Immobilization of heteropolyacids in PEM fuel cell membranes via copolymerization

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Introduction

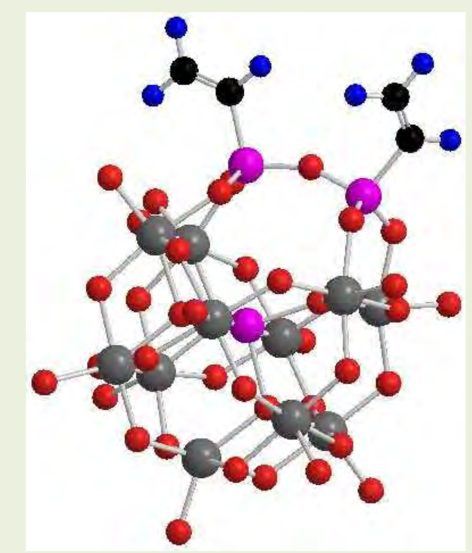
Nafion© is the current standard by which PEM fuel cell membranes are measured. It is a PFSA (perfluoro sulfonic acid) polymer that is used to conduct ions such as protons. This material is only useful at low temperature (<100ºC) and high relative humidity due to protons being transported by water which is not practical for a fuel cell. Research is currently being done to create a new membrane that does not contain PFSA, instead membranes are made using heteropolyacids (HPAs). HPAs are useful because they are strong inorganic acids that have a high water of hydration, meaning a humidifier may not be necessary in a fuel cell. Another positive aspect of HPA's are the ability to for protons to hop from HPA molecule to HPA molecule. One limitation of HPA's is their solubility in water. This research is focused on immobilizing the HPA by functionalizing it with an easily polymerizable group so that it becomes a monomer that can be used to make copolymers. Two HPA systems are being presented here, HPA-ethylene and HPA-butyl acyrlate. It is possible that these systems will be more effective than PFSA membranes.

UV Polymerization

In the butyl acrylate system UV polymerization was used to polymerize the two monomers. HMPP, a photo initiator, was used. The membrane is cast on Teflon sheets and exposed to strong UV light using a Fusion UV. Five different membranes have been made using different weight percents of heteropolyacids in the mixture.

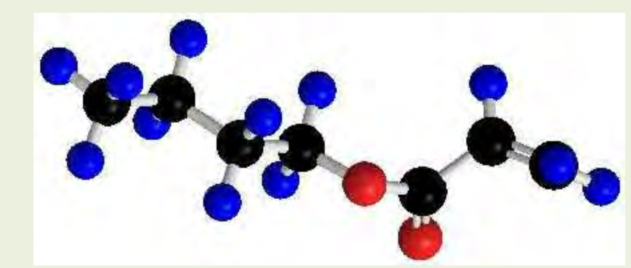
Bomb Reactor

The bomb reactor is used to create a closed system reaction that allows the system to be compressed to high pressures (~1500 PSI). The high pressures and temperature initiate free radical polymerization of the HPA and ethylene. Tert-butyl peroxide (TBPO) and azo-bis-isobutyronitrile (ABIN) were used as initiators. Experiments varied the reaction temperature, initiator and length of experiment.

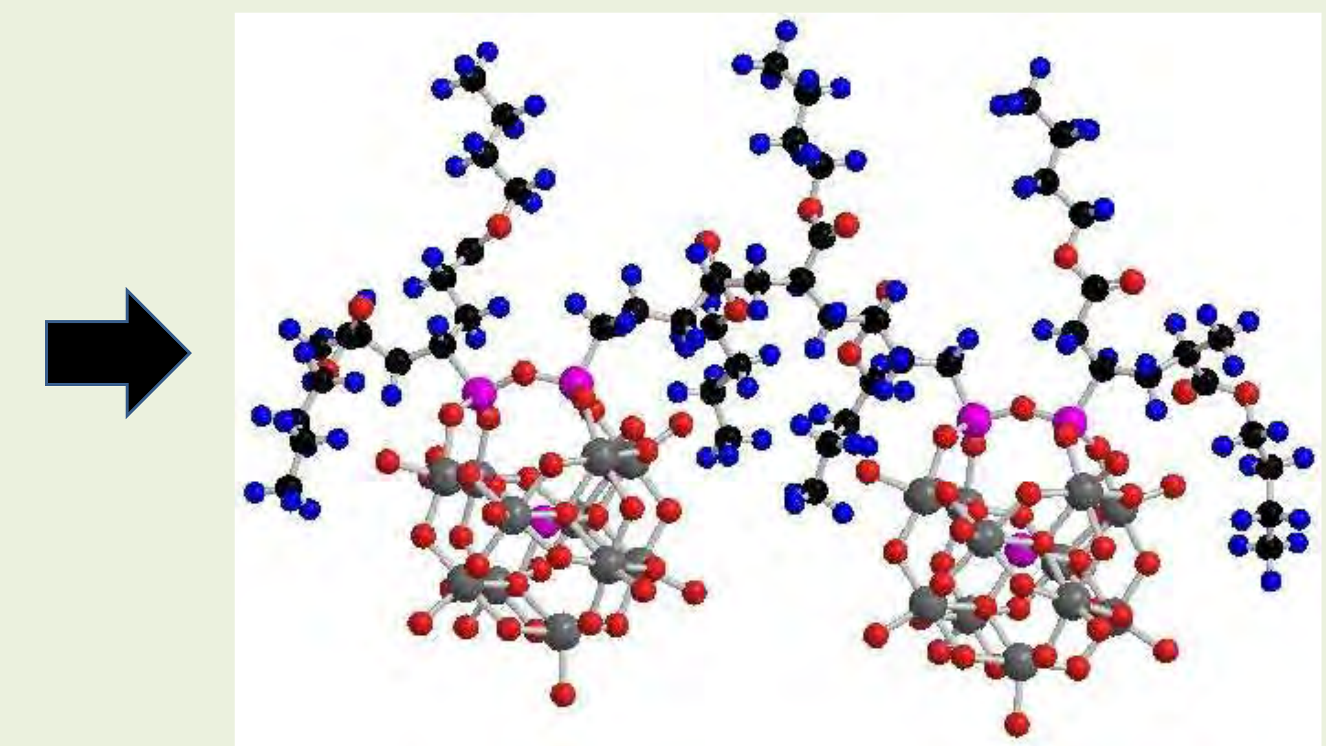


$HSiW_{11}O_{39}(vinyl)_2$

+



Butyl Acrylate

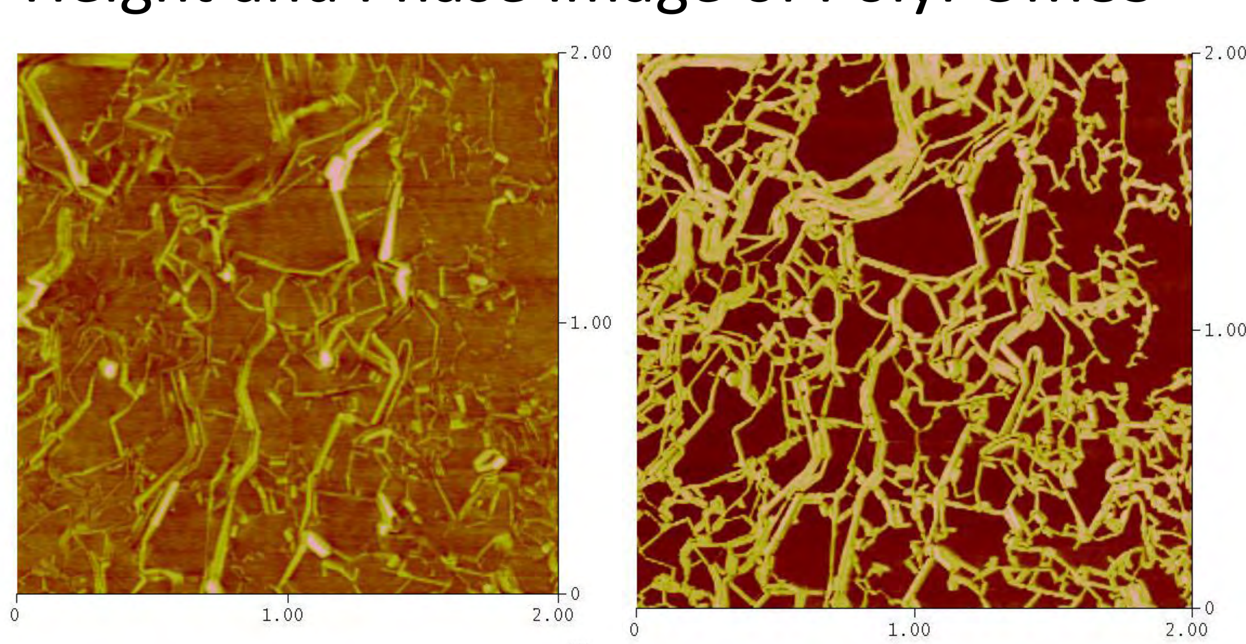


$HSiW_{11}O_{39}(vinyl)_2$/butyl acrylate co-monomer

Pink = SI
Red = O
Gray = W
Black = C
Blue = H

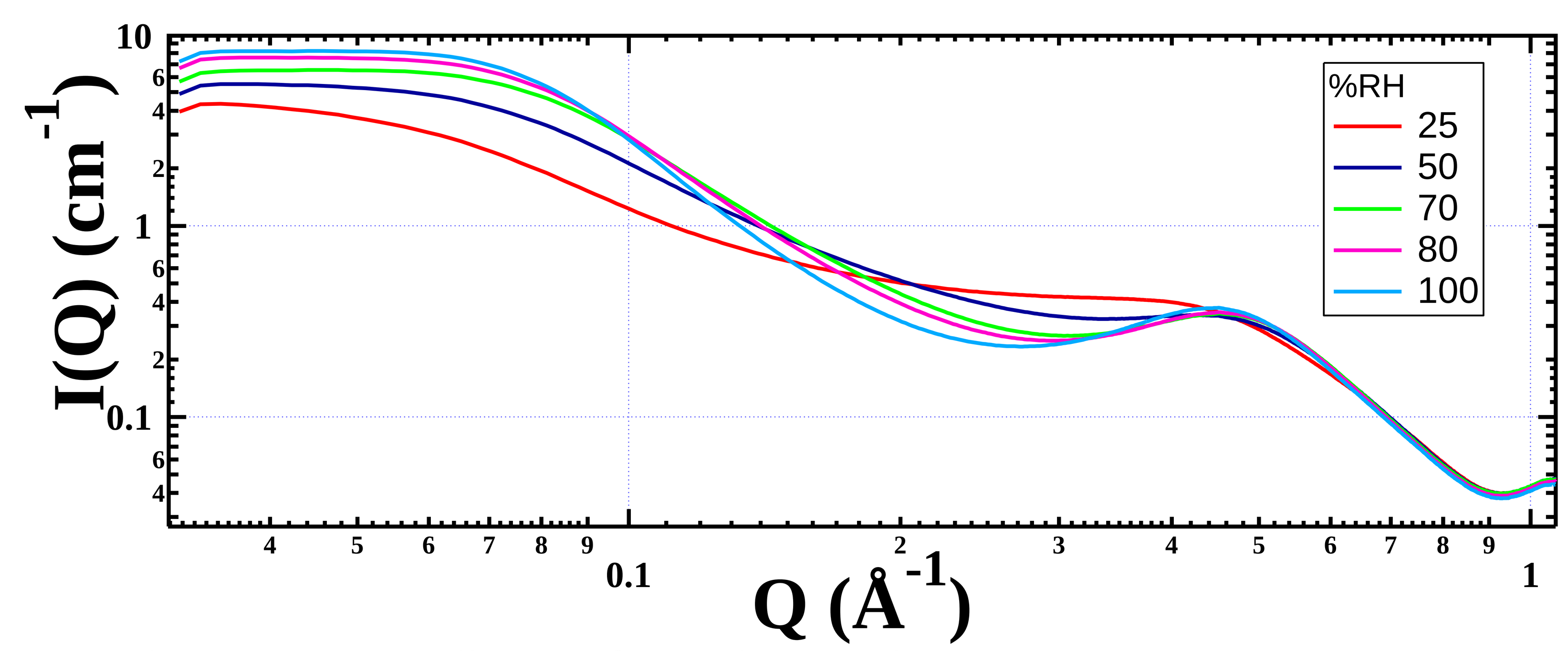
This is the first HPA-ethylene membrane made in the lab. After removing the co-monomer from the bomb the excess solvent was evaporated in a vacuum oven. To create a flexible backbone it was necessary to mix the co-monomer with solid polyethylene and dissolve in a like solvent creating a liquid. This liquid was evaporated off leaving a thick flexible membrane. Much needs to be improved upon to make the membrane more homogenous and thinner.

Height and Phase Image of PolyPOM85

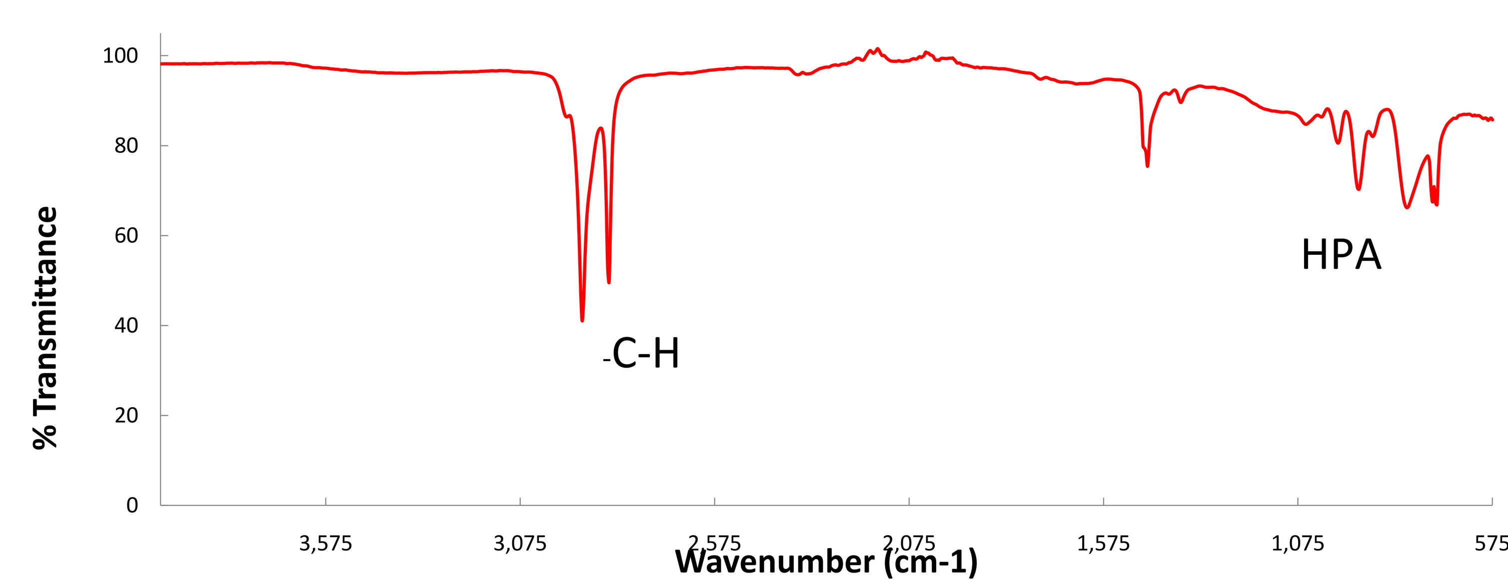


AFM images that depict phase segregation and channeling in butyl acrylate membrane system

SAXS of PolyPom25 Varying %RH



Above is data collected from the synchrotron at Argonne National lab, this trend shows how the morphology of the heteropolyacids in the membrane change as relative humidity changes



IR of HPA/ethylene co-monomer with polyethylene backbone. There are no carbon-carbon double bonds indicating that the polymerization did indeed occur yielding the desired polymer.

Conclusions and Future Work

The butyl acrylate system is more developed than the ethylene system. One of the downfalls of using butyl acrylate is that it does not participate in proton conduction, ethylene is potentially better than butyl acrylate because it is incorporated into the proton exchange network and theoretically should improve proton conduction. Another benefit of using ethylene is that it is relatively inexpensive and plentiful making an ethylene membrane a more economical choice. Some further research needs to be done to test how well the ethylene co-monomer will work as a membrane and to determine the optimal amount of HPA in the system. Furthermore it will be necessary to perfect the bomb reactor polymerization, to determine optimal synthesis conditions.

Acknowledgements

We thank the Renewable Energy MRSEC REU program for the opportunity to do this research. The CFCC provided us the lab space to conduct these experiments and research. Use of the Advance Photon Source was supported by the U.S. Department of Energy, Office of Basic Science, Office of Basic Energy Sciences, under Contract No. W-31-109-Eng-38. Lastly, we thank the National Science Foundation for funding this research under Grant No. DMR-0820518.