

A New Vanadium Redox Flow Battery Using Mixed Acid Electrolytes

Liyu Li, Soowhan Kim, Wei Wang, M. Vijayakumar, Zimin Nie, Baowei Chen, Jianlu Zhang, Jianzhi Hu, Gordon Graff, Jun Liu, Gary Yang*

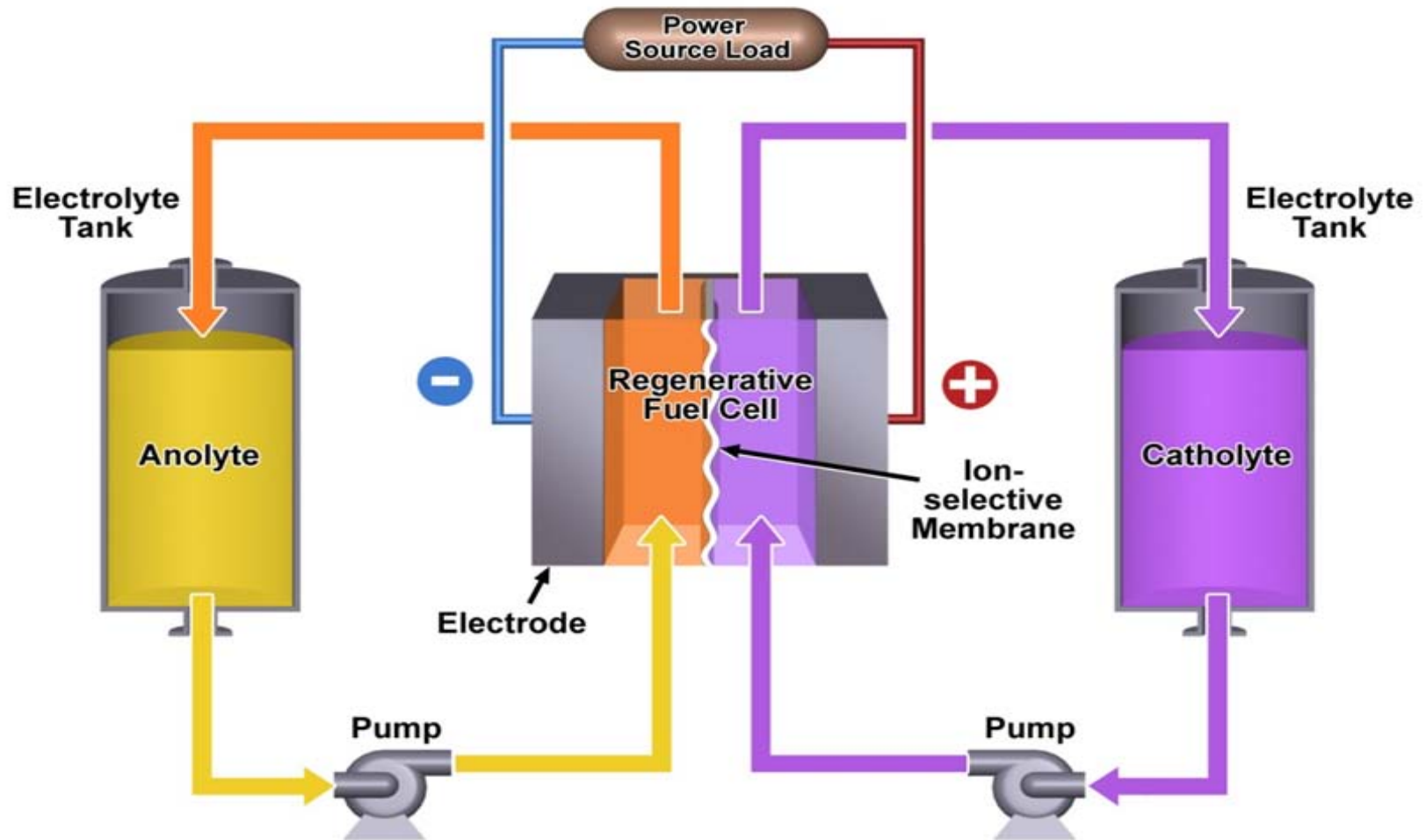
Funded by the Energy Storage Systems Program of the U.S. Department Of Energy through Pacific Northwest National Laboratories

November 2, 2010

US DOE Energy Storage Systems (ESS) Program Review

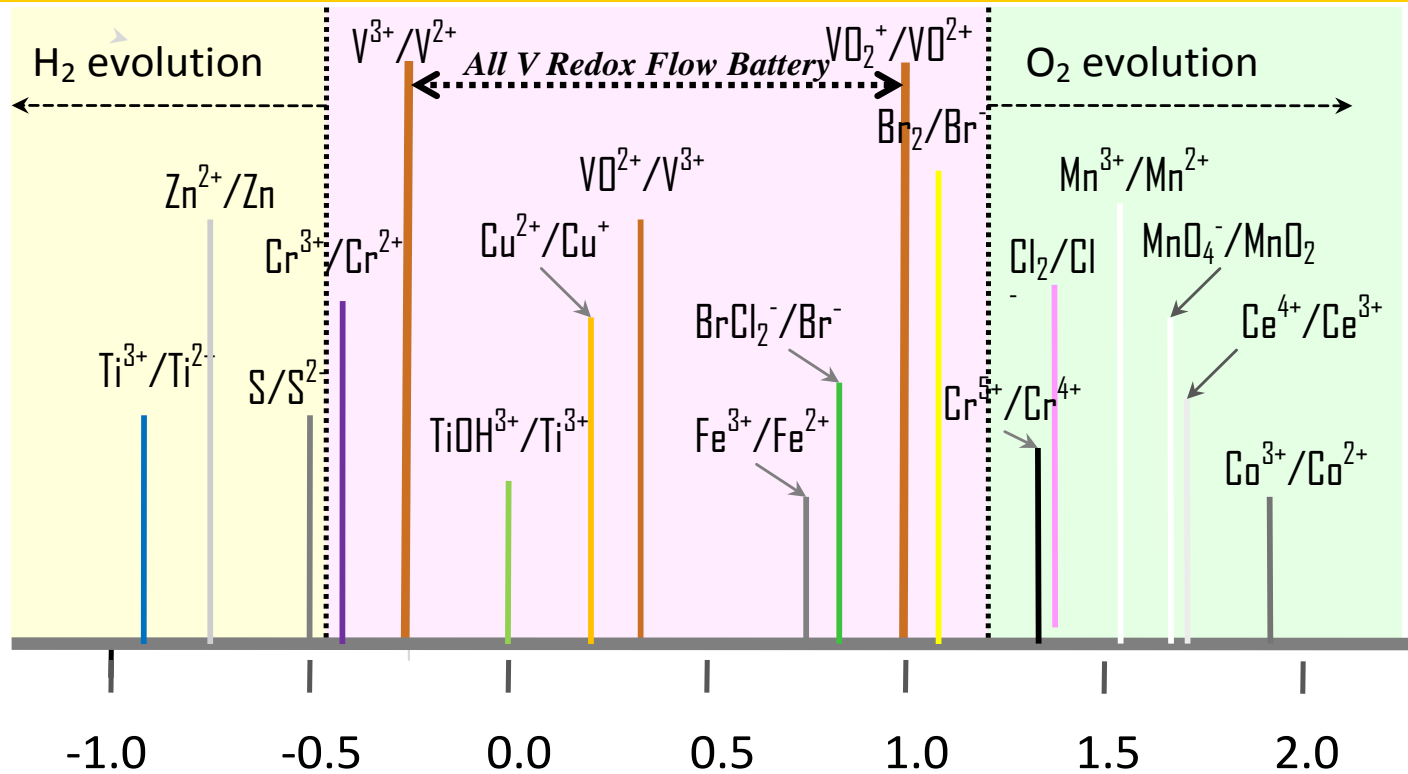
Washington DC

Redox Flow Battery (RFB)



- A redox flow battery is a promising technology for large scale energy storage .

Potential RFB Systems



Standard potential (V) of redox couples

- The use of vanadium in both the anolyte and catholyte effectively eliminate the cross-contamination between the electrolytes through the ion-exchange membrane.

Challenges for All Vanadium Sulfate RFB

V specie	V ⁿ⁺ , M	H ⁺ , M	SO ₄ ²⁻ , M	Temp, °C	Time for p.p.
V ²⁺	2	6	5	-5	419 hr
	2	6	5	25	Stable (>30 d)
	2	6	5	40	Stable (>30 d)
V ³⁺	2	4	5	-5	634 hr
	2	4	5	25	Stable (>30 d)
	2	4	5	40	Stable (>30 d)
V ⁴⁺ (VO ²⁺)	2	6	5	-5	18 hr
	2	6	5	25	95 hr
	2	6	5	40	Stable (>30 d)
V ⁵⁺ (VO ₂ ⁺)	2	8	5	-5	Stable (>30 d)
	2	8	5	25	Stable (>30 d)
	2.2	7.8	5	40	95 hr
	1.8	8.4	5	40	358 hr

- ❑ Low energy density: Vⁿ⁺ concentration <1.7M, decided by the low solubility of V⁴⁺ at low temperatures and the poor stability of V⁵⁺ at high temperatures.
- ❑ Limited operation temperature window: 10 to 40°C, requiring active electrolytes temperature management during hot/cold weathers.

Stability of V^{n+} Cations in HCl Solution

V^{n+} specie	V^{n+} , M	H^+ , M	Cl^- , M	T, °C	Time for precipitation
V^{2+}	2.3	5.4	10	-5	Stable (>10 d)
	2.3	5.4	10	25	Stable (>10 d)
	2.3	5.4	10	40	Stable (>10 d)
V^{3+}	1.5	3.0	7.5	-5	Stable (>10 d)
	1.8	3.0	8.4	-5	124 hr
	2.3	3.1	10	-5	96 hr
	2.3	3.1	10	25	Stable (>10 d)
	2.3	3.1	10	40	Stable (>10 d)
V^{4+} (VO_2^+)	2.3	5.4	10	-5	Stable (>10 d)
	2.3	5.4	10	25	Stable (>10 d)
	2.3	5.4	10	40	Stable (>10 d)
V^{5+} (VO_2^+)	2.3	7.7	10	-5	Stable (>10 d)
	2.3	7.7	10	25	Stable (>10 d)
	2.3	7.7	10	40	Stable (>10 d)

- Cl^- anions can effectively stabilize V^{5+} , V^{4+} , and V^{2+} .
- It is likely that high concentration of V^{2+} , V^{3+} , V^{4+} , and V^{5+} cations can be stabilized in a mixed sulfate and chloride electrolyte solution.

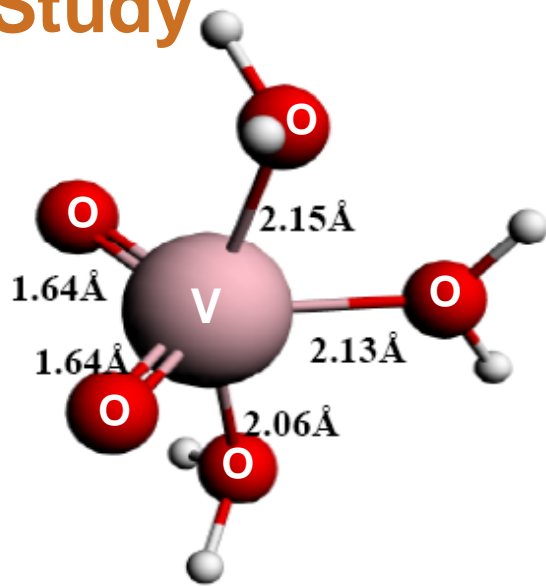
Vⁿ⁺ Stability in SO₄²⁻-Cl⁻ Mixed Solutions

V ⁿ⁺ specie	V ⁿ⁺ , M	T, °C	Time for precipitation	V ⁿ⁺ specie	V ⁿ⁺ , M	T, °C	Time for precipitation
V ²⁺	3	-5	Stable (>10 d)	V ⁴⁺ (VO ²⁺)	3	-5	Stable (>10 d)
	2.5	-5	Stable (>10 d)		2.5	-5	Stable (>10 d)
	2.5	25	Stable (>10 d)		2.5	25	Stable (>10 d)
	2.5	40	Stable (>10 d)		2.5	40	Stable (>10 d)
	3	40	Stable (>10 d)		3	40	Stable (>10 d)
V ³⁺	3	-5	192 hr (8 d)	V ⁵⁺ (VO ₂ ⁺)	3	-5	Stable (>10 d)
	2.5	-5	Stable (>10 d)		2.5	-5	Stable (>10 d)
	2.5	25	Stable (>10 d)		2.5	25	Stable (>10 d)
	2.5	40	Stable (>10 d)		2.5	40	Stable (>10 d)
	3	40	Stable (>10 d)		3	40	Stable (>10 d)
					2.7 V ⁵⁺ 0.3 V ⁴⁺	50	Stable (>10 d)
					2.7 V ⁵⁺ 0.3 V ⁴⁺	60	Stable (>10 d)

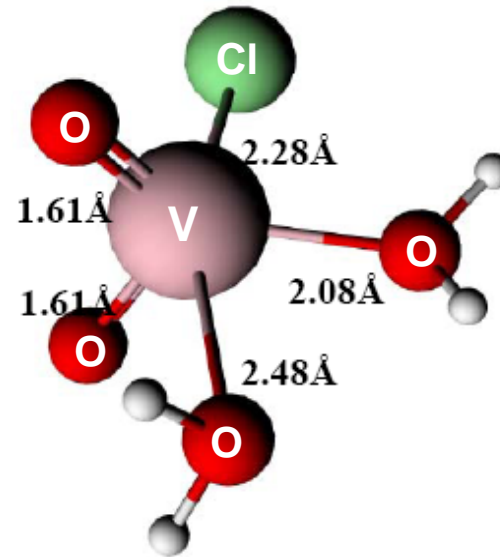
The overall stability of vanadium is decided by V³⁺ at low temperatures.

- ❑ SO₄²⁻/Cl⁻ mixtures can effectively stabilize >2.5M V⁵⁺, V⁴⁺, V³⁺ and V²⁺.
- ❑ Much broad operation temperature window (-5 to 60 °C) can be achieved using SO₄²⁻/Cl⁻ mixed electrolytes.

Solution Chemistry of the Mixed Electrolytes- DFT Study

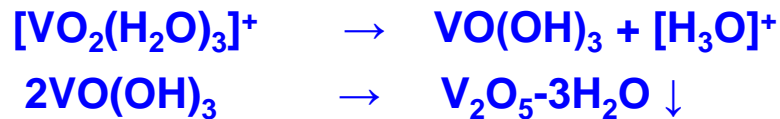


V⁵⁺ in Sulfuric Acid



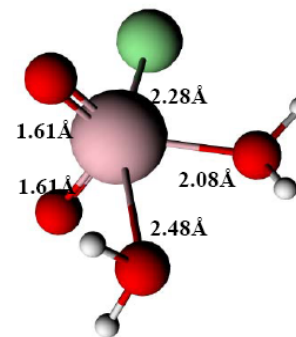
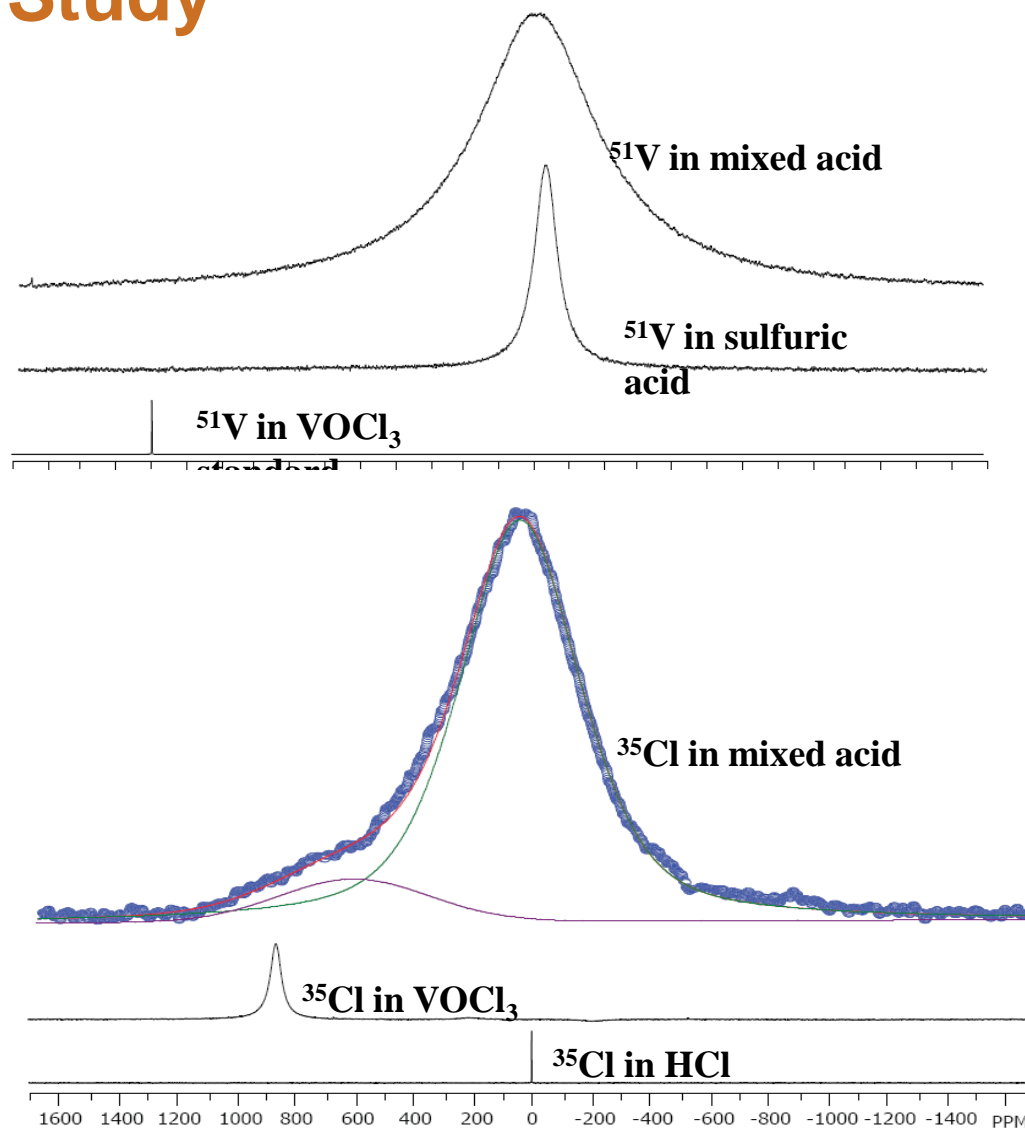
V⁵⁺ in Mixed Acid

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

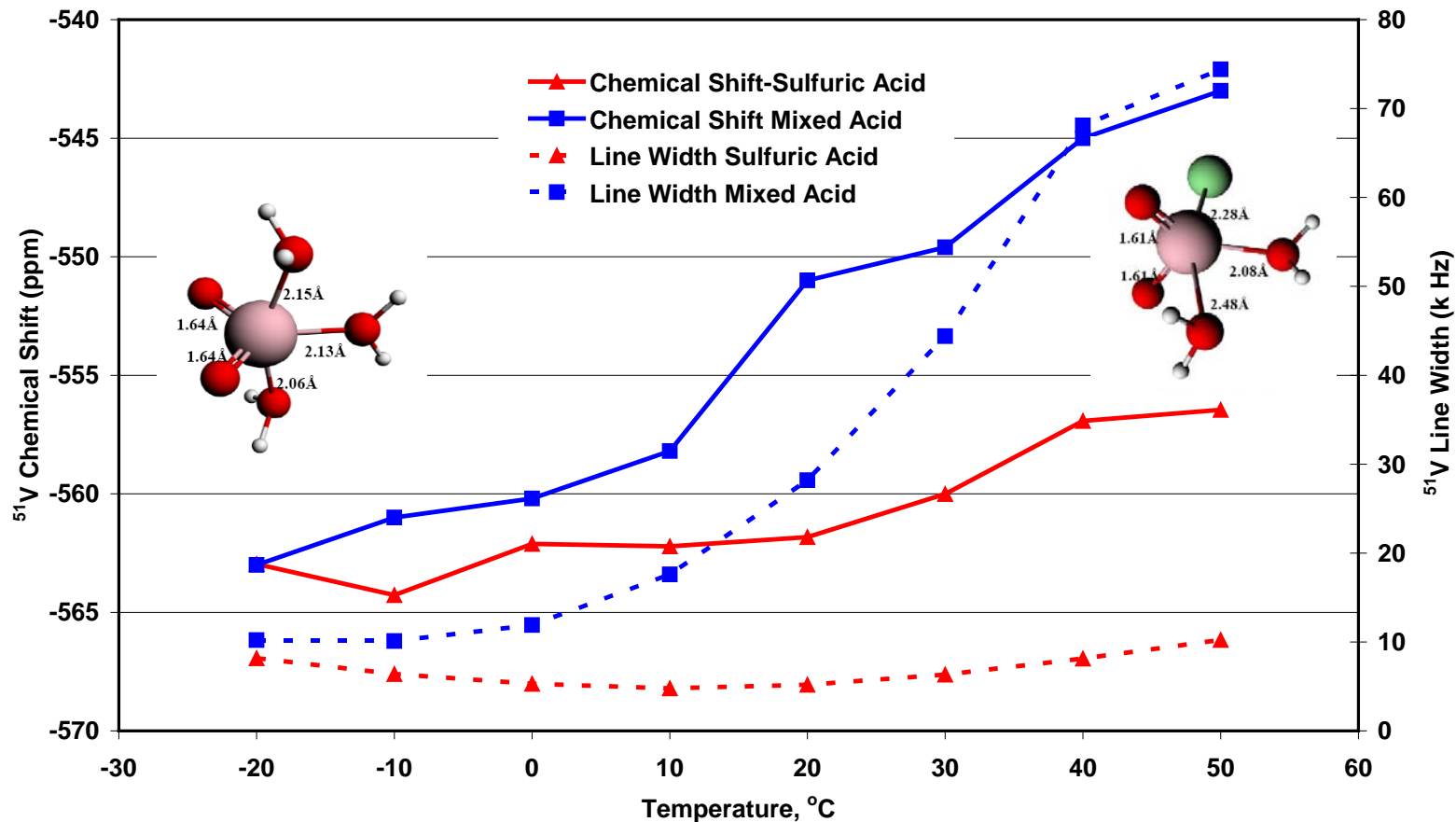


Solution Chemistry of the Mixed Electrolytes-

NMR Study



Temperature Dependence of $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$ Formation



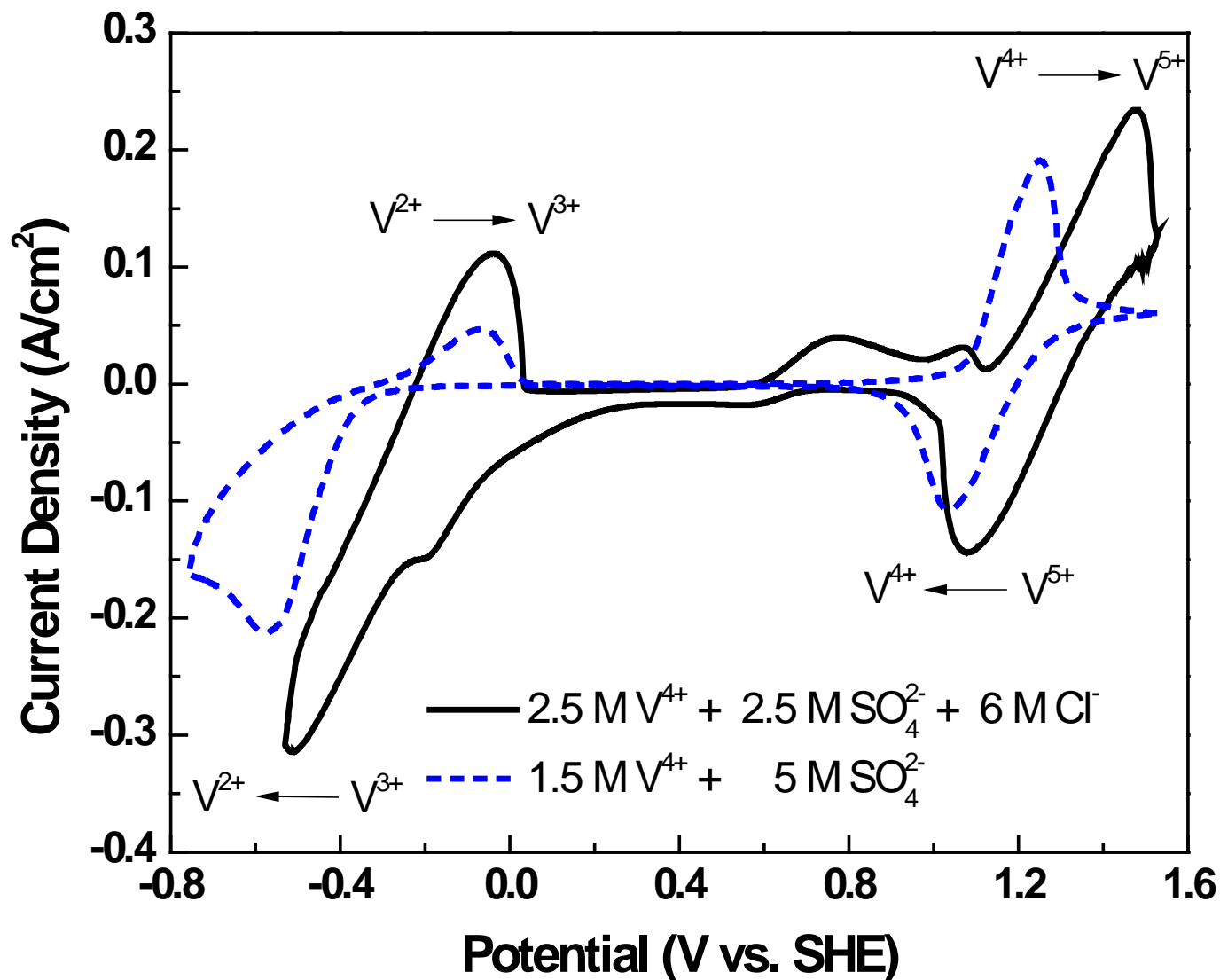
□ $\text{VO}_2\text{Cl}(\text{H}_2\text{O})_2$ complex starts to form in the mixed solutions when temperatures reaching $\sim 20^\circ\text{C}$.

Solution Chemistry of the Mixed Electrolytes-

DFT and Stability Studies

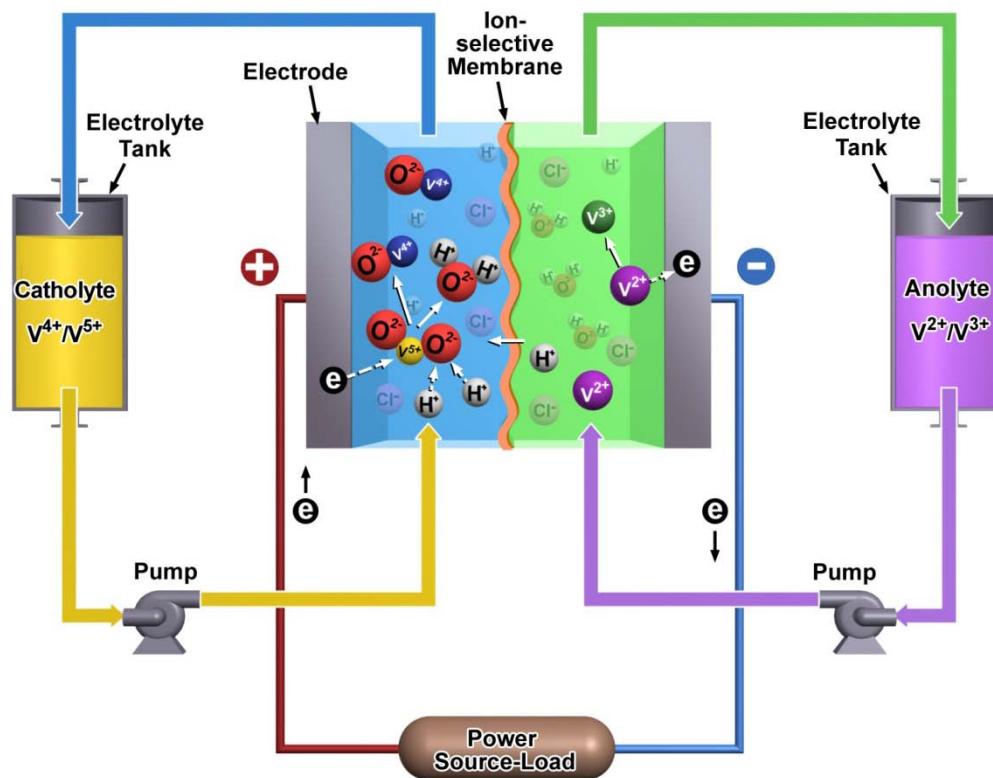
- ❑ Same V^{2+} , V^{3+} and V^{4+} -containing structures was predicted in both electrolyte solutions: $[V(H_2O)_6]^{2+}$, $[V(H_2O)_6]^{3+}$ and $[VO(H_2O)_5]^{2+}$.
- ❑ According to SEM-EDS, and XRD analysis, in the mixed systems, the stability of V^{4+} is controlled by the solubility of $VOSO_4$, the stability of V^{3+} is controlled by the solubility of $V_2(SO_4)_3$ and $VOCl$, the stability of V^{2+} is controlled by the solubility of VSO_4 .
- ❑ The improvement of stability of V^{2+} , V^{3+} , and V^{4+} in the mixed system over the current sulfate systems is due to the decrease of SO_4^{2-} concentration in the solutions.

Electrochemical Properties of Mixed Solutions

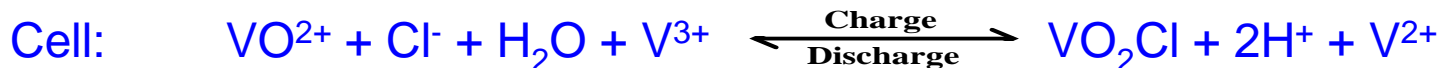
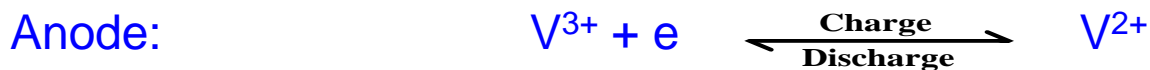
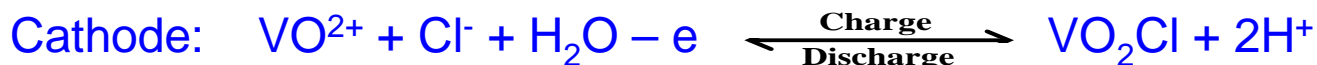
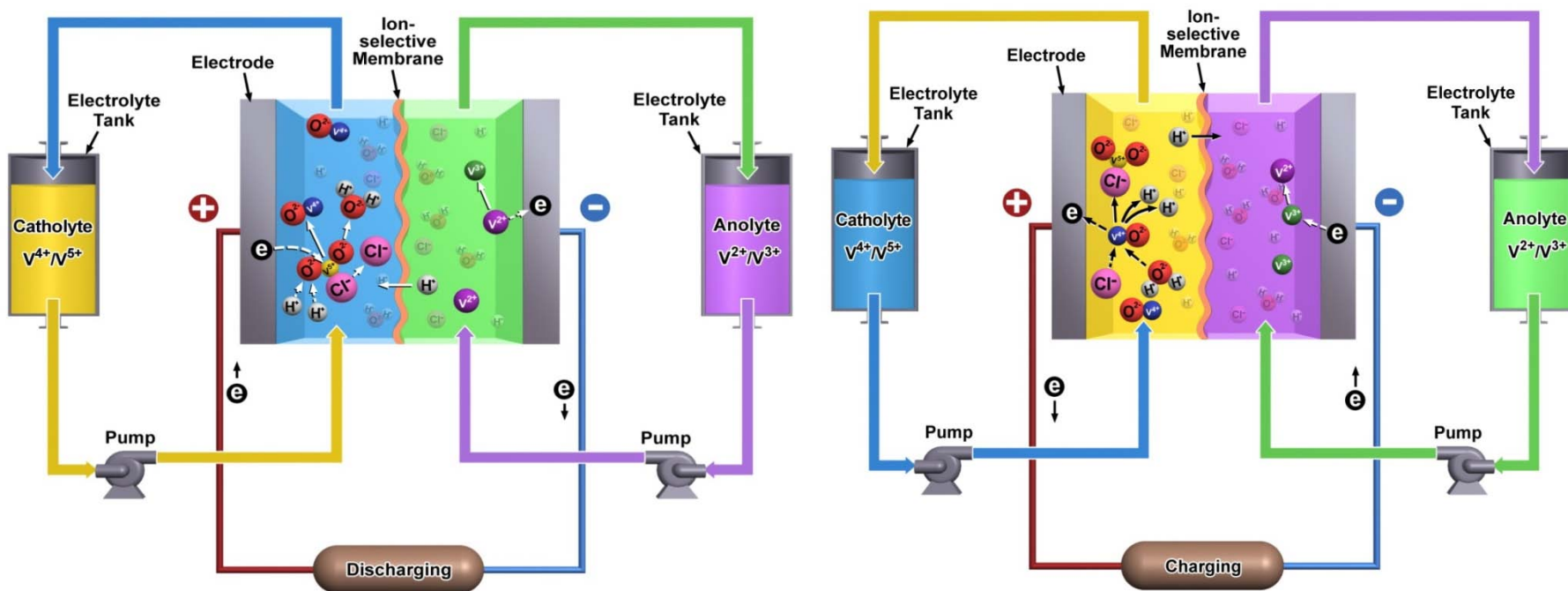


□ No chlorine gas evolution.

Electrode and Cell Reactions ($T < 10^\circ\text{C}$)



Electrode and Cell Reactions ($T > 10^\circ\text{C}$)

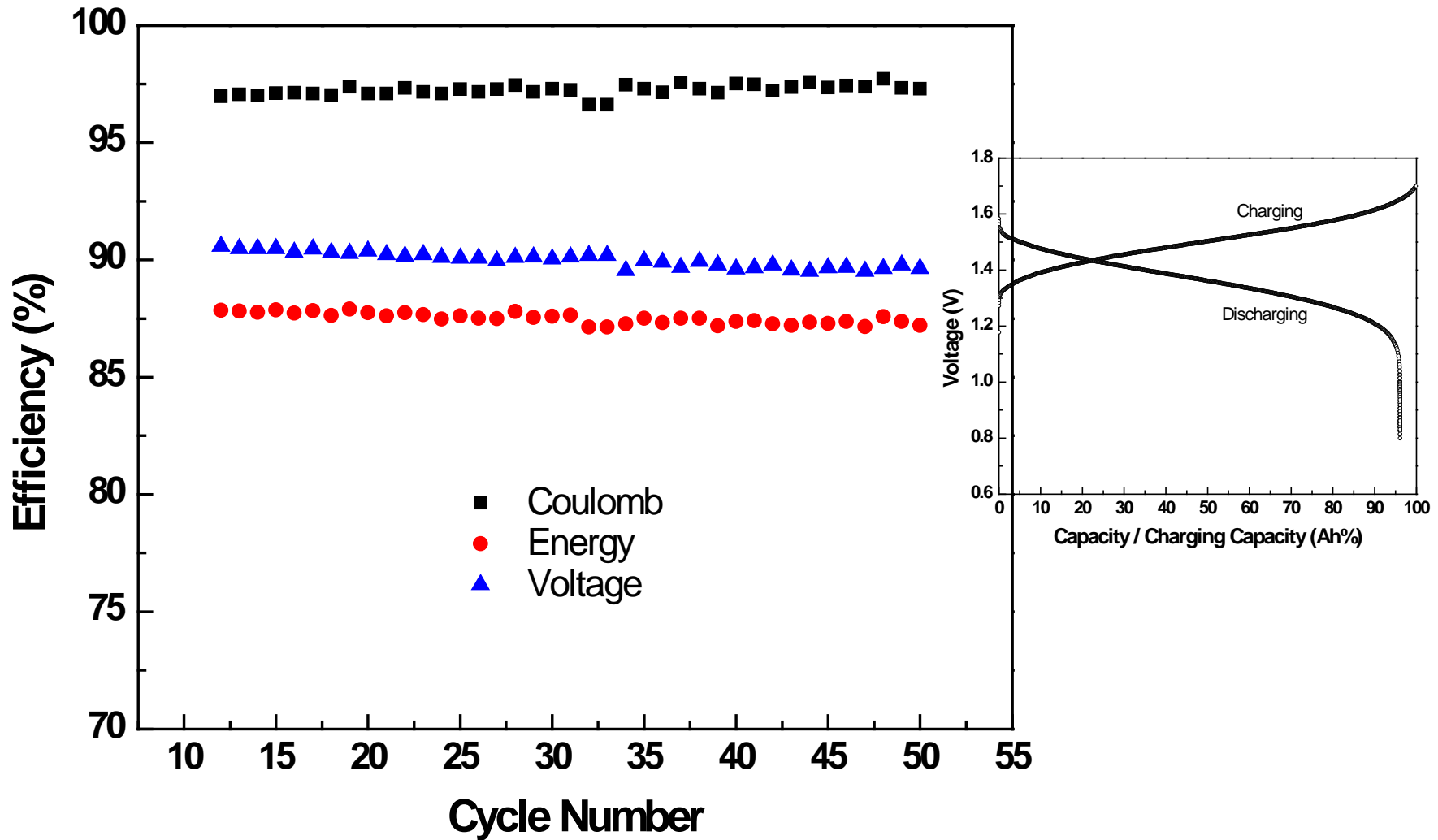


Cell Testing and RFB Evaluation



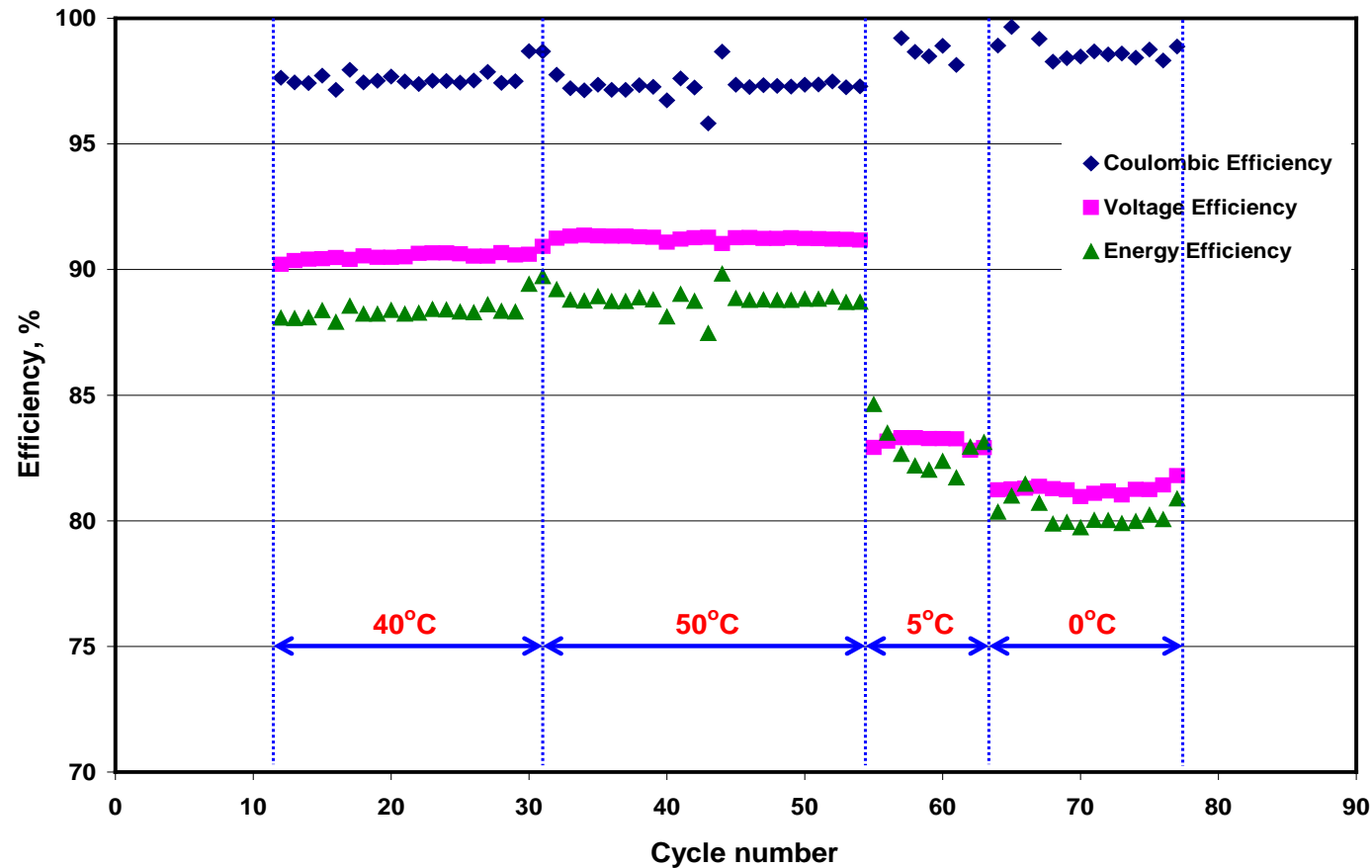
- Cell and reservoirs are inside the environmental chamber.
- Circulating pump is out side of the chamber.
- Pressure monitoring.

Cell Performance at Ambient Temperature



□ Stable performance with 88% energy efficiency at 50 mA.cm⁻²

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.

Cell Performance at Varied Current Densities

Discharge Current, (mA.cm ⁻²)	Energy Density (Wh.L ⁻¹)			Columbic Efficiency			Energy Efficiency		
	Mixed		sulfate	Mixed		sulfate	Mixed		sulfate
	2.5MV	3MV	1.6MV	2.5MV	3MV	1.6MV	2.5MV	3MV	1.6MV
100	36.2	39.5	22.3	0.95	0.95	0.94	0.81	0.76	0.83
75	37.5	40.8	22.4	0.96	0.96	0.94	0.84	0.81	0.85
50	38.5	41.8	22.6	0.96	0.97	0.94	0.87	0.85	0.87
25	39.2	43.1	22.6	0.96	0.97	0.94	0.90	0.89	0.88

Cell operation conditions: 10 cm² flow cell, Charged to 1.7V by 50 mA/cm² current.

The VRBs using mixed sulfate-chloride electrolytes were able to deliver 70 to 80% more energy than the sulfate system, while still being highly efficient.

Summary

- ▶ A new vanadium redox flow battery with a significant improvement over the current technology was developed.
- ▶ This battery utilizes sulfate-chloride mixed electrolytes, which are capable of dissolving 2.5 M vanadium, representing about 70% increase in energy density over the current sulfate system.
- ▶ More importantly, the new electrolyte remains stable over a wide temperature range of -5 to 60°C, potentially eliminating the need of energy-consuming solution temperature management.
- ▶ Battery tests indicated no concern of chlorine gas evolution during the battery operation.



BatteryAnm2.wmv
(965 KB)

Further Work

- ▶ Optimize the mixed electrolyte for further improvement in energy density and stability.
- ▶ Demonstrate a 2.0 kWh (0.3 kW) bench-top prototype FRB with the newly developed mixed electrolyte.
- ▶ Build up strong collaborations with industry, university, and other national laboratory partners.
- ▶ Prepare for larger systems demonstration within 2-3 years.

Acknowledgements

Financial support :

1. DOE Office of Electricity Delivery and Energy Reliability
Energy Storage Program (Manager: Dr. Imre Gyuk)
2. PNNL LDRD program for NMR and DFT-related work.

The NMR work was carried out at the Environmental and Molecular Science Laboratory, a national scientific user facility sponsored by the DOE's Office of Biological and Environmental Research (BER).

