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### **Flow Battery Membrane**

#### Energy Storage Systems Program (ESS) Peer Review and Update Meeting 2012

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#### Vanadium redox batteries (VRB) for energy storage require improved ionselective membranes.

- Vanadium permeation across current membranes leads to self-discharge and decreases cycling efficiency:
  - Negative half cell:  $V^{2+} \leftrightarrow V^{3+} + e^{-}$   $E_0 = -0.255V$
  - Positive half cell:  $e^- + VO_2^+ + 2H^+ \leftrightarrow VO^{2+} + H_2O$   $E_0 = 1.00V$ .
- Current perfluorosulfonic acid polymer membranes are costly.
- TIAX is developing a novel composite bipolar membrane:
  - Composite anionic membrane minimizes content of costly perfluorosulfonic acid polymer
  - Made bipolar by a cationic surface layer to improve selectivity for monovalent protons over larger, poly-cationic vanadium species
- TIAX has completed a Phase I SBIR program
  - contract # DE-SC0006457



The bipolar composite membrane is designed to maximize selectivity for proton conductance while minimizing vanadium permeation and content of costly perfluorosulfonic acid polymer (PFSA).





We have achieved a >10X increase in vanadium rejection with no proton conductance sacrifice, a >100X increase in vanadium rejection with modest proton conductance loss, and >90% reduction in content of costly PFSA.

Proton Conductance and Vanadium Rejection Results					
Membrane	VO <sup>2+</sup> Permeation moles/cm <sup>2</sup> /day	Proton area specific resistance: ohm∙cm²	Vanadium Rejection: Ratio to Nafion 117	Thickness: microns	PFSA content: mg/cm <sup>2</sup>
Bipolar 117	6.0 X 10 <sup>-6</sup>	0.30	32X	180-185	18
Composite	5.0 X 10 <sup>-6</sup>	0.30	38X	19-20	1.2
Composite Bipolar	3.95 X 10 <sup>-7</sup>	0.83	480X	19-20	1.2
Nafion 117 control	1.9 X10 <sup>-4</sup>	0.29	1X	180-185	18



# We monitor selectivity ratio = (test membrane ratio of proton conductance to vanadium permeation)/(Nafion membrane ratio of proton conductance to vanadium permeation).





Phase I results show very favorable permeability characteristics, with chemical stability and electrochemical performance remaining to be assessed.

- Very promising results to date:
  - Bipolar modification of Nafion 117 achieved 32X reduction in vanadium permeation with no loss of proton conductance.
  - Composite membrane achieved 38X reduction in vanadium permeation and 93% reduction in PFSA content with no loss of proton conductance relative to Nafion 117.
  - Bipolar composite membrane achieved 480X reduction in vanadium permeation and 93% reduction in PFSA content relative to Nafion 117, with proton conductance 35% of Nafion's.
- Important questions remaining to be investigated:
  - Membrane oxidative stability/durability (VO<sub>2</sub><sup>+</sup> exposure)
  - Permeability to monovalent  $VO_2^+$  ions
  - VRB performance measurements

