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Pure Award Final Report and Reflection

Investigating Proton Conduction using Guest-Loaded Metal-Organic Frameworks

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Introduction

Proton exchange membrane fuel cells (PEMFC) are a class of hydrogen fuel cells with a proton conducting electrolyte separating the cathode and anode.¹ The only product from the cell's reduction-oxidation reaction is water. Efficient hydrogen fuel cells are a clean alternative to the combustion engine, which releases pollutants such as CO₂. PEMFC efficiency is heavily dependent on how effective the electrolyte is at conducting protons between the anode and cathode. The most common electrolytes are polymers that only function below 100°C.² The reactions are more favourable at high temperatures, which allows for faster reaction rates. Anhydrous conditions, obtained at temperatures above 100°C, allow manufacturers to avoid liquid water, allowing for a simplified cell design.³ Under humidified conditions, water is the charge carrier, however, anhydrous conditions require an alternative. Solid acids can be used under anhydrous conditions, as the acids conduct protons, however, the cell breaks down if the acid leaches out.⁴ Therefore, the membrane must restrict acid movement and withstand heat for prolonged periods of time to maximize the life and efficiency of the fuel cell. The current standard for proton conduction is Nafion, a fluorinated polymer which can achieve proton conductivity of up to 10⁻¹ S/cm.⁵ However, a conductivity on the scale of 10⁻³ S/cm is sufficient for a material to be considered conductive.¹

Ion conduction is hypothesized to occur via the Grotthuss mechanism, where protons “hop” from a donor site on one molecule to an acceptor site in close proximity, continuing until the proton has reached its destination.⁶ The other mechanism is by vehicle transport, where the protons are shuttled on a single carrier.⁶ Pathways through a material are broken up between particles. Proton conduction in a PEMFC is resisted by the grain boundary effect, a resistive force experienced by charges travelling through powdered materials, and the largest deterrent to efficient conduction.⁷ Protons cannot cross the spaces between grains in the powder, resulting in a buildup of charge on the grains and preventing efficient conduction. At temperatures below 100°C, water can facilitate

conduction by bridging the gaps between grains and serving as a hopping site; however, at higher temperatures water is evaporated from the system and alternative carriers between the grains must be used to overcome the boundary. An example of this is to form a phase at the grain boundary with high ionic conductivity, such as by doping the material with conductive materials.⁸

Metal organic frameworks (MOFs) are coordination polymers composed of metals joined by organic linkers. By changing the core or the linkers, MOFs can form 1, 2 or 3-dimensional structures and topologies, some of which are porous, or have different chemical properties.⁹ MOFs have been used in synthesis, catalysis, and proton conduction. Proton conduction with MOFs is possible, provided the MOFs are stable under the operating conditions, such as high temperatures and resistance to acid.¹⁰ Extra groups incorporated inside the MOF may be applicable in proton conduction, as long as those groups can be a hopping site for protons, such as acids.¹¹

The objective of this project is to study acid stable MOFs capable of proton conduction at temperatures up to 200°C. Phosphoric acid is used as an alternative proton carrier and loaded in the pores of specific MOFs. It is tested for ion conductivity using impedance spectroscopy. To prevent the acid from escaping the pore, MOFs with window diameters less than 0.6 nm will be examined. This diameter will prevent anything larger from being released, which will prevent acid leaching. To overcome the grain boundary, polybenzimidazole (PBI), a proton-conductive polymer, was synthesized as a powder and mixed with the MOF to facilitate ion conduction under anhydrous conditions. The end goal is both the successful synthesis of these materials as well as an investigation into their capabilities for proton conduction at a range of temperatures.

Methods

ZIF-65 and ZIF-90, two MOFs with large pore sizes and window diameters below 0.4 nm were synthesized following previous literature with modifications.^{12,13} A trialkyl phosphate ester was used as the solvent in the synthesis of all ZIF materials. The ZIF materials GL7 and GL8 were

synthesized following a procedure for ZIF-90, with GL7 being synthesized in triethyl phosphate and GL8 in trimethyl phosphate. GL9 and GL10 were synthesized following the procedure for ZIF-65, with GL9 and GL10 using trimethyl phosphate and triethyl phosphate, respectively.

Following synthesis, samples were vacuum dried and a portion of each was held for 16 hours in an oven at 180°C to convert the ester to the acid. The ZIFs were characterized by powder x-ray diffraction (PXRD), which identifies phases in a crystalline material that can be matched against patterns in literature. To identify activation conditions of MOFs and track the conversion of the esters, thermal gravimetric analysis (TGA) was used. Physisorption analysis to determine the space within a porous sample was performed by the surface area and porosity analyzer (ASAP).

PBI was synthesized as previously reported.¹⁴ The product was characterized by infrared (IR) and nuclear magnetic resonance (NMR) spectroscopy. By matching peaks in both spectra against literature spectra, the structure of PBI and its successful synthesis can be confirmed.

To test conductivity, the MOF was tested alone or mixed with PBI and crushed to a fine powder. For the mixtures, the ratio of MOF:PBI was quantified by weight, at 80:20 and 50:50. The powder was loaded into a press between carbon tape and pressed at 5000 psi for 5 minutes to make a pellet. It was placed in an oven between platinum electrodes and its conductivity was tested using electrochemical impedance spectroscopy, which measures current relative to changing frequencies. The temperature was increased by 25°C increments up to a maximum temperature of 200°C, with a 24 hour equilibration time between measurements. The resulting Nyquist plot was analyzed to obtain the resistance and conductivity of the material. Due to the restrictions of the cell setup, only one material could be tested at a time. Due to time constraints, only ZIF-65 materials were tested.

Results

A breakthrough material would conduct above 10^{-2} S/cm above 120°C. The following results do not achieve this but are very promising. Most importantly, there are logical paths forward

based on systematic changes. Figure 1 and 2 imply that the incorporation of the ester solvent within the pore of all four materials was successful. There was a decrease in gas sorption from the literature to the synthesized materials. More N_2 was adsorbed by the ZIF materials without guests, relative to materials which were synthesized to have guest molecules. The decrease in gas adsorbed by each sample is due to the presence of the guest blocking further access to that pore. Conversely to what was expected, the choice of phosphate ester did not appear to direct the packing of pores. Trimethyl phosphate is smaller than triethyl phosphate, due to a methyl group being smaller than an ethyl group. It could be inferred that because of the limited space within the pores of a MOF, smaller molecules could pack in more efficiently, leading to less gas adsorbed during physisorption analysis. This is seen in the isotherm of ZIF-90 in Figure 1, where GL8 is less porous compared to GL7. However, this observation is reversed in the isotherm of ZIF-65 in Figure 2, where less N_2 adsorbs to GL10, despite GL10 having been synthesized with a more bulky solvent.

Nyquist plots are the graphs generated by electrical impedance spectroscopy. They depict the resistance of a material as the diameter of the semicircle plotted. The larger the semicircle's diameter, the larger its resistance, and the less conductive it is. ZIF-65 was tested in the cell, as it was hypothesized that the nitro group on the imidazole could serve as an additional hopping site. As is observed in Figure 3, increasing temperatures made the material less conductive. This could be due to the grain boundary effect becoming more prominent as water evaporates at the elevated temperatures, disrupting ion transport between individual crystallites in the bulk material.

PBI is an efficient proton conductor that has been used for fuel cell applications.¹⁵ PBI can be doped with acid and remain stable, therefore, the synthesized PBI was not fully neutralized before it was pressed into a pellet, with the idea that the acid within the polymer would also aid in proton conduction. The PBI was tested for its conductivity as further proof of successful synthesis

after characterization with IR and NMR spectroscopy. As seen in Figure 4, as the temperature increased, the diameter of the semicircle decreased, which corresponds to an increase in conductivity. The highest conductivity of the sample was 1.46×10^{-3} S/cm at 175°C.

The conductivity test was repeated with a pellet containing a mixture of PBI and GL9. It was hypothesized that the incorporation of PBI would facilitate proton conduction across the grain boundary, decreasing the diameter of the semicircle on the Nyquist plot meaning better conduction. The effect of this was first tested using an 80:20 ratio of MOF:PBI by weight. The highest conductivity was obtained at 200°C on the scale of 10^{-9} S/cm. This was repeated with a pellet with a 50:50 mixture. The highest conductivity of this material can be seen in Figure 5, and was obtained at 200°C, at 1.27×10^{-5} S/cm. The increase in conductivity implies that the addition of PBI increased proton conduction through the bulk. However, it is unknown whether the increase in conductivity is due to PBI conducting protons through the grain boundary between crystals of ZIF-65 or whether the protons are selectively travelling through the polymer now that it is in higher abundance.

Conclusion

While metal organic frameworks show promise as proton conductors, further investigation towards using MOFs as the electrolyte layer in a PEMFC at high temperatures is still required. More research must be done on the incorporation of additional hopping sites within the framework. This involves the synthesis and characterization of new or different porous solids which could either trap the proton carriers in a higher concentration in each pore, or have more acidic sites incorporated within the framework itself to aid in proton conduction. The grain boundary continues to challenge the conductivity of crystalline materials, although future work would involve investigating methods to mitigate its resistive effects. An improved cell design and the ability to test multiple pellets at a time would be useful for the investigation, in order to save time.

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Reflection.

Over the summer, I improved upon skills which were beneficial to my professional development. Two of which I found most important were managing information from a variety of sources, and planning, designing, and carrying out a project with defined objectives. I would like to continue with research in the future, and my ability to work independently and collaboratively makes me as a good candidate for an industry-aligned career or for graduate studies. These skills are highly transferable, and will also help me become a better, more organized leader, which is useful as I am heavily involved with an undergraduate club on campus.

An experience that I valued was learning to manage information from a variety of sources. Due to the nature of my project, I had to learn how to use many different programs and applications in order to interpret my data, such as XRD, TGA, impedance spectroscopy, NMR, ASAP, and IR. Learning to interpret and compile all of the information given allowed me to stay organized and work efficiently. I also refined my organic synthetic skills by helping out on other synthesis-heavy projects during my down time. If I pursue future graduate studies, I will be working with much more data, and my PURE research experience has given me the chance to practice data handling and analysis on a smaller scale.

Another learning experience was working on a project which I planned and completed. At the start of the project, I was given basic expectations for my investigation and suggestions on where to start. I used the suggestions to plan my approach to the issue, possible experiments, and how to interpret results which let me reach my own conclusions. The freedom to test my own ideas was something that I enjoyed during my 16-week research period. Even though the results were not as successful as I had hoped, I learned a lot and I am proud of the work that I was able to do. A goal for my future learning is to be able to plan a new project from start to finish. I will be able to practice this skill as I work towards planning events with my fellow club members this year.