Advanced Electrochemical Carbon Dioxide Separation Methods Enabled by Sorbent and Electrolyte Co-design

by

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ABSTRACT

Electrochemically mediated carbon capture (EMCC) is gaining attention as a promising alternative to traditional thermochemical methods, owing to its ambient operating conditions and potential integration with renewable energy sources. In these systems, an electrical potential was applied to adjust the chemical state or the electrolyte environment of EMCC sorbents, enabling reversible CO_2 capture and release. Although various electrochemical techniques have been proposed, challenges persist in creating capture chemistries that combine strong CO_2 affinity, efficient electrochemical regeneration, and stability against oxygen and moisture. This thesis investigates molecular and electrolyte design strategies to facilitate efficient electrochemical CO_2 separation and provides insights into the mechanisms governing the thermodynamics of capture and redox behavior.

Initially, this thesis examines an electrochemical cation-swing process that alters CO_2 loading on liquid amine sorbents via reversible shifts of Lewis-acid cations in the electrolyte. This process involves a reversible conversion between carbamic acid and carbamate, where strong Lewis acid cations favor carbamate formation with low CO_2 loading, and weaker cations promote carbamic acid formation with high CO_2 loading. The equilibrium was systematically studied as a function of amine and salt concentrations and cation type to identify optimal conditions for capture and release. Spectroscopic and calorimetric measurements reveal that the reaction driving force originates from charge interactions of cations, which tune the relative energy states of carbamic acid and ammonium carbamate. These findings were translated into an electrochemical cell that cyclically adjusts cation populations in the electrolyte, resulting in reversible changes in CO_2 loading on amines. This work highlights how electrochemical control of ion speciation can be linked to CO_2 capture and release, offering a new strategy for tuning amine-based capture chemistry.

Next, the thesis introduces N-heterocyclic imines (NHIs) as a novel class of redox sorbents for EMCC process. Unlike many existing systems that require an initial electrochemical reduction to activate CO_2 binding, NHIs bind CO_2 in their neutral form and release it upon electro-oxidation. This capture-oxidation process avoids operating at highly negative potentials that could trigger oxygen reduction reactions. Systematic studies of NHI derivatives show that molecular substituents influence the thermodynamics of CO_2 binding and loading capacity. Although early designs exhibited irreversible redox behavior due to hydrogen abstraction by the NHI radical cation, a bis(NHI) structure linked by a phenylene ring was developed to stabilize the radical cation. This design enables reversible redox behavior, operates at potentials 500 mV more positive than oxygen reduction, and allows for a two-CO_2-per-electron release, demonstrating how molecular engineering can fundamentally alter the stoichiometry and operating conditions of electrochemical capture.

Finally, this thesis investigates how electrolyte composition affects the thermodynamics and electrochemical behavior of NHI-based EMCC systems. Reaction calorimetry combined with spectroscopy shows that Lewis acid cations directly stabilize the NHI–CO_2 adduct via charge interactions. Solvent and anion donor number further tune this stabilization by modifying the effective Lewis acidity of the cations. Additionally, electrolyte composition affects both NHI redox potential and electron-transfer kinetics, as well as competing oxygen reduction pathways, underscoring the importance of balancing electrolyte effects to ensure operational stability.

Together, these studies demonstrate how molecular and electrolyte design and electrochemical control of solution speciation can be integrated to regulate CO_2 binding thermodynamics and electrochemical operation, establishing design principles for future EMCC systems.

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