Development of High Performance Redox Flow Batteries at PNNL

A DOE Office of Electricity Delivery and Energy Reliability

Energy Storage Program (Manager: Dr. Imre Gyuk)

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DOE OE Program Review
San Diego, CA, Oct. 21, 2011

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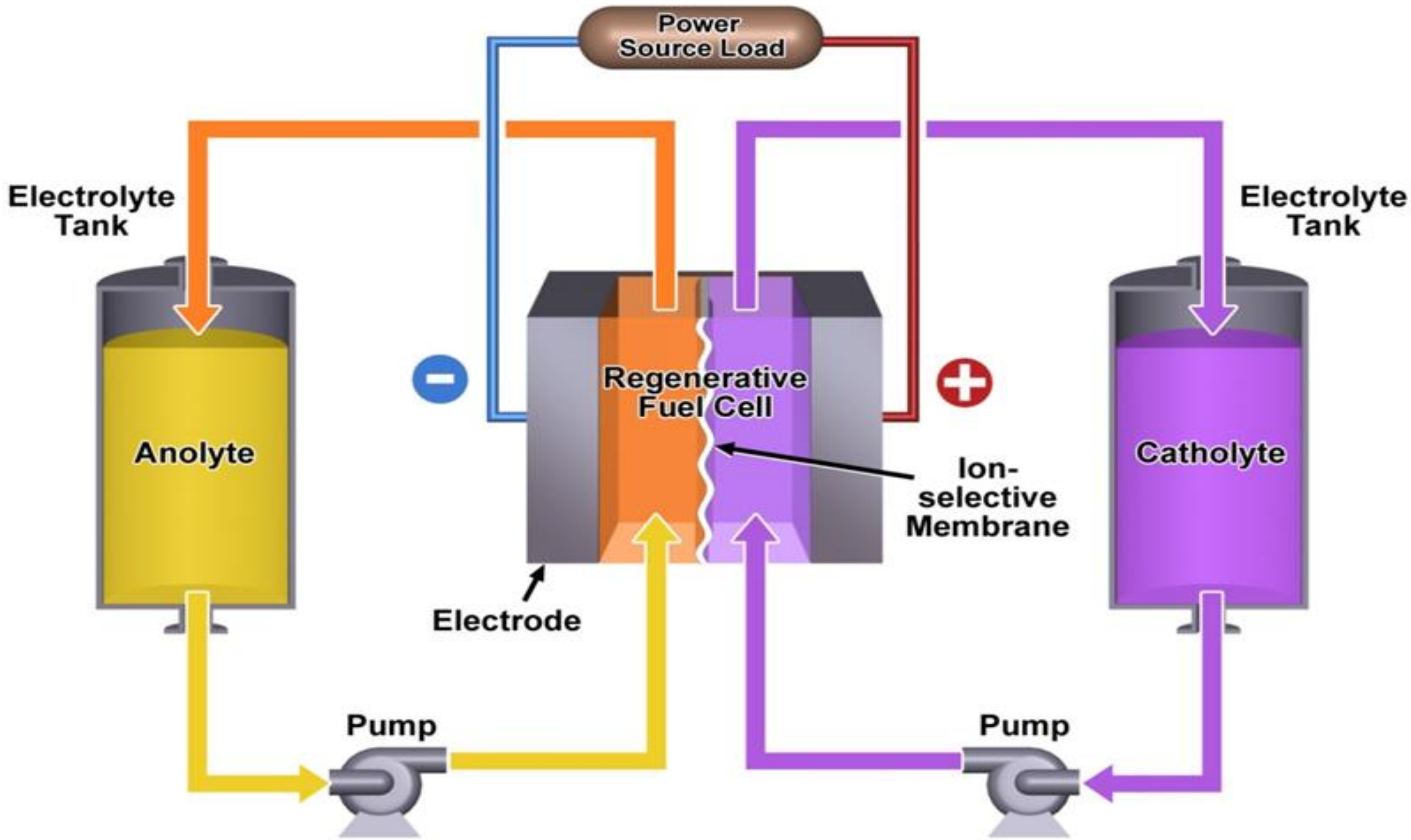
Redox Flow Battery (RFB)



- Redox flow battery is a promising technology for large to medium scale renewable and grid energy storage: active heat management, low self discharge, low maintenance, long life-time, and independent tunable power and storage capacity.

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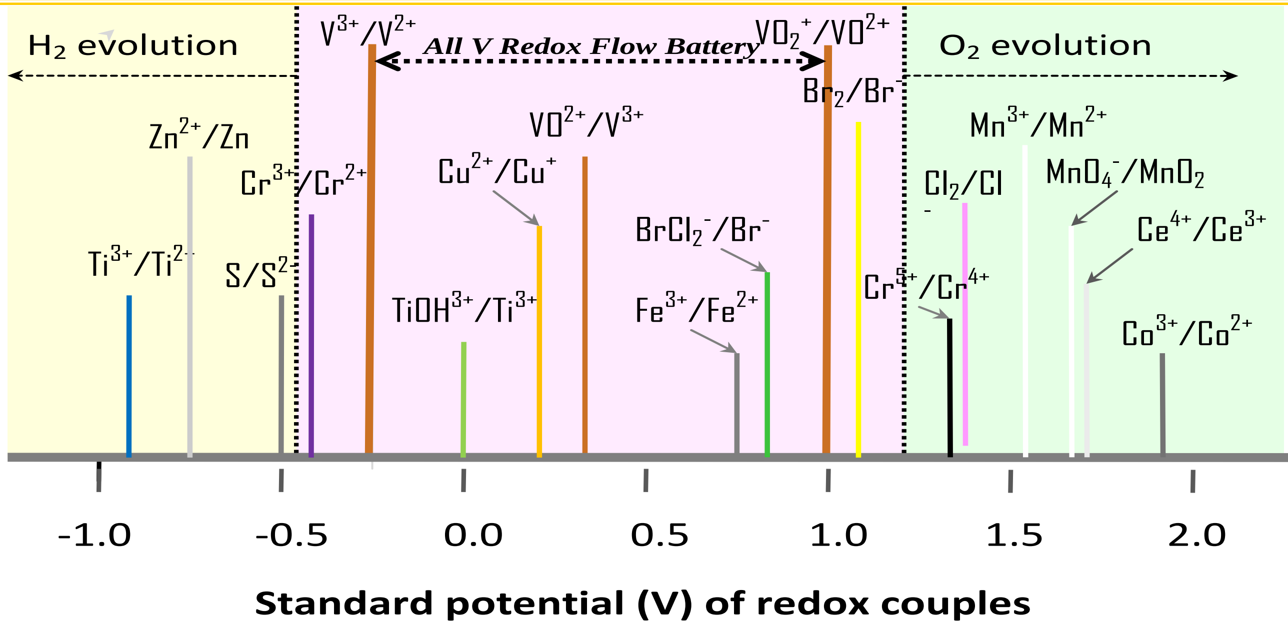
Challenges for RFB Technologies



- Fe-Cr chloride system
  - Safety issue (H_2 generation)
  - Elevated operation temperatures (40-60 ^oC)
  - Use of expensive catalysts for Cr^{2+}-Cr^{3+} reaction.
  - Low energy density ([Fe,Cr] ~1.25M; <10 Whr/L)
  - Low cost (Fe, Cr cost, and separator cost)
- All vanadium sulfate system
  - Energy density ([V]< 1.7 M; <20 Whr/L)
  - Narrow operation temperature window (10-40^oC)
  - High cost (V cost, and membrane cost)

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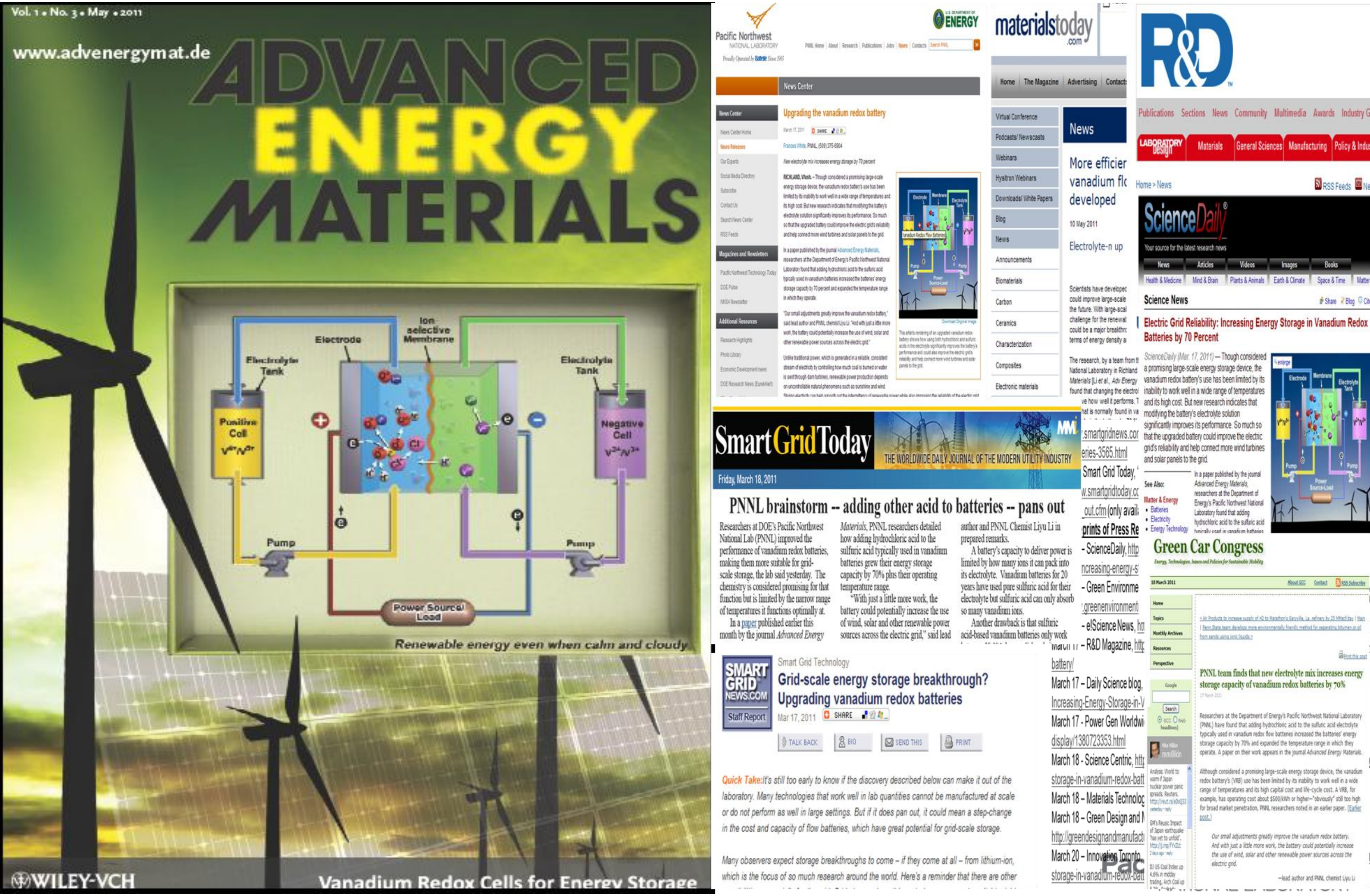
Accomplishments

- Developed New $V^{2+/3+}$ - $Fe^{2+/3+}$ systems
  - Energy density as good as current VRB system
  - Wide operation temperature window (0-60 ^{o}C)
  - Reduced membrane cost by using hydrocarbon separator (~1% of Nafion membrane)
  - No hydrogen evolution or V_2O_5 precipitation

- Developed Advanced $V^{2+/3+}$ - $V^{4+/5+}$ systems
  - 100% increase in energy density vs. current VRB.
    - Less space requirement
    - Less balance-of-plant cost
  - Wide operation temperature window (0-60 ^{o}C).
    - No active cooling/heating required
    - Less parasitic energy loss
    - Less equipment cost

More than 100 Related Media Coverage about PNNL's Redox Battery Progress



Some publications and intellectual properties

- W. Wang, Z. Nie, B. Chen, F. Chen, Q. Luo, G. Xia, M. Skyllas-Kazacos, Liyu Li, Zhenguo Yang, "A New Fe/V Redox Flow Battery Using Sulfuric/Chloric Mixed-Acid Supporting Electrolyte", *Advanced Energy Materials* (submitted, **2011**)
- S. Kim, M. Vijayakumar, Wei Wang, Jianlu Zhang, Baowei Chen, Zimin Nie, Feng Chen, Jianzhi Hu, Liyu Li and Zhenguo Yang, "Chloride Supporting Electrolytes for All Vanadium Redox Flow Batteries", *Phys. Chem. Chem. Phys.,* DOI:10.1039/C1CP22638J. (**2011)**.
- Liyu Li, S. Kim, W. Wang, V. Murugesan, Z. Nie, B. Chen, J. Zhang, G. Xia, J. Hu, G. Graff, J. Liu, and Z. Yang, "A Stable Vanadium Redox Flow Battery with High Energy Density for Large-scale Energy Storage", *Advanced Energy Materials, **2011**, **1**, 394-400.*
- B. Schwenzer, J. Zhang, S. Kim, Liyu Li, J. Liu, and Z. Yang, "Membrane Development for Vanadium Redox Flow Batteries (VRFB)", *CHEMSUSCHEM* (10.1002/cssc.201100068) (**2011)**.
- J. Zhang, Liyu Li, Z. Nie, B. Chen, M. Vijayakumar, S. Kim, W. Wang, B. Schwenzer, J. Liu, Z. Yang, "Effects of Additives on the Stability of Electrolytes for All-Vanadium Redox Flow Batteries", *Journal of Applied Electrochemistry, DOI 10.1007/s10800-011-031201.* ***(2011)***
- W. Wang, S. Kim, J. Zhang, B. Chen, Z. Nie, G. Xia, Liyu Li, and Z. Yang*, "Investigation on the Fe/V Redox Flow Batteries for Stationary Energy Storage", *Energy and Environmental Science*, DOI: 10.1039/c0ee00765j. (**2011)**
- M. Vijayakumar, Liyu Li, Z. Yang, G.L. Graff, J. Liu, H. Zhang, and J.Z. Hu. "Towards Understanding the Poor Thermodynamic Stability of V5+ Electrolyte Solution in Vanadium Redox Flow Batteries". *Journal of Power Sources* **2010**, 196, 3669-3673.
- S. Kim, J. Yan, B. Schwenzer, J. Zhang, Liyu Li, J. Liu, Z. Yang, M.A. Hickner, "Cycling Performance and Efficiency of Sulfonated Poly(sulfone) Membranes in Vanadium Redox Flow Batteries", *Electrochemistry Communications,* **2010** **12**(11): 1650-1653**.**
- M. Vijayakumar, S.D. Burton, C. Huang, Liyu Li, Z. Yang, G. L. Graff, J. Liu, J. Hu, M. Skyllas-Kazacos, "Nuclear Magnetic Resonance Studies on Vanadium(IV) Electrolyte Solutions for Vanadium Redox Flow Battery", *Journal of Power Sources,* **2010, 195**: 7709–7717**.**
- B. Schwenzer, S. Kim, M. Vijaykumar, Z. G. Yang, J. Liu, Correlation of structural differences between Nafion/polyaniline and Nafion/polypyrrole composite membranes and observed transport properties, *Journal of Membrane Science* **2011***,* **372** (1-2): 11-19.
- M. Vijayakumar, M.S. Bhuvaneswari, P. Nachimuthu, B. Schwenzer, S. Kim, Z. G. Yang, J. Liu, G. L. Graff, S. Thevuthasan, J. Z. Hu, "Spectroscopic investigations of the fouling process on Nafion membranes in vanadium redox flow batteries", *Journal of Membrane Science,* **2011***,* **366 (1-2):** 325-334..
- Li, Liyu; Kim, Soowhan; Yang, Z Gary; Zhang, Jianlu; Wang, Wei; Nie, Zimin; Chen, Baowei; Xia, Gordon. "Fe-V Redox Flow Batteries". US patent application filed (9/**2010**). WO patent application filed (6/**2011**)
- Li, Liyu; Kim, Soowhan; Yang, Z Gary; Zhang, Jianlu; Wang, Wei; Nie, Zimin; Chen, Baowei; Xia, Gordon. "Redox Flow Batteries Based on Supporting Solutions Containing Chloride". US patent application filed (9/**2010**). WO patent application filed (6/**2011**)
- G. Xia, G.Z. Yang, Liyu Li, S. Kim, J. Liu, and G. Graff. "A Novel Iron-polysulfide Redox Flow Battery System". US Patent Application filed (3/**2011**).
- W. Wang, Liyu Li**,** Z. Nie, G. Z. Yang, **"**Hybrid Fe/V Flow Battery". US Patent Application filed (9/**2011**)
- More than 20 presentations at scientific conferences.

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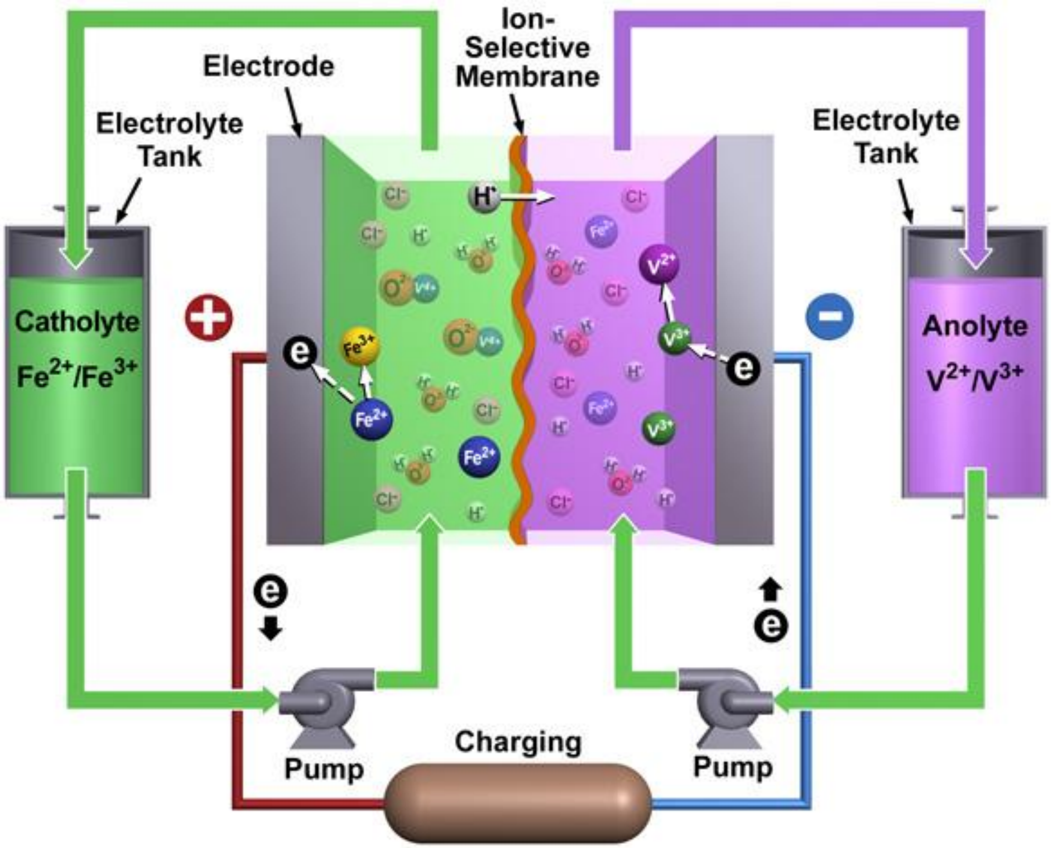
V - Fe Redox Flow Battery



Catholyte: $Fe^{2+} - e$ $\underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}}$ Fe^{3+}

Anolyte: $V^{3+} + e$ $\underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}}$ V^{2+}

Overall: $Fe^{2+} + V^{3+}$ $\underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}}$ $Fe^{3+} + V^{2+}$

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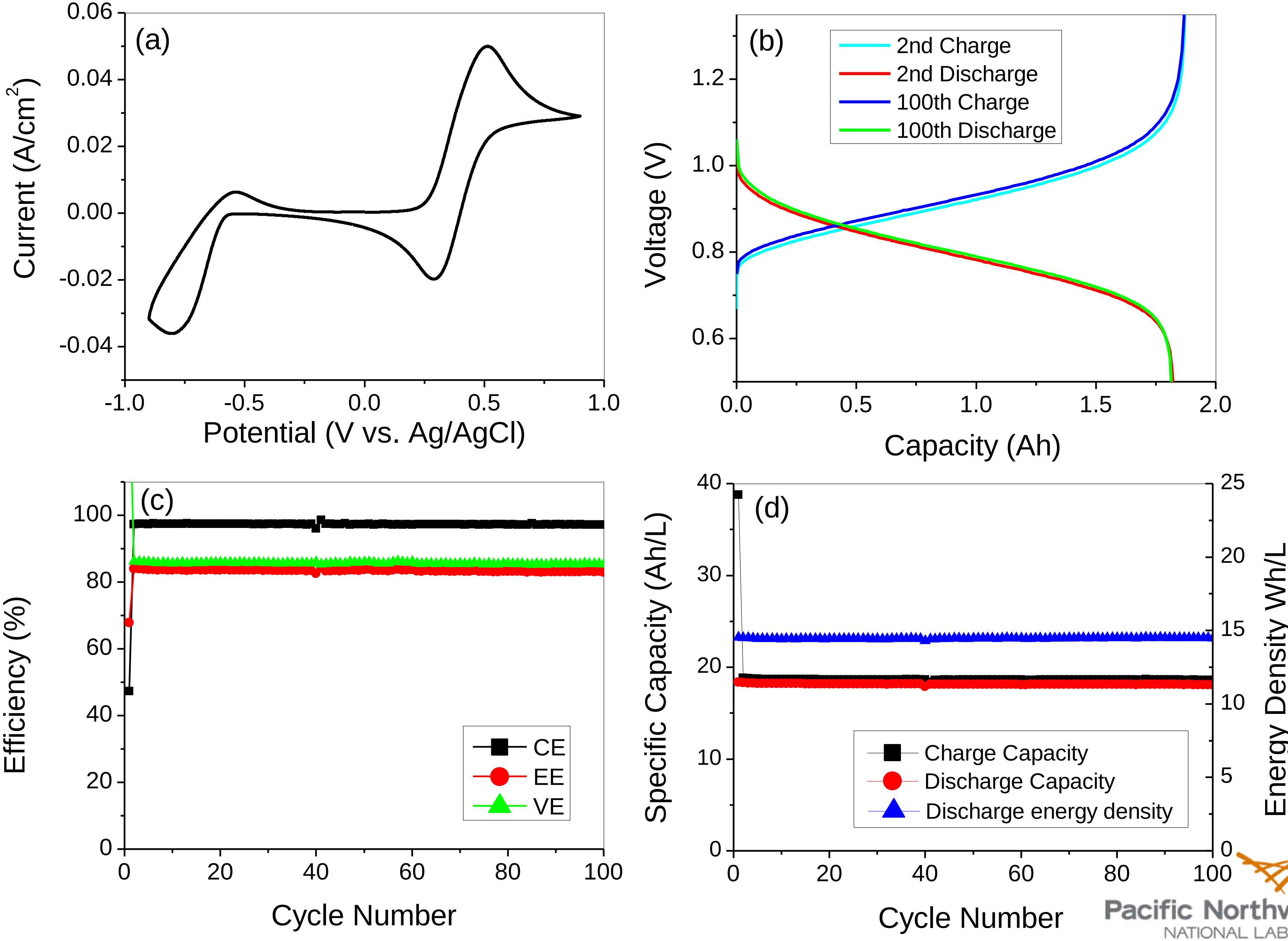
Performance of Fe/V Redox Flow Battery



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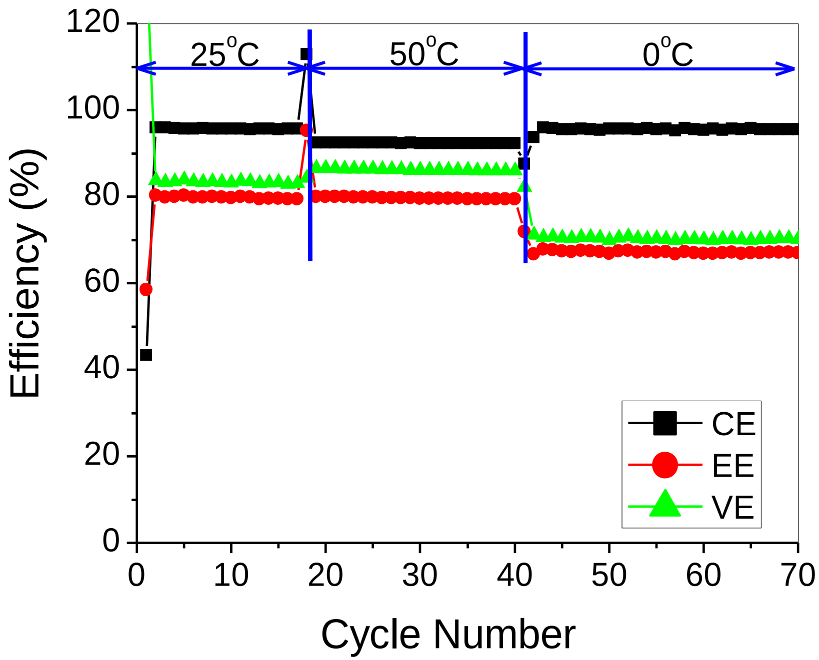
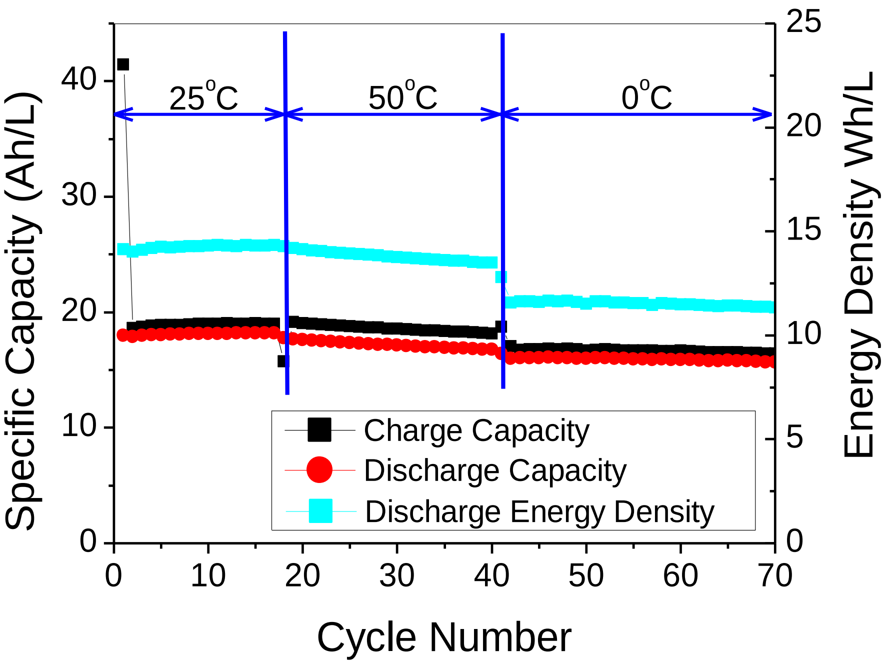
Operating Fe-V Battery at Different Temperatures

1.5M Fe/V mixed acid solution with Nafion membrane





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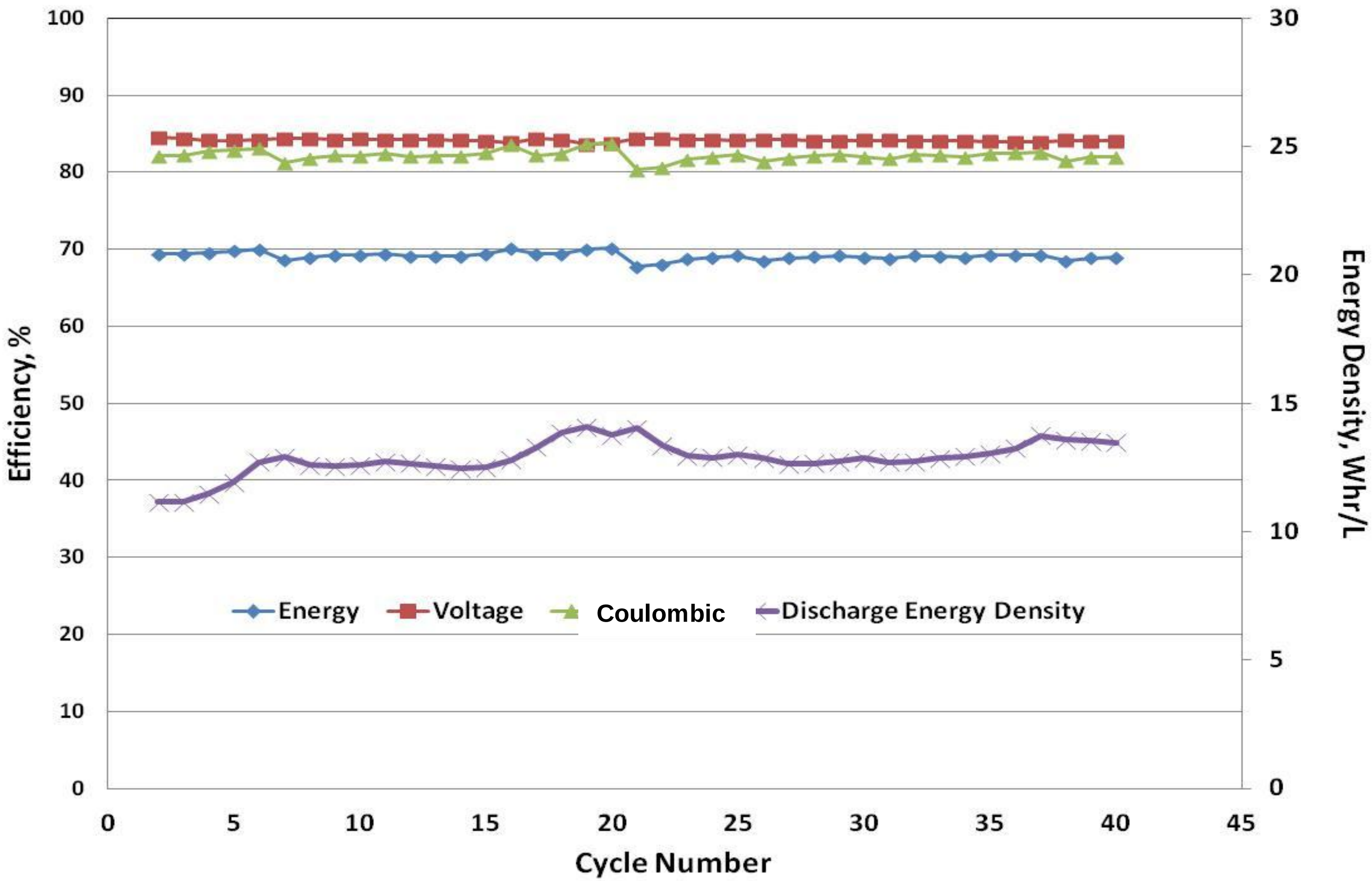
Performance of Fe/V Battery with Hydrocarbon Separator (~1% cost of Nafion membrane)



1.5M Fe/V mixed acid solution, no capacity loss, 50 mA/cm^2.

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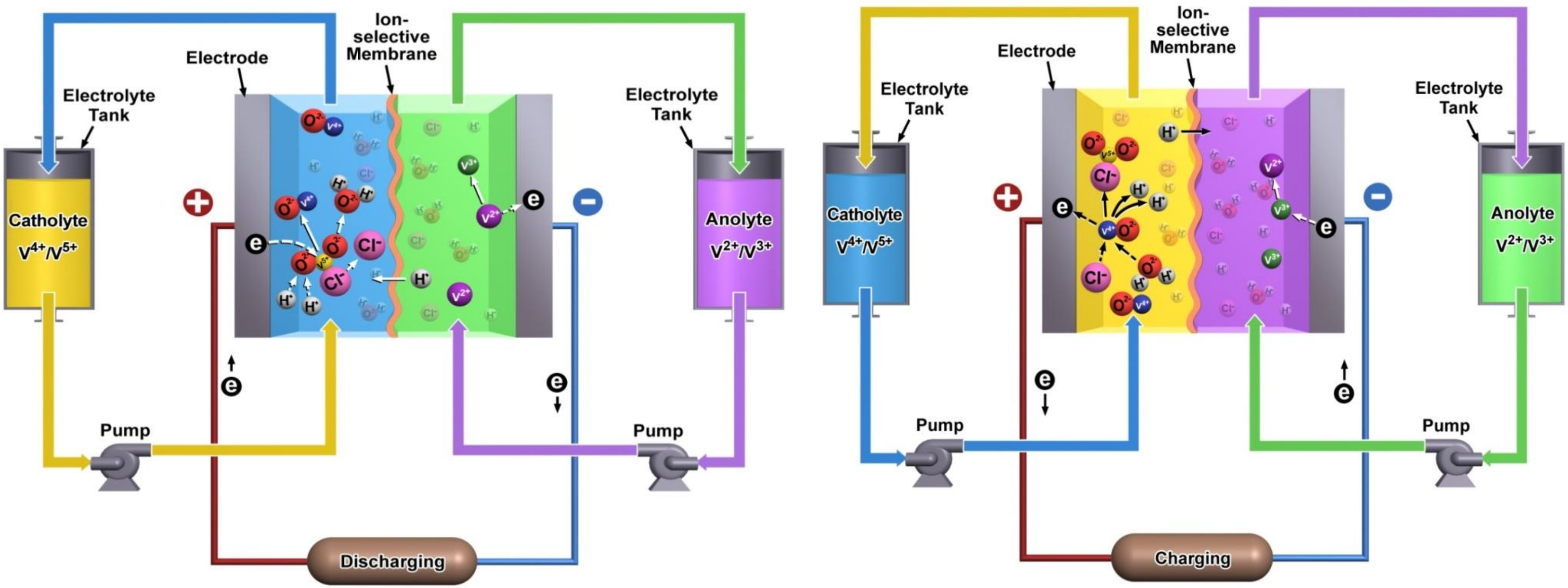
All Vanadium Mixed Acid Redox Flow Battery



Catholyte: $VO^{2+} + Cl^{-} + H_2O - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^{+}$

Anolyte: $V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$

Overall: $VO^{2+} + Cl^{-} + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^{+} + V^{2+}$

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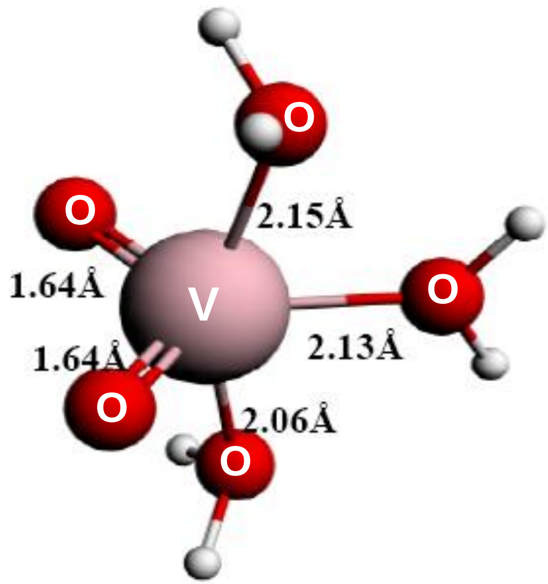
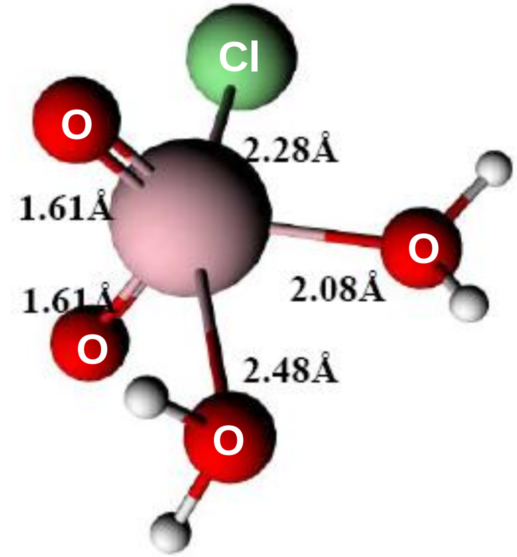
Solution Chemistry of the Mixed Acid Electrolytes



V^{5+} in Sulfuric Acid



V^{5+} in Mixed Acid

- In sulfate solution, V^{5+} exists as $[VO_2(H_2O)_3]^+$, which tends to convert to V_2O_5-$3H_2O$ precipitation via:

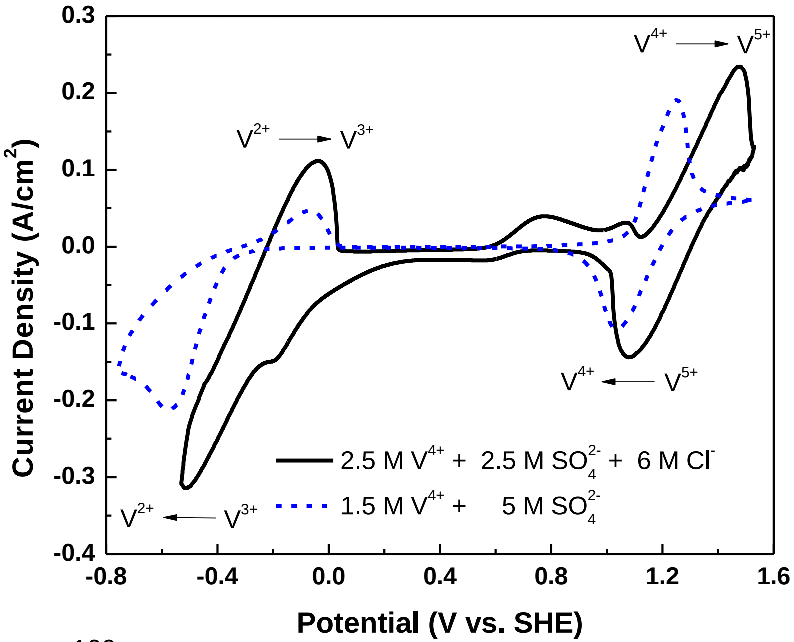
  $[VO_2(H_2O)_3]^+ \rightarrow VO(OH)_3 + [H_3O]^+$

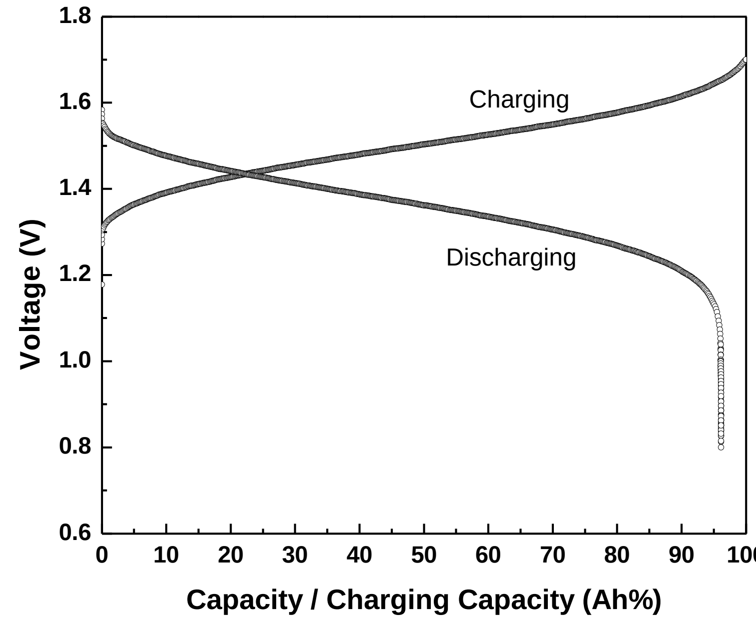
  $2VO(OH)_3 \rightarrow V_2O_5\text{-}3H_2O \downarrow$

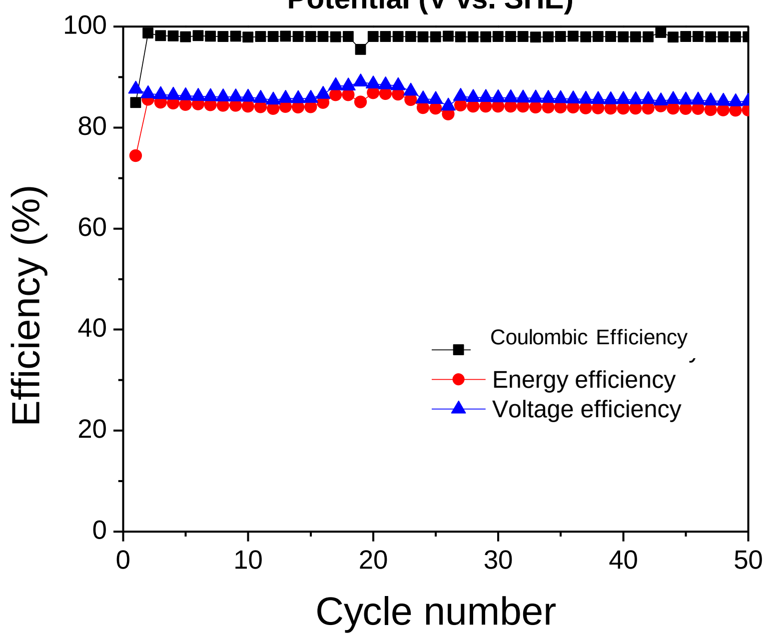
- In the mixed sulfate-chloride solution, a stable neutral specie, $VO_2Cl(H_2O)_2$, forms via:

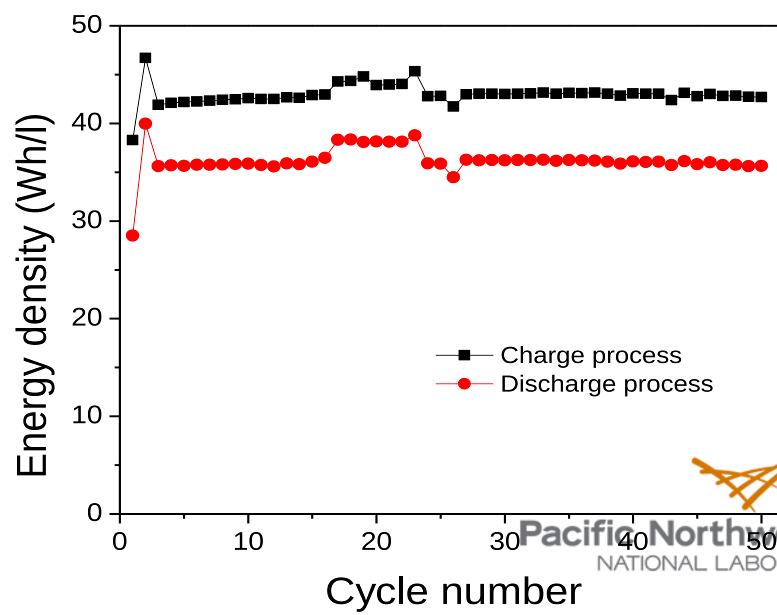
  $[VO_2(H_2O)_3]^+ + HCl \leftrightarrow VO_2Cl(H_2O)_2 + [H_3O]^+ \qquad \Delta H > 0$

Performance of Vanadium Mixed Acid Battery









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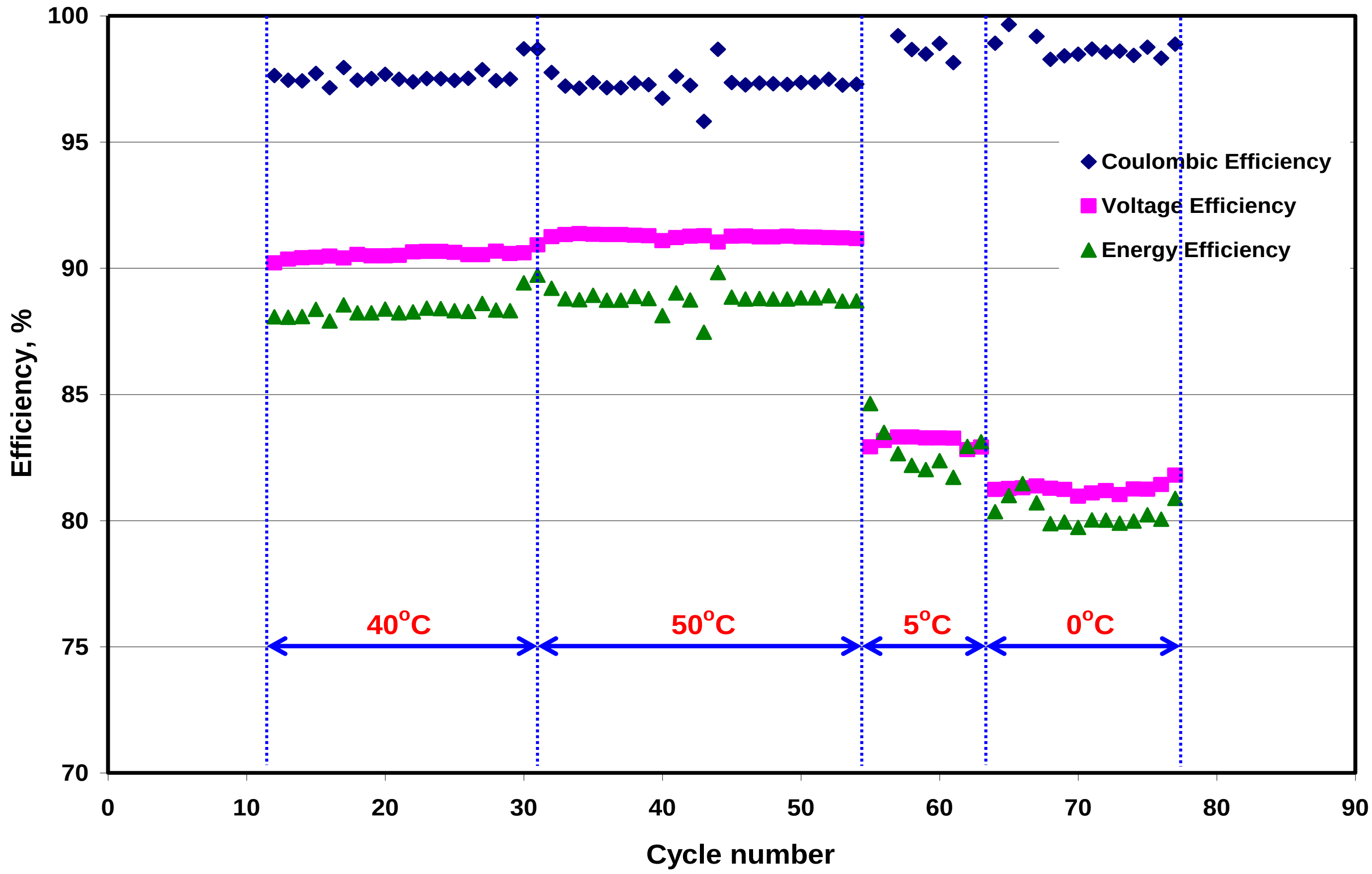
Cell Performance at Varied Temperatures



- A VFB with 2.5 M V mixed acid electrolyte can be operated under a broad temperature range of 0 to 50 °C.
- Redox reactions are temperature dependent.
- No noticeable gas evolution over 25 days.

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Development of New Redox Flow Battery Systems at PNNL

Redox flow batteries		All vanadium sulfate V^{5+}/V^{4+} vs. V^{2+}/V^{3+}	Fe/Cr chloride Fe^{3+}/Fe^{2+} vs. Cr^{2+}/Cr^{3+}	PNNL Fe/V system Fe^{3+}/Fe^{2+} vs. V^{2+}/V^{3+}	PNNL All Vanadium V^{5+}/V^{4+} vs. V^{2+}/V^{3+}
Redox reactions	Positive	$VO_2^{+}+2H^{+}+e=VO^{2+}+H_2O$, 1.0V	$Fe^{3+}+e=Fe^{2+}$ 0.77V	$Fe^{3+}+e=Fe^{2+}$ 0.77V	$VO_2^{+}+2H^{+}+e=VO^{2+}+H_2O$ 1.0V
	Negative	$V^{2+} - e = V^{3+}$ -0.25V	$Cr^{2+}=Cr^{3+} -e$ -0.41V	$V^{2+}=V^{3+} -e$ -0.25V	$V^{2+} - e = V^{3+}$ -0.25V
Voltage	Theoretical	1.0 V-(0.25V)=1.25 V	0.77V – (-0.41V) = 1.18 V	0.77V – (-0.25V) = 1.02 V	1.0 V-(0.25V)=1.25 V
Membrane		Ion exchange Nafion	Ion exchange or micro porous	Ion exchange or micro porous	Ion exchange Nafion
Electrolyte	Catholyte Anolyte	1.5M $VOSO_4$ 1.5M $V(SO_4)_{1.5}$	1.25M$FeCl_2$ + 1.25M$CrCl_3$ 1.25M$FeCl_2$ + 1.25M$CrCl_3$	1.75M Fe/1.75M V 1.75M Fe/1.75M V	2.5M V^{4+}/V^{5+} 2.5M V^{2+}/V^{3+}
Energy Efficiency		~85%	~70%	70~80%	~85%
Current Density		50 mA.cm^{-2}	50 mA.cm^{-2}	50mA.cm^{-2}	50 mA.cm^{-2}
Depth of charge or discharge		20% - 80%	20% -80%	10% - 90%	15% -85%
Fuel utilization		~60%	~60%	~80%	~70%
Energy density	100%	27 Wh.L^{-1}	15 Wh.L^{-1}	19 Wh.L^{-1}	45 Wh.L^{-1}
	Practical	~16 Wh.L^{-1}	~9 Wh.L^{-1}	~15 Wh.L^{-1}	~32 Wh.L^{-1}
Operation ^{o}C		10—40 ^{o}C	40-60^{o}C	0 to 60^{o}C	0-60 ^{o}C
Other major disadvantages			H_2 evolution at anode. Catalyst needed at anode.		

Future Work

- Demonstrate a 5.0 kWh (1.0 kW) bench-top prototype FRB with the newly developed electrolytes.
- Build up strong collaborations with industry, university, and other national laboratory partners.
- Prepare for large system demonstrations (1 MW-hr) within 2-3 years.

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