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Degradation of Model Sulfonated Polyphenylene Proton Exchange Membranes

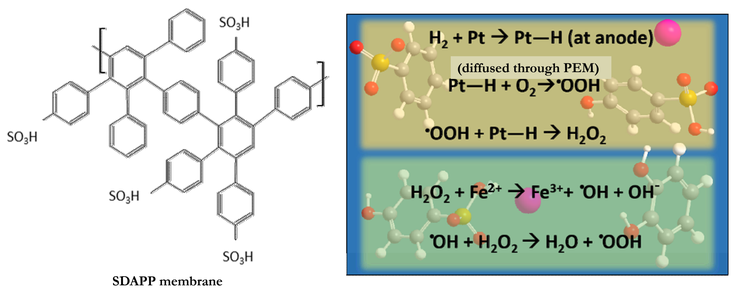
Cassandria Miller*[1], Todd M. Alam[1], and Cy Fujimoto[2]

[1]Department of Organic Material Sciences, Sandia National Laboratories, Albuquerque, NM 87185 USA

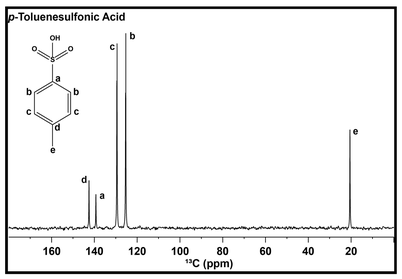
[2]Department of Nanoscale Sciences, , Sandia National Laboratories, Albuquerque, NM 87185 USA

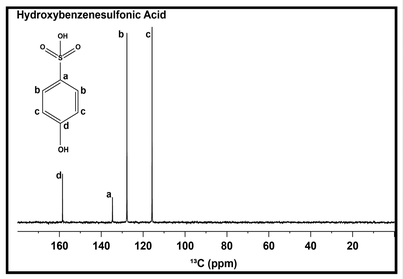
Proton-exchange membrane or polymer-electrolyte membrane (PEM) fuel cells are becoming increasingly popular due to their versatility, high efficiencies and low pollutant output. One of the main failure modes of PEM fuel cells is the degradation of the polymer membranes, and therefore considerable research and resources are being committed to understand the important aspects of the process. One key degradation pathway is initiated by peroxide radical attacks at the membrane electrode interface; peroxides that are generated as the result of the associative oxygen reduction reactions when in contact with low concentrations of transition metal ion impurities. Previous work on the degradation of the Sandia developed sulfonated poly(phenylene) (SDAPP) membranes used solution ^{1}H and ^{13}C NMR to characterize the decomposition products However, the complicated chemistry of the full polymer led to inconclusive identification of all the resulting chemical species. The work described in this poster focuses on the intentional degradation of simpler constitutive model compounds that will ultimately lead to a better understanding of the degradation chemistry that occurs in SDAPP PEMs. These model compounds underwent testing with Fenton's reagent, in which the compounds are directly exposed to varying concentrations of both H_2O_2 and trace ferrous iron contaminants. Solution ^{13}C NMR is used to observe the decomposition as a function of time and identify the degradation products of each reaction at various temperatures. These results are then used to evaluate the degradation of the complete SDAPP membrane.

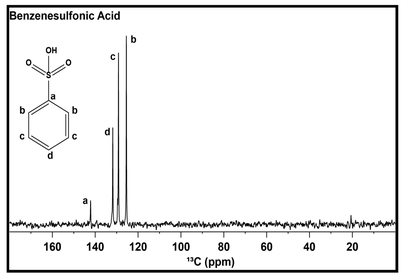
Methods and Materials

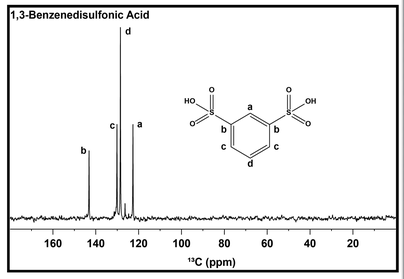


- Peroxide radicals created using Fenton's reagent at varying peroxide and Fe^{3+} concentrations.
- 10% H_2O_2/water , 25ppm Fe^{3+} environments at 50˚C, 60˚C, 70˚C, and 80˚C
- NMR experiments performed on a Bruker Avance-III 500 spectrometer at 125.78 MHz equipped with a 5 mm broadband probe using a single pulse with ^{1}H decoupling.
- ChemDraw© software used to predict ^{13}C NMR resonances

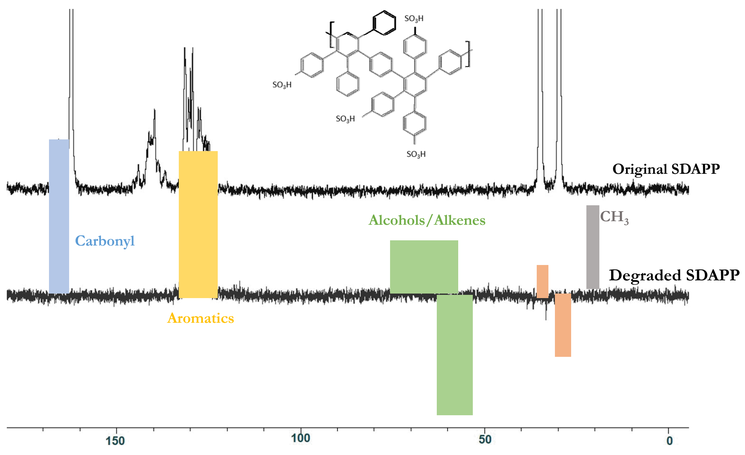




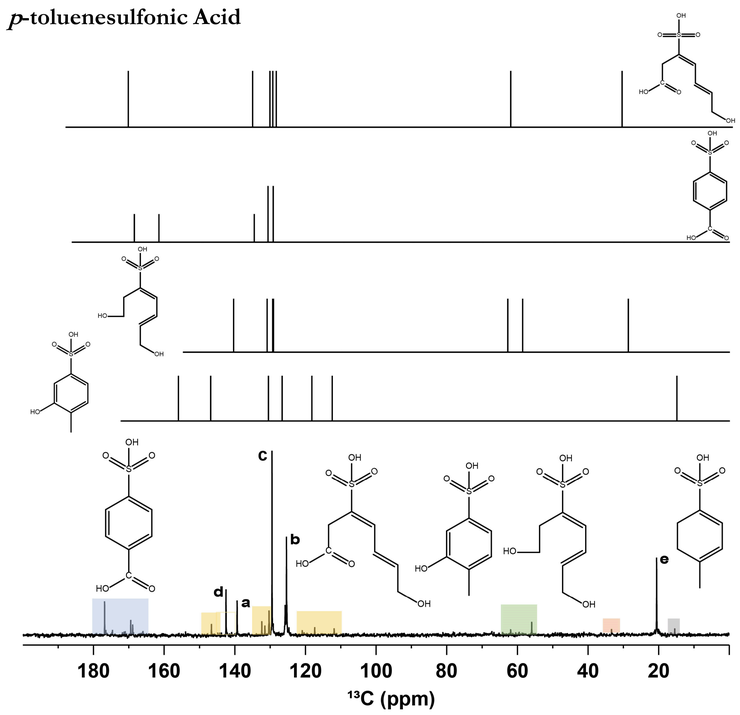


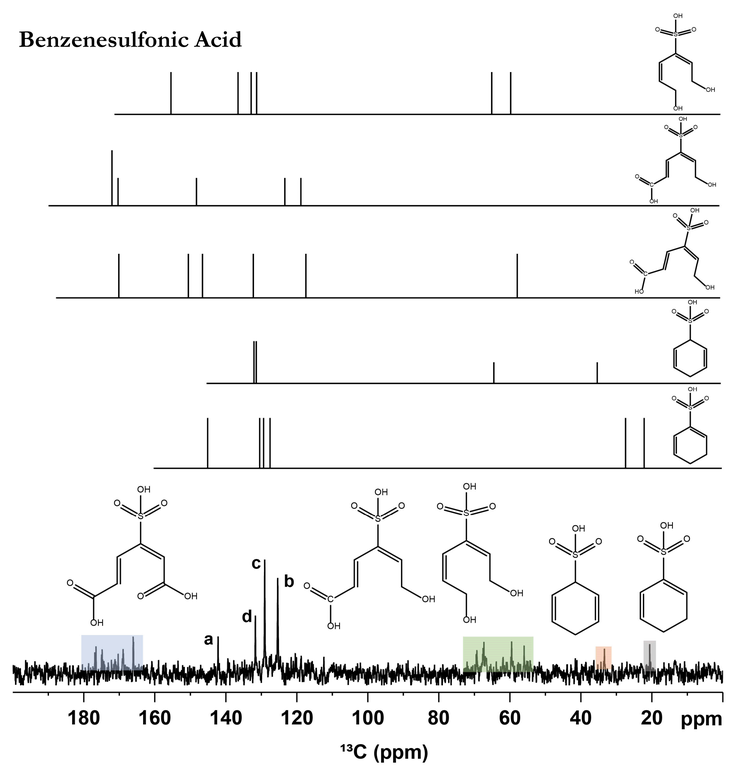


Degradation of SDAPP Membrane

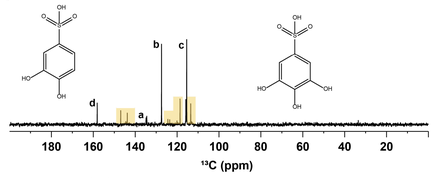


Degradation of Model Compounds

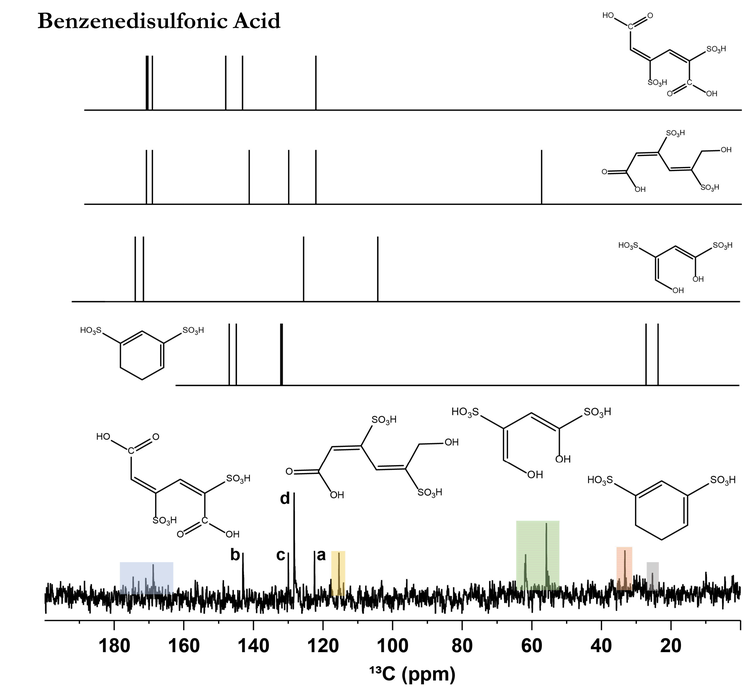




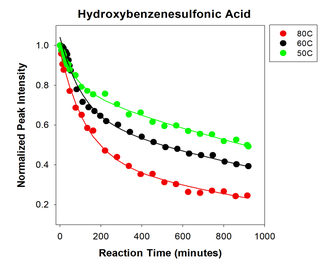
- Hydroxybenzenesulfonic Acid degradation products show hydroxy groups attached in the ortho and meta positions.



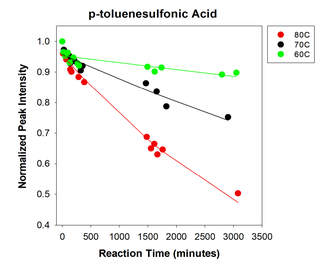
- Radical •OH molecules attack benzene ring, causing ring to open
- Radical •OH and •OOH molecules attach to the opened benzene ring, adding hydroxy and carbonyl groups
- Consistent with products formed in the degradation of original SDAPP membrane
- Benzenedisulfonic and benzenesulfonic acids bubble and expel gas, assumedly CO_2



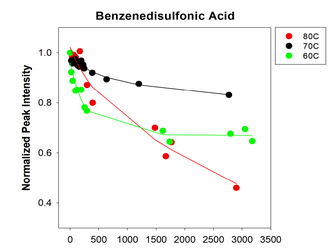
Degradation Kinetics



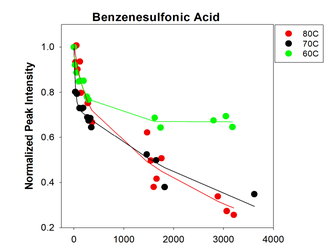
Temperature (C)	Parameter a	Parameter c	T1 (min)	T2 (min)
80	0.51	0.46	120	1347
60	0.39	0.65	105	1795
50	0.20	0.80	75	1928



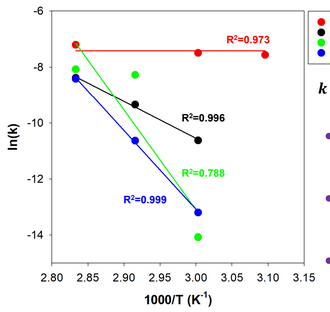
Temperature (C)	Parameter a	T1 (min)
80	0.96	4373
70	0.96	11400
60	0.95	40994

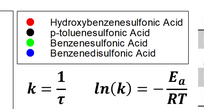


Temperature (C)	Parameter a	Parameter b	T1 (min)	T2 (min)
80	0.12	0.91	303	4528
70	0.09	0.89	510	41,386
60	0.29	0.67	265	5.4E5



Temperature (C)	Parameter a	Parameter c	T1 (min)	T2 (min)
80	0.24	0.78	164	3223
70	0.25	0.74	27	3908
60	0.29	0.67	270	1.3E6





$$k = \frac{1}{\tau} \qquad ln(k) = -\frac{E_a}{RT}$$

Compound	Activation Energy (kJ)
Hydroxybenzenesulfonic Acid	0.17
p-toluenesulfonic Acid	1.58
Benzenedisulfonic Acid	3.38
Benzenesulfonic Acid	4.28

- The e- withdrawing properties and resonance stability from the hydroxy group protects benzene ring from cleaving, instead adding OH groups
- Benzenesulfonic and benzenedisulfonic acids behave similarly in both degradation product formation and activation energies--addition of second sulfonic acid does not protect the ring
- *p*-toluenesulfonic acid has a low activation energy, though the methyl group on the benzene ring allows for eventual degradation

Future Efforts

- Employing mass spectrometry and infrared spectroscopy will allow for further analysis of degradation species
- Synthesize SDAPP with added hydroxy groups to determine if membrane degradation ceases
- Investigate new model compounds with similar properties to hydroxybenzenesulfonic acid
- Acquire proposed degradation compounds and run ^{13}C NMR to ensure legitimacy

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