

PhD thesis Technical summary

Electrochemically Mediated Separations and Catalysis

Sahag Voskian

Electrochemical processes are generally considered to be superior to their thermal counterparts due to the control that manipulating the applied potential offers over the free energy of a process. Moreover, redox-active molecule mediated electrochemical processes present the added advantage of chemical tunability of the mediator for enhanced selectivity, and adaptability of the process for the desired applications. This work showcases the benefits of redox-active molecule electrochemical mediation in separations and electrocatalysis. It addresses the gap in the scale and concentration spectrum of chemical separations by utilizing electrochemical mediation in the development of versatile systems of high selectivity and energy efficiency. It also addresses the problem of electrolyte contamination in electrocatalysis product streams by segregating the electrochemical and chemical reactions spatially and temporally.

The interaction mechanism of a target species with an activated mediator defines the thermodynamics of the process. Hence, a detailed analysis of the electrochemical and chemical reactions of quinone mediators with Lewis acids (mainly CO_2 and SO_2) has been conducted. It was found that the covalent bond formation between the nucleophilic activated quinone and the electrophilic Lewis acid stabilizes the resulting adduct, which lowers the energetics of further activations. This entailed a great increase in the overpotential of activation reactions even when small potential differences were applied, resulting in a surge in currents due to enhanced reaction kinetics. This phenomenon was exploited in the design of electro-swing reactive adsorption (ESRA) parallel passage contactors which allowed for high efficiency and economically viable carbon capture.

Mediated electrocatalysis was also investigated as a means of generating electrolyte-free hydrogen peroxide streams. This was achieved by employing redox mediator phase-transfer (RMPT) to produce and isolate aqueous H_2O_2 from the electrolysis of H_2O and O_2 where the quinone mediator was 'trapped' in an organic phase. Conversely, the mediator was trapped in a solid-state electrode, and exposed to alternating reduction and oxidation environments *via* slug flow. This concept has broad implications because the functionality on the mediator can also be purposefully designed to deliver redox equivalents to reaction/separation environments that would be incompatible with their regeneration. By decoupling the conditions of electrochemistry from the conditions ideal for substrate turnover and separation, the approach established here enables a vast expansion of the utility of electrochemical processes.

Other redox-inactive mediators were also studied in this work. This portion investigated the use of task-specific ionic liquids (TSILs) as inert mediators for (i) solventless, non-volatile, amine-based carbon capture, coupled with electrochemical regeneration *via* the chelation of cupric ions from a corroding copper electrode, for the release of CO_2 ; (ii)

hydrophobic chelators for liquid-liquid extraction of metal ions from aqueous streams, followed by electroplating or acid regeneration; (iii) hydrophobic separators in Li-Br batteries (iv) antimicrobial activity on epidermal wounds and antifouling activity in thin-film ionogels on catheters.

To summarize, this work demonstrates the integration of electrochemical steps into conventional chemical processes *via* the mediation of redox-active and inert organic molecules, which resulted in significant improvements in performance.

Thesis Supervisor: Prof. T. Alan Hatton

Ralph Landau Professor of Chemical Engineering and Director of David H. Koch School of Chemical Engineering Practice