

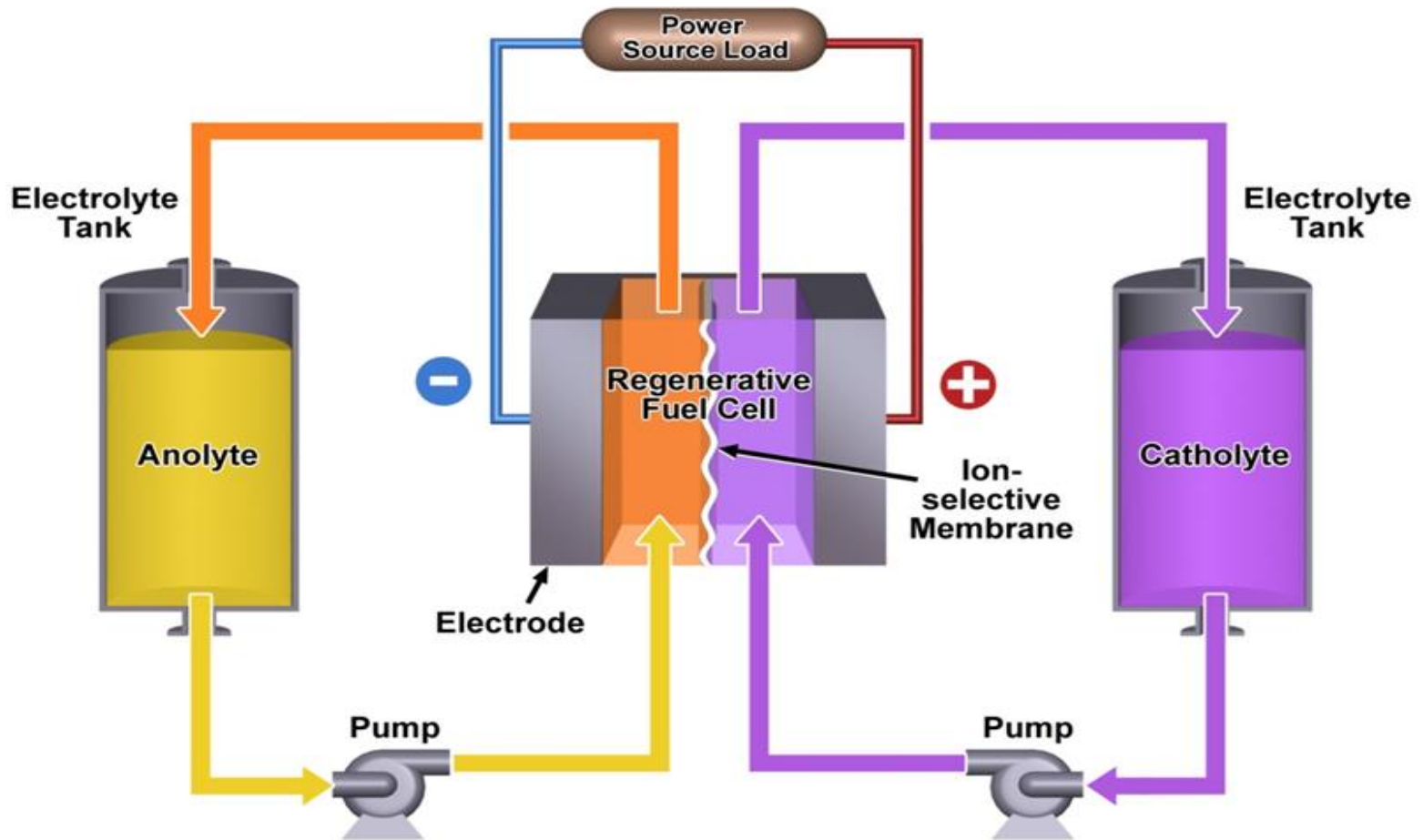
Development of High Performance Redox Flow Batteries at PNNL

A DOE Office of Electricity Delivery and Energy Reliability
Energy Storage Program (Manager: Dr. Imre Gyuk)

Liyu Li, Wei Wang, Zimin Nie, Qingtao Luo, Baowei Chen, M. Vijayakumar, Xiaoliang Wei, Feng Chen, Soowhan Kim, V. Viswanathan, Yuyan Shao, Gordon Xia, Gary Maupin, Dean Matson, Gregrey Coffey, Jianzhi Hu, Gordon Graff, Jun Liu, Gary Z. Yang

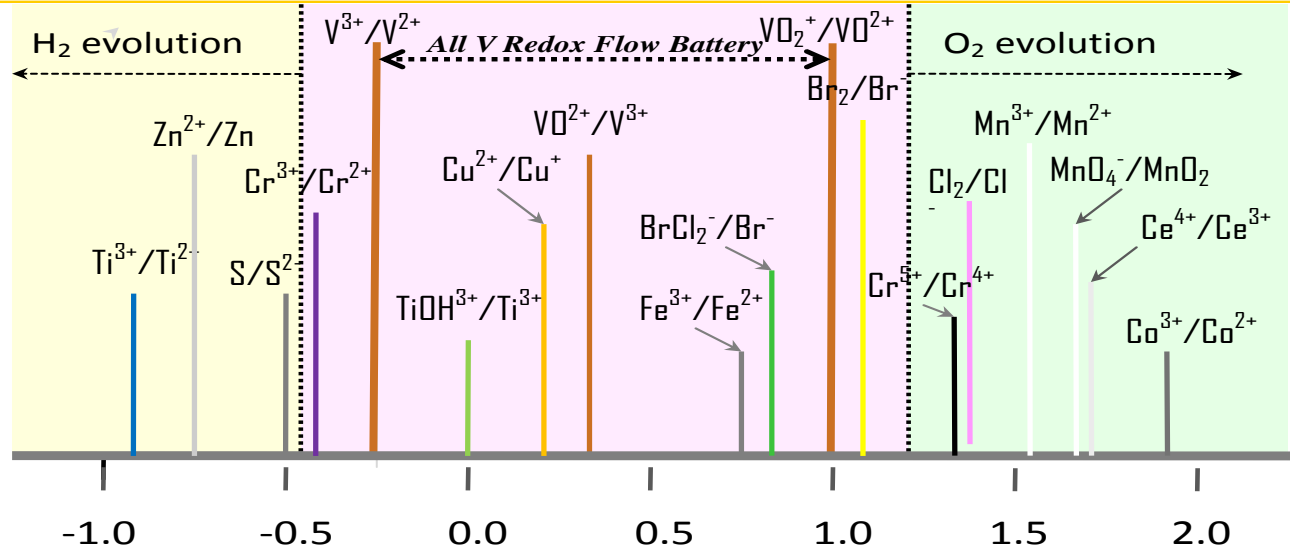
DOE OE Program Review
San Diego, CA, Oct. 21, 2011

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.

Challenges for RFB Technologies



Standard potential (V) of redox couples

► Fe-Cr chloride system

- Safety issue (H₂ generation)
- Elevated operation temperatures (40-60 °C)
- Use of expensive catalysts for Cr²⁺-Cr³⁺ 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°C)
- High cost (V cost, and membrane cost)

Accomplishments

▶ Developed **New $V^{2+/3+}$ - $Fe^{2+/3+}$ systems**

- Energy density as good as current VRB system
- Wide operation temperature window (0-60 °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 °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

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New electrolyte mix increases energy storage by 70 percent

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Reactions and Revisions
In a paper published by the journal *Advanced Energy Materials*, researchers at the Department of Energy's Pacific Northwest National Laboratory found that adding hydrochloric acid to the sulfuric acid typically used in vanadium batteries increased the battery's energy storage capacity by 70 percent and expanded the temperature range in which they operate.

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Keynote
"Our small adjustments greatly improve the vanadium redox battery." said lead author and PNNL chemist Liyu Li. "Not only will this new work, the battery could potentially increase the use of wind, solar and other renewable power sources across the electric grid."

Additional Resources
Under traditional power, which is generated in a reliable, consistent stream of electricity by burning how much coal is burned or water in a geothermal dam system, renewable power production depends on an unpredictable natural phenomenon such as a gusty wind or a sunny day.

Additional Resources
Renewable energy is not just about the abundance of clean energy, it's also about the reliability of the delivery and

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More efficient vanadium flow developed

10 May 2011

Electrolyte-n-up

Scientists have developed a new electrolyte solution that could improve large-scale energy storage. With large-scale challenge for the renewable energy future, the vanadium redox battery's use has been limited by its high cost. But new research indicates that modifying the battery's electrolyte solution significantly improves its performance. So much so that the upgraded battery could improve the electric grid's reliability and help connect more wind turbines and solar panels to the grid.

The research, by a team from the National Laboratory of Energy Research at Pacific Northwest National Laboratory, found that adding hydrochloric acid to the sulfuric acid typically used in vanadium batteries increased the battery's energy storage capacity by 70 percent and expanded the temperature range in which they operate. A paper on their work appears in the journal *Advanced Energy Materials*.

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Electric Grid Reliability: Increasing Energy Storage in Vanadium Redox Batteries by 70 Percent

10 May 2011

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SmartGridToday
THE WORLDWIDE DAILY JOURNAL OF THE MODERN UTILITY INDUSTRY

Friday, March 18, 2011

PNNL brainstorm -- adding other acid to batteries -- pans out

Researchers at DOE's Pacific Northwest National Lab (PNNL) improved the performance of vanadium redox batteries, making them more suitable for grid-scale storage, the lab said yesterday. The chemistry is considered promising for that function but is limited by the narrow range of temperatures it functions optimally at.

In a paper published earlier this month by the journal *Advanced Energy Materials*, PNNL researchers detailed how adding hydrochloric acid to the sulfuric acid typically used in vanadium batteries grew their energy storage capacity by 70% plus their operating temperature range.

"With just a little more work, the battery could potentially increase the use of wind, solar and other renewable power sources across the electric grid," said lead author and PNNL Chemist Liyu Li in prepared remarks.

A battery's capacity to deliver power is limited by how many ions it can pack into its electrolyte. Vanadium batteries for 20 years have used pure sulfuric acid for their electrolyte but sulfuric acid can only absorb so many vanadium ions.

Another drawback is that sulfuric acid-based vanadium batteries only work

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In a paper published by the journal *Advanced Energy Materials*, researchers at the Department of Energy's Pacific Northwest National Laboratory found that adding hydrochloric acid to the sulfuric acid typically used in vanadium batteries increased the battery's energy storage capacity by 70 percent and expanded the temperature range in which they operate. A paper on their work appears in the journal *Advanced Energy Materials*.

Green Car Congress

Energy, Technology, Science and Policy for Sustainable Mobility

March 2011

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440 Studies in Green Energy at 42 in North Carolina, as well as 28 Studies in 15 States (State Dept. Division of Energy Resources), finally, method for separating chlorine at low energy costs (see link)

Post the feed

PNNL team finds that new electrolyte mix increases energy storage capacity of vanadium redox batteries by 70%

17 March 2011

Researchers at the Department of Energy's Pacific Northwest National Laboratory (PNNL) have found that adding hydrochloric acid to the sulfuric acid electrolyte typically used in vanadium redox flow batteries increased the battery's energy storage capacity by 70% and expanded the temperature range in which they operate. A paper on their work appears in the journal *Advanced Energy Materials*.

Although considered a promising large-scale energy storage device, the vanadium redox battery's (VRB) use has been limited by its inability to work well in a wide range of temperatures and its high capital cost and life-cycle cost. A VRB, for example, has operating cost about \$500/kWh or higher—"obviously" still too high for broad market penetration, PNNL researchers noted in an earlier paper. (E&E 305.)

Our small adjustments greatly improve the vanadium redox battery. And with just a little more work, the battery could potentially increase the use of wind, solar and other renewable power sources across the electric grid.

—lead author and PNNL Chemist Liyu Li

Smart Grid Technology

Grid-scale energy storage breakthrough? Upgrading vanadium redox batteries

Mar 17, 2011 SHRE

TALK BACK BIO SEND THIS PRINT

Quick Take: It's still too early to know if the discovery described below can make it out of the laboratory. Many technologies that work well in lab quantities cannot be manufactured at scale or do not perform as well in large settings. But if it does pan out, it could mean a step-change in the cost and capacity of flow batteries, which have great potential for grid-scale storage.

Many observers expect storage breakthroughs to come — if they come at all — from lithium-ion, which is the focus of so much research around the world. Here's a reminder that there are other

March 17 - Daily Science blog, Increasing-Energy-Storage-in-V

March 17 - Power Gen Worldw display/1380723353.html

March 18 - Science Centric, ht storage-in-vanadium-redox-batt

March 18 - Materials Technol

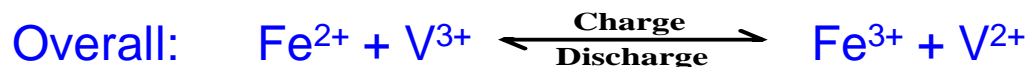
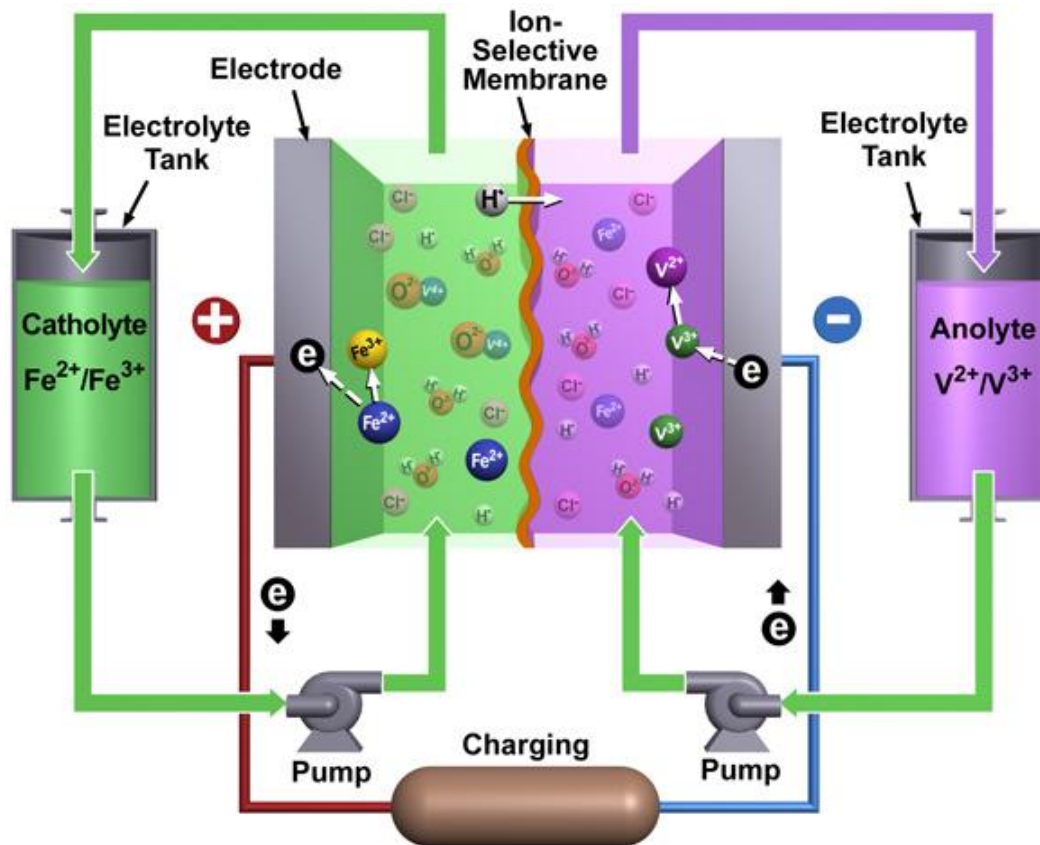
March 18 - Green Design and I http://greendesignandmanufac

March 20 - Innovation Tomor storage-in-vanadium-redox-batt

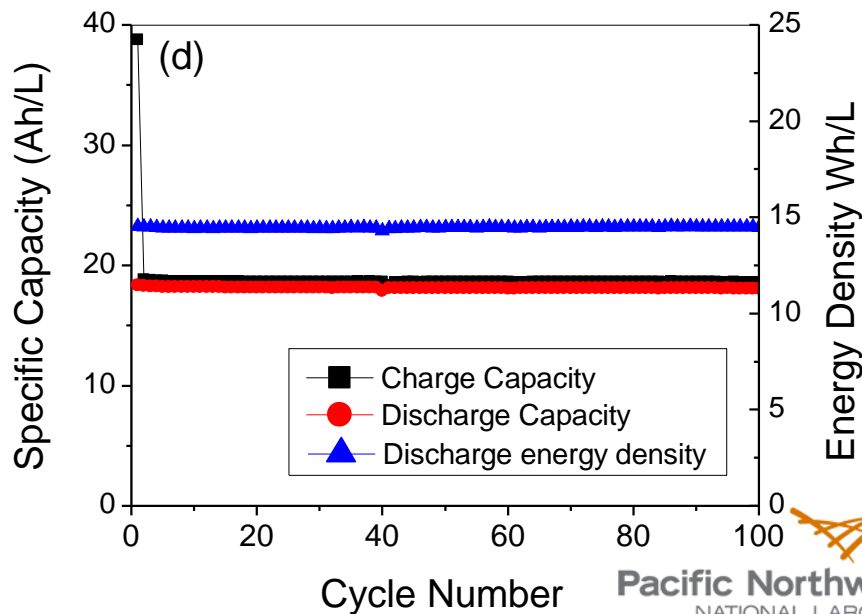
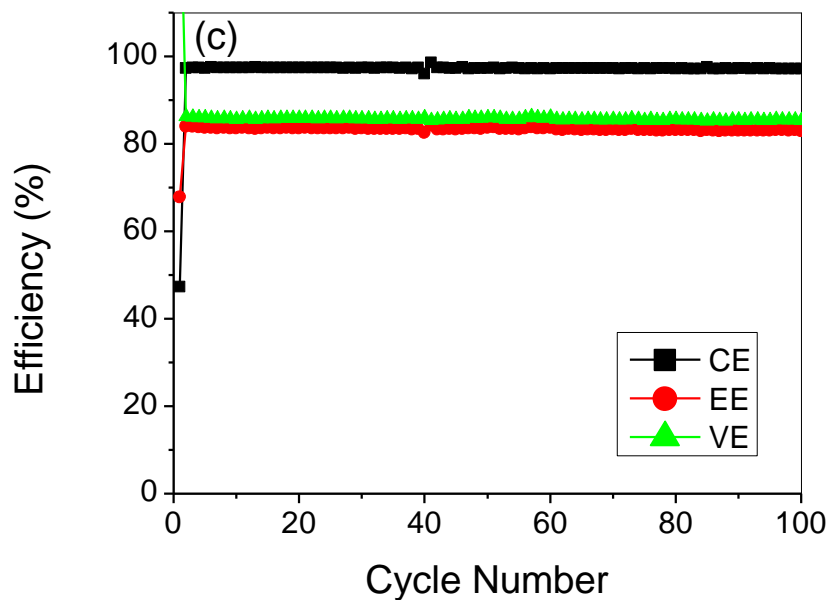
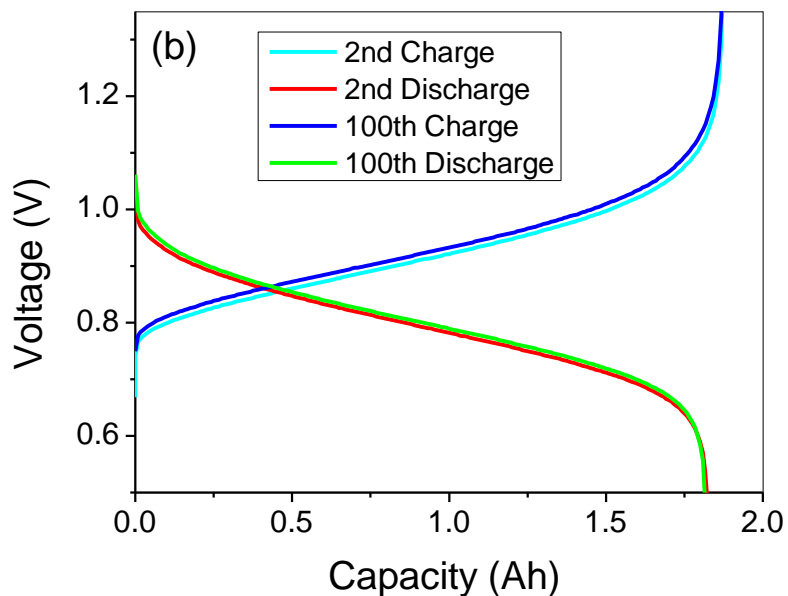
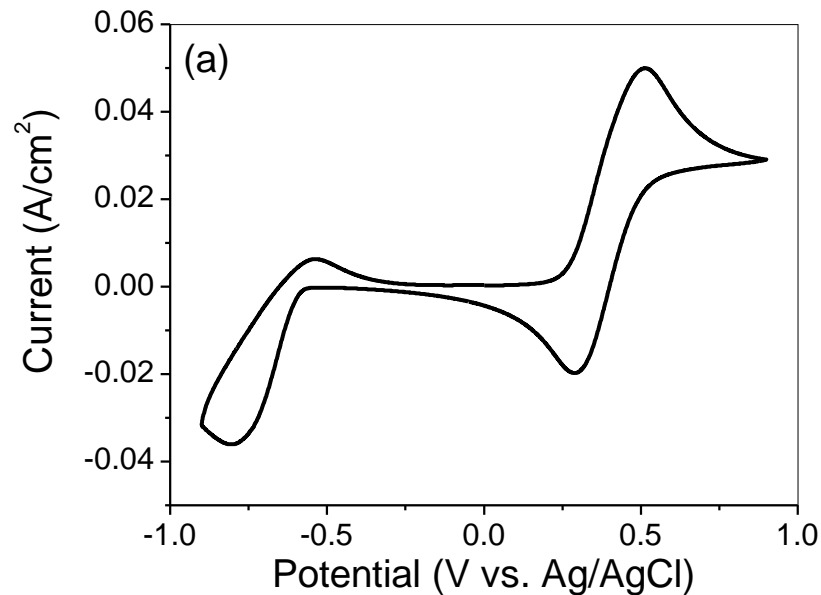
Some publications and intellectual properties

- ▶ 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. Bhuvaneshwari, 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.

V - Fe Redox Flow Battery

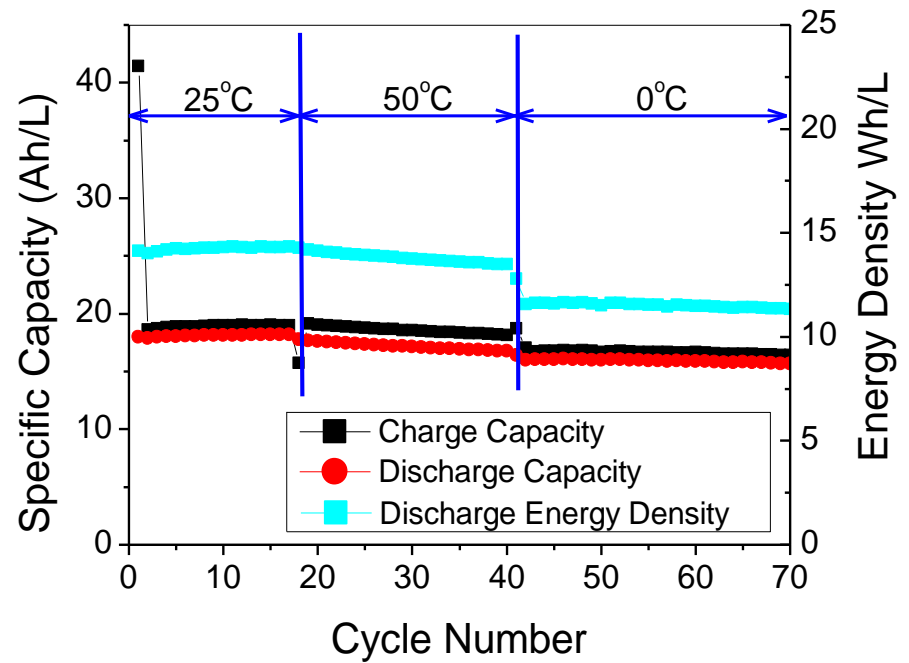
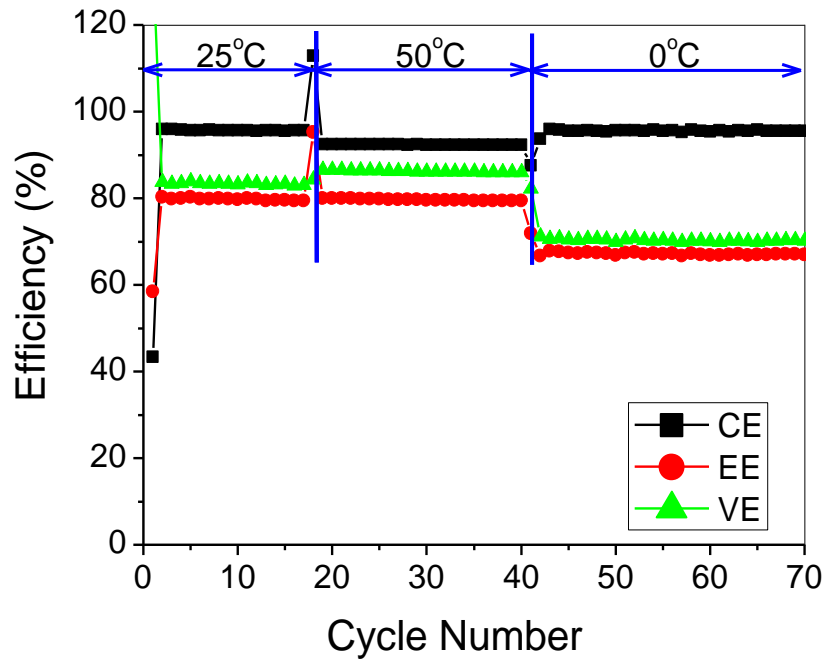


Performance of Fe/V Redox Flow Battery

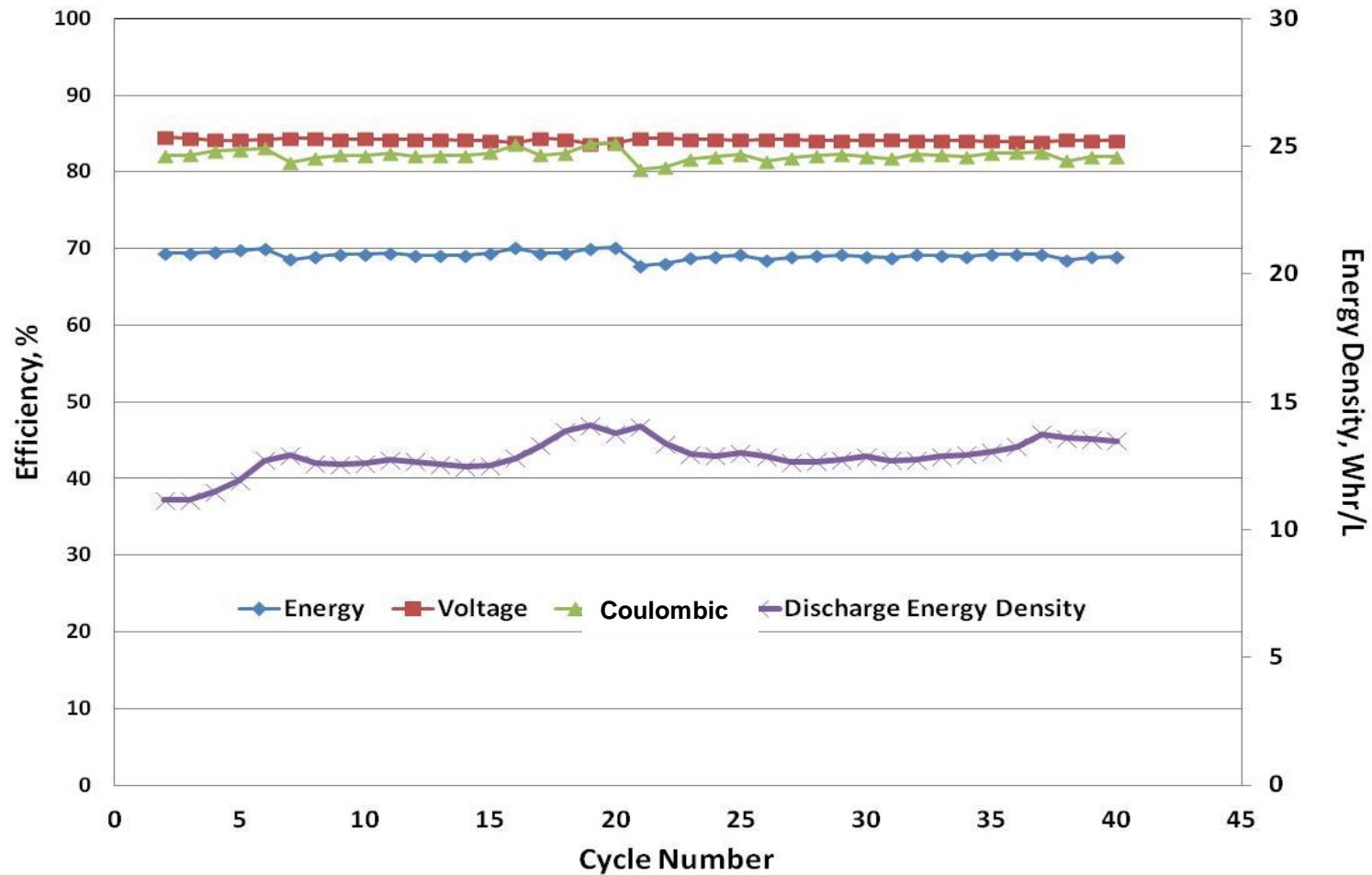


Operating Fe-V Battery at Different Temperatures

1.5M Fe/V mixed acid solution with Nafion membrane

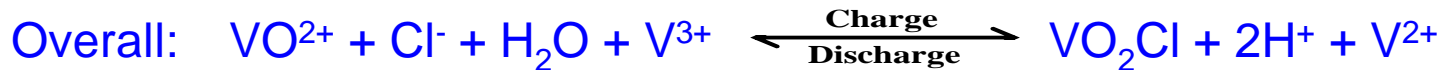
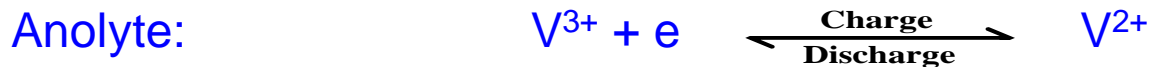
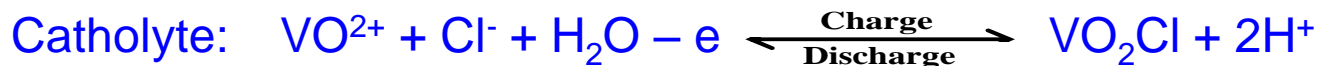
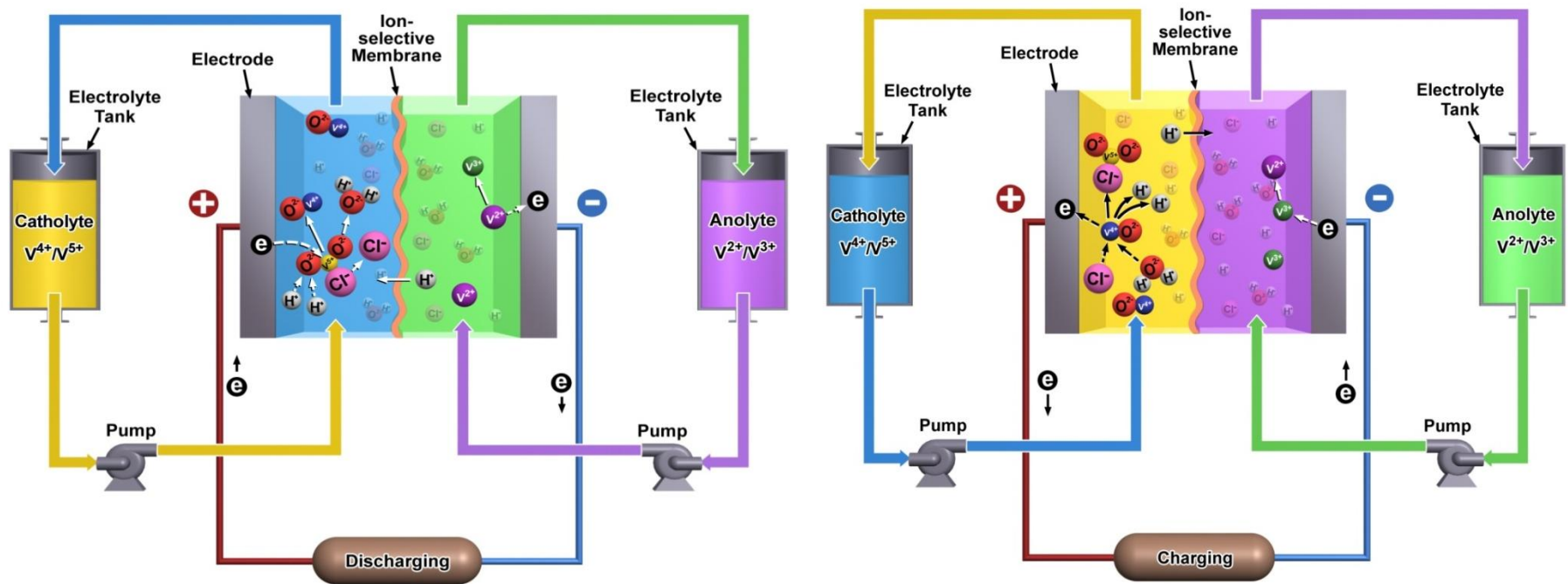


Performance of Fe/V Battery with Hydrocarbon Separator (~1% cost of Nafion membrane)

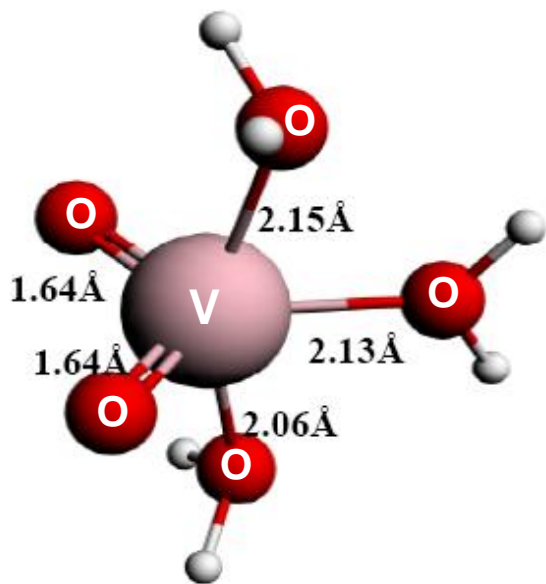


1.5M Fe/V mixed acid solution, no capacity loss, 50 mA/cm².

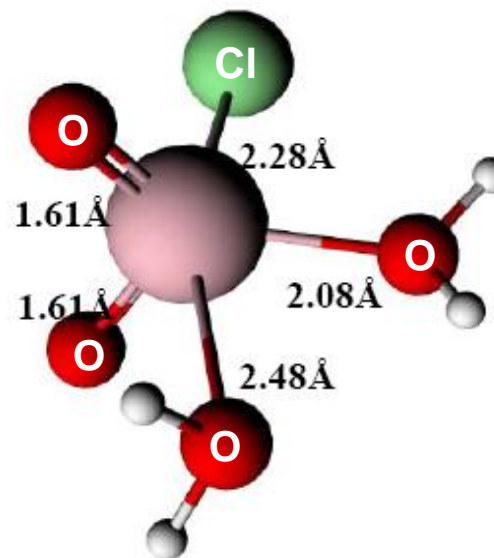
All Vanadium Mixed Acid Redox Flow Battery



Solution Chemistry of the Mixed Acid Electrolytes

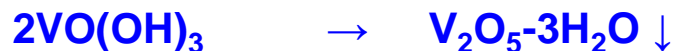


V⁵⁺ in Sulfuric Acid



V⁵⁺ in Mixed Acid

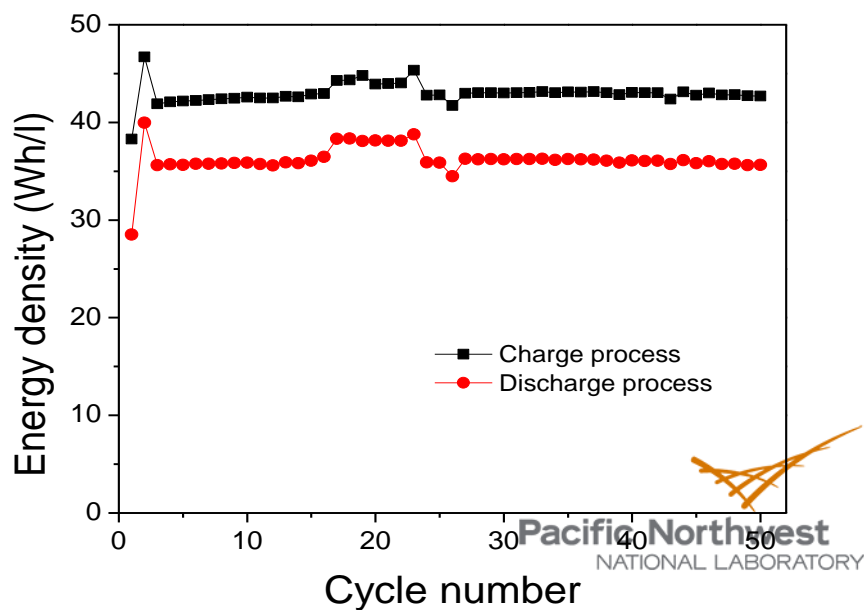
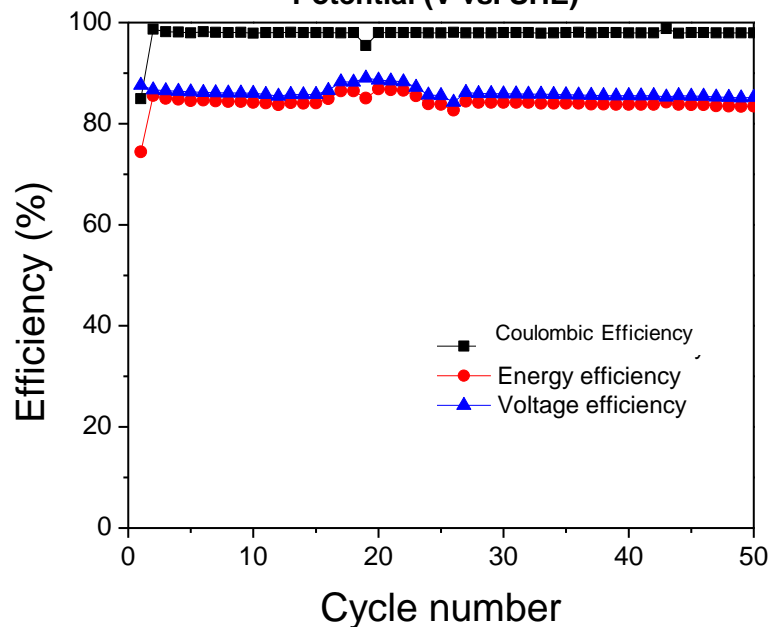
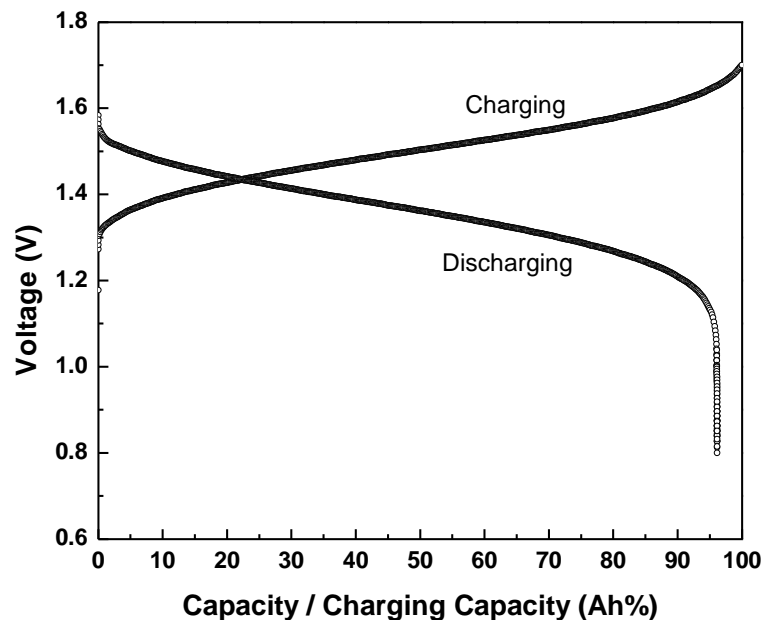
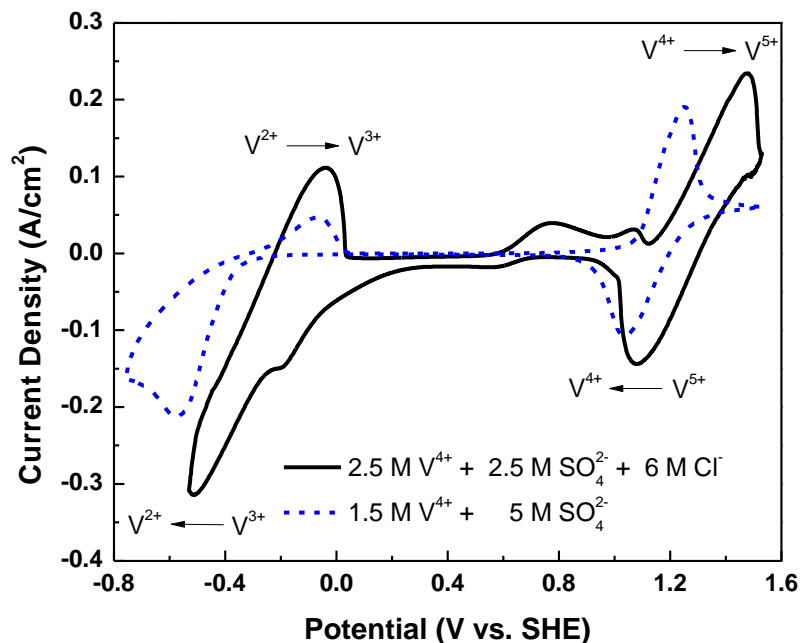
- In sulfate solution, V⁵⁺ exists as [VO₂(H₂O)₃]⁺, which tends to convert to V₂O₅-3H₂O precipitation via:



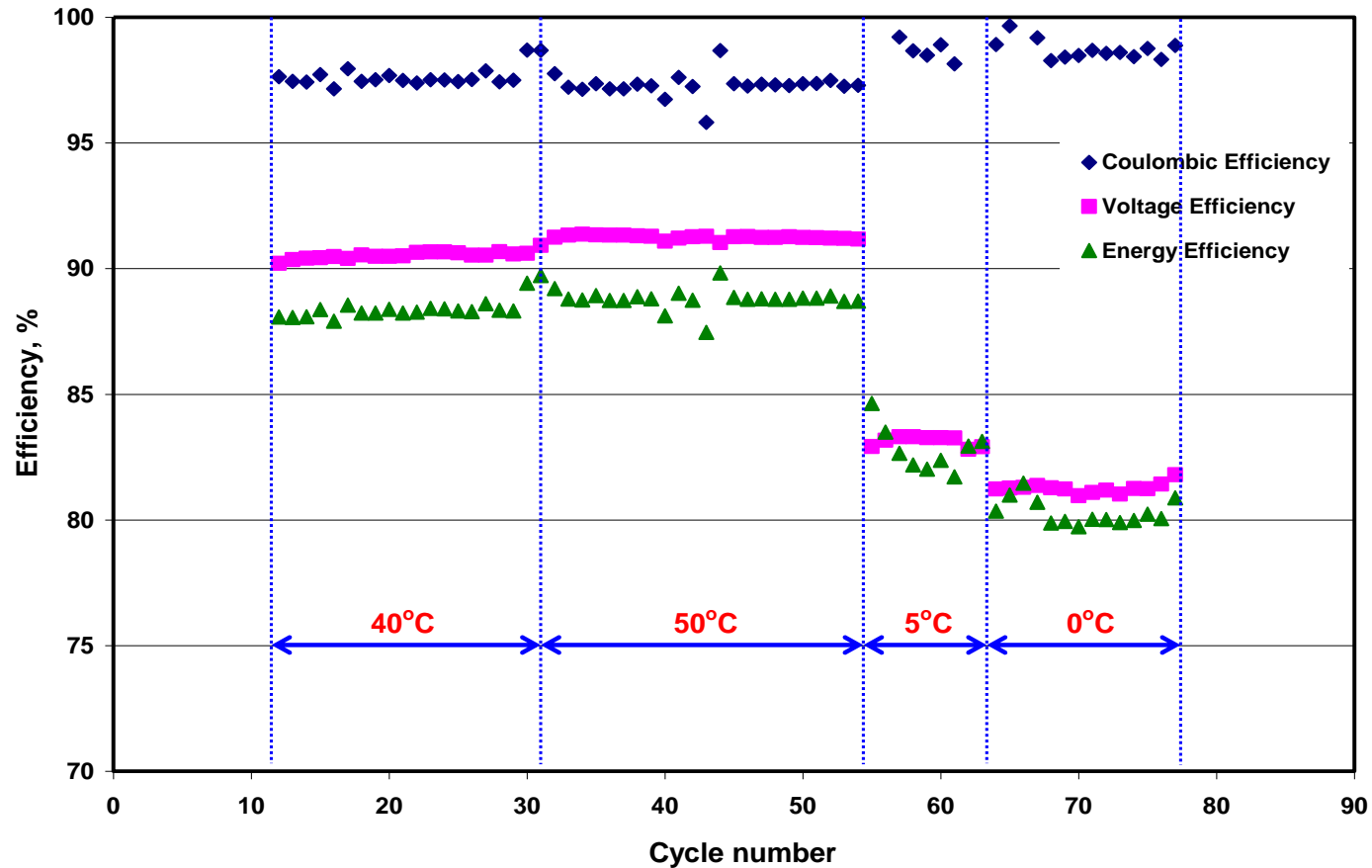
- In the mixed sulfate-chloride solution, a stable neutral specie, VO₂Cl(H₂O)₂, forms via:



Performance of Vanadium Mixed Acid Battery



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.

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 °C		10—40 °C	40-60°C	0 to 60°C	0-60 °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.