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Membranes for Solar Water Splitting Devices

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Sunlight is by far the most abundant and accessible renewable energy source.¹ However, the diurnal nature of sunlight precludes its use as an uninterrupted power supply. Artificial photosynthetic systems overcome this shortcoming by directly storing the energy in sunlight in chemical bonds. However, this is not without added complexity as photosynthetic (light-to-chemical) systems possess additional design constraints relative to photovoltaic (light-to-electrical) devices.² Four such characteristics include the ability to,

- Separate reaction products, i.e. the fuel and the electron source;
- Generate a photovoltage that surpasses the potential required to perform the desired endergonic fuel-forming reactions;
- Catalyze the fuel-forming reactions; and
- Stabilize the materials in aqueous environments

Each can be tailored based on the properties of the ionomer membrane and will be the focus of this presentation.

Microwire arrays partially embedded in a Nafion[®] proton-exchange membrane represent a new and exciting solar fuel-forming architecture.³ Nafion's chemoselectivity greatly attenuates fuel crossover and minimizes ohmic ionic potential drop. Electrical connection of multiple semiconductors in series affords large photovoltages. This was accomplished for two ionomer-embedded microwire arrays, laminated back-to-back as a dual-junction tandem device, using the organic conductive polymer PEDOT:PSS,³ where PEDOT is poly(3,4-ethylenedioxythiophene) and PSS is poly(styrenesulfonate). Replacing a significant fraction of visible-light-absorbing PEDOT:PSS conductor with Ag nanowires alleviated parasitic sunlight absorption by the conductive polymer, while maintaining the favorable ionic and electrical conductivity of the membrane. To further increase the photovoltage in the organic-inorganic functional assembly, a bulk-heterojunction organic photovoltaic was incorporated between the two Nafion-embedded microwire arrays.

To maximize catalytic performance and stabilize individual photoelectrode and catalyst materials, the pH was bifurcated across the membrane. Employing ionomer membranes with charge- and size-selective channels afforded a sustainable pH gradient that did not thermodynamically bias the system. Ionic electric fields in the ionomer membrane opposed chemical proton gradients to generate a stable, equilibrated electric field at the membrane interface.

More effective and economical photoelectrosynthetic functional assemblies can be designed once functional membrane properties become better understood.

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