

Design Principles for Artificial Photosynthetic Cells across the pH Spectrum

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Using a photoelectrochemical cell (PEC) to produce solar fuels, sometimes called artificial photosynthesis, has attracted significant research interest [1-3]. Corrosion remains a significant limitation for PECs. Most electrolysis cells operate under strongly acidic or alkaline conditions. This poses a threat to stability for light absorbers as well as other system components [4]. Progress on an oxygen evolution catalyst that functions at near-neutral conditions has generated optimism for running in buffered systems [5]. However, running under milder conditions presents a host of new problems that must be addressed. Two problems that have been demonstrated experimentally are increased ohmic drop and losses due to pH gradients [6].

To understand these problems and identify ways to mitigate them, a 1-D model of a membrane electrolysis cell is employed. This model is patterned after earlier work on electrochemical reduction of carbon dioxide, and it can be generalized to any number of species and reactions, either at the surface or in the bulk [7]. The cell exhibits limiting current behavior that depends strongly but predictably upon geometry and transport properties. The relative magnitude of losses due to ohmic drop and the various components of the concentration overpotential are characterized for different choices of electrolyte. Results show that adding supporting electrolyte to a dilute strong acid (or base) can reduce ohmic and diffusion losses near limiting current, but it cannot prevent device failure because pH-dependent losses remain.

To overcome this, one strategy is to recirculate the electrolyte between the anode and cathode chambers. Experimental results for a membrane electrolysis cell operating with Nafion and aqueous potassium borate show that the cell develops a large pH gradient and shuts down at PEC-relevant current densities of 10 mA/cm². However, introducing a modest recirculation rate on the order of 60 mL/h can allow the cell to run with tolerable losses. The model predicts recirculation to decrease the pH difference between anode and cathode, in agreement with preliminary experimental findings (see Figure 1).

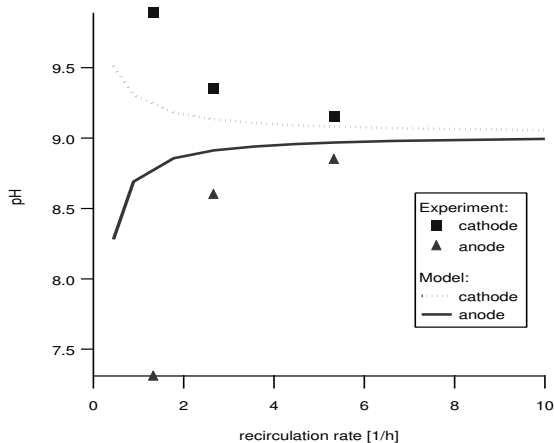


Figure 1: Anode and cathode pH as a function of the recirculation rate (volumetric flow rate divided by volume of electrolyte). Current density is 10 mA/cm².

Furthermore, the model can also account for the undesirable gas crossover that can occur through the recirculating stream or through the membrane. Some of the crossover gases will be consumed at the opposite electrode, contributing to a loss in current efficiency but not contaminating the product stream. Current efficiency and composition of the exit stream are both calculated as a function of current density and flow rate. For 10 mA/cm² and a recirculation rate of 60 mL/min, the model predicts 3.7 vol% H₂ in the oxygen outlet and 2.3 vol% O₂ in the hydrogen outlet. This is in rough agreement with experimental measurements that have yielded 2.8% and 3%, respectively. In this regime, we operate outside the flammability window for mixtures of hydrogen and oxygen, which is 4-94 vol% H₂. Furthermore, the optimum flow rate for overall hydrogen production efficiency is calculated as shown in Figure 2.

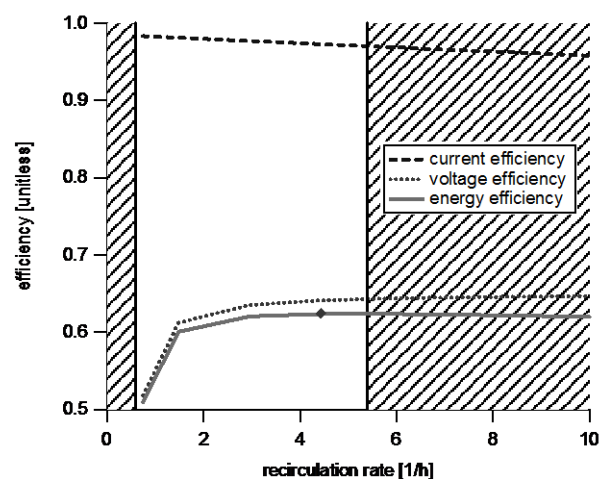


Figure 2: Optimum energy efficiency is 0.624 near a recirculation rate of 4.5 times per hour, indicated by the diamond. The left crosshatched area indicates the minimum recirculation rate to attain a limiting current of 10 mA/cm². The right crosshatched area indicates the maximum recirculation rate, above which the composition of one or both streams will enter the flammability window and present an unacceptable safety hazard.

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