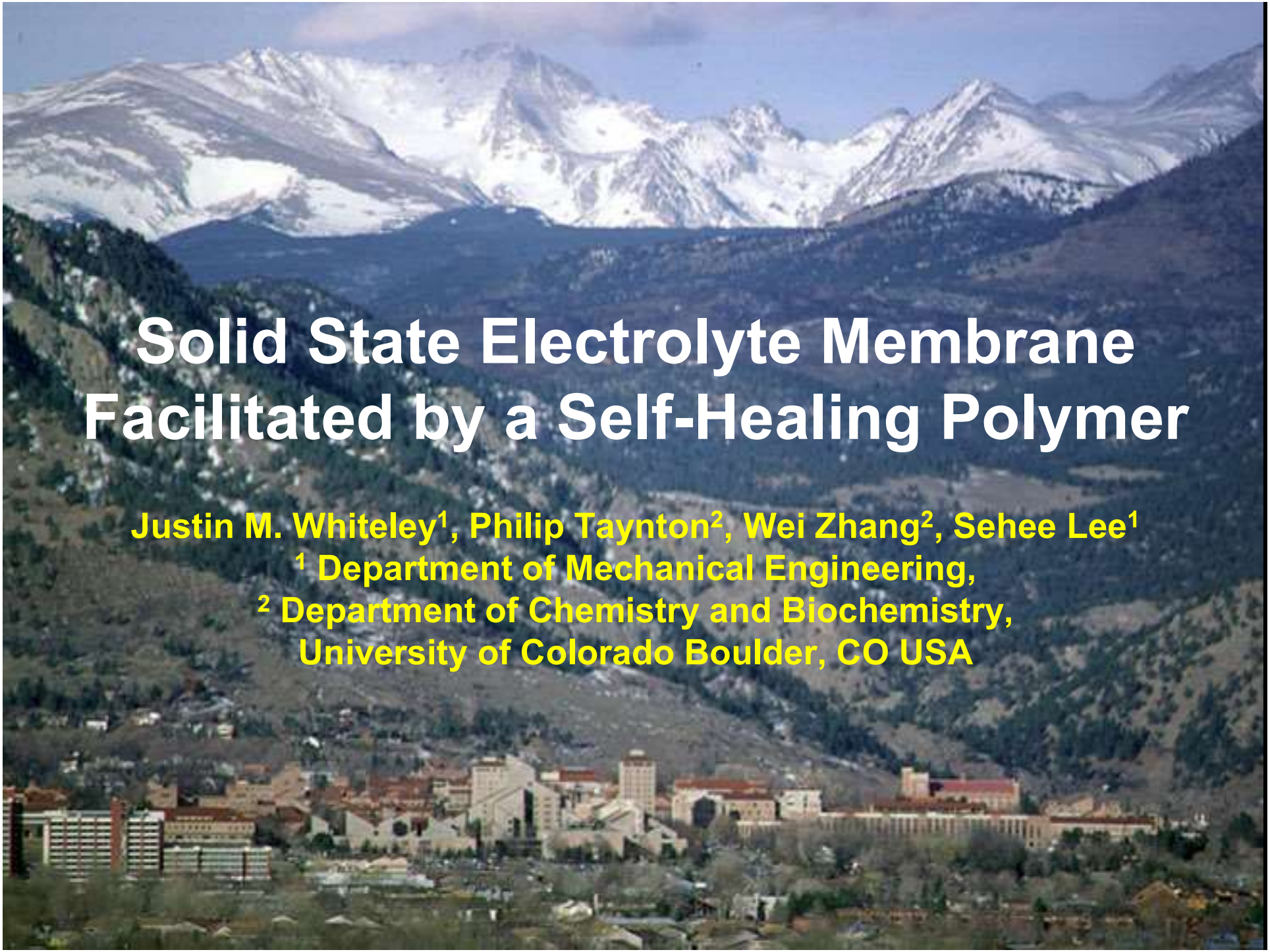

Solid State Electrolyte Membrane Facilitated by a Self-Healing Polymer

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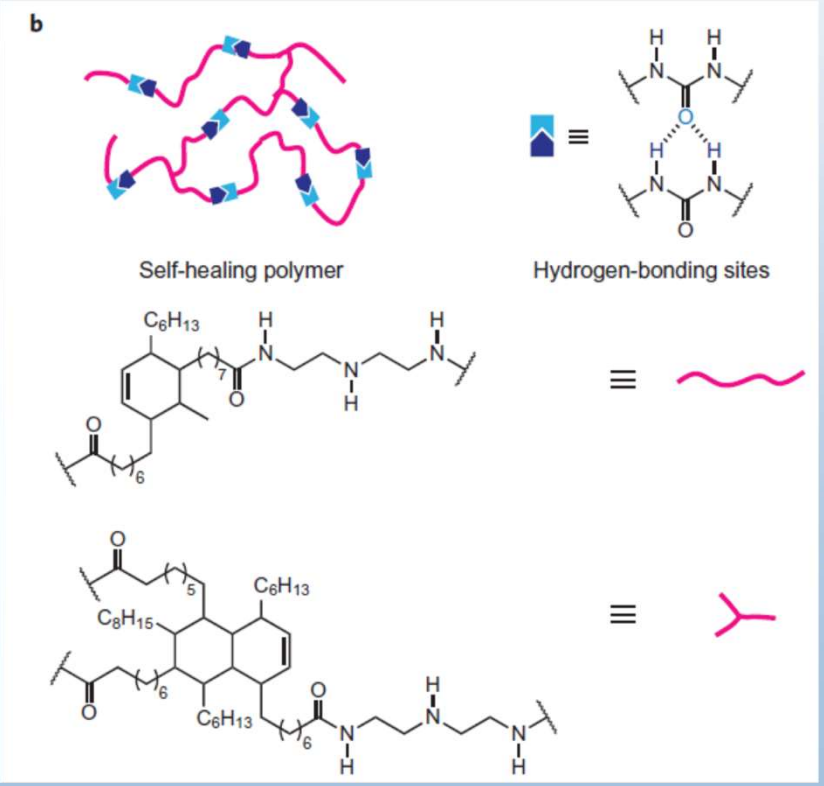
Introduction: Self-Healing Polymer

There are two major categories of SHPs

1. Polymers with **dynamic bonds** (repeatable healing capability)
2. Polymers embedded with microencapsulated healing agents

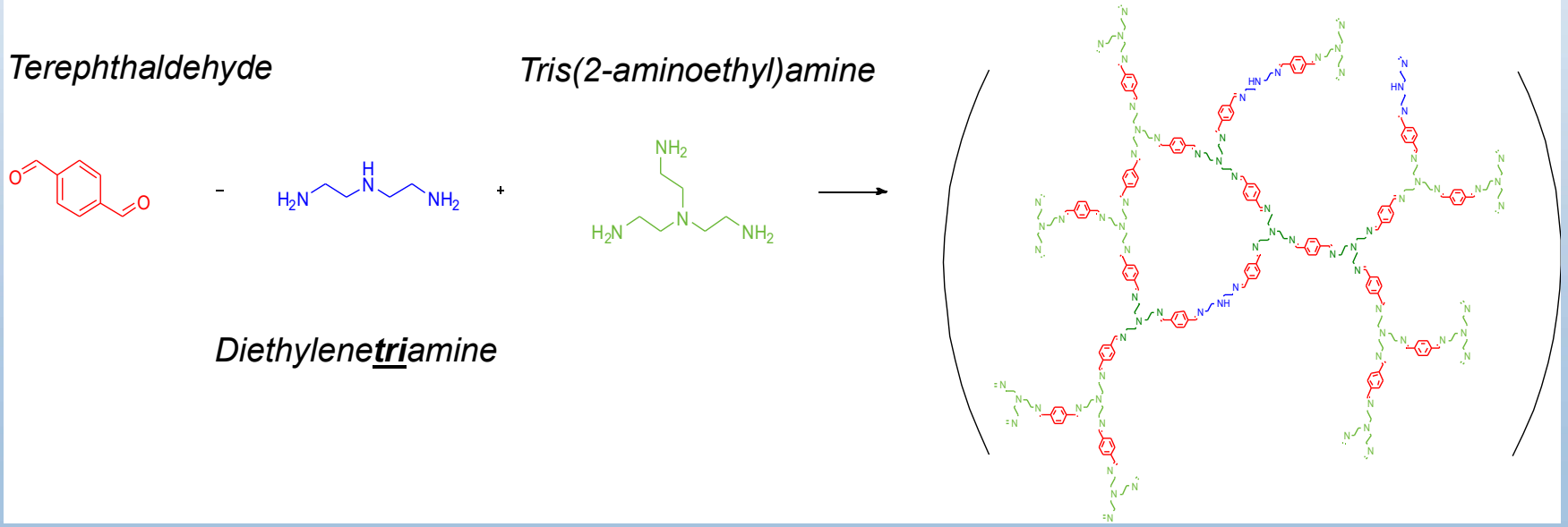


Dynamic bonds: Ionic and hydrogen bonds have been known to achieve self-healing performance but generally vulnerable to heat and water and other polar solvents
and are not as resilient as covalent network polymer.

C. Wang et al., Nature Chemistry 5, 1042 (2013)

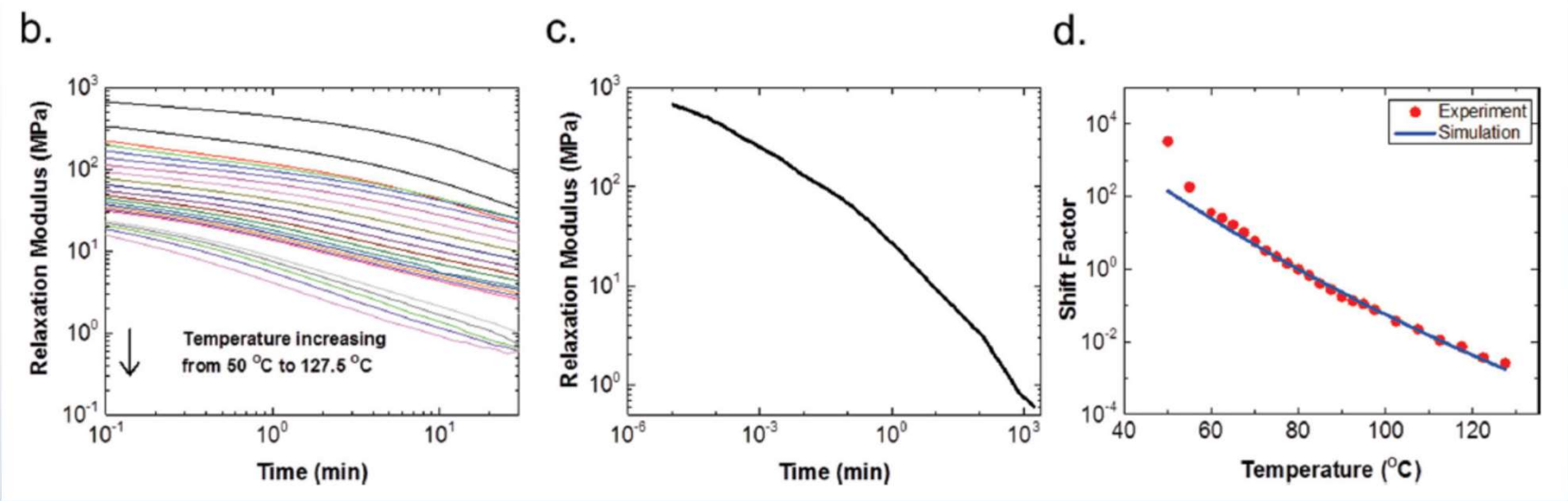
Introduction: Self-Healing Polymer

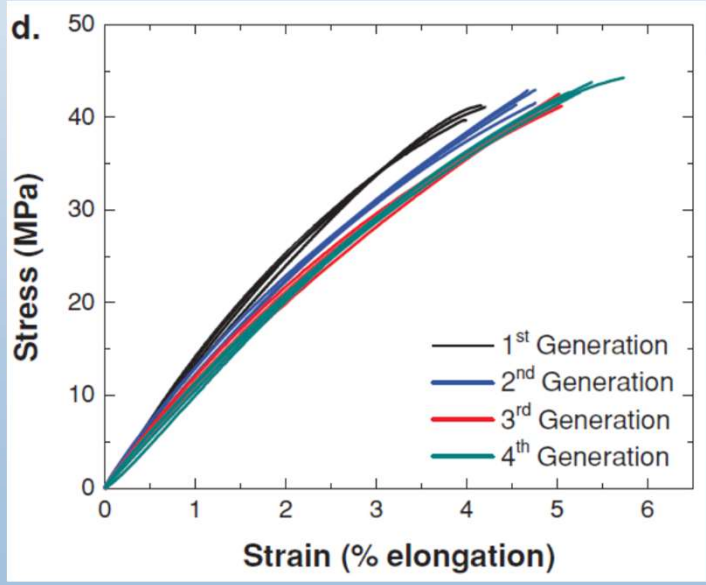
- **Polyimine** (Dynamic Covalent Chemistry)
  - Heat or water activated malleability at low temps (80°C)
  - Thermoset strengths at ambient conditions
  - Processed from powder into film



P. Taynton, et al, *Advanced Materials 26, 3938* (2014).

Stress-relaxation and Recycling Studies

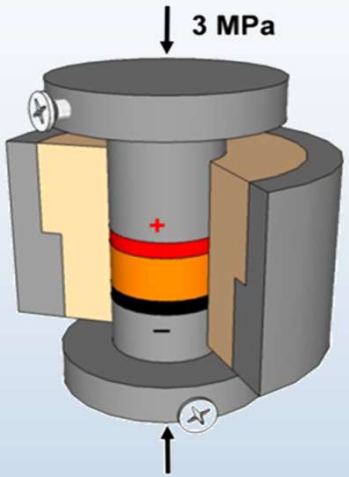




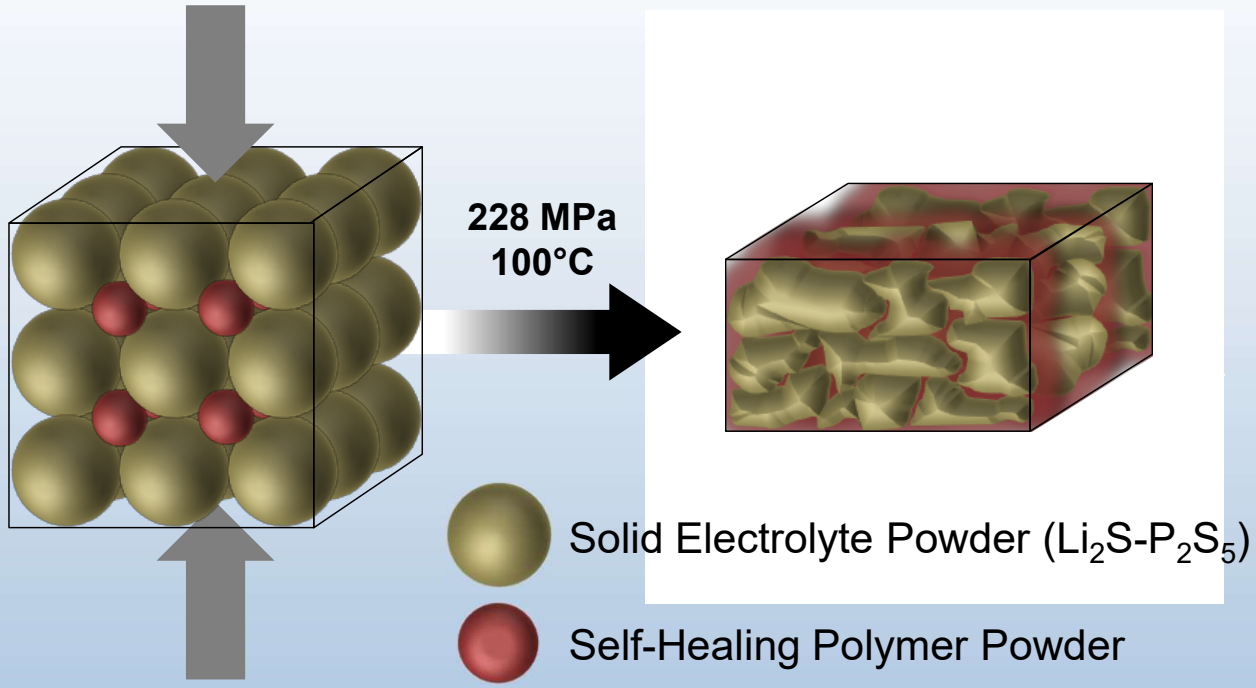
P. Taynton, et al, *Advanced Materials 26, 3938* (2014).

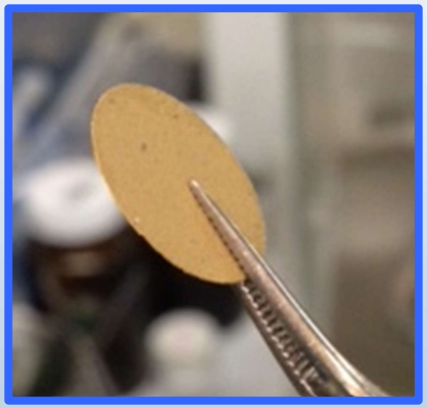
Research Objectives:

- Reduce the thickness of the electrolyte layer - < 0.1 mm
- Maintain mechanical robustness
- Obtain near 0% porosity
- Bulk resistance should be of equal or lesser value than current resistance
- Demonstrate long-term and high rate cycling performance with state-of-the-art cathode and anode



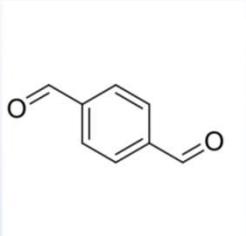
Schematic for forming SEPM





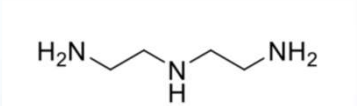
Self-Healing Polymer Formulations

a

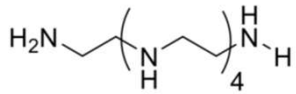


Terephthaldehyde

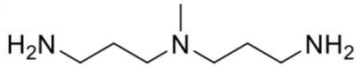
+



*Diethylene**tri**amine*

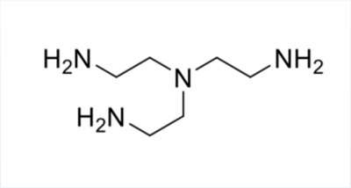


*Pentaethylene**hexa**mine*



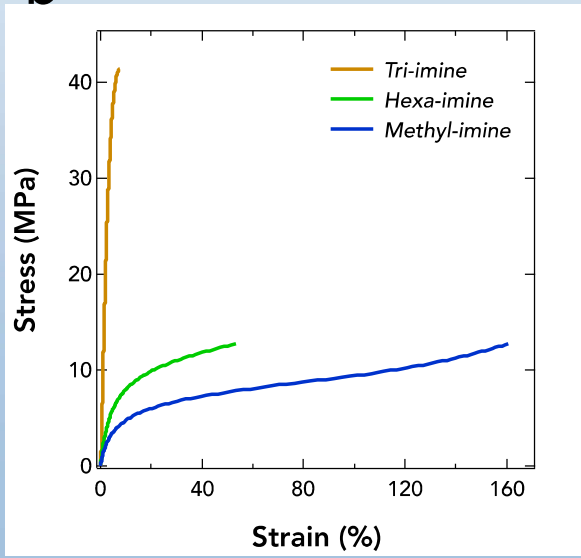
N,N-bis(3-aminopropyl)methylamine

+

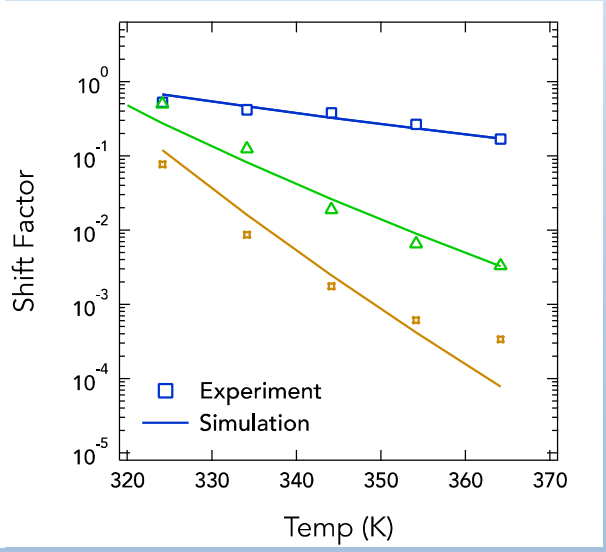


Tris(2-aminoethyl)amine

b



c

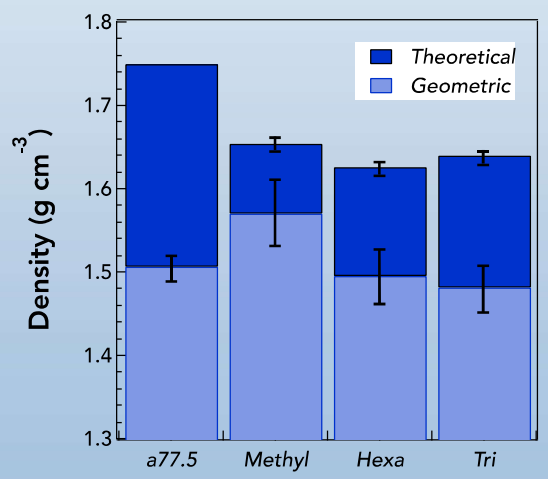


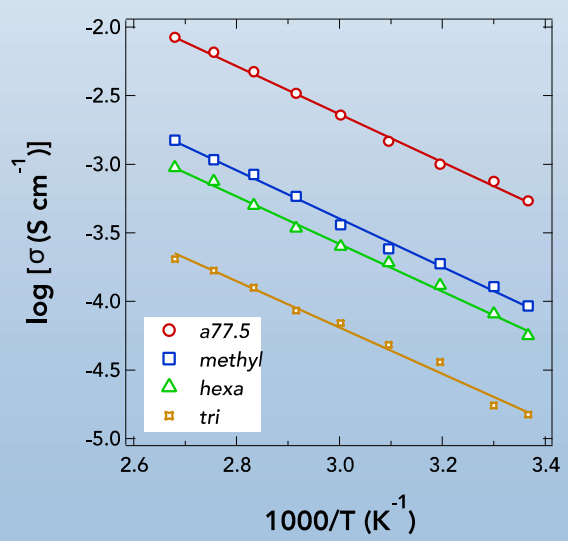
	Activation Energy ($kJ\ mol^{-1}$)
Tri-imine	180
Hexa-imine	109
Methyl-imine	33.5

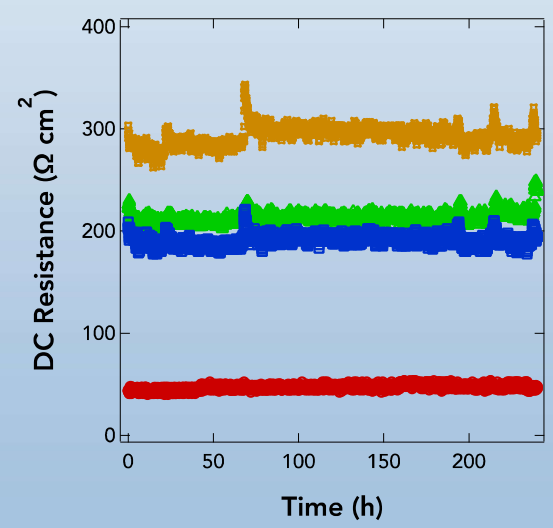
Composite Membrane

Material	Theoretical Density (g cm^{-3})	Composite Relative Density	Composite $\sigma_{25°C}$ (mS cm^{-1})	Composite Activation Energy (kJ mol^{-1})
a77.5	1.75*	0.85 ± 0.01	0.54	34.7
Methyl-imine	1.07 ± 0.02	0.97 ± 0.02	0.092	34.8
Hexa-imine	0.93 ± 0.02	0.94 ± 0.02	0.056	34.5
Tri-imine	1.00 ± 0.02	0.92 ± 0.02	0.015	33.3

* Density tabulated using tie line between Li_2S and P_2S_5 theoretical densities. Value is in good agreement with literature.

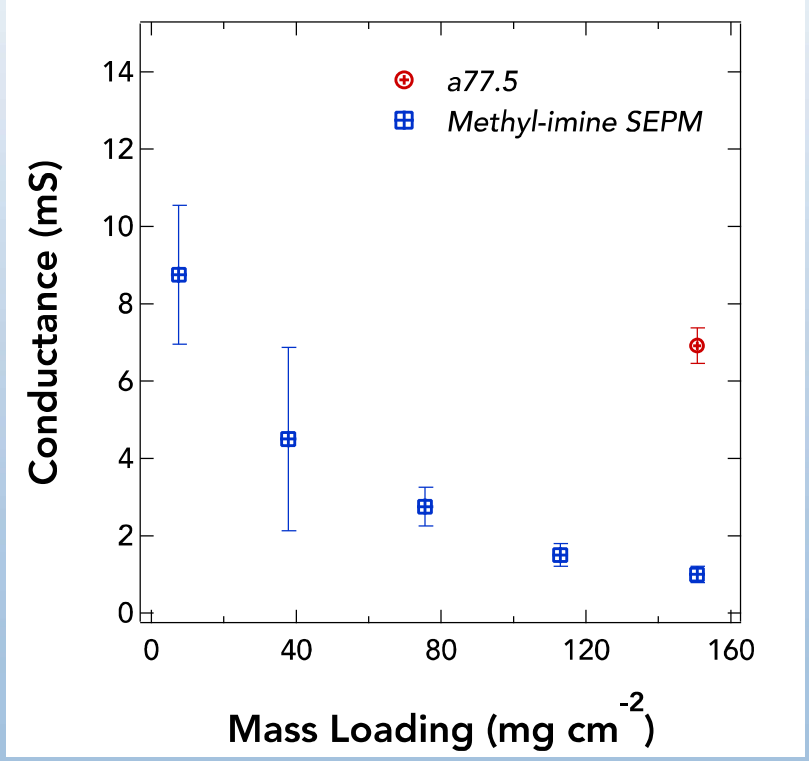






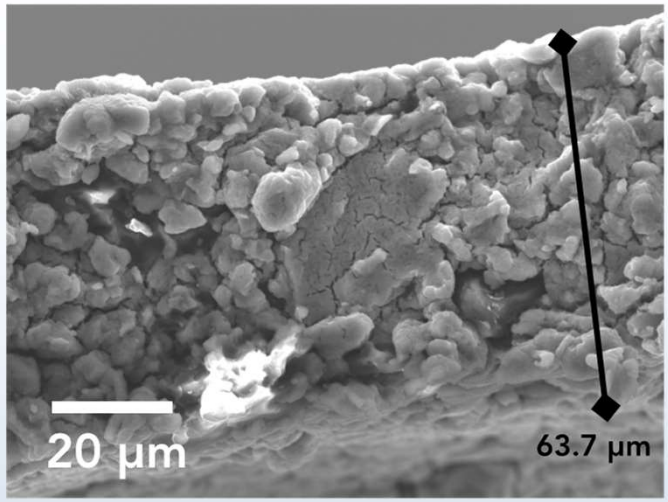
Composite Membrane

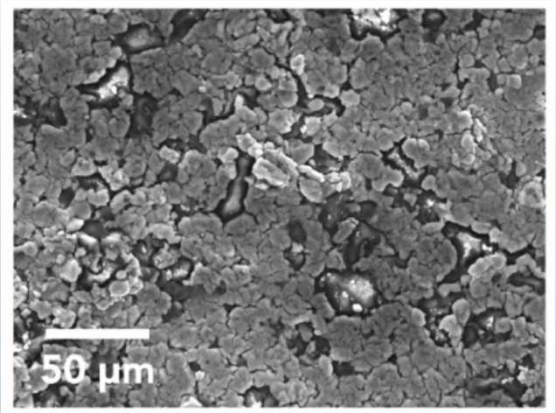
- Optimized 80% weight solid electrolyte
- Achieved greater conductance at 7.5 mg cm^{-2} than pure solid electrolyte

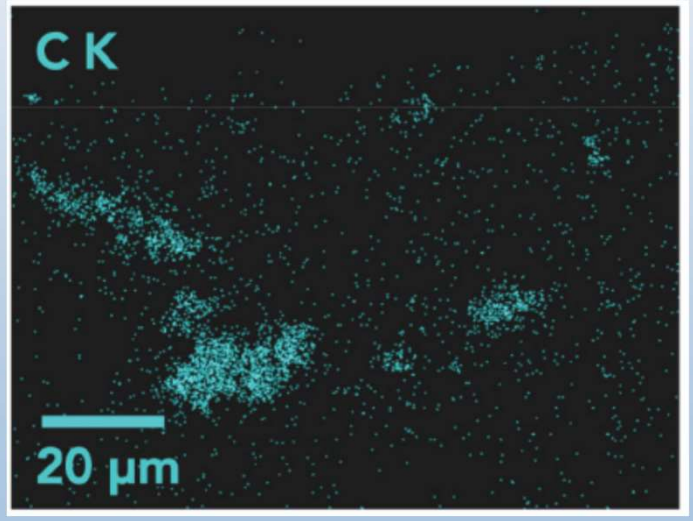


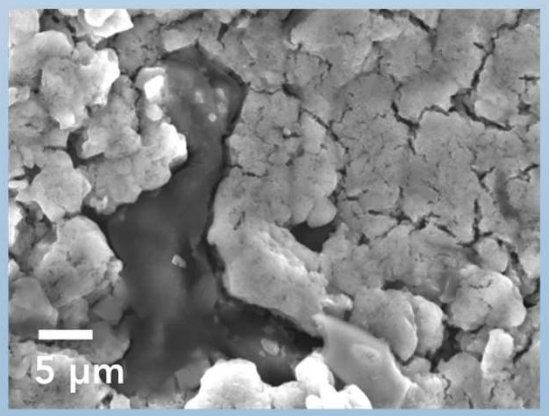
Composite Membrane

- SEPMs developed less than 100 um
- Observed well-dispersed polyimine with EDS
- Intimate contact of polyimine with sulfide solid electrolyte



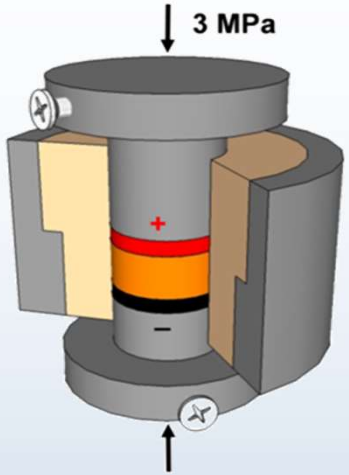


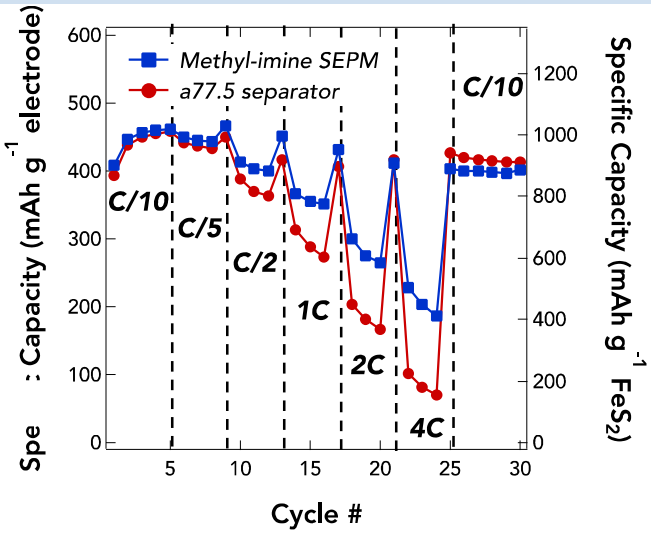


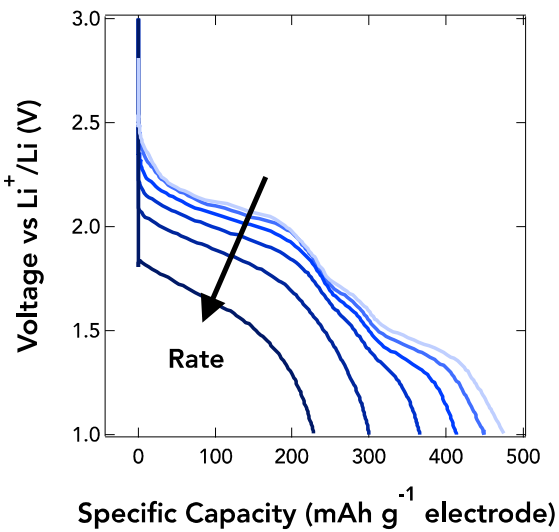


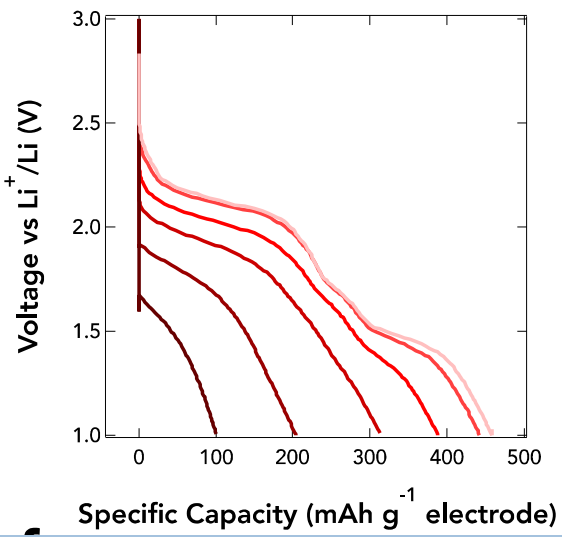
Rate Study

- **FeS_2-based cathode** mounted on top of SEPM
- Rate study performed from C/10 to 4C (15 min charge/discharge)
- Enhanced cycling apparent from lower ohmic overpotential



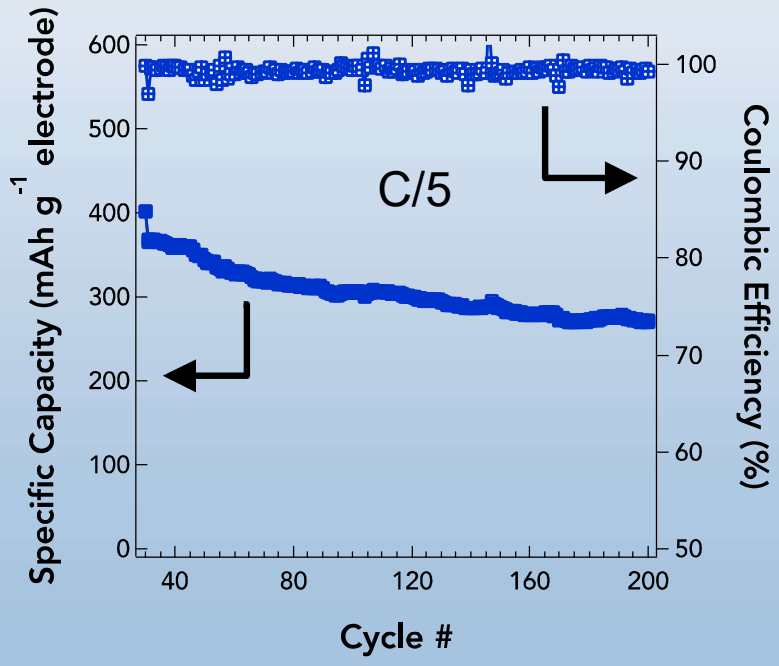


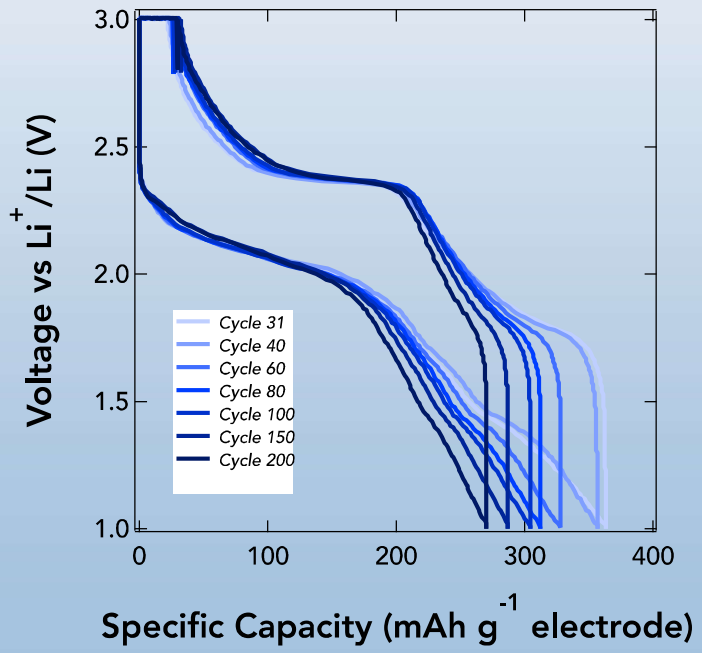




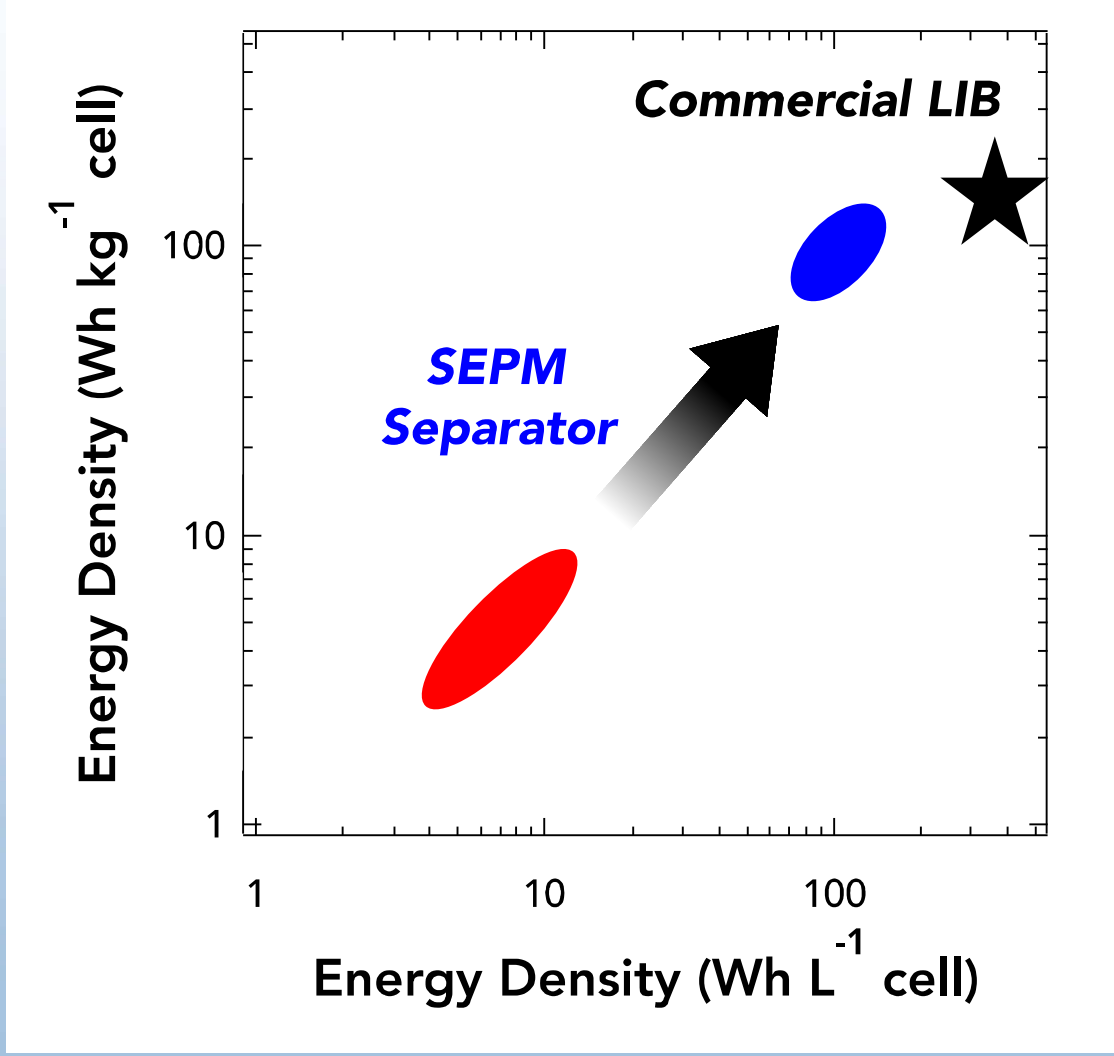
Long-term Cycling

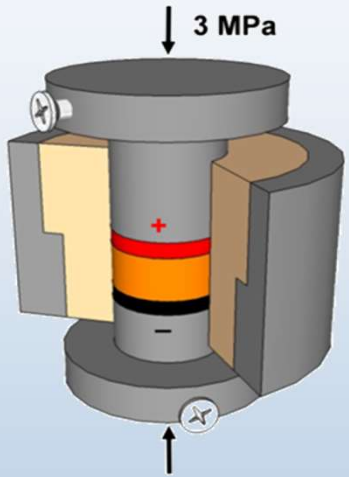
- Successful cycling of FeS_2-based cell for over 200 cycles
- Longest bulk solid-state FeS_2 cell reported to date!
- Degradation appears to be attributed to FeS_2 not loss of separator





Composite Membrane





Future Work

1. Lower crosslinked polyimine and cryogenic ball milling
2. Slurry coating of the SEPM
3. Li metal anode (electrochemical stability against SEPM)
4. High capacity cathode optimization

Thank you very much!

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