Bismuth-Mediated Electrochemical Reductive Amination for Biomass-Derived Monomers

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Electrocatalytic hydrogenation is a sustainable route to access secondary amines by directly utilizing protons from water under mild conditions and high selectivity. Here, electrons from renewable energy sources serve as inexpensive and versatile reducing agents.
Previous studies showed that lead traces (1 ppm) enable >60% amine yields in electrochemical reductive amination of acetone with methylamine in an aqueous system.[1] Recently, it was shown that only sixth-period p-block elements (Tl, Pb, Bi) are active mediators, with non-toxic bismuth (6 ppm) achieving comparable yields at room temperature.[2]
In this work an organic system for the bismuth-mediated electrochemical reductive amination using ethanol as a green co-solvent was developed. This approach enabled the successful electrochemical synthesis of novel secondary amines from biomass-derived carbonyl compounds with 2-amino-1,3-propandiol as the primary amine source.
The substrate scope involved 20 carbonyl compounds, enabling the successful synthesis of 14 secondary amines. While aldehydes were generally active, for ketones it was found that an *ortho*-hydroxyl substituent activates the carbonyl group, thereby enabling the reaction. Secondary amines bearing diol functionalities could be obtained with good quantitative NMR yields (49–69%) and were isolated in good purity by acid-base extraction. The aldehyde substrate scope revealed clear electronic effects controlling both imine formation and the bismuth-mediated reduction.
The electrochemically obtained secondary amines were applied as biomass-derived monomers in a one-pot precipitation polycondensation with hexachlorocyclotriphosphazene (HCCP), affording novel polymer colloids with defined morphology. Moreover, the obtained biomass-derived polymer colloids show high potential as sustainable fire-retardant materials.

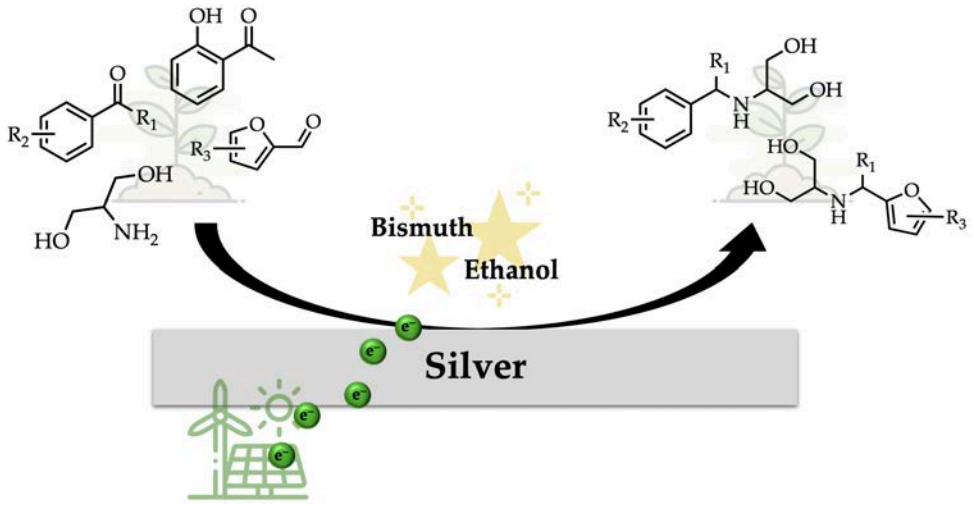

Figure 1: Schematic overview of the research objectives.

Key words
Electrochemical reductive amination, biomass valorization, sustainable monomers

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From Waste to Value: Electrochemical Upcycling into Useful Acetals

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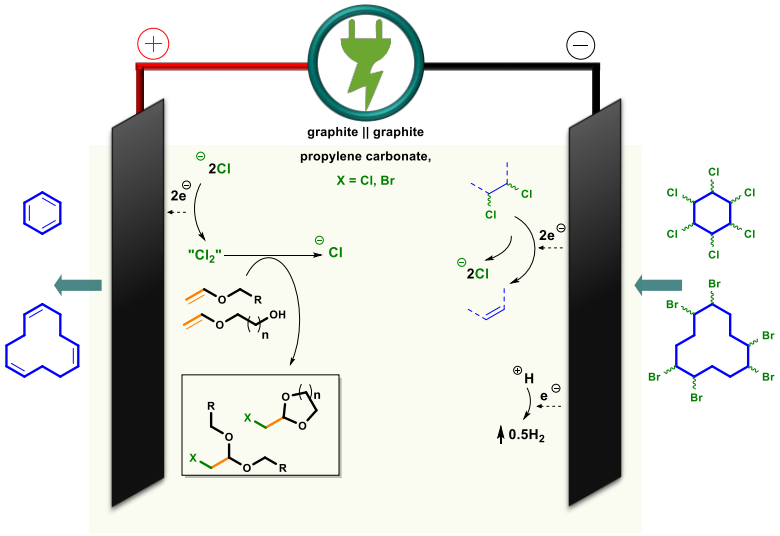
Persistent highly halogenated pollutants such as HCH and HBCD pose a long-standing environmental challenge yet they also represent an untapped chemical resource.[1] Lindane was globally banned in the early 2000s and 2009, all HCH isomers have been listed under the Stockholm Convention on Persistent Organic Pollutants (POPs), restricting their production, use, and transport. In total, an estimated 7.4 megatons of HCH have been produced worldwide additionally HBCD was added to the Stockholm Convention in 2013.[2] In this work, we demonstrate an electrochemical e-shuttle strategy that enables selective conversion of waste into valuable acetals of chloro- and bromo acetaldehyde.[3,4] Due to high selectivity and increasing industrial relevance, 2-chloromethyl-1,3-dioxepane was synthesized as a test substrate. Reaction optimization using fractional factorial designs and response surface methodology identified current density and applied charge as key parameters, with larger ring acetals affording improved yields. Mechanistic studies further revealed that up to 50% of the released chloride is efficiently incorporated into the target products. Importantly, scale-up using a stacked electrode configuration increased the electrode surface area by a factor of 167 and significantly reduced electrolysis time without compromising yields. In addition, product accumulation and electrolyte reusability over multiple cycles highlight the robustness of the system. Overall, this work showcases electrosynthesis as a scalable and sustainable approach for transforming persistent pollutants into valuable platform chemicals.



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Role of oxidative pulse parameters in long-term CO_2 electroreduction on silver

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Electrochemical CO_2 reduction (eCO_2R) using gas diffusion electrodes with silver as catalyst offers a promising pathway to convert CO_2 to CO[1]. However, maintaining high CO selectivity at industrially relevant current densities (>200 mA cm^{-2}) remains challenging due to the onset of the competing hydrogen evolution reaction (HER). Alternating continuous eCO_2R with short oxidative pulses has emerged as a potential strategy to maintain high selectivity, but its effectiveness depends heavily on the operating parameters[2–4]. A mechanistic understanding of these effects is thus needed to optimize the pulsing protocol. In this work, we fabricate silver GDEs using electrospun PVDF-HFP substrates and operate them in a three-compartment electrochemical cell at current densities above 200 mA cm^{-2} using $KHCO_3$ as catholyte. Selectivity is monitored continuously by online gas chromatography, and post-mortem structural characterization is performed by scanning electron microscopy and electrochemically active surface area measurements. We systematically vary the oxidative pulse potential, frequency, and duration to map their individual impacts on selectivity retention and catalyst morphology over operation periods of more than 100 hours. We identify a critical pulse potential threshold that separates two distinct behavioral regimes, linked to distinct structural outcomes of the silver catalyst. Guided by this mechanistic understanding, we find a pulsing protocol that substantially extends selectivity retention relative to continuous electrolysis[5].

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Rhenium-based Electrocatalysts for Water Splitting Processes and Green Hydrogen Production

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Abstract.

The search for efficient, durable, and economically viable electrocatalysts for water splitting remains a critical challenge in advancing sustainable hydrogen production. Conventional noble-metal catalysts such as platinum and iridium continue to set performance benchmarks for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Yet, their scarcity and high cost pose significant barriers to large-scale deployment. In recent years, rhenium (Re) has attracted growing attention as a promising alternative due to its unique combination of electronic structure, chemical stability, and adaptable surface chemistry. These characteristics enable Re-based materials to participate effectively in both HER and OER, offering pathways to modulate reaction kinetics, enhance catalytic efficiency, and improve long-term operational stability.

Progress in electrodeposition, vapor-phase synthesis, and nanostructuring techniques has further expanded the versatility of Re-containing materials, allowing precise control over morphology, oxidation state, and surface composition. Such tunability has led to increasingly favorable activity metrics, with Re demonstrating the ability to lower Tafel slopes, facilitate gas evolution, and serve as a bifunctional catalyst in alkaline, neutral, and acidic environments. Moreover, Re's resistance to structural degradation under harsh electrochemical conditions positions it as a strong candidate for next-generation electrolyzers aimed at renewable hydrogen production.

As the drive to reduce reliance on scarce noble metals intensifies, Re has emerged as a compelling intermediate solution—combining strong catalytic performance with improved economic practicality. Continued advances in identifying Re-based active sites, refining deposition and synthesis techniques, and incorporating rhenium into alloyed or composite structures are steadily strengthening its position as a viable catalyst for both HER and OER. Together, these developments underscore the growing relevance of Re in enabling scalable, efficient water electrolysis. In this talk, we explore the ever-increasing role of Re in water-splitting technologies and discuss the prospects of Re and its derivatives in the broader field of electrocatalysis.

Keywords: electrocatalysis, water splitting, hydrogen evolution reaction (HER), oxygen evolution reaction (OER), rhenium

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Preparation method influences of Ni-based catalysts on alkaline oxygen evolution reaction

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Alkaline water electrolysis is commonly investigated as an approach for the production of green hydrogen. The oxygen evolution reaction (OER) constitutes the bottleneck of the reaction, due to its sluggish 4 e^- -transfer kinetics. In recent years, binary and ternary Ni- or Co-based catalyst often mixed with Fe showed promising OER activity.[1] Different preparation methods, like co-precipitation or electrodeposition are commonly used to synthesize these particles or catalyst films. Although the preparation method is typically chosen to tune certain catalyst properties like uniformity or thickness of the catalyst layer, or for simplicity of synthesis,[2] the influence of different preparation methods for the same catalyst composition on the OER activity is less known.

In this study, multiple ternary Ni-based catalysts are prepared with electrodeposition, co-precipitation and flame spray pyrolysis. The resulting properties are investigated with transition electron spectroscopy (TEM), scanning electron spectroscopy (SEM) and X-ray diffraction (XRD), as well as Raman spectroscopy. The catalytic activity of the catalysts is tested in a gas diffusion electrode (GDE) setup to mimic conditions of an anion exchange membrane water electrolyzer (AEM-WE) while still having a setup easy to assemble.[3] In this way, the effect of the incorporation of different metals (Fe, Co, Mn, Cr) in $Ni(OH)_2$ on the OER is explored. The resulting activities are correlated to the characterized catalyst properties to gain new insights into the influence of the choice of preparation method on the OER performance, valuable for the design of future catalysts.

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Electrocatalytic Reduction of Nitrate on Model Copper Electrodes: Facet-Dependent Activity

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Electrocatalytic reduction of nitrate-ions (NO_3^-) to ammonia (NH_3) is promising both for the application in water purification and for the simultaneous synthesis of a valuable product. Copper exhibits high electrocatalytic activity toward the electroreduction of NO_3^- in both acidic and alkaline media [1]. At the same time, the overpotential for nitrate anion reduction depends significantly on the surface structure of a Cu electrocatalyst [2]. In this work, the influence of the crystallographic surface orientation of single-crystal Cu(hkl) electrodes on the rate and selectivity of nitrate ion electroreduction in alkaline media was systematically and quantitatively investigated for the first time. According to the obtained dependences of faradaic efficiency (FE_{NH3}) and time-averaged partial current density (j_{NH3}) of NH_3 formation on potential (Fig. 1), the activity increases in the order Cu(111) < Cu(110) < Cu(100). A structurally sensitive deactivation of Cu electrodes during electrolysis was revealed, being most pronounced for the Cu(111) face. Furthermore, we employed a potentiodynamic oxidation–reduction protocol in halide-containing solutions to nanostructure polycrystalline Cu foils [3], creating surfaces enriched in (n10) domains that displayed enhanced activity towards NO_3^--to-NH_3 conversion. The results are discussed based on voltammetric data, product analysis, and *in situ* Raman spectroscopy data.

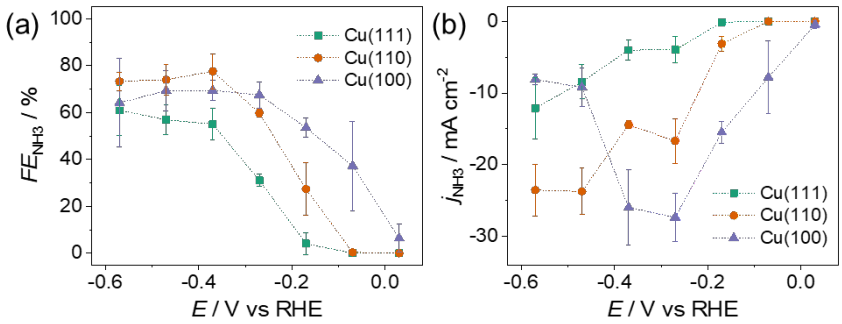

Fig. 1. (a) FE_{NH3} and (b) j_{NH3} as a function of applied potential in 1 M KOH + 0.02 M KNO_3. Potentiostatic electrolyses were carried out until a charge of −10 C had passed.

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Statistical Convergence and Uncertainty in Electrocatalytic Benchmarking of Ir and Ru Oxygen Evolution Catalysts

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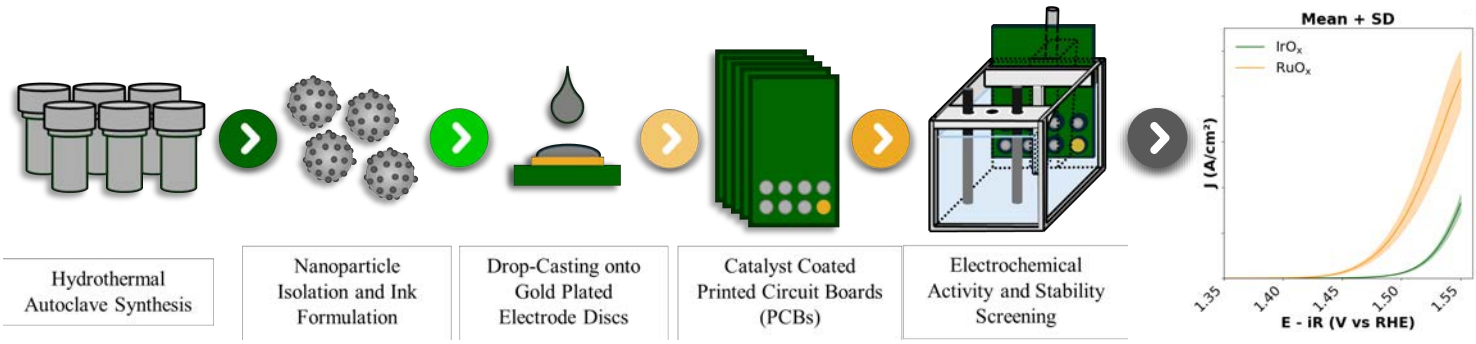
Electrocatalytic oxygen evolution reaction (OER) catalysts are frequently benchmarked using only a small number of measurements, although apparent activity differences may be comparable to experimental variability. Here, we combine parallel hydrothermal synthesis with multi-working-electrode electrochemical screening to generate statistically meaningful datasets for IrOx/ATO and RuOx/ATO catalysts under acidic OER conditions. More than sixty independent measurements per catalyst were used to compare intrinsic dispersion, confidence intervals, batch-to-batch reproducibility, and sample-size convergence. IrOx/ATO showed narrow distributions, near-normal behaviour, and reproducible activity across independent synthesis batches. RuOx/ATO exhibited higher initial activity but broader, non-normal distributions, stronger degradation, and statistically significant batch-dependent behaviour. The comparison demonstrates that standard deviation alone is insufficient for catalyst benchmarking, because it describes data spread but not uncertainty in the estimated mean. Confidence intervals and robust sample-size analysis provide a more defensible basis for comparing electrocatalytic performance. This work establishes a medium-throughput statistical workflow for acidic OER benchmarking and gives practical guidance for reporting reproducibility and uncertainty in catalyst screening studies.



Pulsed-electrodeposited Ni/Ni-foam anodes for flow-through HMF electrooxidation coupled with CO_2 reduction to formate

Paired electrolysis that combines anodic biomass oxidation with cathodic CO_2 reduction is an attractive strategy to improve electrolyzer energy efficiency while co-producing value-added chemicals. In this work, pulse-electrodeposited nickel on porous nickel foam (Ni/NF) were investigated as a flow-through anodes for the electrochemical oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA), paired with CO_2 reduction to formate at a Bi-based gas-diffusion electrode. A flow-through configuration was developed in which the anolyte permeates directly through the three-dimensional Ni/NF electrode, enabling convective transport across the full electrode thickness and improving utilization of the internal catalyst surface. Compared with untreated and cathodically treated nickel foams, pulse-electrodeposited Ni/NF exhibited a more homogeneous catalyst layer, a stronger Ni(II)/Ni(III) redox response, and substantially improved HMF oxidation performance. By systematically varying foam thickness and pore size, we show that porous-electrode geometry strongly affects catalyst utilization, mass transport, and the competition between HMF oxidation and the oxygen evolution reaction. Although some Ni/NF anodes displayed a larger cyclic-voltammetry response, this did not translate directly into higher FDCA selectivity under flow-through operation, highlighting the importance of productive catalyst utilization under realistic transport conditions. The optimized Ni/NF anodes delivered high FDCA selectivity in paired HMFOR/CO_2RR electrolysis, while flow-rate studies revealed a trade-off between single-pass conversion and selectivity. Sustained paired electrolysis was achieved for 96 h at 150 mA, with FDCA and formate remaining the dominant anodic and cathodic products, respectively. These results demonstrate that efficient and durable paired HMFOR/CO_2RR requires not only an active catalyst, but also appropriate porous-electrode architecture and reactor design.

Electrodeposition: A Synthesis Platform for Experimental Models in Electrocatalysis

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The High Entropy Alloys (HEAs) are metastable materials constituting of different principal elements in the same lattice.[1,2] The intrinsic property of chemical diversity in HEAs offer a range of adsorption energies for different molecules. So, tuning the composition can offer optimized adsorption energies is desirable in electrocatalysis. Currently, HEAs are being considered as materials platform to find better sensitivity, selectivity and stability, the three major fronts (3S) in electrocatalysis.[3,4] However, searching better electrocatalysts across all the three fronts for electrochemical reactions is an academic challenge to establish HEA's as a materials platform for catalyst discovery. Therefore, medium throughput experimental screening methods are required which demands faster and controlled synthesis of multielement nanoparticles.[5,6] Current work highlights the synthesis of Au-Ir-Pt-Pd-Rh-Ru nanoparticles using electrodeposition in aqueous media.[7] It uses a pulsed electrodeposition protocol to synthesize one sample within 90 seconds. We introduce an adjustment factor using monometallic depositions bridging the precursor compositions of the synthesis and the mesoscale compositions found using energy dispersive spectroscopy (EDX). Herein, a synthesis model is built using compositional space, particle size and coverage obtained using 250 experiments which allows better prediction of the mesoscale composition expected in the nanoparticles. A Gaussian process regressor is used to train different objectives like compositions found in the nanoparticles, particle size, coverage and synthesis charge during electrodeposition. Compositional analysis at different length scales from different microscopes using EDX, suggests random mixing at mesoscale along with a presence of compositional order at nanoscale.

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Atomic Ordering Effects in PtCo/C Intermetallic Catalysts for Durable PEMFC Cathodes

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Intermetallic Pt-based alloy catalysts with long-range atomic ordering and well-defined stoichiometry have emerged as promising oxygen reduction reaction (ORR) electrocatalysts for proton exchange membrane fuel cells (PEMFCs). To improve precursor dispersion and facilitate the formation of ordered phases, a facile strong electrostatic adsorption (SEA) strategy was employed. In this approach, the negatively charged Co precursor ($[CoCl_4]^{2-}$) is selectively anchored onto acid-treated Pt/C supports.[1] Subsequent optimized annealing under controlled H_2/Ar or vacuum atmospheres at elevated temperatures promotes the formation of ordered PtCo/C intermetallic nanoparticles, as confirmed by high-resolution scanning transmission electron microscopy (STEM).

To further understand the impact of atomic ordering on structural evolution during operation, *in-situ* high energy resolution fluorescence detected X-ray absorption spectroscopy (HERFD-XAS) was performed to monitor potential-dependent changes in the local coordination environments of Pt and Co. Membrane electrode assembly (MEA) fuel cell measurements were conducted to evaluate the macroscopic catalytic performance and durability. The ordered PtCo@Pt/C catalyst exhibited only a 24.2% loss in mass activity (MA) at 0.9 V after 10,000 accelerated stress test (AST) cycles, significantly outperforming its disordered alloy counterparts. Moreover, it delivered an initial mass activity of 0.35 A mg_{Pt}^{-1} at 0.9 V after activation.

Overall, this study demonstrates that atomic ordering in PtCo intermetallic catalysts enhance ORR activity and significantly improves electrochemical stability, providing valuable insights for the rational design of next-generation PEMFC cathode catalysts.

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From biomass-derived acids to chemicals: electrochemical decarboxylation on BDD electrodes

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Electrodes made from boron-doped diamond (BDD) are a powerful material class for electro-organic synthesis, especially for transformations requiring high anodic stability and wide potential windows while parasitic side reactions are suppressed.[1] When it comes to converting biomass into valuable chemicals, the electrochemical decarboxylation of short-chain carboxylic acids is an attractive process because it can be done under mild conditions.[2]

BDD electrodes behave differently than conventional platinum anodes, favouring non-Kolbe-type pathways that form oxygenated and olefinic products. The wide anodic potential window and low surface reactivity of BDD electrodes suppress extensive radical recombination and electrode fouling, thereby enhancing selectivity and process stability. By optimising operating conditions using BDD, it is possible to adjust the oxygenated-to-olefinic ratio, demonstrating the tunability of the system.[2,3]

This study explores the electrochemical conversion of propionic acid on BDD electrodes, with a particular focus on the selective formation of ethanol and ethylene. Propionic acid, an abundant carboxylic acid derived from biomass, is used as a model substrate to study structure-reactivity relationships in anodic decarboxylation processes. Systematic variation of electrolysis parameters such as current density, applied charge, temperature, electrolyte composition, and BDD electrode properties shows that optimising the reaction system depends on multiple parameters simultaneously and is adjustable.

The findings reveal the potential of BDD-based electrolysis in the sustainable conversion of biomass-derived carboxylic acids into platform chemicals, whilst also emphasising the importance of electrode design in advancing selective electrochemical synthesis routes.

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How We Measure Matters: Investigating the Influence of Electrochemical Measurement Conditions on the Characterization of Photoanodes

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Photoelectrochemical (PEC) cells are widely regarded as a promising technology for directly converting solar energy into chemical fuels and high-value products.[1] However, progress in this field is significantly hindered by a lack of comparability between studies. While much of this variability is attributed to differences in material synthesis, there is strong evidence that the electrochemical measurement protocol itself exerts a profound and often underestimated influence on the observed performance. This includes the choice of technique, scan rate, illumination history, electrolyte composition and electrode conditioning.[2] Another major factor is the cell design. Key parameters include the choice of transparent conductive substrate and the quality of its ohmic contact with the back of the semiconductor, illumination geometry, electrolyte composition and pH, and the configuration of the electrochemical cell itself.[3,4]

This study systematically investigates how measurement conditions affect the electrochemical characterisation of benchmark materials such as hematite and bismuth vanadate, as well as photoanodes based on new materials such as metal sulfides and double perovskites. These materials have very different surface chemistries and defect landscapes. By systematically varying conditions such as scan rate, applied bias voltage, light-chopping frequency and prior electrochemical history, the study aims to distinguish between intrinsic material properties and measurement artefacts — a distinction that is crucial for drawing meaningful conclusions about the performance of photoanodes.

The photocurrent-voltage characteristics are determined using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) and the onset potentials are identified. Particular attention is paid to hysteresis effects that may arise from charging surface states and ion redistribution at the semiconductor-electrolyte interface.[5,6] Electrochemical impedance spectroscopy (EIS) is used to determine the frequency-dependent charge transfer response and high/low-frequency resistance.[7] Chronoamperometry under prolonged irradiation is primarily employed to investigate operational stability. Optical characterisation using UV-Vis spectroscopy provides important information for interpreting the electrochemical data. All techniques must be applied within the framework of a uniform, systematically varied protocol to allow a direct assessment of the effect of the sequence of measurements, conditioning steps and environmental parameters on the reported performance metrics.

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Reproducible Data Management for Multi-Technique Electrocatalysis Research

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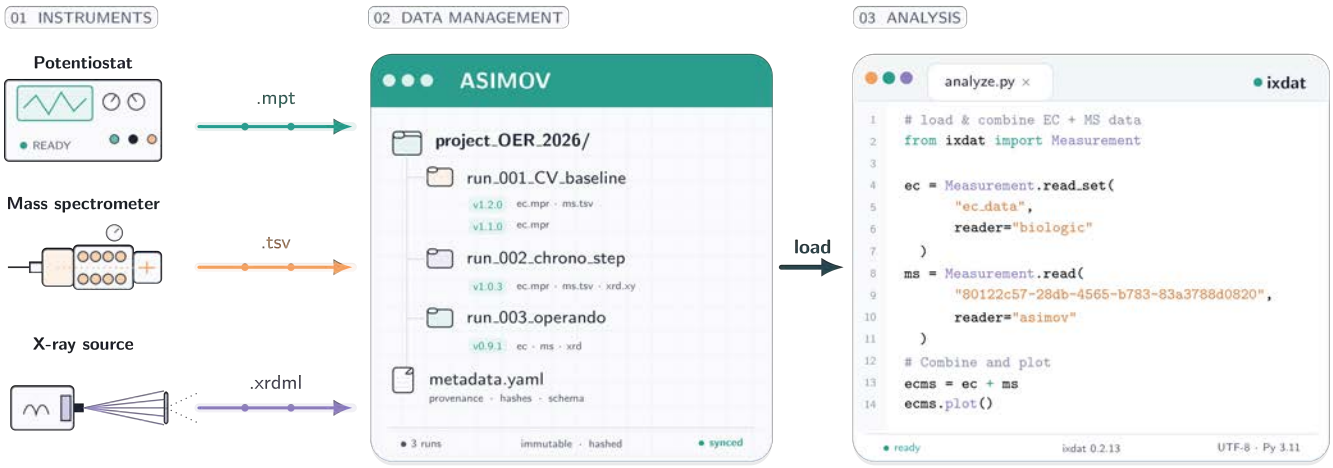
Modern electrocatalysis experiments routinely produce heterogeneous data streams from electrochemistry, mass spectrometry, X-ray spectroscopy, and more; all which might be acquired simultaneously from multiple instruments and stored in proprietary formats. Parsing, combining, and sharing these datasets while maintaining full provenance from raw acquisition to publication remains a persistent bottleneck for reproducible science. Here we present an open-source *software stack* addressing this challenge: **ixdat**[1] and **ASIMOV**.

Ixdat (**I**n-situ E**x**perimental **Da**ta **T**ool) is a Python library providing a unified, object-oriented interface for importing, processing, and analyzing data over various instrument formats used in electrochemical research. Technique-specific classes handle EC, MS, XRD, XPS, NMR and more, enabling time-synchronized merging of multi-technique datasets, with built-in calibration and publication-ready plotting tools.

ASIMOV is an online research data platform that brings samples, instruments, measurements, and datasets together in a shared, searchable project space, replacing fragmented local folder hierarchies. Accessible from anywhere via authentication, researchers can track and annotate their data directly through the website or access it programmatically from Python via ixdat, which returns fully reconstructed measurements. Beyond storage, ASIMOV is being developed as a lightweight presentation tool for browsing, visualizing, and narrating experimental data within the same platform where the data lives. Our architecture directly embeds the FAIR[2] principles into day-to-day workflows: data is complete and labeled at upload, scripts are stored alongside the data they operate on, and the structured project format ensures datasets remain interpretable and reusable by collaborators and future researchers.

Together, ixdat and ASIMOV establish a traceable, shareable path from instrument output through collaborative analysis to publication, built for the multi-technique, multi-researcher reality of modern electrocatalysis research.



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Statistical Benchmarking of MnOx Thin-Film Catalysts for Alkaline OER: A Medium-Throughput Approach

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The lack of statistical rigor in electrocatalytic measurements, where catalyst performance is traditionally determined based on a few representative measurements of thin catalyst films, limits the reliability of benchmarking reactions such as the oxygen evolution reaction (OER). This study reports a medium-throughput, statistically rigorous benchmarking framework that converts anecdotal claims of catalytic activity into quantitatively validated evidence. Two MnO_x-based OER catalysts synthesized via different hydrothermal routes were evaluated across 144 identically prepared thin-film electrodes to explicitly resolve film-to-film variability. The data distribution, intrinsic dispersion, and required sampling size for robust benchmarking were quantified statistically. The HCl-derived catalyst, MnO_x(H), exhibits narrow, near-Gaussian activity distributions with low relative standard error of the mean (RSEM < 8%) and tight confidence intervals, indicating statistically converged performance at moderate sample sizes. In contrast, the H_2SO_4-derived catalyst, MnO_x(S), displays broad, right-skewed, non-Gaussian distributions with persistent high-activity outliers and wide confidence intervals (±25-50%), reflecting intrinsic catalyst-film heterogeneity. Importantly, population-level statistics demonstrated that reliance on a small number of selected measurements can substantially overestimate apparent activity and obscure statistically relevant variability. The findings demonstrate that statistical robustness is as essential as electrochemical metrics for meaningful comparison of OER activity data and that variability can arise from both intrinsic material heterogeneity and measurement artefacts. Taken together, this study highlights the limitations of conventional representative-curve reporting and provides a generalizable framework for statistically robust benchmarking of electrocatalysts.

Toward Enhanced Catalyst Evaluation in CO_2 Electroreduction

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Gas diffusion electrode (GDE)-based flow cells have driven a breakthrough in CO_2 electroreduction (CO_2R) by achieving industrially relevant current densities, yet their complexity introduces numerous interdependent operational parameters that critically influence performance. These parameters are inconsistently controlled and reported across studies, leading to poor inter-laboratory reproducibility and making objective catalyst evaluation increasingly challenging.[1] Addressing this, NCCR Catalysis,[2] the Swiss national research center for sustainable chemistry, has initiated standardization efforts toward more reliable catalyst benchmarking, including the establishment of the Swiss national electrocatalysis platform capable of precisely controlling a broad range of operational parameters (Figure 1a). Here, we demonstrate the importance of systematic and comprehensive control for accurate catalyst evaluation, illustrated by determination of the apparent activation energy (E_a^{app}), a key kinetic descriptor. This requires precise control of temperature and other parameters affecting mass transfer, among which the gas-liquid differential pressure over a GDE was found to significantly affect measured activities. The determination of E_a^{app} allowed identification of the rate-determining steps in the complex chain-growth mechanisms on Ni- and Co-based CO_2R catalysts (Figure 1b).[3,4] This work highlights that accurate catalyst evaluation allows more reliable benchmarking and enables translation into fundamental understanding.

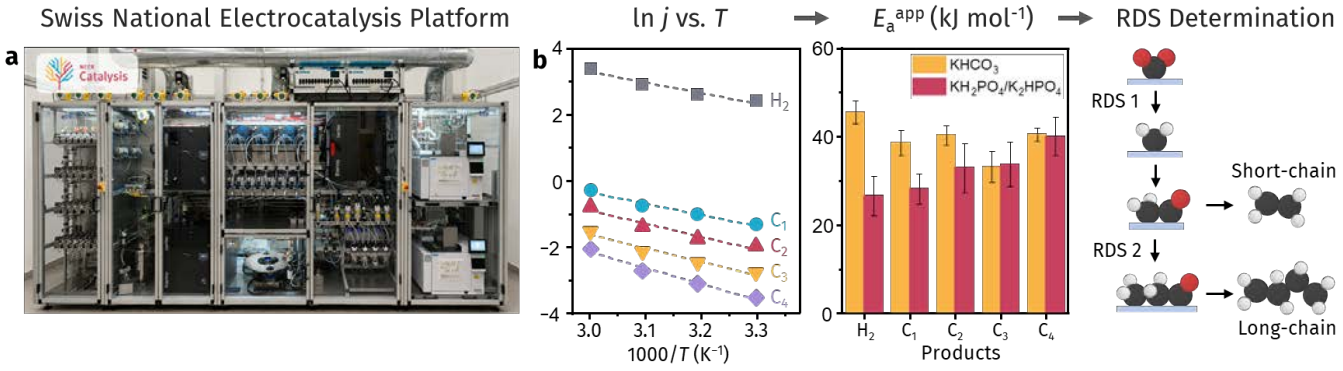

Figure 1. a) Swiss national electrocatalysis platform at ETHZ, and b) determination of E_a^{app} of gaseous CO_2R products on Ni-based catalysts, by measuring product current density (j) vs. temperature (T) to obtain Arrhenius slopes, from which E_a^{app} values were calculated, leading to identification of rate-determining steps (RDSs).

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Oxygen evolution in mildly alkaline solutions: An analytical model to describe stepped polarization curves of rotating disk electrodes

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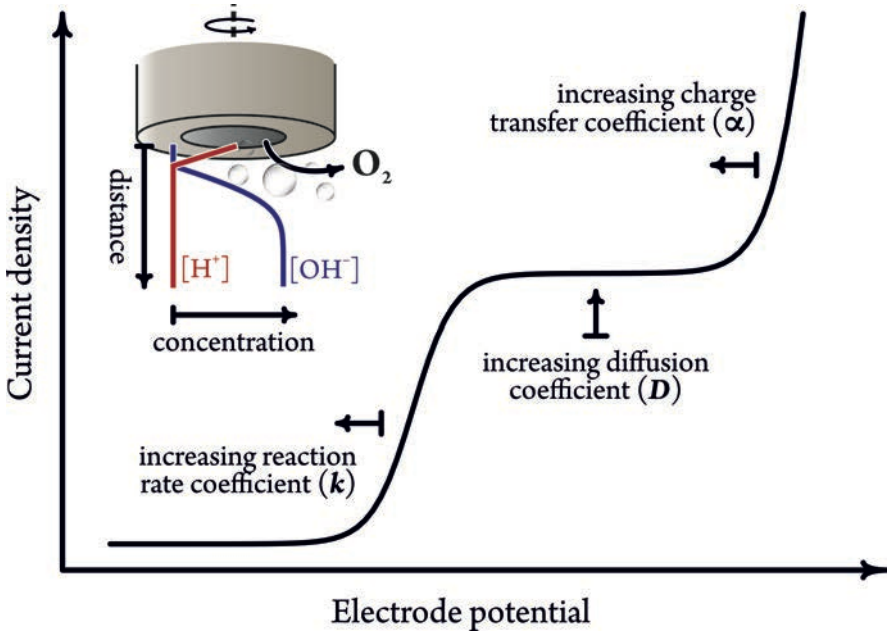
Oxygen evolution reaction (OER), an anode process of most electrochemical reactors, shows strong dependence on the composition of the electrolyte solution, with particular emphasis on the *p*H. Although near-neutral conditions would be beneficial to eliminate corrosion effects, only a scarce number of studies focus on OER under such conditions. We present here a robust analytical model to describe OER polarization curves recorded on rotating disk electrodes in mildly alkaline media. These polarization curves exhibit a stepped shape: two exponentially rising segments (the first commonly assigned to OH^-, the second to water oxidation) are separated by a limiting current plateau. Our model uses only three model parameters for the full polarization curve by assuming that OER proceeds according to a single two-electron charge transfer reaction, $OH^- \rightleftharpoons \frac{1}{2} O_2 + H^+ + 2e^-$, obeying the Erdey-Grúz–Volmer–Butler equation. The presented model can well be fitted to experimental data obtained for OER on oxidized iridium, platinum, and gold, over a broad range of *p*H, rotation rate, and electrode potential. The determined kinetic parameters (reaction rate and charge transfer coefficients) can be used to benchmark the catalytic activity of different electrode materials, while the obtained transport parameter (diffusion coefficient) can effectively support system optimization processes. Using the presented model framework, it is also possible to estimate the variation of *p*H as a function of distance measured from the electrode surface. Such modelled *p*H profiles may become useful in catalyst development and system optimization processes, and could even aid in gaining a deeper understanding of the mechanism of OER.



Electrochemical Synthesis of Disulfonamides as a novel Sulfamoyl Building Block

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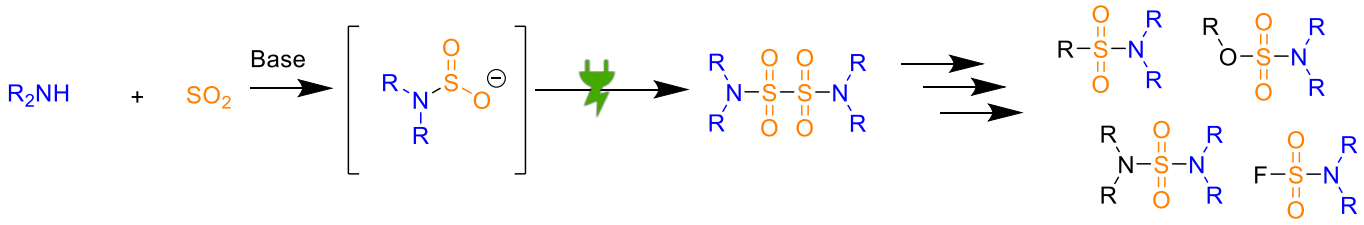
Sulfonamides, sulfamides and sulfamates are important classes of chemicals in pharmaceutical chemistry.[1,2] They are typically prepared by using sulfurylchloride as sulfuryl precursor, which are highly moisture sensitive, lead to chlorine waste and can produce chlorinated byproducts. Intrigued by the work of Maes et. al.[3] using disulfones as sulfonylradical precursors, we imagined similar nitrogen compounds could act as sulfamoyl precursors.

In the presented work we show the first successful synthesis of disulfonamides. The transformation was performed by forming an amidosulfinate intermediate from sulfur dioxide dissolved in acetonitrile and a secondary amine. This Intermediate could be oxidized via a constant current electrolysis resulting in the dimerized product. The methodology could be extended synthesizing multiple examples in gram scale. By reacting these novel structures with a diverse range of nucleophiles the utility as sulfamoyl building blocks could be demonstrated.



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Operando X-ray Studies on the Structural and Compositional Degradation of $Pt_{0.7}Co_{0.3}$ Under Accelerated Stress Testing

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In this study, the performance and structural degradation of $Pt_{0.7}Co_{0.3}$ were investigated using operando X-ray diffraction (XRD), X-ray fluorescence (XRF), and X-ray Absorption Near Edge (XANES) during an accelerated stress test (AST). These tests simulate the long-term operating conditions of proton exchange membrane fuel cells (PEMFCs), commonly used in hydrogen fuel cells. The oxygen reduction reaction (ORR) is the primary rate- and efficiency-limiting step in these systems. Previous studies have demonstrated that the bimetallic PtCo alloy exhibits excellent ORR performance. To further assess its stability, activity, and the potential for future catalyst development, the material was analyzed under AST conditions using operando XRD, XRF, and EXAFS, enabling direct observation of changes in composition, atomic structure, and local coordination. [1-3]

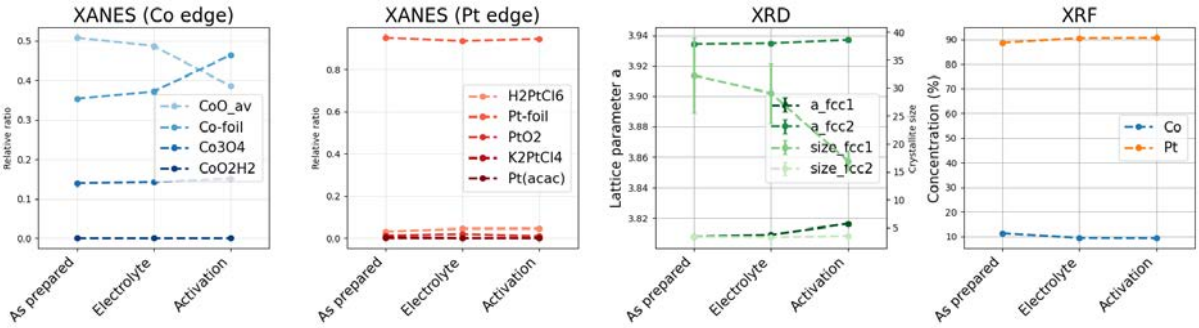

Figure 1: XANES (Co edge), XANES (Pt edge), XRD and XRF parameters during the activation of the catalyst layer.

This study presents initial findings that indicate substantial Co degradation during catalyst activation (Figure 1). XRD reveals the presence of two distinct crystalline phases. The first one is attributed to a mixed CoPt alloy (fig 2: fcc1), while the second phase corresponds to pure Pt (fig 1: fcc2). During the activation process, the CoPt phase shows a shift in the lattice parameter toward that of pure Pt. This suggests dealloying and leaching of Co, which was confirmed by XRF measurements (fig 1). In the Pt phase the crystallite size increased towards the end of the AST protocol, possibly via Ostwald ripening. Whereas the mixed phase decreased in crystallite size, which indicates nanoparticle dissolution, respectively Co leaching.

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Laser-Induced Surface Doping of Ni-Based Electrocatalysts for the Oxygen Evolution Reaction in Alkaline Water Electrolysis

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Electrochemical water splitting is a cornerstone technology for the decarbonization of the chemical sector, yet its efficiency and long-term stability critically depend on the performance of earth-abundant electrocatalysts, particularly for the anodic oxygen evolution reaction (OER). Pulsed Laser Diffusion Enhancement in Liquids (PUDEL) represents a scalable, low-energy post-processing strategy that enables surface-selective modification [1-4] and cation doping [5] of nanoparticle catalysts under continuous-flow conditions, without altering bulk structure or particle size. In this contribution, we systematically investigate PUDEL as a tool for tailoring the surface chemistry of Ni-based OER catalysts relevant for anion exchange membrane water electrolysis (AEM-WE). NiO, $NiFe_2O_4$, and NiFe nanoparticles are modified using Li^+, Fe^{3+}, and Ce^{3+} dopants across a broad parameter space encompassing laser fluence, pulses per volume, wavelength, counter-anions, and electrostatic environment. The impact of laser-induced surface modification is quantified using the OER as a functional electrochemical readout, directly linking surface chemistry to catalytic performance. Comprehensive surface and structural characterization (XPS, XRF, XRD, TEM-EDX), complemented by adsorption studies, reveals that PUDEL selectively alters near-surface chemical states while preserving bulk crystallinity. Distinct parameter-activity relationships are identified, with moderate fluences (20-40 mJ/cm^2), single pulse-per-volume, and intermediate zeta potentials (~10 mV) yielding the most favourable OER performance. Mechanistically, the results support an adsorption-controlled process, in which pre-adsorbed dopant species govern laser-induced diffusion and surface restructuring. [6] Overall, this work demonstrates how laser-based surface engineering can be integrated into electrocatalyst development, providing mechanistic insight and practical guidelines for tuning anodic catalyst surfaces in electrochemical energy-conversion systems.

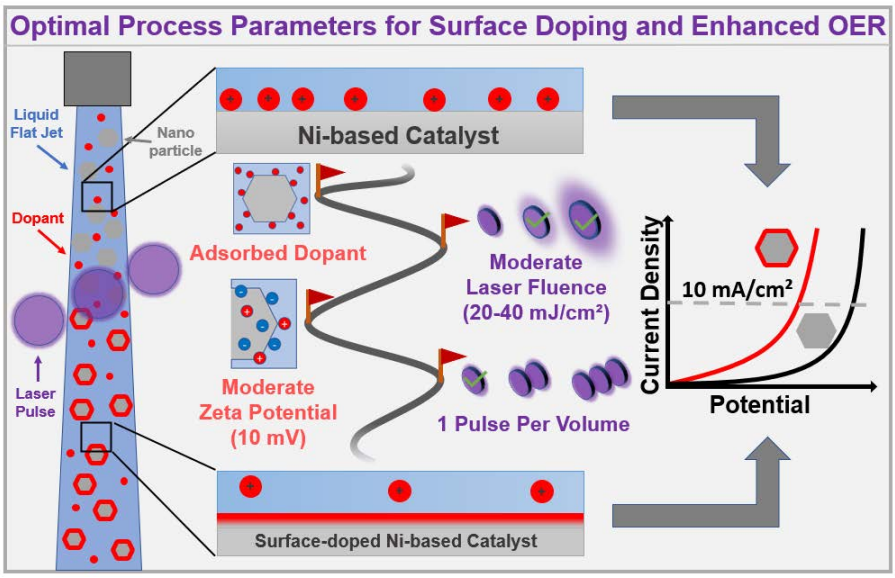

Figure 1: Schematic representation of the assumed surface doping caused by the PUDEL treatment under optimized process parameters and their influence on OER activity.

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Towards unified catalyst discovery through transferable composition–activity relationships

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Abstract: Multinary materials provide vast compositional flexibility for optimizing electrocatalytic reactions, yet systematic exploration of their composition space is challenging. Density functional theory (DFT)-derived models, thin-film materials libraries for high-throughput characterization, and nanoparticle-based electrochemical screening provide complementary routes for catalyst discovery. However, it has to be shown that composition–activity trends obtained from these different approaches are transferable, which would allow their combination into a unified approach. Here, we evaluate the transferability of composition–activity relationships across these experimental and theoretical approaches, using the oxygen reduction reaction (ORR) in the quaternary system Ir–Pd–Pt–Ru as a model case. Three complementary datasets, consisting of ORR data from DFT-derived theoretical activities, thin-film materials libraries, and electrodeposited nanoparticles, were used to independently construct continuous composition–activity landscapes using Gaussian Process Regression. To enable direct cross-platform comparison despite differences in electrochemical techniques, absolute activity metrics and sample density across the quaternary system, the data were converted into rank-normalized activity landscapes. It is shown that, regardless of their differences, all three approaches consistently identify Pd-rich compositions with moderate Pt incorporation and low Ru/Ir content as high-activity regions. While the detailed shapes of the obtained activity landscapes differ between the approaches, the dominant compositional trends are consistent. These results demonstrate that the composition–activity trends are transferable across theory-based, thin-film, and nanoparticle catalyst screening platforms, providing the basis for a general strategy of accelerated catalyst discovery combining different datasets.

Keywords: Nanoparticles; thin-film material libraries; density functional theory; multi-metal electrocatalysis; oxygen reduction reaction; Gaussian Process Regression

Electrochemical Dehydration of Carboxamides to their Nitriles

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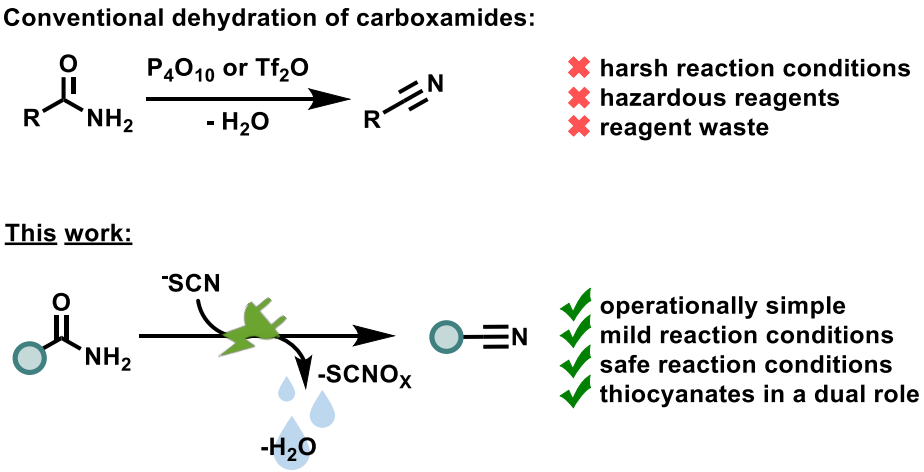
An efficient electrochemical strategy for the dehydration of carboxamides to their corresponding nitriles is reported. This method replaces conventional dehydrating reagents with a thiocyanate-mediated electrochemical activation, providing a safer, milder, and more sustainable alternative. Under optimized conditions in an undivided cell, 18 examples of aromatic and aliphatic carboxamides were smoothly converted to the corresponding nitriles at ambient temperature in good to excellent yields (up to 84%). Hexafluoroisopropanol proved to be essential for reaction efficiency, while tetrabutylammonium thiocyanate acted as a redox mediator, as confirmed by cyclic voltammetry studies, which revealed an EC-type mediated oxidation process. The method demonstrates broad functional-group tolerance, including halogenated, methoxylated, and sterically hindered substrates, as well as complex molecules derived from pharmaceuticals and natural products. Importantly, the protocol was successfully scaled up eight-fold with minimal loss in yield, illustrating its robustness and practical applicability. Mechanistically, anodic oxidation of thiocyanate generates highly reactive species that activate the amide functionality, leading to nitrile formation via an oxidative dehydration pathway, while hydrogen evolution occurs at the cathode. This work expands the synthetic utility of electrochemical dehydration reaction and offers a valuable, environmentally responsible route to nitrile-containing compounds of broad relevance for pharmaceuticals, agrochemicals, and materials science



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Beyond Binding: How Ionomer-Defined Microenvironments Direct Selectivity in Acidic CO_2 Reduction to Formic Acid

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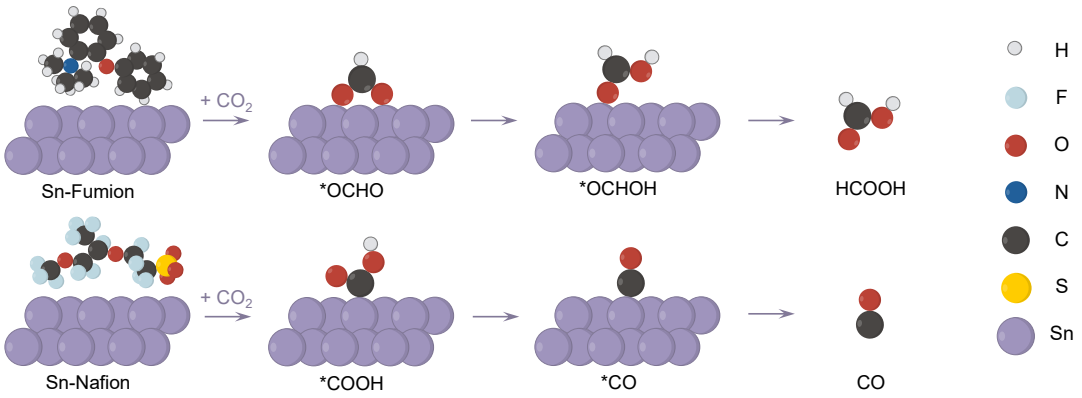
The electrochemical CO_2 reduction reaction (CO_2RR) offers a promising route to renewable feedstocks and a circular carbon economy. In neutral and alkaline electrolytes, however, carbonate formation severely limits CO_2 conversion efficiency, complicating downstream separation and undermining industrial feasibility. Operating in acidic media avoids carbonate formation, but high proton availability facilitates the competing hydrogen evolution reaction (HER). Using pH 1 media, we address this challenge through strategic control of the catalyst microenvironment, specifically by application of an anion-exchange ionomer, Fumion. *Operando* Raman spectroscopy revealed the presence of carbonate species on the Sn-Fumion surface during catalysis at high current densities, indicating a locally alkaline environment despite the strongly acidic bulk. Density functional theory calculations show that the positively charged Fumion side chains and H-down water orientation creates a proton-repelling yet charge-stabilizing interface, enhancing *OCHO intermediate stabilization and thereby promoting selective formate generation over CO and H_2 pathways. This enables CO*2*RR to remain competitive even under high-conversion conditions where CO*2* availability depletes. High Faradaic efficiencies for formic acid (> 70%) could be achieved up to 400 mA cm−*2*, as well as conversion rates of 69% whilst operating at 200 mA cm−*2*. This demonstrates a simple yet effective strategy for tailoring a catalyst microenvironment to achieve high performance in acidic media under industrially relevant conditions.



Electrochemical Depolymerisation of PLA in Suspension

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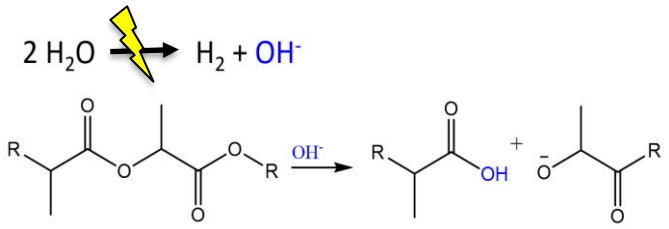
Plastic pollution has become one of the most pressing global environmental challenges.[1–3] Recycling represents a key strategy to mitigate this issue. However, mechanical recycling, while widespread, involves uncontrolled bond scission, leading to inferior properties afterwards and a limited number of recycling cycles.[4] Another method, chemical recycling, remains comparatively underdeveloped, resulting in high costs.[1]. In addition, most of the currently studied methods are highly specialised for specific polymers.[5] Thus, research into new and innovative recycling systems – especially those capable of handling multiple polymers – is needed to find the solution for the pollution problem.[1] In a previous publication, we showed the feasibility of depolymerizing poly(lactic acid) (PLA) electrochemically to its monomer lactic acid using a mixture of 9:1 1,4-dioxane: water to dissolve the polymer. This system had a maximum yield of 87 % lactic acid after transferring an electric current of 28.5 C mg^{-1}.[3] First mechanistic insight revealed the mechanism proceeds *via* water splitting producing hydroxide anions, which cleave the ester group connecting the repeating units with a nucleophilic attack.[3,6] However, this system has only been investigated for PLA so far, limiting its applicability for alternative, more challenging polyesters and mixtures of polyesters.



Scheme 1: Electrochemical depolymerisation of PLA through hydroxide anions, generated by water splitting.

Herein, we present first insights in the adaption of this system towards additional polyesters. For this, the restricted solubility of most polyesters in 1,4-dioxane was identified as the limiting key factor for a successful transfer. Thus, a screening of various organic solvents was employed as a first step in opening the reaction system for new polyesters. With 4.29 C mg^{-1} transferred charge over platinum electrodes in an undivided cell only three of the tested organic solvents showed activity: tetrahydrofuran, acetonitrile and 1,3-dioxolane. However, the yields, determined by HPLC, remained under 10 %, compared to the 30.2 (± 1.7) % of the reaction in dioxane. A suspension of PLA particles in water generated a lactic acid yield of 4.1 (± 1.7) %, showcasing a similar activity to the substituted solvents while circumventing the need for expensive and more toxic solvents.

The suspendability of the PLA particles in water, determined by their particle size and zeta potential, was found as a key limiting factor for the lower depolymerization yield in suspension. Particles with a highly negative zeta potential, synthesized *via* a salting out method, exhibited a limited suspendability in water and yielded lactic acid, while cryogenically milled particles with a more neutral zeta potential did not. Employing mixtures of water with ethanol improved the stability of the suspension. Adding ethanol to water with a ratio of 9:1 resulted in a lactic acid yield of 24.2 (± 1.6) %, which is only 6.2 % less than the comparable reaction in aqueous dioxane solution. The best results were obtained with an increased

transferred charge of 25 C mg^{-1} achieving a yield of 50.2 %. In summary, we were able to transfer the depolymerisation of PLA from a solution in 1,4-dioxane to a suspension in an ethanol-water mixture, providing a greener alternative, while maintaining high activities and enabling further investigation into other polyesters.

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Engineering metal-support interaction for manipulate microenvironment: single-atom platinum decorated on nickel-chromium oxides towards high-performance alkaline hydrogen evolution

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Rational construction of platinum (Pt)-based single-atom catalysts (SACs) with high utilization of active sites holds promise to achieve superior electrocatalytic alkaline HER performance, which requires the assistance of functional supports. In this work, we report a novel catalytic configuration, namely, Pt SACs anchored on the nickel-chromium oxides labeled as Pt_{SACs}-$NiCrO_3$/NF. The mechanism associated with the metal-support interaction (MSI) for synergy co-catalysis that empowers efficient HER on Pt_{SACs}-$NiCrO_3$/NF is clarified. Specifically, the modulated electron structure in Pt_{SACs}-$NiCrO_3$/NF manipulate the interface microenvironment, mediating a more free water state, which is beneficial to accelerate front water dissociation behavior on the oxide support. Besides, the homogeneously distributed Pt sites with the created near-acidic state ensure the subsequent fast proton-involved reaction. All these determine the comprehensively accelerating HER kinetics. Consequently, Pt_{SACs}-$NiCrO_3$/NF deliverers considerable HER performance, with overpotentials (η_{10}/η_{100}) of 23/122 mV, high mass activity of 382.77 mA mg^{-1}_{Pt}. When serving in alkaline water-based anion exchange membrane electrolytic cell (AEMWE), Pt_{SACs}-$NiCrO_3$/NF also presents excellent performance (100 mA cm^{-2} at the cell voltage of 1.51 V and stable up to 100 hours), confirming its good prospect.

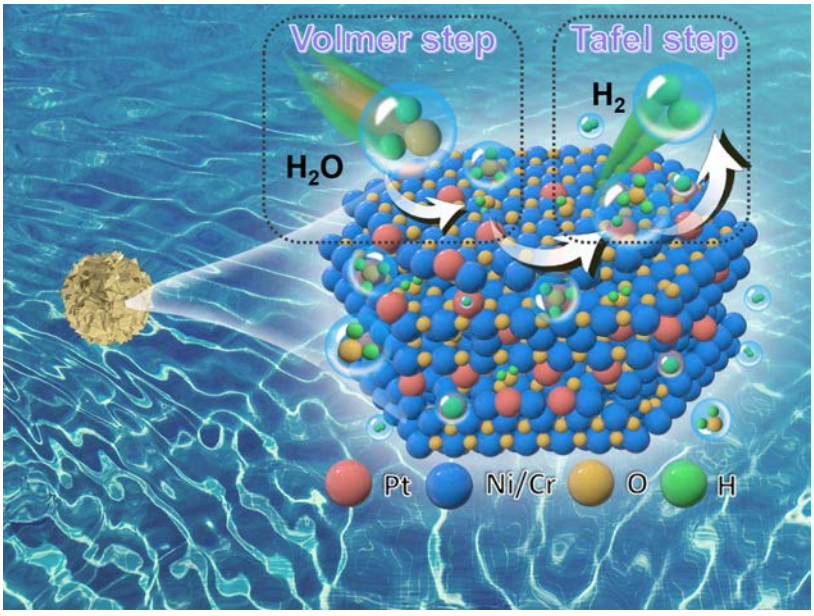

Figure 1. Schematic illustration of the dynamic proton-concentrated catalyst surface.

Disentangling the Pitfalls of Rotating Disk Electrode-Based OER Stability Assessment: Bubble Blockage or Substrate Passivation?

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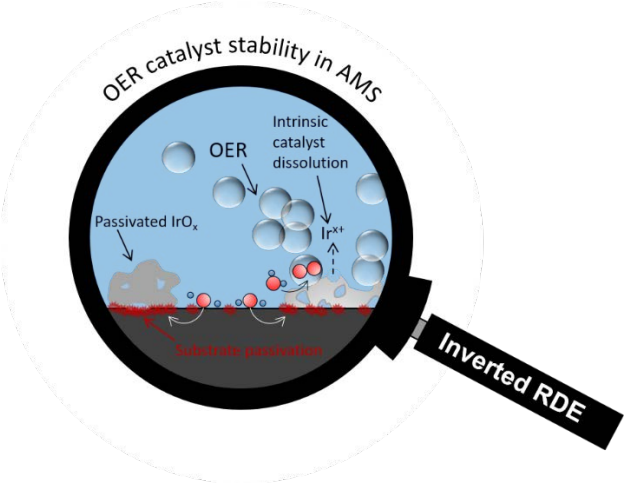
Currently, the **stability benchmarking of electrocatalyst materials** is increasingly driving the attention of the oxygen evolution reaction (OER) community since device operation in the 10-years range is an essential requirement for the widespread deployment of proton exchange membrane water electrolyzers (PEMWEs). Since the testing of the powdered catalyst materials in real devices (i.e., membrane electrode assemblies, MEAs) is prohibitively expensive and time-consuming, catalyst assemblies in aqueous model systems (AMSs) consisting in dropcasted thin-film rotating disk electrodes (TF-RDEs) are more frequently resorted to for such determinations. However, researches are increasingly aware of **the limitations of this approach that fails to produce transferable material stability metrics to technical approaches due to operational issues that are not related to intrinsic material degradation**. The groups of Dr. Serhiy Cherevko[1] and Prof. Linsey C. Seitz[2] have demonstrated that stability investigations carried out with these simplified platforms suffer from artifacts originating from the use of insufficiently inert materials used as backing RDE electrodes under the oxidizing OER conditions. In addition, El-Sayed et al.[3] have identified pitfalls of the employed RDE-based AMS approaches due to accumulation of oxygen microbubbles within the porous structure of the catalyst that leads to performance decline of the electrode assemblies. **Despite the independently developed understanding of these two processes (e.g., substrate passivation and catalyst blockage by O_2 bubbles), their interplay and relative impact on the intrinsic and operational material stability have not yet been established and elucidation of whether they occur simultaneously or sequentially in the course of TF-RDE-based OER investigations remains an open question**. This ambiguity along with major discrepancy in stability metrics between AMS and MEA have stimulated criticism of the ubiquitous RDE-based screening method and its suitability for OER catalyst durability benchmarking.

Our work tackles this debate. **We employ an inverted RDE (iRDE)-based approach coupled to online gas quantification that excludes the influence of bubble retention on the surface of the catalyst and allows dissecting the electrode assembly degradation process occurring during TF-(i)RDE-based OER stability studies**. The strength of our approach is rooted in the following points:

- Due to its upward-facing configuration, the iRDE exploits buoyancy and hydrophilicity of the anodes operated at high anodic current densities in acidic electrolytes,
- The electrochemical experiments are coupled to quantitative gas analysis that enables unambiguous dissection of the electrochemical processes involved in TF-(i)RDE-based OER catalyst screenings,
- Through advanced characterization techniques and specifically devised experiments that provided spatiotemporal insights, we were able to propose a mechanism that reveals the electrode assembly degradation occurring in typical TF-RDE-based OER stability studies.

Thus, we identify the origins of the apparent catalyst degradation and allow accurate quantification of intrinsic catalyst material loss. **We demonstrate that even when bubble accumulation within the catalyst layer can be avoided using the iRDE, the stability misalignment between galvanostatic NP-TF-RDE- and MEA-derived data is still observed and is due to the use of corrosion-prone substrate materials in AMSs.** Furthermore, we propose experimental measures to mitigate or circumvent TF-RDE-related limitations when the technique is to be applied to OER stability assessment. It is our contention that these findings advance the transferability between AMS and MEA approaches.



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