Decarbonization of the chemical industry through electrification: Barriers and opportunities

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Electro-organic synthesis presents opportunities to produce chemicals through more sustainable pathways, but practical implementation faces barriers including low selectivity and production rates. This presentation will discuss approaches to overcome these challenges using the electrohydrodimerization of acrylonitrile to adiponitrile as a model reaction. Electrolyte engineering strategies reveal how tuning the electrochemical double layer composition impacts selectivity. Dynamic electrochemistry through pulsed potentials can balance mass transport limitations and reaction kinetics. Enhancing transport with forced or bubble convection alleviates mass transport limitations and leads to high permorfance. Integrating these advances with process modeling, in situ monitoring, and autonomous optimization provides a framework to accelerate the development of selective, efficient, and scalable electrochemical processes as chemical manufacturing alternatives to conventional fossil-fuel-powered thermal production routes.

INTRODUCTION

The chemical industry produces more than 70,000 products (1.2 billion tons in total) via thermal processes powered by fossil fuel combustion, accounting for ~5% of the US energy utilization and >30% of the US energy-derived industrial CO_2 emissions.[1] Amongst these processes, the production of organic chemical commodities accounts for most of the energy utilization (>1200 TBTU/y), and the electrification of these processes via the implementation of electro-organic reactions could enable the integration of renewable electricity sources with chemical plants and accelerate the decarbonization of the chemical industry.[2] Currently, however, two major challenges prevent the deployment of electro-organic reactions at scale: their low selectivity and their low production rates. To circumvent these barriers, my group combines electrochemical reaction engineering principles and machine-learning methods to accelerate the development of high-performing electro-organic reaction processes. In this presentation, I will discuss our work on understanding and improving the production of adiponitrile (ADN), a precursor to Nylon 6,6, via the electrohydrodimerization of acrylonitrile (AN). This is the largest and most successful electro-organic reaction deployed in industry and serves as a test case for the development of large-scale organic electrochemical processes.

ENGINEERING ELECTROLYTES FOR ORGANIC ELECTROSYNTHESIS

Our investigations on ADN are aimed at uncovering the relationship between the electrochemical environment at and near the electrical double layer (EDL) and reaction performance metrics (i.e., selectivity, efficiency, and productivity). I will discuss general guidelines for electrolyte formulation and provide insights into the role of different electrolyte species (e.g., buffer ions, chelating ions, selectivity-directing ions, and supporting ions) in achieving conversions of AN to ADN with selectivity as high as 83%.[3] Our results demonstrate that tetraalkyl ammonium (TAA) ions strongly impact reaction selectivity. Larger TAA ions (e.g., tetrabutyl ammonium) can enhance the solubility of organic reactants in the bulk electrolyte, impacting the local concentration of AN at the EDL and ultimately enhancing the electron selectivity towards organic products. At high current densities (> 80 mA cm^{-2}) the selectivity towards ADN starts to decrease due to mass transport limitations, and the selectivity towards propionitrile (PN) increases. These transport limitation can be partly mitigated by increasing the concentration of AN in the bulk electrolyte. Our results also demonstrate that mantaining an intermeadiate pH in the electrolyte is important to achieve high ADN selectivity. High pH environments lead to undesired bulk reactions between AN and hydroxide ions. Low pH environments lead to increased rates for the hydrogen evolution reaction (HER). We also observed that larger alkali cations can enhance ADN selectivity, suggesting that the structure of the EDL and the solvation of intermediates can have strong effects in the selectivity of the reaction.[4]

To further understand the role of electrolyte species on the selectivity of the reaction, our team developed an *in situ* electrochemical cell integrated with an attenuated total reflectance (ATR) Fourier

Transform Infrared (FTIR) spectroscopy system. This cell allowed us to gain insights into the relationship between local concentrations of TAA ions, AN, water and applied potentials. Our experiments demonstrate that TAA ions migrate towards the electrode interface upon the application of cathodic potentials, lowering the concentration of water and suppresing the competing hydrogen evolution reaction (HER). The increased concentration of TAA in the electrode interface also leads to an enhanced concentration of AN molecules at the EDL, which ultimately leads to efficient electron transfer from the electrode surface to the organic substrates, resulting in high selectivity towards ADN.

Our initial studies on engineering electrolytes for ADN electrosynthesis informed the design of electrolytes used for other electro-organic reactions, such as the electrohydrogenation of ADN to hexamethylene diamine (HMDA), one of the monomers used in the manufacture of Nylon 6,6.[5] These studies also demonstrated that transport limitations have strong impacts in the selectivity of organic reactions, and that mitigating them could lead to higher performing electrochemical manufacturing processes.

DYNAMIC ELECTROCHEMISTRY: BALANCING TRANSPORT AND KINETIC PROCESS BY MODULATING POTENTIAL

Achieving high selectivity in transport limited reactions requires adequate balance between transport rates from the bulk electrolyte to the surface of electrodes and the rates of the electrochemically-promoted reactions. To control and optimize this balance between transport and kinetic processes, our team explored the implementation of pulsed potential conditions in the electrosynthesis of ADN. Under pulsed electrosynthesis, a cathodic pulse can be applied to promote the electro-organic reactions, and a resting pulse can used to allow the replinishment of AN in the diffusion layer. To identify the appropriate leght of cathodic and resting pulses that enhanced ADN selectivity, our team develop 1D transport models of the reactions which suggested that pulses in the range of 10-100's ms could lead to measurable changes in the interfacial concentration of AN at the electrode surface. Using this timescale, our team experimentally explored a number of pulse sequences and then implemented a machine learning optimization framework to identify the optimal sequence that enhanced the production rate of ADN by >30%.[6]

Based on the learnings from ADN electrosynthesis, our team has implemented similar dynamic electrochemistry techniques, together with machine learning optimization, to identify optimal pulse sequences for applications in redox-mediated hydrogen generation devices,[7] and in the reduction of CO_2.[8] To further accelerate the development of high-performing electro-organic processes, my group has recently developed new machine-learning methods for rapid reactor outflow analysis using inexpensive spectroscopic tools[9] and Bayesian optimization methods that leverage physical models to maximize process performance.[10] These new tools are critical components of future autonomous workflows that will help us accelerate the electrification of petrochemical processes with large carbon footprints.

OVERCOMING MASS TRANSPORT LIMITATIONS VIA CONVECTION

Convective forces can help minimize transport losses in organic electrosynthesis. To better understand the interplay between convection and the performance of electro-organic reactions, we explored the impact of forced and bubble-induced convection on mass transport limitations in ADN electrosynthesis. In our work, we uncovered relationships between electrochemical conditions and the characteristics of convective flows by developing predictive surrogate models. Our results demonstrate that forced convection and bubble-induced convection result in nearly equivalent mass transport conditions, as measured by the non-dimensional Sherwood Number (Sh). These convection conditions control the microenvironment composition at the electrode/electrolyte interface and ultimately the selectivity of the reaction. Our study demonstrates that ADN selectivity fundamentally scales with Sh, current density and AN concentration, and that the uncovered relationships can be implemented in the scale-up of electrochemical processes.[11]

CONCLUSIONS

In conclusion, this work demonstrates promising approaches to overcome key challenges in electro-organic synthesis through electrolyte engineering, dynamic electrochemistry, and enhanced mass transport. Our findings on optimizing the electrolyte composition highlight the importance of controlling the electrochemical double layer to direct selectivity. Implementing pulsed potentials enabled better

balancing of mass transport and reaction kinetics. Convective flows induced through forced or bubble convection can alleviate transport limitations that hinder performance at scale. Taken together, these advances provide new insights and tools to enhance the viability of electro-organic routes as a sustainable alternative to traditional thermal processes in the chemical industry. Ongoing efforts integrating process modeling, advanced in situ characterization, and autonomous optimization workflows will further accelerate the development of selective, efficient, and scalable electrochemical processes to produce commodity chemicals.

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