Anhydrous Polymeric Proton Conductors

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JPL

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Development of "Water-Free" Proton Conductors for High Temperature PEM Fuel Cells

Program Objectives :

Develop " water free" proton conductors

- 125°-160°C, thermally and electrochemically stable
- ionic conductivity >100 mS/cm
- low gas permeability
- low-cost and easy to manufacture

Overall Approach:

- Identifying/Engineering candidate "water- free" proton conducting systems
- Preparation of materials and fabrication of membranes
- Characterization of membrane properties for fuel cells

Designing Proton Conductors

- Maximize acidity of the proton
- Providing time average basis sites for proton hopping/diffusion
- Development of structured arrays with minimal re-organization and short path length for proton hopping/diffusion.
- Materials stable to thermal and oxidative conditions.

<u>Computational Outputs:</u>

- Effect of structure on acidity (proton availability)
- Quantification of temporal and spatial re-organization that affect proton hopping frequency, activation barriers
- Proton hopping/ diffusion rates for flexible and ordered systems

Novel Proton Conducting Systems

1. Organic Amine Sulfates and Phosphates

2. Polymeric Amine Sulfates and Phosphates

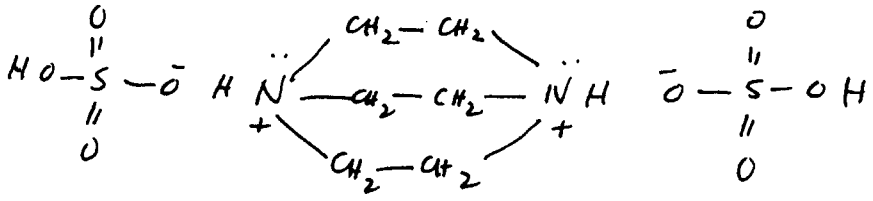
3. Ordered array single component polymeric systems with high charge carrier and site availability.

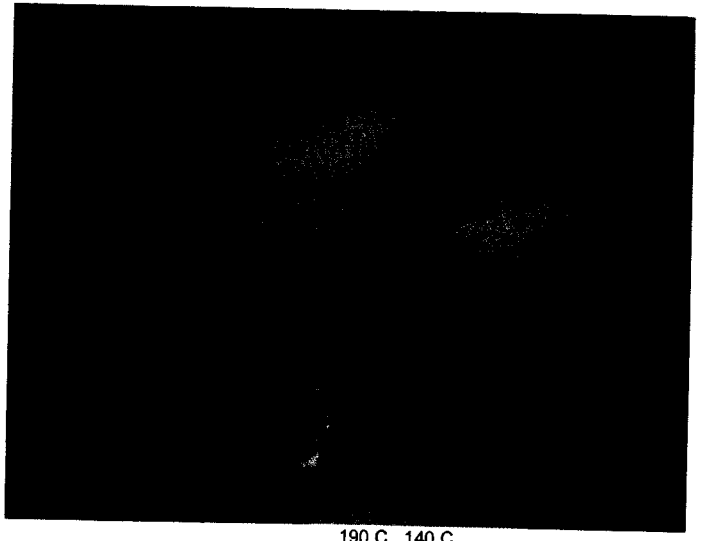
4. Two-component polymer system with acid and base groups

5. Inorganic silica perfluorosuflonic acid hybrids

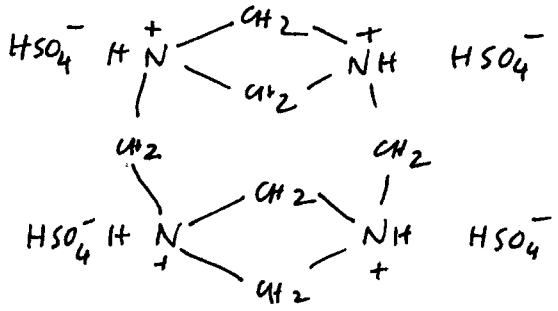
Organic Amine Sulfates

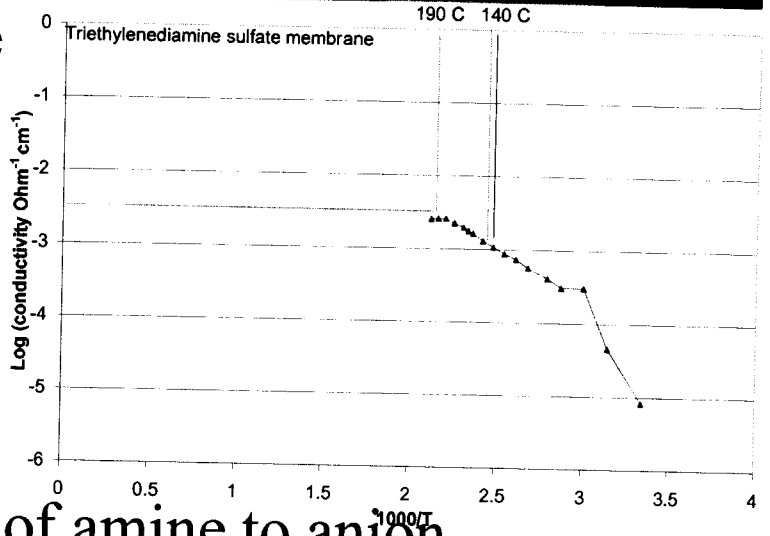
Triethylenediamine bisulfate





Hexamethylenetetramine bisulfate





Conductivity varies with the ratio of amine to anion

Activation energy is about 0.15 –0.2 eV suggest facile mobility

Polymeric Salt Materials Under Study

Preparation completed:

- *poly-2-vinylpyridinium bisulfate and phosphate*
- *poly-4-vinylpyridinium bisulfate and phosphate*
- *polyvinylimidazolinium bisulfate and phosphate*

Preparation in progress:

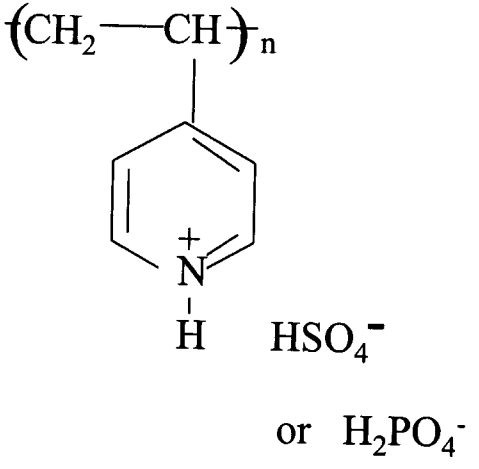
- *Polyvinylethoxyimidazolinium bisulfate and phosphate*

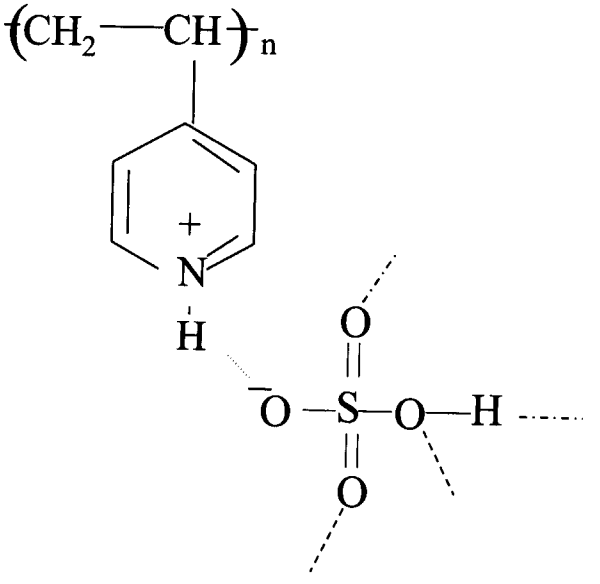
Prepared substrate supported membranes for studies

- *Bisulfates polymers have been tested*
- *Testing in progress for phosphates*

Polymeric Amine Bisulfates and Phosphates

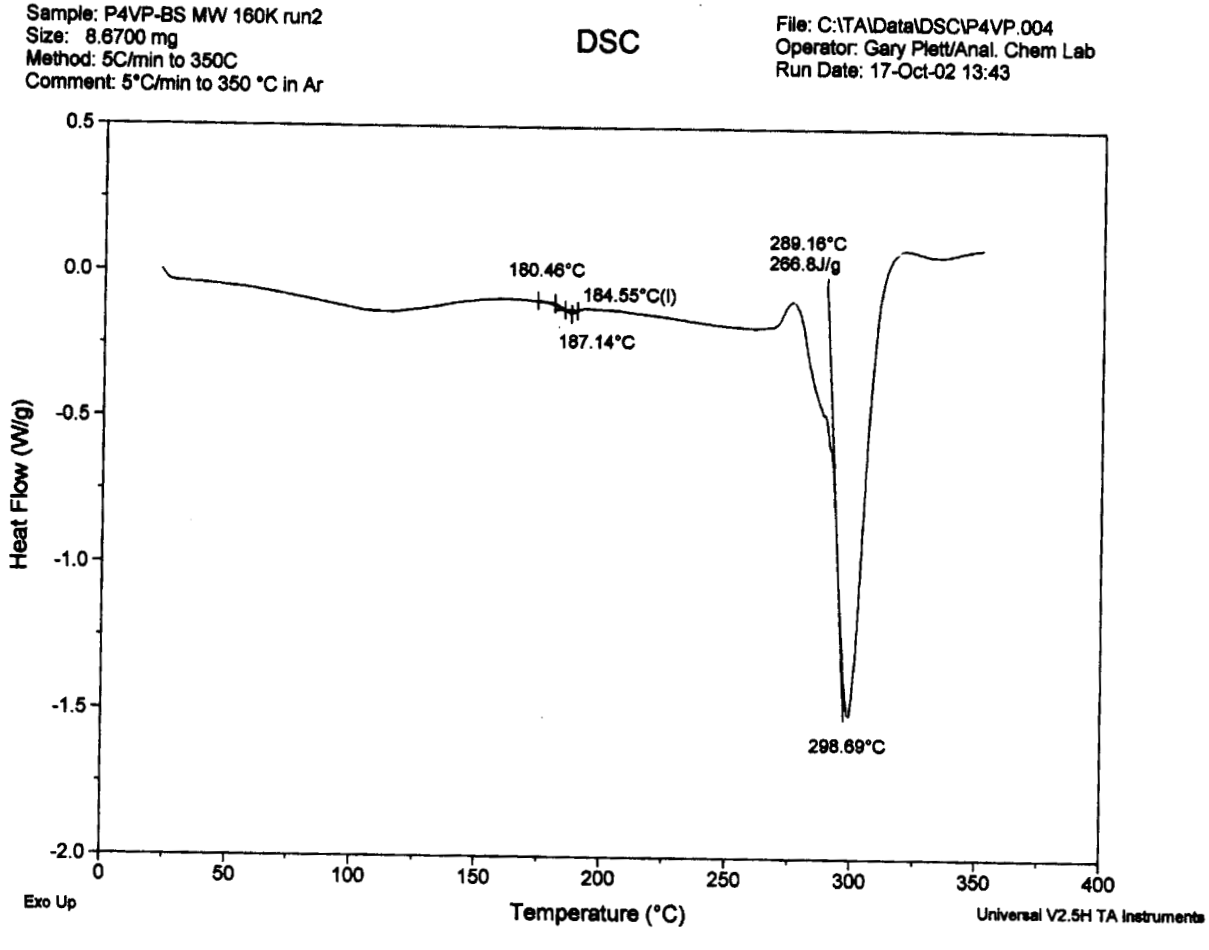
Poly-4-vinylpyridinium bisulfate and dihydrogenphosphate





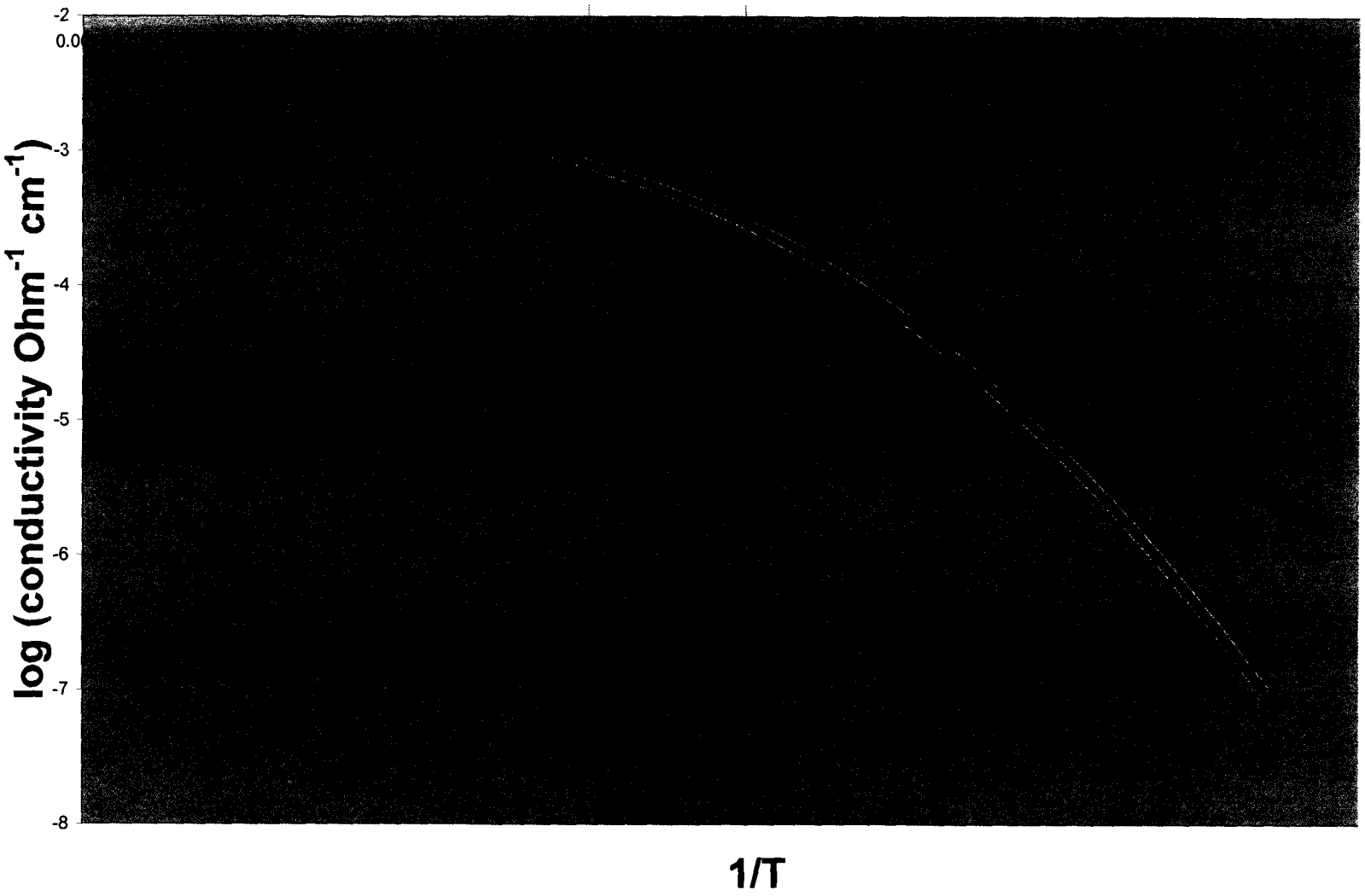
Proton transport through
Hydrogen bonded network?

Thermal Studies on Poly-4-vinyl pyridinium sulfate



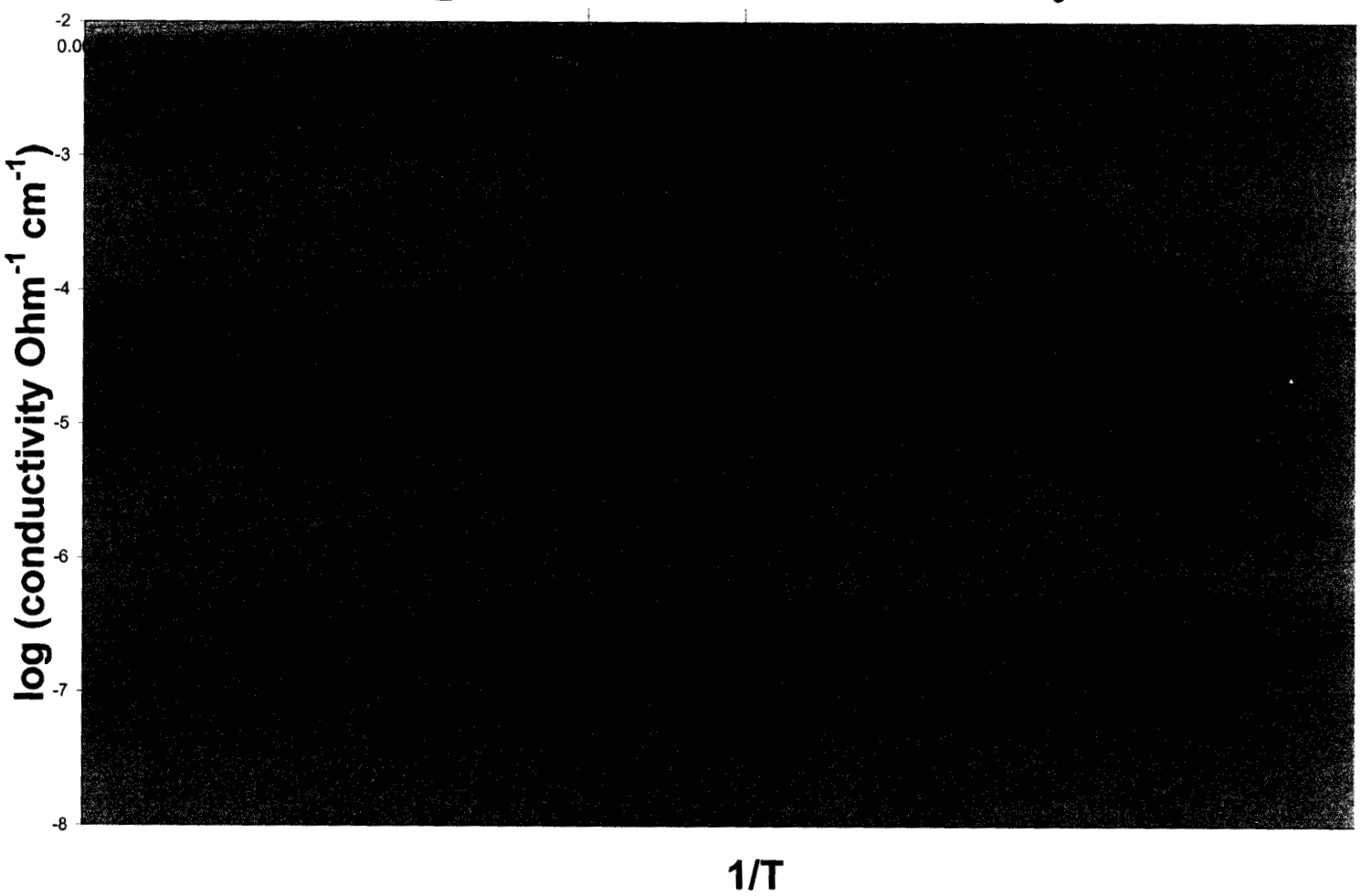
•Good thermal stability until 300°C.

Conductivity of Phosphate and Sulfate Polymers



Phosphate polysalts are found to be more conducting than sulfates

Effect of Silica on Conductivity of Phosphate and Sulfate Polymers



•Silica enhances the low temperature conductivity of polysalts

SUMMARY OF RESULTS

- All Polymer materials tested are stable until 180°C tested
- Activation energies for proton conduction are about 10-15 kcals/mole
- Polymer back-bone flexibility is key factor in conductivity
  - -Polyvinylpyridinium (PVP) polymers more conducting than Polyvinylimidazolinium
- Phosphate polymers are more conducting than sulfate polymers
- Nanoparticulate silica affects the conductivity at low temperatures