New Generation Aqueous Base Redox Flow Battery Component Development

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U.S. DEPARTMENT OF ENERGY

Dr. Imre Gyuk

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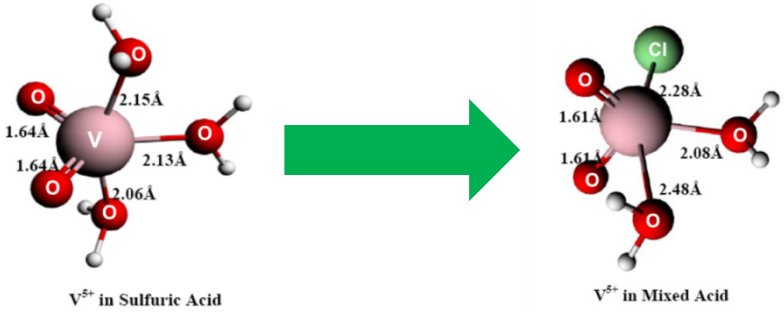
Review of previous work

Mixed-acid VRB



Double Energy Density
Extend temperature window

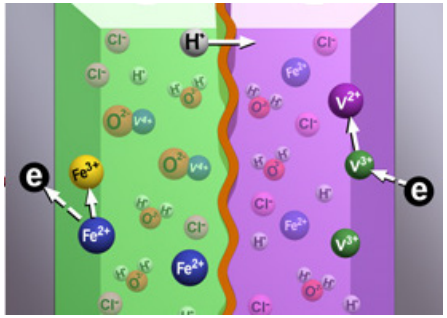
2.5M, ~30Wh/L, -5~50°C

Catholyte: $VO^{2+} + Cl^- + H_2O - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+$ ε_{co}=1.0 V

Anolyte: $V^{3+} + e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$ ε_{ao}=-0.25

Overall: $VO^{2+} + Cl^- + H_2O + V^{3+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} VO_2Cl + 2H^+ + V^{2+}$ E_o=1.25 V

Fe/V RFB



Higher utilization, stable cycling
Low-cost membrane

1.5M, ~15Wh/L, 0~50°C

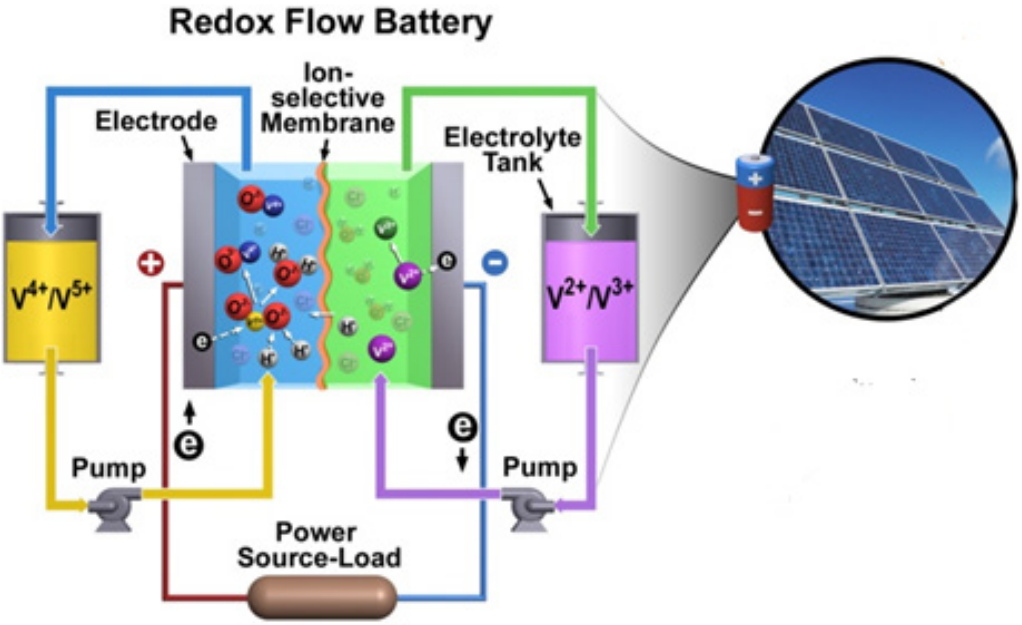
Positive: $Fe^{2+} - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} Fe^{3+}$ $E^o = 0.77\,V$

Negative: $V^{3+} - e \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+}$ $E^o = -0.25V$

Overall: $V^{3+} + Fe^{2+} \underset{\text{Discharge}}{\overset{\text{Charge}}{\rightleftharpoons}} V^{2+} + Fe^{3+}$ $E^o = 1.02\,V$

W. Wang, *et al*, *Energy & Environmental Science*, **4**, 4068, 2011
L. Li, *et al*. *Advanced Energy Materials*, **1**, 394, 2011

Outline



- **Electrolyte Study**
  - Investigation of V/V electrolyte;
  - Optimization of Fe/V electrolyte;
- **VRB transport Phenomenon**
  - *In-situ* V ions crossover study;
  - Capacity decay mitigation.
- **Separator Development**
  - Low-cost separator for VRB;
  - Screening commercial separator.
- **Improvement of Power Output**
  - Catalyst.

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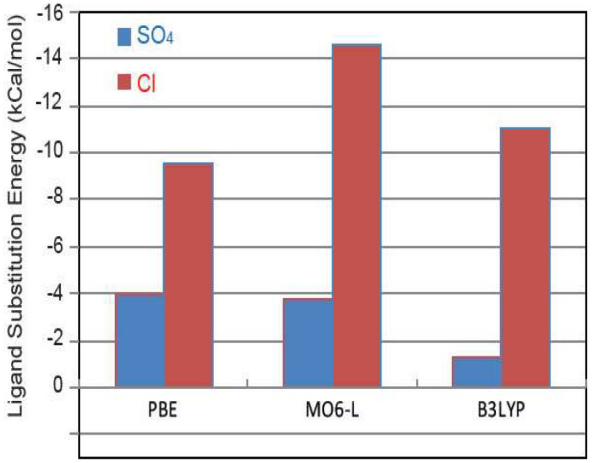
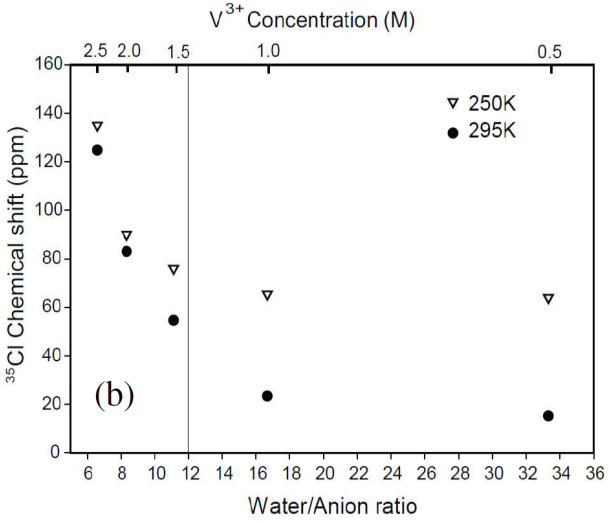
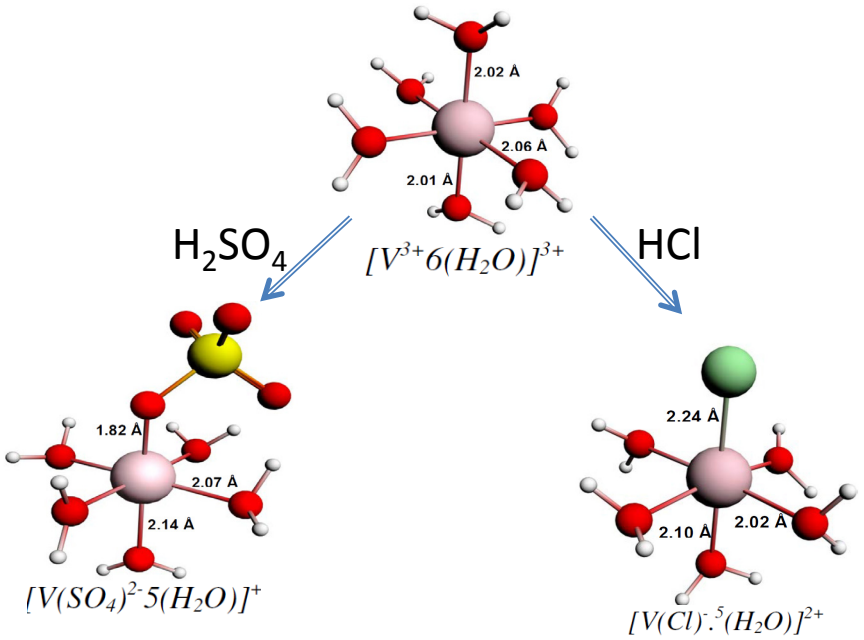
Electrolyte Study - V/V electrolyte

In mixed-acid electrolyte, vanadium (III) precipitate beyond 2.5M



Reaction pathway from NMR





Anion complexation of V^{3+} molecule in Electrolytes leads to neutral molecules and subsequent precipitations,

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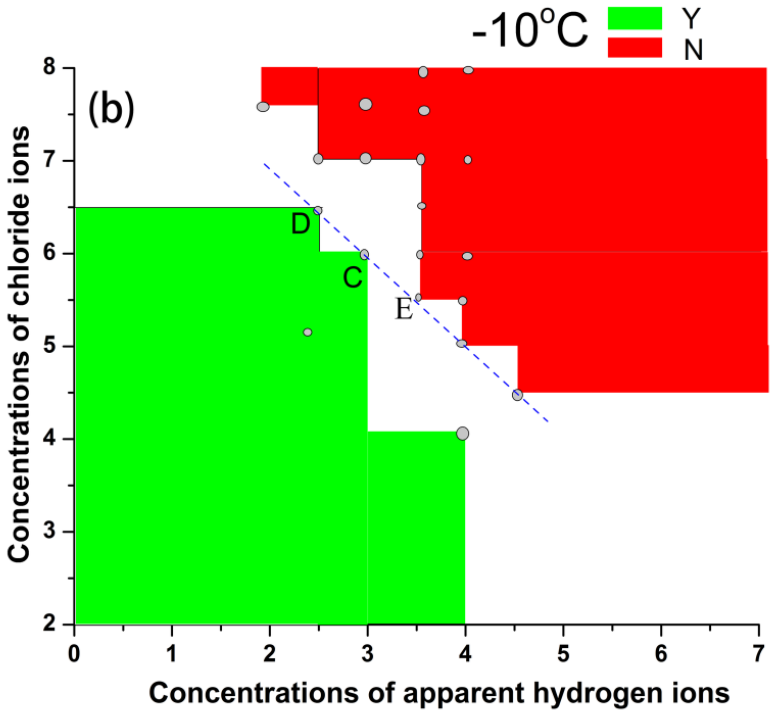
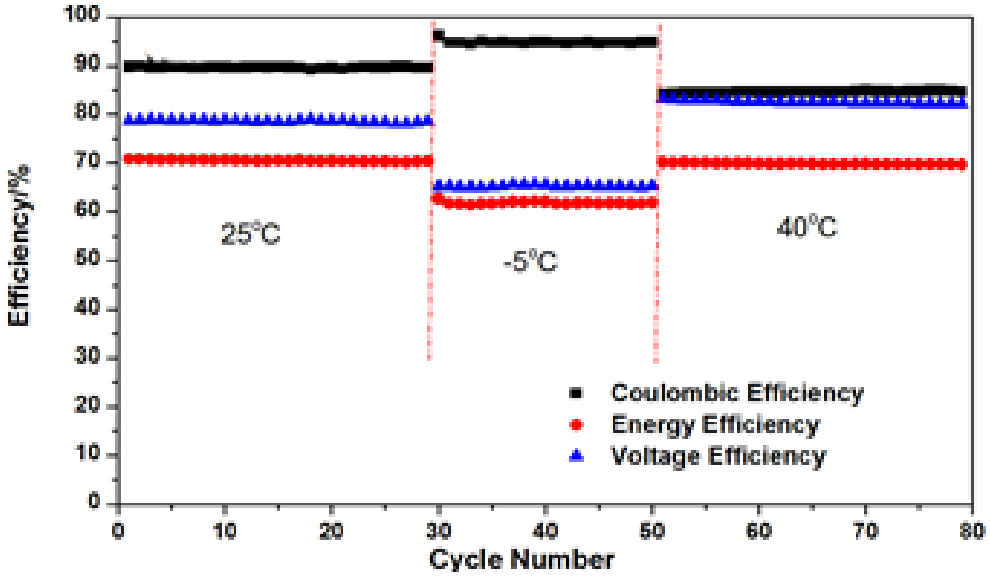
M. Vijayakumar, *et al*, *PCCP,* 2012, **14**, 10233-10242.

Electrolyte Study - Fe/V electrolyte

Expand the temperature window of Fe/V RFB from 0~50°C to -10~50°C





Electrochemical performance of Fe/V RFBs with optimized electrolytes

1.5M Fe^{2+}/V^{4+} electrolyte stability with respect to apparent hydrogen and chloride ions concentrations at -10°C.

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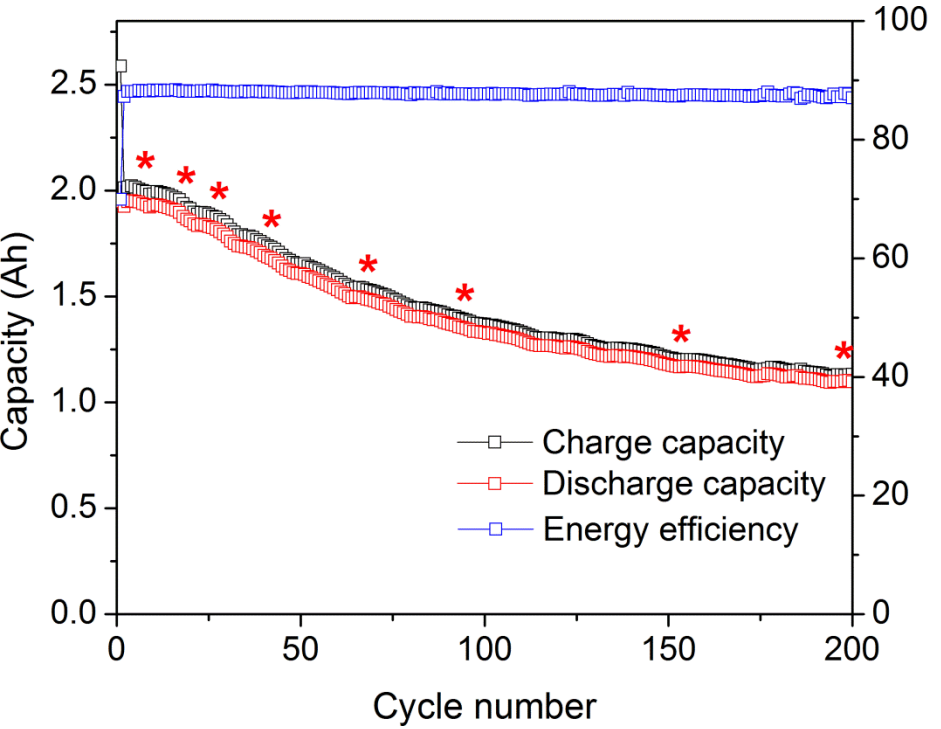
B. Li, *et al*, Submitted.

VRB transport Phenomenon-Capacity Decay along Cycling

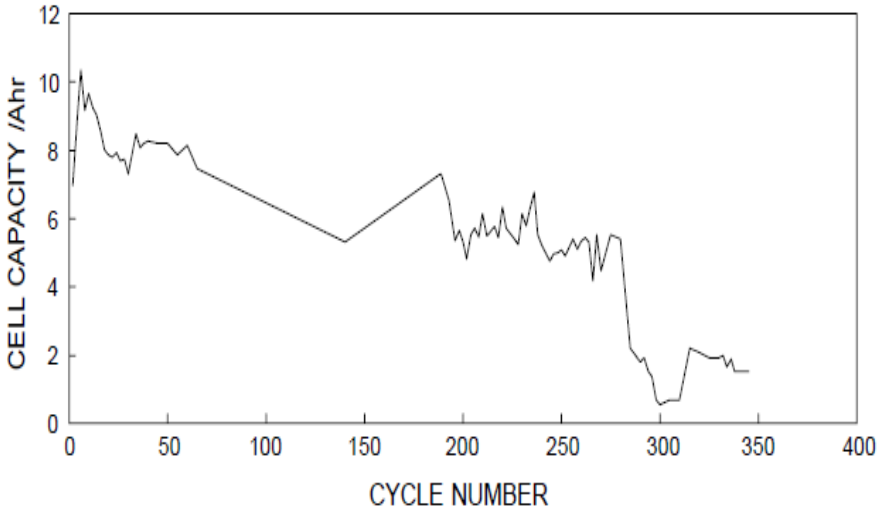
On-line investigation of capacity decay and composition change



Cycling performance of a VRB using 1.7 M V and 5 M S electrolytes and N115 as the membrane.

Capacity decay of VRB

- Increase the maintenance cost
- Threat to the long-term stability



Capacity decay of a vanadium cell using Gore Select L-570 membrane

- Withdrawn 1mL sample from positive electrolyte
- Added back 1mL pre-prepared electrolyte with constant SoC
- Samples were analyzed by ICP and UV-Vis.

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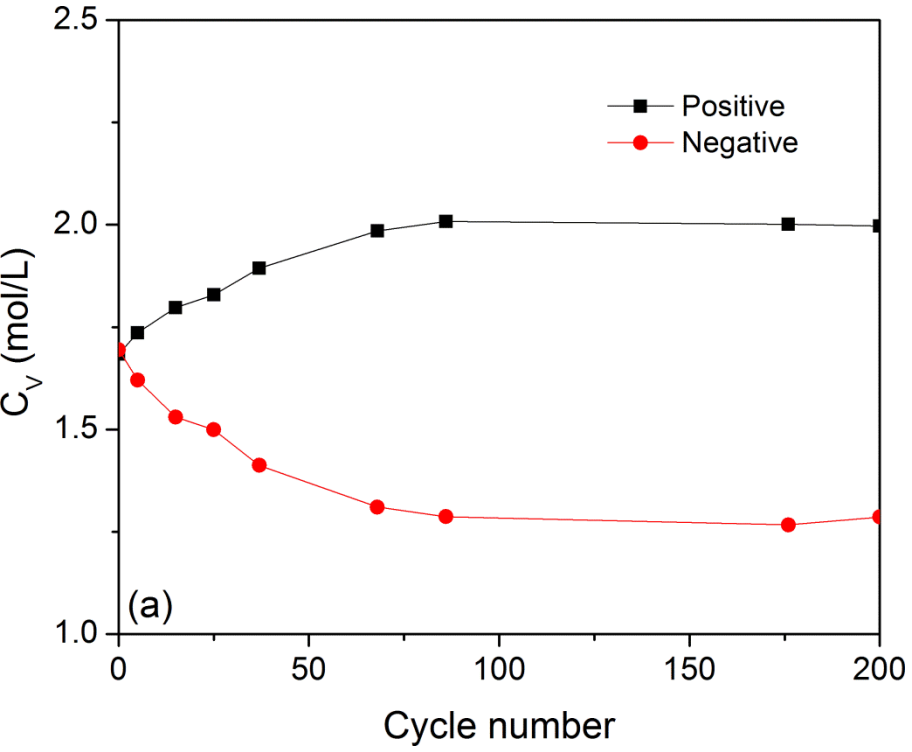
T. Sukkar, *et al*, *J. of Applied Electrochemistry* **34** 137–145, 2004
Q. Luo, *et al*, Submitted.

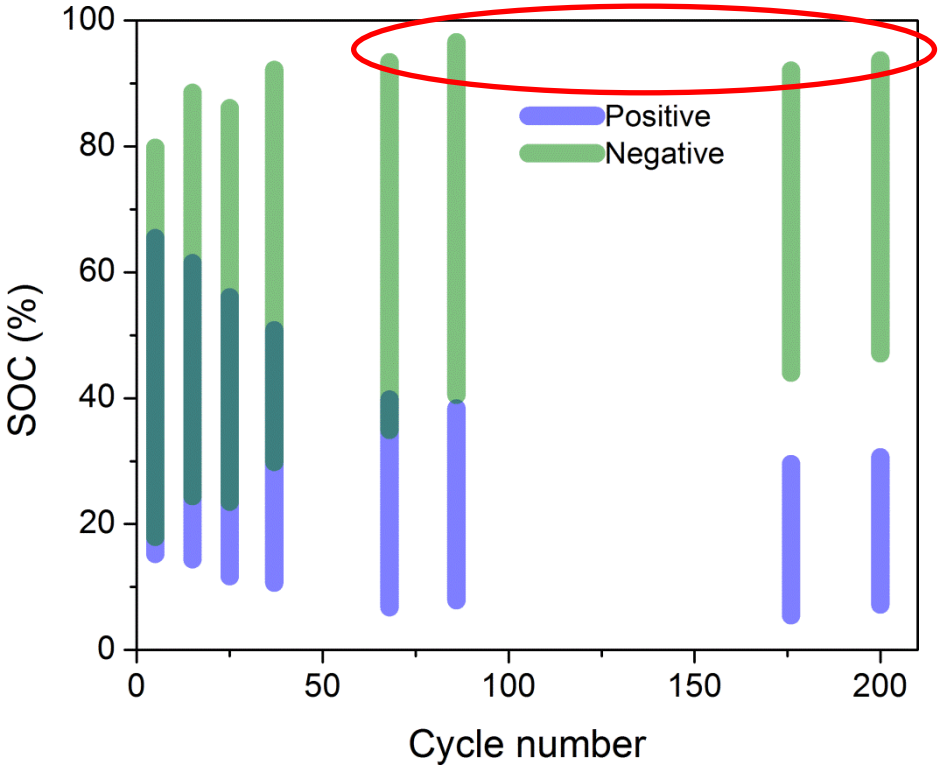
VRB transport Phenomenon- Cause of Capacity Decay

Differential transfer of vanadium ions



Variation of total vanadium ion concentration along cycling

Imbalance of vanadium ion valence



Positive and negative electrolyte SoC change along cycling

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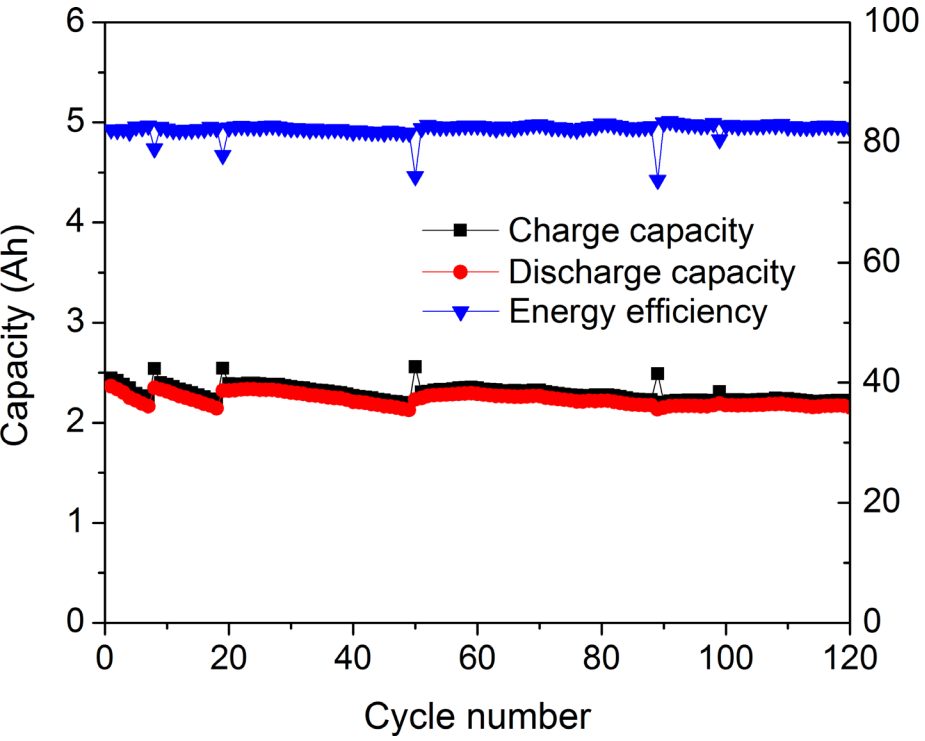
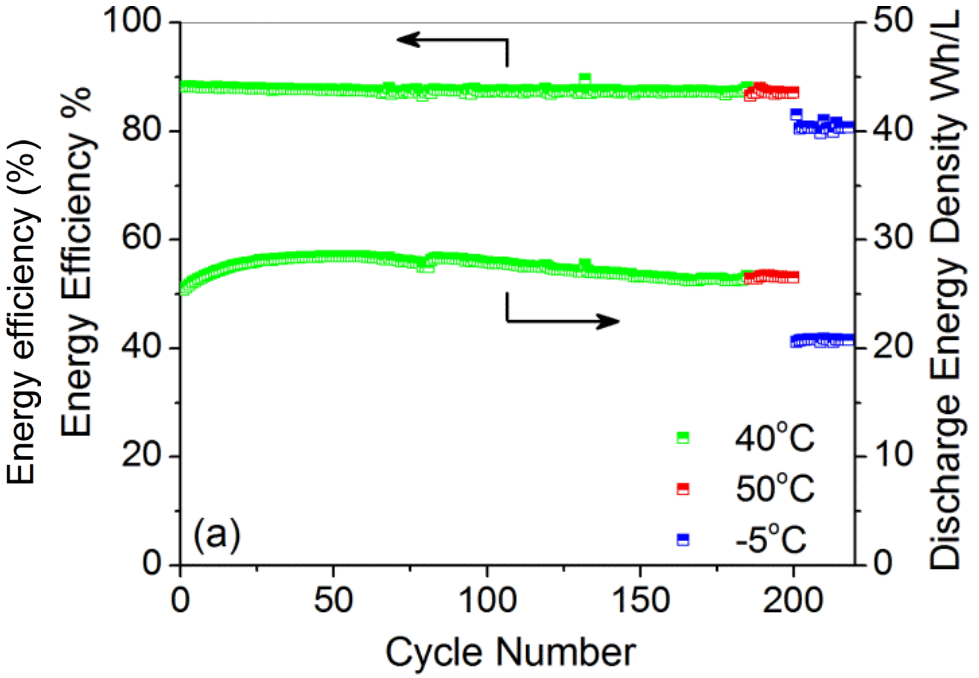
Q. Luo, *et al*, Submitted.

VRB transport Phenomenon- Remediation of Capacity Decay

Capacity stabilization through periodic electrolyte transfer



Long-term cycling of VRB using electrolyte transfer with 1.7M V and 5 M S as the positive and negative electrolytes, respectively, and N115 as the membrane.



Long-term cycling performance of the optimized mixed-acid RFB at different temperatures and a current density of 50 mA/cm2 with Nafion 115 as membrane.

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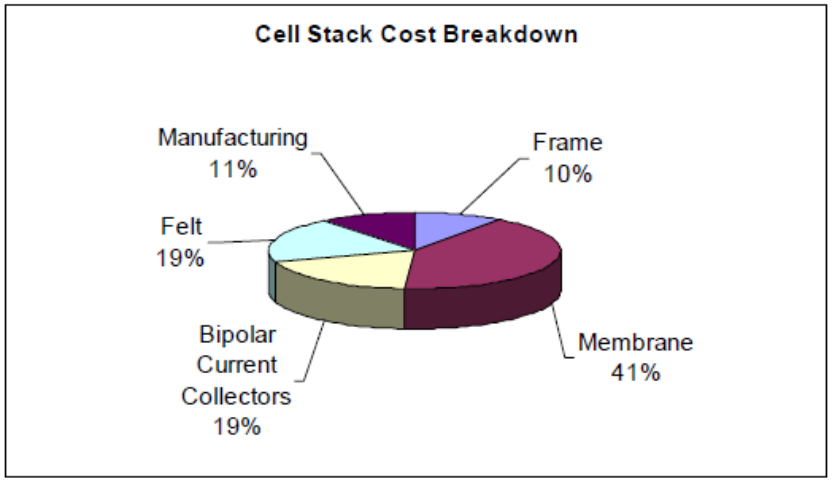
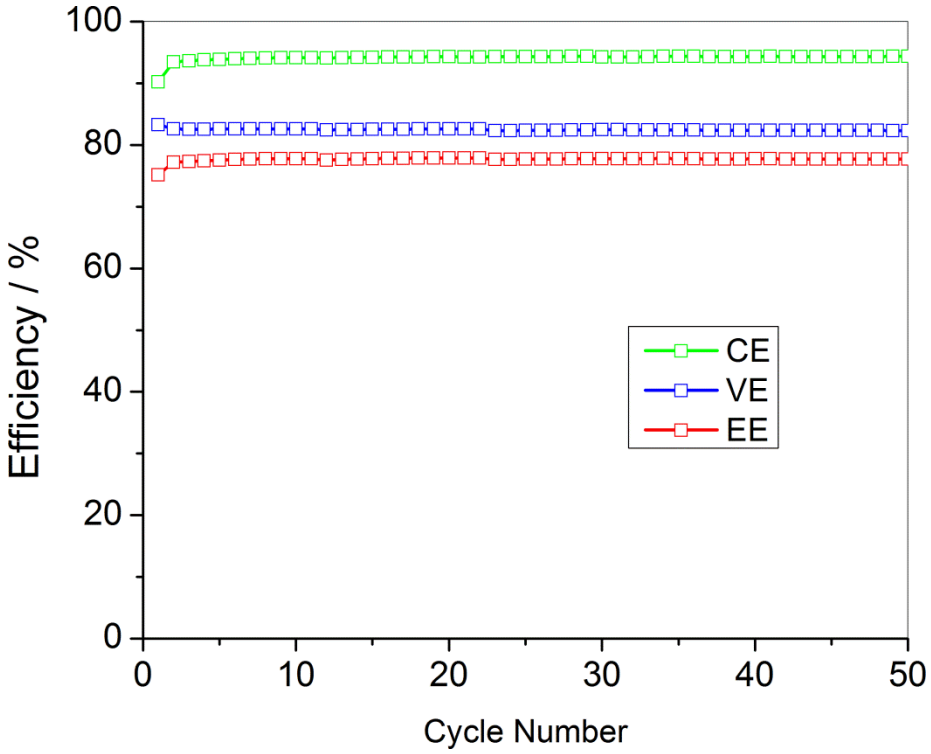
Q. Luo, *et al*, Submitted.
W. Wang, *et al, Advanced Functional Materials*, in press

Separator Development-Low cost VRB separator

PNNL developed low-cost VRB separator

- **Proven chemical stability in long-term VRB operation**
- **Cycling capacity stability**
- **Cost <5% of Nafion**



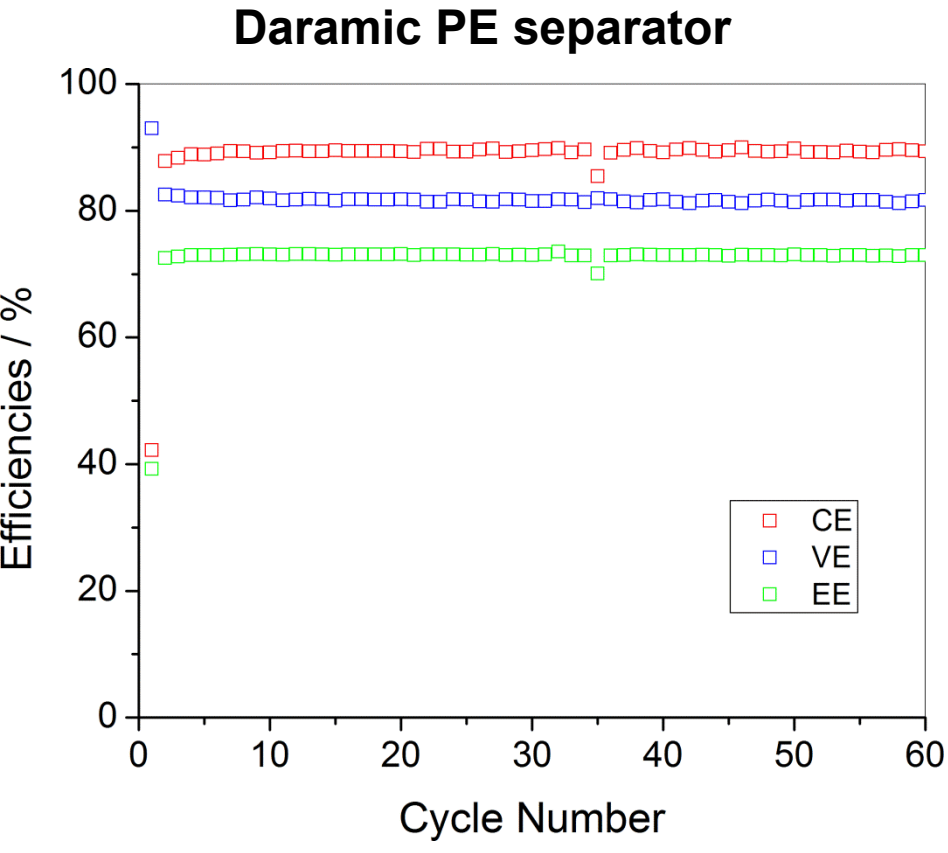


Efficiencies of the PNNL separator in a 2.5M mixed acid VRB at 50mA/cm^2 current.

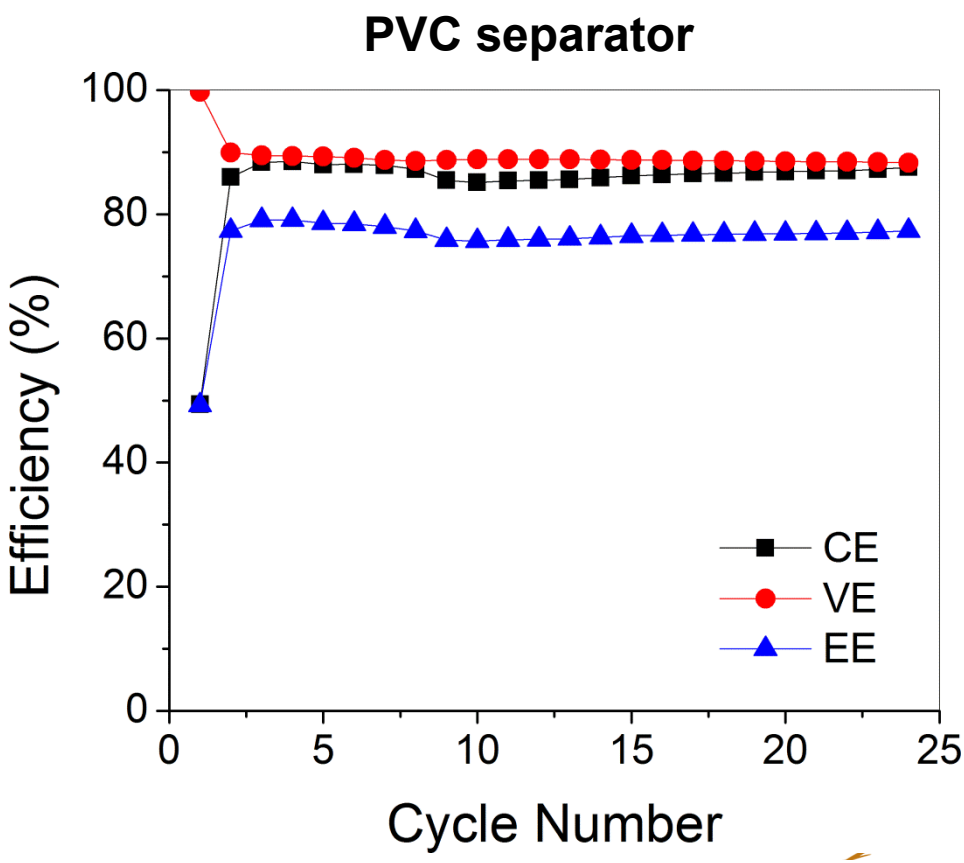
EPRI report, Palo Alto, CA, USA, 2007
X. Wei, et. al. In preparation

Separator Development-Commercial separator

Separator development in lead-acid battery provide a wide selection of potential low cost separator for RFB application.



Efficiencies of the PE separator in a 1.5M Fe/V at 50mA/cm^2 current.

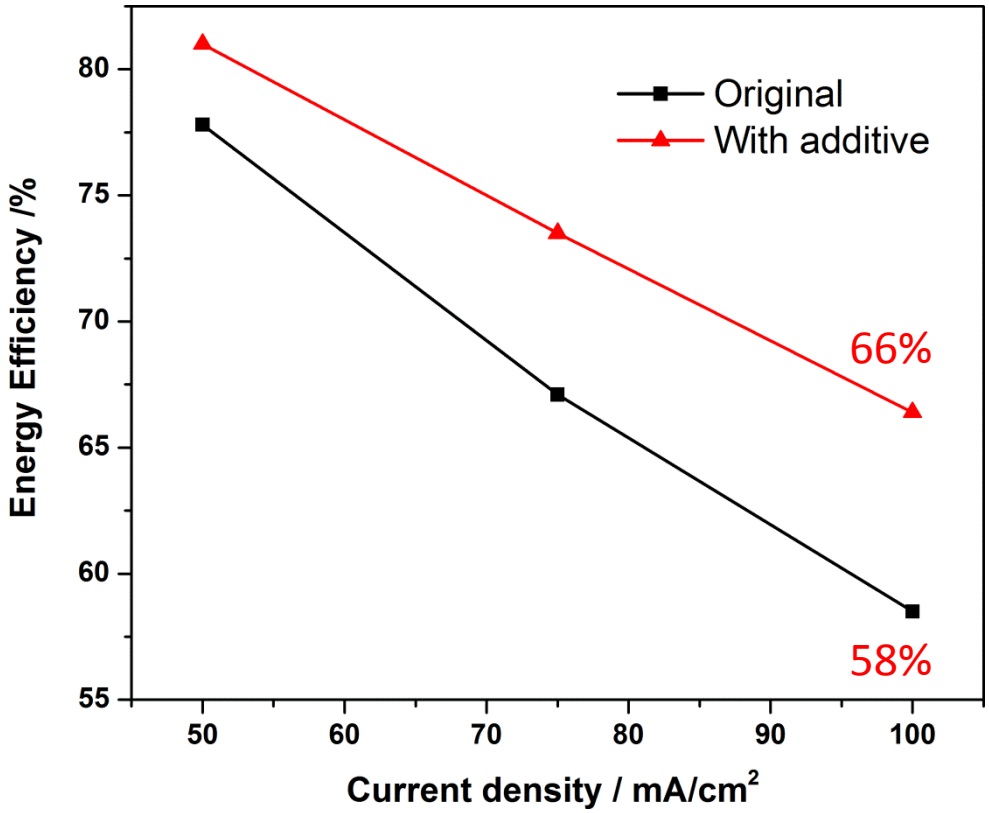


Efficiencies of the PVC separator in a 2.5M mixed acid VRB at 50mA/cm^2 current.

X. Wei, et al, *JPS*, **218**, 39-45, 2012
X. Wei, *et al*, in preparation.

Improvement of Power Output-Catalyst

Improvement in the current density of RFB leads to a smaller stack size, therefore dramatically reduce the cost.



Improvement in the energy efficiency of 8% at 100mA/cm^2 in a 1.5M Fe/V flow battery using Nafion 212.

Accomplishments

1. Identified the cause of V(III) electrolyte precipitation.
2. Optimized Fe/V electrolyte expand the temperature from 0~50^{o}C to -10~50^{o}C.
3. Identified the cause of VRB capacity decay.
4. Developed various methods to mitigate the capacity decay.
5. Developed Low-cost separators for VRB application.
6. Identified catalyst to improve the RFB energy efficiency at high current density.

Future Work

- Continuous optimization of V/V and Fe/V electrolyte
- Investigation of V composition change in mixed-acid VRB
- Development and validation of low-cost membrane/seperator
- Improve the RFB power output.

Publication

- **Wei Wang, Qingtao Luo, Bin, Li, Xiaoliang Wei, Liyu Li, Zhenguo Yang, "Recent progress on the redox flow battery research and development"** ***Advanced Functional Materials*****, DOI: 10.1002/adfm.201200694**
- Qingtao Luo, Liyu Li, Zimin Nie, Wei Wang, Xiaoliang Wei, Bin Li, Baowei Chen, Zhenguo Yang, "In-situ investigation of vanadium ion transport in redox flow battery" *J. Power Sources*, **218**, 2012, 15-20.
- Xiaoliang Wei, Liyu Li, Qingtao Luo, Zimin Nie, Wei Wang, Bin Li, Guan-Guang Xia, Eric Miller, Jeff Chambers, Zhenguo Yang, "Microporous separators for Fe/V redox flow batteries" *J. Power Sources*, **218**, 2012, 39-45.
- Wei Wang, Liyu Li, Zimin Nie, Baowei Chen, Qingtao Luo, Yuyan Shao, Xiaoliang Wei, Feng Chen, Guan-Guang Xia, Zhenguo Yang, "A new hybrid redox flow battery with multiple redox couples" *Journal of Power Sources*, **216**, 2012, 99-103.
- Wei Wang, Wu Xu, Lelia Cosimbescu, Daiwon Choi, Liyu Li and Zhenguo Yang, "Anthraquinone with tailored structure for a nonaqueous metal–organic redox flow battery" *Chem. Commun.*, 2012, **48**, 6669-6671
- Qingtao Luo, Liyu Li, Wei Wang, Zimin Nie, Xiaoliang Wei, Bin Li, Baowei Chen, Zhenguo Yang, Vincent Sprenkle, Submitted.
- Bin Li, Liyu Li, Wei Wang, Zimin Nie, Xiaoliang Wei, Qingtao Luo, Zhenguo Yang, Vincent Sprenkle , Submitted.

Acknowledgements

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