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.

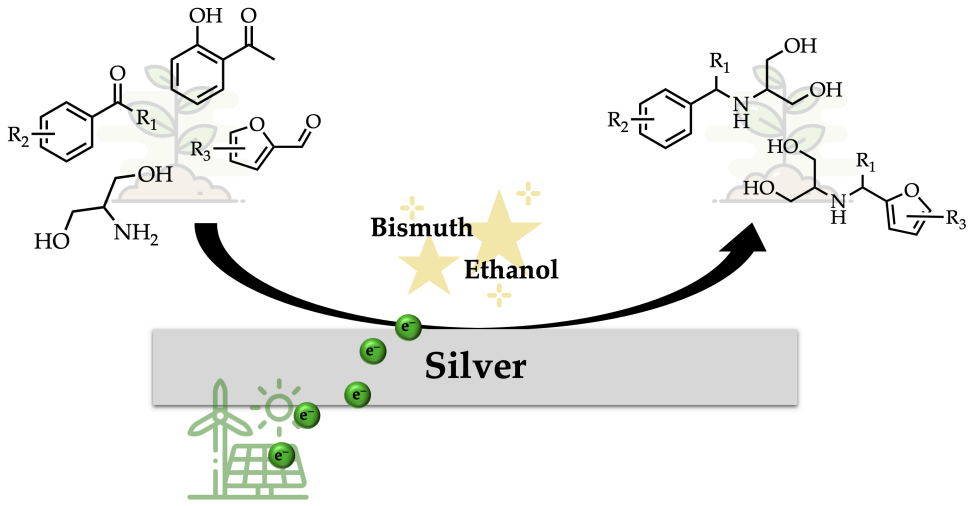

Figure 1: Schematic overview of the research objectives.

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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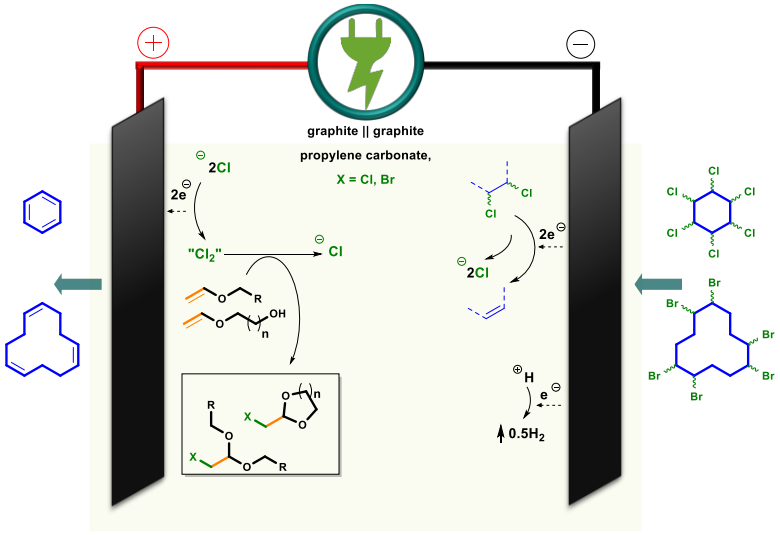
Persistent highly halogenated pollutants such as HCH and HBCD pose a long-standing environmental challenge yet they also represent an untapped chemical resource.[1] Lindane was globally banned in the early 2000s and 2009, all HCH isomers have been listed under the Stockholm Convention on Persistent Organic 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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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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Surface-enhanced infrared absorption spectroscopic elucidation of the electrochemical promotion of the thermocatalytic hydrogenation of 3-nitrostyrene

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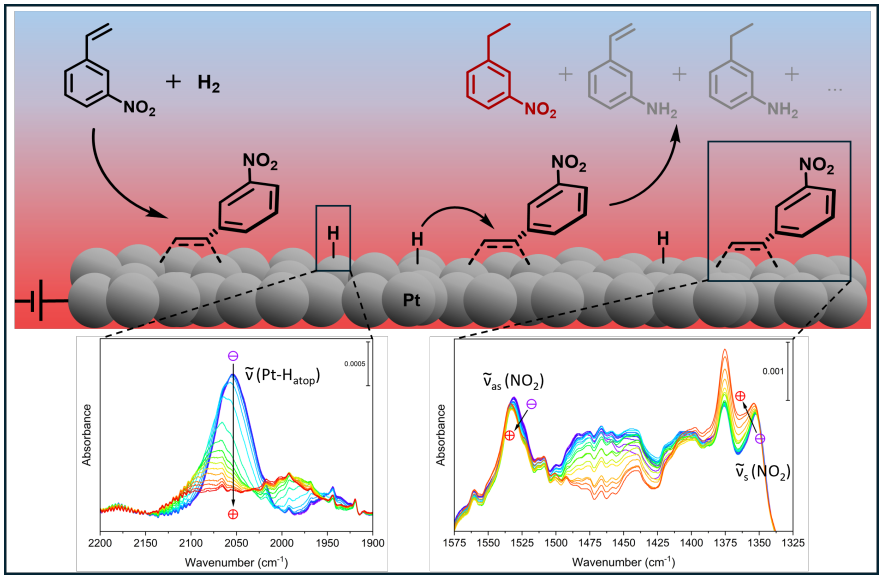
Surface-enhanced infrared absorption spectro-electrochemistry (EC-SEIRAS) is as a powerful analytical technique to study surface-bound species and electric field effects at electrified solid-fluid interfaces.[1] EC-SEIRAS could thereby provide key information on the interfacial chemistry that directs 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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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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ZnO Nanoparticles for Electrochemical Urea Synthesis

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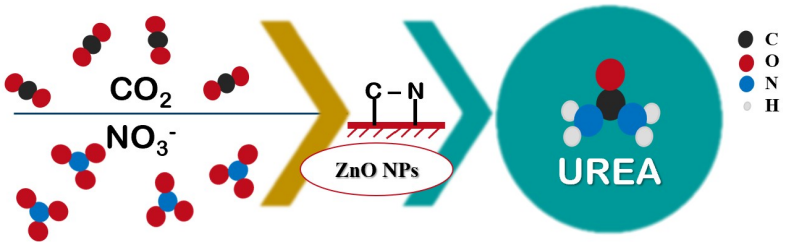
The electrochemical conversion of CO_2 and nitrate into urea provides a promising route to reduce carbon emissions and nitrogen pollution while producing a valuable chemical feedstock. Efficient C-N coupling is challenging, requiring a catalyst that can simultaneously activate CO_2 and nitrate and mediate 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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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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Electrochemical synthesis of imidazolines from aldehydes

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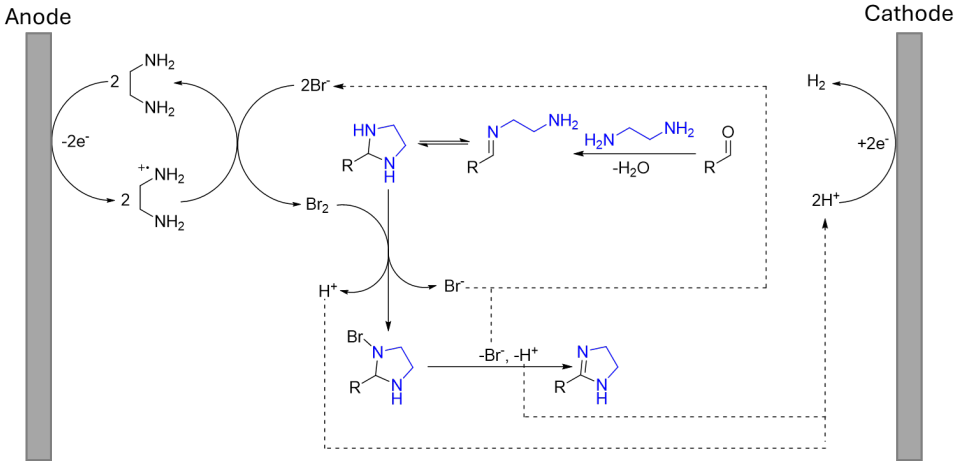
2-Imidazolines are non-aromatic 5-membered rings that contain two nitrogen atoms and a carbon-nitrogen double bond. They have a broad range of applications, such as pharmaceuticals, surfactants and herbicides.[1] Additionally to this applications, a large amount of the imidazolines synthesized are used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