

New Generation Aqueous Base Redox Flow Battery Component Development

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Dr. Imre Gyuk

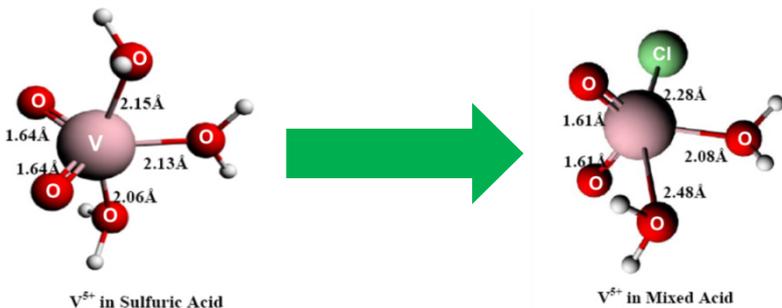


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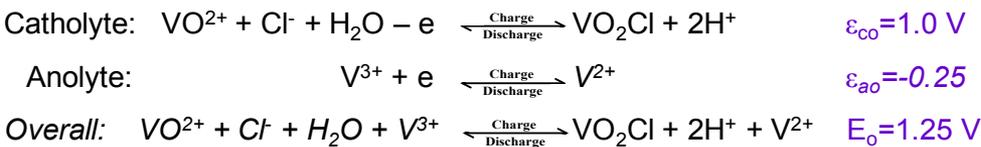
Review of previous work

Mixed-acid VRB

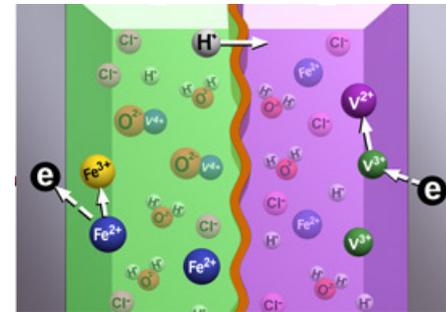


Double Energy Density
Extend temperature window

2.5M, ~30Wh/L, -5~50°C

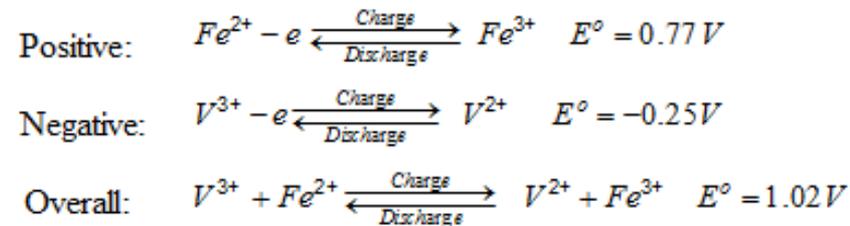


Fe/V RFB

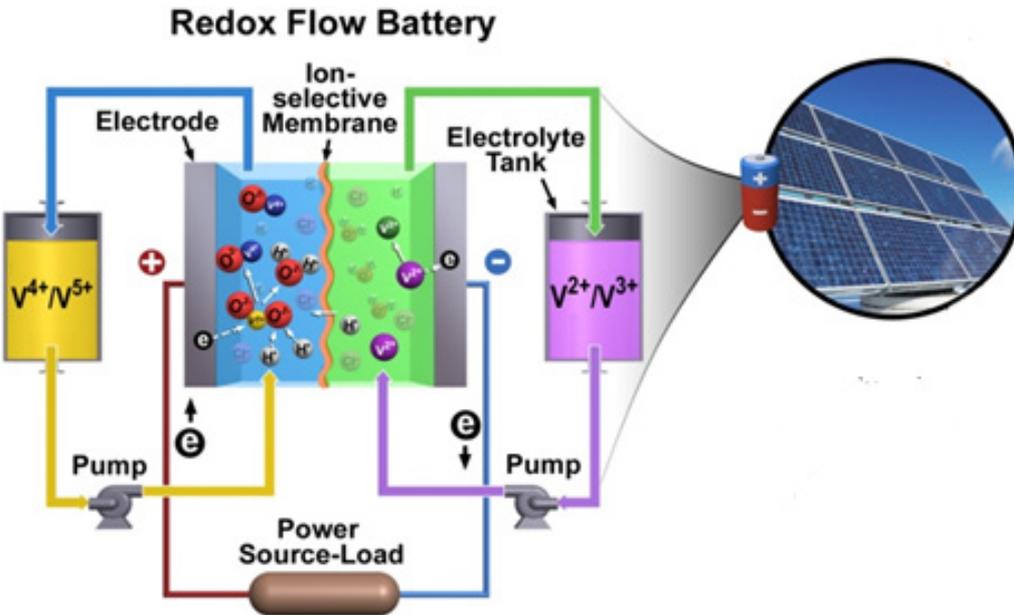


Higher utilization, stable cycling
Low-cost membrane

1.5M, ~15Wh/L, 0~50°C



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

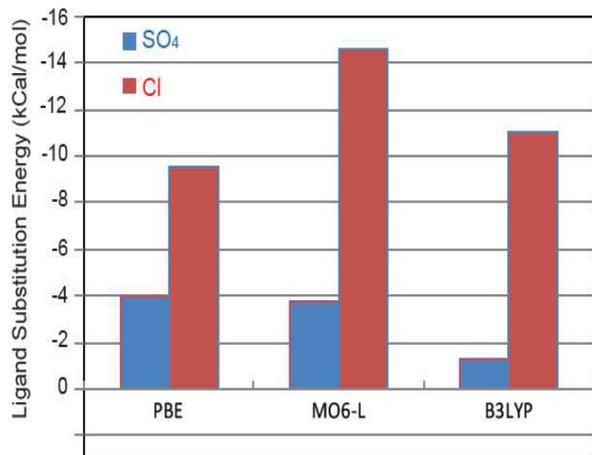
- Low-cost separator for VRB;
- Screening commercial separator.

□ Improvement of Power Output

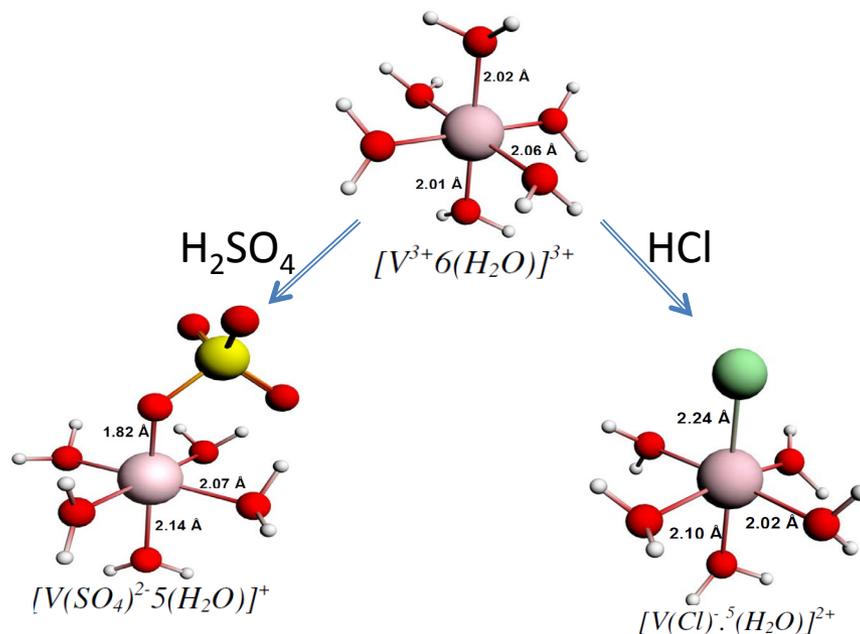
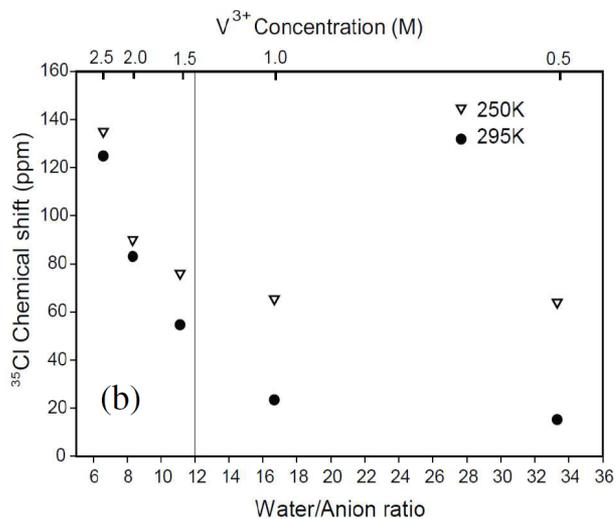
- Catalyst.

Electrolyte Study - V/V electrolyte

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



Reaction pathway from NMR



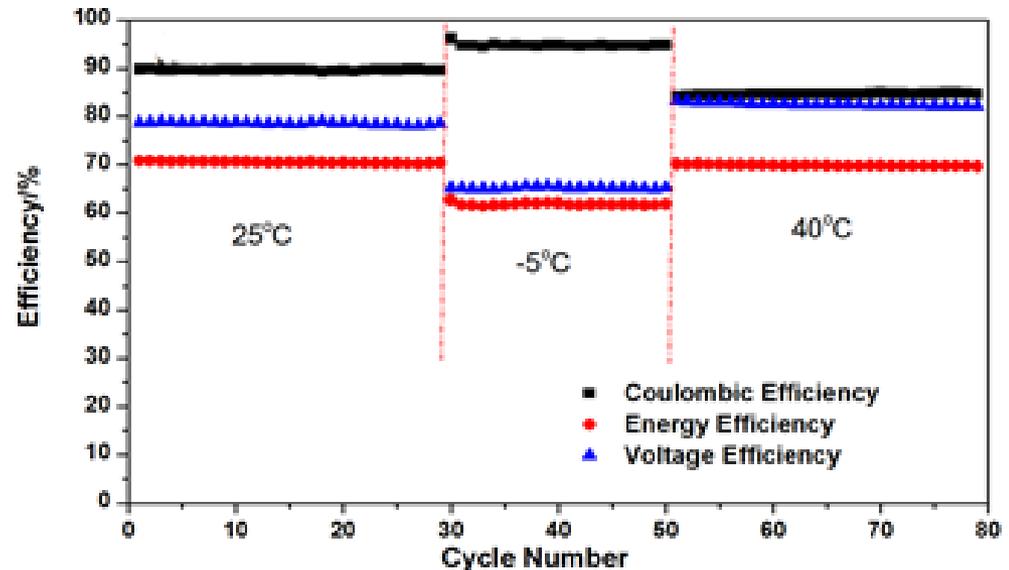
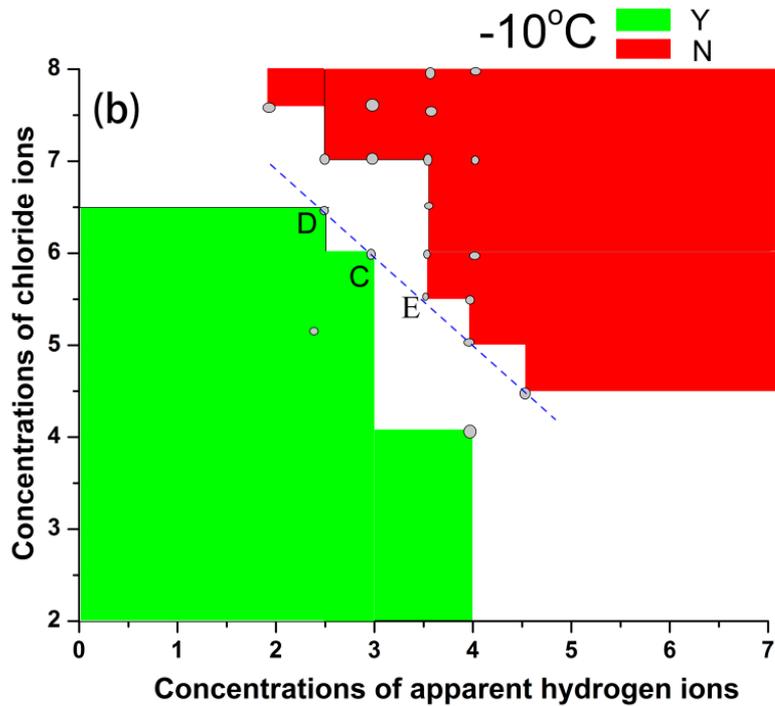
Anion complexation of V^{3+} molecule in Electrolytes leads to neutral molecules and subsequent precipitations,



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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 Fe²⁺/V⁴⁺ electrolyte stability with respect to apparent hydrogen and chloride ions concentrations at -10°C.

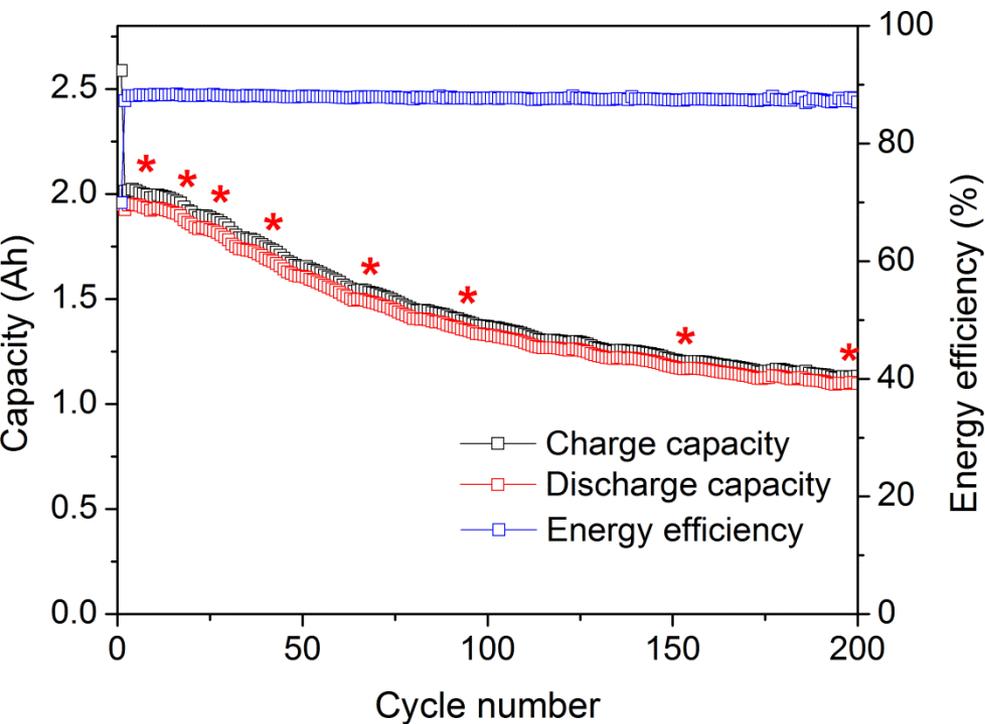


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VRB transport Phenomenon-Capacity Decay along Cycling

On-line investigation of capacity decay and composition change

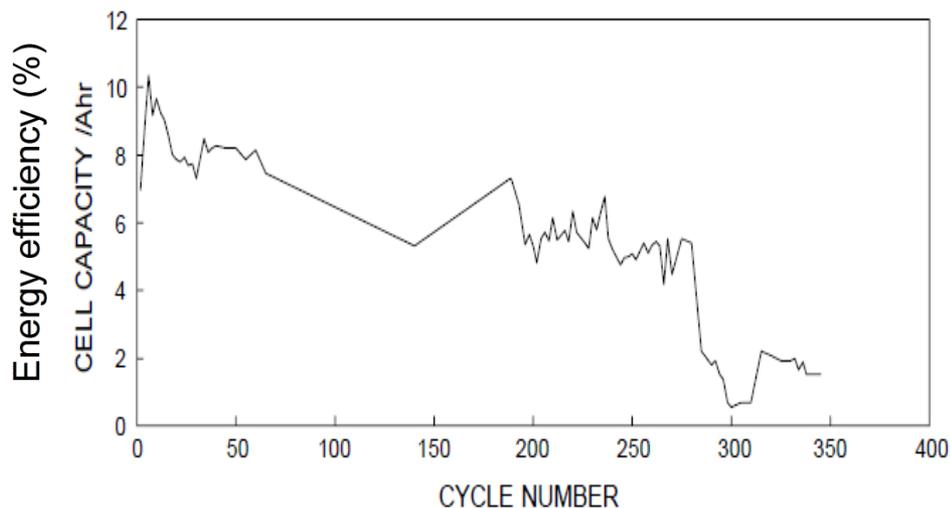


Cycling performance of a VRB using 1.7 M V and 5 M S electrolytes and N115 as the membrane.

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

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

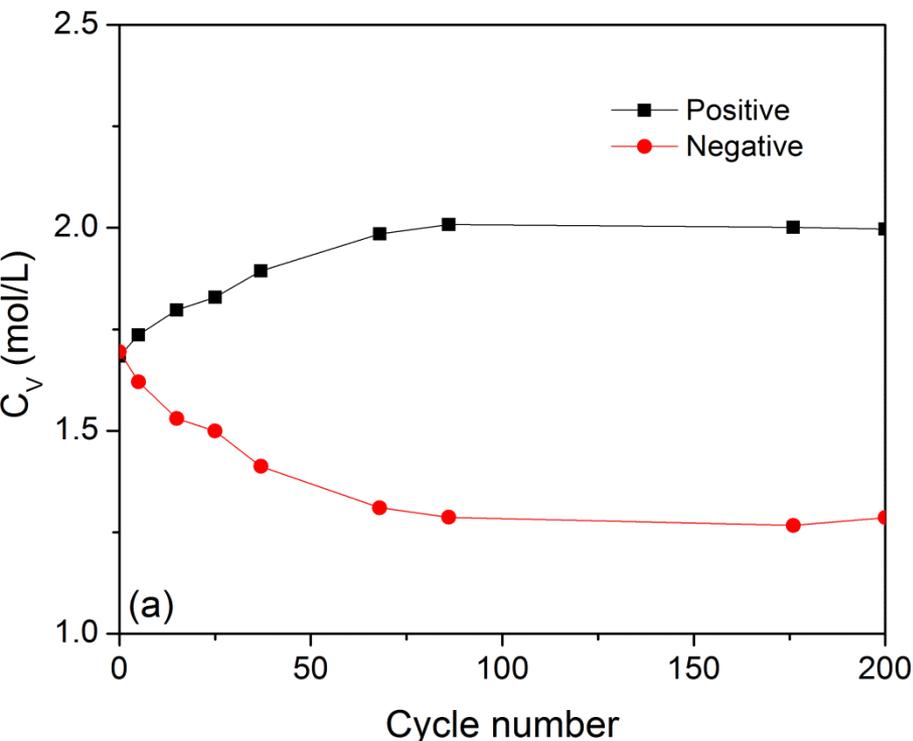


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T. Sukkar, et al, *J. of Applied Electrochemistry* **34** 137–145, 2004
Q. Luo, et al, Submitted.

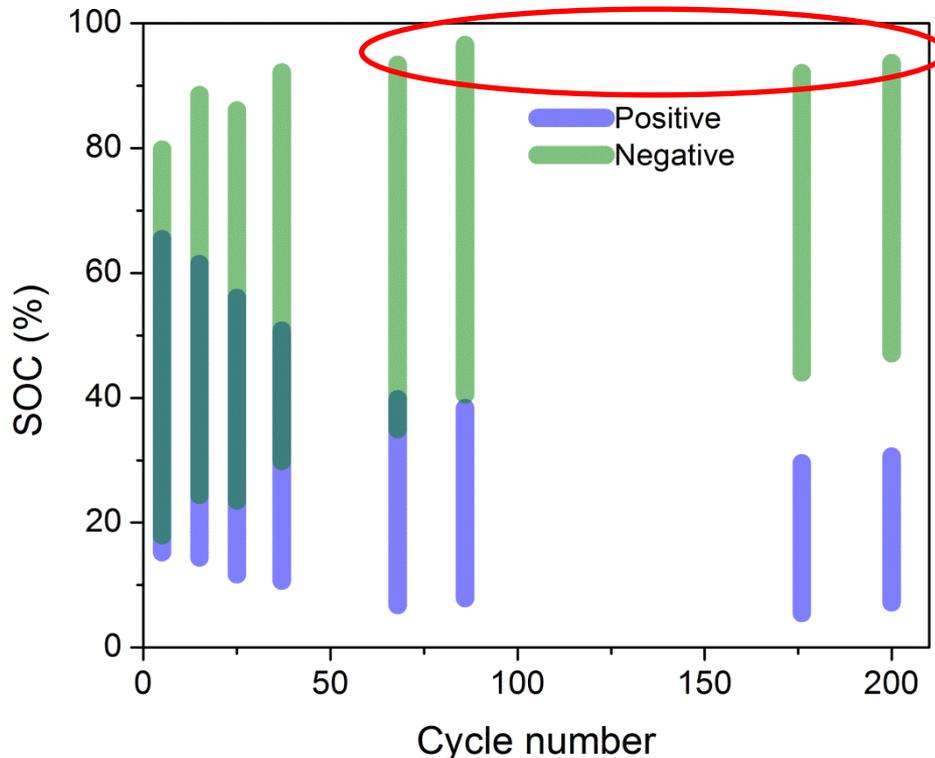
VRB transport Phenomenon- Cause of Capacity Decay

Differential transfer of vanadium ions



Variation of total vanadium ion concentration along cycling

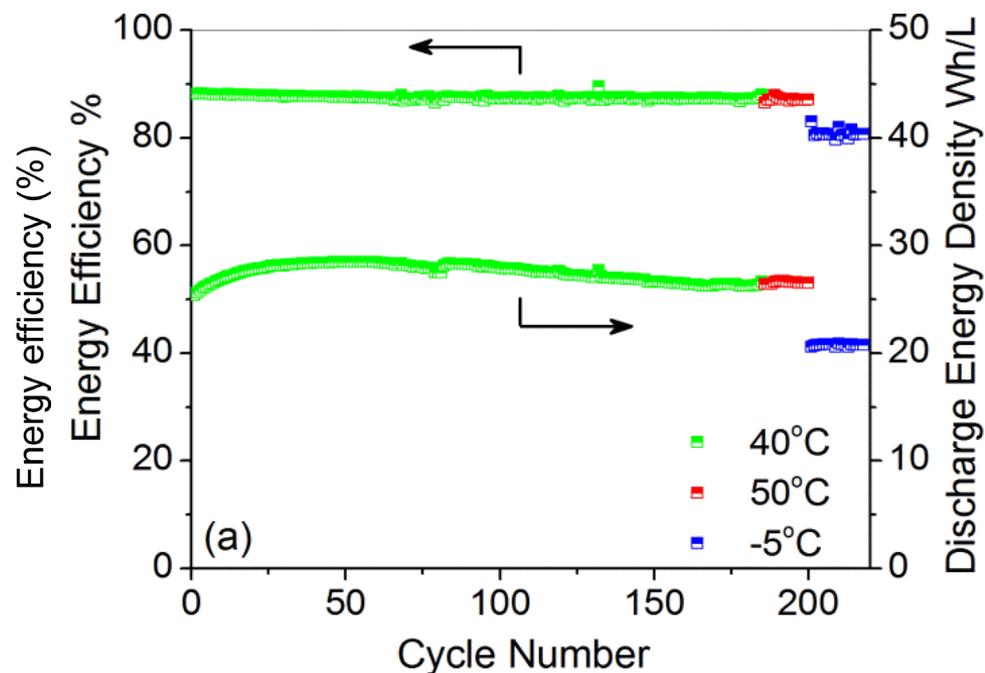
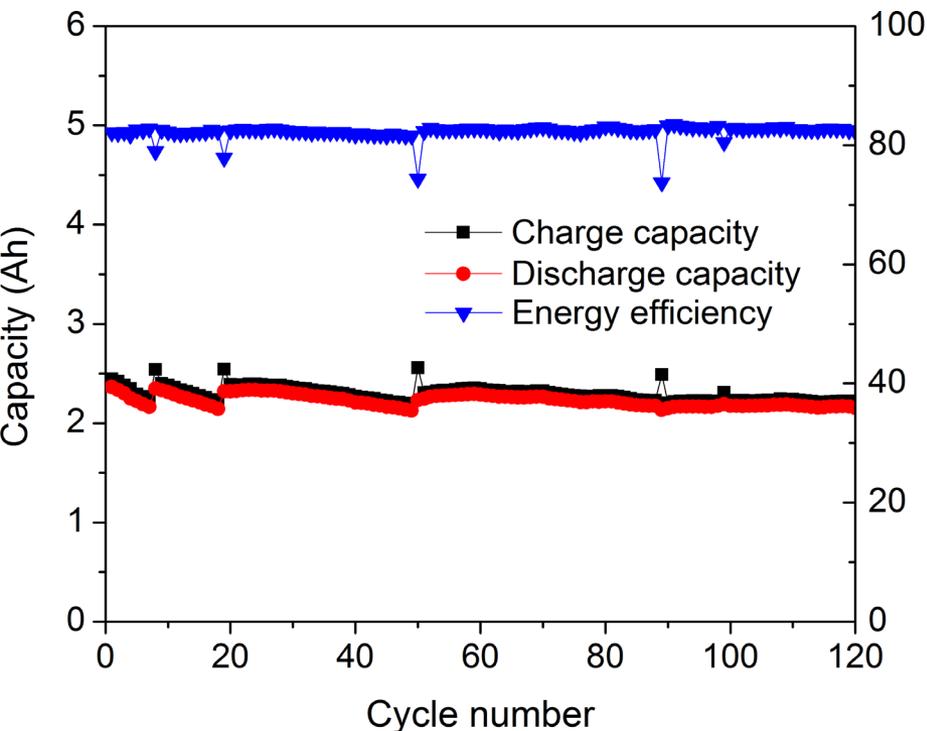
Imbalance of vanadium ion valence



Positive and negative electrolyte SoC change along cycling

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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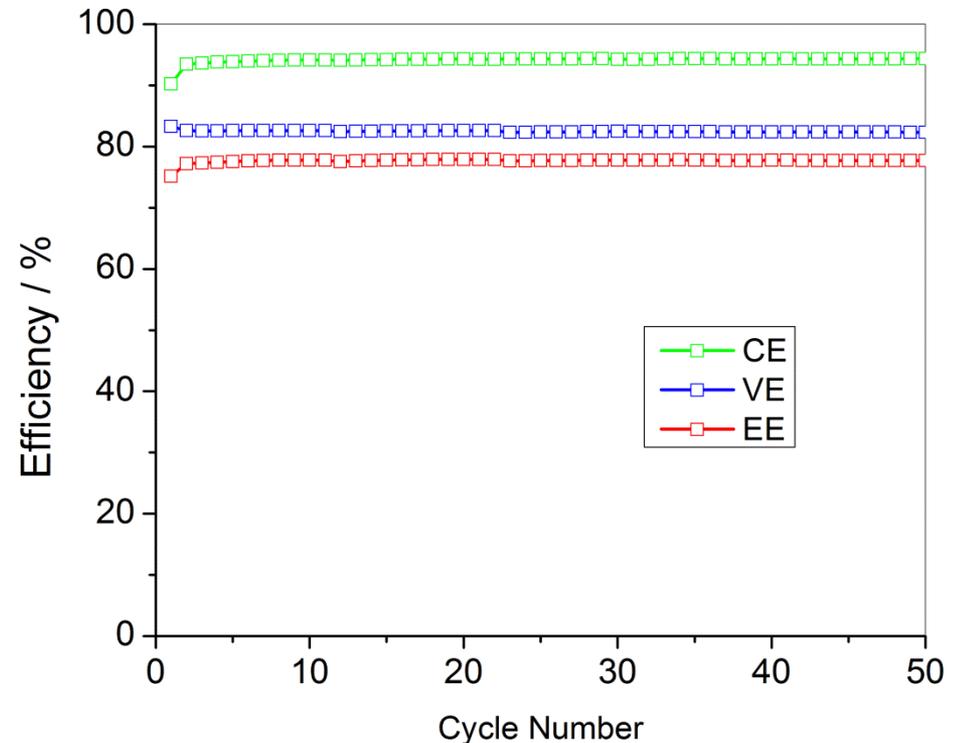
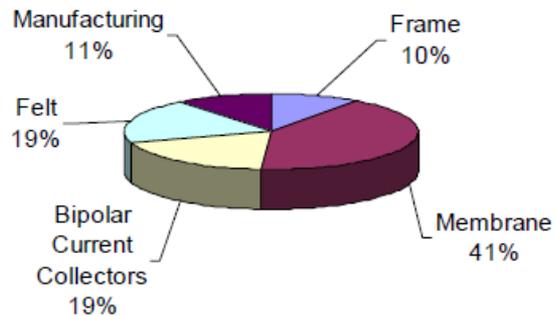
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Separator Development-Low cost VRB separator

PNNL developed low-cost VRB separator

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

Cell Stack Cost Breakdown

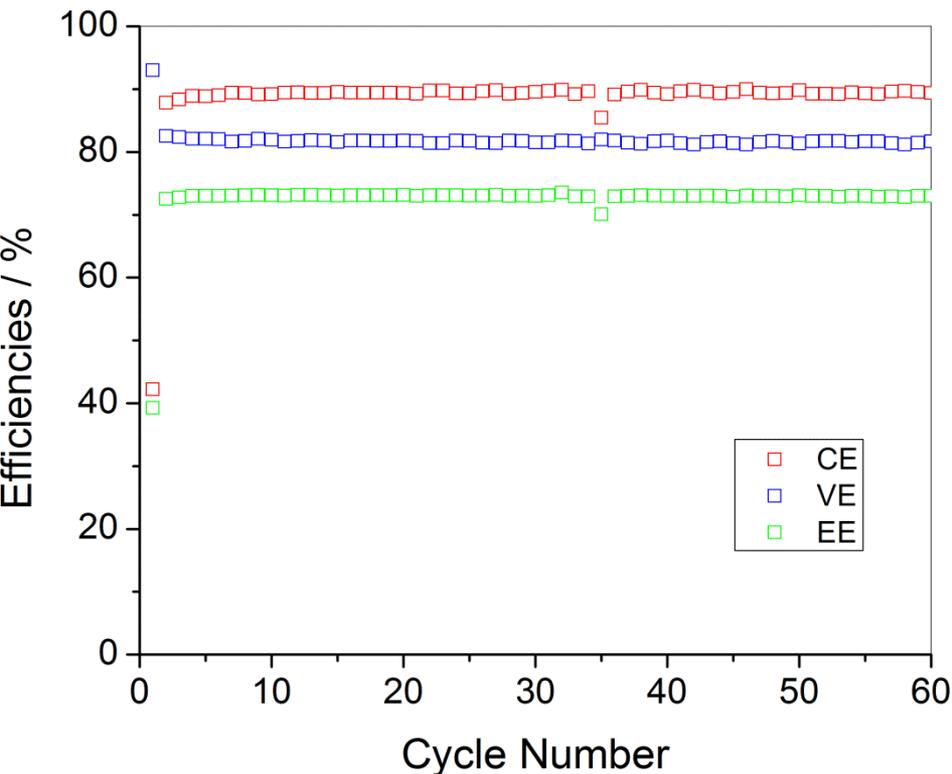


Efficiencies of the PNNL separator in a 2.5M mixed acid VRB at 50mA/cm² current.

Separator Development-Commercial separator

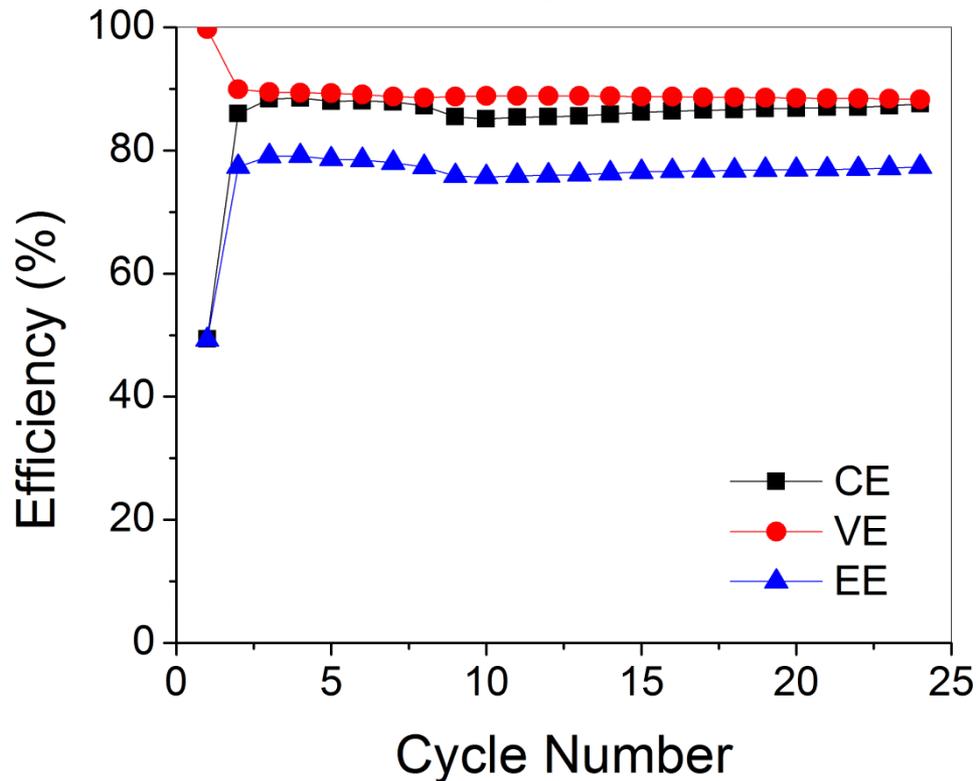
Separator development in lead-acid battery provide a wide selection of potential low cost separator for RFB application.

Daramic PE separator



Efficiencies of the PE separator in a 1.5M Fe/V at 50mA/cm² current.

PVC separator



Efficiencies of the PVC separator in a 2.5M mixed acid VRB at 50mA/cm² current.

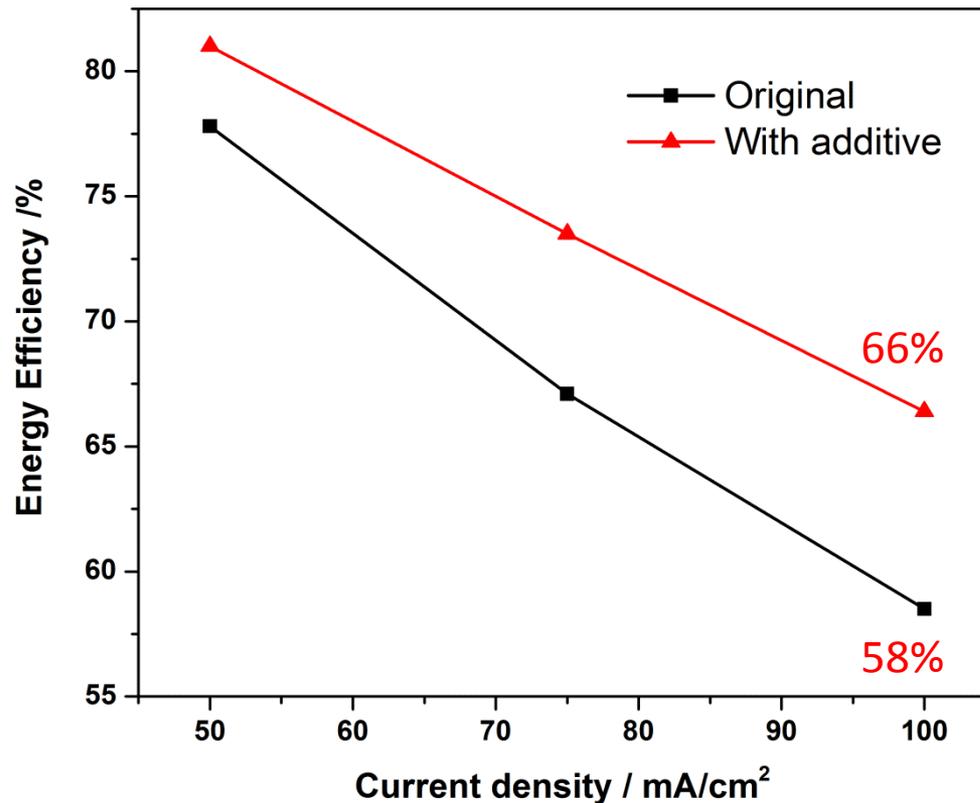
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X. Wei, et al, *JPS*, **218**, 39-45, 2012
X. Wei, et al, in preparation.

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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/cm² in a 1.5M Fe/V flow battery using Nafion 212.



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Accomplishments

1. Identified the cause of V(III) electrolyte precipitation.
2. Optimized Fe/V electrolyte expand the temperature from 0~50°C to -10~50°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.

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