

Maintaining pH gradients in solar fuel technologies using bipolar membranes: defining parameters and evaluating materials

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Emergent technologies capable of efficiently converting solar energy into fuel for widespread practical use will very likely require specifically engineered membranes.¹ These membranes must physically compartmentalize the electrode chambers where product gases are evolved while remaining as passive to the photoelectrochemical process as possible. Specifically, the membranes must be both chemically and physically stable over long operation times and in extreme conditions (temperature, salinity, pH) while transmitting visible light and conducting charge with minimal resistance.²

Recently, our research groups have defined and reported the figures of merit for a membrane optimized for microwire array solar fuel devices using current state-of-the-art polymeric materials,³ and have since defined them for general photoelectrochemical systems.¹ A consideration not previously evaluated focuses on the redox reactions occurring at the electrodes. In general, the oxidation reaction at the anode and reduction reaction at the cathode occur optimally in basic and acidic conditions, respectively, due to catalyst stability and kinetics. Given solar conversion efficiencies are very sensitive to potential losses in the systems, it is paramount that novel catalysts being developed for these applications operate in optimal conditions. Therefore, to operate at the desired pH, a membrane arrangement must be developed to maintain a pH gradient while still meeting the design criteria described above.

Our proposed solution is a system incorporating a *bipolar membrane* which consists of an anion (OH⁻) conducting membrane, contacting the basic electrolyte in the anode compartment, laminated to a cation (H⁺) conducting membrane in contact with the acidic electrolyte in the cathode compartment. The interface of these two membranes resembles that of a solid-state semiconductor p-n junction, due to the fixed charge functional groups in each membrane. Given electrolyte counterions ideally cannot cross the permselective membranes, current is passed by the dissociation of water at the interfacial region and the pH gradient across the cell is maintained. This technology has already been developed and studied for electrodialysis for the last ~35 years for acid and base concentration.⁴ The challenge now lays in uniting the vast knowledge of electrodialysis with our defined needs for solar fuel membranes. For example, the sunlight-limited current densities attainable in solar fuel systems require more stringent demands on conversion efficiency including limiting counterion and product crossover as well as potential losses by the composing materials. Additionally, the specially tailored interfacial region consisting of polyelectrolyte and catalysts in the most recent bipolar membranes⁵ must now be composed of materials that meet the above requirements but also offer rapid water dissociation kinetics.

This presentation will collect and evaluate key findings in both fields and use these values to determine

the figures of merit for the application of state-of-the-art bipolar membranes to solar fuel devices. Recent experimental results from our groups will be discussed in addition to details on fabrication and characterization of various membrane arrangements and compositions.

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