Impact of Different Comonomers (PEGMA, PEGMEA, AND PEGMEMA) on Solute Co-transport in PEGDA and PEGDA-AMPS Membranes

Ryan Wozniak[1,], and Bryan S. Beckingham[2]*

[1] Undergraduate Student, Department of Chemical Engineering, Auburn University
[2] Associate Professor, Department of Chemical Engineering, Auburn University

CO_2 emissions have become an important environmental concern due to the increasing usage of various fossil fuels that release CO_2 upon combustion.[1] Therefore, researchers are working on finding methods to mitigate CO_2 emissions into the atmosphere. The three main methods to reduce atmospheric CO_2 are CO_2 capture, CO_2 storage, and CO_2 conversion.[2] This research focuses on CO_2 conversion by using an electrochemical cell that converts CO_2 by a reduction process into various, low carbon footprint chemicals and fuels such as carbon monoxide, methanol, ethanol, formate, etc.[2] In particular, the electrochemical cell has two half-cells, an anode and cathode that are separated by a polymer membrane known as an ion-exchange membrane (IEM). The reduction reaction occurs in the cathode, and an oxygen evolution reaction occurs in the anode. The IEM must selectively permeate the hydron molecule from the anode half-cell into the cathode half-cell for the reduction reaction to occur. However, the IEM must also be highly impermeable to all other molecules in the described reactions to avoid significant efficiency losses in the electrochemical cell.[3]Therefore, researching and characterizing various membranes is essential in determining an effective IEM.

The current research focuses on investigating single solute transport (sodium formate and sodium acetate) through a cation exchange membrane consisting of poly(ethylene glycol) diacrylate (PEGDA) and acrylamido-2-methyl-1-propanesulfonic acid (AMPS). In these membranes, different comonomers are implemented to determine their relative impacts on the membrane's water volume fraction and permeability. These comonomers are poly(ethylene glycol methacrylate) (PEGMA), poly(ethylene glycol methyl ether acrylate (PEGMEA), and poly(ethylene glycol ethyl ether methacrylate) (PEGMEMA). The first set of polymer membranes without AMPS had a constant pre-polymerization water content mol percent of 20% with varying comonomer and PEGDA mol percent. The second set of membranes with AMPS had a constant pre-polymerization water content mol percent of 20%, constant PEGDA mol percent of 54.4%, and varying comonomer and AMPS mol percent.

The first characterization method was implemented to measure water uptake and water volume fraction of the different polymer membranes. This method consisted of soaking the membranes in distilled water and weighing them at their "swelled weight". The membranes were then vacuum dried and weighed at their "dry weight". The dry membranes' hydrostatic weight was then measured to determine the water volume fraction of the membranes. The resulting data is displayed in Figure 1 and Figure 2.

The second characterization method was implemented to measure the permeability of the different polymer membranes. A diffusion cell was set up with one side filled with distilled water and measured by an FTIR probe that measured conductivity. The other side was filled with a 1M solution of either sodium formate or sodium acetate. The conductivity was measured over five hours and best fit with the Yasuda model to extract the permeability values of each solute. The resulting data is displayed in Figure 3 and Figure 4.

*Corresponding author:rjw0048@auburn.edu

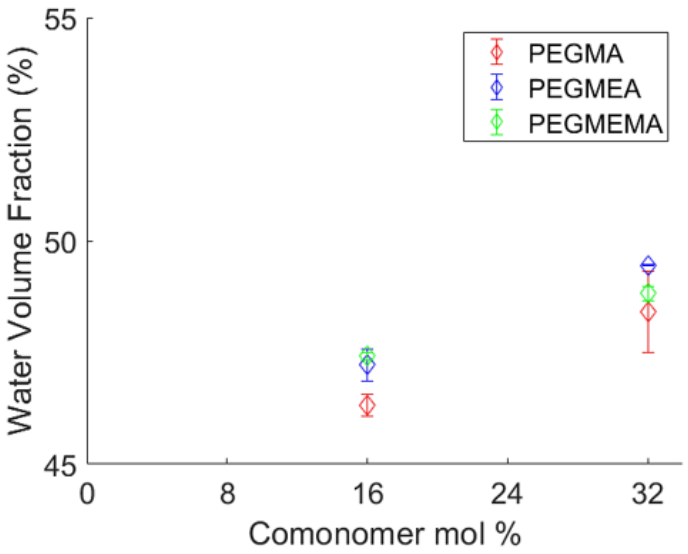


Fig. 1 Water volume fraction vs. comonomer mol percent with no AMPS

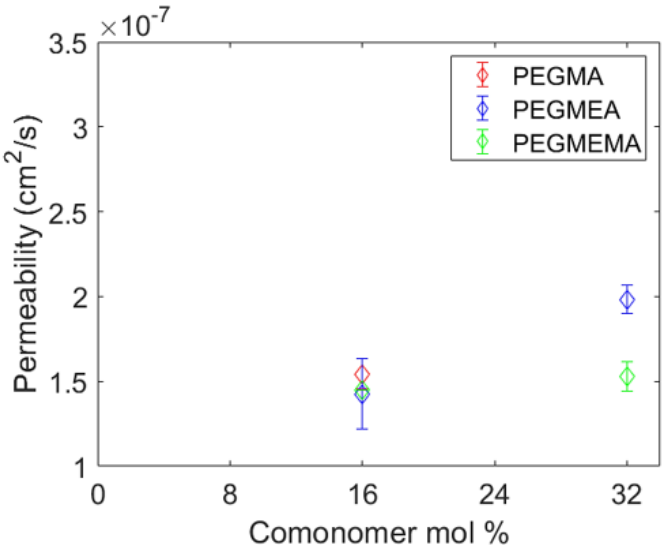


Fig. 3 Permeability vs. comonomer mol percent with sodium acetate and no AMPS

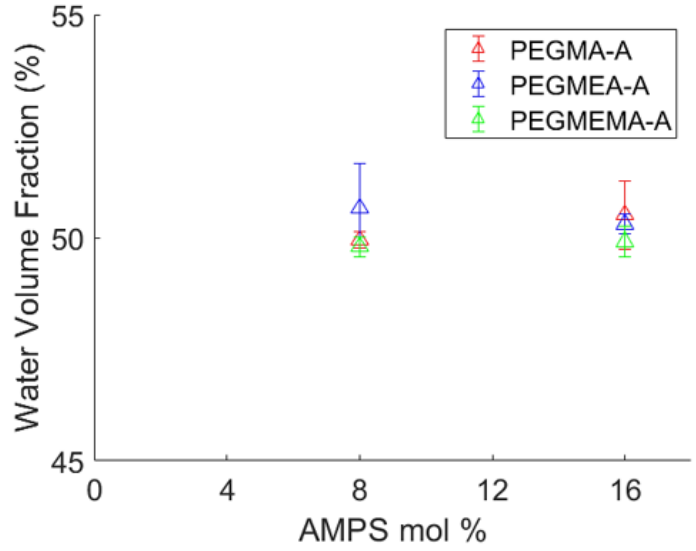


Fig. 2 Water volume fraction vs. comonomer mol percent with AMPS

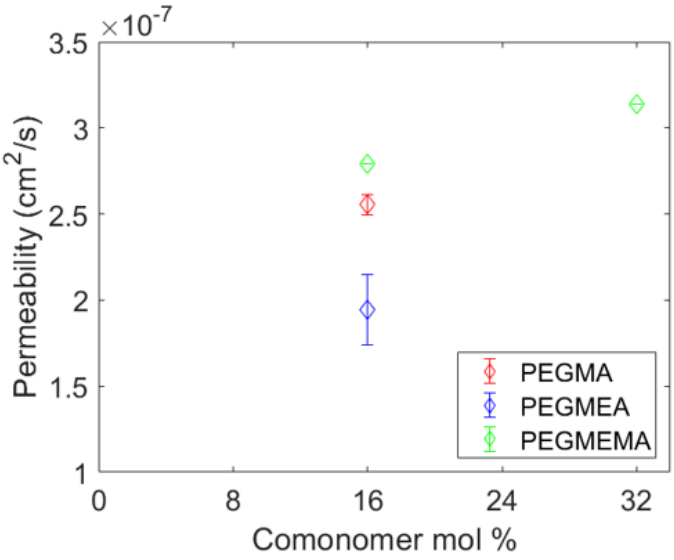


Fig. 4 Permeability vs. comonomer mol percent with sodium formate and no AMPS

Results from the first characterization method indicate that water volume fraction increases with increasing comonomer mol percent. Results from the second characterization method indicate that, in the case of sodium formate without AMPS, PEGMEMA has a higher permeability than PEGMA, and PEGMA has a higher permeability than PEGMEA at 16 mol percent. Further trials are being run at 32 mol percent to see if these trends are upheld. In the case of sodium acetate without AMPS, all three comonomers have roughly the same permeability at 16 mol percent.

Further trials are being run at 32 mol percent, but early data suggests that PEGMEMA membranes have a lower permeability than PEGMEA membranes. Trials using PEGDA-AMPS membranes will be run in the future to determine permeability values with varying AMPS and comonomer mol percents.

Statement of Research Advisor

Mr. Ryan Wozniak investigated how the chemistry of polymer networks could be used as a handle for tuning the polymer membrane behavior in solar fuels devices. Solar fuels devices convert carbon dioxide into chemicals or fuels such as methanol, acetate, and formate.

Ryan synthesized two series of polymer membranes (with and without ionic groups) and characterized their water uptake and permeability to formate and acetate. Overall, his work showed that water content could be controlled through the neutral comonomer content, but that even at similar water contents these different neutral comonomers had different impacts on the permeability of the solar fuels product molecules. This type of behavior is poorly understood, but important as the ability to design membranes with desirable permeability characteristics relies on knowledge of these kinds of structure-property relationships with Ryan's work adding to our growing knowledgebase.
- Bryan S. Beckingham, Department of Chemical Engineering, Samuel Ginn College of Engineering

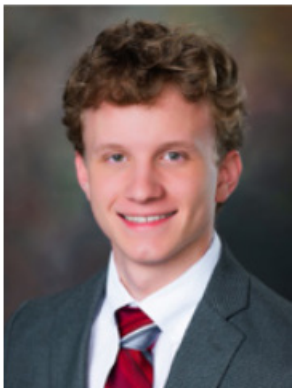
References

[1] Roy, N.; Suzuki, N.; Terashima, C.; Fujishima, A. Recent Improvements in the Production of Solar Fuels: From CO2 Reduction to Water Splitting and Artificial Photosynthesis. Bull. Chem. Soc. Jpn. 2019, 92, 178–192. https://doi.org/10.1246/bcsj.20180250.

[2] Liang, S.; Altaf, N.; Huang, L.; Gao, Y.; Wang, Q. Electrolytic Cell Design for Electrochemical CO2 Reduction. J. CO2 Util. 2019, 35, 90–105. https://doi.org/10.1016/j.jcou.2019.09.007.

[3] Chen, Y.; Lewis, N.S.; Xiang, C. Operational Constraints and Strategies for Systems to Effect the Sustainable, Solar-Driven Re- duction of Atmospheric CO2. Energy Environ. Sci. 2015, 8, 3663–3674. https://doi.org/10.1039/c5ee02908b.

Authors Biography



Ryan Wozniak is a junior-year student pursuing a B.S. degree in Chemical Engineering at Auburn University. He has played a key role in conducting research on single solute transport in PEGDA and PEGDA-AMPS membranes.

Dr. Bryan S. Beckingham is an Associate professor in the department of Chemical Engineering and is Director of the Center for Polymers and Advanced Composites. His research focuses on leveraging synthetic polymer chemistry and materials characterization to inform design of novel polymer materials, with an emphasis on polymer membranes, hierarchically structured matter and additive manufacturing of polymer functional polymer systems.