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Innovative electrolyzers for carbon capture and valorization

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Summary

As global warming accelerates - driven primarily by anthropogenic CO₂ emissions - developing effective climate mitigation strategies has become a global priority. Among emerging solutions, carbon capture, utilization, and storage (CCUS) technologies stand out for their potential to reduce atmospheric CO₂ levels. In particular, carbon capture and utilization (CCU) not only reduces emissions but also transforms CO₂ into valuable products. This thesis investigates advanced electrochemical technologies for CCU, with a focus on integrated systems that maximize energy efficiency.

Currently, the most widely used CO₂ capture methods rely on chemical absorption using amine-based solvents or alkaline aqueous solutions. However, these processes require a thermal regeneration step to recover pure CO₂ for subsequent use. Similarly, the most established CO₂ conversion techniques are thermocatalytic and energy-intensive, typically requiring high temperatures and expensive hydrogen as a reactant. This dependence on thermal energy leads to significant efficiency losses, undermining the potential of CCU systems. In contrast, electrochemical technologies offer a compelling alternative - operating at lower temperatures and easily powered by renewable energy sources - making them ideal for a future increasingly driven by electrification.

Electrochemical carbon capture leverages the distribution of dissolved inorganic carbon (DIC) in aqueous solutions, which shifts with pH. At high pH, CO₂ is captured as (bi)carbonate via OH⁻-CO₂ interaction; at low pH, CO₂ is released as a gas. Electrolyzers can exploit this mechanism by inducing a pH swing between their compartments. Typically, this is achieved via water splitting reactions, which require a minimum cell voltage of 2.06 V. In this work, a bipolar membrane electro dialysis (BPMED)-based pH-swing electrolyzer was optimized to capture and release CO₂ at a flow rate sufficient to feed a gas-diffusion electrode (GDE) flow cell for electrochemical conversion into CO using a ZnO-based catalyst. The integration was successful, achieving a Faradaic efficiency (FE) of 50% for CO production. However, the BPMED configuration - comprised of two bipolar membranes (BPMs) and a cation exchange membrane (CEM) - required high cell voltages, increasing the system's overall energy demand.

To lower the energy requirements, an anthraquinone derivative, 2,7-AQDS, was identified as a redox carrier with proton coupled electron transfer (PCET) redox potentials within the water stability window. It was demonstrated that a 25 mM solution of 2,7-AQDS could reversibly capture and release CO₂ from a CO₂/N₂ mixture. Higher concentrations of the redox carrier enabled operation at greater current densities, though the system's capture efficiency was ultimately limited by mass transport. As a result, integrating a packed column into the setup is necessary to enhance CO₂ absorption efficiency.

For CO₂ electroreduction, anion exchange membrane (AEM)-based membrane electrode assembly (MEA) electrolyzers are currently the most widely used and efficient systems. This configuration provides the alkaline environment favourable for CO₂ reduction reactions. This thesis includes a study on the use of copper nanocubes (CuNCs) as catalysts for ethylene production within an AEM-based MEA configuration. The results showed that smaller CuNCs (40–75 nm) achieve FE for ethylene up to 35%. However, the system suffers from salt deposition on the GDE, leading to low

carbon efficiency and poor durability. Switching to a CEM creates a more acidic environment, which mitigates crystal formation. However, this requires redesigning the GDE to suppress the hydrogen evolution reaction (HER). Through optimization of the catalyst layer composition - specifically, the Ag:CB:AEI ratio (1:1:2) - the CO Faradaic efficiency was improved from 5% to 40%.

To obtain a pure CO₂ stream to feed the above mentioned electrolyzer, a thermal process is needed. To eliminate this expensive step, bicarbonate electrolyzers (BEs) have emerged as a promising alternative, enabling direct conversion of a CO₂-capturing (bicarbonate) solutions into valuable products. This thesis presents the optimization of a low-loaded Ag electrode for use in BEs, achieving nearly 80% FE for CO production. Additionally, the device architecture was evolved from a BPM to a CEM-based configuration, reducing energy demands in formate production by enhancing the local pH during CO₂RR. These results demonstrate that CCU platforms based on bicarbonate electrolyzers offer a more energy-efficient pathway compared to those relying on gas-fed systems.

In conclusion, this thesis presents viable electrochemical solutions to reduce the energy burden of CCU technologies. PCET-based carbon capture systems avoid the need for thermal regeneration of sorbents, significantly lowering operating costs. Simultaneously, bicarbonate electrolyzers represent a breakthrough technology that enables direct CO₂ conversion without requiring the gas to be isolated first. Altogether, this work supports the vision of a circular carbon economy, where CO₂, once the main driver of global warming, becomes a feedstock for the sustainable industries of the future.