

Investigation of Structure-Transport Relationships of an Anion-Exchange Membrane Platform for CO₂ Reduction Devices

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Abstract

The membrane is essential to maintaining efficiency within the photoelectrochemical cell because it mediates the transport of both CO₂ reduction products and charge carriers. A better understanding of the physicochemical properties that mediate transport in these materials as they relate to performance in membrane-electrode assembly (MEA) type devices is needed. Herein, we modulated the structure of anion-exchange membranes (AEMs) by controlling the synthesis of the polymer platform, which consists of a poly(phenylene oxide) (PPO) backbone and cationic imidazolium pendant groups. The changes in structure were correlated to the transport performance relevant to artificial photosynthesis devices. These studies revealed a tradeoff in the transport properties desirable for artificial photosynthesis: materials demonstrating high charge-carrier transport of also demonstrated high transport of reduction products.

Introduction

The membrane plays a vital role in the MEA. A high-performing membrane will:

- Mitigate transport of CO₂ reduction products to the anode
- Facilitate ion transport between the electrodes
- Demonstrate mechanical and chemical stability

Achieving this set of properties is challenging because high solute transport often correlates with high conductivity.

Team



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Outlook

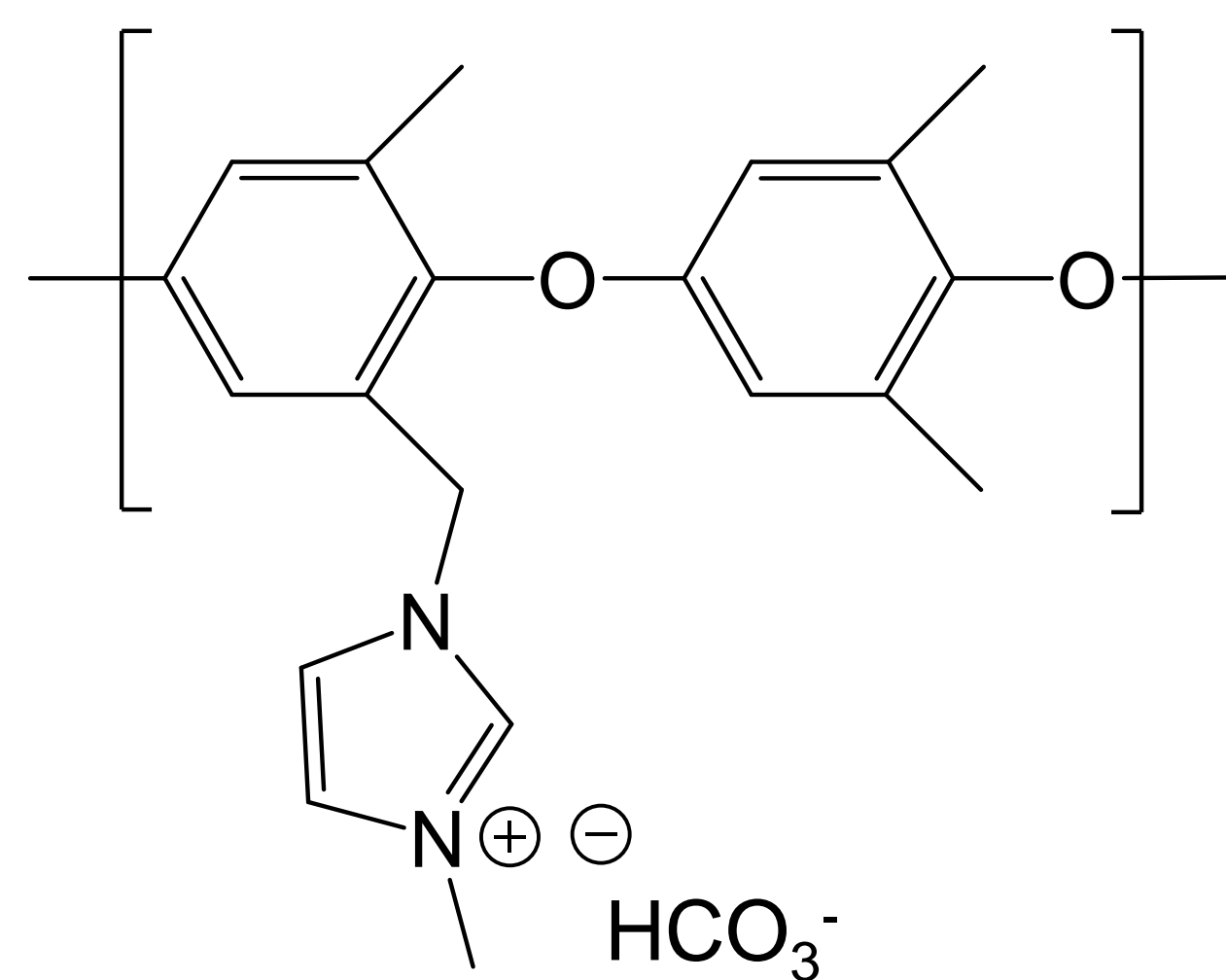
In light of the tradeoff in transport properties desirable for artificial photosynthesis devices, it is necessary to consider the minimum ionic conductivity necessary to support high MEA-device performance so as to mitigate the crossover of liquid fuel products. Alternative membrane architectures should be considered to break this tradeoff and decouple ion and ethanol transport.

Acknowledgments

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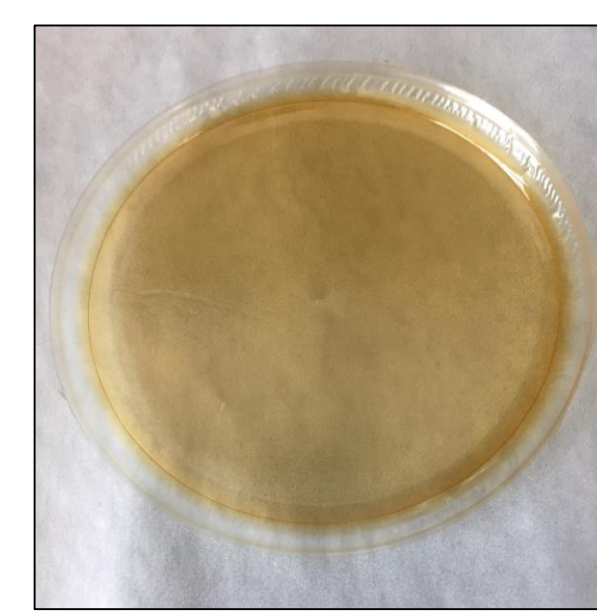
Results, Highlights, and Accomplishments

Anion exchange polymer platform



Imidazolium-functionalized poly(phenylene oxide) (ImPPO)

The degree of functionalization, X, is controlled via synthesis, and counterion is exchanged for Br⁻ by soaking the fabricated membrane in a sodium bromide solution.



thickness: ~120 μm
density: 1 g/cm³

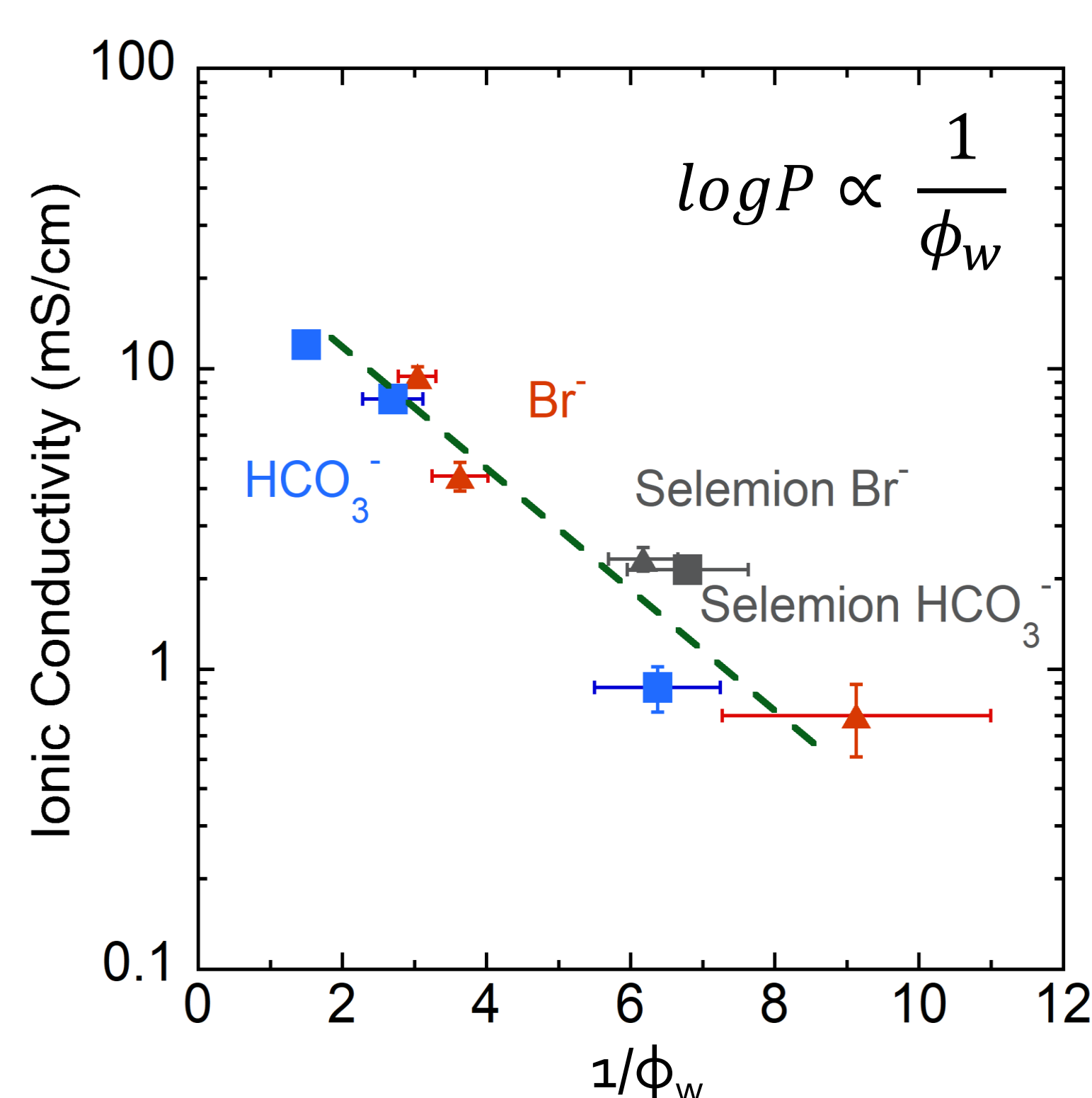
Free-standing membranes were fabricated from the various modifications of the ImPPO polymer platform. The upper limit of X was determined by the value of X at which the fabricated membrane dissolved in water.

Properties of ImPPO membranes in the bicarbonate form

Polymer ID	X (%)	IEC (mmol/g dry polymer)	Water uptake (wt%)	Ethanol perm. (x 10 ⁻⁶ cm ² /s)	Ionic cond. (mS/cm)
ImPPO-11	11	1.4	19 ± 3	0.10 ± 0.01	0.9 ± 0.2
ImPPO-19	19	2.1	61 ± 4	0.79 ± 0.04	7.9 ± 0.6
ImPPO-24	24	2.4	209 ± 9	3.2 ± 0.4	12.0 ± 0.9
Selemion AMV		1.85	15 ± 2	0.03 ± 0.03	2.1 ± 0.2

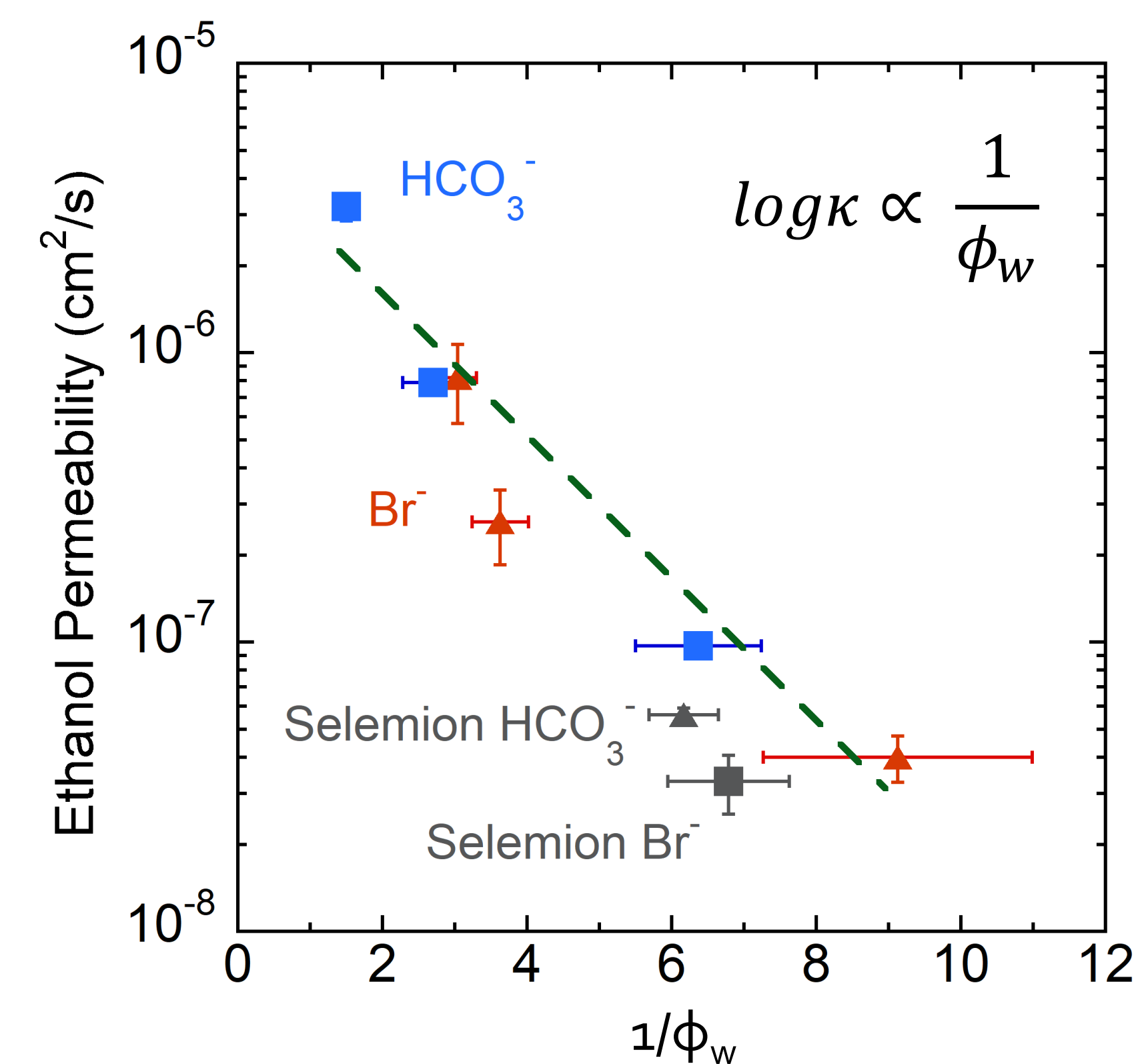
The transport properties of the ImPPO membrane platform can be modulated through synthetic control of the degree of functionalization, X, as well as exchanging the counterion (values not included in the table).

After demonstrating the ability to control the transport properties of this ImPPO polymer platform, we looked to the transport theory applicable to dense polymer membranes in order to understand the observed trends.



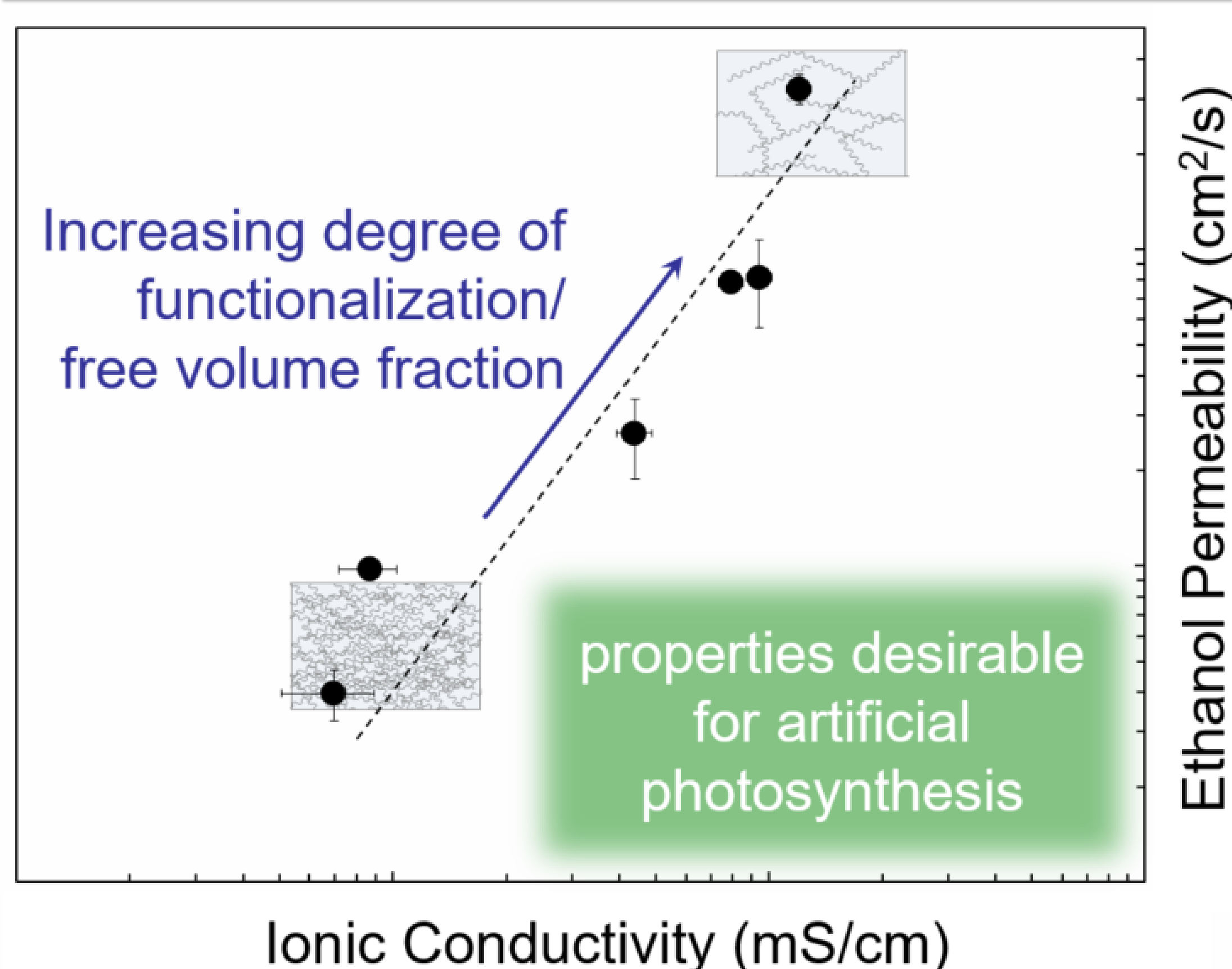
Free Volume Theory:

1. The space available for solute transport in dense polymer films is proportional to the free volume present between the polymer chains.
2. The free volume between polymer chains is proportional to the water volume fraction, $1/\phi_w$.



For the ImPPO materials fabricated herein, the log of ionic conductivity and the log of ethanol permeability are linearly proportional to the inverse of the water volume fraction, demonstrating that the free volume theory describes the observed transport trends and that each of these species is transporting through the free volume available within the polymer.

BOTH the degree of functionalization and the counterion impact BOTH the ethanol permeability and the ionic conductivity of the ImPPO platform because these two controlled factors change the free volume within the polymer.

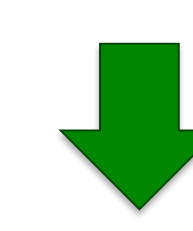


Considering a given ImPPO material's ionic conductivity and ethanol permeability simultaneously, we observe that materials with a lower free volume fraction had a lower ionic conductivity and a lower ethanol permeability than materials with a higher free volume fraction.

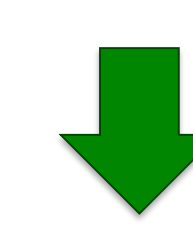
The performance demonstrated by this set of materials represents a **tradeoff** in the transport properties desirable for artificial photosynthesis (i.e., high transport of charge carriers and low transport of liquid fuel products).

Summary

Chemical Change
(degree of functionalization)



Structural Change
(free volume fraction)



Change in Transport Properties
(ethanol permeability
ionic conductivity)

Dischinger, et al., *Ind. Chem. Engr. Res.* (2019)