Thermo-Cross-Linked Anion Exchange Membranes with Improved Mechanical Strength

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Anion Exchange Membrane Fuel Cell

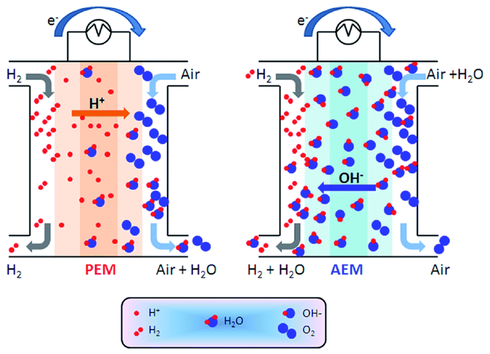
Advantages

Proton Exchange Membranes

- Require pure hydrogen fuel
- Require precious metal catalysts
- Environmentally destructive fluorocarbon synthesis

Anion Exchange Membranes

- Allow variety of fuels
  - Low-carbon alcohols can be oxidized in high pH environments
- Allow non-precious metal catalysts
  - Kinetically favorable oxidation reduction reactions at electrodes in high pH environments
- Environmentally friendly synthesis



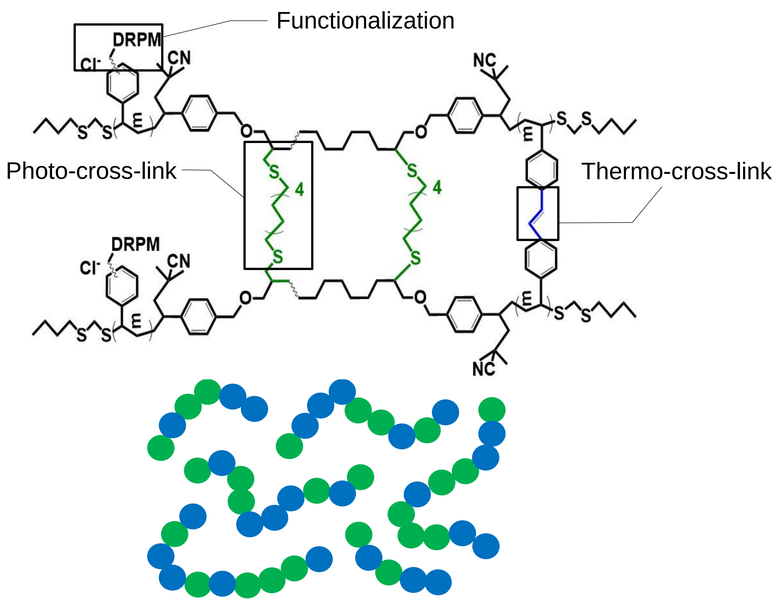
**Energy & environmental science* 7.10 (2014): 3135-3191.

Requirements

- High conductivity
- Chemical stability
- Mechanical strength in humid environments
  - Water is a reactant and mechanical strength decreases when water uptake increases
  - Mechanical strength is thought to increase with increased cross-linking

Membrane Fabrication with Thermo-Cross-Linking

Shown below is an example of the cross-linking structure and functionalization that could occur in the triblock co-polymer PCMS-b-PCOE-b-PCMS.



Methods to Determine the Extent of Cross-Linking

Cross-linking is thought to increase mechanical strength. The amount of cross-linking can be indicated with dimensional analysis tests and conductivity tests.

Dimensional Analysis

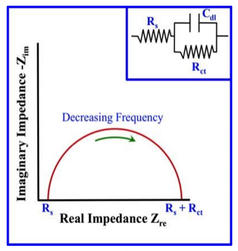
Large water uptake indicates weaker membranes with less cross-linking

Electrochemical Impedance Spectroscopy (EIS)

Calculates in-plane conductivity from membrane resistance

Membrane Conductivity: $\sigma = \frac{L}{Rwt}$ — L: Distance between electrodes; w: Membrane Width; t: Membrane Thickness; R: Membrane Polarization Resistance

**Macromolecules* 49.1 (2015): 153-161.



**EIS | GSCSG | Boston MA*. N.p.

- large conductivity indicates less cross-linking
- Membranes loaded into four-probe cell (platinum electrode probes)
- Bio-Logic VMP3 Potentiostat for data collection
- Test Equity H1000 environmental chamber to control temperature and relative humidity

Thermodynamic Prediction of Extent of Cross-Linking

$$\upsilon_i \quad 2C_2H_2Cl \xrightarrow{\Delta} 2HCl + C_4H_2$$

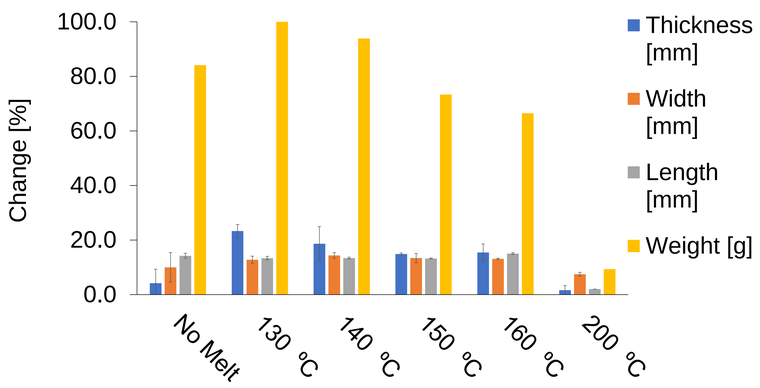
Equilibrium Constant: $K = \frac{n_2^2 P^2}{n_{Total}^2}$ — υ_i: Species #; υ_{Total}

$$e^{\left(\frac{\Delta g^0 rxn}{RT^0} - \boxed{\frac{\Delta h^0 rxn}{R} * \left[\frac{1}{T} - \frac{1}{T^0}\right]}\right)} = \frac{n_2^2 P^2}{n_{Total}^2}$$

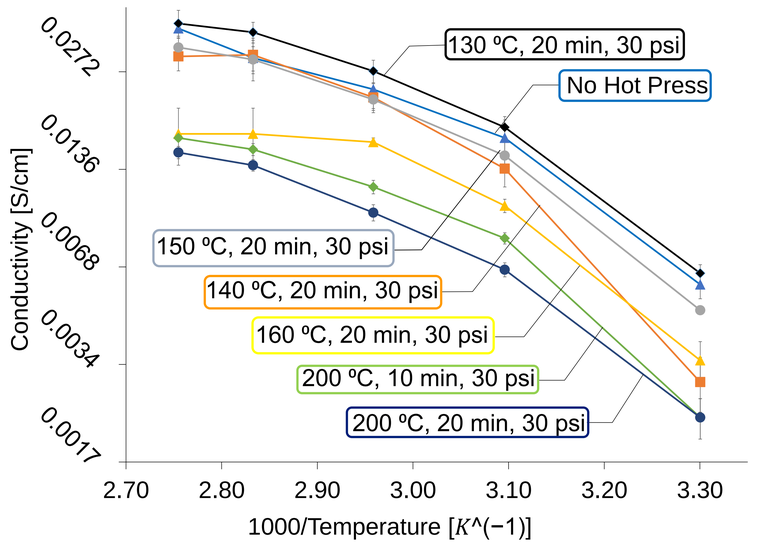
Temperature Correction Factor

Effect of T and P on the Extent of Cross-linking

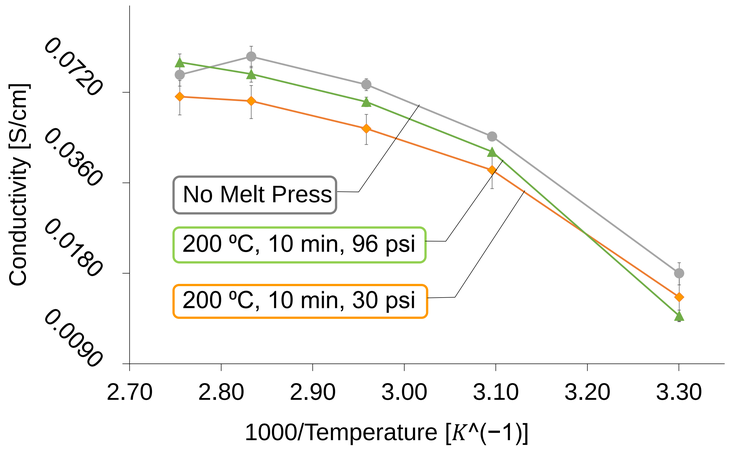
- 20% DT photo-cross-linked membrane melt pressed for 20 minutes at 30 psi and various temperatures
- Samples measured when dry and when wet to determine percent change



- Photo-cross-linked (20% DT)
- Melt pressed at various temperatures (thermo-cross-linking)



- No photo-cross-linking (0% DT)
- melt pressed at different pressures (thermo-cross-linking)



Conclusions and Future Work

Conclusions

1. Extent of Cross-linking can be adjusted by T and P results matched thermodynamic equilibrium equations
   -Thermo-cross-linking increases with lower melt press pressure
   -Thermo-cross-linking increases with higher temperature
2. Introducing cross-links effectively withheld water absorption and dimensional swelling membranes appeared to have higher mechanics in humid conditions

Future Work

1. Tensile testing should be done to compare the strength before and after cross-linking
2. More testing should be done to confirm relationships between temperature, pressure, and cross-linking

Acknowledgements

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