vector that is expected to solve the energy crisis and global warming issues. Photocatalysis is reported as a promising technology that could lead to the production of green H_2 using photocatalytic materials.

TiO_2 coupled to Au nanoparticles was found to be an efficient combination that is capable of producing H_2 under light excitation. Recently, our group found that covering Au nanoparticles (AuNPs) with a thin TiO_2 overlayer significantly enhances hydrogen production. Furthermore, altering the location of the AuNPs within the structure (Au/TiO_2 or TiO_2/Au) greatly affects hydrogen production efficiency. The reasons behind this difference remain unclear and require further investigation. In our group, we developed a new electrochemical device coupled to nonlinear optical spectroscopy for in situ monitoring of the chemical intermediates and species that adsorb, desorb, or dissociate at the extreme surface of the photocatalysts during the photocatalytic production process. Sum-frequency generation (SFG) spectroscopy, which works as an effective in-situ optical probe for monitoring interfaces, enables us to observe and track the steps involved in production at the surfaces of these nanostructures. We have developed a technique for depositing these core-shell nanostructures onto suitable substrates and have characterized them both structurally and optically to gain a deeper understanding of these materials. The chemical signature of all the absorbed intermediates was monitored in situ, and an attempt to establish the reaction mechanism occurring during the photocatalytic process on each system is proposed. This study provides valuable insights into the mechanisms of photocatalytic hydrogen production, offering a foundation for the design of more efficient materials for green energy applications.

POSTER #30

Cl-doped Polypyrrole for photocatalytic green H_2O_2 production

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Hydrogen peroxide (HO) is a promising green oxidant for various industrial applications. However, its synthesis is primarily achieved through the environmentally costly anthraquinone process. Consequently, several alternative routes for eco-friendly HO synthesis are under investigation. Photocatalytic HO production via H_2O oxidation and O_2 reduction stands out as a sustainable option, as it generates no harmful byproducts. Conjugated polymers, as organic semiconductor have emerged as one of promising candidates for photocatalytic H_2O_2 generation active under visible light in recent years. Here, we report a facile one step synthesis of Cl-doped polypyrrole (Cl-PPy) conjugated polymer via -radiolysis for photocatalytic HO production. We investigated the effect of Cl doping on HO production and studied various parameters (pH, light source, influence of oxygen, etc.) affecting HO yield. Several analytical and characterization techniques were employed to understand the behavior of the Cl-PPy photocatalyst and its role in HO generation. We found that Cl-PPy is highly active for photocatalytic HO production (0.90 mmol/g/h) from H_2O and O_2 without any sacrificial agent, under UV-Vis illumination. Its higher photocatalytic activity, ease of synthesis, and recyclability confirm its potential for sustainable photocatalytic HO production.

Copper-based electro-catalysts for sustainable chemical production from carbon oxides conversion

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Electro-catalytic conversion of carbon monoxide (CO) and carbon dioxide (CO_2) is a promising strategy to reach the sustainable energy future. Herein, several copper-based catalysts selective for electrochemical conversion of CO and CO_2 will be presented. A nitride-derived silver or gold doped copper (CuAuN or CuAgN) material showed the record value of faradaic efficiency (FE) of 76% for multicarbon alcohols production including ethanol and n-propanol. Detailed studies about morphology and chemical structure of the electro-catalysts by TEM, XANES, ECSA measurements will be presented.

References

1. H.P. Duong et al., Angewandte Chemie, 62, e202310788 (2023).
2. H.P. Duong et al., ACS Catal., 12, 10285-10293 (2022).

Crosslinked electron transport layer for stable perovskite solar cells

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At the beginning of the 21st century, carbon neutral and sustainable energy sources need to be considered instead of exhaustible fossil fuels to meet the growing demand and combat global warming. Within this very challenging race for alternative energy sources, metal halide perovskite solar cells (PSCs) have undergone unprecedented progress with efficiencies reaching now 26.7% and even over 30% in tandem configuration(i) and sparked great excitement in the photovoltaics community due to their flexibility and ability to be synthesized at low cost. However, since hybrid halide perovskites have a highly ionic character, they can decompose under external stresses such as moisture, solvents and heating cycles.(ii),(iii),(iv) Reducing environmental stresses imposed by moisture or oxygen for example, in order to improve the long-term stability of perovskite solar cells, is critical to the deployment of this technology.

In this communication, we will discuss the preliminary development of new electron transport layers (ETL) and their use in inverted PSCs. It is expected that these materials can create a more compact layer protecting the perovskite layer from oxygen and water, which is an important challenge in the field of PSCs and barely studied.(v)It is also expected that crosslinking improves mechanical strength, which is important for durability. Crosslinkable ETLs might also act as an insulating layer against harmful environment and for lead sequestration. Furthermore, these new materials will be integrated in devices to study the stability of perovskite solar cell while maintaining efficient devices

(i) National Renewable Energy Laboratory, (2021); www.nrel.gov/pv/cell-efficiency.html
(ii) Berhe, T. A. *et al.* Energy Environ. Sci. 9, 323–356 (2016) Organometal halide perovskite solar cells: degradation and stability
(iii) Leijtens, T. *et al.* Adv. Energy Mater 5, 1500963 (2015). Stability of Metal Halide Perovskite Solar Cells
(iv) Rong, Y. *et al.* Adv. Energy Mater 5, 1501066 (2015) the Challenge of Stability in Mesoscopic Perovskite Solar Cells
(v) Alex K.-Y. Jen et al., Energy Environ. Sci., 2015,8, 1160-1189 Recent progress and perspective in solution-processed Interfacial materials for efficient and stable polymer and organometal perovskite solar cells.

Energy production from wastewater-galvano-fenton process

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The chemical, textile, and pharmaceutical industries manufacture a wide variety of products. As a result, the waste streams generated by these industries can be heavily laden with contaminants, toxins, nutrients, and organic pollutants that pose unique treatment challenges. Synthetic dyes are one of the most common contaminants released into wastewater by these industries. Their elimination (degradation) can be a challenge for conventional wastewater treatment methods, which will require the development of effective methods for their degradation. In this brief study, the capacity of the Galvano-Fenton process as an advanced technique in terms of the simultaneous oxidation of the model pollutant (Direct Blue 14) and the energy production and saving is evaluated. The Galvano-Fenton technique utilises electrochemical oxidation to generate hydroxyl radicals, which efficiently degrade synthetic dyes while promoting energy recovery. The experiments were conducted in a galvanic cell using iron as a sacrificial anode and copper as a cathode and a 10 mg/L DB14 aqueous solution of pH of 3 (Pourbaix diagram) as a reaction medium. In this study, we investigated the effect of the pre-immersion time on the energy production as well as on the dye degradation. The pre-immersion time was varied from 1 to 10 min.

The obtained results showed that with a pre-immersion time of 5 min, a total conversion (100%) of the dye was achieved within 20 min and 32.23 mW/m^2 for every 1 μmol/L of dye, indicating a highly efficient degradation process. Furthermore, extending the pre-immersion time to 10 minutes resulted in similar energy production levels but a slight decrease in dye conversion efficiency, highlighting the importance of optimising pre-immersion conditions for maximising both energy output and pollutant degradation.

Expanding the applications of the SAFT-γ Mie Group-Contribution Equation of State: polycyclic aromatic hydrocarbons (PAH) and liquid organic hydrogen carriers (LOHC)

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Liquid organic hydrogen carriers (LOHC) are being studied as a promising and feasible alternative for hydrogen storage and transportation due to their high hydrogen uptake capacity, low flammability and stability at ambient conditions. This work focuses on expanding the applications of the SAFT-γ Mie Group-Contribution Equation of State by estimating the parameters of three new groups: aromatic bridgehead carbon (aC), methylene ”elbow” group connecting two aromatic rings (aCCH2aC), and molecular hydrogen (H2), starting from readily available experimental data on polyaromatic hydrocarbons (PAH), molecular hydrogen, and LOHC candidates such as alkylcarbazoles, diphenylmethane, and isomers of benzyl- and dibenzyl toluene. The model is able to predict with great accuracy the vapor pressure and saturated liquid density of said substances, with a %AADPsat,overall of 8.26%, and a %AADρliq,overall of 0.93%, as well as the vapor-liquid equilibria of PAH-alkane mixtures, but has important limitations when describing the structural nuances of molecules that present the same functional groups, which requires the definition of second-order interaction parameters for isomers like anthracene and phenanthrene.

Experimental investigation of hydrogen-enriched biogas deflagration for various compositions

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Experimental studies on the deflagration of hydrogenated biogas, taking into account different percentages of carbon dioxide (0%, 10%, 20% and 30%) and the addition of hydrogen at two different percentages (5% and 10%), were carried out in a constant cylindrical combustion chamber, for three equivalence ratios (ER=0.8, 1, 1.2). The aim was to explore the potential for recycling CO_2 in biogas applications. Analysis of the experimentally recorded pressure profile enabled crucial parameters to be calculated, including the net heat release rate (NHRR) and the deflagration index (K G). The results of the study highlight the effect of CO_2 concentration in biogas on combustion efficiency compared with CH_4/air combustion. It was found that an increase in the volume fraction of CO_2 in biogas leads to a reduction in the net heat release rate (NHRR), particularly in stoichiometric and rich mixtures. This finding is important because it provides insight into the combustion dynamics of biogas with varying levels of CO_2, contributing to the understanding of the efficiency of biogas combustion under different conditions. Under lean conditions (ER = 0.8), the combustion tests failed. However, the injection of 5% H_2 proved sufficient to improve the reactivity of the lean mixtures and promote flame propagation. The results indicate a superior performance of the biogas-hydrogen mixtures compared with the stoichiometric and rich mixtures of CH_4/air combustion. Nevertheless, the addition of hydrogen increased the deflagration index, an important parameter for managing explosion risks. This nuanced understanding provides valuable information for optimising the removal of CO_2 from biogas and combustion processes involving hydrogenated biogas, with implications for both efficiency and safety considerations.

High performance triple mesoscopic perovskite solar cells under real outdoor working conditions

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To successfully enter the photovoltaic market, perovskite solar cells (PSCs) still face several tough challenges. Scalability of the processes and long-term stability of the devices must be ensured. The latter, in particular, has been one of the main causes of skepticism for a long time and is still underestimated in most studies.

The best-performing devices all use gold or silver as the back contact, in conjunction with holetransporting materials (HTMs) acting as electron-blocking layers. The use of such noble metals limits the large-scale application of PSCs. In 2017, we published a structure proven to be stable for more than 10,000 h, measured under controlled standard conditions, by engineering an ultrastable 2D/3D perovskite junction. This structure is based on a fully printable architecture made of three mesoporous layers in which the perovskite is embedded. Triple mesoscopic devices use a carbon counter electrode, which has proven to be an effective method to significantly enhance the device's lifetime and has become one of the most prevalent scaffolds for constructing stable PSCs. Since then, carbon electrode-based perovskite solar cells have established themselves as highly promising device architectures for the next generation of photovoltaics, with efficiencies over 20% and unprecedented stabilities.

Outdoor operational conditions are rarely considered, and only a few reports can be found. All reports show that, as the testing time increases, devices suffer both reversible and, more importantly, irreversible degradations, which might not be detected in a constant temperature, constant one-sun irradiance Maximum Power Point (MPP) tracking procedure. For perovskite technologies to reach the level of consistent outdoor reliability seen with silicon and become commercially viable, more extensive outdoor testing is needed to identify and address potential failure modes in the field. In this communication, we will disclose preliminary results on triplemesoscopic perovskite solar cells in real indoor and outdoor working conditions.

Hydrogen-substituted Graphdiyne combined with hybrid Perovskites toward photocatalytic CO_2 reduction

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In response to the urgent need for sustainable and clean energy sources for the upcoming generations, converting CO_2 into fuel or chemical feedstock compounds could reduce, in principle, fossil fuel consumption and climate-changing CO_2 emission. One strategy aims to convert solar light to chemical fuel through the reduction of CO_2. In this context, photocatalysis involving light-irradiated catalysts offers both sustainable and relatively low-cost solutions to face the challenge. In this work, we investigate the CO_2 reduction under organic solution using Hsubstituted graphdiyne (HGDY) and perovskite composite. The perovskite was obtained by the dissolution-precipitation process, allowing the formation of the $Cs_4PbBr_6/CsPbBr_3$ junction in pyridine. Then, in situ growth of HGDY was performed under the presence of the perovskite, allowing solid composite formation. The material was characterized by TRPL, PL, TRMC, TPC, EIS, XRD,and TEM to shed light on the electronic and morphological properties. The results enable defining the charge transfer mechanism and the electronic properties of the composite, which was proven to be suitable for CO_2 reduction reactions. Indeed, our funding shows that H-GDY was revealed to play a crucial role in preventing the dissolution of perovskites in an aqueous solution, reducing photogenerated charge recombination, and improving charge separation efficiency. The hybrid HGDY/perovskite exhibits good activity and high selectivity to CO in CO_2 conversion.

Innovative Synthesis and Characterization of Non-Toxic Gold-Based Double Perovskites

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Renewable energy sources are increasingly recognized as the most viable solution for lowcarbon electricity production across various sectors, including industry, transportation, and buildings, while significantly reducing dependence on fossil fuels (1). Among these, photovoltaic energy, harnessing the sun as an inexhaustible resource, plays a pivotal role in accelerating the global energy transition. Within the diverse solar technologies, halide perovskites semiconductors stand out as particularly promising. Since their emergence in 2009 (2), these materials have demonstrated exceptional advantages, including remarkable optoelectronic properties (power conversion efficiency exceeding 25%, excellent charge carrier mobility, and low defect density) and cost-effective, energy-efficient fabrication processes (low-temperature synthesis), surpassing traditional silicon-based technologies in several aspects. However, perovskites face two major challenges: environmental instability and toxicity due to the presence of lead, which limit their widespread industrial adoption.

To address the issue of toxicity, numerous lead substitution strategies are being explored. In this work, we focus on Gold-based double perovskites, *Cs2Au(I) Au(III)X6* (*X = Cl, Br, I*), a promising non-toxic alternative to the conventional *APb(II)X3* composition . These new materials exhibit bandgaps in the range of 1–1.6 eV, which are highly suitable to maximize photovoltaic efficiencies.

We present an innovative synthesis method for these materials and provide comprehensive data on their structural (XRD, SEM, EDX, XPS) and optical (photoluminescence, Raman, absorption spectroscopy) characterization. These characterizations not only confirm the successful formation of the target phase but also unveil the intricate interactions between charge carriers and lattice vibrations, which could directly limit charge mobility while enhancing heat dissipation processes. Our analysis offers valuable insights into the potential of these semiconductor materials for applications such as photovoltaics, as well as photocatalysis, which is less dependent on charge carrier diffusion length.

(1) *International Energy Agency, 'Net Zero by 2050 – A Roadmap for the global sector'.*
(2) *Kojima, A., Teshima, K., Shirai, Y., Miyasaka, T. Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. J. Am. Soc. 2009, 131, 6050-6051.* https://doiorg/10.1021/ja809598r.

MOF-based catalysts for enhanced CO_2 conversion using non-thermal plasma-assisted methods

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Keywords: MOFs, Plasma, CO_2

Since the industrial revolution, the consumption of fossil fuels has accounted for most anthropogenic carbon dioxide (CO_2) emissions, resulting in environmental pollution and contributed in an increasing global warming effect (IPCC). In this regard, while the capture of CO_2 (point source, direct capture...) seems unavoidable to mitigate the effect of CO_2, considering the actual massive amount of this gas as a feedstock to be converted into useful chemicals and energy vectors has aroused as a sound strategy. Among the possible valorisation pathways, catalytic hydrogenation of CO_2 is a promising option that can to high energy density fuels (e.g., CH_4; methanol...).

Thus, in MOFPlasma project, we are focusing on developing new hybrid catalysts to improve the conversion of CO_2 into CH_4 (i.e., selectivity, kinetics, productivity rate, lower temperature, pressure) by means of Non Thermal Plasma (NTP)-assisted catalysis (2). This, combined to sustainable catalytic systems (higher stability /durability), is expected to enable a drastic decrease of the overall energy penalties, in comparison with conventional thermal hydrogeneration (3,4). This project specifically relies on the rational design of new Metal-Organic Framework (MOF)-based catalysts carefully loaded with catalytically active Ni-NPs (5).

Metal–organic framework materials, are a family of hybrid organic–inorganic crystalline porous solids, built-up of inorganic building units (IBU) (isolated or multinuclear metal ions) linked together by organic linkers (bridging ligands). The high and fine tunability of MOFs in terms of composition (organic ligand, inorganic moieties) and geometrical features (pore size and shape), (1) make them appealing candidates for catalytic CO_2 conversion.

In this presentation, we will explain our strategy in designing MOF-based catalyst through eco-compatible methodologies (Figure1). We will also share preliminary results obtained with our in-house developed catalysts.

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References

- Wang, S., Kitao, T., Guillou, N., Wahiduzzaman, M., Martineau-Corcos, C., Nouar, F., ... & Serre, C. (2018). A phase transformable ultrastable titanium-carboxylate framework for photoconduction. *Nature communications*, *9*(1), 1660. DOI:10.1038/s41467-018-04034-w. Da Costa, P., Hasrack, G., Bonnety, J., & Henriques, C. (2021). Ni-based catalysts for plasma-assisted CO2 methanation. *Current opinion in green and sustainable chemistry*, *32*, 100540. https://doi.org/10.1016/j.cogsc.2021.100540
- Mikhail, Maria & Da Costa, Patrick & Amouroux, Jacques & Cavadias, Simeon & Tatoulian, Michael & Galvez, Maria & Ognier, St´ephanie. (2021). Tailoring physicochemical and electrical properties of Ni/CeZrOx doped catalysts for high efficiency of plasma catalytic CO2 methanation. Applied Catalysis B: Environmental. 294. 120233. 10.1016/j.apcatb.2021.120233.
- Chen, H., Mu, Y., Shao, Y., Chansai, S., Xiang, H., Jiao, Y., Hardacre, C., & Fan, X. (2020). Nonthermal plasma (NTP) activated metal– *AICHE Journal*, *66*(organic frameworks (MOFs) catalyst for catalytic CO2 hydrogenation. 4), Article e16853. https://doi.org/10.1002/aic.1
- R. Del Angel et al., Metal-Organic Frameworks in Biomedical and Environmental Field. Springer, Cham, 2021. 10.1007/978-3-030-63380-6 1.

Plasmonic Photocatalysis on Noble Metal-Modified Titania

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Titania has been proposed as a photocatalyst to solve environmental problems and energy demand. Unfortunately, it is well-known that titania suffers from lack of vis-absorbing properties, which leads to limitation in its application, i.e., the utilization of titania usually requires UV light as an irradiation source. Hence, modification of titania has often been reported to improve the photoabsorption properties. One of the possible methods is based on deposition of noble metals (NM) on the titania surface. Photodeposited noble metal can induce titania activation under vis via localized surface plasmon resonance (LSPR). Here, the effect of properties and crystalline-phase composition of titania on the resultant properties of NM-deposited titania and their photocatalytic activities have been investigated. Although correlations between photocatalyst properties and photocatalytic activity have been reported, the experiments are usually performed under UV/vis irradiation, while the study under vis is still limited (1,2). Here, the research has been focused on the photocatalytic activity under vis to understand deeper the photocatalysis induced by LSPR activities.

Several samples of commercial and self-sensitized (e.g., inverse opal photonic crystals) titania with different properties and composition of crystalline phases were used in this study. The photodeposition of noble metals was conducted by irradiating titania suspension in 50 vol% aqueous methanol in the presence of noble metal precursor solution. The photocatalytic activity test under vis irradiation was conducted to evaluate the performance of photocatalysts. Photocatalytic activity evaluation was also conducted for: (i) pristine titania samples, (ii) reference experiment without photocatalyst, and (iii) inactive material (e.g., silica) modified with noble metals. The product was evaluated by gas and/or liquid chromatography. The properties of the materials were confirmed by diffuse reflectance spectroscopy (DRS), X-ray diffractometer (XRD) and field-emission scanning electron microscopy (FE-SEM).

Indeed, titania does not show photocatalytic activity under vis irradiation unless sensitization occurs. It has been found that properties of both deposited NM NPs and titania influence the photocatalytic activity under vis irradiation. Additionally, since commercial titania does not show photocatalytic activity under vis, confirming that no sensitization occurs, and thus it has been concluded that the photocatalytic activity of NM-modified titania must be caused by LSPR feature. The further mechanism clarifications and discussion on key factors for activity will be presented during this meeting.

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References

(1) Prieto-Mahaney, O. O.; Murakami, N.; Abe, R.; Ohtani, B. Correlation between photocatalytic activities and structural and physical properties of titanium(IV) oxide powders. *Chem. Lett.* **2009**, *38* (3), 238-239. DOI: 10.1246/cl.2009.238.

(2) Kowalska, E.; Mahaney, O. O. P.; Abe, R.; Ohtani, B. Visible-light-induced photocatalysisthrough surface plasmon excitation of gold on titania surfaces. *Phys. Chem. Chem. Phys.* **2010**, *12* (10), 2344-2355. DOI: 10.1039/b917399d.

Predictions of thermodynamic properties of CF_3I and its mixtures with no binary interaction parameter using the Multipolar SAFT-VR-Mie equation of state

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There is a renewed interest in the use of the refrigerant CF_3I for refrigeration and airconditioning applications, driven by its low global warming potential (GWP) and low (but nonzero) ozone depletion potential (ODP). In this communication, The M-SAFT-VR Mie model was successfully applied to predict the vapor-liquid equilibrium (VLE) behavior of CF_3I with alkanes and refrigerants by combining the existing thermodynamic data for this fluid. The model takes into account the effects of dipole-dipole, quadrupole-quadrupole, and dipole-quadrupole interactions to obtain more accurate predictions without the need for binary interaction parameters (kij=0). The suitability of the model was evaluated by combining the existing mixture data with the thermodynamic modeling method to simulate the properties of these mixtures. This study optimizes and obtains new interaction parameters for CF_3I, providing a theoretical basis for its use as a refrigerant or refrigerant mixture component in air conditioning or organic Rankine cycle (ORC).

POSTER #42

Silicon micropillar arrays decorated with Ag_xCu_{100-x} as enhanced photocathodes for solar-driven CO_2 reduction

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The development of efficient and sustainable photoelectrochemical (PEC) systems is crucial for addressing global CO emissions. Indeed, photoelectrochemical CO reduction (PEC-CO) using semiconductors (SCs) as photocathodes can convert harmful anthropogenic CO into lowcarbon fuels and valuable products, using solar radiation as a renewable energy input. Despite notable advances, PEC-CO is still at an early stage of maturity, and key aspects such as photoelectrode activity (current density, overpotential), selectivity and stability need to be optimized. This study explores the integration of Ag_xCu_{100-x} on silicon micropillars (Si MPs) as innovative photocathodes for solar-driven CO2 reduction (1). Si MPs offer several advantages for PEC reactions compared to flat surfaces, such as increased contact surface area with the electrolyte, higher catalytic loading, and enhanced light absorption. Given the interest of bimetallic catalyst, and particularly Ag_xCu_{100-x}, to improve the CO_2 conversion performance (2,3) the combination of SiMPs and Ag_xCu_{100-x} appears promising. The synthesis method chosen is Metal-Assisted Chemical Etching (MACE), a scalable and effective deposition technique. To the best of our knowledge, this is the first time MACE has been applied for bimetallic deposition on 3D structures.

Our results demonstrate that bimetallic deposition via MACE is feasible to 3D structures, providing relatively good control over NP composition and distribution of NPs along the micropillars. The as-synthetized 3D photocathodes (Ag_xCu_{100-x}/Si MPs) show a significant reduction in light reflectance (up to 45% in the visible spectrum) compared to flat Ag_xCu_{100-x}/Si. This translates to improved performances for solar energy conversion, including enhanced light trapping and photocurrent generation. For instance, $Ag_{50}Cu_{50}$/SiMPs achieved a radiometric power saved of 4.7%, compared to 3% observed for an equivalent flat photocathode (2). A clear influence of the bimetallic composition on the position of the PEC responses was observed, with $Ag_{20}Cu_{80}$/Si MPs emerging as the most favorable catalyst in terms of photocurrent and overvoltage (+220 mV *vs.* Ag/SiMPs and +600 mV *vs.* bare Si MPs). Regarding selectivity, the bimetallic photocathodes exhibit enhanced CO and CH production compared to their monometallic counterparts. For example, $Ag_{50}Cu_{50}$/Si MPs achieved faradaic efficiencies (FE) of 16.7% for CO and 9% for CH production. These results highlight the potential of bimetalliccoated Si MPs for PEC-CO applications.

Despite the advantage of SiMPs/Ag_xCu_{100-x} over flat surfaces in driving PEC reactions with lower external energy input, their CO_2 reduction performance remains limited, with H_2 being the dominant product. Our studies reveal NP agglomeration and detachment after PEC (especially for Cu/SiMPs), leaving exposed Si surfaces prone to the HER. We believe that the stability of the catalysts is negatively impacted due to intense gas evolution between MPs, combined with the intrinsic instability of Cu-based nano-electrocatalysts (4). While bimetallic interactions stabilize the catalyst to some extent, further improvements are necessary. Current efforts are focused on developing methods to prevent catalyst detachment (e.g., higher catalyst loadings, improved anchoring, etc.).

1. H. Chaliyawala, ChemElectroChem. (2024). Just accepted, doi.org/10.1002/celc.202400405.
2. H. A. Chaliyawala, ACS Appl. Energy Mater. **6**, 8397 (2023).
3. P. Guo, Energy Fuels **38**, 5659 (2024). 4. P. Wilde, Chem. Sci. **12**, 4028 (2021).

POSTER #43

Tailoring the performance of Pt/TiO_2 catalysts in the dehydrogenation of perhydrobenzyltoluene

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Introduction

Today hydrogen is considered a key energy vector in the transition to renewable energy. As a method of hydrogen storage Liquid Organic Hydrogen Carrier (LOHC) technology, particularly the perhydrobenzyltoluene (H12BT)-benzyltoluene (H0BT) couple, is gaining significant attention for its favorable physical properties and competitive H_2 storage density (6.2 wt%). To release hydrogen from LOHCs, Pt catalysts are currently used both in industry and academia. Our study explores the effect of TiO_2 supports on the structural and catalytic properties of Pt nanoparticles (NPs), intending to achieve higher activity and selectivity compared to a commercial Pt/Al_2O_3 catalyst.

Materials and Methods

TiO_2 supports were selected from commercial sources, some of which were subjected to heat treatment to change the ratio of polymorphs in the sample. TiO_2 supports are named A_x, where *x* stands for the percentage of anatase phase in the titania.

The 0.4 wt% $Pt/\gamma\text{-}Al_2O_3$ catalyst was provided by Heraeus. Pt/TiO_2 catalysts were synthesized via incipient wetness impregnation using $Pt(NH_3)_4(NO_3)_2$ precursor with subsequent calcination and reduction treatments. The loading of Pt was 0.5 wt%.

Catalytic tests were performed in a glass reactor with continuous removal of hydrogen connected to a GC-TCD. Recycling tests were performed in a stainless steel autoclave connected to a micro-GC. Reaction conditions : n(Pt)/n(H12BT) = $9*10^{-5}$, 260 °C, 4 h.

Results and Discussion

The preparation of Pt/A_x catalysts resulted in the formation of Pt NPs of 1.0-1.6 nm in average size. The performance of the catalysts depends on the nature of the support as well as on the structure of the particles. Compared to Pt/Al_2O_3, Pt/TiO_2 catalysts show higher productivity (*P*) and degree of dehydrogenation (DoD), except for Pt/A100. In particular, using Pt/A_0, 47 % of DoD was achieved with an initial productivity of 2.2 $g(H_2)/g(Pt)/min$, while for Pt/Al_2O_3 the values of DoD and *P* are 35 % and 1.4 $g(H_2)/g(Pt)/min$. As for the selectivity, Pt/TiO_2 catalysts lead to less methylfluorene (MF) side-product. Namely, at an H0 yield of 11 % using Pt/Al_2O_3, the MF yield reaches 0.40 %, whereas with Pt/A_0 only 0.09 % MF is formed. Selectivity improvement can be ascribed to both support and NP properties. Firstly, MF production can be promoted by acidic sites. Titania has lower acidity than alumina and rutile is less acidic than anatase1. Currently, FTIR measurements with a pyridine probe are being conducted to rationalize this behaviour. Secondly, undercoordinated Pt sites (steps, corners) can strongly adsorb H0BT, which can be subsequently converted into MF2. CO-DRIFTS analysis confirmed that the most selective catalyst has the lowest fraction of undercoordinated Pt. During the recycling, a mild deactivation of the Pt/A_0 catalyst was observed. A post-characterization and a regeneration of the catalyst will be presented during the conference.

References

1. H. Li, M. Vrinat, G. Berhault, D. Li, H. Nie and P. Afanasiev, *Mater. Res. Bull.*, **2013**, *48*, 3374–3382
2. F. Auer, A. Hupfer, A. B¨osmann, N. Szesni and P. Wasserscheid, *Catal. Sci. Technol.*, **2020**, *10*, 6669–6678.

Triple-mesoscopic perovskite solar cells with tunable bandgap for hydrogen production

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Today's development of the hydrogen fuel automotive industry is strongly limited by the lack of processes and technologies capable of providing sufficient amounts of hydrogen at acceptable costs without polluting the environment or increasing the CO_2 footprint. A very promising solution has been found in the use of solar energy, in combination with photovoltaic devices, to perform water splitting and produce hydrogen in an ecological manner. While the use of expensive catalysts and multi-junction solar cells has shown potential for high performance and a good solar-to-hydrogen (STH) conversion efficiency, the cost of such produced hydrogen remains prohibitive.

Various low-cost PV cells including silicon, perovskite and dye-sensitised solar cells have been investigated as a means of supplying the additional bias to the photoelectrodes made of earthabundant elements to achieve spontaneous water splitting.(i),(ii),(iii),(iv) Impressive STH efficiencies previously unattainable have been reported in the last few years. Among the PV devices, solution-processed organohalide perovskite cells are excellent candidates for tandem configurations with photoelectrodes due to their inexpensive solution processing, high efficiencies and bandgap tunability.(v),(vi)While the performance characteristics of perovskite devices are very well suited for water splitting, their extreme sensitivity to water makes them very difficult to use, directly as photoelectrodes.

Printable perovskite solar cells based on MAPbI3 in a TiO_2/ZrO_2/Carbon triple-layer mesoporous scaffold have shown a simple fabrication process(vii) and impressive stability.(viii) In addition, the hydrophobic mesoporous carbon layer protects the perovskite absorber from moisture penetration.

In this communication, we will discuss the development of tunable bandgap perovskite solar cells using triple mesoscopic architecture (Figure 1) as a stable solution and their potential application in water splitting.

(i) M. Grätzel *et al*., Nano Lett. 2015, 15, 3833.
(ii) J. H. Park *et al*., Nano Energy 2015, 13, 182
(iii) J. S. Lee *et al*., ACS Nano 2015, 9, 11820
(iv) S. Yang *et al*., J. Mater. Chem. A 2017, 5, 19091
(v) M. Grätzel *et al*., Science 2014, 345, 1593
(vi) S. I. Seok *et al*., Science 2017, 356, 1376
(vii) (vii) H. Han *et al.*, J. Nanophotonics 7 (2013) 073090-073090.
(viii) G. Grancini *et al*., Nat. Comm., 8, 15684, (2017).

Tuning the intrinsic catalytic activity of W and V doped MoS_x for hydrogen evolution reaction

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With low CO_2 emission and high energy density, green hydrogen is an alternative source to replace fossil fuels. At present, noble metals (Ir, Ru, Pt) and their oxides are the most effective electrocatalysts for hydrogen production from water via the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER), due to their high current density and low overpotential requirement. [1, 2] However, scarcity and their high cost limit their practical application.

Molybdenum disulfide (MoS_2) is considered as a potential electrocatalyst to replace precious metals for HER, due to its availability and stability.[1] However the active sites of MoS_2 are only localized to the edges of the crystallites, while the basal planes are catalytically inert. Thus, numerous methods such as doping, phase engineering and heterostructure approaches are proposed to improve its HER performance. Element doping is another promising solution to activate the catalytically inert in-plane hexagonal MoS_2 for efficient hydrogen adsorption besides promoting charge transport and modulating electron mobility. [2]

Here, we describe the *in situ* synthesis of amorphous W- or V-doped MoS_x via a one-step microwave synthesis. To alter the mechanical, electronic and electrochemical properties, the bulk materialis further exfoliated using sonication in solution and microwave treatment.[1,2] Electron microscopy and atomic force microscopy show the decrease in size from bulk MoS_x to few-layers crystallites. W- and V-doping improved the catalytic efficiency of the exfoliated materials by reducing the overpotential to reach 10 mA/cm^2 in H_2SO_4 (pH ˜2) from 235 to 192 mV.

Further work is now devoted to depositing exfoliated doped-MoSx materials onto a transparent conductive electrode in contact with a light-harvesting semi-conductor for photoinduced hydrogen production within the European project PH2OTOGEN (ph2otogen.eu). This project is cofunded by the Clean Hydrogen Partnership and the European Union (grant number HORIZONJTI-CLEANH2-2023-01-04).

References

1. Morozan, A.; Johnson, H.; Roiron, C.; Genay, G.; Aldakov, D.; Ghedjatti, A.; Nguyen, C. T.; Tran, P. D.; Kinge, S.; Artero, V. Nonprecious Bimetallic Iron-Molybdenum Sulfide Electrocatalysts for the Hydrogen Evolution Reaction in Proton Exchange Membrane Electrolyzers. ACS Catal. 2020, 10 (24), 14336– 14348, DOI: 10.1021/acscatal.0c03692
2. Quirós-Ovies, R.; Laborda, M.; Martín Sabanés, N.; Martín-Pérez, L.; Moreno-Da Silva, S.; Burzurí, E.; Sebastian, V.; Pérez, Emilio M.; Santamaría, J. Microwave-Driven Exfoliation of Bulk 2H-MoS2 after Acetonitrile Prewetting Produces Large-Area Ultrathin Flakes with Exceptionally High Yield. *ACS Nano* **2023**, 17, 5984–5993

Urchin-like TiO_2 nanostructure obtained using cellulose nanocrystals as growth biotemplate for Oxygen Evolution Reaction

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The oxygen evolution reaction is known as the limiting step in the water-splitting reaction. To overcome this issue, structuring material oxides such as TiO_2, and at the same time controlling the crystalline structure of the active phase, appear as promising alternatives to costly metallic nanoparticles. In this work, we demonstrated the synthesis of urchin-like TiO_2 using a soft method including cellulose nanocrystal (CNC) as a growth-directing biotemplate. It is found that modifying the ratio between the titanium precursor and the CNC amount allows controlling the crystalline structure and morphology of TiO_2. The proposed growth mechanism involved the reaction of surfacial hydroxyl groups of CNCs with TiCl, where the hydroxyl groups act as binding sites, ensuring the uniform distribution of metal precursors on the CNC surface. This interaction promotes the ordered growth of the inorganic material, ultimately resulting in the formation of urchin-like TiO_2 nanostructures. Furthermore, the surface hydroxyl groups of CNCs lower the surface free energy required for crystal nucleation through hydrogen bonding and charge interactions, which prior promotes the nucleation of the anatase/rutile mixed crystalline TiO_2 structure. The TiO_2, with its higher conductivity and superior electron transport properties, exhibited interesting electrocatalytic oxygen evolution reaction (OER) properties. The mixedphase TiO_2 significantly enhanced the catalytic activity compared to pure rutile TiO_2. The OER performance is attributed to the optimized electron transport within the mixed-crystalline phase and the increased surface activity sites of the sea urchin-like TiO_2, producing a synergistic effect. The finding provides a new idea into the design of efficient OER catalysts.

Hydrogen production through dehydrogenation of morpholine borane in the presence of PSSA supported PdAg catalyst

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For the transition to hydrogen economy, the challenges of producing hydrogen in a clean and efficient manner, as well as storage, must be resolved. Since solid hydrogen storage materials are lightweight materials containing high amounts of hydrogen by weight, they can store hydrogen safely and can be an alternative way for clean hydrogen production. Solid hydrogen storage materials can be easily hydrolyzed at room temperature in the presence of a catalyst. As a result of the hydrolysis reaction, high amounts of hydrogen gas and by-products (e.g., H3BO3, NaBO2, BO2) which are entirely harmless to the environment are released. In this study, four different catalysts, PSSA (Poly(4-styrenesulfonic acid-co-maleic acid)) stabilized Pd, PdNi, PdCo, and PdAg, were investigated for hydrogen production from morpholine borane (C4H12BNO). Among the PSSA stabilized bimetallic catalysts, PdAg showed the best catalytic activity at room temperature, and the optimum (metal)/(PSSA) ratio and metal ratios were 1/4 and Pd50Ag50. respectively. As a result of the kinetic studies, it was determined that the reaction was first order according to the catalyst and zero order according to the substrate. PSSA stabilized PdAg catalyst maintained its stability during the first 10 cycles, showed 100% catalytic activity in the first two cycles, and retained more than 70% of its activity at the end of the twentieth cycle. The activation energy and the enthalpy of the hydrolysis reaction was calculated as 55.68 kJ/mol and -53.22 kJ/mol respectively.

A Field-Controlled High-Temperature Superconducting Switch: Experiment and Simulation

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High-temperature superconducting (HTS) switches leverage dynamic and/or flux flow resistance to achieve on and off states, offering advantages such as high current capacity and low onstate power consumption compared to semiconductor switches. These switches can be triggered in various ways, including mechanically, thermally, by field, or by current. The field-controlled HTS switch, in particular, exhibits zero resistance in a low magnetic field (on-state) and finite resistance in higher fields (off-state). This work specifically focuses on the AC field-controlled HTS switch, where dynamic resistance increases with the amplitude, frequency, and DC transport current, while it decreases with the critical current. The paper presents the fabrication, testing, and simulation of such a switch, using a 2D unidirectional electromagnetic-thermal finite element model (FEM) validated by experimental results to investigate switch resistance.

The behavior of the field-controlled HTS switch is explored through both experimental and simulation methods. The HTS switch consists of a YBCO tape placed in the air gap of an iron-core copper-wound electromagnet. Resistance measurements were taken for varying amplitudes and frequencies of the electromagnet current, as well as for different DC transport currents through the HTS tape. To efficiently and accurately simulate the switch's performance, a 2D electromagnetic-thermal finite element model with unidirectional coupling was developed. The fabricated HTS switch achieves an on-state resistance of 93 $\mu\Omega$, which meets the specific requirements for applications such as transformer-rectifier HTS flux pumps. The developed model reduces computational time by 96% compared to a general bidirectional coupling model while maintaining accuracy.

Experimental results show that the HTS switch generates a 14 mV DC voltage with a 150 A DC transport current and a 0.28 T, 100 Hz magnetic field, resulting in an off-state resistance of 93 $\mu\Omega$. This performance is well-suited for applications such as HTS flux pumps. Furthermore, the 2D model developed here is highly effective for integration into HTS flux pump simulations.

POSTER #49

Energy management in a fuel cell-based hybrid electric vehicle using machine learning

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The emergence of PEM fuel cell hybrid electric vehicles marks a crucial step in the pursuit of sustainable and environmentally friendly mobility. At a time when challenges related to greenhouse gas emissions and the depletion of fossil resources urge us to rethink our modes of transportation, emerging technologies offer innovative solutions for reconciling energy efficiency and operational performance. At the core of this revolution lies energy management, a major issue that directly impacts the autonomy, reliability, and carbon footprint of electric vehicles. In fact, this paper studies energy management in fuel cell hybrid electric vehicles, focusing on energy efficiency and operational performance. Through careful evaluation of key components of the hybrid powertrain, we have mathematically modelled the behaviour of the fuel cell, lithium-ion battery, supercapacitors and power converters. Integrating the principles of artificial intelligence, particularly neural networks, and the dissertation proposes innovative and optimized energy management strategies.

In this context, this research sits at the intersection of fuel cell technology, electro mobility, and artificial intelligence, focusing specifically on the application of machine learning for proactive energy management in hybrid fuel cell electric vehicles. This innovative approach aims to overcome the complex challenges related to energy source variability, propulsion system performance optimization, and overall vehicle efficiency maximization.

Simulations are realized in Python via the Jupyter environment make it possible to assess the viability of these strategies, with the aim of improving fuel consumption and promoting sustainable mobility. Synthetic data is used for training and validation of models, suggesting significant improvements using machine learning techniques.

Laboratory Measurements for Machine Learning-based Modelling of LV Harmonic Sources for Harmonic Frequency Simulation

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The rapid integration of renewable energy sources such as solar and wind power, and new electric usages such as electric vehicles and heat pumps has necessitated the widespread adoption of power electronic converters. These converters, essential for interfacing renewable energy sources with the grid, introduce non-linear loads that generate harmonic currents. These harmonic currents distort the sinusoidal waveform of the grid voltage, leading to various power quality issues. As a result, the study of harmonic propagation and its impact on power systems has gained significant importance. Traditional modelling approaches, such as time-domain and frequencydomain methods, present limitations. Time-domain simulations, while offering high accuracy, often require detailed converter models, which may not always be readily available. Moreover, these simulations can be computationally expensive. Conversely, frequency-domain analysis, simpler and suitable for conventional nonlinear loads modelled as current sources, struggles to accurately capture the complex harmonic interactions observed in modern power systems. This is because many contemporary loads and sources exhibit voltage-source characteristics, necessitating more sophisticated modelling techniques.

In this work, we propose a novel methodology for modelling harmonic currents using machine learning techniques trained on laboratory-derived datasets. The methodology is validated through experimental tests on two representative cases: an electric vehicle charger and a threephase diode rectifier. A variety of machine learning algorithms, including regression neural networks, decision trees, and random forests, are used and compared to identify the most effective predictive models for harmonic current estimation. The results demonstrate the potential of these models to accurately predict harmonic disturbances under diverse operating conditions.

Furthermore, the integration of these predictive models into low-voltage grid frequency simulations is explored. The thesis investigates how these models can enhance frequency-domain analysis while addressing convergence challenges inherent to such simulations. Proposed solutions to mitigate these convergence issues are also to be presented to improve power quality assessment and grid reliability.

A shape optimization framework to design robust distance elements considering uncertainties

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Objectives and context

This work presents a robust design of a distance element in a protection relay that considers both the uncertainties of the impedances and the measurement errors. With the increase in electricity demand and the decrease in total grid inertia, the transmission power system will be operated closer and closer to its security limits. That is why there is a need to ensure both the sensitivity and reliability of the distance protection elements that protect lines. To ensure these properties, the grid operator must consider the measurement errors and the uncertainty on the line impedance parameter values. To do so, the proposed method uses Monte-Carlo simulations to estimate the probability density function (PDF) of the apparent impedance seen by a distance relay during a fault. Knowing this PDF, a shape optimization algorithm is then used to distort the shape of the distance element.

Method

The shape design is composed of two main steps. First, electrical computations of the voltage and current at the relay location are performed. The uncertainties and errors are considered using a Monte-Carlo process to estimate the probability distribution of the apparent impedance considering different fault locations and fault resistance values. In the second step, a fast and flexible optimization algorithm based on shape derivative is used to distort an element, maximizing the wanted criteria, e.g., selectivity for a fault on the downstream line or reliability for a fault on the protected line. Moreover, additional constraints on the shape can be considered, such as its desired area or perimeter.

Outcome and conclusion

Compared to classical methods (heuristic or finite-difference-based optimizations), our framework is based on a gradient-descent algorithm, the gradient being computed by shape derivatives. Therefore, our approach is fast and can handle as many control points as the user requires. So, the main advantage of this framework is that it can lead quickly to the design of more complex shapes than the most commonly used for better reliability and selectivity.

A robust fault location method for MV distribution feeders

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This paper presents a probabilistic fault location method (FLM) designed for Medium Voltage (MV) distribution feeders. Usually, the only instrumented nodes in a MV feeder are located at the primary substation, leading to significant limitations in the performances of impedancebased FLMs, such as multiple estimations (1). With emerging smart grids, Distribution System Operators (DSOs) are more likely to install measurement devices in some secondary substations. Most of the FLMs discussed in the literature have not been designed for distribution feeders but adapted from the transmission level. Precisely locating a fault is challenging when considering a radial topology and limited measurements. Nevertheless, a precise location is not mandatory since huge gains in reliability could be obtained with a localization zone between two manual switches. We aim to provide the DSOs with an area - whose size is as small as possible - where the fault is occurring while keeping the number of additional measurements as low as possible for cost constraints. In (2), a FLM is proposed and relies on estimating the zero-sequence voltage sags along the paths from the primary substation to each measurement node and vice-versa. Performing estimations as if the grid was sound leads to accurate estimates for the nodes which are upstream of the fault in the Top-Down process. In contrast, inaccurate estimates are computed in the Bottom-Up estimation. A solution area is defined as the lateral nodes to the one where the two estimates agree. However, this method proves to be very sensitive to measurement or line impedance value errors. To consider those potential errors, a series of Monte Carlo simulations are performed to estimate the 4-dimension Gaussian probability density functions (PDFs) of voltage and current along the paths. The volume of the intersection of the two estimates gives us an indication of the probability of the fault being lateral to the considered node. The robustness has been assessed with respect to various parameters such as fault resistance value, fault position, measurement error or line impedance estimation error. The results are obtained on the CIGRE MV distribution network benchmark considering a single-line-to-theground fault with resistance and uniformly distributed measurement errors and line impedance errors Here, to ensure that all the branches with more than 50% fault probability are put in the solution area, we would need to consider the lateral nodes to both nodes 3 and 4, meaning that only node 4 would need to be added to the non-robust solution area of (2).

References

(1) T. D. Le et M. Petit, “Earth fault location based on a Modified Takagi Method for MV distribution networks”, in *2016 IEEE International Energy Conference (ENERGYCON)*, 2016, 1-6. doi
(2) A. Bach, T.-D. Le, et M. Petit, ” A zero-sequence impedance-based fault location method for MV distribution feeders with sparse measurements ”, in *16th International Conference on Developments in Power System Protection (2022)*, Newcastle, UK, mars 2022, 7-12. doi

Energy Arbitrage Potential of Bidirectional Electric Vehicles Considering Virtual Mileage Impact on Vehicle Residual Value

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Vehicle-to-grid (V2G) technology knows an increasing interest with the rapid uptake of electric vehicles (EVs). This technology allows the EVs to leverage the periods it sits idle (i.e. not driving), which represents 97% of the time. When a bidirectional vehicle is plugged, it can either provide services to the grid (for example: frequency regulation, voltage support) or arbitrate its electricity consumption (for example: behind-the-meter energy optimisation, or trading energy on the market by using the EV battery as storage). We focus on the second use case since we observe a saturation of the most profitable markets such as primary frequency reserves by stationary batteries. In this work, we present a new approach as to how to assess vehicle economic degradation caused by additional cycles on the battery due to V2G operations. In most studies, this economic impact is represented by a fraction of the battery price depending on the storage capacity loss of the battery. However, this approach lacks realism as this cost is never actually paid by any actor. Upcoming standards and regulations will force EVs to account and display so-called ”virtual mileage”, which is an image of the energy discharged by the battery when performing V2G services. One virtual kilometre (*vkm*) is meant to represent the same vehicle degradation as a real (driving) kilometre. If virtual mileage is interpreted as such by the consumers, V2G will have a considerable impact on the vehicle retail value, also called ”residual value”. This devaluation depends on the age and accumulated mileage of the vehicle but is on average 1.09 c€/vkm and can go up to 4.07 c€/vkm according to our data. This translates as 0.054 € per discharged kilowatt-hour, which constitute a substantial hinderance to V2G profitability. We analysed the economic potential of V2G with EVs simulated to participate to the day-ahead electricity market for the French bidding zone and the year 2019, considering devaluation induced by virtual mileage. Our results show that the average economic benefits to V2G are much lower than the figures found in the literature, with an average of 8.54 €/EV over the simulated year. In an alternative scenario in which we do not account for devaluation, all things being equal, we reach a potential value of 39.7 €/EV. Virtual mileage could therefore become one of the largest inhibitors to V2G whereas a virtual kilometre is not as damaging to the vehicle as a real kilometre: the tires, the powertrain, and other equipment used while driving are not used when the EV is performing V2G. Moreover, virtual mileage only accounts for additional cycling ageing of the battery, which is only a component of the full battery degradation, so that, for instance, an EV with a high virtual odometer may retain a higher residual battery capacity than an EV with a low virtual odometer but stored fully charged for a long time. This paper hence highlights the limits to the concept of virtual mileage and proposes to favour alternative indicators for vehicle degradation.

POSTER #54

Loadflow method for long-term planning and the valorization of new levers

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The production of renewable energy plants on the network (renewable energies), and the diversification of electrical uses (private solar panels, electric vehicles, storage) create a change in the distribution of loads on the medium voltage network leading to the appearance of high voltage constraints.

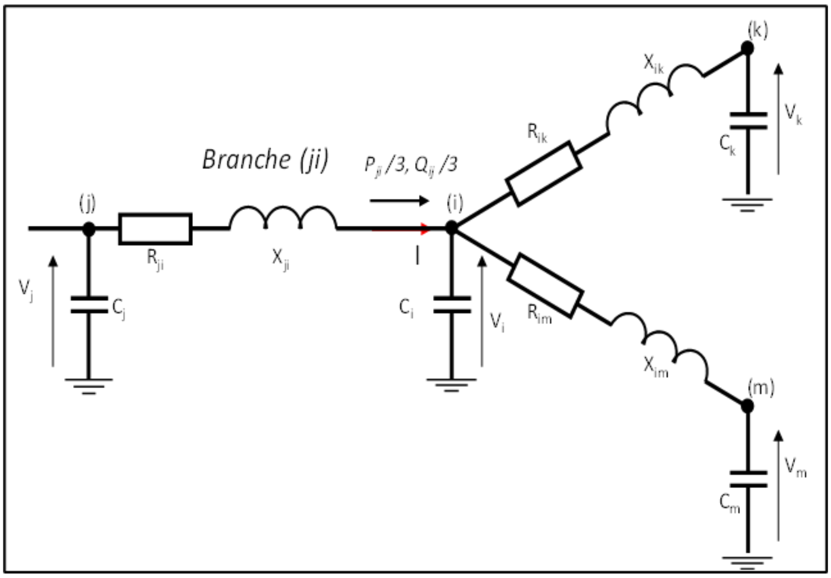
This new context forces distribution system operators (DSOs) to carry out long-term planning studies, which are characterized by a high calculation (1) cost, to maintain a time step of an hour.

In addition, DSOs have many levers to resolve the appearance of constraints, these can take different forms such as reinforcement, operation, or flexibility levers.

To assess the relevance of each solution in a long-term planning framework, it is essential to have a fast and precise calculation model.

The loadflow model developed in this article is based on the linearization of the voltage equations and on the principle of load additivity, to achieve a low calculation cost.

With the assumption of voltages close to the set voltage of the source substation, the accuracy error of the calculations is only a few percent. However, since the appearance of high voltage constraints is defined by a 2% increase in voltage along a feeder, this condition is mostly met on French networks.



Generic PI model on a radial structure

Thus, the linearization of the voltage equations developed in this article allows the matrix writing $U = M_P * P + M_Q * Q$, where:

- U the column vector of the voltages at the nodes.
- P,Q the column vectors of the active and reactive powers at each node.
- M_P, M_Q : the sensitivity matrices of the node voltages as a function of the powers at the network nodes

But also, the writing $U = M_R * R + M_X * X$ where :

- U the column vector of the voltages at the nodes.
- R,X the column vectors of the resistances and reactance of the lines connecting the nodes.
- M_R,M_X the sensitivity matrices of the node voltages as a function of the electrical characteristics of the lines.

This equation allows us to extract the network sensitivity matrices and thus analytically obtain several parameters:

- The capacity to accommodate production and consumption at a node k, without creating any constraint at a node i.
- The costs of the levers (line replacement, coil installation, capping in production, etc.) in (€/V), i.e. the cost to invest for the number of volts by which we wish to lower the voltage.

In conclusion, we manage to obtain a fast and precise loadflow allowing to carry out long-term planning studies with a time step of the order of an hour.

A long-term study in planning medium-voltage networks will be carried out subsequently to grasp all the benefits of this approach combined with the advantages provided by flexibilities.

(1) O. R. a. J. Bartels, Evaluation of Temporal Complexity Reduction Techniques Applied to Storage Expansion Planning in Power System Models, DLR–Institut für Vernetzte Energiesysteme e.V., Carl-von-Ossietzky-Str. 15, 26129 Oldenburg, Germany; 2020.