Linking Dissolution Phenomena to Selectivity in Pulsed CO_2 Electrocatalysis in Cu Gas Diffusion Electrodes

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Mitigating global warming requires transitioning to a carbon-neutral economy. Electrocatalysis powered by renewable energy is a promising approach to convert CO_2 into valuable chemicals like CO, formate, and ethylene, where the product depends on the catalyst.[1] Copper is widely studied as catalyst for its ability to selectively produce C_{2+} products such as ethylene, but maintaining high selectivity over extended periods of operation remains a challenge.[2]
Applying positive potential pulses between electrolysis periods was shown to extend copper catalyst selectivity, possibly by inducing favourable changes in catalyst morphology via copper dissolution and redeposition and/or changes in oxidation state, although the precise mechanism remain unclear.[3,4]
Employing X-ray absorption spectroscopy (XAS) combined with inductive coupled mass spectrometry (ICP-MS), we can investigate local copper concentrations on the electrode surface and the oxidation state of the copper. Preliminary data shows that the rate of copper dissolution and the oxidation state of copper depend on the electrolyte anions, electrolyte pH, and the pulse potential. Fig. 1 illustrates that copper concentration reduces under positive potential pulses. Copper oxide formation was detected only for electrolytes based on $KHCO_3$ at very high potentials. ICP-MS verified the dissolution of the copper catalyst.

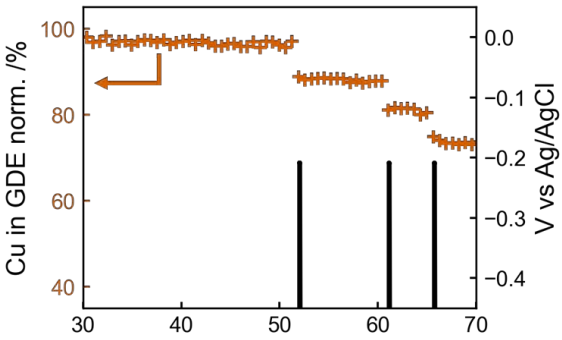

Fig. 1: Evolution of Cu concentration on the gas diffusion electrode as measured by the intensity of the Cu K edge at 8.9789 keV by XAS as a function of time in KCl electrolyte.

Understanding the relationship between the dissolution, redeposition, and oxidation of copper during electrolysis is thus essential for maintaining high selectivity for C2+ products.

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Rigorous statistical benchmarking of Pt/C catalysts for the oxygen reduction reaction: reaffirming particle size-dependent activity and dissolution behavior

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Reliable catalyst comparison requires statistically meaningful datasets that are difficult to obtain with conventional single-electrode measurements. Here, we establish a medium-throughput platform and integrated measurement protocol for statistical benchmarking of oxygen reduction reaction (ORR) catalysts. A glassy-carbon multi-working electrode enables six catalysts to be measured simultaneously, while a sequential protocol combines electrochemical surface area and ORR activity measurements with accelerated stress tests (ASTs) and step-resolved Pt dissolution analysis by inductively coupled plasma mass spectrometry. Applied to commercial Pt/C catalysts, the platform provides 13-17 valid replicate datasets per catalyst and reduces measurement time to approximately one fifth of that required for conventional measurements.

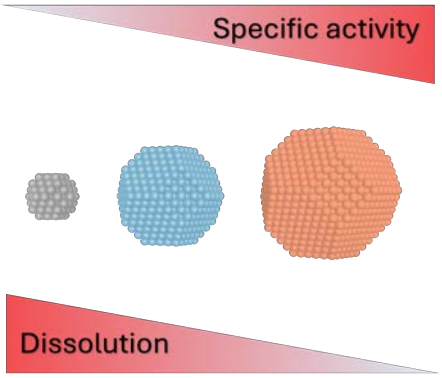

Fig 1. Schematic illustration of the particle-size-dependent activity–stability relationship.

Statistical benchmarking reveals a clear particle-size-dependent activity–stability relationship (Fig. 1) consistent with previous reports: smaller Pt particles exhibit lower ORR specific activity and higher Pt dissolution. [1,2] Testing a 46% Pt/C catalyst with an intermediate particle size yields intermediate specific activity, dissolution, and apparent S-number, confirming that these trends persist across the catalyst series. To probe their mechanistic origin, under-coordinated edge and corner Pt atoms in the smallest-particle 19.4% Pt/C were selectively replaced by Au through galvanic replacement. This modification increases ORR specific activity by approximately 1.5-2 times while markedly suppressing Pt dissolution. These results identify under-coordinated Pt surface atoms as common sites governing both enhanced dissolution and reduced intrinsic activity, and demonstrate how medium-throughput statistical benchmarking can connect catalyst performance distributions with mechanistic insight.

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Advances in Halo-mediated Electrosynthesis

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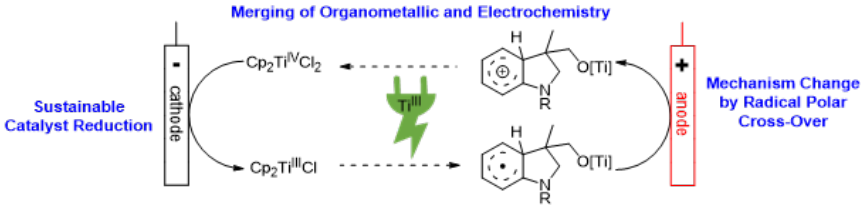
The field of organic electrosynthesis is currently experiencing unprecedented interest from both academic and industrial laboratories. This is due to the highly attractive advantages in terms of sustainability and increased process safety that this approach offers, while simultaneously opening up new regions of chemical space. Organometallic catalysis has also greatly contributed to the exploration of chemical space. Consequently, combinations of electrosynthesis and organometallic catalysis have also appeared. However, in these examples only one half-cell reaction (usually the reduction) is used in conjunction with the catalyst, leaving the second half-cell reaction unutilized.[1]
Simultaneously, the titanocene-catalyzed radical arylation provides access to a number of scaffolds of great interest for the pharmaceutical and fine-chemical industries.[2] This reaction requires a low-valent metal center, which is regenerated through the oxidation of the substrate by a high valent Ti-species. As such, this method cannot be applied to electron poor substrates which are hard to oxidize.



However, by merging the titanocene-catalyzed radical arylation with electro-organic synthesis, we could perform both the reduction, to form the active catalyst, and the oxidation necessary for the rearomatization electrochemically in a simple, galvanostatic setup. This also led to a change in the mechanism, substituting the critical proton-coupled electron transfer by a radical polar cross-over. This is achieved in a unique manner by consecutive paired galvanostatic electrolysis through a decoupling of the electron and proton transfer steps by spatially separating the critical redox processes, the anodic oxidation of the radical σ–complex to the cationic σ–complex and the mild in-situ preparation of the active catalyst by cathodic reduction of Cp2TiCl2.[3]
As such, this galvanostatic approach allows for the generalization of the titanocene-catalyzed radical arylation and may also remove limitations on other reactions, thus opening up new regions of chemical space.

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Automated Electrochemical Synthesis and Characterization of Multimetal Electrocatalysts for Hydrogen Evolution and Formic Acid Oxidation

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Electrocatalysis paired with renewable energy sources is a promising route towards decarbonizing the chemical sector [1]. Key metrics in electrocatalytic performance include activity, stability, selectivity, and cost [1]. Existing metal catalysts are optimal in some metrics and suboptimal in others, and thus, combining catalysts in bimetallic to high-entropy alloy (≥5 metal) systems is an effective strategy to design and optimize electrocatalysts [1, 2]. The combination of multiple metals, however, opens a vast compositional space which necessitates increased experimental throughput [3, 4]. Here, we present an automated, medium-throughput system to synthesize multimetal catalysts and evaluate their performance for model cathodic (hydrogen evolution, HER) and anodic (formic acid oxidation, FAO) reactions.

Our medium-throughput system features an extrusion 3D printer with electrochemical cell, microfluidic pump, and computer interface. To synthesize dual and ternary metal systems, metal precursor concentrations were varied and pumped into the cell, which was moved across 32 discrete spots on a glassy carbon substrate. Particles were deposited via pulsed electrodeposition. The morphology and composition of the resulting particles were determined with automated scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX). Two material systems were explored for trends in activity: Pd-Au-Pt for HER and Pd-Au for FAO, both in acidic media. The results were compared with literature values as an initial benchmark [5, 6]. These results further demonstrate the platform's versatility across material systems and reaction types, spanning cathodic and anodic transformations. Our future work includes exploring higher-dimensional systems (e.g., HEA catalysts) and incorporating stability measurements to understand activity-stability trends and trade-offs. Finally, we aim to use medium-throughput experiments to explore statistical methods, predict optimized compositions, and establish data-driven compositional design.

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Electrocatalytic Hydrodeoxygenation of Aldehydes in Pd@CNT-stabilized Pickering Emulsions.

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ABSTRACT

The global transition toward a sustainable chemical industry requires processes to shift from fossil to renewable carbon and energy sources. Many important platform molecules contain carbonyl functionalities such as aldehydes (e.g. furfural, HMF, vanillin, etc.), which need to be hydrodeoxgenated to produce bio-derived intermediates for the production of fuels and value-added chemicals.[1,2] High temperatures and pressures are typically needed for conventional thermal catalytic processes, and these harsh conditions can also promote side reactions such as polymerization and coke production, which can reduce yield and selectivity.[3]

With the ability to fine-tune electron transfer and redox transformations under moderate conditions without the need of stoichiometric oxidants or reductants, electrocatalysis and organic electrosynthesis have lately become attractive approaches.[4,5] One direct and atom-efficient method for removing oxygen from carbonyl substrates is electrochemical deoxygenation; yet, direct hydrodeoxygenation (HDO) of these substrates is still a major obstacle due the high bond dissociation energies (BDEs) of C−O and C=O bonds.[6]

Building on a concept recently established by our team,[7] this study investigates the electrocatalytic HDO (ECHDO) of aldehydes using a Pd@CNTs catalyst within a Pickering emulsion system. The unique properties of this Pickering emulsion system, such as enhanced mass transfer and optimized interactions between the catalyst, organic phase and electrolytes, provides a conducive environment for complex catalytic reactions enabling effective dissociation of C−O and C=O bonds to tolyl products with higher selectivity and Faradaic efficiency than previously reported (Figure 1b). The hydrophilic carboxylated-CNTs stabilize the aqueous phase, while hydrophobic Pd NPs generate adsorbed hydrides (H_{ads}) at the interface and drive selective C–O bond cleavage in the organic phase (Figure 1a). This integrated catalytic–emulsion platform enables the selective hydrodeoxygenation of C=O bonds to alkanes, effectively overcoming the limitations of traditional hydrogenation pathways.

This method demonstrates a synergistic integration of electrocatalysis and emulsion chemistry for the sustainable upgrading of biomass-derived carbonyl compounds, advancing the frontier toward a green chemistry-energy nexus.

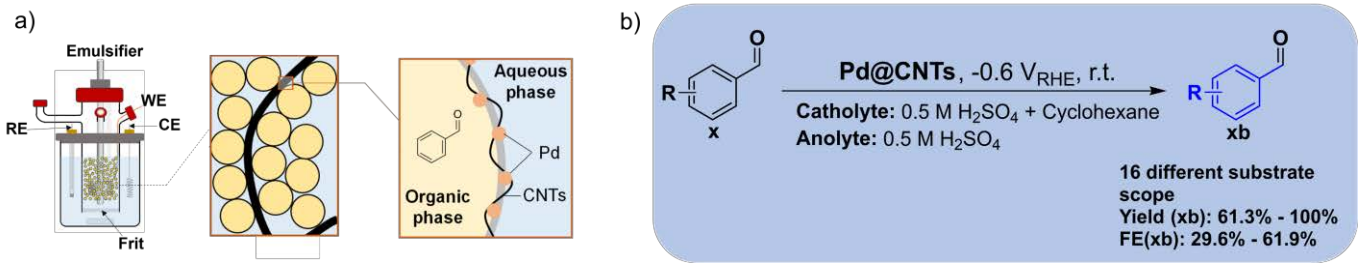

Figure 1: a) Pickering emulsion system, with CNT-stabilized oil-in-water emulsion on Ag electrode (WE: Working Electrode) enabling interfacial ECHDO of aromatics (where; CE: Counter Electrode, and RE: Reference Electrode). b) Optimized conditions for aldehyde ECHDO across substrates.

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Surface-enhanced infrared absorption spectroscopic elucidation of the electrochemical promotion of the thermocatalytic hydrogenation of 3-nitrostyrene

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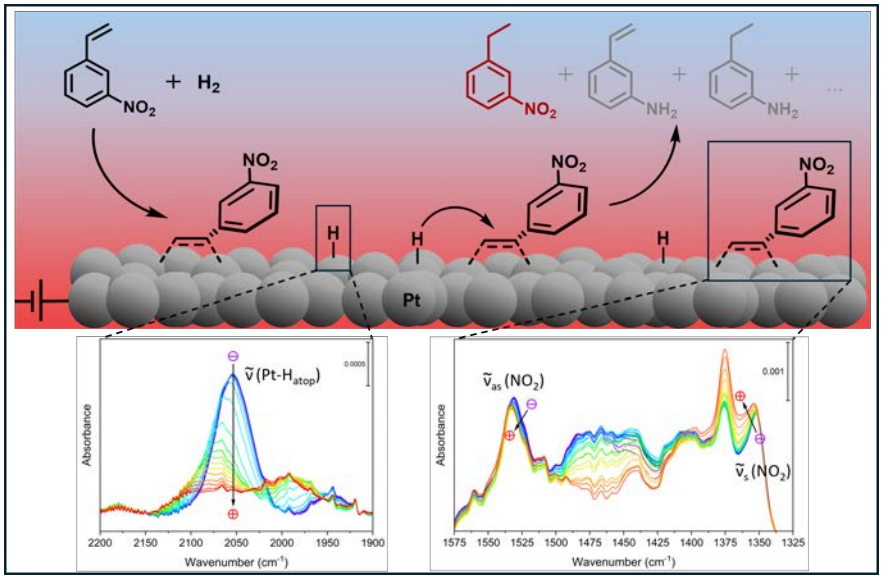
Surface-enhanced infrared absorption spectro-electrochemistry (EC-SEIRAS) is as a powerful analytical technique to study surface-bound species and electric field effects at electrified solid-fluid interfaces.[1] EC-SEIRAS could thereby provide key information on the interfacial chemistry that directs heterogeneous catalysis.[2] Electrochemical promotion of catalysis (EPOC) offers an elegant way to enhance catalytic performance *in situ* with applied electric fields. For instance, recent work has demonstrated spectacular rate enhancements of thermal catalysis by applied electrochemical potentials in a few transformations, including hydrogenation reactions. [3-8] We hypothesized that with a better fundamental understanding of such processes through EC-SEIRAS, EPOC may be further developed, for instance, to also allow enhancement of chemoselectivity in thermal reactions.

Here, we show that the application of a positive potential during the thermocatalytic hydrogenation of 3-nitrostyrene with H_2 on a heterogeneous Pt catalyst delivered one single product (1-ethyl-3-nitrobenzene) with six-fold enhanced yield, meanwhile a complex product mixture was obtained at open circuit voltage. Examining this system by EC-SEIRAS combined with kinetic studies suggested that a tuned surface coverage and a modified affinity of the Pt catalyst for electron-rich versus electron-poor functional groups at positive applied potential is responsible for the enhancements in rate and chemoselectivity. Our work thereby provides fundamental understanding of the effect of an applied potential on a thermal hydrogenation and opens the road for tuning chemoselectivity in other transformations.



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Direct Electrolysis of Flue Gas to Valuable Products by Advanced Electrode Design

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Background and motivation. Electrochemical CO_2 reduction (CO_2RR) has attracted strong interest as a route to mitigate emissions, offering ambient operation, compatibility with renewable electricity, and access to diverse value-added products. However, most studies still rely on pure CO_2, whereas practical streams (e.g., flue gas and biogas) typically contain ≤40% CO_2. Developing advanced electrodes that enable in situ upgrading/purification of mixed feeds could simplify the process by reducing downstream separation steps [1,2].

Materials and methods. Herein, I showcase the scenarios to integrate adsorption and membrane separation within gas diffusion electrodes (GDEs) and present our recent research data of CO_2 conversion in an ionic liquid-mediated CO_2-selective GDE [1]. The designed GDE has an inter-layer for CO_2 purification coated on a PTFE membrane as the substrate. The interlayer is made of a polymer with intrinsic porosity incorporated with a CO_2-phil ionic liquid. CO_2RR was performed in an MEA-type cell with Ni as anode and anion exchange membrane. Results and discussion. A uniform interlayer was successfully coated on PTFE, and then it was sputtered with a thin layer of silver for CO/syngas production from CO_2. Surface SEM image show that this layer is very porous, therefore it does not resist gas permeation. Also, the intrinsic porosity of the layer acts as CO_2 reservoir, owing to the high CO_2 adsorption of the layer. The preliminary CO_2RR results showed that this design can keep performance with less pure CO_2 feed (such as 50% or 15% with 5% O_2, resembling flue gas). While the untreated sample showed a sharp reduction in CO_2RR products (CO selectivity reduced from 92% to 22% when CO_2 feed changed from pure to 15% purity), the treated sample exhibited the same selectivity for CO production.

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Keywords: CO_2 Electrolysis, Electrode design, Ionic liquid, syngas production and gas-diffusion electrode

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ZnO Nanoparticles for Electrochemical Urea Synthesis

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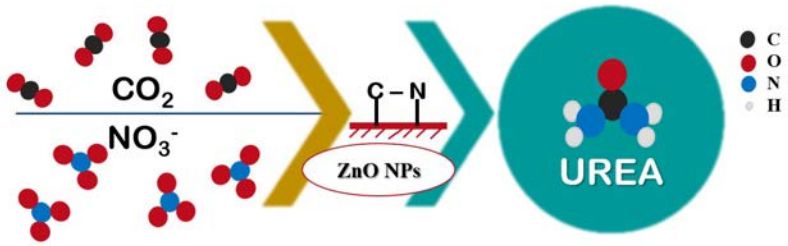
The electrochemical conversion of CO_2 and nitrate into urea provides a promising route to reduce carbon emissions and nitrogen pollution while producing a valuable chemical feedstock. Efficient C-N coupling is challenging, requiring a catalyst that can simultaneously activate CO_2 and nitrate and mediate a complex 16-electron, 18-proton transfer. Despite recent progress in electrochemical C–N coupling, both the mechanistic pathways and the structure-composition-activity relationships governing urea formation remain under debate.



In our study, ZnO nanoparticle-based materials are explored as promising catalysts for electrochemical urea synthesis. Building on the intrinsic activity of ZnO, we systematically investigate the impact of transition metal incorporation on catalytic performance and selectivity. In parallel, we explore the influence of electrochemical operation modes, including static and pulsed techniques, to modulate reaction pathways and enhance C–N coupling efficiency. Additionally, the role of different carbon and nitrogen precursors is examined to elucidate their effect on urea formation mechanisms.

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Electrochemical Alcohol Oxidation with Transition Metal Oxides

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Electrochemical alcohol oxidation is a sustainable and cost-effective method of converting alcohols into valuable chemicals, such as aldehydes and carboxylic acids. At the same time, green hydrogen is also produced through reduction at the cathode. Therefore, electrochemical alcohol oxidation could replace sluggish water oxidation in electrolysis. The catalytic active oxides typically operate under alkaline conditions with high activity and stability. Nickel-based oxides, in particular, are known to be effective catalysts for both the oxygen evolution reaction (OER) and alcohol oxidation (AOR).[1]

In this study, we present cobalt-nickel-iron (Co-Ni-Fe) oxides with different molar ratios that were annealed under an oxygen-poor atmosphere (1 vol% air in argon) to generate oxygen vacancies.[2] We studied these materials as anode catalysts for the oxidation of various alcohols (e.g., ethanol, 2-propanol, and ethylene glycol) at different current densities (10, 20, and 30 mA/cm^2) in an H-cell set-up. We discussed the obtained potentials in terms of stability and compared them with the corresponding behavior of the material for OER. To investigate product formation and distribution, we applied the nuclear magnetic resonance (^{1}H-NMR) technique. XRD, XPS, and TEM measurements were conducted to detect changes in the material. Nickel oxide, the best-performing material, catalysed the oxidation of ethanol to acetate with Faradaic efficiencies of over 75% @ 20 mA/cm^2 without significant cleavage of C-C bonds. This study demonstrates the application of transition metal oxides with oxygen deficiencies for alcohol oxidation.

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Operando X-ray Diffraction Studies of Co Oxide Model Catalysts during Oxygen Evolution Reaction and Alcohol Oxidation

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Overcoming the slow kinetics of the anodic oxygen evolution reaction (OER) is a key challenge for the sustainable production of green hydrogen via electrolysis. Transition-metal oxides such as Co_3O_4 are among the best precious-metal-free electrode materials for the anodic OER in alkaline electrolysis [1]. Moreover, these spinel-type transition metal oxides are an important class of catalysts for the selective oxidation of organic compounds in the liquid phase under thermal and electrocatalytic conditions [2].

Here, we present *operando* surface X-ray diffraction (SXRD) studies of OER model catalysts, consisting of thin epitaxial Co_3O_4(111) films electrodeposited on Au(111) substrates [3]. Previous studies have shown pronounced reversible changes in the near-surface oxide's structure of these catalysts [1,4]. In particular, a sub-nm $CoO_x(OH)_y$ skin layer starts forming in the pre-OER potential range which is accompanied by a volume change of the underlying Co_3O_4 lattice [4]. Since the skin layer formation already starts several 100 mV negative of the onset of the OER, it is not induced by the catalytic reaction itself, but rather reflects the oxide's electrochemistry, and may thus be expected also for other catalytic reactions.

In a more recent work, we investigated the role of defects in the reversible surface restructuring and the activity of these electrocatalysts during OER [5]. Combined *operando* SXRD and electrochemical impedance spectroscopy as well as *operando* X-ray absorption spectroscopy measurements demonstrated that thermal annealing leads to a defect-free Co_3O_4(111) surface and completely suppresses the skin layer formation. Potential-induced surface restructuring consequently only occurs in the presence of surface defects. The presence of this skin layer promotes oxygen evolution at low overpotentials but results in higher Tafel slopes. As a result, defect-free Co_3O_4(111) surfaces are more active at high current densities than defective Co_3O_4 surfaces that undergo surface restructuring.

Furthermore, studies of electrocatalytic ethylene glycol (EG) oxidation on Co_3O_4 films revealed similar structural changes, even though they appear to be less pronounced under alcohol oxidation conditions, especially at higher EG concentrations. Recent studies have shown that similar structural changes may also occur during liquid thermal oxidation of organic compounds such as 2-propanol or ethylene glycol.

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Low-Pt High-Entropy Intermetallics as Oxygen Reduction Catalysts

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Platinum-rich PtM (M = Fe, Co, Ni; up to 25 at. %) materials are the state-of-the-art catalysts for the acidic oxygen reduction reaction (ORR) in fuel cell applications. [1,2] However, Pt is scarce, which severely limits the upscaling of Pt-dependent technologies. One possible solution to this problem is to further reduce the amount of Pt used in catalyst materials below the currently used minimum of 75 at. % Pt. In this study, we apply the concept of high-entropy alloys (HEA) to reduce the Pt content. HEAs are characterized by the random arrangement of the constituent elements in the crystal (sub)lattices, which results in a continuum of adsorption energies for reaction intermediates.[3] A subset of these sites exhibits optimal interactions with the reactants and thereby dominates the catalytic activity. The HEA space includes both high-entropy solid solutions and high-entropy intermetallics. In solid solutions, the elements are randomly distributed within a single lattice, whereas in intermetallics the elements are on distinct sublattices.
Using a recently developed incipient wetness impregnation approach [4], the deliberately chosen sample composition of $Pt_5MnFeCoNiCu$ allows us to synthesize both high-entropy solid solutions and intermetallics of identical composition. Electrochemical testing of ORR activity in a gas diffusion electrode setup ($J > 1$ A cm_{geo}^{-2}) showed that samples containing the intermetallic phase outperform the solid solutions in both specific and mass activity. We used DFT calculations to understand the origin of the intermetallics' improved activity. The calculations suggest that while the cubic solid solutions experience isotropic strain, the tetragonal lattice of the intermetallics introduces anisotropic strain. The anisotropic strain results in favourable reactant binding energies for the intermetallics at 50 at. % Pt, whereas the isotropic strain in solid solutions at such low Pt contents leads to over-straining effectively reducing ORR activity.
Strain anisotropy therefore emerges as a useful design principle for low-Pt ORR catalysts, enabling further reductions in Pt content while potentially improving both activity and stability. Conceptually, anisotropic strain engineering provides a more general principle for tuning catalytic properties applicable to other electrocatalytic processes and materials.

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Electrocatalytic Nitrile Synthesis with Cobalt-Based Polyoxometalates

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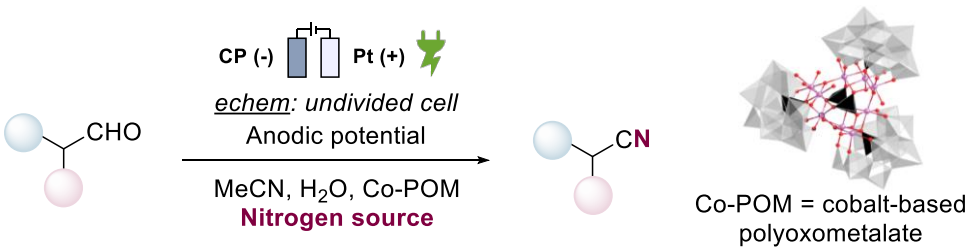
The electrocatalytic preparation of nitriles offers a sustainable alternative to conventional methods that rely on toxic or stoichiometric oxidants and harsh conditions,[1] which suffer from poor atom economy and significant waste generation. In contrast, electricity serves as a clean redox reagent under mild conditions to access valuable synthetic intermediates.[2] Herein, we report the development and optimization of this transformation under anodic oxidation conditions using a cobalt-based electrocatalyst, with particular emphasis on improving selectivity and catalyst performance. Reaction parameters were systematically investigated, including ammonia concentration, water content, and applied potential, to maximize nitrile formation while suppressing over-oxidation, particularly the formation of the corresponding carboxylic acids. Careful control of the reaction pH proved essential for maintaining catalyst stability and preserving the nucleophilicity of ammonia, both of which are critical for efficient conversion to the desired nitrile products. The protocol employs a cobalt-substituted polyoxometalate (Co-POM), a versatile catalyst class with broad applicability in diverse chemical transformations,[3] which mediates selective oxidation under mild electrochemical conditions via efficient electron transfer between the substrate and the electrode interface. To evaluate the influence of the catalyst environment on reactivity, immobilization of the Co-POM on conductive electrode surfaces was investigated, resulting in enhanced catalytic performance while enabling efficient recovery without loss of activity. The methodology exhibits a broad substrate scope, encompassing aromatic and aliphatic aldehydes as well as alcohol-derived precursors that can be converted in situ to the corresponding carbonyl intermediates. This versatility demonstrates the general applicability of this electrocatalytic system to structurally diverse feedstocks. Mechanistic investigations, supported by targeted control experiments, provide evidence for the reaction pathway and enable identification of key intermediates involved in cobalt-mediated anodic electrocatalytic nitrile formation. In conclusion, this study establishes a sustainable electrocatalytic system for nitrile synthesis enabled by cobalt-based polyoxometalate catalysis. The combination of mild operating conditions, broad substrate scope, robust catalytic performance, and mechanistic insight highlights the potential of this approach as an efficient and environmentally benign alternative to conventional nitrile synthesis methods.



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Electrochemical synthesis of imidazolines from aldehydes

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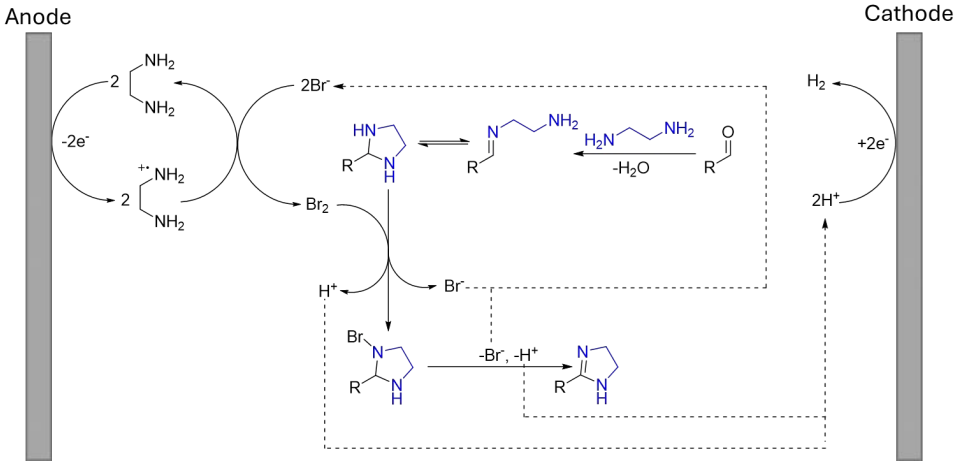
2-Imidazolines are non-aromatic 5-membered rings that contain two nitrogen atoms and a carbon-nitrogen double bond. They have a broad range of applications, such as pharmaceuticals, surfactants and herbicides.[1] Additionally to this applications, a large amount of the imidazolines synthesized are used for the further oxidation to the aromatic imidazoles.[2]

In the main industrial synthetic pathway, a carboxylic acid derivative or nitrile is reacted with ethylenediamine (EDA) at high temperatures with a alumina-acid catalyst (see figure 2). Similar procedures are known in industry, but they all use harsh reaction conditions such as high temperatures and high acidity.[2]

More recently, alternative pathways have been developed where aldehydes are reacted with EDA in the presence of an oxidant such as NBS, I_2 or H_2O_2.[3-5] However, harsh conditions like elevated temperatures, toxic oxidants and/or toxic solvents remain. Green alternatives have been found, where *Zhang et al.* use photochemistry for the synthesis of 2-imidazolines, albeit needing a very complex photocatalysts.[6]

Using benzaldehyde as the model substrate together with EDA, a electrochemical method for the synthesis of 2-imidazolines was developed. This resulted in a bromide catalyzed reaction performed in a green reaction mixture of water and acetonitrile (MeCN) at room temperature and ambient pressure with a faradaic efficiency (FE) of up to 43% and yields up to 96%. On these conditions a substrate scope was performed which gave very good yields for other aromatic aldehydes, and even good yields for aliphatic aldehydes. Control experiments and electrochemical analytical methods such as cyclic voltammetry were performed to elucidate the reaction mechanism.

Our protocol possesses several advantages: 1) the main byproduct is the cathodic production of hydrogen gas, a potentially useful product, 2) utilization of renewable electricity in ambient reaction conditions, 3) water and acetonitrile as green solvents, 4) catalytic amount of bromide through the electro-regeneration of the active bromine compound.



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Tuning the Oxygen Evolution Activity in Rutiles and Perovskites via the Fermi Level

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In this presentation, we introduce a design principle for developing active and potentially stable rutile catalysts for the acidic oxygen evolution reaction (OER). Our density functional theory calculations demonstrate a volcano-type relationship between the catalytic activity and the Fermi level on TiO_2-coated conductive rutiles (see Figure 1a).[1] According to our charge and structure analysis, this trend originates from the non-oxidisability of the Ti sites in the rutile structure. Therefore, a TiO_2-coated rutile with a suitable Fermi level can be highly active and potentially stable under acidic OER conditions, consistent with experimental reports that TiO_2 coatings improve stability in acid while preserving OER activity.[2,3] Moreover, we propose a composition-based model that successfully identifies Ir- and Ru-free substrate compositions ($W_xPt_{1-x}O_2$ and $W_{0.46}Pd_{0.54}O_2$) that can activate the TiO_2 coating layer.

A similar volcano-type relationship between OER activity and the Fermi level is observed on the La-termination of $LaBO_3$ perovskites (B: Ni, Co, Fe, Cu, Cr and Mn; see Figure 1b).[4] This tunability is attributed to the non-oxidisable La sites, analogous to the role of Ti in the rutile structure. La-terminated perovskites have been reported in the literature,[5] supporting the feasibility of our design approach. The same tuning mechanism operates across rutiles and perovskites, establishing a broad design principle for efficient OER electrocatalysts.

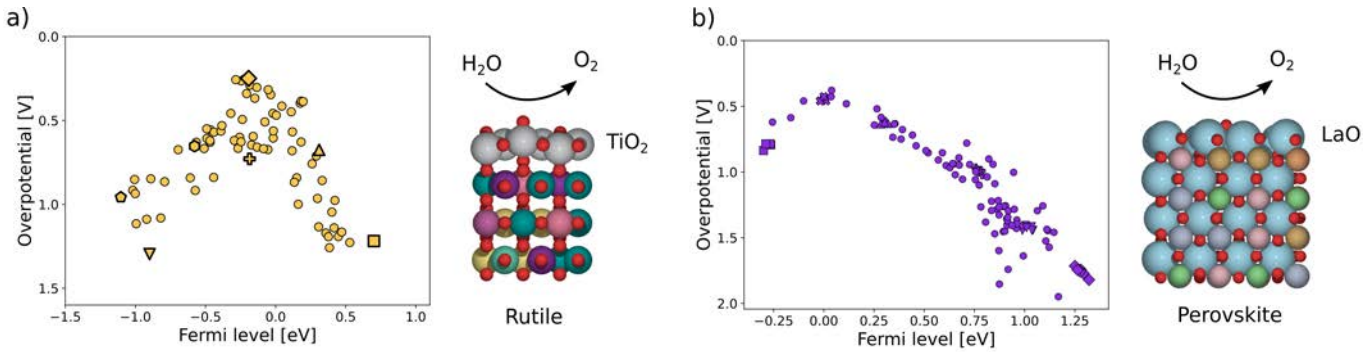

Figure 1: Volcano-type relationships between OER activity and the Fermi level of a) TiO_2-coated rutiles and b) La-terminated perovskites.

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Bayesian Optimization–Driven EXAFS Fitting of High-Entropy Alloy Nanoparticles

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High-entropy alloys (HEAs) have emerged as a promising platform for the discovery of highly active and stable electrocatalysts. The central hypothesis is that compositional complexity generates a distribution of active sites that can be tuned via composition, provided that single-phase structures are maintained. [1, 2] Common characterization methods for HEA materials include phase analysis and elemental mapping. [3, 4]

In this project, we build on the synthesis of phase-pure Pt-based HEA nanoparticles (NPs) prepared by incipient wetness impregnation (IWI), an industrially relevant and scalable method. Two supported HEA NPs catalysts, PtPdRuNiFe/C and PtPdMoNiFe/C, were specifically designed to avoid overlap of X-ray absorption edges and thereby enable element-resolved, multi-edge EXAFS analysis. This approach provides access to the local coordination environment around each absorbing element and complements other techniques to follow structural changes during synthesis, activation, and degradation. Incorporating EXAFS analysis into *in situ/operando* XRD/XAS experiments offers complementary insight. XRD and PDF analysis probe long-range order, local disorder, and structural evolution, while XANES captures changes in electronic structure and oxidation state, and EXAFS resolves local coordination environments.

Because conventional least-squares EXAFS refinement can be sensitive to starting parameters, whereas reverse Monte Carlo approaches are often computationally expensive, we explore a hybrid fitting strategy that combines Bayesian optimization with least-squares refinement. This workflow aims to provide a more efficient and robust route for analyzing EXAFS data from structurally complex HEA NPs.

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A convolutional kernel approach for efficient simulation of diffusion in complex electrode geometries

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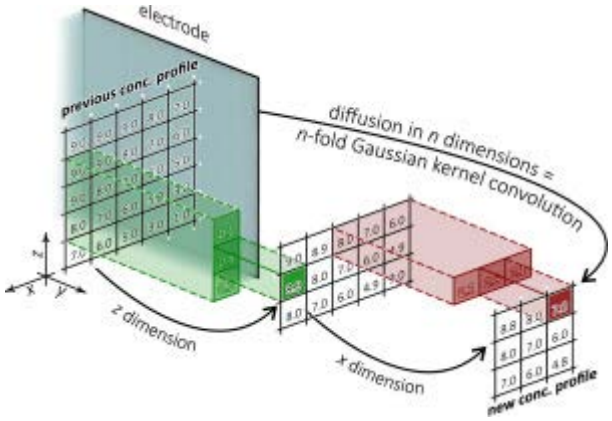

A fast, robust, and low-error method is described for the simulation of transient diffusion in electrochemical systems, particularly those featuring complex, high surface area geometries in one, two, or three dimensions—like porous electrode structures used in electrocatalysis. Our approach reformulates the discrete solution of Fick's laws by approximating the propagation matrix with a Gaussian convolution kernel. This methodology leverages the known spectral decomposition of symmetric tridiagonal matrices, significantly reducing computational cost compared to traditional methods that rely on large-scale matrix inversion or exponentiation. Furthermore, this method is highly amenable to parallelization and GPU acceleration. We detail the implementation of various electrochemical boundary conditions, including diffusion control and mixed kinetic-diffusion control, demonstrating the potential of the method as a fast, user-friendly, and powerful tool for electrochemical simulations. Building upon this theoretical foundation, we present practical simulation examples on realistic 3D topographies, focusing specifically on highly porous metal foam electrodes. To handle these intricate geometries, we introduce simplifying spatial calculations that translate 2D microscopic imagery into bounded 3D computational domains. By modeling specific diffusion layer envelopes to represent various macroscopic mass-transport regimes, we demonstrate how this workflow can be used to predict the expected transport-controlled currents on porous catalyst structures under suitable convection conditions.

Electrochemical Synthesis of Sodium Perborate: Towards Sustainable and Scalable Platform Oxidizer Production

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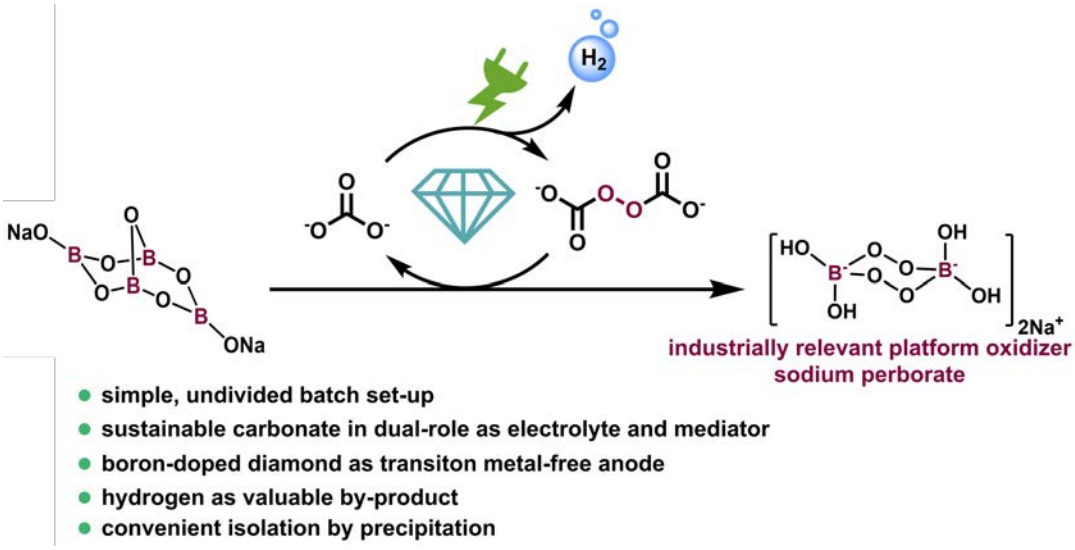
The development of sustainable oxidation processes is a key challenge in modern chemistry, particularly in replacing energy-intensive and waste-generating conventional methods. Sodium perborate is an inexpensive and stable oxidant widely used in detergents, bleaching, and organic synthesis; however, its conventional production relies on external oxidants and alkaline pretreatment of borax.

Electrochemical synthesis offers a promising alternative by enabling the in-situ generation of oxidizing species driven by electricity, ideally from renewable sources, while simultaneously allowing hydrogen evolution at the cathode. In this work, we investigate the electrosynthesis of sodium perborate in aqueous media using carbonate as the sole electrolyte in an undivided batch cell with a boron-doped diamond (BDD) anode.

After optimization, a solid product with up to 80% yield was obtained, showing good agreement with a commercial reference based on FTIR analysis. Mechanistic studies, including cyclic voltammetry and electrolyte variation, indicate a carbonate-mediated oxidation pathway as the most plausible reaction mechanism.

This study demonstrates a scalable and sustainable route for the electrochemical production of inorganic oxidants under mild conditions, contributing to the advancement of green electrosynthesis.



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Compositional Data Analysis in High-Entropy Alloy: Toward Machine Learning–Guided Autonomous Experimental Optimization

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High-Entropy Alloys (HEAs) offer a vast compositional design space for electrocatalyst discovery, but their analysis is complicated by the constrained nature of composition data. In this work, we apply Compositional Data Analysis (CoDA), using the centered log-ratio (CLR) transformation, to experimental datasets linking precursor ratios to actual alloy compositions measured by EDX. The CLR approach enables meaningful regression and accurate prediction of EDX-derived compositions from precursor inputs, overcoming limitations of raw fraction-based representations. This methodology establishes a critical foundation for integrating machine learning into self-running optimization experiments, where reliable prediction of composition is essential for closing the experimental feedback loop.

Adaptive *IR* Compensation and Multi-Nodal Electrometry Control Concepts for Electrolysers: An Instrumentation Roadmap

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Electrocatalysis is rapidly moving from catalyst discovery toward device-relevant operation, where meaningful benchmarking requires high current densities, long durations, and realistic architectures (membranes, GDEs, flow cells). In this regime, however, a fundamental measurement problem becomes dominant: the electrical quantity we command (applied potential or current) is often not the electrical quantity the catalyst experiences, because significant —and frequently time-dependent— voltage losses occur outside the interface. Uncompensated and drifting solution resistance (IR drop) can therefore obscure activity/selectivity trends, distort integrated charges and Faradaic efficiencies, and compromise reproducibility across laboratories.

We argue that robust electrolyser experimentation requires an instrumentation shift: from single-working-electrode-centred control toward electrolyser-native observability and closed-loop stabilisation. The roadmap begins with adaptive, oscillation-free IR compensation as a prerequisite for high-current potentiostatic studies. We present a fully software-based method that achieves 100% dynamic IR compensation using commercially available potentiostats by continuously monitoring the high-frequency resistance and DC current, then adapting the setpoint so that the IR-corrected electrode potential remains constant throughout electrolysis. Crucially, the control strategy is designed to remain stable even when resistance decreases during operation (e.g., due to Joule heating or evolving multiphase conditions), which is exactly where conventional analogue positive-feedback compensation becomes unstable or forces users to under-compensate. Demonstration in nitrate-to-ammonia electrolysis at high current density shows that static partial compensation can lead to artefact-prone currents and misinterpreted selectivity, while adaptive digital control enables stable operation without oscillations and yields reliable potential-dependent performance metrics under drift.

Adaptive IR control solves one critical “single-electrode” problem, but electrolysers are multi-domain systems in which cathode, separator, and anode jointly set performance and failure. The next step in the roadmap is therefore multi-nodal electrometry: simultaneous measurement of cathode and anode potentials vs local references, separator-associated losses, and full-cell voltage, enabling real-time partitioning of where voltage (and therefore energy) is spent as conditions evolve. Building on this observability, we outline an electrolyser-centric control instrument concept that supports modes aligned with system constraints—including constant-power regulation in addition to constant-current/constant-voltage—so that operation can be stabilised under shifting resistive and transport conditions.

A further enabling element is bias-under-load, frequency-aware diagnostics embedded into the controller: controlled AC (including multi-tone) perturbations superimposed on DC operation to extract rapid impedance-informed signatures during electrolysis, localise emerging bottlenecks, and trigger protective or performance-preserving interventions before catastrophic drift occurs.

Exploring the cation effect on NiNC single metal atom electrocatalysts for CO_2-to-CO Conversion

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The microenvironment plays a crucial role in determining the reactivity of the electrochemical CO_2 reduction reaction (CO_2RR).[1-2] On metallic surfaces, the presence of cations, anions, and other additives can modulate electrocatalytic performance by affecting reaction mechanisms, kinetics, and mass transport. In contrast, single-site catalysts—characterized by unique geometric and electronic configurations of active sites—have been relatively underexplored in this context. In this study, we seek to broaden our fundamental understanding of cation effects on the solid-state NiNC catalyst. By varying the identities and concentration of conventional alkali metals (Li^+, Na^+, Cs^+), we observe minimal changes in the electrochemical CO_2-to-CO reactivity. Interestingly, the presence of organic-based tetramethylammonium (TMA^+) provides a different trend for this and exerts a pronounced CO reactivity at higher concentrations. Our findings emphasize the critical influence of cation type and concentration in CO_2RR on single-atom NiNC catalysts, positioning TMA^+ as a promising direction for future electrolyte research in this field.

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How to boost TRLs in Glucose Oxidation Reaction

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Starting from lignocellulosic biomass, valuable platform chemicals can be produced.[1,2] This allows for the creation of material streams based on renewable resources that have a low CO_2 footprint. In order to rapidly achieve high technology readiness, all process steps involved must be considered at various scales. An example of this is the E-GLUCO project, which has been initiated within the Cluster Electrification of Technical Organic Syntheses (ETOS). E-GLUCO aims to establish selective glucose oxidation from the laboratory scale to TRL 4.

The focus lies on electrochemical oxidative dehydrogenation – an energy-efficient reaction principle that enables high selectivities at low cell voltages.[3] Hydrogen is the sole byproduct, resulting in a resource-saving process (Figure 1). A key component involves the development of novel nickel-based catalysts optimized for high activity, stability, and selectivity.[4–6] Additionally, membrane electrode assemblies (MEAs) are designed to ensure the scalability of the process. The technical feasibility is demonstrated, with cell areas of up to 100 cm² being investigated.

Through these efforts, the E-GLUCO project makes a significant contribution to sustainable chemistry by enabling the material utilization of biomass-based raw materials while reducing energy and resource consumption. The project results will pave the way for future industrial implementation.

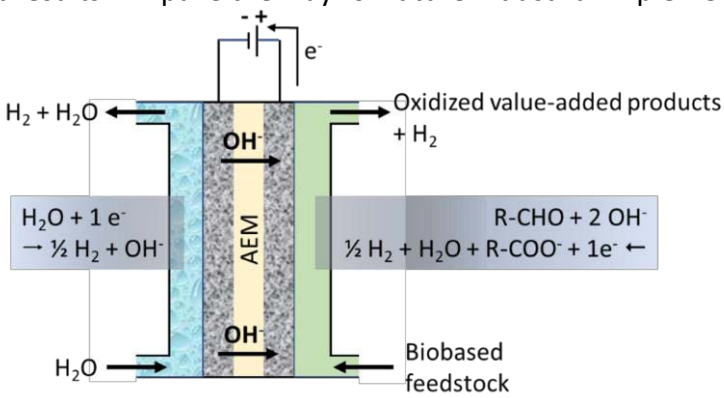

Figure 1. Representation of an electrochemical cell for glucose oxidation and the respective half-cell reactions.

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Quantification of Urea in Electrocatalytic Systems

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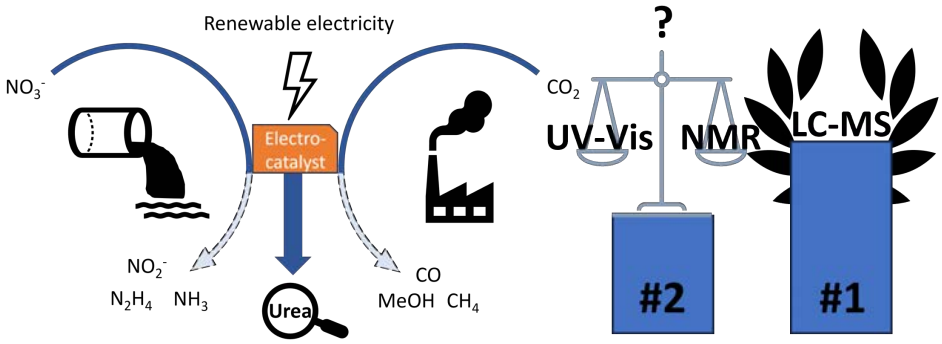
Electrochemical urea synthesis (EUS) from CO_2 and nitrates has recently emerged as a promising and more sustainable alternative to conventional nitrogen fertilizer production [1]. By utilizing captured CO_2 and nitrate-containing wastewater streams, this approach could contribute to both carbon utilization and nitrogen waste valorization. On the road EUS technology development, accurate and reliable quantification is an undeniable cornerstone. Because the field is still in its infancy, urea is often produced at very low concentrations alongside numerous side-products [2], making reliable analysis difficult and leading to reported false positives and negatives [3,4]. Although it is widely accepted that at least two independent analytical methods should be used, the choice of appropriate quantification protocols remains an open question [3–6].



Here, we present a comparative study of the most commonly used urea quantification methods, highlighting their advantages, limitations, and recent developments [7]. In addition, preliminary case-study results are presented to illustrate the reproducibility challenges of electrochemical measurements [8].

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Simulating First Principle Electrochemistry in the Grand-canonical Way

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Accurate first principle modelling of electrochemical systems requires a realistic description of the electrode potential under operating conditions. In most conventional density functional theory (DFT) simulations, the number of electrons in the simulation cell is fixed. This corresponds to a constant-charge description, where the total charge of the electrode is fixed while the electrode potential is an outcome of the calculation and may vary along a reaction pathway. However, electrochemical experiments are typically performed under constant-potential conditions: the applied voltage is controlled externally, and the electrode exchanges electrons with an external circuit so that the interfacial charge adjusts in response to the chemical environment.

This mismatch between standard DFT simulations and experimental electrochemistry can lead to an incomplete or biased description of electrochemical interfaces, especially when modelling charged intermediates, potential-dependent reaction energetics, and electrocatalytic mechanisms. A rigorous route to overcome this limitation is to describe the electrode within a grand-canonical ensemble, where the electron chemical potential, or equivalently the work function, is fixed, while the number of electrons is allowed to vary.

In a series of recent publications [1–3], we implemented a grand-canonical DFT framework in the open-source CP2K code. The developed computational toolbox combines:
(1) a grand-canonical self-consistent field formalism to converge the target work function,
(2) a planar counter-charge method to compensate excess interfacial charge and maintain electrostatic stability, and
(3) a solvent-aware self-consistent continuum solvation model, with the possibility to extend it to anisotropic continuum solvation in order to account for direction-dependent interfacial solvent response.

Importantly, these developments have been validated and benchmarked on representative bulk, surface, and electrified interface models, including implicit water, TiO_2, Pt, and Ag(111)/water systems, as well as reaction-relevant interfacial processes such as electrochemical half-reactions and OH* adsorption at metal/water interfaces.

Together, these developments enable more realistic and efficient simulations of electrified solid–liquid interfaces under experimentally relevant constant-potential conditions. We expect this framework to facilitate the mechanistic investigation of electrocatalytic reactions and to improve the connection between computational predictions and electrochemical experiments.

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An Electrochemical Synproportionation Reaction: Concerted Anodic and Cathodic Production of Formate from CO_2 and Ethylene Glycol at High Current Densities

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In this contribution we present a tandem electrolysis approach where formate is produced cathodically from gaseous CO_2 using a fluidic gas-diffusion electrode design in combination with a nanoparticulate CO_2-absorbing bismuth-oxycarbonate (denoted $(BiO)_2CO_3$) catalyst and anodically from dissolved ethylene glycol (EG, hydrolysis product of PET) by applying a highly porous, electrodeposited Ni foam catalyst. As evidenced by *operando* Raman spectroscopy, metallic Ni transforms under oxidative conditions into a NiOOH active catalyst converting EG into formate with a near-unity Faradaic efficiency at potentials below the onset of the parasitic OER. Similar high Faradaic yields for formate were observed for the cathodic counterreaction. We will demonstrate that ampere level reaction rates (geometric current densities) can be achieved using this tandem electrolysis approach. Possible catalyst degradation pathways will be discussed and affect mainly the NiOOH catalyst on the anode side of the electrolyzer whereas the bismuth-oxycarbonate demonstrates a high stability against reduction into metallic Bi even under such harsh electrolysis conditions as long as the supply of gaseous CO_2 is sufficient, and electrolyte flooding is prevented.

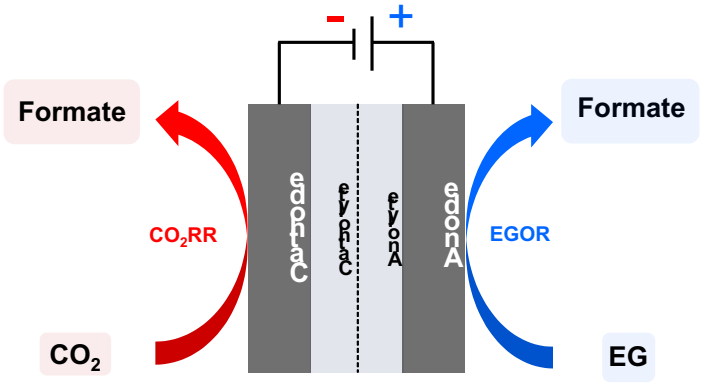

Figure 1. Schematic illustration of the tandem electrolysis approach utilizing CO_2 and ethylene glycol (EG, hydrolysis product of PET).

Separating Charge Throughput from Degradation Behavior in Pulsed High-Current OER Testing of NiFe Foam Electrodes

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Abstract

High-current oxygen evolution reaction (OER) stability tests under pulsed operation are difficult to compare when degradation is reported only as potential drift per elapsed time, because different duty cycles impose different cumulative charge throughput over the same test duration[1]. Here, dynamic-hydrogen-bubble-templated (DHBT) NiFe foam electrodes[2] were evaluated in an alkaline GDE-type dry-anode setup[3, 4] under pulsed galvanostatic OER at 1-3 $A \cdot cm^{-2}$. Two protocols, 6 s on/1 s off (86% active operation) and 24 s on/1 s off (96% active operation), were compared using electrodes from two independent deposition batches. In the time domain, the iR-corrected potential drift increased from 19.3 to 51.5 $mV \cdot h^{-1}$ for the 86% protocol and, at 2 $A \cdot cm^{-2}$, was higher for the 96% protocol than for the 86% protocol. When the same cleaned active-period data were analyzed versus cumulative areal charge, these differences were substantially reduced. For the 86% protocol, charge-normalized degradation rates remained close to 5.6-6.2 $mV \cdot (kC \cdot cm^{-2})^{-1}$ across 1-3 $A \cdot cm^{-2}$, whereas the 96% protocol showed no monotonic current-density dependence. At 3 $A \cdot cm^{-2}$, late-stage potential fluctuations and post-electrolysis SEM/EDX evidence of structural and compositional heterogeneity indicated additional failure processes. These results support the use of charge-normalized metrics to separate charge-throughput effects from changes in degradation behavior during pulsed high-current OER testing.

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