Pacific Northwest
NATIONAL LABORATORY

Presentation #303: Polycomplex Ion Additive for Aqueous Organic Redox Flow

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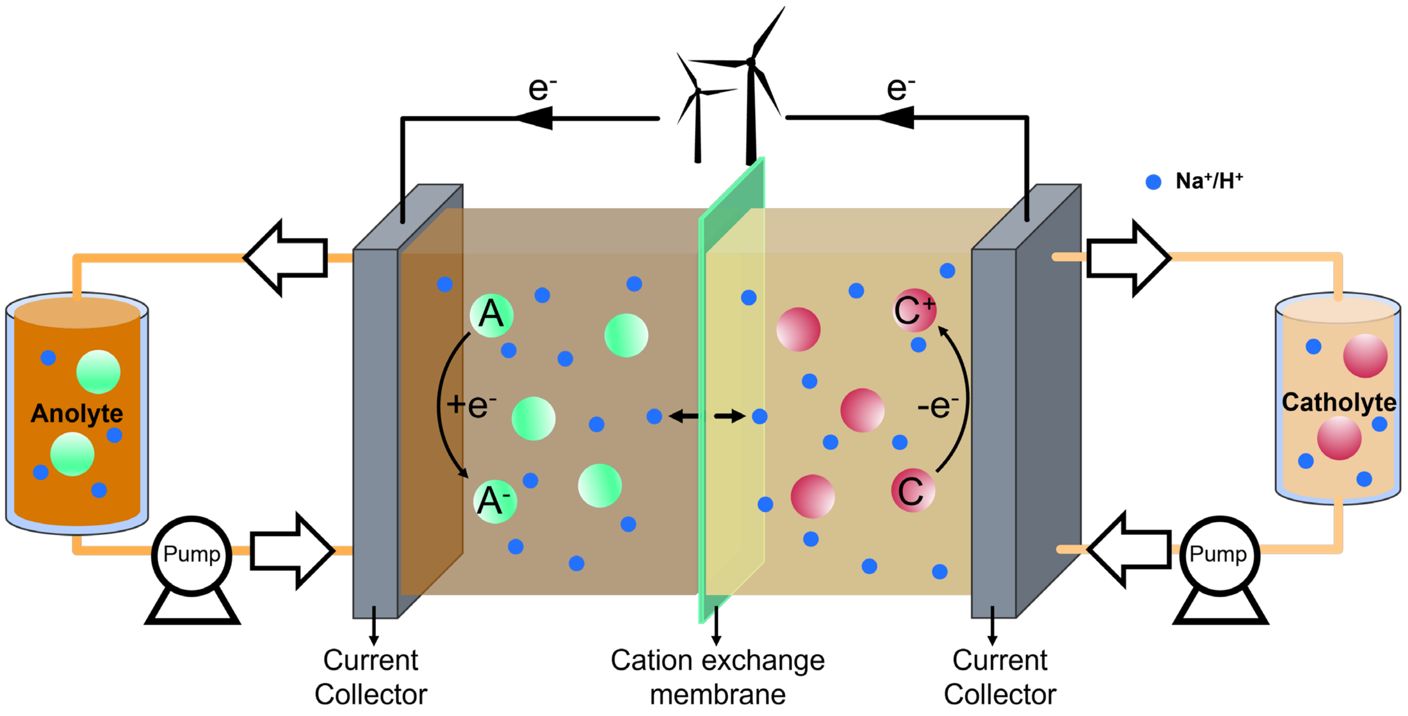
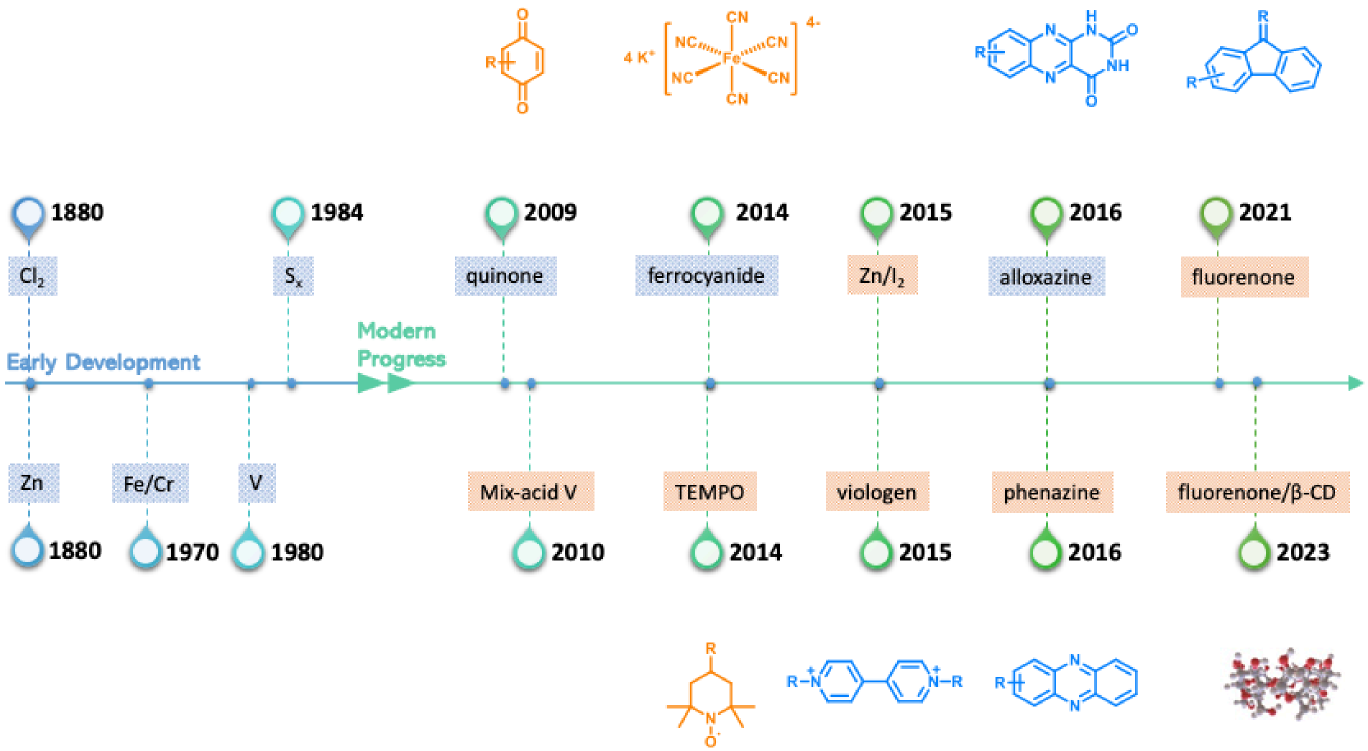
U.S. DEPARTMENT OF ENERGY BATTELLE

Redox Flow Batteries (RFBs)



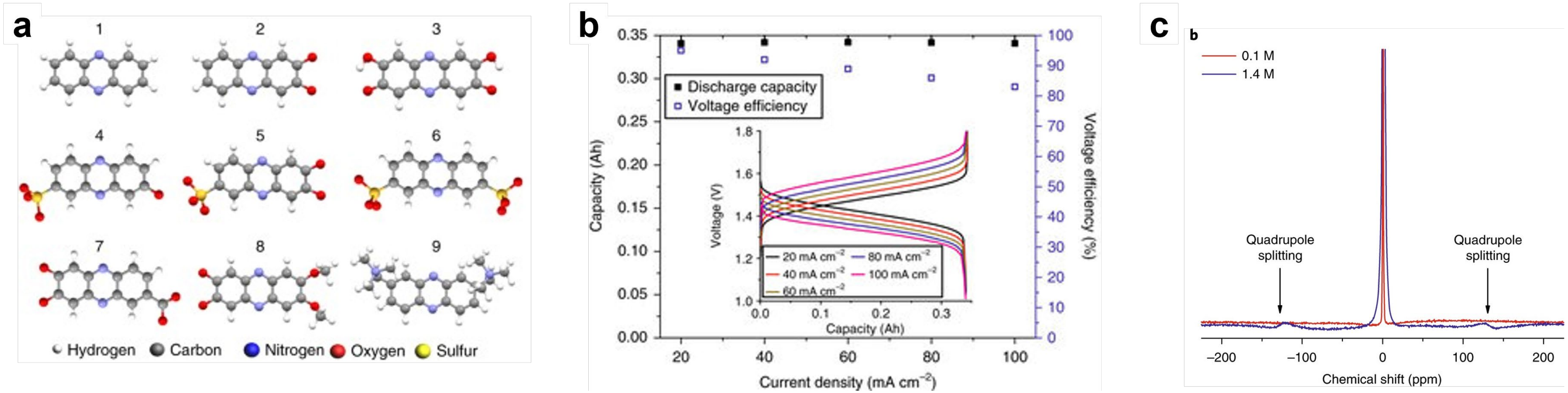
- Decoupling of Power and Capacity
- Size and Capacity Scalability
- Long duration
- Earth abundant materials

Development of Redox Active Species for RFBs



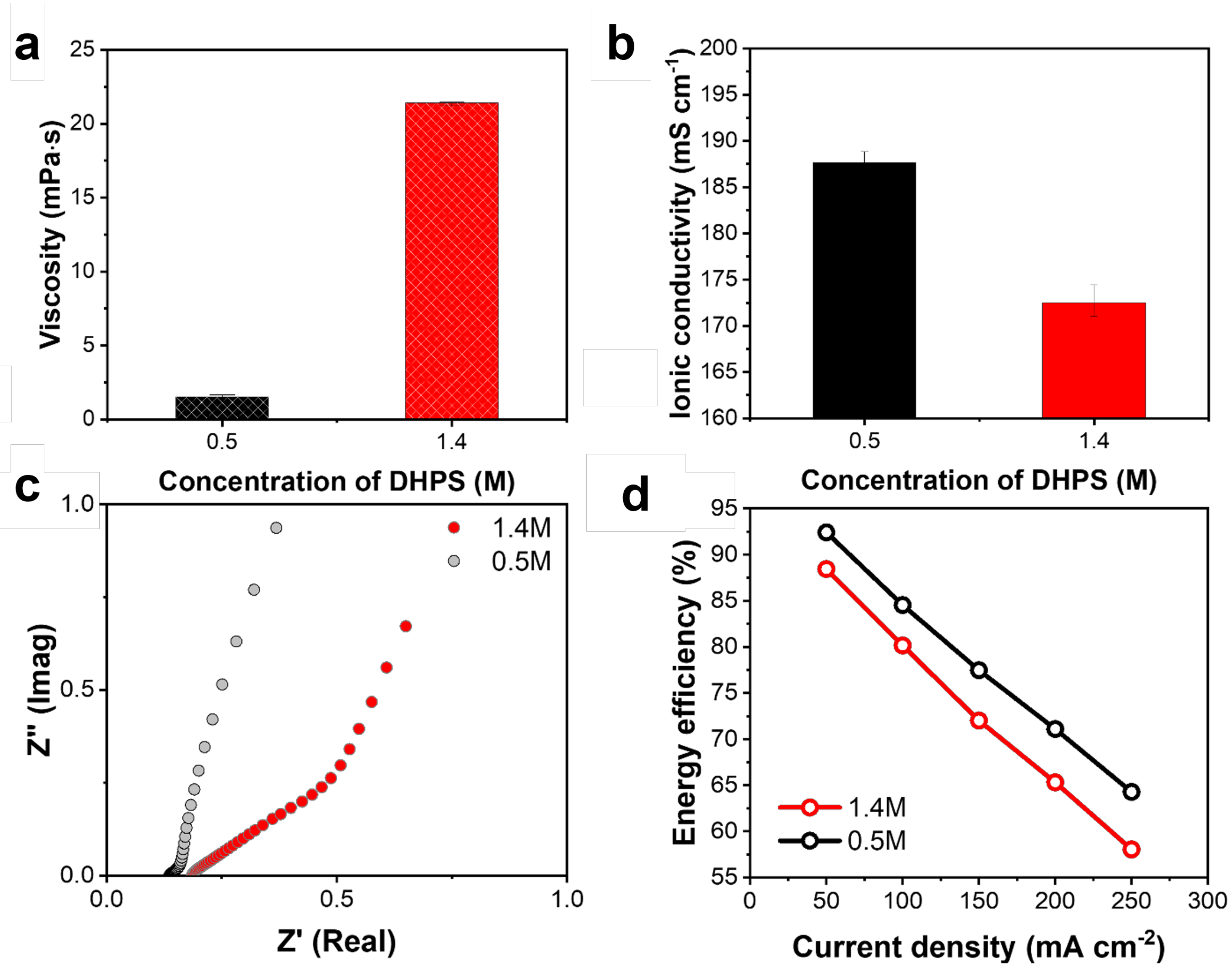
- PNNL have discovered and developed wide variety of different chemistries for various redox flow batteries.
- We currently focused on developing organic redox materials for AORFBs due to the competitive cost, good solubility, chemical stability and electrochemical performance.

Challenges for Organic Redox Molecules



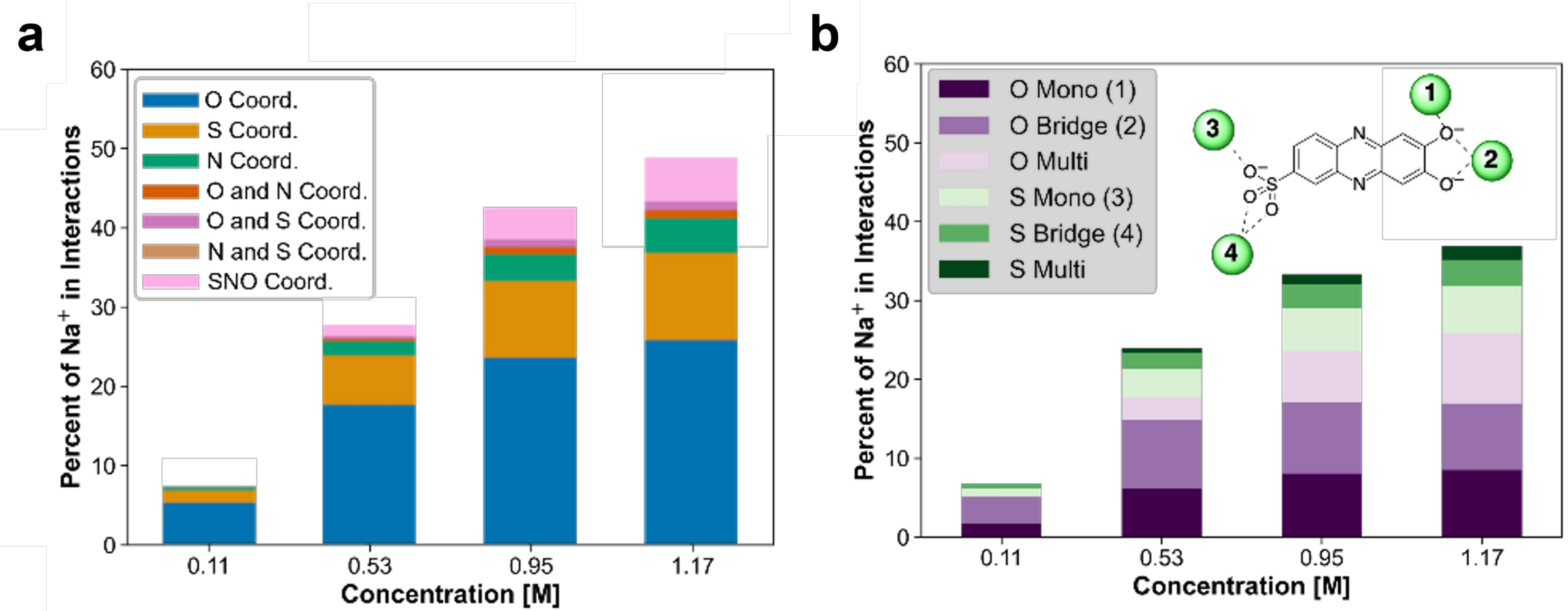
- ✧ The developed 7,8,-dihydroxyphenazine-2-sulfonic acid (DHPS) is promising organic redox materials demonstrated the good solubility, chemical stability and electrochemical performance.
- ✧ Limited solubility → Increases solution viscosity at high concentrations
- ✧ Design/synthesis/modification of new molecules are such a challenge.

Challenges for Organic Redox Molecules



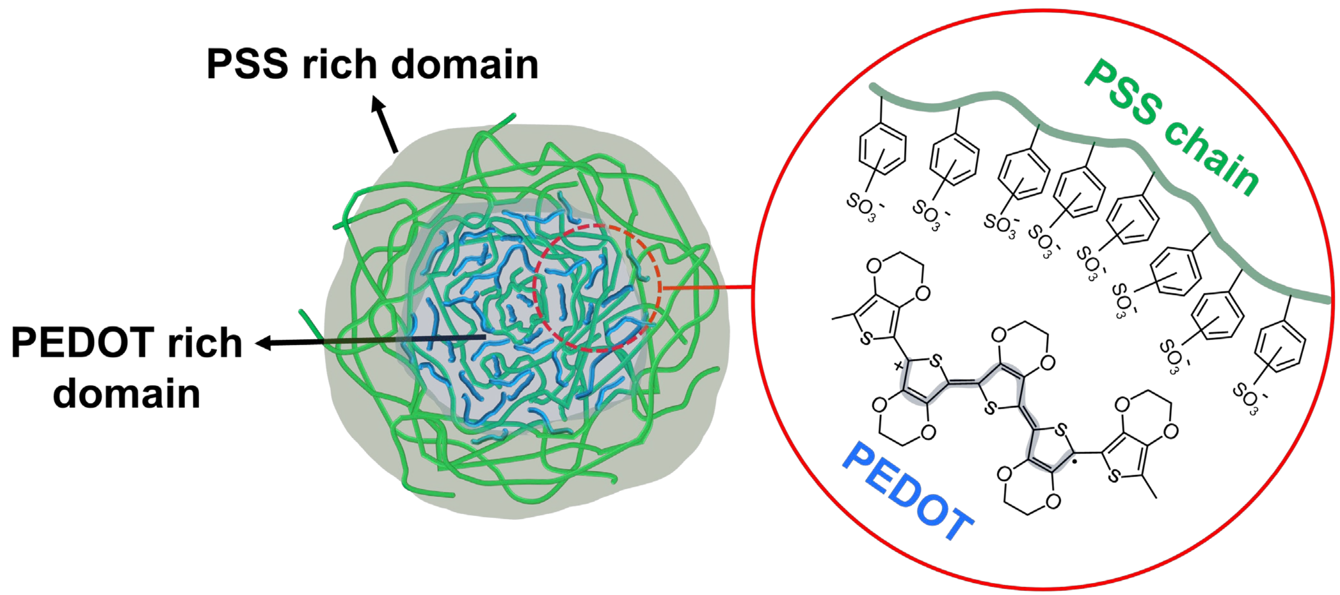
- Electrolyte properties and electrochemical behaviors strongly depend on the concentration of DHPS anolyte solutions.
- Rigid solvation structure forming at high concentration → increasing cell resistance and decreasing energy efficiencies.
- Need to understand the solvation environment derived from increasing electrolyte concentrations

Understanding Solvation Structure at High Concentrated Electrolytes



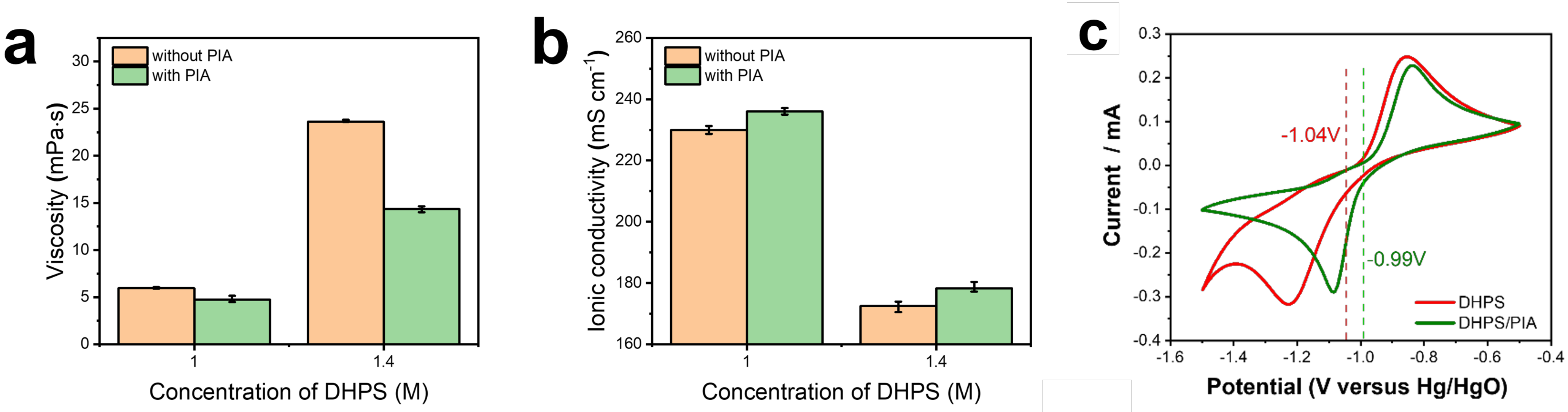
- Molecular dynamics (MD) simulations results provided the oxygen atom and sulfonate groups of DHPS are mainly involved in coordinating networks with Na^+ ions.
- At high concentrated electrolyte, mono-, bridge, and multiply coordination occur → rigid cluster formation leading to high solution viscosity.
- Need to modulate the solvation structure for enhancing solubility and energy density

Modulating Solvation Structure with Polycomplex Ion Additives (PIA)



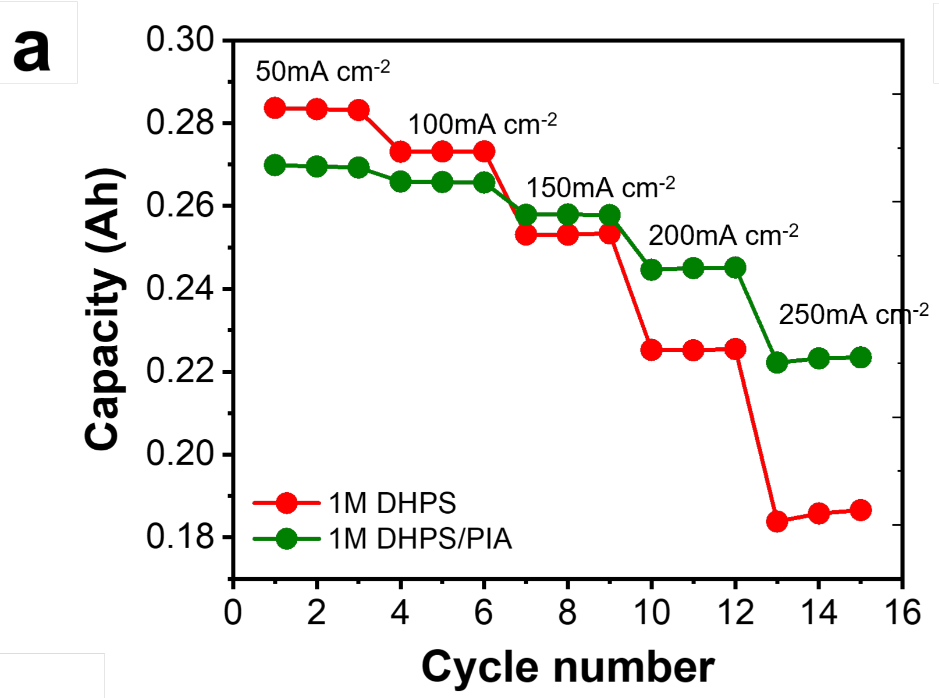
- Without significant work on design/synthesis/modification of organic molecules, the solvation environment can be modulated by introducing polycomplex ion additives.
- Negatively charged surface of PIA can interact with Na ions and disrupt the formation of rigid solute-salt-solute coordination at highly concentrated electrolytes.

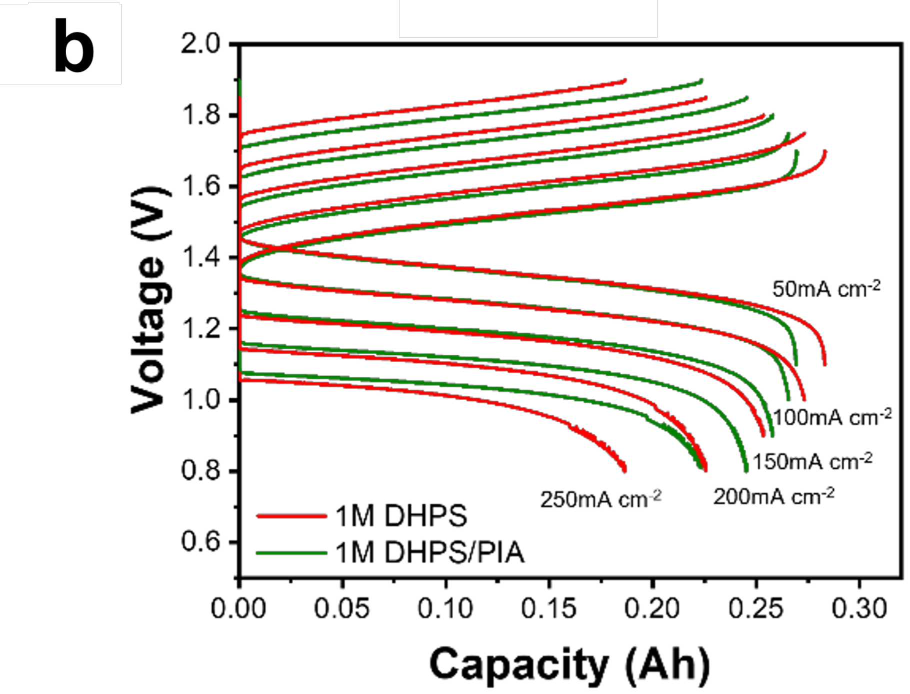
Modulating Effect of PIA on Electrolyte Properties



- Reduced solution viscosity and improved ionic conductivity with PIA (20µL/1M DHPS solution) even at high concentrated solutions (1.4 and 1.6M DHPS in 1M NaOH solutions, respectively)
- Shifting reduction peak with PIA toward positive potential → reduction of DHPS molecules is more reversible

PIA Effect on AORFB Cell Performance





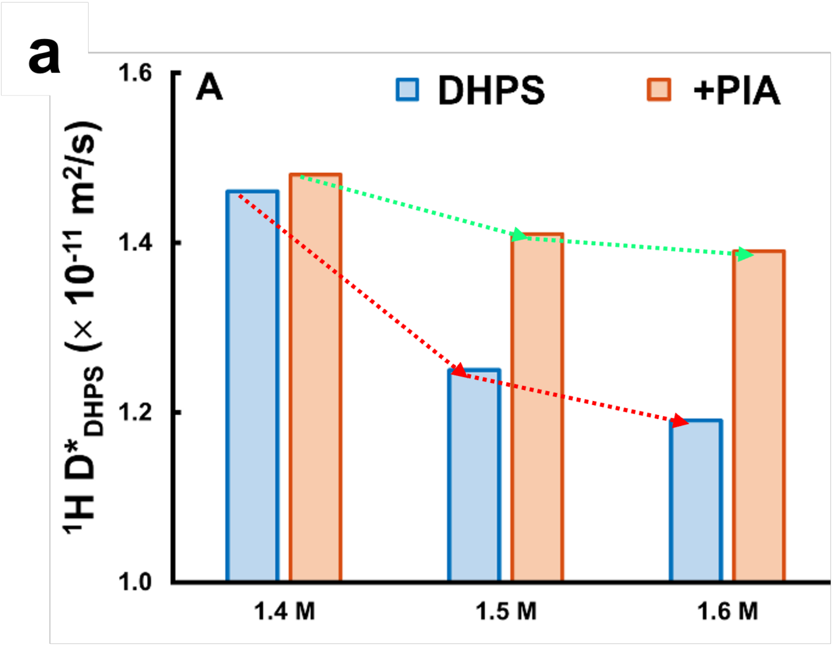
- Reduced capacity decay (about 18% from 50 mA cm^{-2} to 250 mA cm^{-2} current densities) with PIA compared to large capacity loss (about 34%) m pristine DHPS cell.

- Reduced cell over potential with PIA.

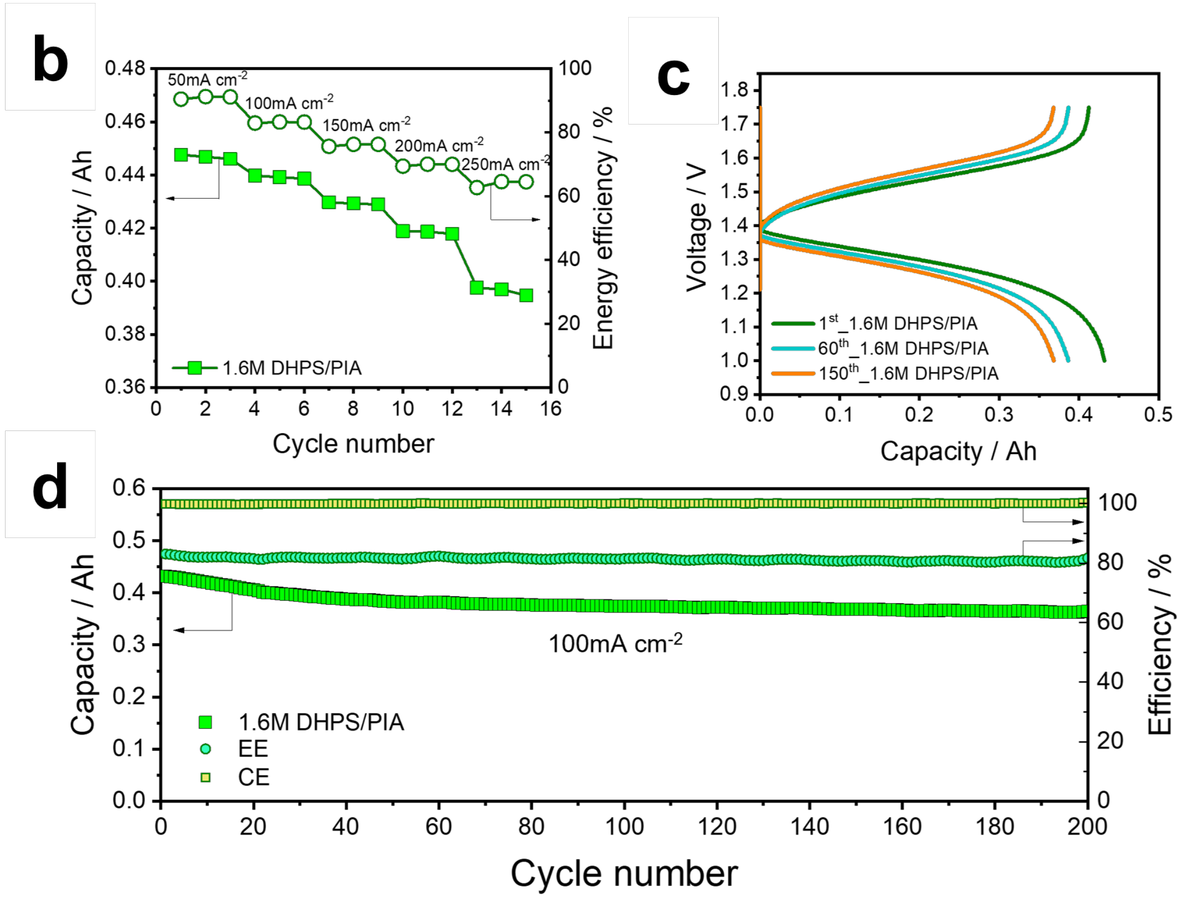
Surpassing Limited Solubility with PIA

- ✧ Increased the concentration of DHPS with PIA to 1.6 M which is higher (about 14%) than the saturation concentration of pristine DHPS (1.4M)
- ✧ Good fluidic properties with much lower viscosity (22% lower than pristine solution), without any blocking and precipitation problems, similar cell resistance

Surpassing Limited Solubility with PIA for Enhancing Energy Density of AORFB



- Reduced diffusion of DHPS with PIA from 1.4 M to 1.6 M while a much larger reduction without PIA ([1]H diffusivity measurements).
- PIA provides less constrained pathways for ion transport.



- Stable cycling stability and good rate capability with high capacities at all current densities (only about 12% of capacity decay from 50mA cm^{-2} to 250 mA cm^{-2} current densities)

Summary and Acknowledgements

Summary

- Enhancing solubility and energy density of AORFBs were obtained with introducing polycomplex ion (PIA) without new synthesis/design/modification of organic molecules.
- ^{23}Na-NMR and MD simulations were studied to understand and modulate solvation structures.
- PIA significantly reduces solution viscosity, enhance ionic conductivity and energy density achieved 74.3 Ah L^{-1} (anolyte), one of the highest demonstrated among all the organic flow batteries.

Future Direction

- Utilized with other potential redox active species in progress
- Pursue modified PIA which enable more enhanced solubility

Support

- This material is based upon work supported by the U.S. Department of Energy, Office of Electricity (OE), Energy Storage Division.
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Thank You For Your Attention

Questions?

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