

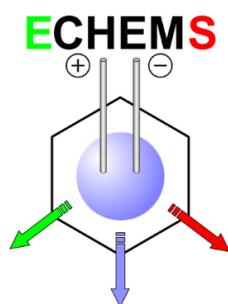
Abstracts of ECHEMS 2024

Welcome to the ECHEMS 2024 conference!

Electrochemistry in Molecular Transformations

Where? Raitenhaslach TUM Academy Center,
Burghausen, Bavaria, Germany

When? 28th to 31st of October 2024



Hour	Monday	Tuesday	Wednesday	Thursday
08		Breakfast	Breakfast	Breakfast
		Shuttle to Venue	Shuttle to Venue	Shuttle to Venue
09		<i>Kevin Lam</i>	<i>Kim Daasbjerg</i>	<i>Cyrille Constantin</i>
		<i>Mickaël E. Avanthay</i> <i>Svenja Bechtold</i> <i>David Moser</i>	<i>Santanu Ghorai</i> <i>Abhishek Saini</i> <i>Michael Papadakis</i>	<i>Ben Johnson</i>
10	Bus Transport			<i>Darren Buesen</i> <i>Mark Potter</i>
		Coffee Break	Coffee Break	Coffee Break
11		<i>Rok Narobe</i> <i>Alexandra Matei</i> <i>Tingran Liu</i>	<i>Daniel A. Scherson</i> <i>Matthieu Haake</i> <i>Yoshua Moore</i>	<i>Matthieu Etienne</i>
				Closing Ceremony
12	Registration & Lunch	Lunch	Lunch	Lunch
13				
	Opening Ceremony	<i>Helena Lundberg</i>	<i>Christophe Léger</i>	Bus Transport (Venue to Munich Airport)
14	<i>Serena Arnaboldi</i>	<i>Darryl Nater</i> <i>Laurent Bouffier</i> <i>Xiuming Sun</i> <i>Kathryn Toghill</i>	<i>Steffen Hardt</i> <i>Léonard Olivotto</i> <i>Andrea Fasano</i> <i>Maya Landis</i>	(RedoxShield participants may stay)
15	<i>Wanmai Srisuwananno</i> <i>Sara Grecchi</i>			
	Coffee Break	Coffee Break	Coffee Break	
16	<i>Chularat Wattanakit</i>	<i>Omer Yehezkeli</i>	<i>Sylvie Chardon</i>	
	<i>Claudio Fontanesi</i> <i>Alexander Kuhn</i> <i>Florian Breitschaft</i> <i>Abdulaziz Al-romema</i>	<i>Claudio Righetti</i> <i>Yvonne Schöbaw</i> <i>Joshua Lawrence</i> <i>Paniz Izadi</i> <i>Tobias Vöpel</i>	Shuttle to Burghausen & Privately Guided Tour at the Castle	
18		Conference Dinner at Klostergasthof Raitenhaslach		
	Welcome Buffet & Poster Session			
19				
	Shuttle to Hotels in Burghausen		Free time! Walk through the historic city center of Burghausen and grab dinner!	
20				
21				
22		Shuttle to Bar Mathilda in Burghausen	Shuttle to Raitenhaslach	

Please refer to the full program schedule for the exact times.

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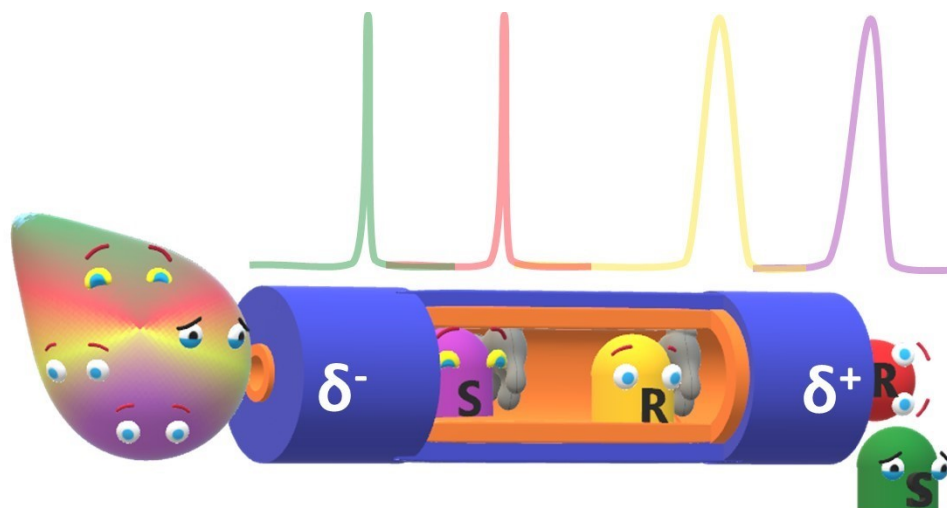
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Keynote Talks

Wireless Synthesis, Detection, and Separation of Chiral Analytes

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While the enantioselective separation of chiral molecules, induced by external stimuli, has been well established, the development of miniaturized chiral soft systems capable of swiftly and wirelessly distinguishing such molecules is still a challenge. However, the unique synergy between the mechanical properties and the enantioselectivity of conjugated polymers, powered by bipolar electrochemistry (BPE), could lead to so far unexplored effects. The soft tubes we've prepared mimic chiral columns typically used in HPLC but with the added advantage of wireless operation, a feature inherent to BPE. This allows for the in-situ synthesis and separation of molecules in the enantiopure form without needing a physical connection to an HPLC apparatus, making it a cost-effective and rapid solution. The miniaturized nature of this system also hints at the potential for using these devices in wireless chiral separation scenarios that demand low-cost, quick, and in situ analyses. [1, 2]



References:

- [1] S. Grecchi, G. Salinas, R. Cirilli, T. Benincori, S. Ghirardi, A. Kuhn, S. Arnaboldi, *Chem* 2024,10, 660–674.
- [2] S. Grecchi, F. Malacarne, R. Cirilli, M. Dell'Edera, S. Ghirardi, T. Benincori, S. Arnaboldi, *Anal. Chem.* 2024, 96, 4901–4908.

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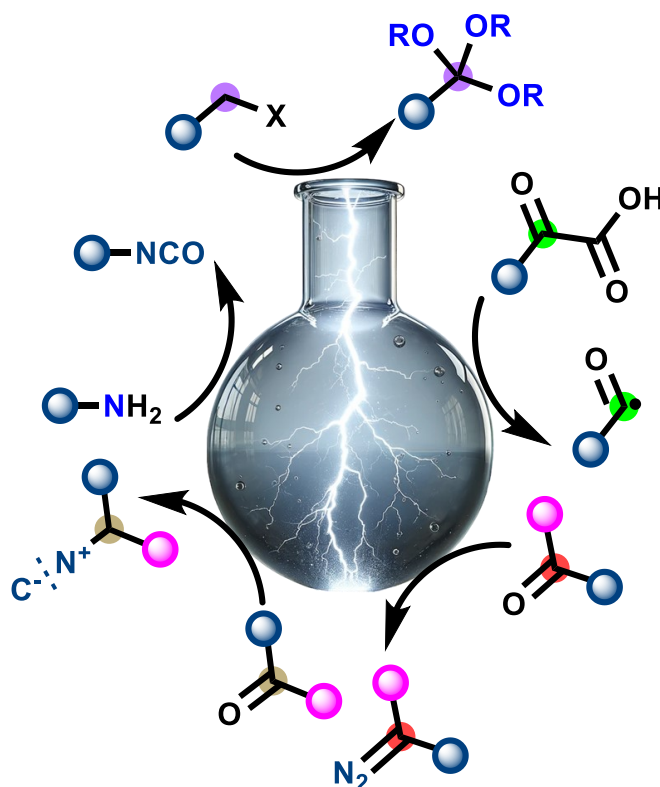
Your Chemistry Has Got Potential: Highly Reactive Intermediates Without the “Bang”

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Synthetic organic electrochemistry has its roots in the classic work of Faraday and Kolbe on the electrolysis of aliphatic carboxylic acids. Although a large number of transformations have been developed since then, many of which have been successfully applied in various industrial processes, the potential of preparative organic electrochemistry remains underestimated. However, the growing impetus to find greener and more cost-effective alternatives to traditional synthetic methods has recently led to the development of novel electrosynthetic methods.

In this talk we will present new, safe, green, affordable and efficient ways to generate highly reactive organic intermediates such as iso(thio)cyanates, isocyanides, orthoesters or even diazo compounds! We will also discuss their scale-up using flow electrosynthesis and demonstrate their real-world application in the pharmaceutical industry by reviewing case studies carried out with GSK, AstraZeneca and Johnson & Johnson.



Electroreductive Transformations via C–O and C–S Bond Activation

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In this work, a net reductive approach is demonstrated to afford new electrochemically driven synthetic methods for C–O and C–S bond cleavage in alcohols and thiol derivatives. The bond activation result in alkyl radical intermediates that may be trapped with electron deficient alkenes in Giese-type transformations. Alternatively, the open shell intermediates can undergo radical-polar crossover to the corresponding anions with subsequent cross-coupling with different classes of electrophiles.

Steering Carbon Dioxide Reduction Toward C–C Coupling Using Copper Electrodes Modified with Organic Films

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Copper offers a unique capability as a catalyst for producing multicarbon compounds in the electrochemical CO₂ reduction reaction (eCO₂RR). However, despite recent progress, designing catalytic systems with high product selectivity remains a significant challenge. This study systematically investigates how eCO₂RR is affected by film thickness and porosity. On a polycrystalline Cu electrode, immobilizing porous bipyridine-based films of varying thicknesses results in nearly a tenfold enhancement of the intrinsic current density for ethylene formation, while multicarbon product selectivity increases from 9.7% to 61.9%. Supported by a microkinetic model, we propose that porous and thick films increase both local carbon monoxide partial pressure and surface coverage by retaining in situ generated carbon monoxide. This reroutes the reaction pathway toward multicarbon products by enhancing carbon–carbon coupling.¹

Next, we derivatize Cu electrodes using the spontaneous grafting of benzenediazonium salt to elucidate the effect of surface restructuring. These electrodes show a remarkable sixfold improvement in Faradaic efficiency for C₂₊ products compared to unmodified Cu, while hydrogen evolution is reduced significantly. Comprehensive characterization reveals that the grafted organic film induces changes in the valence state of Cu and triggers surface reconstruction. Overall, these studies highlight the significance of customizing both the molecular film and Cu surface structures to improve the selectivity of Cu catalysts in eCO₂RR.

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Outer-Sphere Effects on the Catalytic Properties of Hydrogenases

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The comparison of homologous metalloenzymes, in which the same inorganic active site is surrounded by a variable protein matrix, has demonstrated that residues that are remote from the active site may have a great influence on catalytic properties. I shall exemplify this idea by summarizing recent findings on the diverse molecular mechanisms by which the protein matrix may define the oxygen tolerance, catalytic directionality and catalytic reversibility of hydrogenases, enzymes that catalyze the oxidation and evolution of H₂. These mechanisms involve residues in the second coordination sphere of the active site metal ion, more distant residues affecting protein flexibility through their side chains, residues lining the gas channel and even accessory subunits. Such long-distance effects, which contribute to making enzymes efficient, robust and different from one another, are a source of wonder for biochemists and a challenge for synthetic bioinorganic chemists.

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Recent Advances in Mechanistic Analysis of Molecular Catalysis of Electrochemical Reactions

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Molecular catalysis of electrochemical reactions is an area of intense research, with significant focus on both small molecule activation and the electrification of chemical transformations. Understanding reaction mechanisms is essential for the rational design of more efficient catalysts. In this context, cyclic voltammetry, when combined with controlled potential electrolysis and spectroelectrochemistry, is recognized to be a valuable analytical tool.

In this presentation, we will explore recent advances in the mechanistic analysis of molecular catalysis in electrochemical reactions. Specifically, we will discuss: (i) the key factors governing the transition between fast and slow catalytic regimes in controlled potential electrolysis, (ii) self-modulation phenomena in catalysis, and (iii) the potential of cyclic voltammetry for investigating electrophotocatalytic processes—an emerging field in molecular electrochemistry.

Asymmetric Synthesis of Chiral Organic Compounds at Electrochemically Generated Enantioselective Metal Surfaces

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The asymmetric synthesis of chiral compounds is of crucial importance, especially in modern chemistry. Typically, the rational design of catalysts for the highly efficient enantioselective synthesis is still challenging as they can be used to selectively produce the desired enantiomer, which can exhibit a positive effect on biological activity, whereas the other even shows toxicity. In this contribution, we report new perspectives using chiral encoded mesoporous metals prepared via electrodeposition in the simultaneous presence of non-ionic surfactants and chiral molecules acting as mesoporogens and chiral templates, respectively, as electrocatalysts for asymmetric synthesis¹⁻⁶. For example, we have successfully generated a series of chiral imprinted metals, ranging from noble to non-noble metals and alloys, including Pt, Ni, and PtIr, imprinted with various chiral molecules, such as the enantiomers of 3,4-dihydroxyphenylalanine (DOPA), mandelic acid and phenylethanol¹⁻⁶. The chiral features are perfectly retained confirmed by the discrimination between two enantiomers using Differential Pulse Voltammetry (DPV) even after removing the chiral templates.

We were able to improve the efficiency of these chiral imprinted metals in terms of their stability by elaborating alloys with chiral features obtained by co-electrodeposition of Pt and Ir in the presence of a liquid crystal phase and chiral templates. Their stability can be significantly enhanced when using them for electrocatalysis and also as a heterogeneous catalyst for the reduction reaction of model compounds, eventually leading to high enantiomeric excess (>85-95 %) ⁴⁻⁵. We extended this approach also to the synthesis of real pharmaceutical compounds with very high enantiomeric excess (>95 %) ⁶⁻⁷. In addition, we explore new ideas for the design of chiral encoded metals for CO₂ upgrading to chiral compounds with high enantiomeric excess via an electrochemical approach. In summary, this novel family of nanostructured metal layers exhibits promising perspectives in the general frame of catalysis/electrocatalysis, especially for real pharmaceutical applications and CO₂ conversion.

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Photo-Driven Enzymatic or Microbial Fuel Cells for the Conversion of Biomass or Bioplastic to Electricity and Added-Value Chemicals

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Utilizing biomass or bioplastics as an energy source has attracted increasing attention in the last few decades. Crops are composed of ~40% cellulosic materials which are not currently used as food and can be further exploited. Polylactic acid is a widely used polymer in industry that may be utilized as an energy source after first use. Methods to convert biowaste into added-value chemicals or green energy are required for a better and sustainable world. Herein, we present the design of photo-bioelectrochemical cells, that uniquely enable photooxidation of small organic molecules while suppressing competing reactions such as water oxidation. To enable energy-efficient devices, the developed photoanodes were conjugated with enzymes¹ or bacteria that facilitate biomass degradation into soluble molecules, which in turn, enable their consumption as an electron source in bias-free photoelectrochemical cells. The high-energy electrons can be further utilized by conjugated biocathodes to generate electrical energy or valued molecules such as ammonia.²

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Beyond CO₂ Activation: Shedding Light on N₂O Electroreduction Catalyzed by Low Valent Iron Porphyrin

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In addition to its euphoric and anesthetic properties, nitrous oxide (N₂O) is known for its significant impact on the environment. The increase of atmospheric N₂O since the start of the industrial era has contributed to greenhouse gas emission, with a greater global warming potential than carbon dioxide (CO₂), as well as ozone layer depletion.[1] Therefore, N₂O activation is of key interest to help mitigate environmental issues. However, its high chemical inertness makes it challenging.[2] For this purpose, the electrochemical reduction of N₂O into dinitrogen (N₂) using molecular catalysts is a promising approach.[3] Taking inspiration from CO₂ electroreduction catalysis, widely studied with iron porphyrin molecular catalysts, our recent work has revealed the interesting catalytic activity of low-valent iron tetraphenylporphyrin (FeTPP) electrochemically generated for the selective reduction of N₂O into N₂ [4]. Here we illustrate the investigation of the mechanism involved in the N-O bond activation (deoxygenation reaction) and we compare it with the C-O bond activation (in CO₂), using electrochemical and spectro-electrochemical tools. Particular attention has been paid to determine the active form of the catalyst as well as the role of the acidic co-substrate.

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Next Stop, The Kinetic Zone! A Geometric Interpretation of Kinetic Zone Diagrams in Electrochemistry

Ben Johnson

TBA

Bioelectrochemistry Without Potentiostat (or Any Electronics)

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In recent years, we have been interested in performing electrochemistry without potentiostat, i.e. without providing electrical energy as input for running the bioelectrochemical reaction, and without recovering the produced energy, because the potential difference between the involved redox reactions was too low to be meaningfully exploitable and also because maximizing the current density was preferable to maximizing the power density. In practice, two electrodes are simply short-circuited at the same potential, but still specialize into anode and cathode due to differences in the local environment or the nature of the electrode surface.

After a brief overview of this concept in the literature, I would like to present three examples of bioelectrochemistry performed without potentiostat for, 1) nitrate reduction with microbial electrodes, 2) biohydrogen production from organic waste and 2) NADH regeneration with H_2 . The methodology for characterizing the short-circuited system will be discussed and the main results will be highlighted.

Autonomous Chiral Encoded Metal-Motors for Enantioselective Synthesis

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Molecular-imprinted metals hold a promising position as chiral catalysts for asymmetric electrosynthesis with high enantioselectivity[1]. However, the synthesis of enantiomers *via* classic electrochemical reactions may encounter some limitations due to the restricted active surface area and the need for an external electric power supply. To bypass these problems, wireless electrodes, not directly connected to a power supply, have been employed, which allow also avoiding mass transport limitations [2]. In this context, we propose a pioneering design of self-propelled artificial micromotors for heterogeneous enantioselective synthesis. They contain a reactive metal such as zinc, serving as the integrated driving force to propel the micromachine by its spontaneous oxidation, combined with chiral imprinted metal overlayers. A fraction of the liberated electrons is used for hydrogen bubble formation to ensure autonomous motion, whereas the other electrons are transferred to the chiral metal shell, where they trigger the enantioselective production of chiral compounds by reducing a prochiral precursor.

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Wireless Asymmetric Umpolung Electrosynthesis of Enantiopure Lansoprazole

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Electroorganic synthesis has proven to be an exciting tool for the asymmetric conversion of pro-chiral compounds. In this work, we introduced a wireless methodology based on bipolar electrochemistry, in synergy with the enantioselective capabilities of inherently chiral oligomers, to induce an umpolung chirality transfer [1,2]. The success of this approach was demonstrated by the electro-conversion of a racemic mixture of lansoprazole, resulting in an enantio-enriched solution of a single antipode.

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The Role of Spin in Chiral Recognition: An Electrochemical-Based Approach

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In this communication some experimental results will be presented addressing the possible role of spin in the process of chiral recognition. In particular, a rather exhaustive picture, also concerning chiral induction, is based on the use of electrochemical experiments within the so called spin-dependent electrochemistry paradigm. Electrochemical results are critically compared and discussed in the light of X-ray natural circular dichroism (XNCD)[1], magnetoconductive AFM (mcAFM)[2], Kelvin probe AFM (KPFM) and optical rotation resolved photoluminescence results, paper in preparation and [3].

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Magnetic Field-Enhanced Redox Chemistry On-the-Fly for Efficient Enantioselective Synthesis

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Chemistry on-the-fly is an interesting concept, extensively studied in recent years due to its potential use for recognition, quantification and conversion of chemical species¹. It is also a promising approach for asymmetric synthesis, since it can help to overcome mass transport limitations, present for example in conventional organic electrosynthesis. Herein, the synergy between a magnetic field-enhanced self-electrophoretic propulsion mechanism² and enantioselective redox chemistry on-the-fly³ is proposed as an efficient strategy to boost stereoselective conversion. We employ autonomous Janus swimmers as redox-active elements, exhibiting a well-controlled motion with a speed that can be increased by one order of magnitude in the presence of an external magnetic field. While moving, these bifunctional objects convert spontaneously a prochiral molecule into a specific enantiomer with high enantiomeric excess⁴. The magnetic field-enhanced self-mixing of the swimmers, based on the formation of local magnetohydrodynamic vortices⁵, leads to a significant improvement of reaction rate and overall yield.

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Electrochemical Upcycling of SO₂ into Alkyl Alkenylsulfonates using a Multicomponent Approach

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Sulfur dioxide (SO₂) is produced on a million-ton scale via the combustion of elemental sulfur and is mainly used for production of sulfuric acid. But SO₂ is also a potent greenhouse gas, posing serious health and environmental threats.

Our group however has demonstrated the direct electrochemical upcycling of this pollutant into high-value-added products like alkenylsulfonates using styrenes as simple and commercially available starting materials. The metal-free procedure facilitates the generation of monoalkylsulfites from SO₂ and alcohols in-situ. These intermediates serve a dual role as nucleophilic reactants while simultaneously ensuring high conductivity. The feasibility of our protocol was demonstrated by an extensive scope with 44 examples and yields up to 81%, in addition to a gram-scale experiment. Cyclic voltammetry studies facilitated the elucidation of the reaction mechanism.

Currently, our research focuses on the expansion of these techniques to other valuable substrates bearing an electron-rich double bond, like enamines and enol ethers.

In-Situ Electrolyte for Electrosynthesis: Scalable Anodically-Enabled One-Pot Sequence from Aldehyde to Isoxazol(in)es

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Electrochemical transformations are considered a green alternative to classical redox chemistry as it eliminates the necessity for toxic or waste producing reagents. Typical electrochemical reactions require the addition of a supporting electrolyte or additives to enhance the conductivity or reaction outcomes. However, this is often accompanied by an increase in produced waste. Here, we report an "in-situ electrolyte" concept for facile, transition-metal-free, additive-free one-pot electrochemical preparation of isoxazol(in)es from the respective aldehydes. The protocol utilizes no halogenated solvents and no external oxidants, while salt side-products provide the ionic conductivity necessary for electrosynthesis. The Reactions are performed using the state-of-the-art electrodes for the chlor-alkali industry dimensionally stable and scalable mixed metal oxide anode and platinized titanium cathode of high durability. The cascade transformation comprises the condensation of aldehyde to oxime followed by its anodic oxidation and subsequent intra- and/or intermolecular [3+2] cycloadditions with an appropriate dipolarophile with yields up to 97%.

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Bromide-Mediated Silane Oxidation: A Practical Counter-Electrode Process for Nonaqueous Deep Reductive Electrosynthesis

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Organic electrosynthesis delivers transformations that are more efficient, safer and greener than their non-electrochemical counterparts,¹ for example by enabling reductive electrolysis at strongly negative potentials ('deep reductions', < -2 V vs Fc/Fc⁺) without harsh reductants. Existing counter-electrode processes for non-aqueous electrochemical deep reductions have shortfalls: sacrificial metal anodes release stoichiometric amounts of metal ions whereas using divided cells requires specialized reactionware which is costly and resistive.²⁻⁴

Herein, we present a metal-free counter-electrode process for undivided electrochemical deep-reductions that involves a mediated electrochemical silane oxidation. It was applied to our reductive hydrodefluorination of trifluoromethyl arenes⁵ that required a divided cell, enabling a flow adaptation; as well as to other electrochemical reductions that relied on sacrificial anodes or divided cells.

Overall, this novel counter-processes is metal-free, inexpensive and has shown robustness in anhydrous and aqueous electrochemical reduction. It is a potential alternative to separators and sacrificial anodes, enabling flow adaptations and lowering the barrier of entry for electrochemistry newcomers.

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***In-Situ* Spectroelectrochemical Study of Semiconducting Polymers and their Modifications**

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Semiconducting polymers have garnered significant attention in recent years for their potential usage as active layers in opto-electronic devices and bioelectronics. Our contribution will show the electrochemical study of two polymer systems, one of which focuses on carbazole-based redox polymers (1) and one which uses ethylenedioxythiophene-based copolymers (EDOT) (2). In the first case, *in-situ* spectroelectrochemistry is employed to monitor the crosslinking of carbazole units and identify the charge carrier species. Their conductivity behavior is investigated and discussed. With the usage versatility offered by *in-situ* spectroelectrochemistry EDOT and its functionalization before and after copolymerization is shown. A range of polymer analogous reactions including click chemistry are discussed as pathways to tuning not only the properties but also to tailoring the materials for specific demands of various applications, e.g. bioelectronics.

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In-Situ Spectroelectrochemistry as a Tool for Ionization Energy Determination for Organic Solar Cell Applications

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Current organic solar cells systems have been shown to reach higher short circuit currents and high fill factors rendering them as promising competitors to other 3rd generation solar cell materials. A promising material combination is the binary blend of the donor-acceptor copolymer PBDB-T-2F as donor and non-fullerene acceptors (e.g., Y6), reaching efficiencies around 15%[1]. *In-situ* spectroelectrochemistry is a powerful tool to evaluate the oxidation onsets and therefore HOMO energy levels in these systems. Recording the absorption maxima as a function of the applied potential in cyclic voltammetry allows the identification of the different radical cations present in these blends. The energy barrier between the HOMO levels of the donor and acceptor, can be estimated with this method, with higher HOMO differences resulting in better charge carrier separation and carrier transport.

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Practical Electrochemical Hydrogenation of Nitriles at Nickel Foam Cathode

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Despite many positive attributes of catalytic hydrogenation methods, significant safety risks are associated with supply chain of compressed flammable, potentially explosive hydrogen gas (production, transportation, storage) and its handling in a research lab or industrial production plant. In this context, electrochemistry offers a neat solution, as it allows reduction of protons (H^+) at a metal cathode material (M) leading to hydrogen adsorbed onto a metal surface (M-H), which is an essential intermediate in hydrogenation reactions.

We present a readily scalable electrochemical method for hydrogenation of nitriles. In contrast to other electrochemical hydrogenation methods, it relies on the use of readily available commercial materials, which can be reused several times. The use of inexpensive nickel foam as cathode material offers an important advantage in scalability due its availability and excellent mechanical properties. To capitalize on this, we show the ease of scalability from batch screening cells to differently sized flow cells.

On the Use of Propylene Carbonate and Dimethyl Carbonate as Green Solvents in Organic Electrosynthesis

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Polar aprotic solvents such as dimethylformamide, acetonitrile or dichloromethane are commonly used in electroorganic syntheses because of their excellent properties, however, they are highly problematic in terms of sustainability. The propylene carbonate-dimethyl carbonate (PC-DMC) system is a promising alternative with comparable electrochemical properties and with enhanced environmental, health and safety characteristics. This work presents a systematic study on the PC-DMC system as reaction medium for organic electrosyntheses, spanning from the characterization of electrolyte properties to representative test reactions on a preparative scale. Anodic synthesis of diaryliodonium salts, cathodic reduction of ketones, and TEMPO-mediated alcohol oxidations serve as use cases, showing that yields are comparable to the ones obtained in conventional solvents. An interesting feature is the possibility for tuning the physicochemical properties of the reaction medium by varying the PC-DMC ratio, which was shown to impact the catalytic rate of TEMPO-mediated alcohol oxidations and the yield of diaryl iodonium synthesis.

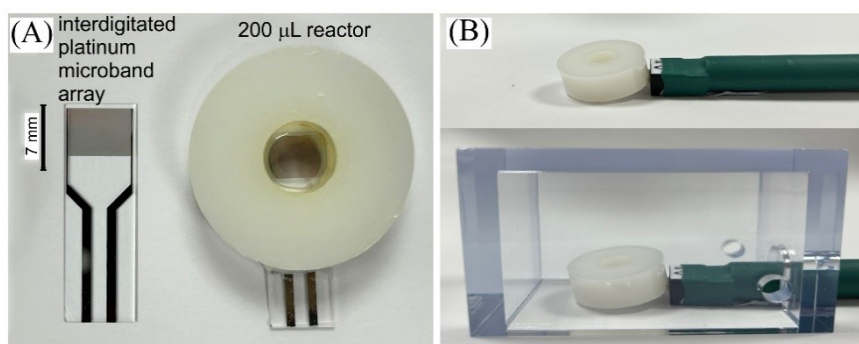
Electrolyte-free Paired Electrosynthesis on Interdigitated Electrodes

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Interdigitated electrodes (IDEs) were introduced to electrosynthesis by Girault and Belmont in 1994.^[1] The properties of interdigitated electrodes help minimizing Ohmic losses between anode and cathode and thereby allow electrolysis without intentionally added electrolyte. IDEs allow a beneficial increase in local rates of inter-electrode mass transport. Due to the closeness of the anode and cathode, IDEs (see Figure) could be used in electrolyte-free electrosynthetic systems.^[2]



In this work, a microreactor with interdigitated microband electrodes was designed and tested. The gap and the width of the microband are 5 µm and the maximum volume of the cell is 400 µL. Starting material was dissolved in the solvent with no electrolyte added, and then electrolyzed in galvanostatic or potentiostatic mode. Tetraethyl ethylenetetra-carboxylate (TET) reduction was investigated and reached over 90% yield. Isotope effects are investigated. A finite element model is employed to explore transport in the absence of electrolyte.^[3] The IDE mechanism is related to localized photocatalysis processes based on single electron transfer reactions (SET) and could lead to a broader range of applications.^[4]

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Electrochemical Hofmann Rearrangement at High Current Densities in a Simple Flow Setup

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Amines and Carbamates are central functional groups in organic chemistry with numerous applications in both the fine chemical and pharmaceutical industries. One of the most used methods towards generating these moieties is the Hofmann rearrangement. However, this reaction relies on the stoichiometric use of harmful halo-compounds. Recently, the electrochemical in-situ generation of halo-species from halide salts has attracted great interest. Application of this methodology also led to the development of an electrochemical Hofmann rearrangement, however, the described methodologies are limited to low current densities. As such, we have developed a reliable electrochemical version for the Hofmann rearrangement, using high current density in a simple, commercial flow electrolysis cell. The protocols have been optimized towards both aromatic and aliphatic substrates, yielding good to excellent yields across a broad substrate scope with high functional group tolerance. The method can also be performed on multi-gram scale with good yield, while being inherently safe.

In Situ Confocal Fluorescence Microscopy: a Toolbox to Decipher Molecular Mechanism

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Recently, the coupling between electrochemistry and fluorescence microscopy has gain a major renewal of interest. Indeed, the simultaneous collection of both analytical signals can provide a new level of space- and time-resolved information, enabling to uncover spatial or temporal heterogeneities of electrode processes [1-3].

We have implemented fluorescence confocal laser scanning microscopy (F-CLSM) under electrochemical control in order to map either in 2D (xy plane of the electrode surface) or in 3D (at different z positions away from the electrode surface) various reaction layers associated with interfacial electron transfer processes.

Two different strategies can be implemented by taking advantage of either a pH-sensitive fluorescence dye such as fluoresceine or by using appropriate electrofluorogenic species like phenoxazine dyes for example [4,5].

In this contribution, we will first describe the instrumental setup, as well as discuss several molecular systems. The comparison between large scale macroelectrodes and much smaller microelectrodes will be used to address the limit of resolution that can be reached [6].

Finally, the application to bioelectrodes decorated with active enzymes will be proposed in order to extend the scope of F-CLSM imaging [7,8].

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In-Situ Spectroelectrochemical Study of N-type Semiconducting Polymers for Bioelectronic Devices

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Semiconducting polymers have become attractive for their potential application as channel materials in organic field-effect transistors (OFETs) and organic electrochemical transistors (OECTs) in bioelectronics. Our research is focused on n-type polymers, namely the donor-acceptor copolymer poly[N,N'-bis(2-octyldodec-yl)-1,4,5,8-naphthalenediimide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) [P(NDI2OD-T2)](1)-(2) and its derivatives modified with oligo(ethylene glycol) side chains and selenophene-vinylene-selenophene as donor units (3). We are using an *in-situ* spectroelectrochemical approach to investigate the electrochemical behavior to identify the redox species at different doping degrees with in parallel recorded UV-vis-NIR spectra. Since the onset reduction potentials of polymers can be determined by mapping the spectral evolution from the neutral in the first reduced state, our operando technique is advantageous over classical cyclic voltammetry to estimate the lowest unoccupied molecular orbital (LUMO) energy level for their integration in devices.

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Understanding the Redox Mediated Alkaline Hydrogen Evolution Reaction

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High-pressure alkaline water electrolysis to hydrogen and oxygen is a century old mature technology that is marked by numerous advantages; more cost effective than other electrolyser methods, no rare or high-cost catalyst materials, routinely delivers >10000 hours continuous operation, and is modular and scalable. However, the technology suffers several challenges related to energy efficiency, material degradation, and operational complexity. In particular, the kinetics of the reaction are sluggish, leading to much higher potentials than thermodynamics predict also requiring higher operating temperatures and pressures.

In this work we describe optimisation of a redox mediated approach to alkaline hydrogen evolution and value-added oxygenation reaction, whereby a core flow battery supplies charged reducing and oxidising agents to indirectly and rapidly produce hydrogen on demand, as well as producing valorised chemicals and materials. Here, a range of redox mediators and catalysts are evaluated and benchmarked for decoupled alkaline hydrogen evolution.

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Exploring *Ch*CODH II for Electrochemical CO₂ Reduction Reaction and Water-Gas Shift Reaction

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[NiFe]-Carbon monoxide dehydrogenase (CODH) catalyses the reversible reduction of CO₂ to CO by high selectivity, activity and near-zero overpotential. CODHs feature a complex multimetallic NiFe₄S₄ active site alongside additional FeS clusters involved in the electron transfer (ET) from the buried active site to the surface^[1,2]. In this study, a highly efficient direct ET is reached by immobilizing *C. hydrogenoformans* CODH-II on functionalized multi-walled carbon nanotubes electrodes. The enzyme's stability and oxygen tolerance were also studied under various solvents, temperatures, and pH conditions. With the aim to perform the multiprotein biological water-gas shift reaction (WGSR) in vitro^[3], we show that the H⁺/H₂ and CO₂/CO redox couples are both reversible at electrodes modified with a bisdiphosphine Ni(II) hydrogenase-mimic^[4] and CODH, opening avenues for direct WGSR. The design of a biofunctionalized nanostructured electrode offers promising pathways for sustainable energy conversion and carbon utilization strategies through the integration into novel biotechnological devices.

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Developing Thermistor Electrodes for Analysing the Heat Fluxes During Extracellular Electron Transfer of Electroactive Microorganisms

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Extracellular electron transfer couples the metabolism of electroactive microorganisms (EAM) with insoluble electron conductors beyond the cellular envelope and allows the transformation of chemical energy into electrical energy and *vice versa*. EAM are being harnessed in microbial electrochemical technologies (MET) for numerous applications including waste water treatment and production of chemicals. To allow reasonable upscaling of MET, thermodynamics of EAM and the energy fluxes during EET needs to be understood. A first step was performed by Korth *et al.* developing bioelectrocalorimetry for measuring the heat production of *Geobacter* enrichment biofilms at graphite anodes. This study revealed the existence of the microbial electrochemical Peltier heat as a considerable energy sink accounting for $27 \pm 6 \text{ kJ e-mol}^{-1}$, but the required sophisticated setup limits experimental data generation. To solve this, we developed simple thermistor electrodes for analyzing the heat fluxes during extracellular electron transfer and the corresponding calibration and validation procedure.

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Analytical Bioelectrochemistry of Thylakoid Membrane Electron Transport

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Analytical electrochemistry has enabled the interrogation of electron transport of various biomolecules, yet its application has generally been confined to *in vitro* studies of isolated proteins and metabolites [1]. This prevents researchers from obtaining a systems-level understanding of the complex electron transport pathways found *in vivo* [2]. To address this, we have developed a bioelectrochemical system for analysing electron transport within cyanobacterial thylakoid membranes. Isolated thylakoid membranes were interfaced with state-of-the-art, structured electrodes [5]. Photocurrents obtained with these electrodes exhibited a distinctive shape which was dependent on multiple electron transport pathways. Further analysis revealed light-dependent and light-independent features of photocurrents, which could be directly related to the electron transport activities of different photosynthetic and respiratory proteins. Spectroelectrochemical analysis confirmed these results were consistent with spectroscopic techniques commonly used to analyse photosynthesis. These results demonstrate that analytical bioelectrochemistry can provide information on complex electron transport processes occurring within native biological membranes.

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On the Way to Reach Industrial Applications in CO₂ Conversion Within Electrobiorefineries

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Electrobiorefineries integrate microbial and electrochemical synthesis to produce chemicals and fuels. For achieving a circular economy, using CO₂ as the sole carbon feedstock in electrobiorefineries is of special interest. Despite the growing interest in electrochemical CO₂ reduction reaction (eCO₂RR), its industrial application remains limited. One reason is the lack in assessment of the system performance, such as carbon conversion (CCE), electron (CE) and energy (EE) efficiencies. Therefore, eCO₂RR was performed at the 10 and 100cm² tin-gas diffusion electrode (Sn-GDE). In conditions being representative of numerous previous studies, CCE was increased from ≈20% to 41% (being only 9% below the theoretical maximum), by adjusting the inlet CO₂ flow rate from ≈35 to 16 mL min⁻¹, while CE was kept high (≈85% for formate) at both conditions and scales. This demonstrated the promising performance not only in laboratory settings but also viability for further scaling up in industrial contexts.

Development of an Oxygen-Insensitive Electrochemical Oxidase-Based Biosensor

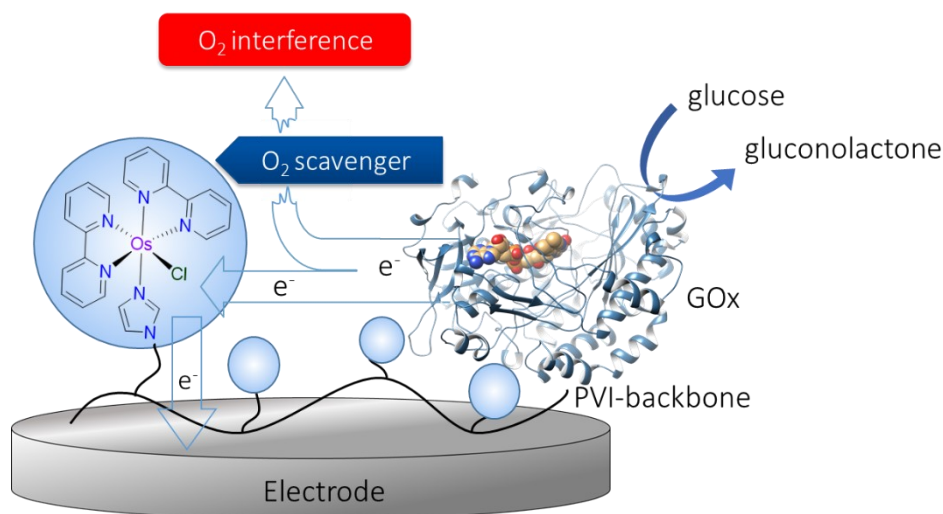
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Continues monitoring of glucose levels in human blood for diabetic patients is very essential. This requires a high-performance biosensor, that is, to oxidize glucose and deliver a generated current, which is proportional to the glucose concentration. Redox-hydrogel film as a mediator can implant an oxidizing enzyme, creating a stable and active glucose sensing system. Os-complex modified redox polymer was tested for glucose biosensing based on GOx enzyme. [1-2] GOx is highly specific and selective to glucose which minimizes the interferences from other substances. The composition of the film was optimized to obtain the highest catalytic current density. An enzymatic O₂ scavenger was developed to remove oxygen interferences on glucose sensing. [3] The oxygen-removing system was patented in 2021 [4] and used to validate its performance. The optimum-modified electrode is adapted to a screen-printed electrode, which is designed to integrate the oxygen scavenger as a final model of the oxygen-free glucose biosensor. Controlled-potential coulometry is used to give accurate quantifying results of glucose concentrations. All combined would lead to a highly reliable minimally invasive self-monitoring blood glucose (SMBG) biosensor.



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Bio-Inspired Catalyst Design Strategy for Green Ammonia Production

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Ammonia is crucial for urea synthesis and for the global chemical economy. NH_3 is synthesized by traditional Haber-Bosch process at high pressure (~ 150 bar) and temperature ($\sim 600\text{K}$) and it leads to global CO_2 emissions around $\sim 1.44\%$ ¹. So far bio-catalytic, enzymatic and microbial, homogeneous catalyst & heterogeneous catalyst are deployed for sustainable ammonia production with poor yield and high over-potential². Here Our findings show that bio-inspired Cobaloxime with axial modification can accomplish electrochemical NO_2^- to NH_4^+ yield $105\text{mg hr}^{-1} \text{mg}_{\text{cat}}^{-1}$ with faradaic efficiency $\sim 99\%$ FE under near-neutral conditions to mild acidic condition. For the device application, we heterogenized best performing electrocatalyst with MWCNT upon Ni foam for electrolyser using flue gas as source of NO_x^- . This work demonstrates promising aspect of molecular catalyst for industry ready green ammonia production.

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A Seawater Electrolyzer with a Designed Metalloprotein

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The quest for sustainable energy sources has notably shifted towards green hydrogen production, given its potential to establish a carbon-neutral energy infrastructure.^{1,2} Our study introduces an innovative biomimetic catalyst design rationale that precisely integrates a hydrogen-producing cobaloxime core into a robust azurin protein scaffold to harness the unique interplay between the transition metal active site and the protein-based outer coordination sphere (OCS). This artificial metalloprotein displayed a substantial enhancement in the electrocatalytic H₂ proficiency compared to the precursor cobaloxime in near-neutral aqueous media under oxic conditions, which reached its apex TON $\sim 4.9 \times 10^5$; Overpotential ~ 0.10 V at pH 6.0 with a faradaic efficiency of $\sim 95\%$. This oxygen-tolerant and robust metalloprotein was further fabricated as an operational electrolyzer that consistently produced hydrogen in 1:1 distilled water/seawater blend (Cell Voltage 2.65 V, output current density 1.5 mA/cm²). Hence, this study accentuates the importance of adopting a systematic expansion of the biomimetic catalyst design strategy for green hydrogen production.

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Stereochemical Tailoring of Nickel-Based Electrocatalyst for Hydrogen Evolution Reaction

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Over the past two centuries, the exponential consumption of fossil fuels has led to their depletion, necessitating a shift towards catalytic systems that generate environmentally friendly fuel sources. Hydrogen is abundant and is considered an “ideal” fuel since its combustion only releases water vapours into the environment. Recent endeavours focus on developing novel methods, such as electrocatalytic and photocatalytic hydrogen evolution reactions (HER), to harness hydrogen from renewable and sustainable resources.¹

Hydrogenases, the biological systems that naturally produce hydrogen, serve as valuable models for designing metalorganic complexes with mimetic catalytic abilities. Drawing inspiration from [NiFe]-hydrogenases, we studied a series of thiosemicarbazone-based nickel complexes and their potential as electrocatalysts for HER.² Additionally, we explored the impact of the methoxy group's positioning on the catalytic properties of these compounds, comparing various configurations with our reference catalyst, NiTSC-OCH₃, featuring the -OCH₃ moiety at the para position. Our investigation focuses on how subtle structural variations in almost chemically identical compounds influence their catalytic performances in electrocatalytic HER.

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Electrostatic Stimulation of Electron Transfer at the Metal-Electrolyte Interface

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This contribution will illustrate the use of electrostatic stimulation techniques developed in our laboratory[1], to explore new aspects of the oxidation of adsorbed carbon monoxide on Pt electrodes, CO(ads)|Pt, and the reduction of selenite in aqueous acidic electrolytes, not as yet unveiled by the use of more conventional methods. This technique relies on modifications in the electrostatic potential in the solution immediately adjacent to the electrode generated by the passage of current between an electrode placed very close to the working electrode polarized at constant potential, and a second electrode far away from it. Judicious application of this novel tactic will make it possible to measure the rates of surface diffusion to be complemented by normal incidence differential reflectance spectroscopy to image in real time the rates of propagation of adsorbates along electrode surfaces.

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Selectivity Control of a Cobalt-Based Molecular Cathode for Aqueous CO₂ Electroreduction Through Molecular Surface Engineering

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The preparation of molecular heterogeneous catalysts stands as an attractive and promising alternative for electrochemical CO₂-conversion into hydrocarbons and/or useful chemicals.¹ These hybrid catalysts combine the robustness of material-based catalysts with the ease of tuning of molecular structures.² In particular, cobalt-based cathodes have shown great promises for selective CO₂-conversion once incorporated into electrolyser devices.³ Therefore, our group recently modified the ligand scaffold of a cobalt complex based on a tetraaza-macrocyclic ligand⁴ with a pyrene-anchoring unit allowing for its smooth and controlled immobilisation onto multi-walled carbon nanotube (MWCNT) based electrodes.

This novel molecular cathode allows efficient CO₂-to-CO conversion in fully aqueous and neutral conditions, giving rise to large turnover number for CO production (TON_{CO}) up to 20x10³ at reasonable overpotentials (η = 450 mV) with faradaic efficiencies of >95%. Furthermore, electrochemical investigations and XAS analysis allowed gaining more insights into the chemical environment of the hybrid catalyst upon reduction and post-electrolysis.⁵

Understanding Mass Transport at Individual and Connected Pores of 3D Electrodes to Access their Morphology and Size Distribution

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3D-structured porous electrodes are necessary for upscaling electrochemical systems in an applied sense. Electrocatalytic performance depends on the pore structure (pore morphology and pore size distribution) as it defines catalyst loading and the efficiency of substrate/product transport to/from the biocatalysts incorporated within. While many methods are available for characterizing the pore morphology and pore size distribution at multiple scales, none are suitable for in-situ characterization of macropores (pores greater than 50 nm) in which the transport of molecules takes place following the laws of bulk diffusion. Such a method would be extremely beneficial as a routine characterization for screening the electrode fabrication or monitoring its degradation over prolonged operation. We use voltammetric simulations to gain a fundamental understanding of how the diffusion of small molecules within pores of various morphologies and sizes impacts the current response, and aim to use this knowledge to demonstrate how the pore morphology and pore size distribution can be extracted from the non-catalytic current read-out of real 3D electrodes.

Bidirectional Catalysis for Protection of Polymer-Embedded [FeFe]-Hydrogenase from O₂ under Intermittent Hydrogen Evolution

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The intermittent availability of renewable energy causes a need for energy storage potentially realized by producing H₂ in electrolyzers. However, abundant electrocatalysts for hydrogen evolution suffer fast degradation under intermittent operation due to oxidative stress.^[1] Hydrogenases incorporated into thin films of viologen-based polymers are highly active electrocatalysts for hydrogen conversion and self-protected from oxidative damage under conditions of unidirectional H₂-evolution.^[2] However, reversing the reaction to achieve protection under conditions optimized for H₂ evolution is a challenge, because H₂ evolution and O₂ reduction are competing for the available electrons.

Here we show that ensuring bidirectionality of catalysis enabled protection of the enzyme from O₂ under conditions of intermittent H₂ production. Open circuit potential experiments were combined with UV/Vis-spectroscopy and simulations demonstrating the equilibration of the Med_{ox}/Med_{red}-ratio to the potential of the proton/hydrogen redox couple. The catalytic bias was controlled by varying the pH-value and the mediator potential. By this, high current densities (0.40 ± 0.04 mA cm⁻² on flat electrodes) were combined with long lifetimes under aerobic conditions (>1h at OCP). The propagation of O₂ into the film was simulated suggesting that increasing the film thickness and optimizing the film homogeneity have the potential to further increase the lifetime by orders of magnitude.

Considering that bidirectionality, high energy efficiency and high O₂ sensitivity are common features of abundant (bio)electrocatalysts,^[3] the demonstrated protection strategy bears great potential to increase the applicability of these catalysts for reduction reactions in general.

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Solvent Tuning to Enable CO₂-to-CO Electrocatalysis by CNT-Supported O₂-Sensitive CODH Under Aerobic Conditions

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A promising approach to selectively reducing CO₂ to CO with low energy costs is to take advantage of efficient biocatalysts such as CO Dehydrogenase (CODH) enzymes¹. CODHs rely on a nickel/iron active site, buried inside a protein scaffold to reversibly reduce CO₂ with near-zero overpotential and exceptional catalytic activity. However, CODH is strongly oxygen-sensitive and must be handled under strictly anaerobic conditions.

Key to achieving efficient bio-electrocatalysis is the design of tailored electrodes with a minimized enzyme-electrode distance to avoid electron transfer rate limitations. For this purpose, carbon nanotube (CNT)-based electrodes are ideal. Once modified with adapted anchoring groups², they enable a high enzyme loading on highly conductive surfaces.

This study uses tailored electrolytes to enhance oxygen tolerance of CODH-modified electrodes. Deep Eutectic Solvents (DESs)³ are particular organic media with low oxygen diffusion properties^{4,5}. The electrocatalytic CO₂ reduction at CNT-supported CODH in DES has been investigated to enable efficient CO₂-to-CO conversion in a non-natural environment as a means of increasing their oxygen tolerance.

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Kinetic Modeling of the Reversible or Irreversible Electrochemical Responses of FeFe-Hydrogenases

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FeFe-hydrogenases catalyse H₂ oxidation and evolution. Prototypical hydrogenases catalyse the reaction in a reversible manner. Reversibility is defined in relation to the thermodynamic driving force that the enzyme needs to start catalyzing the reaction in either direction[1]. Recently, new, “atypical” hydrogenases were discovered, characterized by different catalytic properties[2]. One of those is the first FeFe-hydrogenase to be active in both directions of the reaction, but in an irreversible manner[3]. It has the same active site and the same kind of catalytic cycle of reversible hydrogenases[4]. Therefore, the origins of their different reversibility must reside in kinetic details of their catalytic cycles.

To elucidate the molecular reasons behind reversible and irreversible responses, we developed a kinetic model to quantitatively interpret the catalytic voltametric responses of reversible and irreversible hydrogenases[5]. The results allowed the understanding of the crucial steps of the catalytic cycle in determining the reversibility of the catalytic response[6].

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Tuning Carbon Nanomaterials as Active Supports for Hydrogenases

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The use of hydrogenase enzymes in biotechnology offers possibilities for cleaning up biocatalysis, replacing glucose or formate as reductants with the atom-efficient H₂ gas. Hydrogenases have been employed on carbon supports for the cofactor-free reduction of nitro-compounds, which occurs via an electrochemical mechanism on the conductive support at potentials provided by enzymatic hydrogen oxidation. [Sokolova D, Lurshay T, Rowbotham J, Stonadge G, Reeve H, Cleary S, et al. Cofactor-free biocatalytic hydrogenation of nitro compounds for synthesis of amines. ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-vqfc1 This content is a preprint and has not been peer-reviewed.]. This project aims to exploit electrochemically active carbon nanomaterials which are suited to supporting biocatalysts. Carbon materials are synthesized by chemical vapour deposition while material qualities are achieved both by targeting diverse intrinsic structural properties and through heteroatom doping. Furthermore, electro-analytical and electro-synthetic methods are employed and the synthesized materials are utilised as heterogeneous supports for redox enzymes.

A Kinetic Barrier to Enable Semiconductor-Free Biophotovoltaics

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Despite the outstanding properties of photosynthetic proteins for light-induced charge separation, their integration in semiconductor-free photovoltaic cells remained unproductive until now because of recombination of the charge carrier at the photocathode surface. Herein, we combine a mobile inner-sphere charge carrier and a polymer-bound outer-sphere electron mediator to kinetically suppress charge recombination by regulating their respective electron transfer rates at the photoelectrode. Chemical modification of the surface of the electrode led to an efficient kinetic barrier that decreases the rate of recombination of the inner-sphere charge carrier by two orders of magnitude. Simultaneously, the low activation energy for charge transfer with the outer-sphere electron mediator maintains a favored kinetic pathway for reduction of the photo-oxidized protein and thus generates a net power output under illumination. These findings open a unique and general approach to prevent charge recombination in biophotovoltaic cells that are free of semiconductor materials.

Decoupling Electrochemical CO₂ Reduction via Redox Mediators

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Electrochemical transformation of CO₂ into value added chemicals offers a promising solution to the urgently needed replacement of fossil fuels as a source of small hydrocarbons for use as energy carriers and chemical feedstocks. A range of simple products are commonly reported using various metallic electrode-catalysts; however, most are limited in their effectiveness by poor long-term stability and low activity. The two-dimensional nature of most electrode-catalyst systems limits both the surface area and the mass transport of CO₂. By using a redox mediator to transport the charge from the electrode to the catalyst, the nature of the reaction can be drastically altered. With the delivery of both electrons and CO₂ in the liquid phase, the catalyst is no-longer constrained by the need for electrical conductivity and can be deployed in a non-continuous three-dimensional matrix, possibly expanding the scope for viable materials and simplifying reactor design.

In-Situ Spectroelectrochemistry as a Tool for Ionization Energy Determination for Organic Solar Cell Applications

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Current organic solar cells systems have been shown to reach higher short circuit currents and high fill factors rendering them as promising competitors to other 3rd generation solar cell materials. A promising material combination is the binary blend of the donor-acceptor copolymer PBDB-T-2F as donor and non-fullerene acceptors (e.g., Y6), reaching efficiencies around 15%[1]. *In-situ* spectroelectrochemistry is a powerful tool to evaluate the oxidation onsets and therefore HOMO energy levels in these systems. Recording the absorption maxima as a function of the applied potential in cyclic voltammetry allows the identification of the different radical cations present in these blends. The energy barrier between the HOMO levels of the donor and acceptor, can be estimated with this method, with higher HOMO differences resulting in better charge carrier separation and carrier transport.

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From Trifluoromethylarenes to Functionalized Fluoromethylarenes

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Fluorinated compounds are of interest for pharmaceutical and agrochemical industries owing to their ability to modulate the lipophilicity, activity and molecular conformation.^{1,2} Pharmaceutical agents containing a benzylic fluoride motif have gained interest due to their potential to affect a favourable pharmacokinetic profile.³ Procedures for benzylic fluorination^{4,5} are environmentally unsustainable, employ the use of toxic reagents or are expensive.

Ubiquitous trifluoromethylarenes can be used as feedstocks for defluorinative functionalisation.⁶ However, a challenge in this field is the selectivity of sequential defluorination of trifluoromethylarenes, as there is little difference in the reduction potentials of tri, di, and mono-fluoromethyl groups. Electrochemistry can be used to address defluorination processes by tuning the reduction potential, allowing better selectivity in defluorinative processes. Progress in defluorofunctionalisation has been reported previously.⁷⁻⁹ In this work we will show the combination of hydrodefluorination and defluorofunctionalisation of trifluoromethylarenes, which has not previously been reported. In this electrochemical method, good selectivity to mono-fluorinated compounds from trifluoromethylarenes is demonstrated.

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Tuning Carbon Nanomaterials as Active Supports for Hydrogenases

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The use of hydrogenase enzymes in biotechnology offers possibilities for cleaning up biocatalysis, replacing glucose or formate as reductants with the atom-efficient H₂ gas. Hydrogenases have been employed on carbon supports for the cofactor-free reduction of nitro-compounds, which occurs via an electrochemical mechanism on the conductive support at potentials provided by enzymatic hydrogen oxidation. [Sokolova D, Lurshay T, Rowbotham J, Stonadge G, Reeve H, Cleary S, et al. Cofactor-free biocatalytic hydrogenation of nitro compounds for synthesis of amines. ChemRxiv. 2024; doi:10.26434/chemrxiv-2024-vqfc1 This content is a preprint and has not been peer-reviewed.]. This project aims to exploit electrochemically active carbon nanomaterials which are suited to supporting biocatalysts. Carbon materials are synthesized by chemical vapour deposition while material qualities are achieved both by targeting diverse intrinsic structural properties and through heteroatom doping. Furthermore, electro-analytical and electro-synthetic methods are employed and the synthesized materials are utilised as heterogeneous supports for redox enzymes.

Bromide-Mediated Silane Oxidation: A Practical Counter-Electrode Process for Nonaqueous Deep Reductive Electrosynthesis

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Organic electrosynthesis delivers transformations that are more efficient, safer and greener than their non-electrochemical counterparts,¹ for example by enabling reductive electrolysis at strongly negative potentials ('deep reductions', < -2 V vs Fc/Fc⁺) without harsh reductants. Existing counter-electrode processes for non-aqueous electrochemical deep reductions have shortfalls: sacrificial metal anodes release stoichiometric amounts of metal ions whereas using divided cells requires specialized reactionware which is costly and resistive.²⁻⁴

Herein, we present a metal-free counter-electrode process for undivided electrochemical deep-reductions that involves a mediated electrochemical silane oxidation. It was applied to our reductive hydrodefluorination of trifluoromethyl arenes⁵ that required a divided cell, enabling a flow adaptation; as well as to other electrochemical reductions that relied on sacrificial anodes or divided cells.

Overall, this novel counter-processes is metal-free, inexpensive and has shown robustness in anhydrous and aqueous electrochemical reduction. It is a potential alternative to separators and sacrificial anodes, enabling flow adaptations and lowering the barrier of entry for electrochemistry newcomers.

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Autonomous Ni/Al Swimmers for Enantioselective Synthesis

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The development of chiral metals as electrocatalysts for asymmetric synthesis has gained considerable attention due to their remarkable enantioselectivity.¹⁻³ However, a low yield of chiral products is often observed due to the limited reactive electrode surface. Moreover, the electrode must be physically connected to a power supply. To overcome these limitations, replacing macroscopic electrodes with a group of self-propelled swimmers in which chiral information is encoded at the catalyst surface is an interesting perspective. Herein, we present the concept of the asymmetric synthesis of chiral compounds using chiral-imprinted nickel/aluminum swimmers as self-propelled catalysts in an acidic solution. Interestingly, optimizing the redox potential difference between aluminum oxidation and proton reduction drives spontaneous electron generation. These electrons are partially transferred from the aluminum to the chiral nickel surface, facilitating the asymmetric reduction with significant enantioselectivity. This opens up interesting perspectives for the use of inorganic swimmers in the frame of chiral synthesis.

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***In-Situ* Spectroelectrochemical Study of Semiconducting Polymers and their Modifications**

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Semiconducting polymers have garnered significant attention in recent years for their potential usage as active layers in opto-electronic devices and bioelectronics. Our contribution will show the electrochemical study of two polymer systems, one of which focuses on carbazole-based redox polymers (1) and one which uses ethylenedioxythiophene-based copolymers (EDOT) (2). In the first case, *in-situ* spectroelectrochemistry is employed to monitor the crosslinking of carbazole units and identify the charge carrier species. Their conductivity behavior is investigated and discussed. With the usage versatility offered by *in-situ* spectroelectrochemistry EDOT and its functionalization before and after copolymerization is shown. A range of polymer analogous reactions including click chemistry are discussed as pathways to tuning not only the properties but also to tailoring the materials for specific demands of various applications, e.g. bioelectronics.

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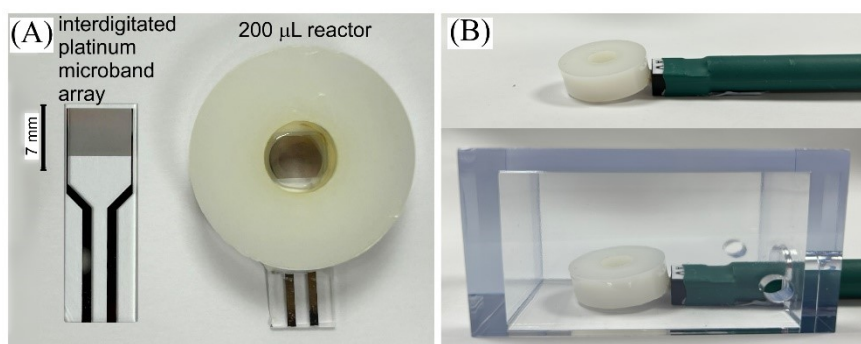
Electrolyte-free Paired Electrosynthesis on Interdigitated Electrodes

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Interdigitated electrodes (IDEs) were introduced to electrosynthesis by Girault and Belmont in 1994.^[1] The properties of interdigitated electrodes help minimizing Ohmic losses between anode and cathode and thereby allow electrolysis without intentionally added electrolyte. IDEs allow a beneficial increase in local rates of inter-electrode mass transport. Due to the closeness of the anode and cathode, IDEs (see Figure) could be used in electrolyte-free electrosynthetic systems.^[2]



In this work, a microreactor with interdigitated microband electrodes was designed and tested. The gap and the width of the microband are 5 μm and the maximum volume of the cell is 400 μl . Starting material was dissolved in the solvent with no electrolyte added, and then electrolyzed in galvanostatic or potentiostatic mode. Tetraethyl ethylenetetra-carboxylate (TET) reduction was investigated and reached over 90% yield. Isotope effects are investigated. A finite element model is employed to explore transport in the absence of electrolyte.^[3] The IDE mechanism is related to localized photocatalysis processes based on single electron transfer reactions (SET) and could lead to a broader range of applications.^[4]

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In-Situ Spectroelectrochemical Study of N-type Semiconducting Polymers for Bioelectronic Devices

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Semiconducting polymers have become attractive for their potential application as channel materials in organic field-effect transistors (OFETs) and organic electrochemical transistors (OECTs) in bioelectronics. Our research is focused on n-type polymers, namely the donor-acceptor copolymer poly[N,N'-bis(2-octyldodec-yl)-1,4,5,8-naphthalenediimide-2,6-diyl]-alt-5,5'-(2,2'-bithiophene) [P(NDI2OD-T2)](1)-(2) and its derivatives modified with oligo(ethylene glycol) side chains and selenophene-vinylene-selenophene as donor units (3). We are using an *in-situ* spectroelectrochemical approach to investigate the electrochemical behavior to identify the redox species at different doping degrees with in parallel recorded UV-vis-NIR spectra. Since the onset reduction potentials of polymers can be determined by mapping the spectral evolution from the neutral in the first reduced state, our operando technique is advantageous over classical cyclic voltammetry to estimate the lowest unoccupied molecular orbital (LUMO) energy level for their integration in devices.

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A Seawater Electrolyzer with a Designed Metalloprotein

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The quest for sustainable energy sources has notably shifted towards green hydrogen production, given its potential to establish a carbon-neutral energy infrastructure.^{1,2} Our study introduces an innovative biomimetic catalyst design rationale that precisely integrates a hydrogen-producing cobaloxime core into a robust azurin protein scaffold to harness the unique interplay between the transition metal active site and the protein-based outer coordination sphere (OCS). This artificial metalloprotein displayed a substantial enhancement in the electrocatalytic H₂ proficiency compared to the precursor cobaloxime in near-neutral aqueous media under oxic conditions, which reached its apex TON $\sim 4.9 \times 10^5$; Overpotential ~ 0.10 V at pH 6.0 with a faradaic efficiency of $\sim 95\%$. This oxygen-tolerant and robust metalloprotein was further fabricated as an operational electrolyzer that consistently produced hydrogen in 1:1 distilled water/seawater blend (Cell Voltage 2.65 V, output current density 1.5 mA/cm²). Hence, this study accentuates the importance of adopting a systematic expansion of the biomimetic catalyst design strategy for green hydrogen production.

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Protection of Hydrogenases from O₂ under Intermittent HER via Bidirectional Catalysis

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The intermittency of renewable energy sources like solar and wind necessitates storing energy as chemical vectors such as H₂ using electrolyzers. However, this intermittency accelerates the aging of electrolyzers, especially those with non-precious metal catalysts that suffer oxidative stress from electrode potential or O₂ in open circuit conditions.

We demonstrate that hydrogenase, a fragile but highly active catalyst for H₂ evolution, can be protected under intermittent use with redox-active films, provided the catalysis is bidirectional and a sufficient bias for H₂ oxidation is maintained. During the off phases, H₂ produced during the on phases is oxidized by hydrogenase, generating electrons that the redox-active polymer diverts to reduce O₂ molecules, thereby protecting the hydrogenases.

Modeling and spectroscopic data show how the redox states of the polymer film equilibrates with H₂ and pH to achieve precise control of the catalytic bias. The protection lifetime and catalytic rates are synergistic, meaning higher bioelectrode activity for H₂ evolution/oxidation extends its lifespan under intermittent use. This protection strategy has great potential to enhance the applicability of catalysts for reduction reactions, considering that bidirectionality, high energy efficiency, and high O₂ sensitivity are common features of many (bio)catalysts for small molecule interconversion.

Intrinsically Microporous Polymers (PIMs) in Electrochemical Transformations

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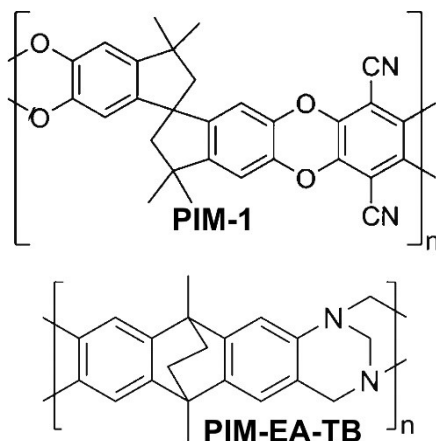
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Polymers of intrinsic microporosity (or PIMs) have been developed over the past decade as molecularly rigid and highly processable materials that are readily applied to electrode surfaces or employed as free-standing membranes. Two prototypical PIMs are PIM-1 [1] and PIM-EA-TB [2] (see Figure). Both possess rigid molecular backbones and pack into porous solid/glassy films with high surface area and with typically 1 nm pore size [3].



PIMs have been introduced into electrochemical applications in energy storage devices [3] and in sensors [4]. They provide fertile ground for fundamental studies on ion transport and electroosmotic water transport [5]. Intrinsic microporosity leads to binding and transport with size selectivity and chemical selectivity. Binding of gases into nanoparticulate PIM materials is responsible for gas activity changes under triphasic conditions [6] and could be beneficial in electrochemical transformations based for example on gaseous oxygen and hydrogen.

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Solvent Tuning to Enable CO₂-to-CO Electrocatalysis by CNT-Supported O₂-Sensitive CODH Under Aerobic Conditions

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A promising approach to selectively reducing CO₂ to CO with low energy costs is to take advantage of efficient biocatalysts such as CO Dehydrogenase (CODH) enzymes¹. CODHs rely on a nickel/iron active site, buried inside a protein scaffold to reversibly reduce CO₂ with near-zero overpotential and exceptional catalytic activity. However, CODH is strongly oxygen-sensitive and must be handled under strictly anaerobic conditions.

Key to achieving efficient bio-electrocatalysis is the design of tailored electrodes with a minimized enzyme-electrode distance to avoid electron transfer rate limitations. For this purpose, carbon nanotube (CNT)-based electrodes are ideal. Once modified with adapted anchoring groups², they enable a high enzyme loading on highly conductive surfaces.

This study uses tailored electrolytes to enhance oxygen tolerance of CODH-modified electrodes. Deep Eutectic Solvents (DESs)³ are particular organic media with low oxygen diffusion properties^{4,5}. The electrocatalytic CO₂ reduction at CNT-supported CODH in DES has been investigated to enable efficient CO₂-to-CO conversion in a non-natural environment as a means of increasing their oxygen tolerance.

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Decoupling Electrochemical CO₂ Reduction via Redox Mediators

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Electrochemical transformation of CO₂ into value added chemicals offers a promising solution to the urgently needed replacement of fossil fuels as a source of small hydrocarbons for use as energy carriers and chemical feedstocks. A range of simple products are commonly reported using various metallic electrode-catalysts; however, most are limited in their effectiveness by poor long-term stability and low activity. The two-dimensional nature of most electrode-catalyst systems limits both the surface area and the mass transport of CO₂. By using a redox mediator to transport the charge from the electrode to the catalyst, the nature of the reaction can be drastically altered. With the delivery of both electrons and CO₂ in the liquid phase, the catalyst is no-longer constrained by the need for electrical conductivity and can be deployed in a non-continuous three-dimensional matrix, possibly expanding the scope for viable materials and simplifying reactor design.

Molecular Copper Complex Driving Rapid Electrocatalytic Hydrogen Production from Water

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The hydrogen economy has emerged as a potential gateway in our pursuit of carbon-neutral power infrastructure¹. In this context, Fe, Ni, and Co-based catalysts are quite common in the literature^{2,3,4}. However, the citations of copper-based molecular complexes capable of active hydrogen production in water are quite rare. We have deployed a macrocyclic transmembrane ion carrier design-inspired nitrogen-containing Cu-N₆ Complex, where it ligates a copper ion with three sets of imine and pyridyl coordination. The flexibility and the ligand environment provide the leeway for the facile structural dynamics and proton movement required for a fast H₂ production cycle. The salient features of our work are its excellent catalytic rate with high turnover number (TON) of ~450 for H₂ production recorded in only 1 hour of bulk electrolysis (with > 90% Faradaic efficiency) at pH 3.0, and its sustainable catalysis in an acidic medium over a broad range of pH (3.0-7.0). Hence, this catalyst can establish the foundation for developing an economical, efficient, and environment-friendly green hydrogen production methodology for our future energy landscape.

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Bio-Inspired Catalyst Design Strategy for Green Ammonia Production

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Ammonia is crucial for urea synthesis and for the global chemical economy. NH_3 is synthesized by traditional Haber-Bosch process at high pressure (~ 150 bar) and temperature ($\sim 600\text{K}$) and it leads to global CO_2 emissions around $\sim 1.44\%$ ¹. So far bio-catalytic, enzymatic and microbial, homogeneous catalyst & heterogeneous catalyst are deployed for sustainable ammonia production with poor yield and high over-potential². Here Our findings show that bio-inspired Cobaloxime with axial modification can accomplish electrochemical NO_2^- to NH_4^+ yield $105\text{mg hr}^{-1} \text{mg}_{\text{cat}}^{-1}$ with faradaic efficiency $\sim 99\%$ FE under near-neutral conditions to mild acidic condition. For the device application, we heterogenized best performing electrocatalyst with MWCNT upon Ni foam for electrolyser using flue gas as source of NO_x^- . This work demonstrates promising aspect of molecular catalyst for industry ready green ammonia production.

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Bioelectrocatalytic H₂–Driven NADP⁺ Regeneration

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NAD(P)H-dependent oxidoreductases are promising biocatalysts to produce many organic commodities owing to their remarkable properties, such as regio- and stereo-selectivity. However, due to the high cost of NAD(P)H, highly efficient regeneration of the cofactor is required for the industrial application of NAD(P)H-dependent oxidoreductases. To address the high cost of NAD(P)H, a H₂-driven enzymatic cascade is proposed for NADPH regeneration, which is composed of hydrogenase and ferredoxin NADP⁺ reductase (FNR). Co-immobilizing hydrogenase and FNR in a redox-active polymer enhances electron transfer and enzyme loading. Additionally, the redox matrix can serve as a shield against the O₂-sensitive hydrogenase under aerobic conditions.

“SS”: A New, Small, O₂-Stable, Ancestral [FeFe] Hydrogenase

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Here, a newly-characterized [FeFe] hydrogenase is presented. It is one of the smallest eukaryotic [FeFe] hydrogenases characterized so far, and its structure is only composed of the main catalytic subunit. Moreover, like other ancestral [FeFe] hydrogenases, it shows a peculiar TSCCCP motif close to the active site that differs from the usual TSCCP present in standard enzymes.

Our efforts to study this enzyme derive from its peculiar capacity to tolerate O₂ exposure, which is very uncommon among [FeFe] hydrogenases. The O₂ tolerance has been tested via an electrochemical set-up, both by exposing the protein to air and via injections of O₂-saturated buffer in the electrochemical cell. Activity is fully retained after air exposure, and only partially lost after the injections.

The exploration of non-standard [FeFe] hydrogenases has only recently started, and the study of enzymes whose features differ from the canonical ones could lead to the discovery of peculiar and interesting properties.

Ionic Liquid (BMIM⁺BF₄⁻) Reactivity on Graphene Foam Electrodes: Humidity Effects on Reversible Cathodic BMIM⁺ Intercalation

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This study investigates the reactivity of 1-butyl-3-methylimidazolium tetrafluoroborate (BMIM⁺BF₄⁻) on graphene foam electrodes, focusing on the effect of ambient humidity on the reversible cathodic intercalation of BMIM⁺ ions. The reversible cathodic intercalation of BMIM⁺ into graphene foam was explored using in situ Raman spectrometer, revealing humidity-dependent shifts in intercalation dynamics. Additionally, BMIM⁺BF₄⁻ was employed with ferrocene and Fe (III) as an adsorbed redox probe on graphene foam electrodes. These systems were studied to understand ion adsorption, charge transfer processes, and their impact on the electrode's surface chemistry. In situ Raman spectral series at different potentials provided real-time insights into the role of humidity in modulating the electrochemical performance of BMIM⁺ insertion and extraction into graphene foam electrode, with potential implications for energy storage and electrochemical devices.

Analytical Bioelectrochemistry of Thylakoid Membrane Electron Transport

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Analytical electrochemistry has enabled the interrogation of electron transport of various biomolecules, yet its application has generally been confined to *in vitro* studies of isolated proteins and metabolites [1]. This prevents researchers from obtaining a systems-level understanding of the complex electron transport pathways found *in vivo* [2]. To address this, we have developed a bioelectrochemical system for analysing electron transport within cyanobacterial thylakoid membranes. Isolated thylakoid membranes were interfaced with state-of-the-art, structured electrodes [5]. Photocurrents obtained with these electrodes exhibited a distinctive shape which was dependent on multiple electron transport pathways. Further analysis revealed light-dependent and light-independent features of photocurrents, which could be directly related to the electron transport activities of different photosynthetic and respiratory proteins. Spectroelectrochemical analysis confirmed these results were consistent with spectroscopic techniques commonly used to analyse photosynthesis. These results demonstrate that analytical bioelectrochemistry can provide information on complex electron transport processes occurring within native biological membranes.

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