ENERGETIC LOSSES IN MEMBRANE-BASED CARBON DIOXIDE ELECTROLYZERS

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Electrolytic products derived from CO_2 electrolyzers provide a potential avenue for bridging renewable electricity with the production of fuels and chemical feedstocks by providing an end use for captured CO_2 while utilizing renewable electricity power sources as an energy input. In this dissertation, three outstanding electrochemical engineering problems for CO_2 electrolysis are addressed: the techno-economic viability gaps for CO_2 electrolysis as a chemical process, the diagnosis and minimization of voltage losses in CO_2 electrolyzers, and minimizing the quantity of iridium used as the anode catalyst while maintaining adequate performance.

First, a techno-economic analysis is conducted for CO_2 electrolysis to carbon monoxide, formic acid, ethylene, and ethanol to assess the state of readiness for existing electrolysis cell configurations based on a large survey of recent experimental works. In this work, minimizing internal cell resistance is identified as one of the key technical issues that must be addressed. Industrially relevant single-pass conversion, cell stability, and current density are also evaluated for each product to inform future cell optimization efforts.

Subsequently, a systematic investigation was conducted to elucidate and address the problem of high internal resistances present in the commonly reported zero-gap anion exchange membrane cell configuration when using a dilute supporting electrolyte. A new diagnostic tool utilizing five electrodes (cathode, anode, two AgBr-coated wires, and a fritted reference electrode) was developed to deconvolute internal cell resistance and overpotentials, leading to a discovery that the dominant bottleneck of the configuration is a poor ionic interface between the cathode catalyst layer and membrane. This bottleneck was addressed by catalyst-coating the membrane using a novel wet decal transfer technique. Then, the diagnostic tool was used to identify the key stability issue as anode ionic passivation induced by end plate corrosion. By understanding the

degradation process, failure issues were mitigated in a follow-up test by making small, rational adjustments to anode components and operating conditions.

Finally, the issue of poor voltammetric performance with low-iridium (Ir) loaded (≤0.1 mg cm^{-2} IrO_2) anodes was addressed for a model system: a proton exchange membrane water-electrolysis (PEMWE) cell. The issue of optimizing the catalyst-coated membrane on the anode side was approached via a bottom-up design methodology. First, the necessary anode catalyst layer sheet conductivity to attain high catalyst utilization was evaluated. Then, the requisite thickness of a microporous layer (MPL) to supplement a very thin anode catalyst layer to achieve that needed sheet conductivity was experimentally evaluated. Finally, MPL-supported PEMWE catalyst-coated-membranes (CCMs) with low-Ir loading and sufficient sheet conductivity were fabricated and benchmarked against unsupported PEMWE CCMs at high current density (up to 4 A cm^{-2}). Results indicate that anode performance using typical loadings (1 mg cm^{-2} IrO_2) can be attained with 0.05-0.2 mg cm^{-2} IrO_2 when the catalyst layer is supported with a 0.4 mg cm^{-2} Pt black MPL. This work establishes a framework for designing promising low-Ir loaded anodes. While commercial Pt black was used as an exemplary support material for this study, future work should explore alternative PGM-free support materials that are currently being developed.

In conclusion, this dissertation explores several facets of electrochemical engineering design for practical CO_2 electrolysis. The three major aspects of this dissertation: technoeconomic analysis, operando performance/stability diagnosis, and composite material design are seemingly disparate topics, but together capture the broad complexity of designing practical electrochemical processes. As a holistic study, this work contributes a collection of scientific findings that enable the further advancement of CO_2 electrolysis toward viability as an industrial chemical process.