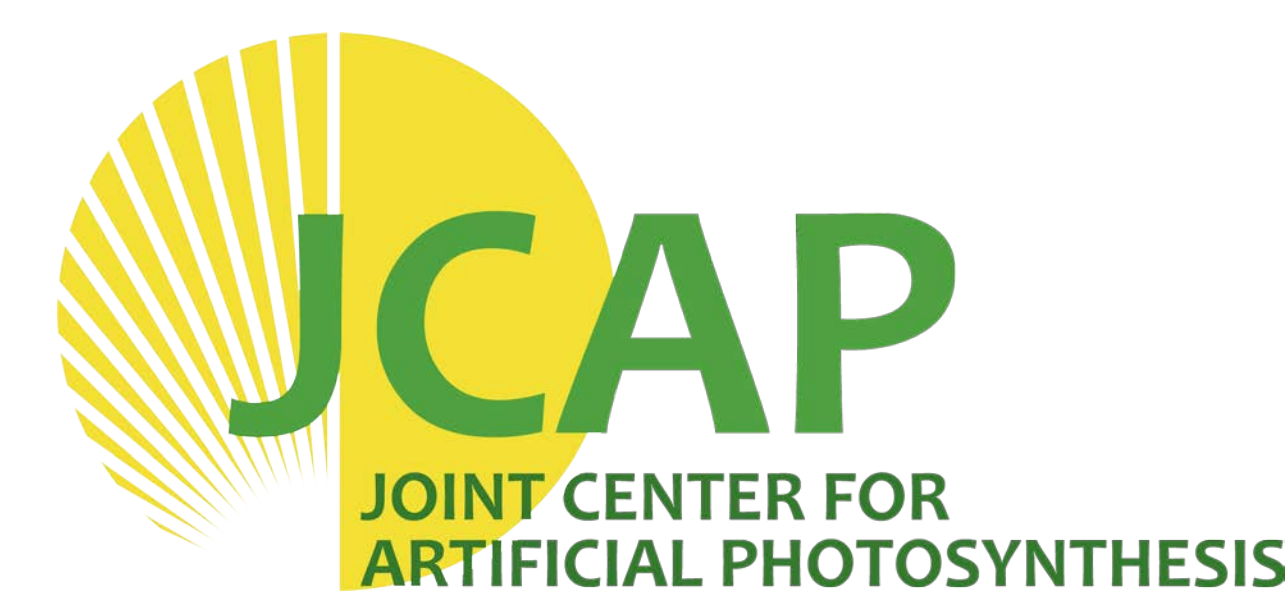


# Perspectives on Membranes for Solar Fuels Devices

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## Abstract

The development of robust membranes that govern fluxes of water, electrolyte ions, and half-reaction reactants and products throughout the microenvironment assembly comprising a solar fuels device is essential to the design of solar fuels devices. Critical science gaps in understanding how to achieve exquisite control of molecular and ionic transport in semipermeable soft matter must be bridged by embracing an interdisciplinary, cross-cutting approach that leverages multi-physics modeling, material synthesis, advanced characterization, and system integration. A key outcome is to understand how to design highly selective, semipermeable soft matter capable of rapidly transporting charge-carrying electrolyte ions between electrodes, which supports high device current density, while simultaneously suppressing crossover of half-cell reduction products, which enhances device efficiency by minimizing parasitic re-oxidation.

## Introduction

Photoelectrochemical devices for water oxidation and CO<sub>2</sub> reduction often utilize polymeric membranes, which must be:

- Conductive to electrolyte ions
- Relatively impermeable to CO<sub>2</sub> reduction products
- Resistant to degradation by electrolyte, light, and heat

Designing materials that have all of these properties is challenging. Significant tradeoffs among these properties are commonly observed with traditional materials.

## Outlook

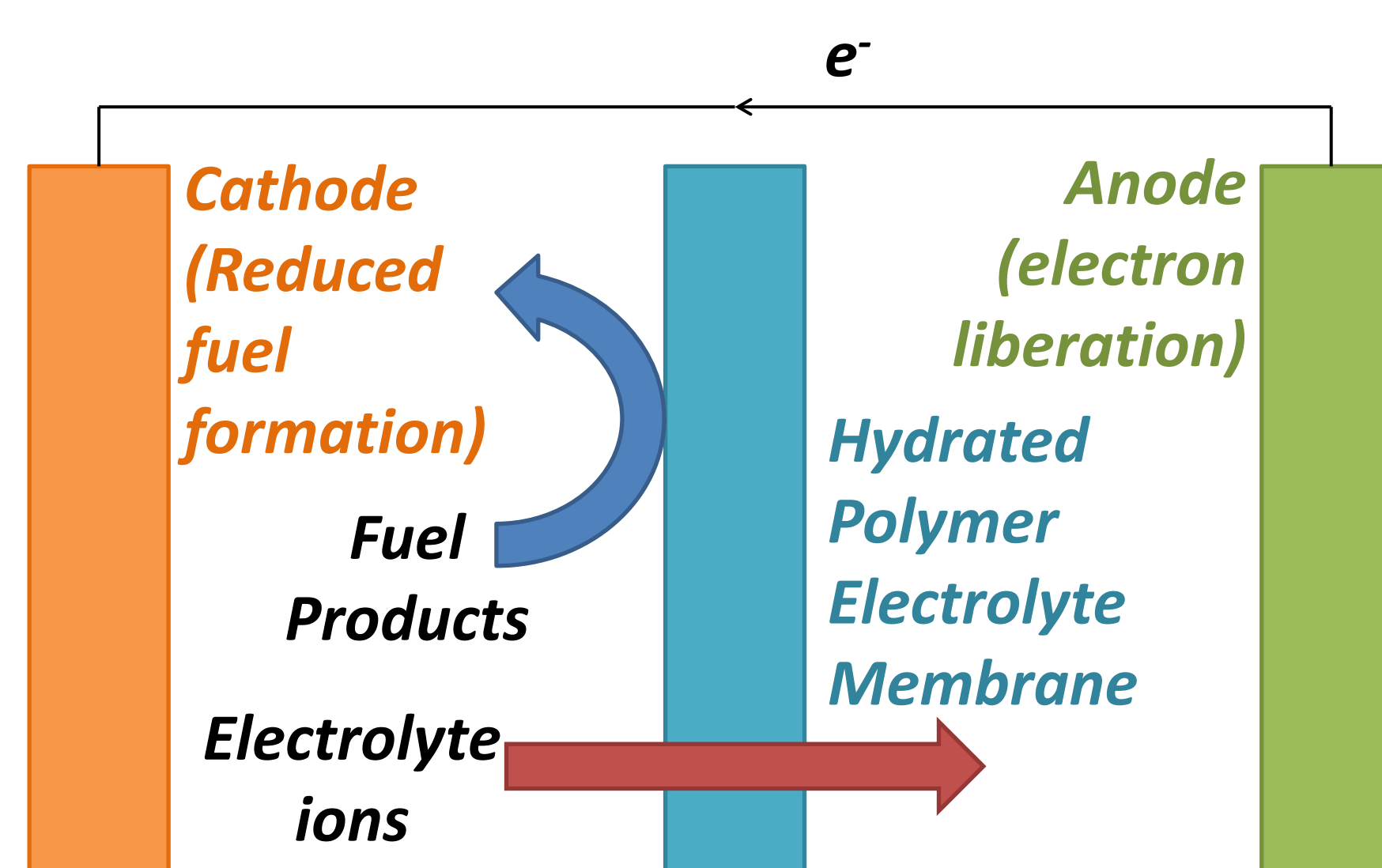
- Membrane ionic conductivity and permeability to CO<sub>2</sub> reduction products can be tuned over a wide range by varying membrane functionality, but both are strongly correlated with water content, resulting in a tradeoff between ionic conductivity and CO<sub>2</sub> reduction product crossover.
- New strategies to de-couple the transport of charge carriers and neutral CO<sub>2</sub> reduction products are needed.
- While bipolar membranes enable the use of anolyte and catholyte at different pH values, new bipolar membranes with reduced resistivities must be developed for use in CO<sub>2</sub> reduction devices
- Membranes resistant to photodegradation and chemical degradation (e.g., alkaline hydrolysis) will likely need to be developed for practical solar fuels devices

## Acknowledgments

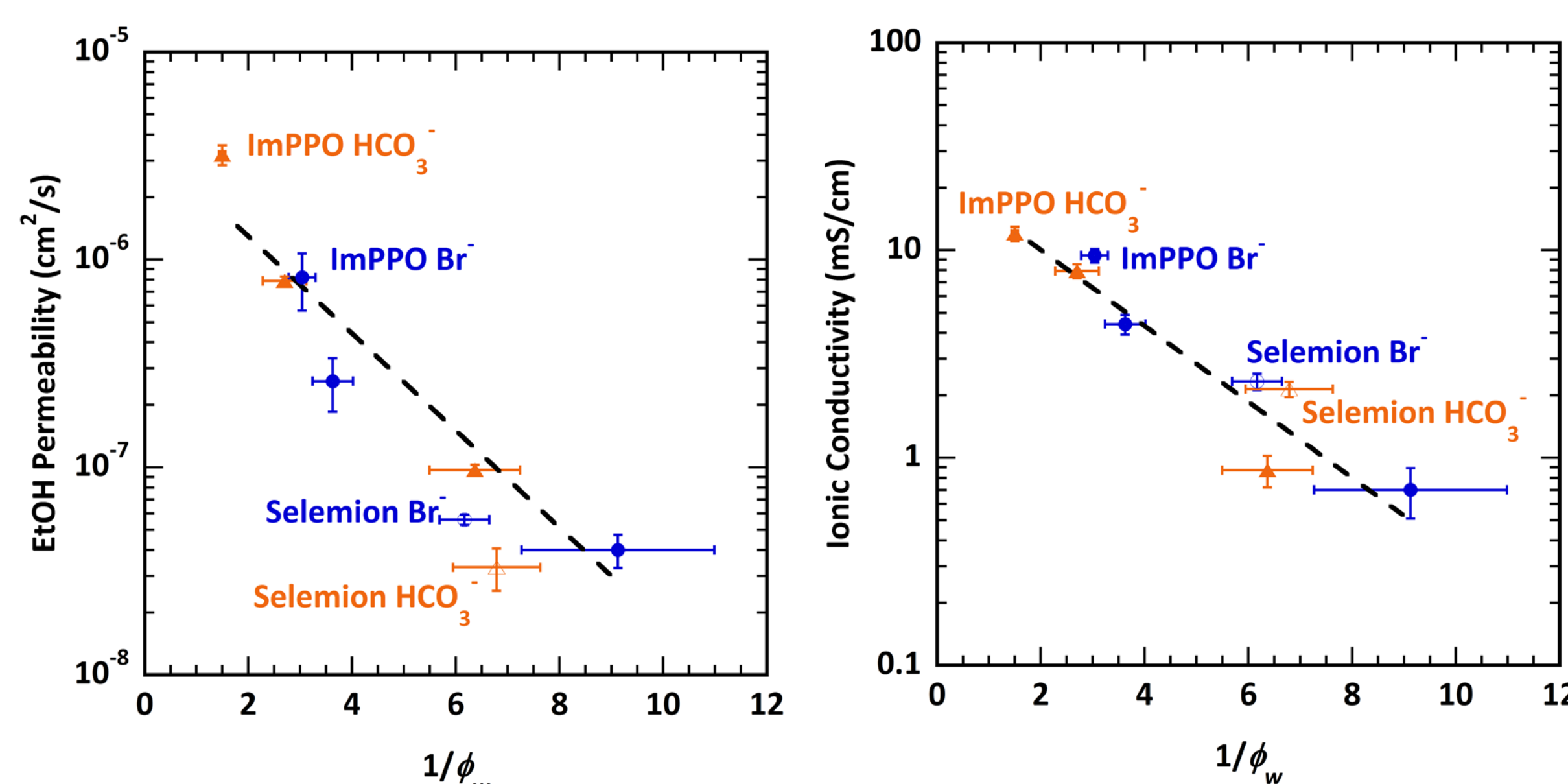
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## Recent Results and Critical Science Gaps

The fundamental selectivity requirement challenging design of polymer electrolyte membranes for solar fuels devices.



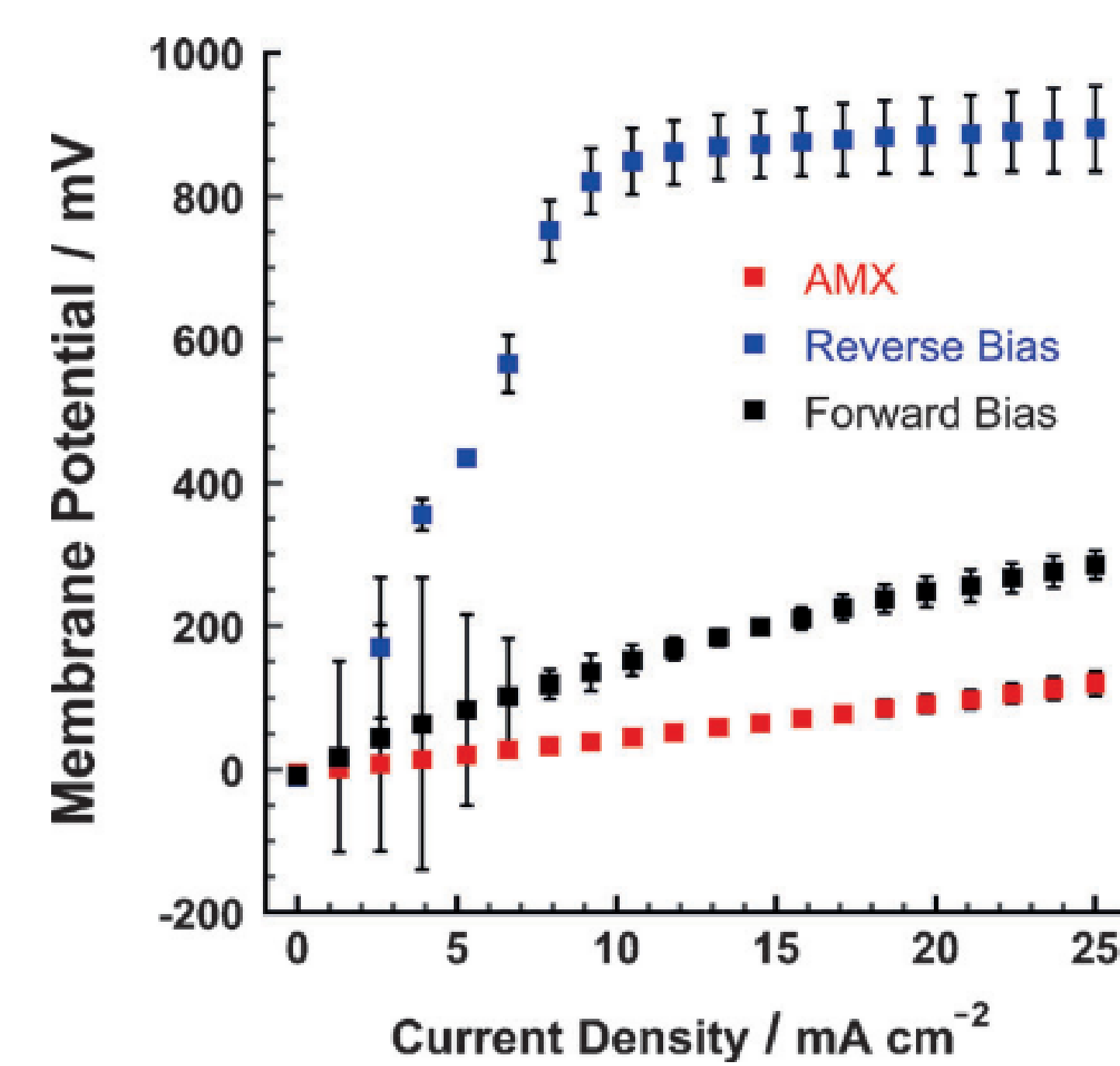
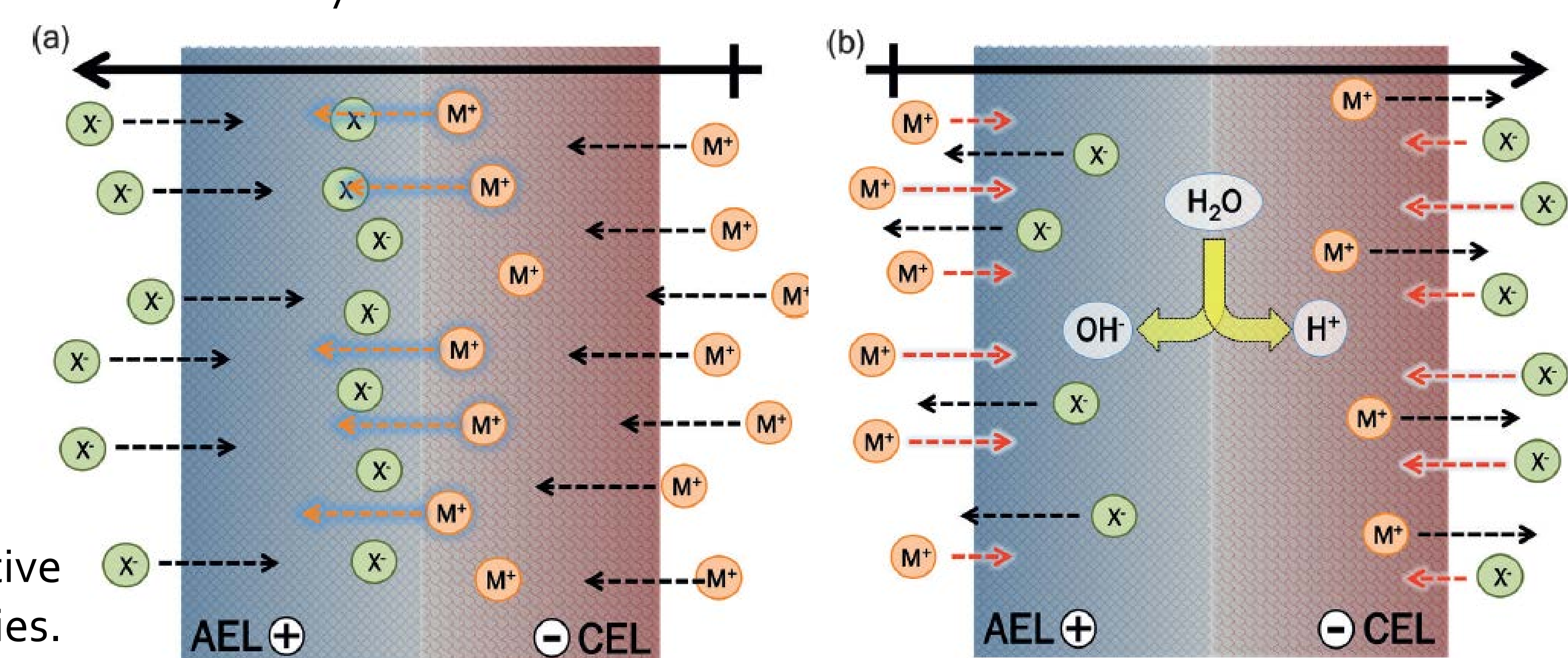
Membranes with high ionic conductivity are attractive because they generally support high current densities. However, membranes with high ionic conductivities also often exhibit high permeabilities to CO<sub>2</sub> reduction products, such as alcohol fuels. Significant CO<sub>2</sub> reduction product crossover may jeopardize device efficiency, because reduced products may migrate to and be re-oxidized at the anode. Transport of both electrolyte ions and CO<sub>2</sub> reduction fuel products is strongly correlated with membrane water content, frustrating design of membranes with high conductivity to electrolyte ions and low permeability to CO<sub>2</sub> reduction products.



Imidazolium-functionalized poly(phenylene oxide) (Im-PPO) membranes with both Br<sup>-</sup> and HCO<sub>3</sub><sup>-</sup> counterions exhibited strong dependence of ethanol permeability (left) and ion conductivity (right) on membrane water content. As a result, these membranes exhibited a tradeoff between ethanol permeability and ionic conductivity (left). A key goal is to de-couple ionic conductivity from CO<sub>2</sub> reduction product permeability.

S. M. Dischinger, S. Gupta, B. M. Carter, and D. J. Miller. *Industrial and Engineering Chemistry Research* 59(12) 5257-5266 (2020).

Bipolar membranes are of considerable interest because each of their two laminated layers promotes transport of ions of differing valences; we hypothesize that use of a bipolar membrane in a solar fuels device will enable tailoring of electrolyte environments to particular oxidation and reduction catalysts.

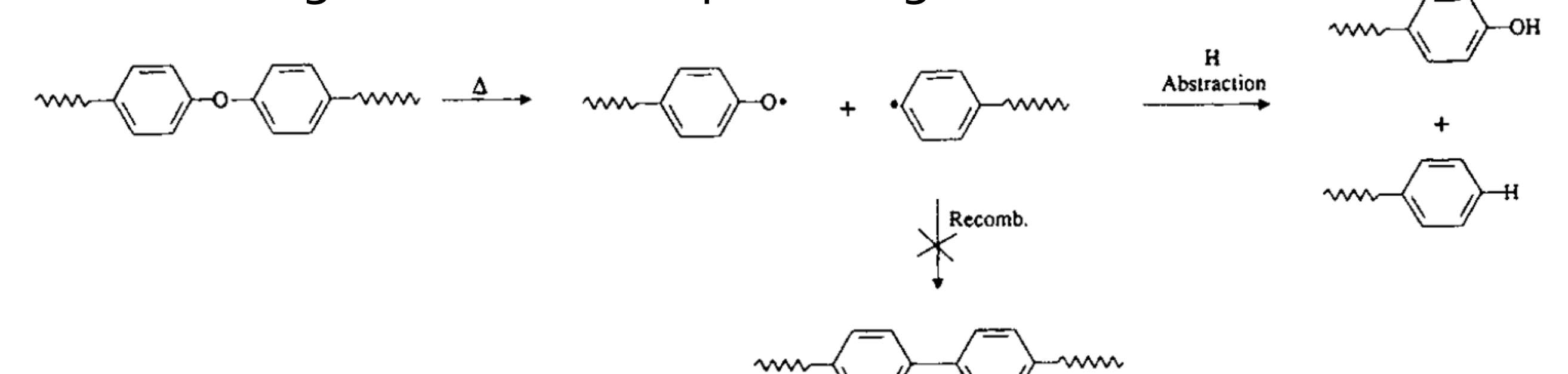


Bipolar membrane under (a) forward- and (b) reverse-bias conditions. The solid dark arrow shows the direction of the applied voltage. Black dashed arrows indicate the direction of ion migration, and colored dashed arrows indicate ion migration that is impeded by the membrane. The figure at left shows the potential of an anion exchange membrane (AMX) and bipolar membranes under forward and reverse bias.

Under reverse bias (the orientation used in solar fuels devices), bipolar membranes tend to be highly resistive relative to anion exchange membranes.

N. M. Vargas-Barbosa, G. M. Geise, M. A. Hickner, and T. E. Mallouk. *ChemSusChem* 7(11) 3017-3020 (2014).

A key science gap is in understanding how to achieve long-term durability in polymeric and hybrid materials exposed to the challenging environment of a solar fuels device, which will drive the development of membranes with longstanding resistance to photodegradation, chemical degradation (especially in the presence of highly alkaline electrolyte), and new approaches to mitigating the effects of carbon dioxide plasticization and physical aging on membrane permeability. For example, poly(phenylene oxide) undergoes irreversible photodegradation (below).



G. Montaudo, C. Puglisi, R. Rapisardi, F. Samperi. *Macromolecular Chemistry and Physics* 195(4) 1225-1239 (1994).