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Advanced Aqueous Redox Flow Battery

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Pacific Northwest National Laboratory

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Redox flow batteries (RFB)

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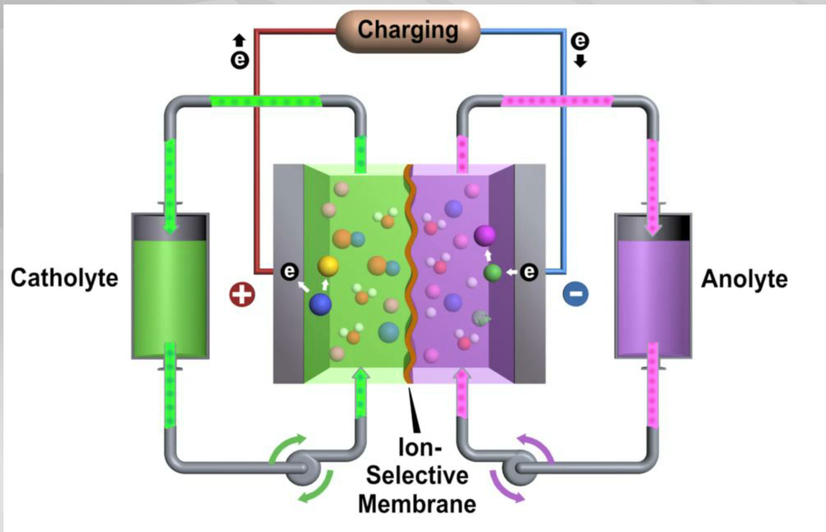
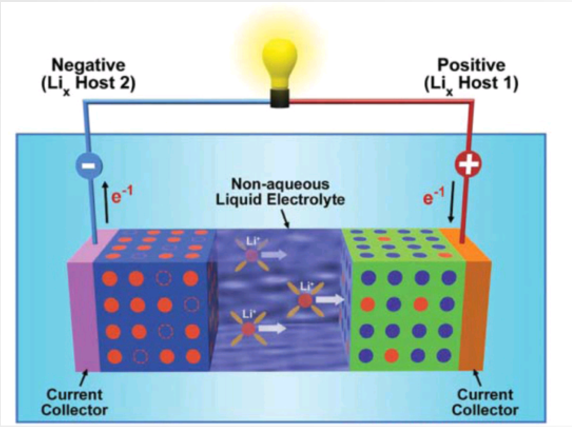
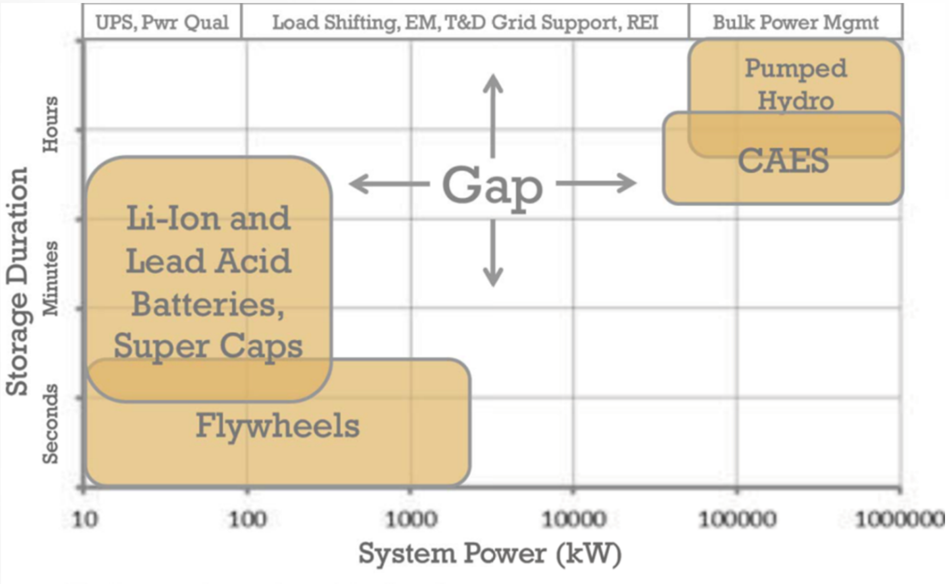


Why RFB?

- **High safety**
  - Na-S Battery: NGK 2MW system fire in September 21 of 2011.
  - Li-ion Battery: Electrovaya 1.5MW lithium polymer system fire in November of 2012.
  - Lead Acid Battery: Xtreme Power 15MW lead-acid battery fire in August of 2012

Separation of reactive materials
Easy thermal management





Zhenguo Yang, *et. al*. *Chemical Reviews*, **111**, 2011, 3577
Wei Wang, *et. al*. *Advanced Functional Materials* , **23**, 970, 2013

An integrated approach to advance the RFB technology

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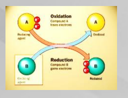
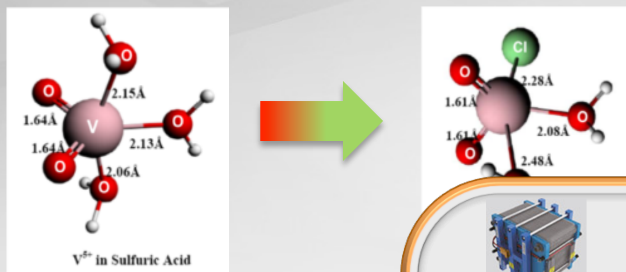
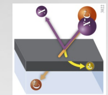


Novel electrolyte

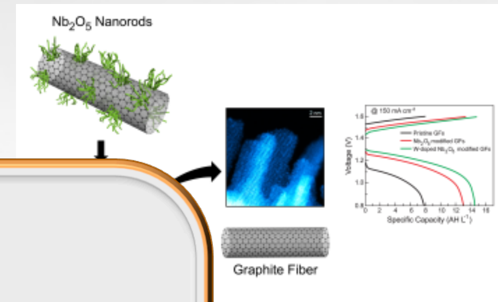


✧ L. Li, etc. *AEM* **2011**

✧ W. Wang, etc. *EES* 2



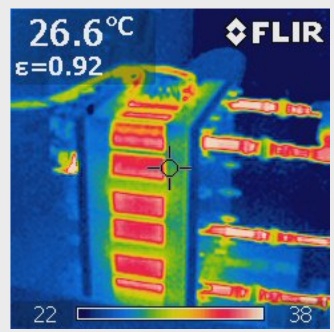
Advanced electrode

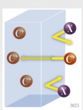


no.lett. **2013**, 1330-1335

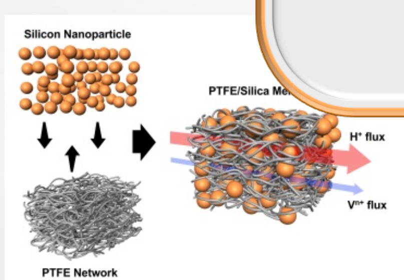
no.lett. **2014**, 158-165

Flow stack R&D





High perform and transport



✧ X. Wei, etc. *AEM* **2013**, 1215-1220

✧ Q. Luo, etc. *ChemSusChem* **2013**, 268

...eous RFB

✧ W. Wang, etc. *ChemComm.* **2012**, 6669

✧ X. Wei, etc. AM, *in press*, **2014**

Review of RFB R&D at PNNL

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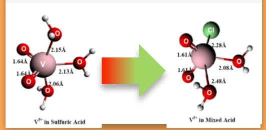
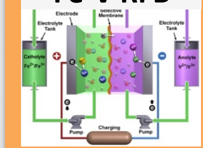
2009
- Program start

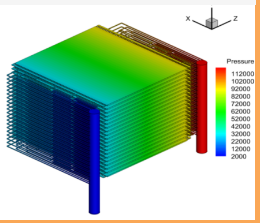
2010
- Mixed-acid VRB



- Fe-V RFB

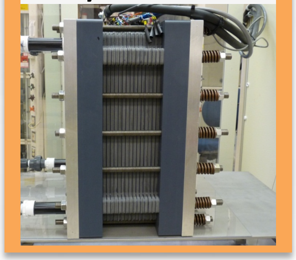


2011
- Stack R&D



- Paper published

2012
- MVRB License
  UET
  Company X
- 1kW/1kWh DEMO



- FLC (Federal Laboratory Consortium for Technology Transfer)

2013
- UET 125kW system

- Fe-V License
  Aartha USA

  New Chemistry

2014
- MVRB License
  Wattjoule

  Patents granted
- UET first commercial system

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

Major challenge of RFB technology

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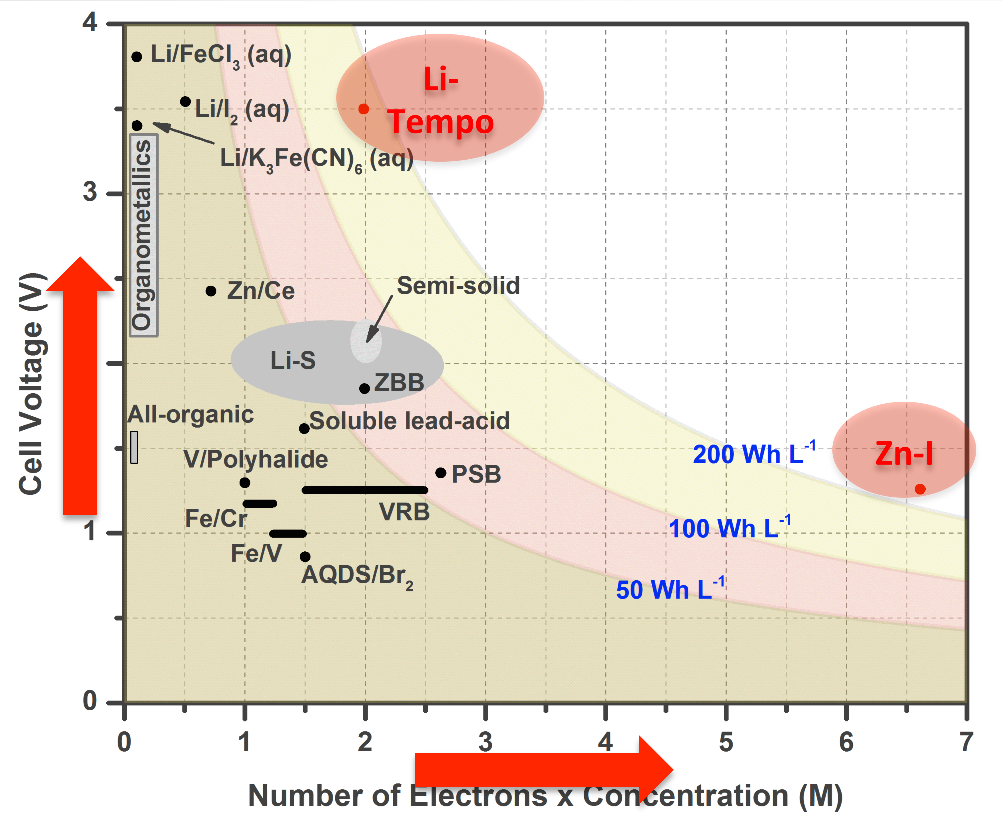
Major Challenge of the current RFB technology: low energy density

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

- Large form factor/footprint
- Limited application



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

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

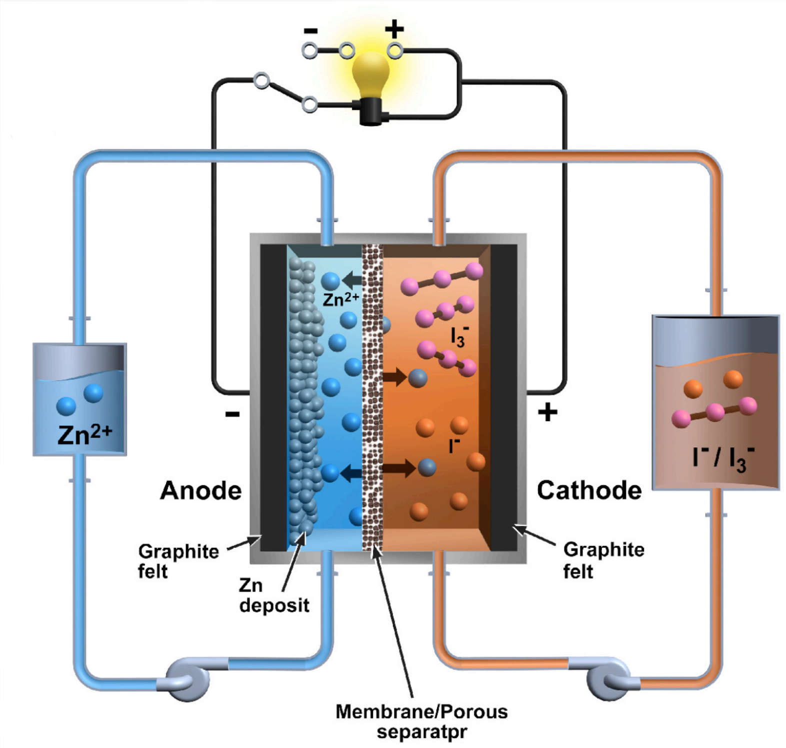
$$Positive: 3I^- \underset{Discharge}{\overset{Charge}{\longleftrightarrow}} I_3^- + 2e^- (E_0 = 0.536V)$$

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

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

Characteristics of the Zn-I RFB

- Ambipolar electrolyte
  Both anion and cation are active species.
- Bifunctional electrolyte
  Active species can act as charge carrier.
- High energy density
- High safety: PH value: 3~4
  No strong acid
  No hazardous materials



Electrochemical performance

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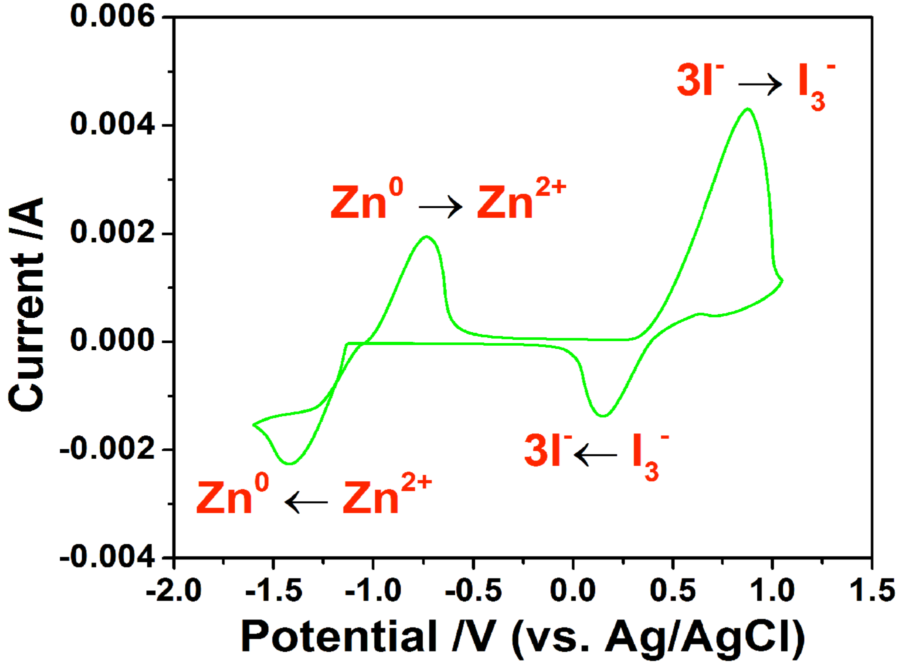
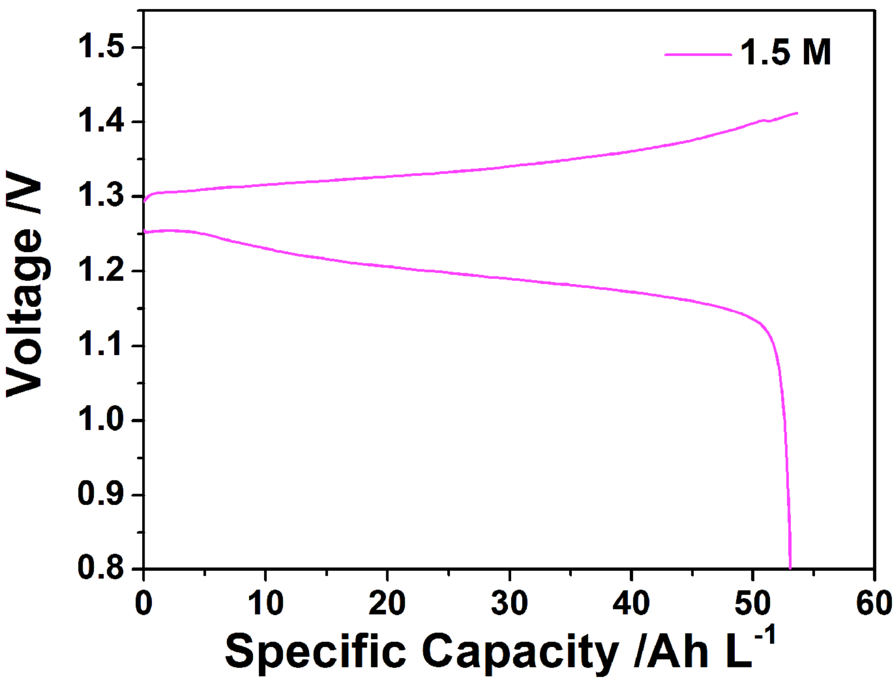


CV of 0.085 M ZnI_2 on a glassy carbon electrode at the scan rate of 50 mV s^{-1}.



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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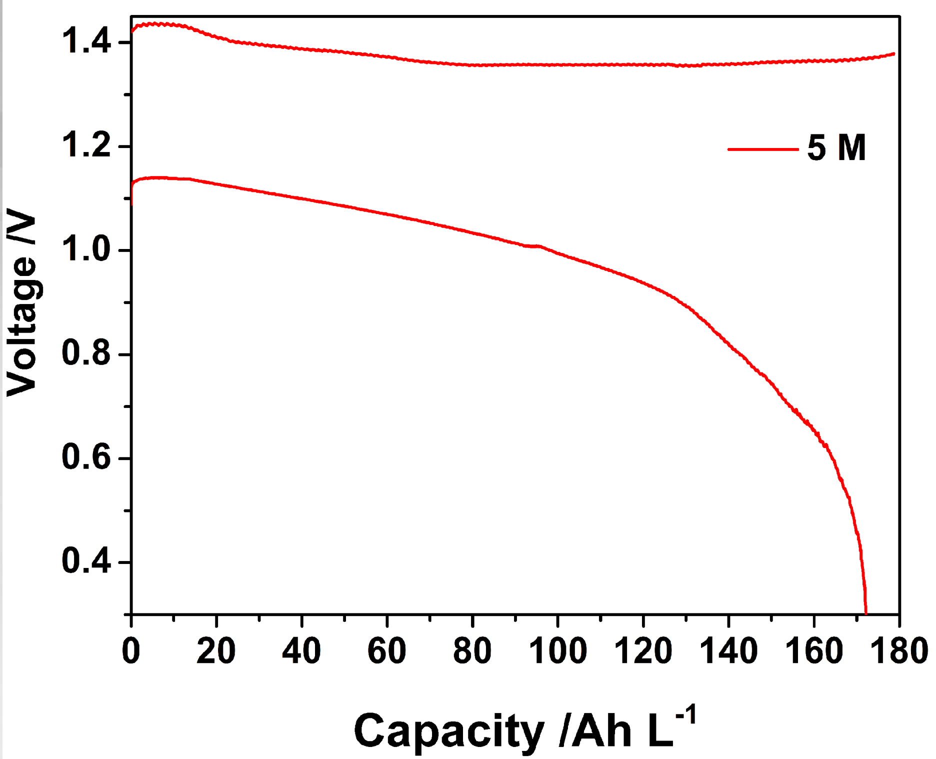
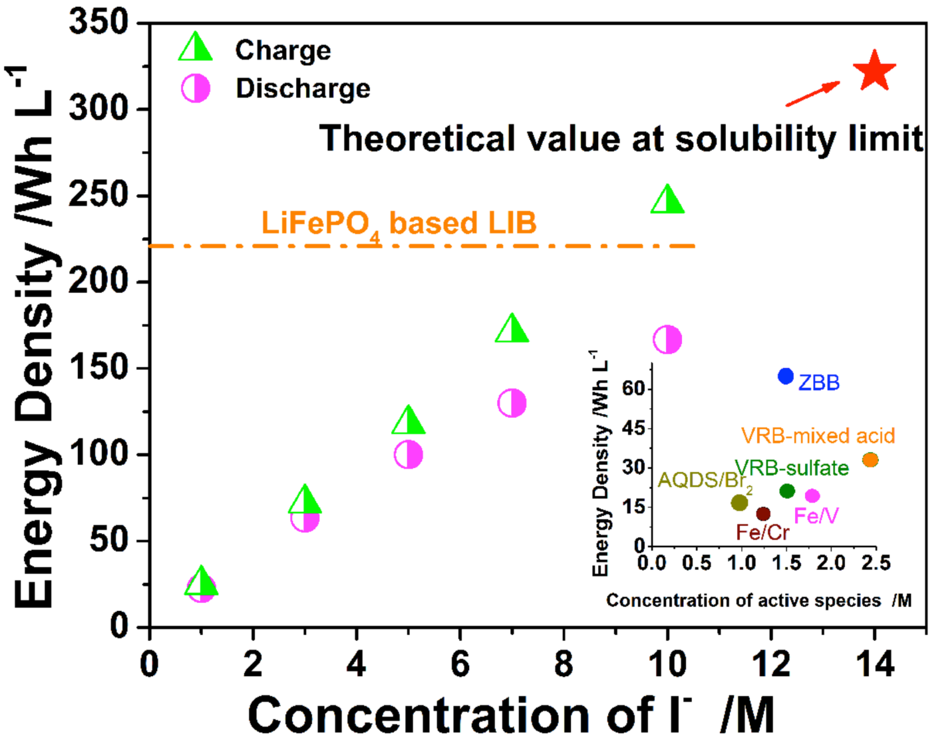
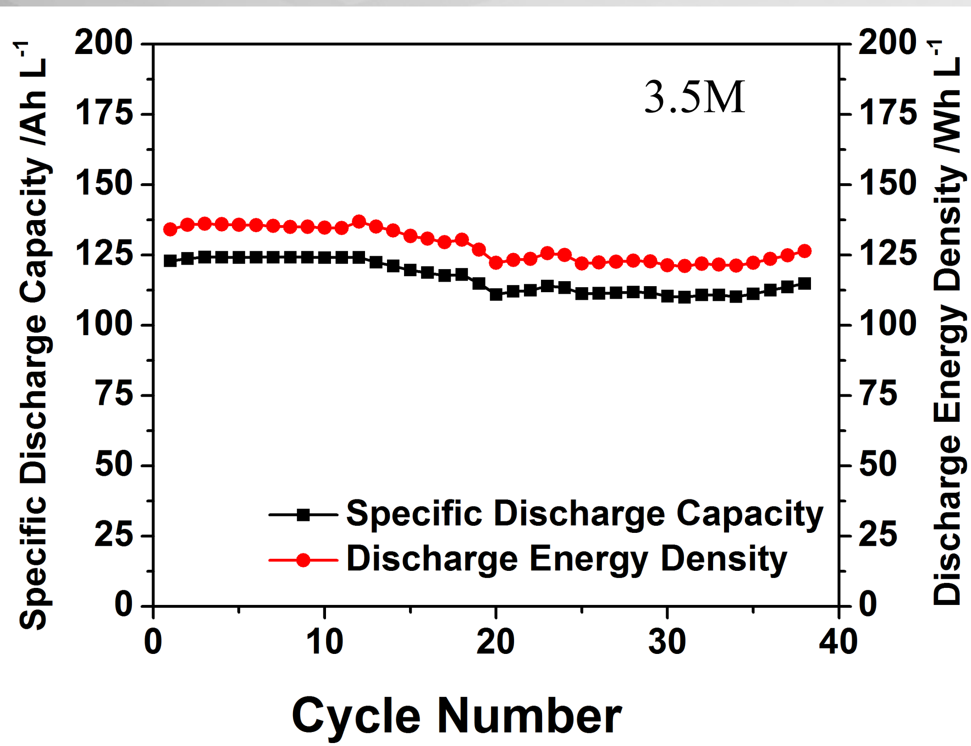


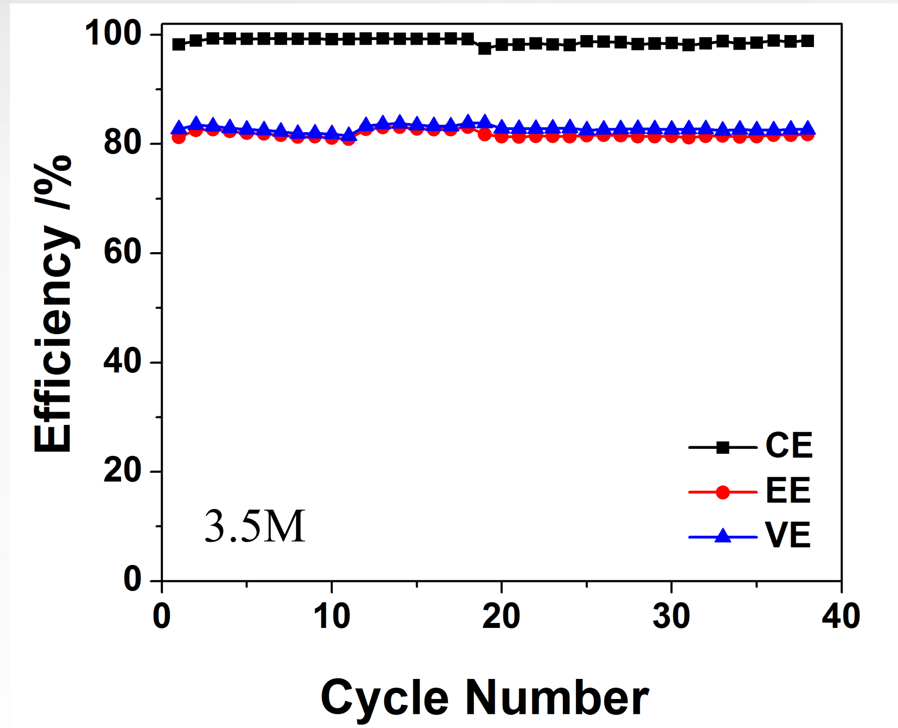


Charge/discharge curves for the cell with 5.0 M ZnI_2 and Nafion 115 as membranes operated at the current density of 5 mA cm^{-2}.

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

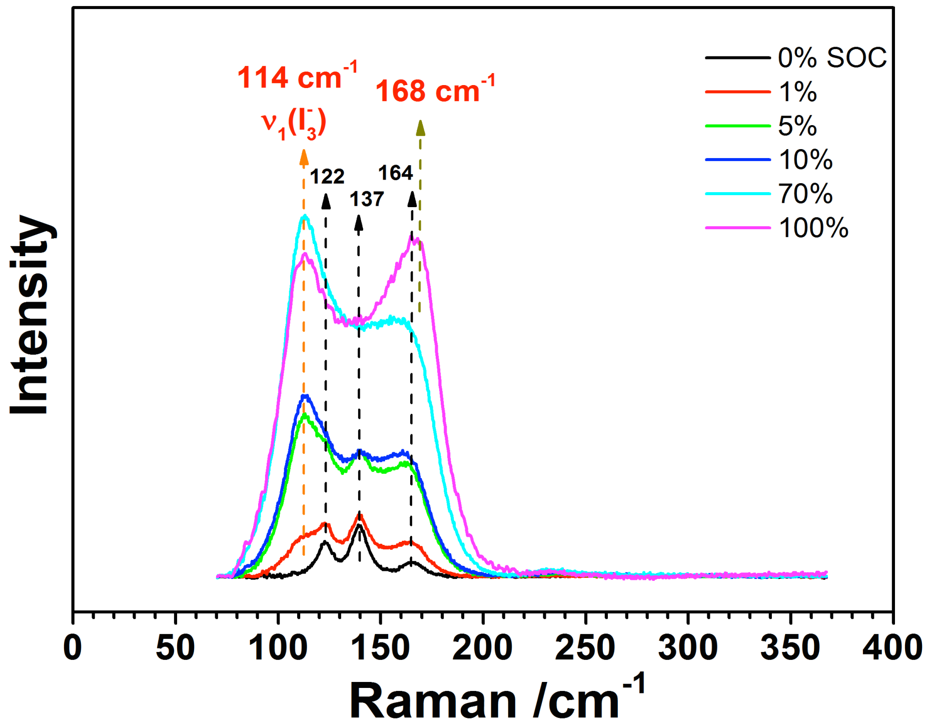


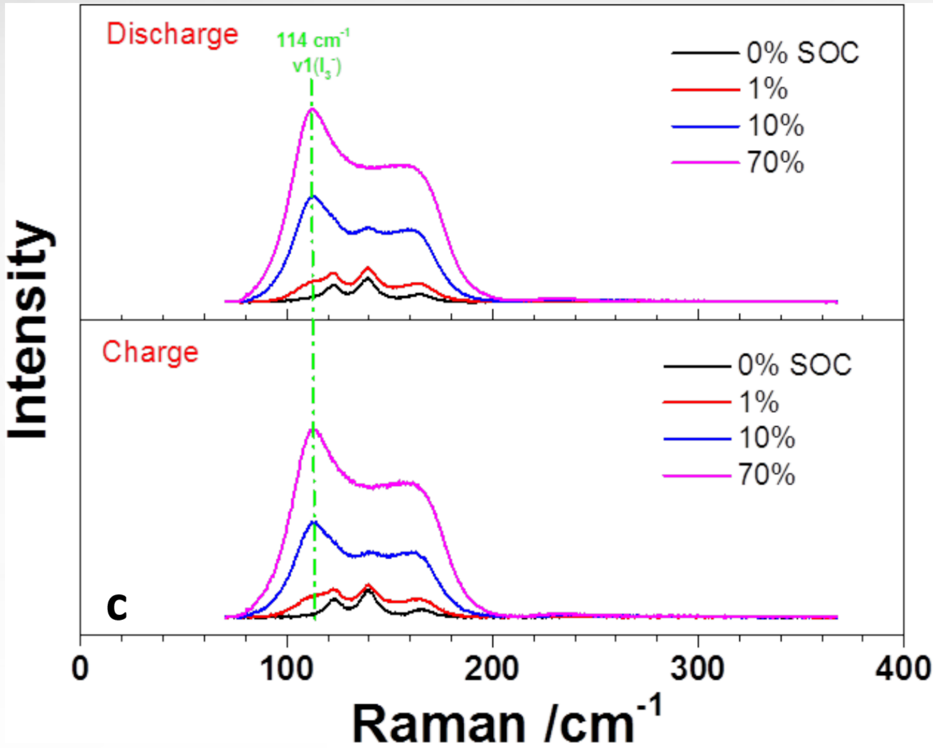


Capacities and energy density of the cell with 3.5 M ZnI_2 and Nafion 115 as membranes under the current density of 10 mA cm^{-2}.

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





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

Delayed Discharge

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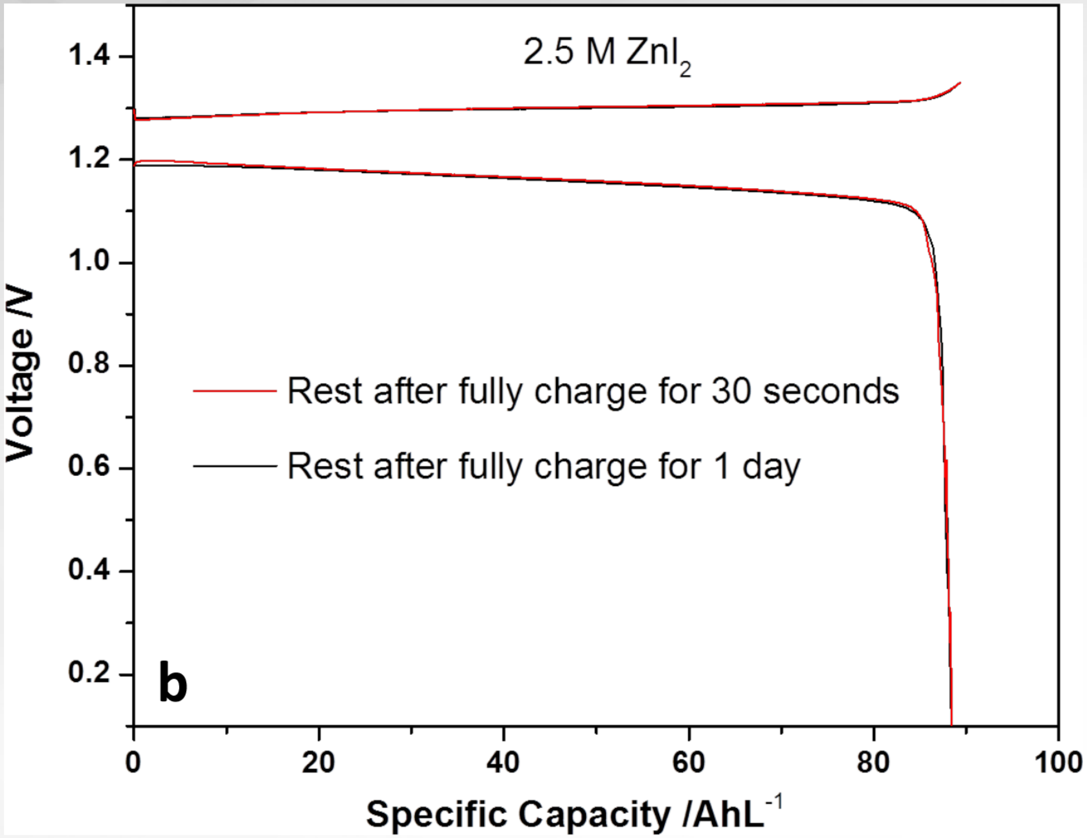


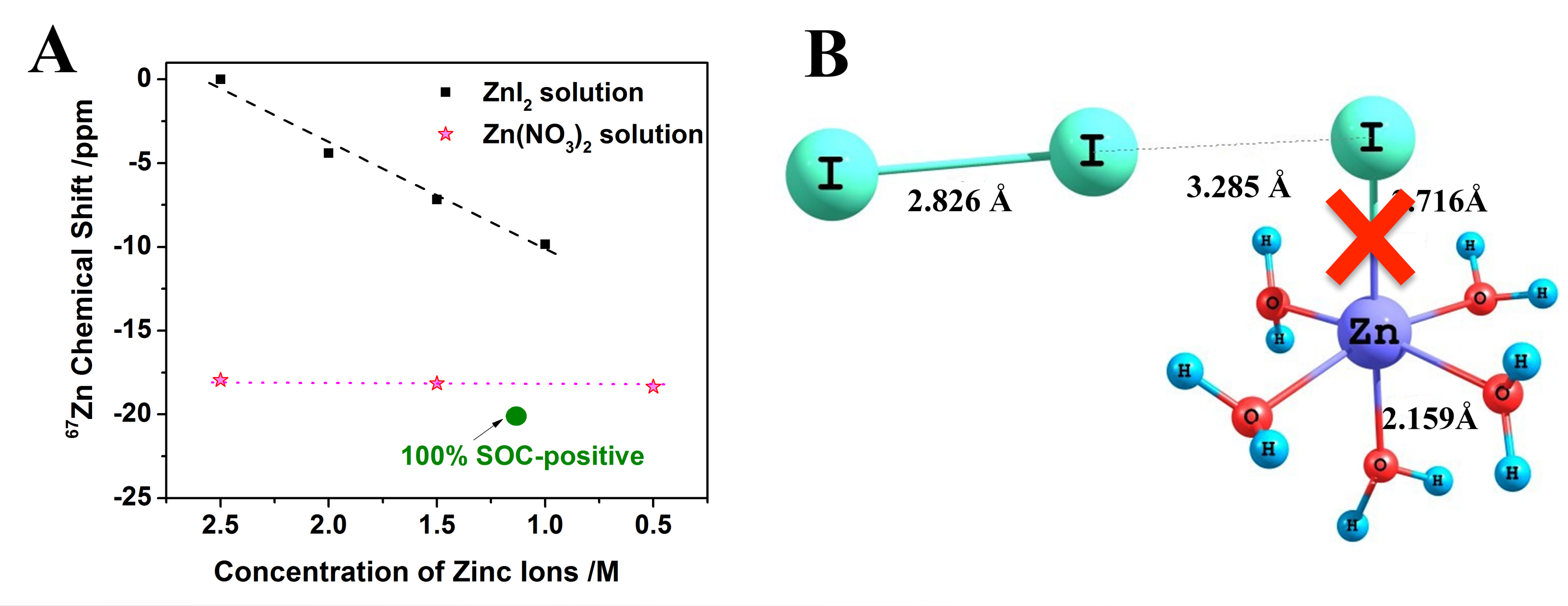
Voltage profiles of the flow cell test with different rest time.

Temperature stability of the catholyte

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

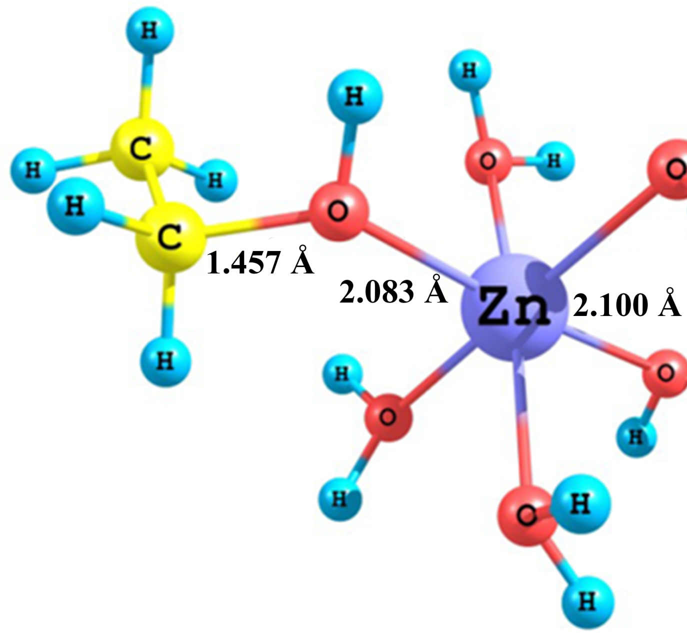
ZnI_2 (M)	50ºC	25ºC	0ºC	-10ºC	-20ºC
3.5	stable	stable	ppt	ppt	ppt
2.5	stable	stable	ppt	ppt	ppt

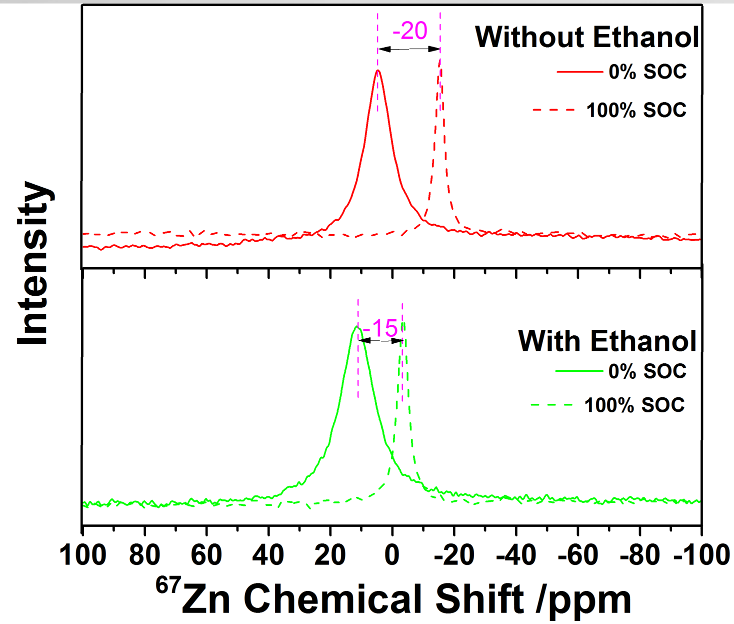
NMR and DFT study of the catholyte solution chemistry



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

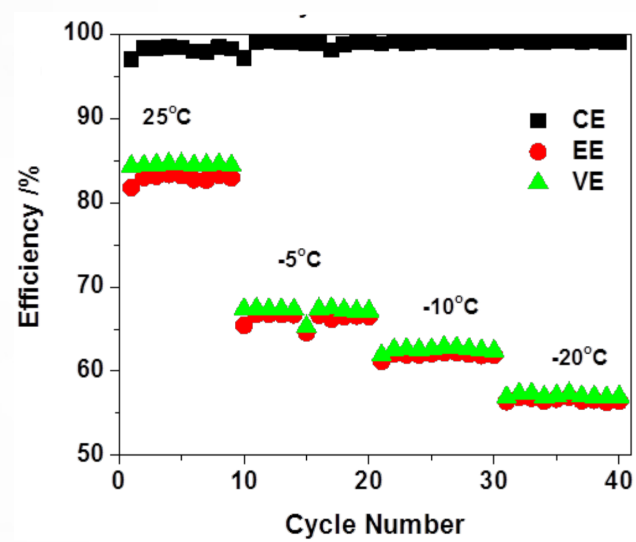
Stablize the catholyte through coordination chemistry





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

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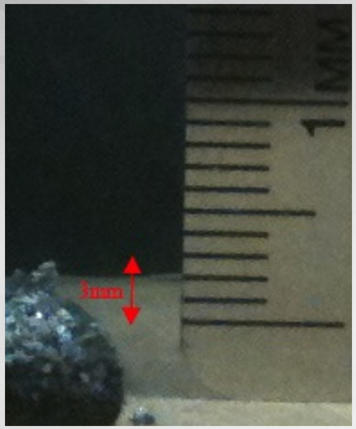
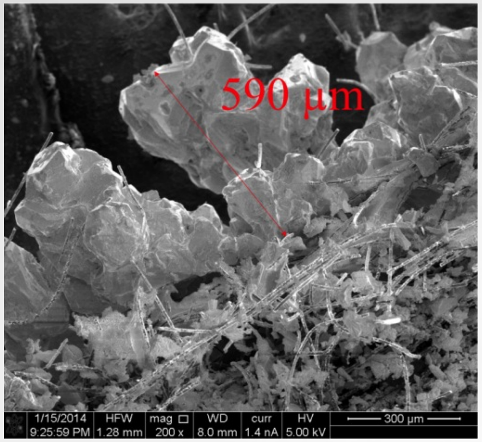
Dendrite growth in the flowing electrolyte



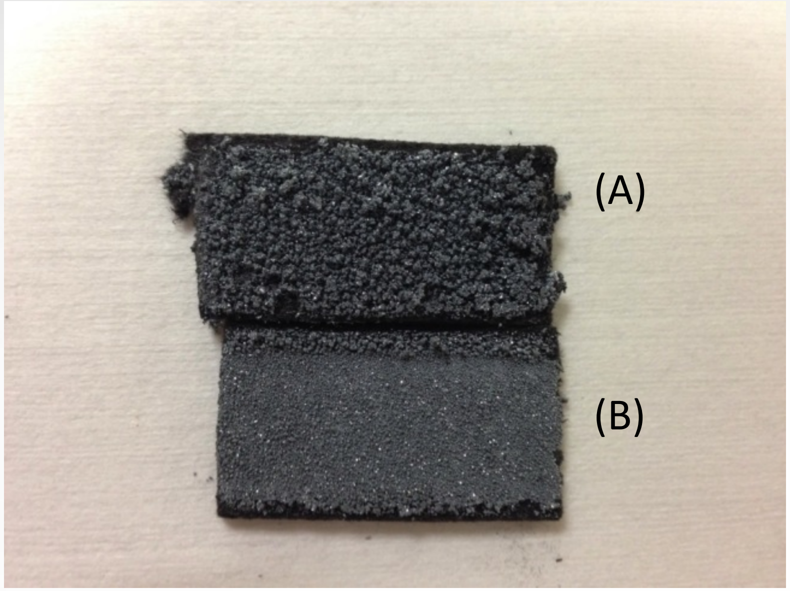
(A)



(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.

Summary

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- 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.

- Improve the kinetics of the polyiodide redox reaction.

Acknowledgements

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

- Pacific Northwest National Laboratory is a multi-program national laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract DE-AC05-76RL01830.

Effect of the Ethanol and anolyte volume

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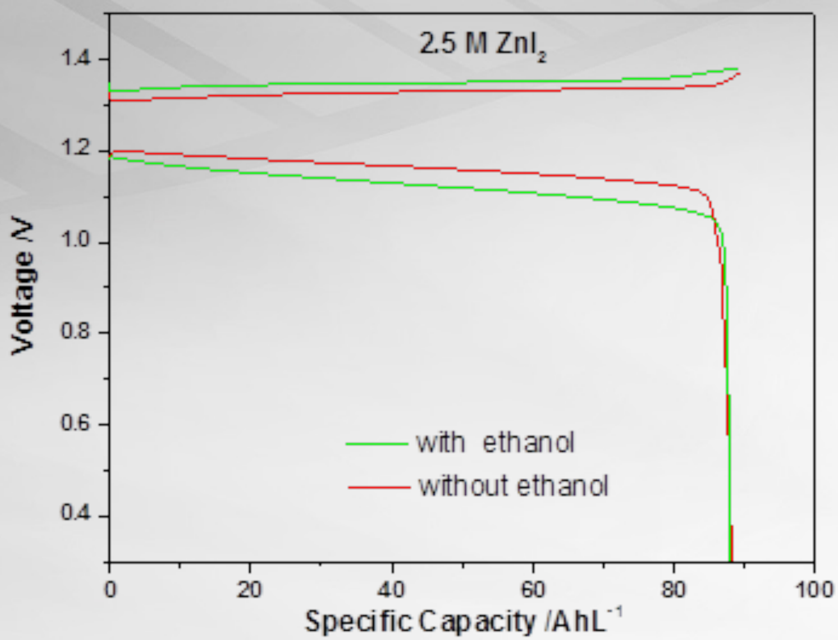

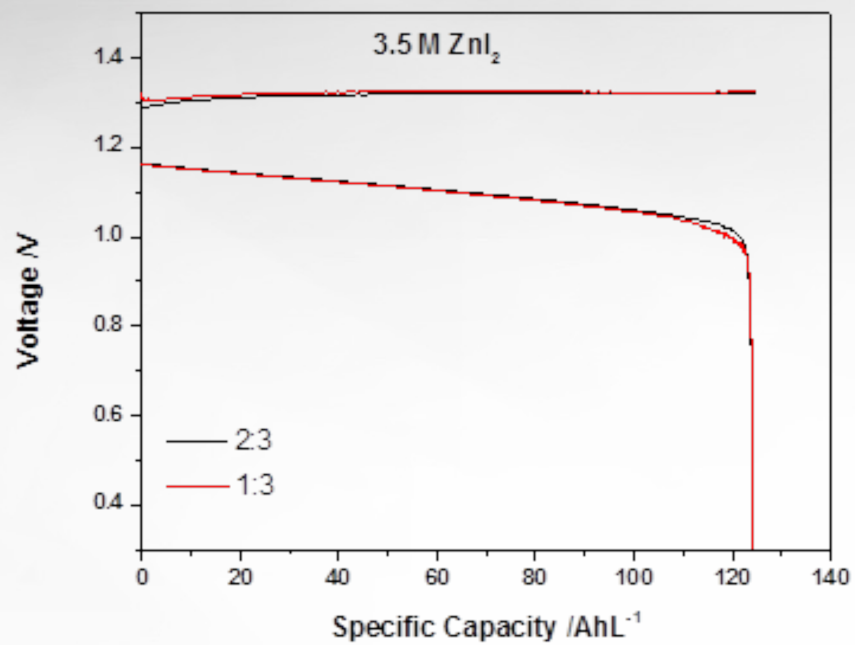

Voltage profiles of a flow cell test on a 2.5M ZnI_2 electrolyte with and without ethanol.

Voltage profile of flow cell tests with different anolyte volumes.

Mass spectrometry analysis of catholyte

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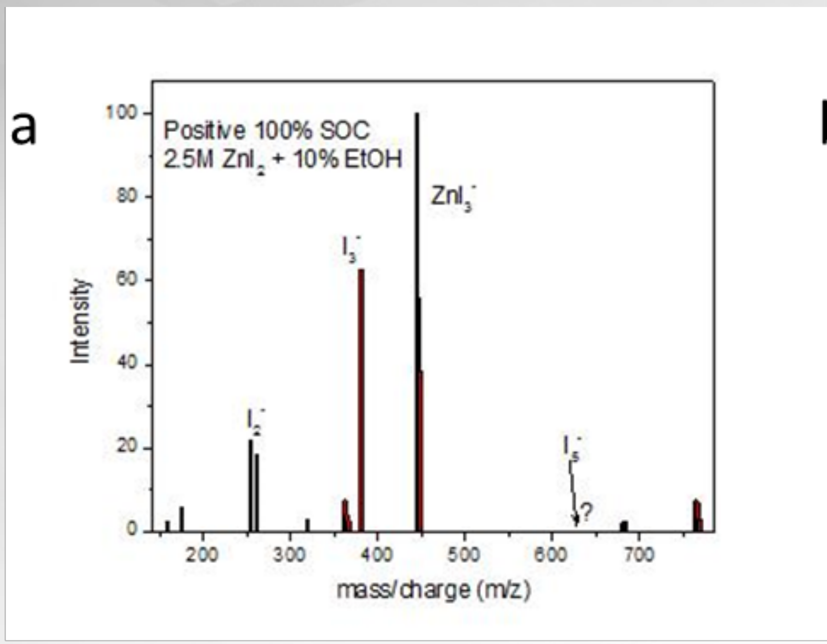

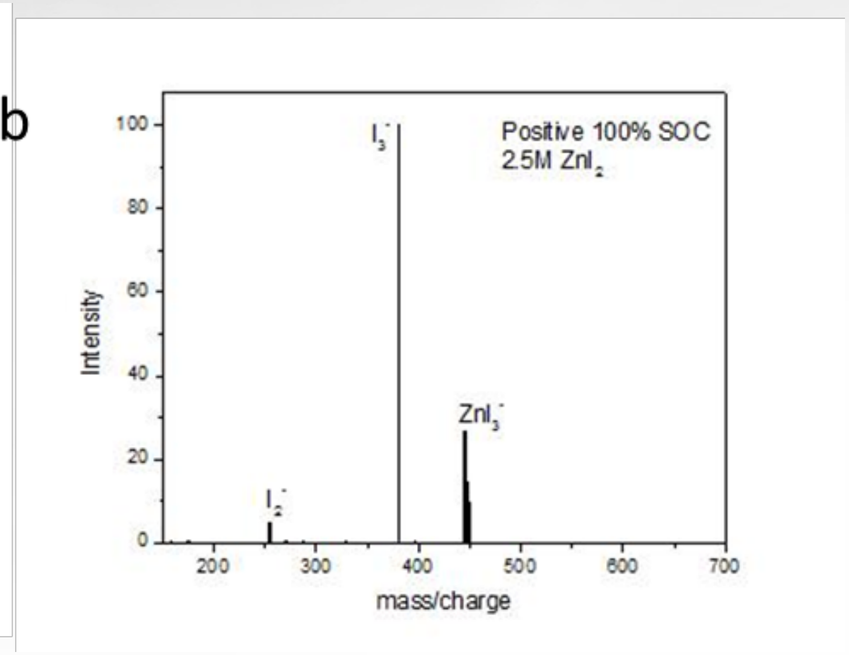

Mass spectrometry analysis of (**a**) pristine and (**b**) EtOH-added catholyte at fully charged condition. The presence of ZnI_3^- and molecular triiodide confirms our NMR and DFT-based analysis.