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Next Generation Aqueous Redox Flow Battery Development

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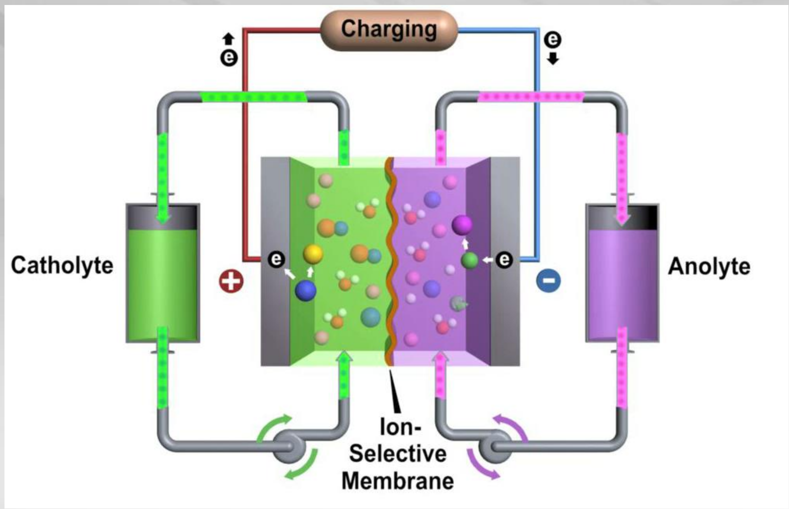
Pacific Northwest National Laboratory
Electrochemical Materials and Systems

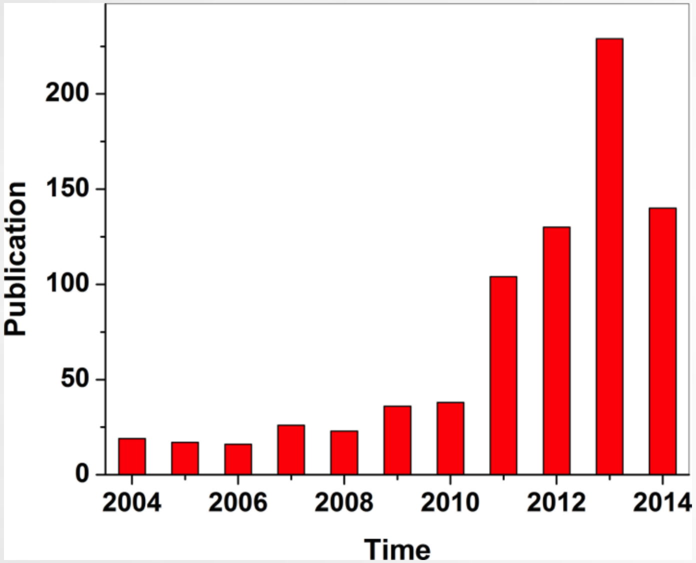
DOE Office of Electricity Energy Storage Program – Imre Gyuk Program Manager.

OE Energy Storage Systems Program Review

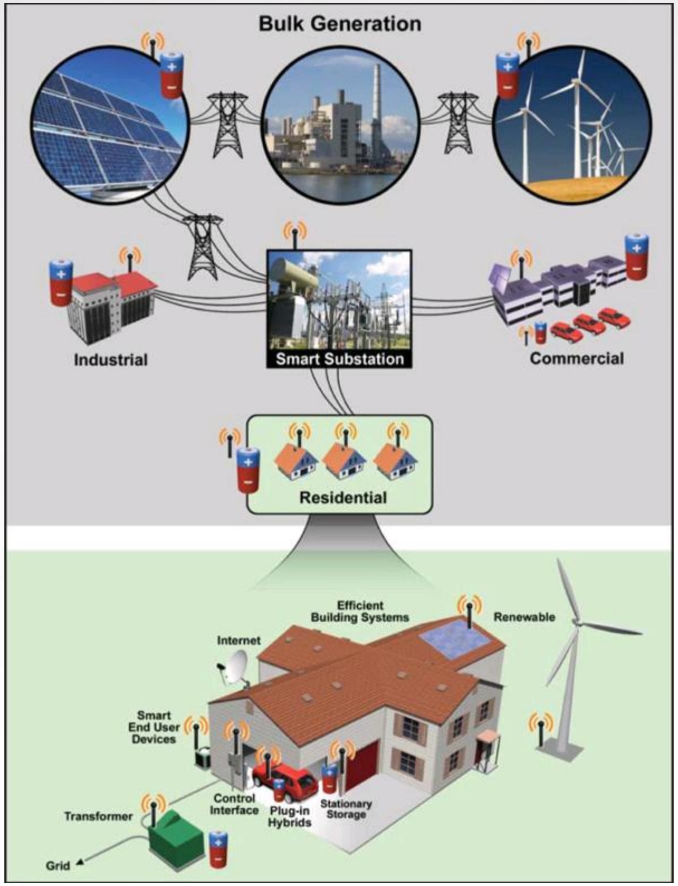
September 16-19th, 2014

Redox flow batteries (RFB)





Applications



An integrated approach to advance the RFB technology

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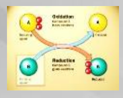
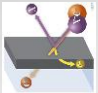


Novel electrolyte

- ➢ Solvation chemistry study
- ➢ Improved stability and energy density
- ➢ New redox chemistries

✧ L. Li, etc. *AEM* **2011**, 3
✧ W. Wang, etc. *EES* **2**
✧ W. Wang, etc. *AEM*

❖ 2 patents, 4 patent



Advanced electrode

- ➢ New electrode materials and structure
- ➢ Powerful catalyst

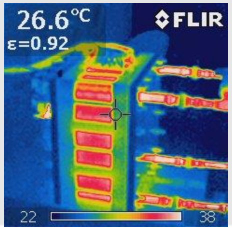
no.lett. **2013**, 1330-1335
o.lett. **2014**, 158-165

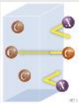
cations

Flow stack R&D

- ➢ Flow field design
- ➢ System integration and analysis

✧ S. Kim, etc. *JPS*. **2013**, 300





High perform
and transport

- ➢ New membrane/se
- ➢ Membrane fouling n
- ➢ Ion transport study

✧ X. Wei, etc. *AEM* **2013**, 1215-1220
✧ Q. Luo, etc. *ChemSusChem* **2013**, 268
✧ B. Li, etc. *ChemSusChem* **2014**, 577

❖ 1 patent applications

eous RFB

redox chemistries
r non-aqeuous systems
➢ New electrode

✧ W. Wang, etc. *ChemComm.* **2012**, 6669
✧ X. Wei, etc. *AEM, in press*, **2014**
✧ X. Wei, etc. AM, *in press*, **2014**

❖ 4 patent applications

Review of RFB R&D at PNNL

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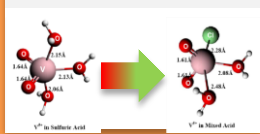
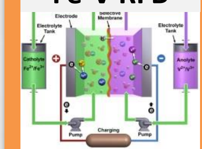
Discovery → Deployment | IP | R&D | Demo | License: UET/ X /Aartha/Wattjoule

Program start

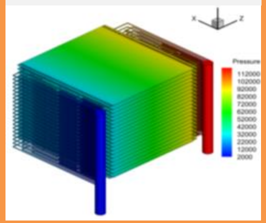
Mixed-acid VRB



Fe-V RFB

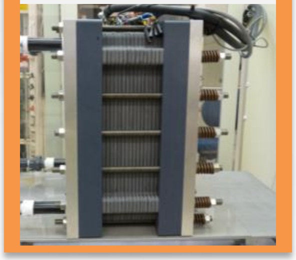


Stack R&D



Paper published

1kW/1kWh DEMO



MVRB License
UET
Company X

FLC

UET 125kW system

Fe-V License
Aartha USA

New Chemistry

MVRB License
Wattjoule

Patents granted

UET first commercial system

What's next ?

Major Challenge of the current RFB technology: low energy density

120MWh system, peak power ~15MW.
Each tank holds 1800m^3 of electrolyte.

- Large form factor/footprint
- Limited application

How to design a high energy RFB ?

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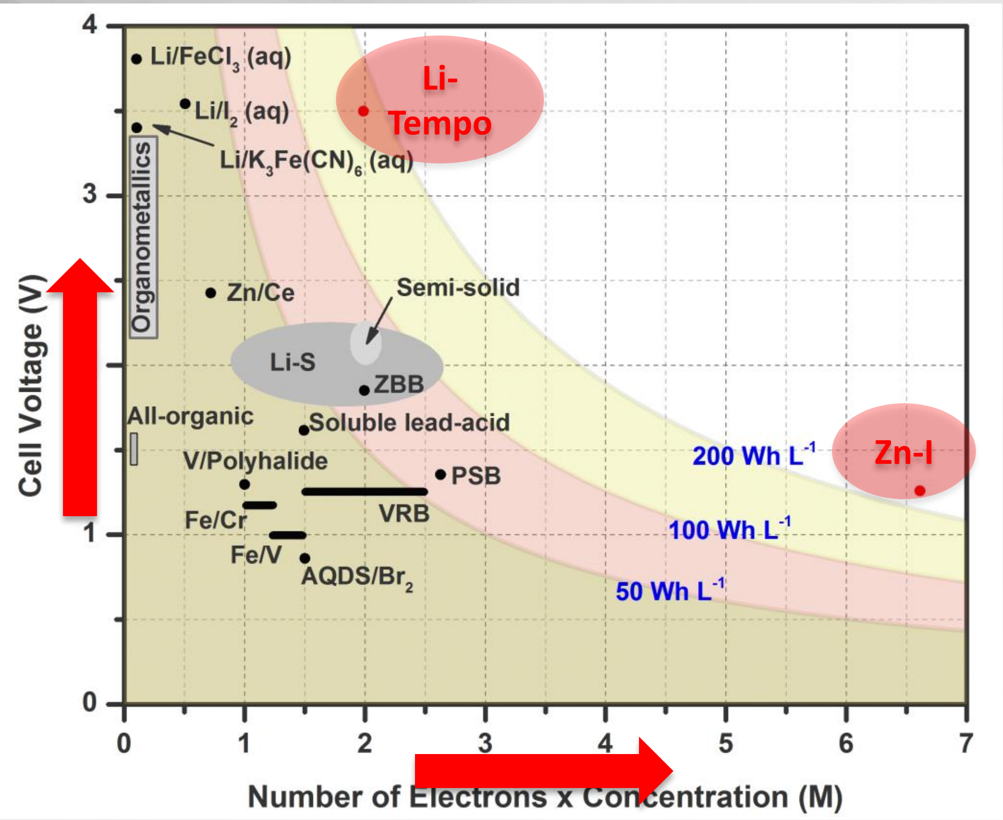
$$E = \frac{NC_a FV}{n}$$



E, system energy density based on the electrolyte composition and volumes

N, the number of electrons involved in the redox reaction

F, Faraday constant (26.8 Ah mol^{-1})

C_a, Max concentration of active redox species

V, Voltage of the cell

n, number of electrolyte tanks

- Hybrid flow battery design
- Ambipolar electrolyte
  Both anion and cation are active species.
- Bifunctional electrolyte
  Active species can act as charge carrier.

High energy density Zn-Polyiodide aqueous RFB

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Solubility of ZnI_2 is 7M in water → theoretical energy density ~322Wh/L

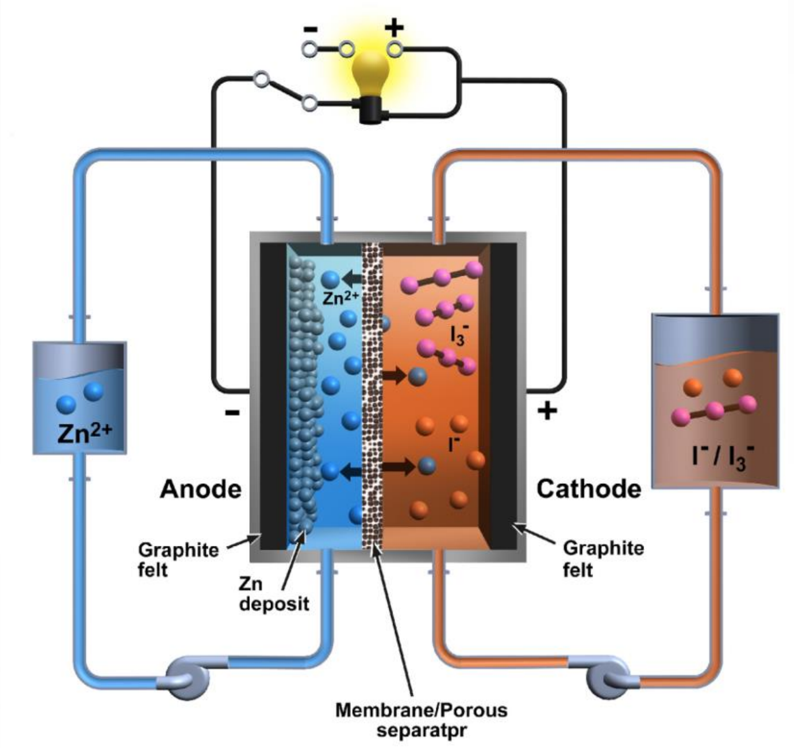
Identify high solubility redox active species

$$I_2(s) + I^- \leftrightarrow I_3^- \qquad K \approx 720 \pm 10 (298K)$$

$$Positive: 3I^- \underset{Discharge}{\overset{Charge}{\longleftrightarrow}} I_3^- + 2e^- (E_0 = 0.536V)$$

$$Negative: Zn^{2+} + 2e^- \underset{Discharge}{\overset{Charge}{\longleftrightarrow}} Zn (E_0 = -0.7626V)$$

$$Overall: Zn^{2+} + 3I^- \underset{Discharge}{\overset{Charge}{\longleftrightarrow}} Zn + I_3^- (E_0 = 1.2986V)$$



Characteristics of the Zn-I_x RFB

- Ambipolar electrolyte
- Bifunctional electrolyte
- High energy density
- High safety: PH value: 3~4
  No strong acid
  No hazardous materials

Electrochemical performance

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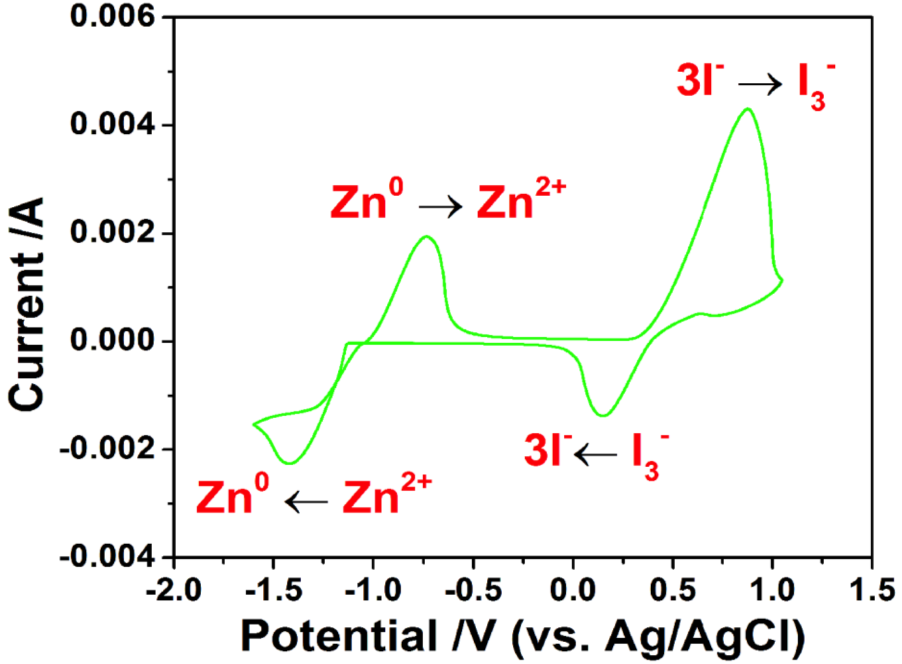
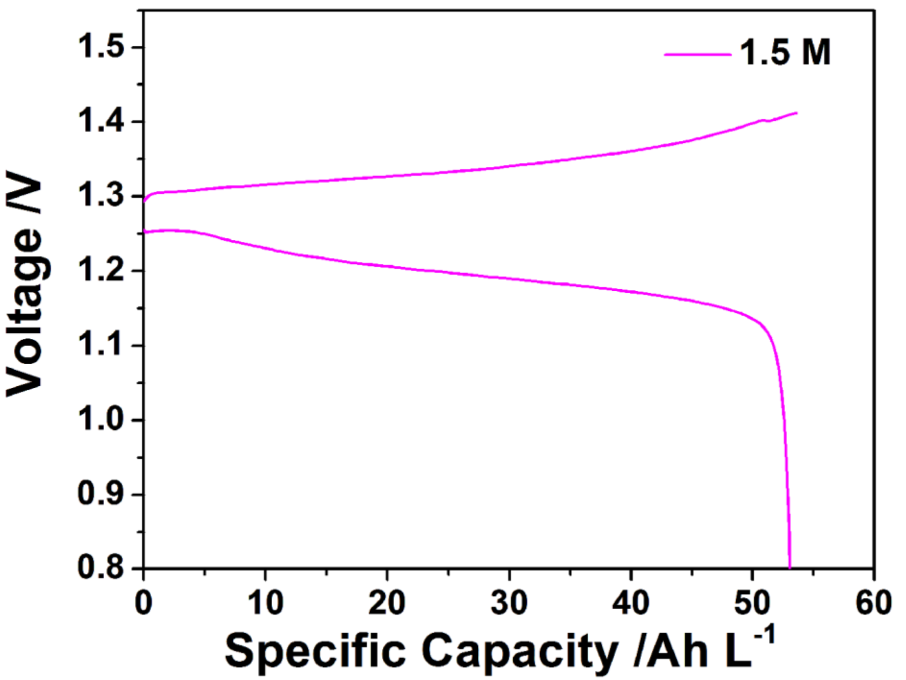


CV of 0.085 M ZnI_2 on a glassy carbon electrode at the scan rate of 50 mV s^{-1}.



Typical charge-discharge curves at 1.5 M ZnI_2 at a current density of 20 mA cm^{-2}.

Electrochemical performance

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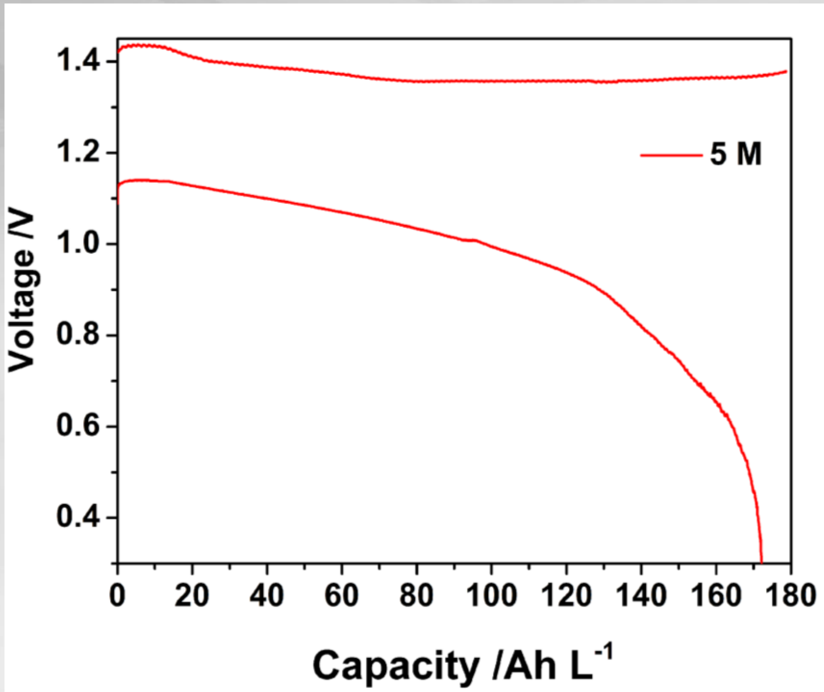
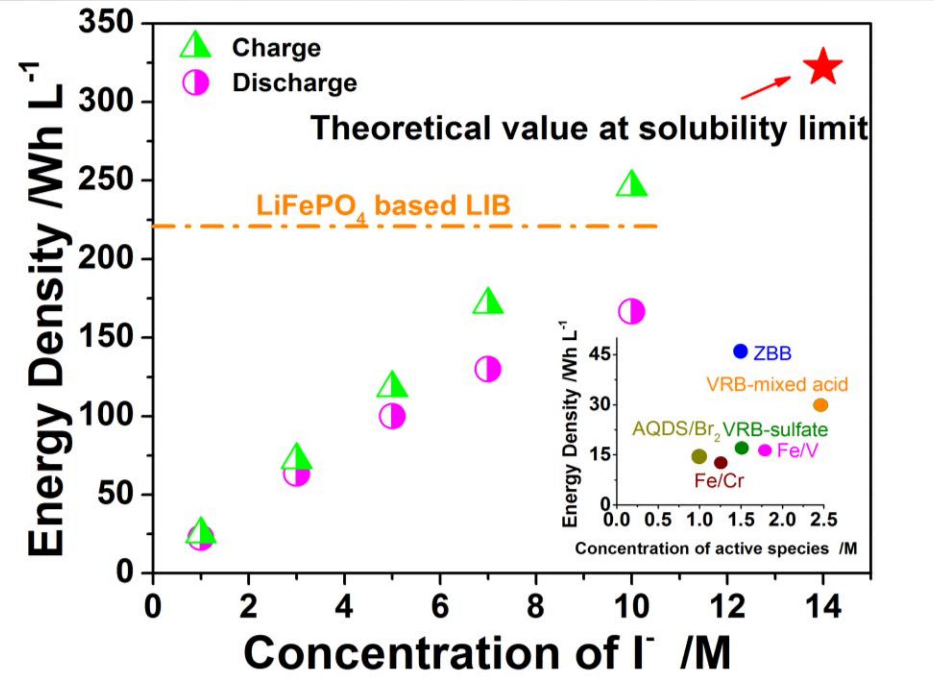


Charge/discharge curves for the cell with 5.0 M ZnI_2 and Nafion 115 as membranes operated at the current density of 5 mA cm^{-2}.



The charge and discharge energy density as a function of the concentration of I^-. The inset lists concentration vs. energy density of several current aqueous redox flow battery chemistries for comparison.

Cycling performance

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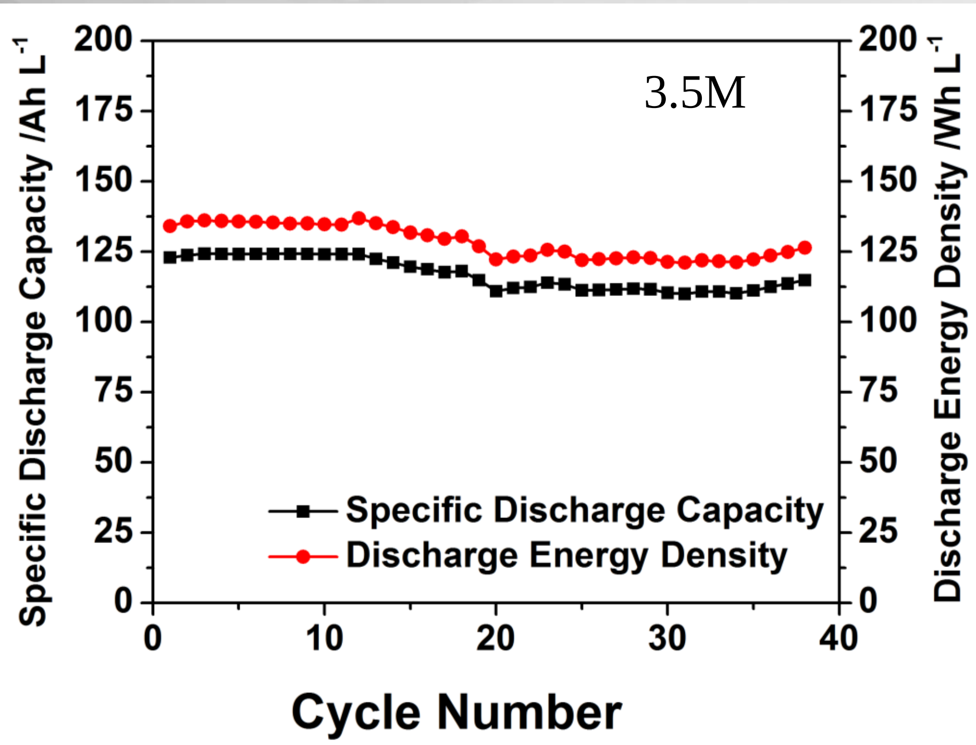

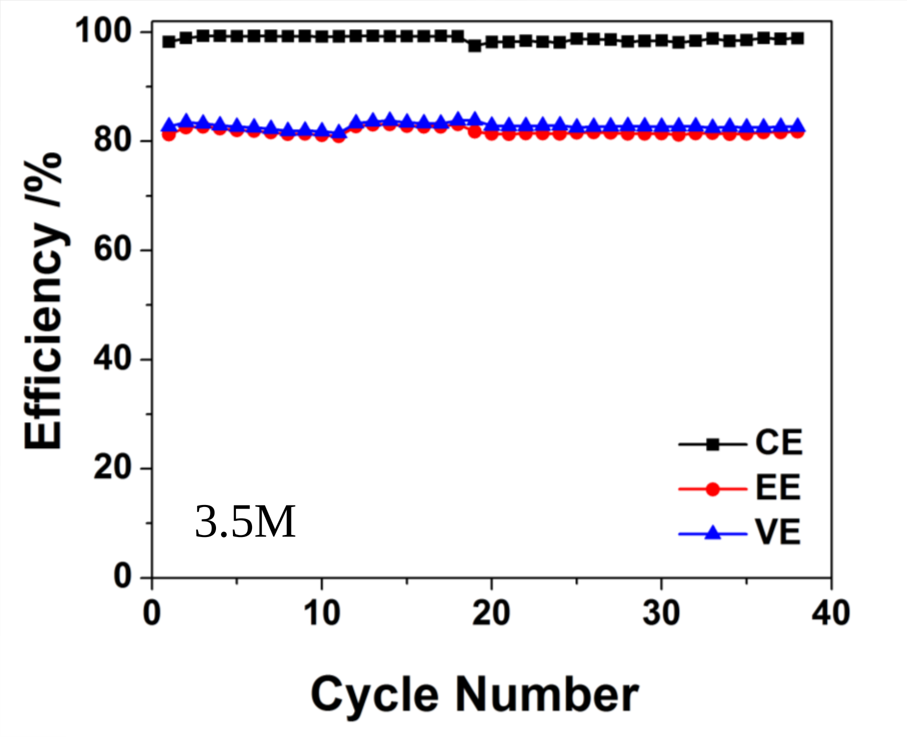

Capacities and energy density of the cell with 3.5 M ZnI_2 and Nafion 115 as membranes under the current density of 10 mA cm^{-2}.

Efficiencies of the cell with 3.5 M ZnI_2 and Nafion 115 as membranes under the current density of 10 mA cm^{-2}.

Polyiodide species in the catholyte

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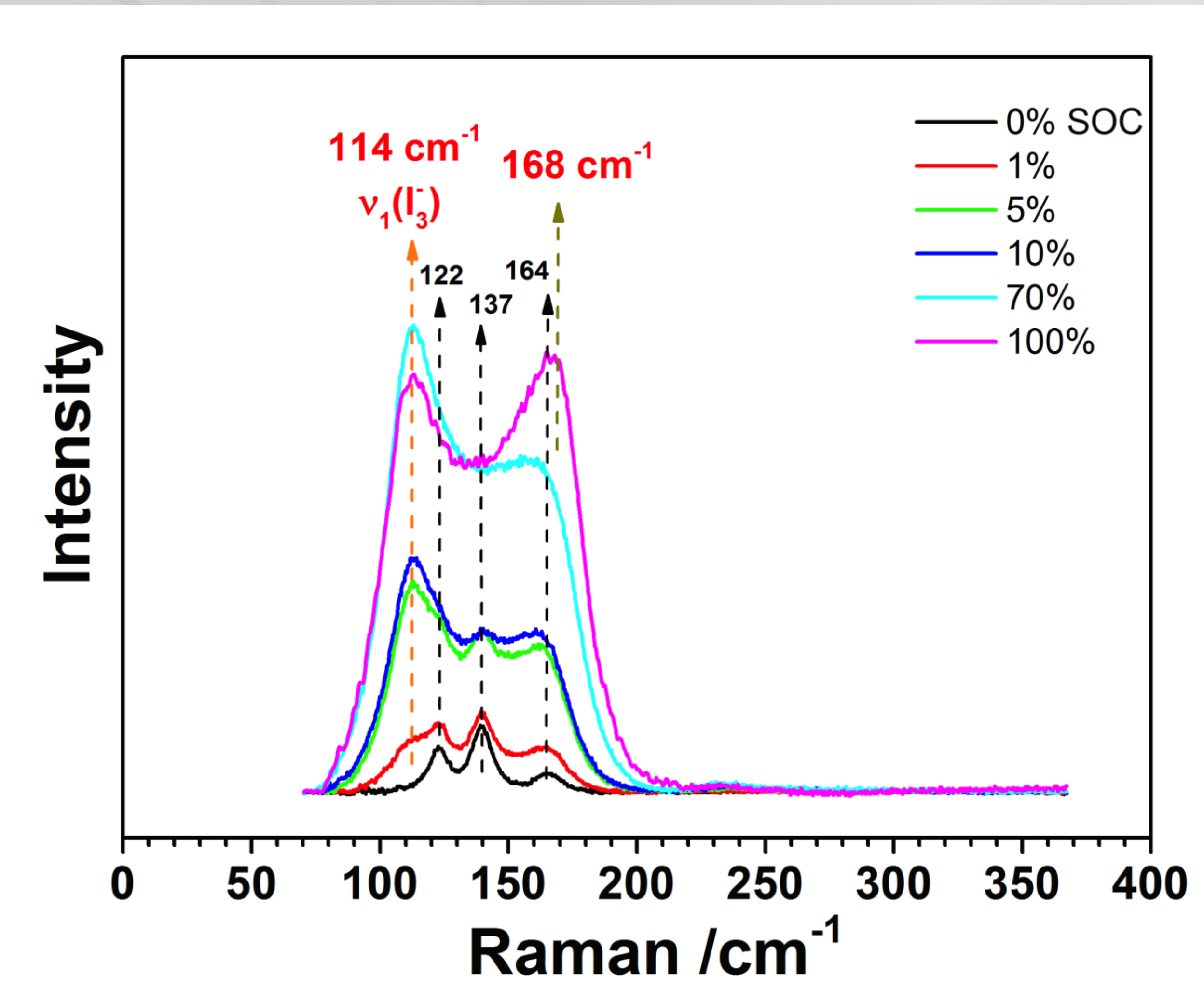

Raman spectra of catholytes at different state of charges (SOCs) from 0 to 100% SOC.

Temperature stability of the catholyte

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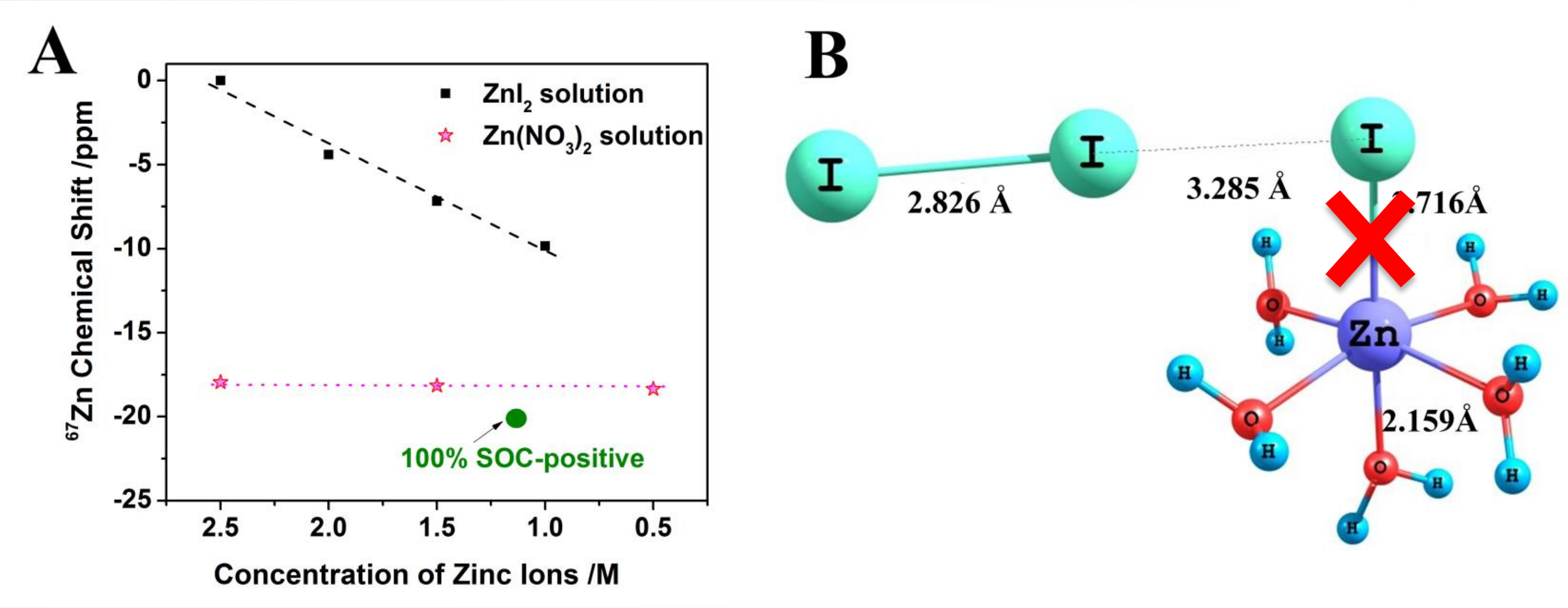
Temperature stability (off-line) of 100% SOC catholytes

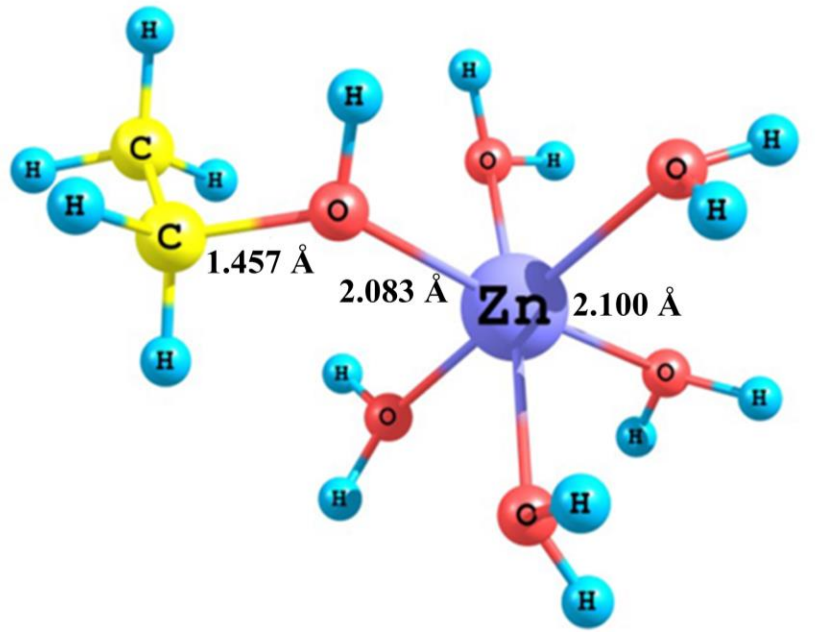
ZnI_2 (M)	50°C	25°C	0°C	-10°C	-20°C
3.5	stable	stable	ppt	ppt	ppt
2.5	stable	stable	ppt	ppt	ppt

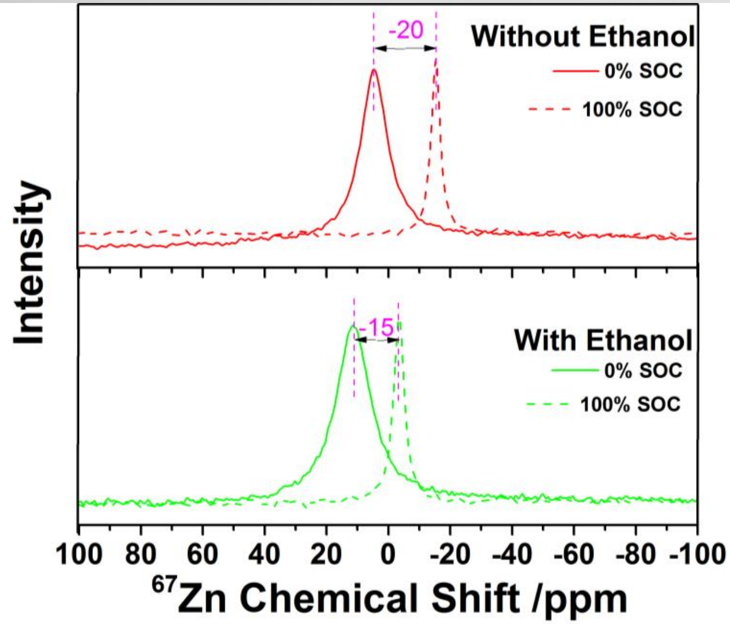
NMR and DFT study of the catholyte solution chemistry



$$[Zn^{2+}.I_3^-.5H_2O]^+ \leftrightarrow [Zn^{2+}.I^-.5H_2O]^+ + I_2(s)$$

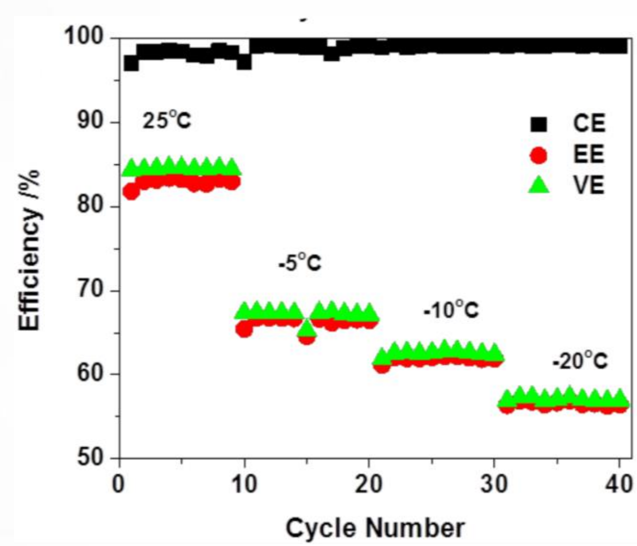
Stablize the catholyte through coordination chemistry





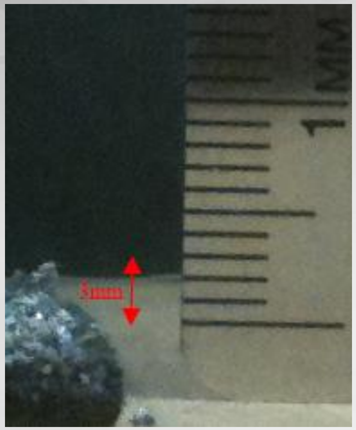
Temperature stability with alcohol additives

ZnI_2 (M)	Vol% EtOH	50°C	25°C	0°C	-10°C	-20°C
3.5	25	stable	stable	stable	stable	stable
	25 (EG)	stable	stable	stable	stable	stable
2.5	25	stable	stable	stable	stable	stable

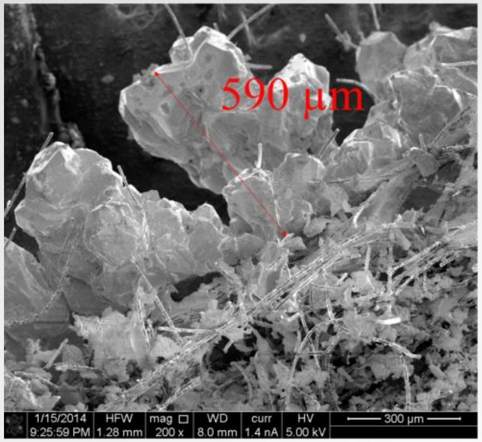


Mitigation of Zinc dendrite growth

Dendrite growth in the flowing electrolyte



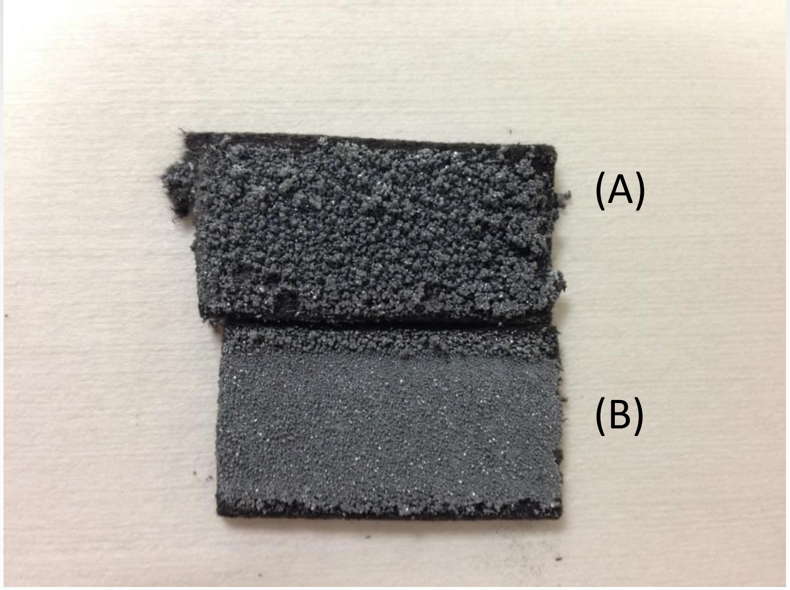
(A)



(B)

Morphologies of zinc dendrites after charge for the cells with 3.5 M ZnI_2 operated at the current density of 10 mA cm^{-2} (**A**) in the static cell and (**B**) the flow rate of 100 mL min^{-1}.

Alcohol complexing ameliorate the dendrite growth



Morphologies of zinc dendrites after charge (**A**) without EtOH and (**B**) with EtOH in the electrolytes.

Development on Membrane and Electrode

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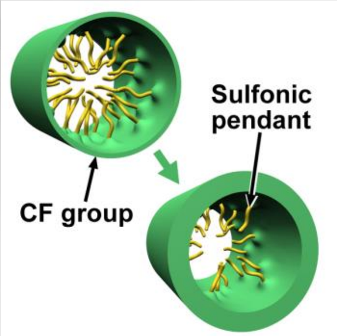
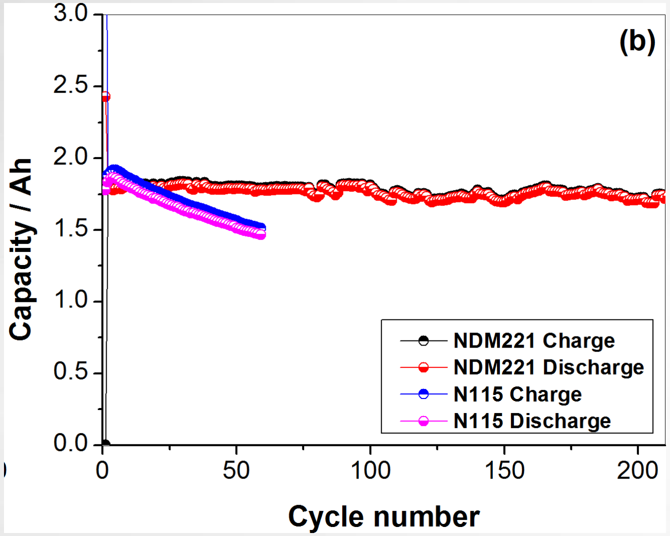
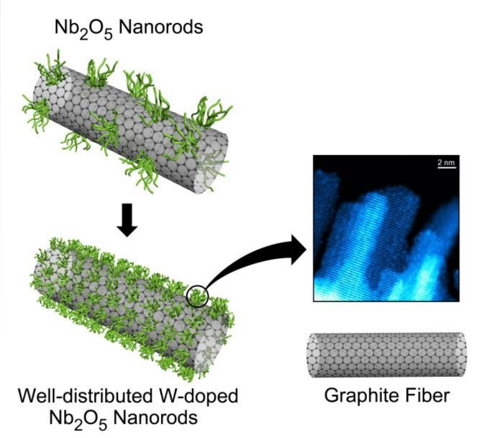
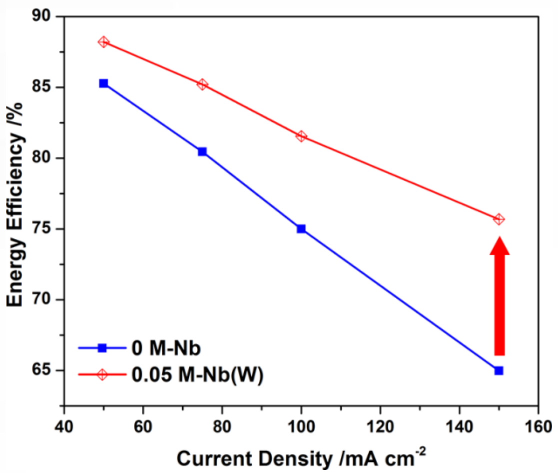
Development of high selective PFSA membrane with Dupont





Development of advanced RFB electrode





Please check out our membrane and electrode research at poster session

Summary

- High energy density Zn-I RFB (>150Wh/L) has been designed and demonstrated
- Alcohol molecules are found to complex with the Zn ions, which improve the temperature stability and ameliorate Zn dendrite growth.

Future work

- Investigation of the Zn dendrite formation mechanism and development of mitigation methods.

Acknowledgements

- US Department of Energy's Office of Electricity Delivery and Reliability – Dr. Imre Gyuk, Energy Storage Program Manager.
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