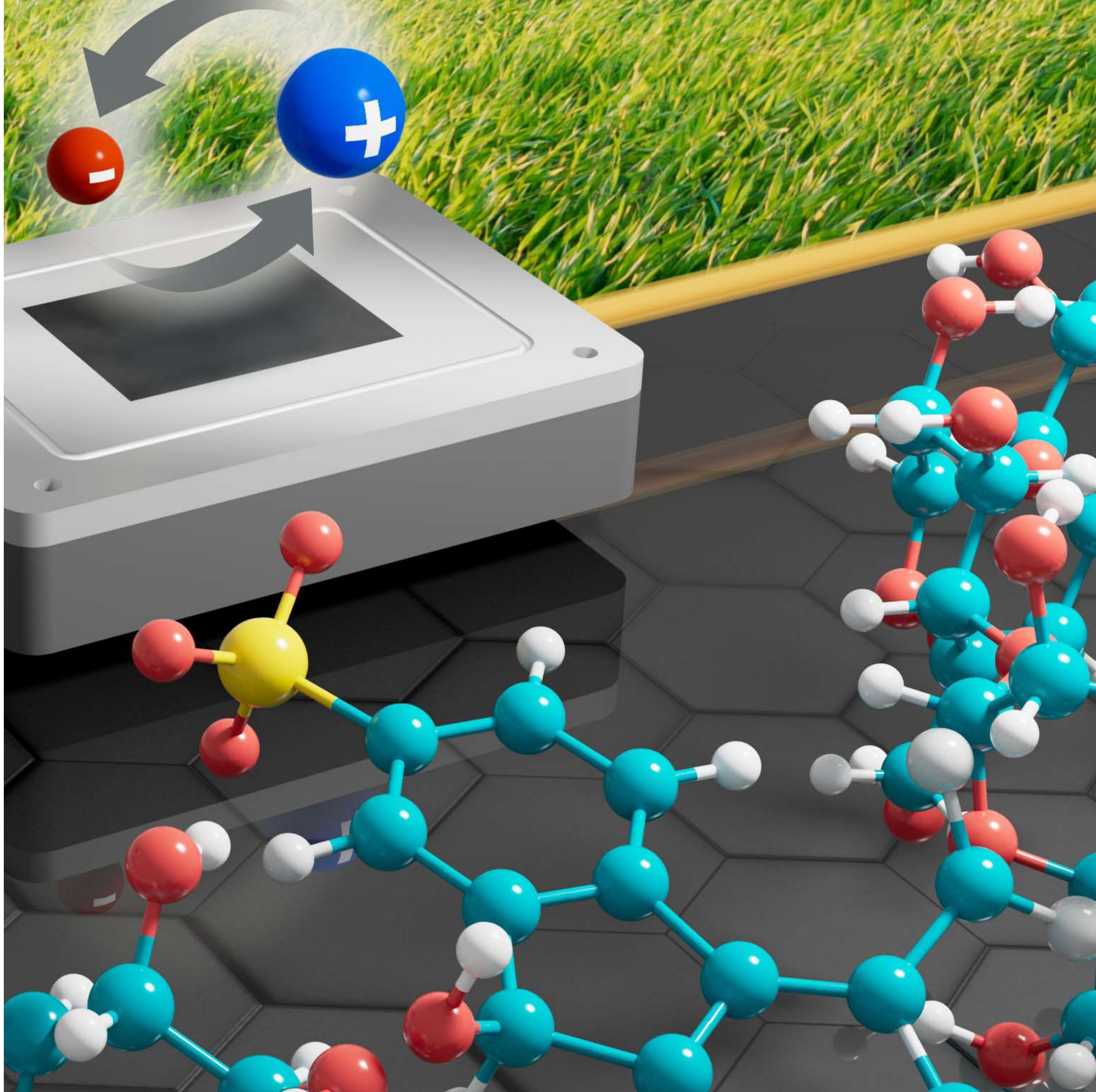
Pacific Northwest NATIONAL LABORATORY

Sugar additive enabled high-capacity and long-life aqueous organic flow battery

Presentation # 603

Ruozhu Feng

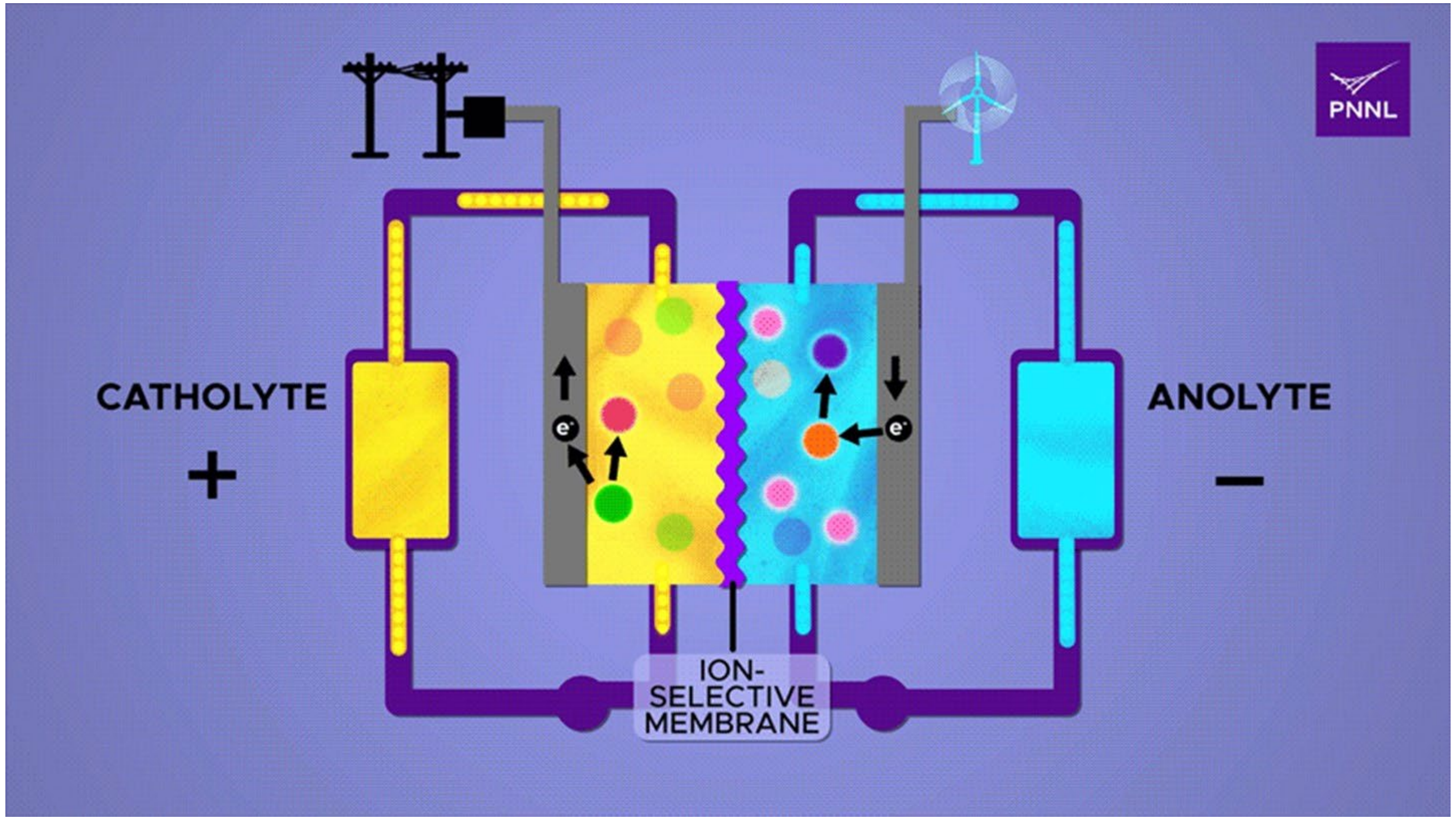
October 24, 2023



U.S. DEPARTMENT OF ENERGY BATTELLE

PNNL is operated by Battelle for the U.S. Department of Energy

Redox flow battery: suitable for long duration energy storage

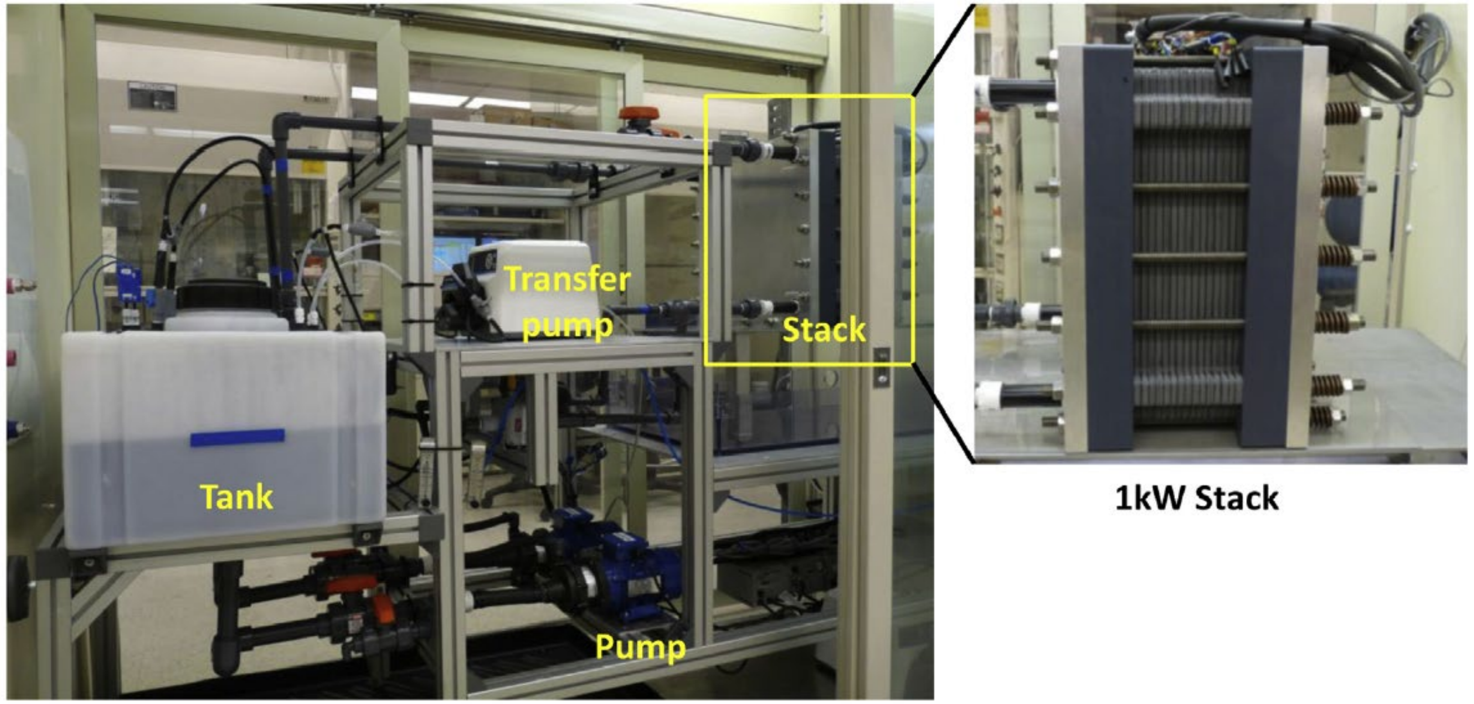


Modular structure

- fluidic electrolyte
- spatial separation of energy storage and power generation
- individually tuning of energy capacity and power capability

Objective:
discovery of the "ideal" electrolyte and redox chemistry for flow battery application

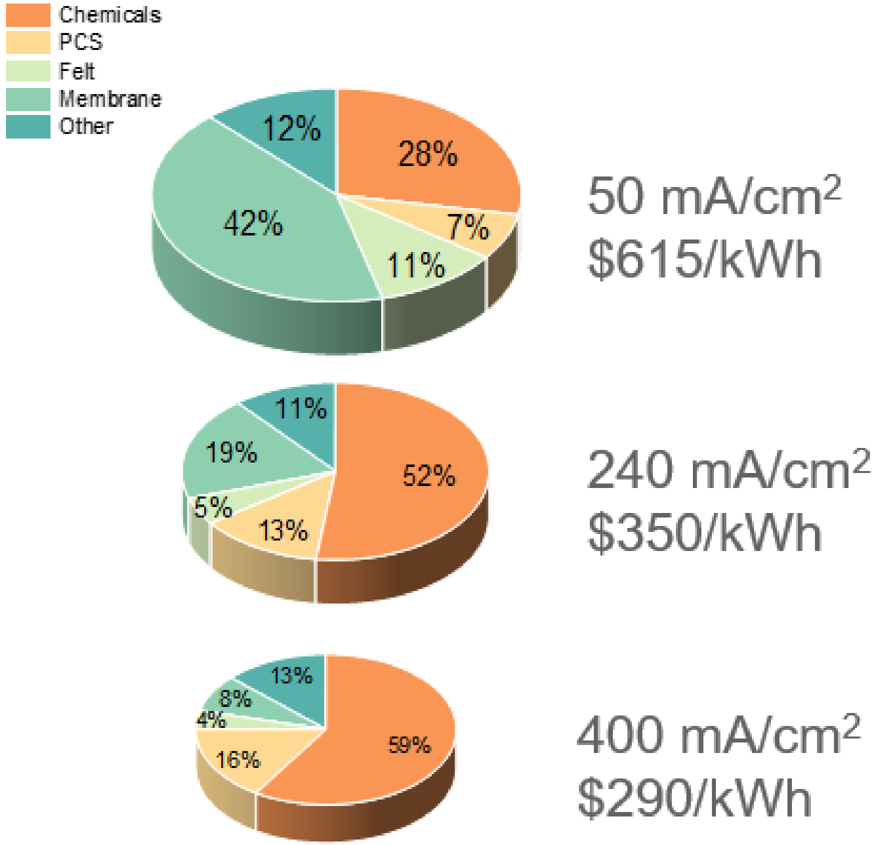
Vanadium redox flow battery research at PNNL



1kW / 1kWh VRFB System

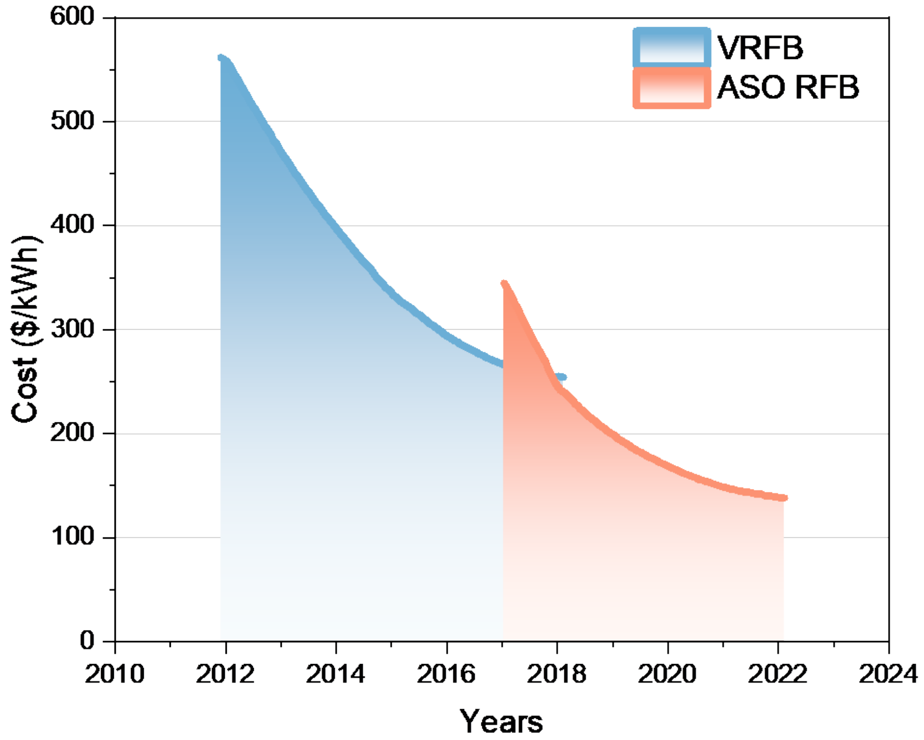
Advanced mixed acid electrolyte in vanadium flow battery

J. Power Sources **2013**, *237*, 300–309.

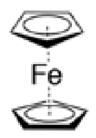
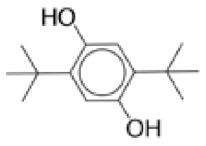
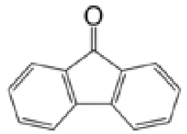
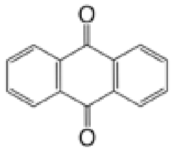
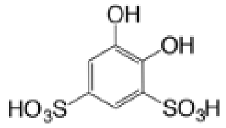
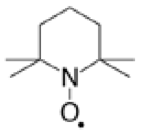
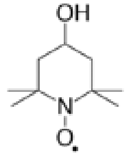
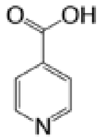
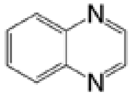
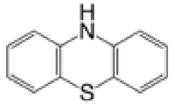
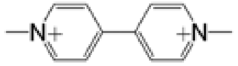


Material cost can NOT be further optimized !

Aqueous soluble organics can be good alternative



Bulk Prices of Prominent ROMs or Their Precursors in \$ kg^{-1} at a Scale of 25 kg from Alibaba.com, unless Otherwise Indicated

ROMs	 ferrocene	 precursor of DBBB & ANL-8	 9-fluorenone	 anthraquinone	 quinone	 **TEMPO**
Prices	1	1~5	2	4.74	5-10	5-7
ROMs	 4-hydroxy-TEMPO	 precursor of **16 & 17**	 quinoxaline	 phenothiazine	 methyl viologen	V_2O_5
Prices	7	1~20	1~2	1~2	1	10-12

ACS Energy Lett. **2019**, *4* (9), 2220-2240.

Benefits of Organic Materials

- lower material cost on large scale
- tunability of electrolyte : battery energy density/ power density/lifetime

Development of organic flow battery

1970

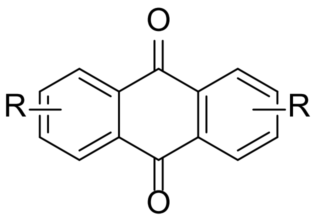
NASA Fe/Cr

1980

Skyllas-Kazacos

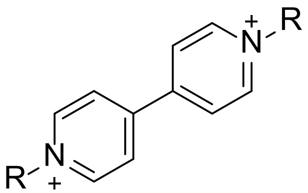
Vanadium RFB

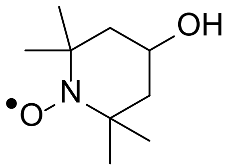
2014



Nature Aziz, et al, Anthraquinone

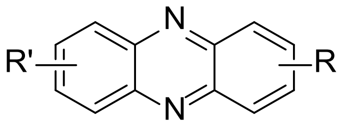
2015





Nature Schubert, et al, TEMPO Viologen polymer

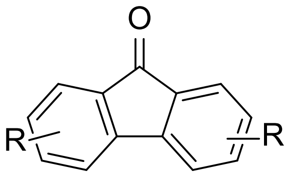
2018



PNNL

Nature Energy, Wang, et al, Phenazine

2021



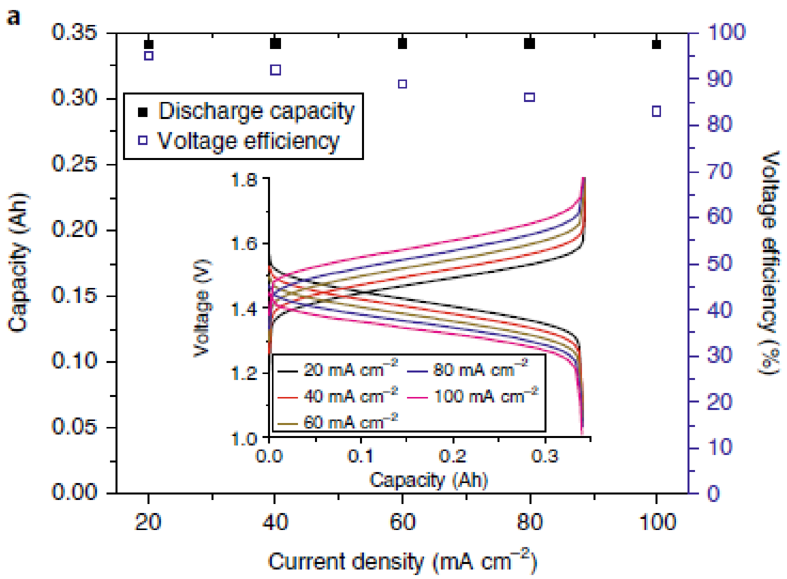
PNNL

Science, Wang, et al, Fluorenone

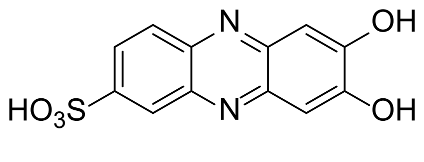
Incredible stability!

ACS Energy Lett. **2019**, *4* (9), 2220-2240. *Nature* **2015**, *527* (7576), 78–81. *ACS Energy Lett.* **2017**, *2 (9)*, 2187–2204. *Nature* **2014**, *505*, 195. *Nat. Energy* **2018**, *3* (6), 508–514. *Science* **2021**, *372* (6544), 836–840.

FL kinetics comparing to other organic systems

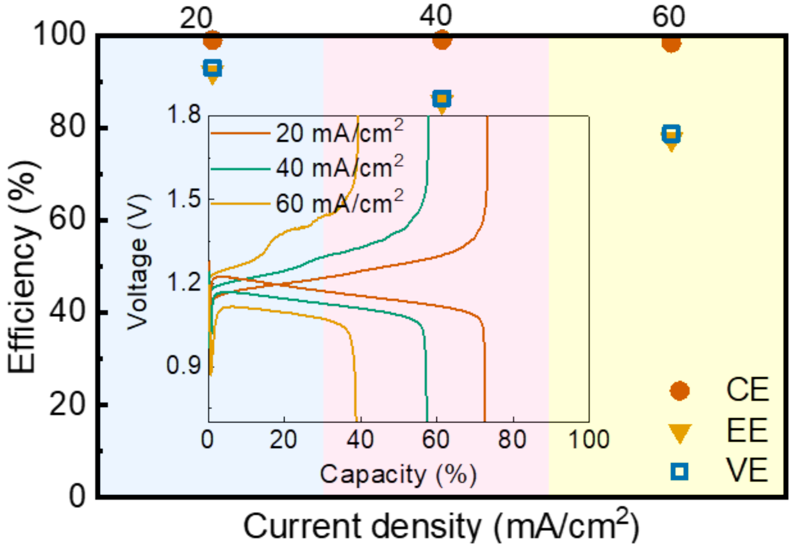


DHPS 75 Ah/L

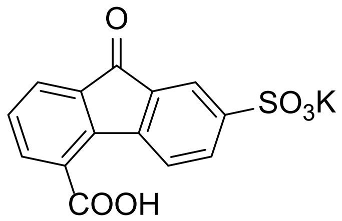


Nat. Energy **2018**, *3* (6), 508-514.

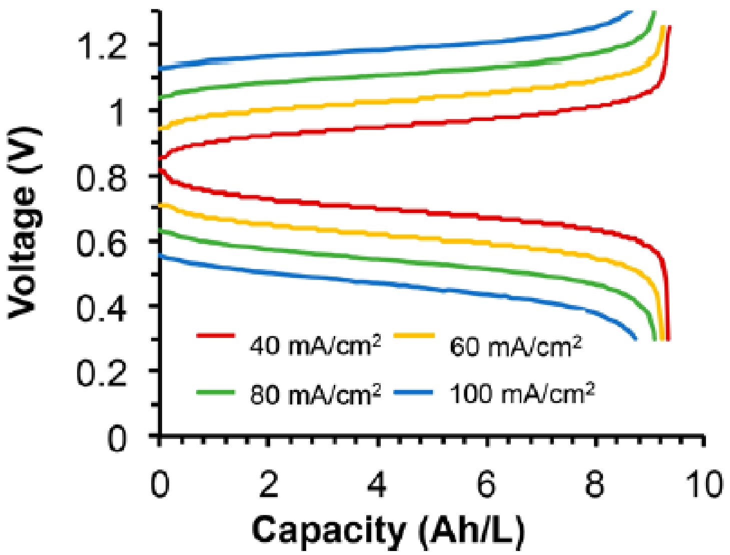
Alkaline system



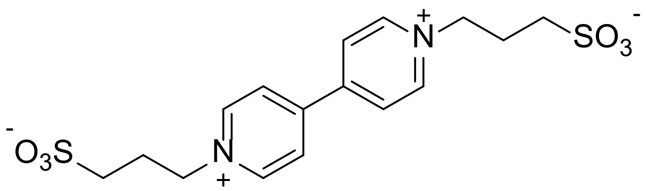
4C7SFL 73 Ah/L



Alkaline system



$(SPr)_2V$ 13.4 Ah/L

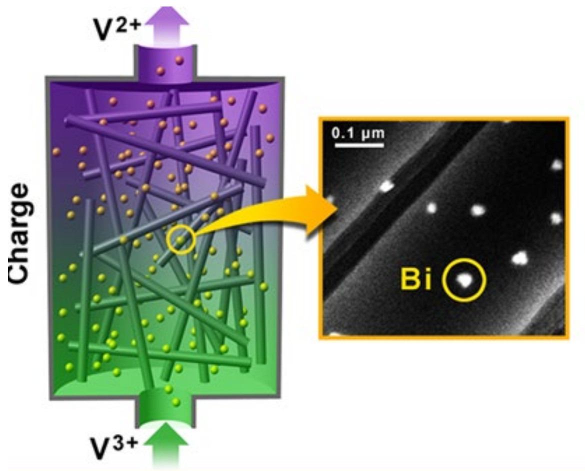


ACS Energy Lett. **2018**, *3*, 663–668.

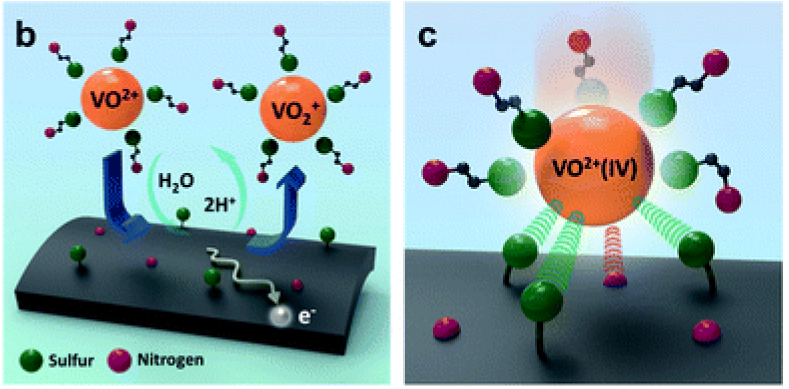
pH neutral system

Key problem to solve in this project:
How we tune kinetics in flow battery?

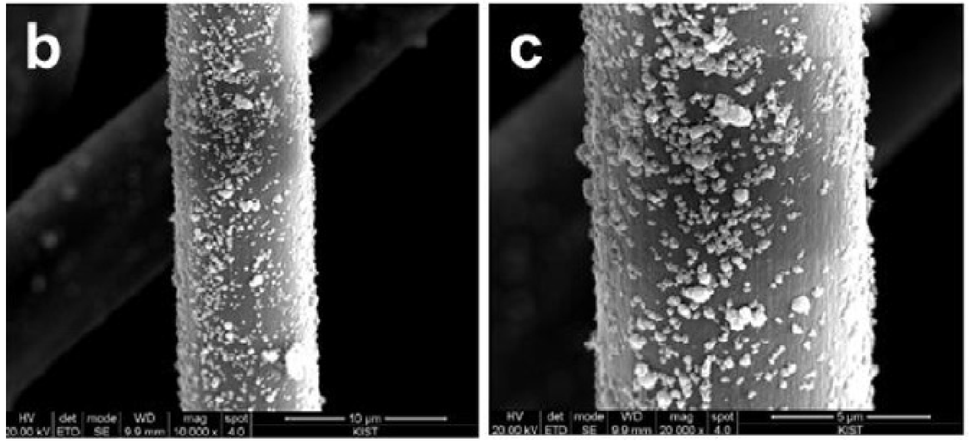
Tunning kinetics in redox flow battery: Heterogeneous catalysis



Nano Lett. **2013**, *13*, 1330−1335
PNNL



J. Energy Chem. **2018**, *27*, 1269-1291.



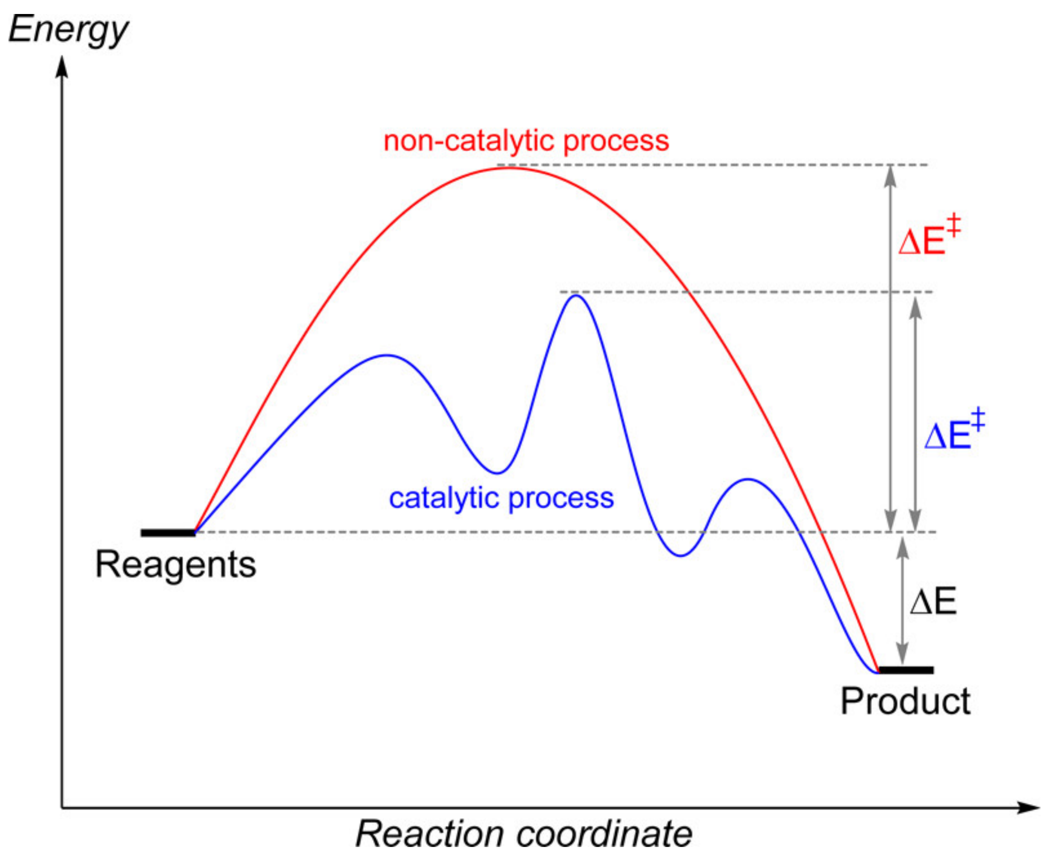
J. Mater. Sci. Technol. **2021**, *75* , 96–109.

Heterogeneous catalysis

- **Electrode modification** with metal/metal oxide electrocatalyst
- **Catalyst loss during long time service**

New strategy: Homogeneous catalysis

A background information



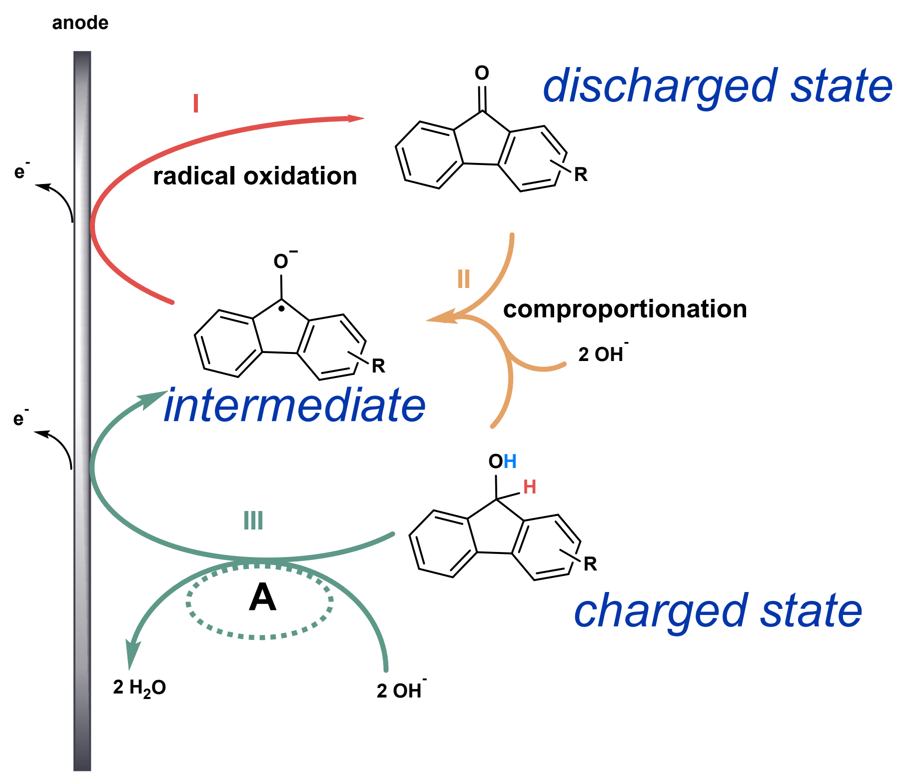
- Both reagents and catalyst dissolved in solution phase
- Lower reaction kinetic barrier

ACS Catal. 2015, 5, 3, 1964–1971

- Has been adopted in catalysis and organic synthesis
- Not been used in energy storage

For fluorenone flow battery: mechanism-informed homogeneous catalysis

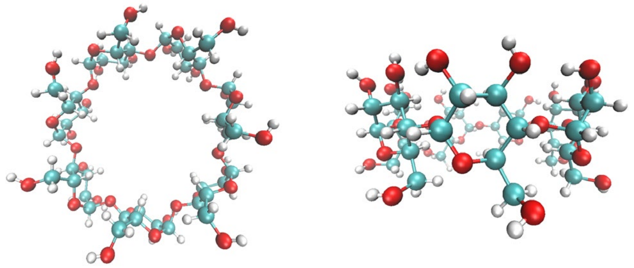
- **Proposed method:** facilitate proton transfer with proton regulator, lower reaction kinetic barrier
- **Why β-cyclodextrin (sugar) as catalyst:** “pKa equalization principle”
- **Expected effect:** higher current density, faster generation of intermediate

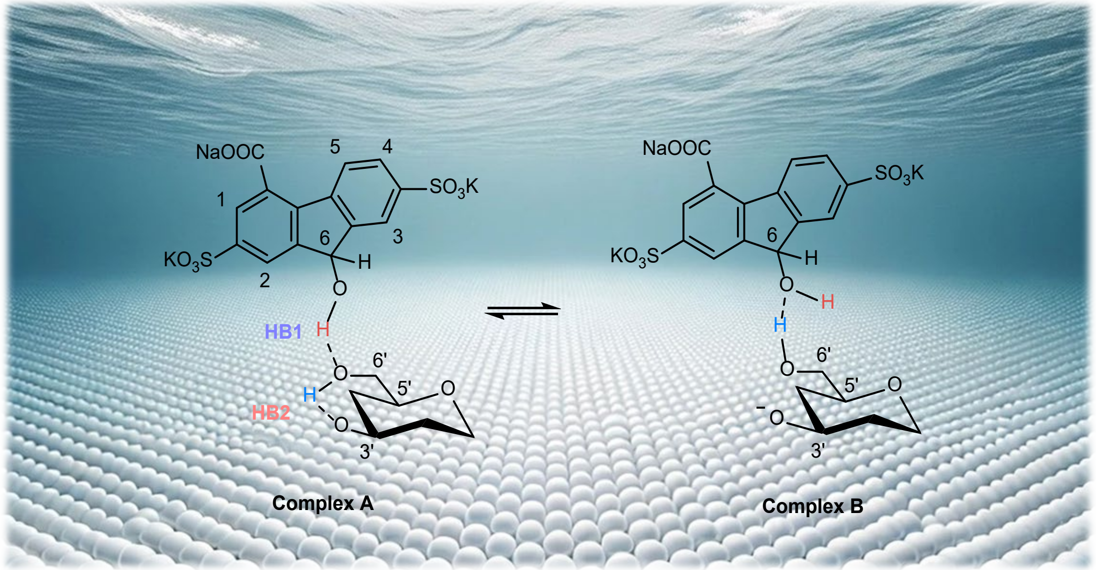


On discharge

accelerate the radical anion supply

Joule **2023**, *7*, 1609

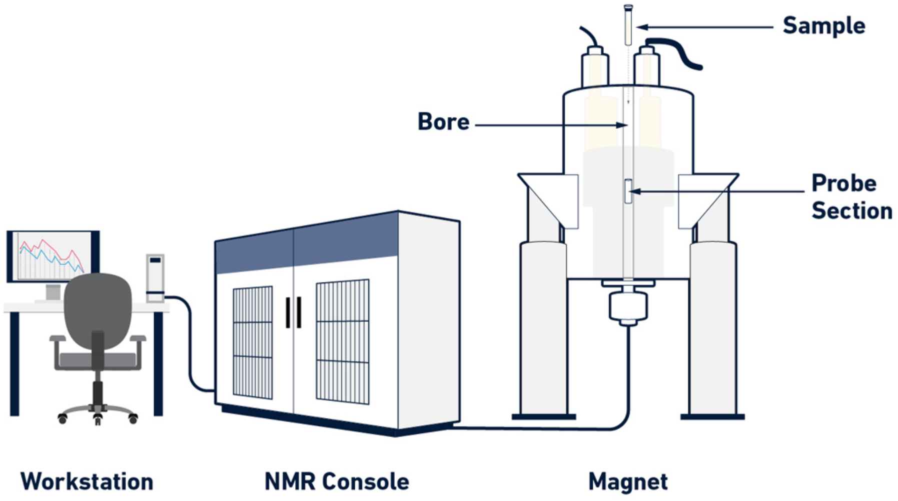




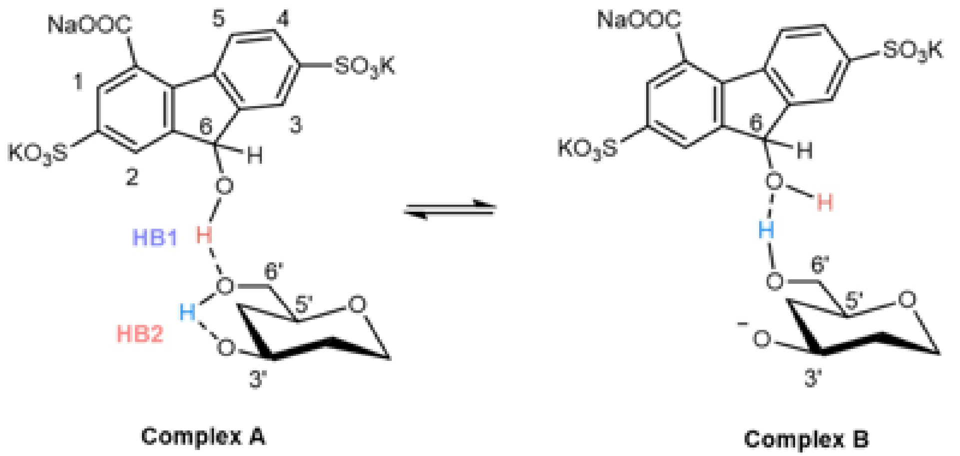
3D art generated by DallE3

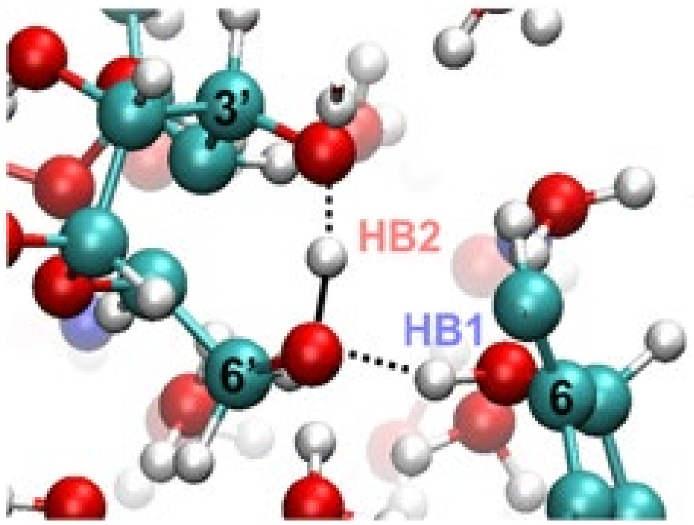
Foundation: Molecular level interaction

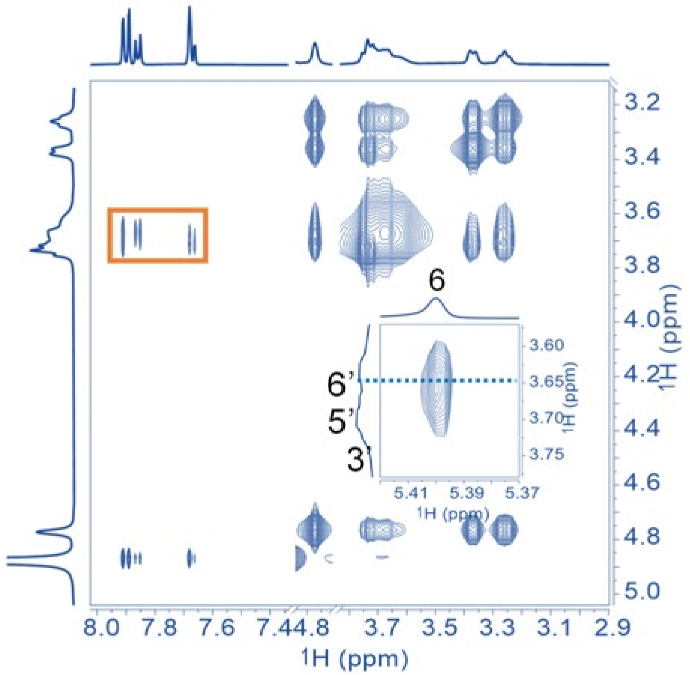
Nuclear Magnetic Resonance (NMR)



https://www.technologynetworks.com/analysis/articles/nmr-spectroscopy-principles-interpreting-an-nmr-spectrum-and-common-problems-355891



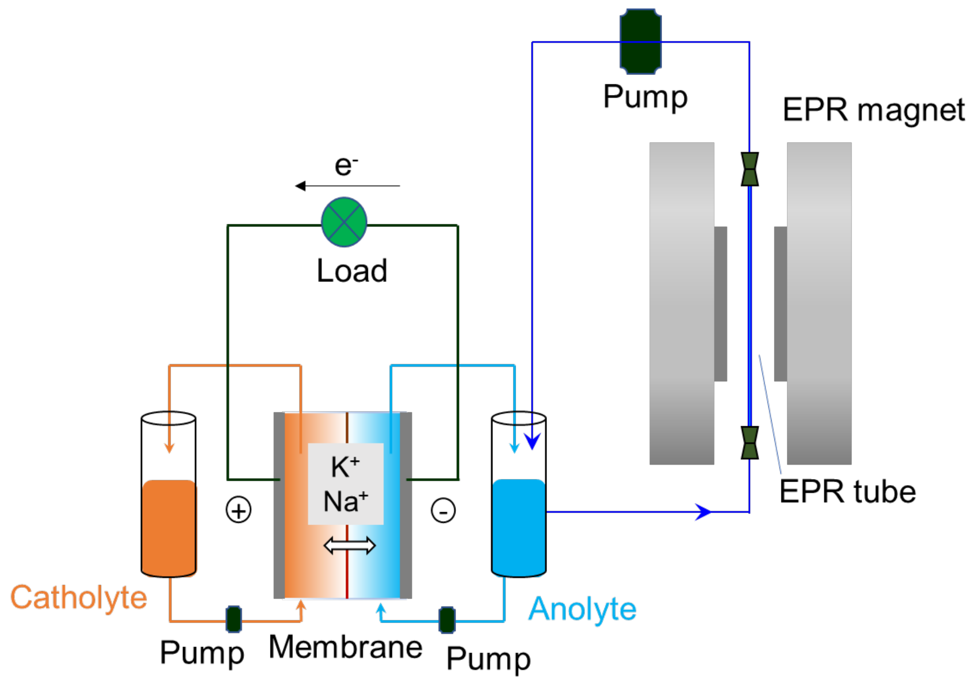


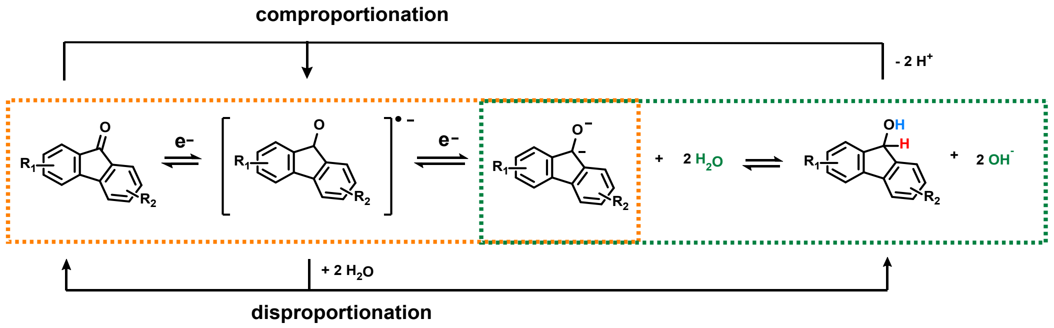


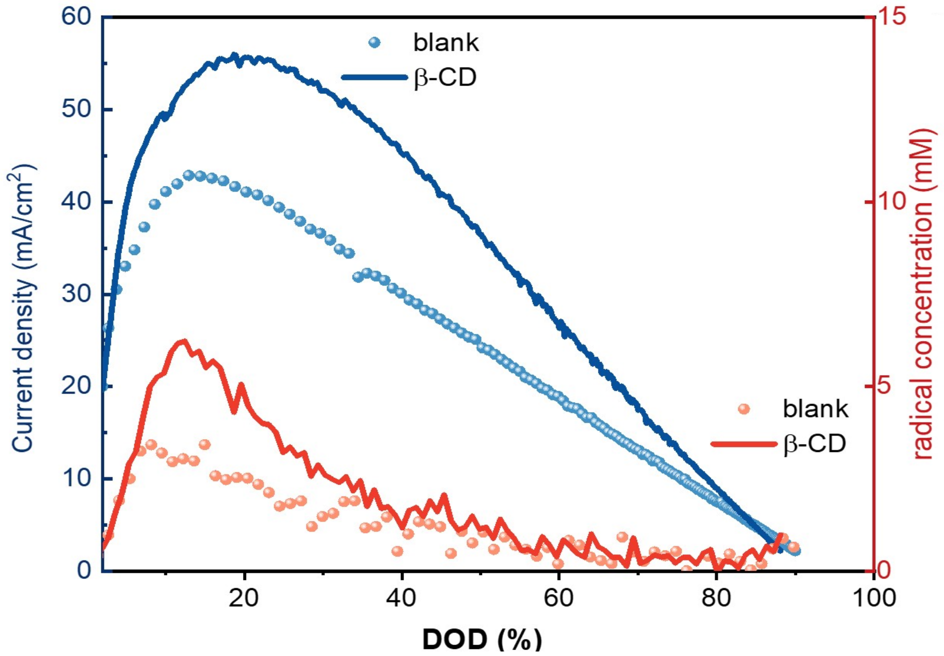
Confirmation of H-bonding complex!

Electrochemical validation in flow cell for catalytic effect

In situ Electron Paramagnetic Resonance (EPR)







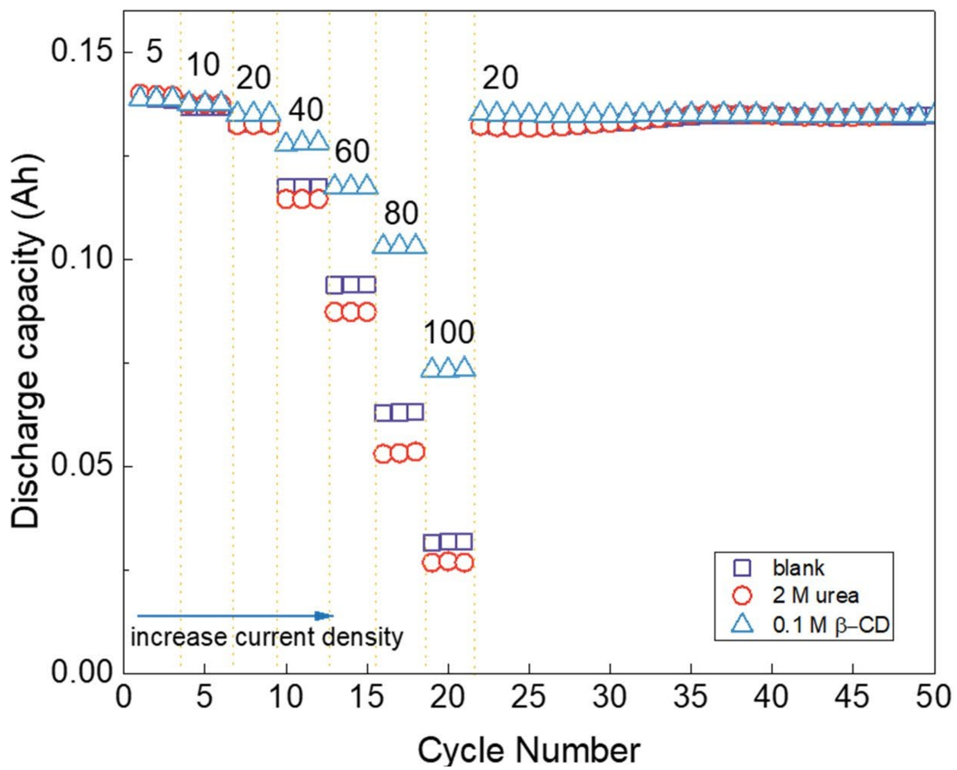
Using pseudo reference under controlled potential

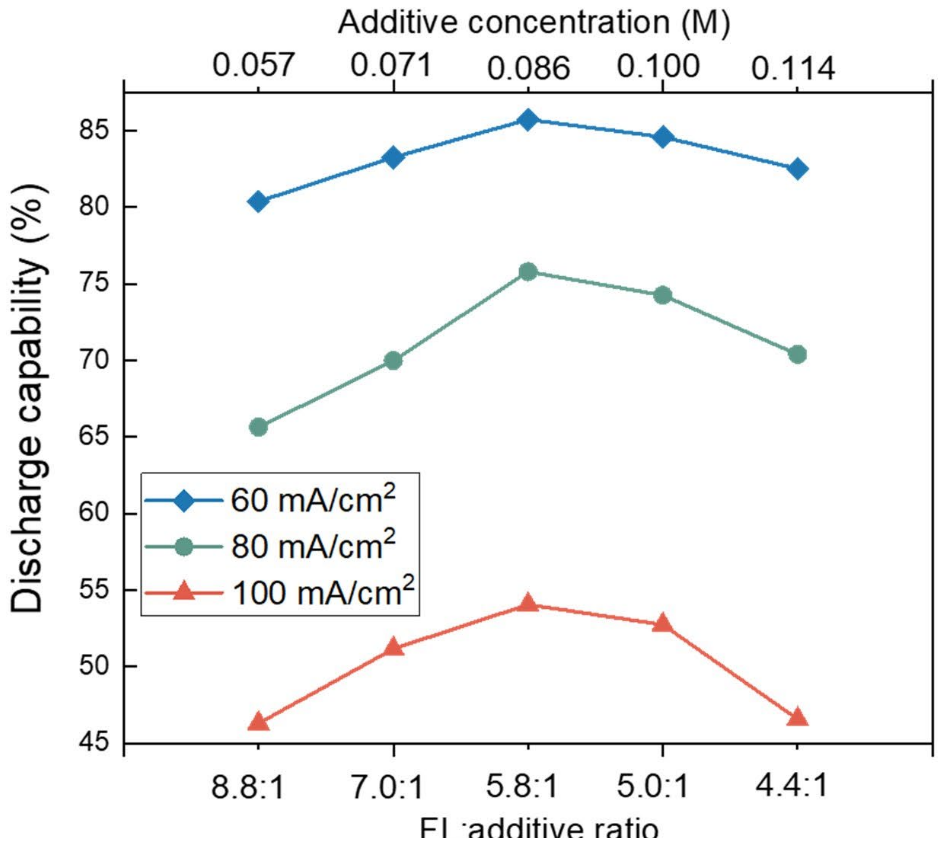
-Higher current density

-Higher intermediate (radical) concentration

-Faster kinetics

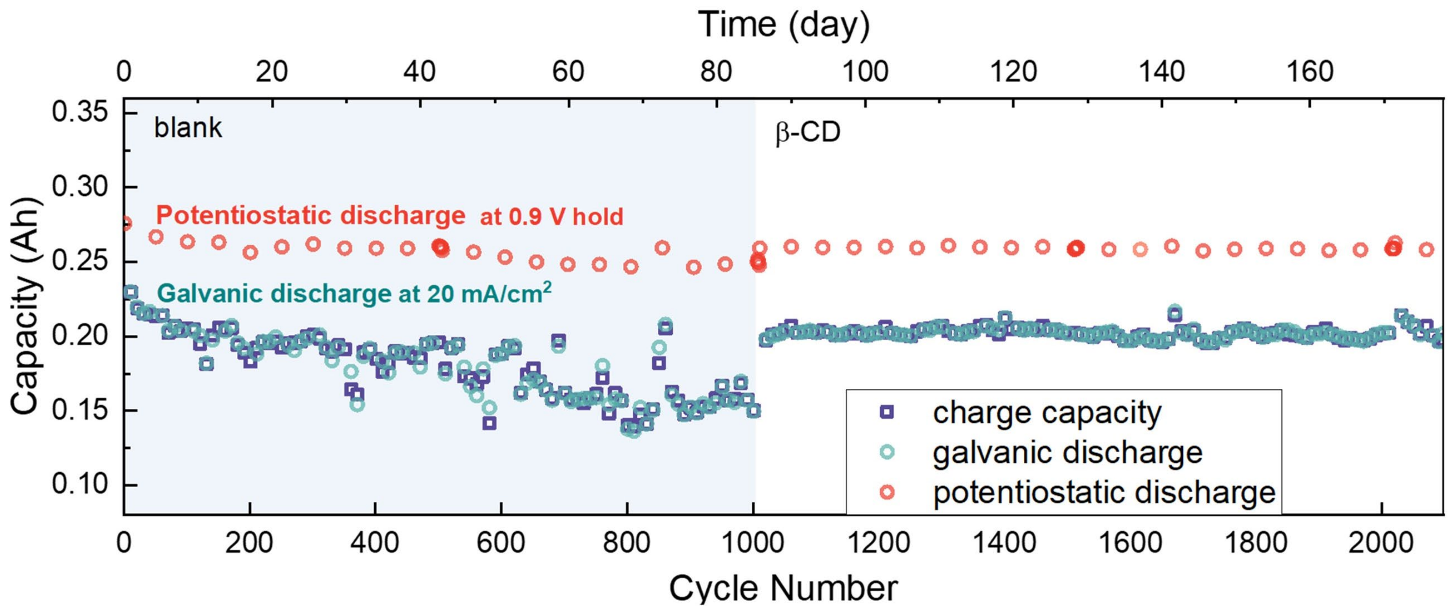
Current density test in battery

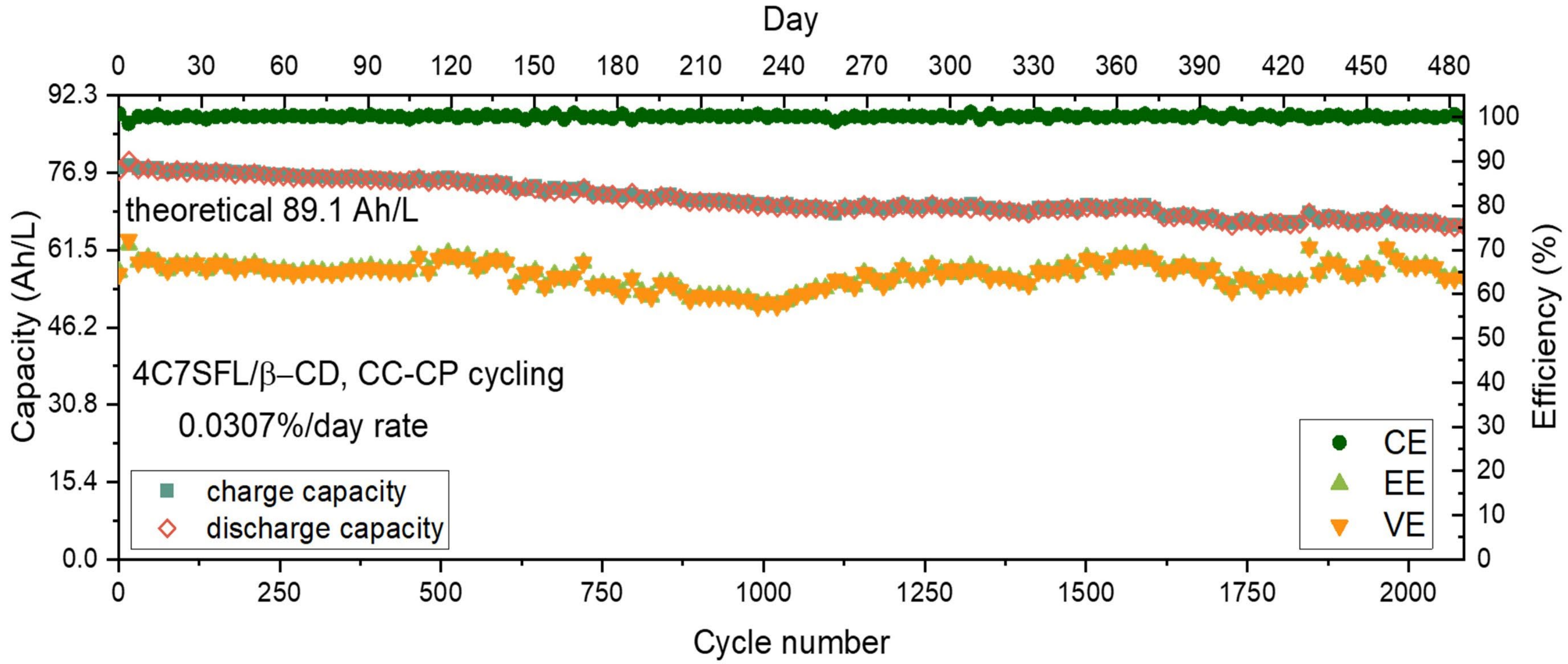




- Net positive effect
- *Kinetic enhancement (+)* outcompete *viscosity negative impact(-)*
- Optimal ratio

Long term stability test





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Summary

	Redox active material	Demonstrated capacity (Ah/L)	Demonstrated time (day)	Demonstrated fade rate (%/day)	Demonstrated energy density (Wh/L)	reference
ASO RFB	47FL/Additive	89.1Ah/L[1]	>500 days	0.0307%/day	100Wh/L[2]	Joule **2023**, 7, 1609 Wei Wang, etc.
ASO RFB	$Na_4[Fe^{II}(Dcbpy)_2(CN)_2]$	26.8Ah/L[4]	>13 days	0.25%/day	32.2Wh/L[5]	Nat. Energy **2021**, 6, 873-881. Wei Wang, Yu Zhu, etc.
Redox targeting RFB	Prussian blue/ ferrocyanide	56.3Ah/L[6,7]	>20 days	0.078%/day[8]	97.4Wh/L[9]	Joule **2019**, 3, 1–13. Qing Wang, etc.
Chelate RFB	KCrPDTA	32.2Ah/L[10]	>4.6 days	- [11]	52.2Wh/L[12]	Chem Asian J. **2022**, 17, e202200700 Michael Marshak, etc.
Vanadium RFB	V^{3+}/V^{4+}, V^{4+}/V^{5+}				~35-40Wh/L	

(1)Calculated based on anolyte solution, battery demonstrated with excess ferrocyanide (2)Calculated based on theoretical battery voltage (1.1 V) and anolyte volumetric capacity (3)Initial EE ~70% at room temperature (~20 °C), VE dropped >10% during > 500 days operation (4)Calculated based on catholyte solution, battery demonstrated with excess Spr-Bpy (5)Calculated based on theoretical battery voltage (1.2 V) and catholyte volumetric capacity (6)Effective volumetric capacity from both solution phase and solid phase, battery demonstrated with $Zn(OH)_4^{2-}$ (7)Solid phase material utilization calculated to be 17.4% (8)Calculated based on reported retention rate 99.991%/cycle (9)Calculated based on theoretical battery voltage (1.73 V) and catholyte effective volumetric capacity (10)Calculated based on anolyte solution, battery demonstrated with excess ferrocyanide (11)Capacity limit of 80% applied during cycling (12)Calculated based on theoretical battery voltage (1.62 V) and anolyte volumetric capacity

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Acknowledgement

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Team:

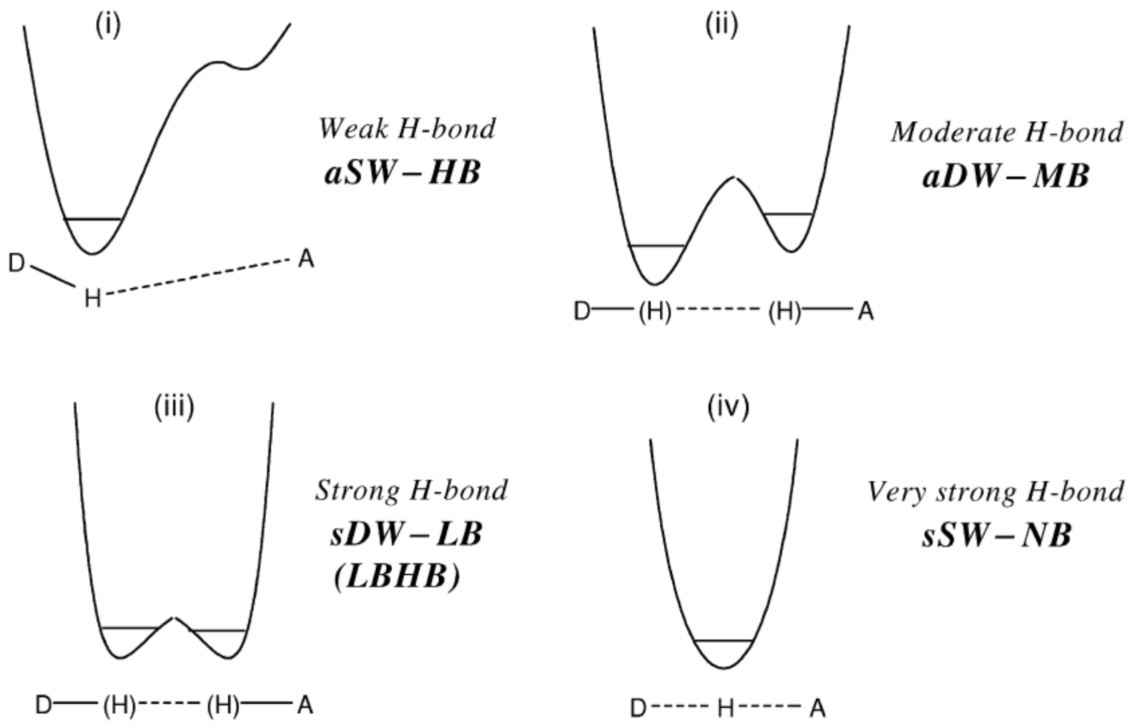
Wei Wang
Yuyan Shao
Aaron Hollas
Xin Zhang
Ying Chen
David Reed
Vijayakumar Murugesan
Hyung-Seok Lim
Yangang Liang
David J. Bazak
Soowhan Kim
Litao Yan
Qian Huang
Peter S. Rice

Collaborators:

Yale University
Sharon Hammes-Schiffer
Benjamin. J. G. Rousseau

Intermolecular interaction: H-bonding

pKa match theory



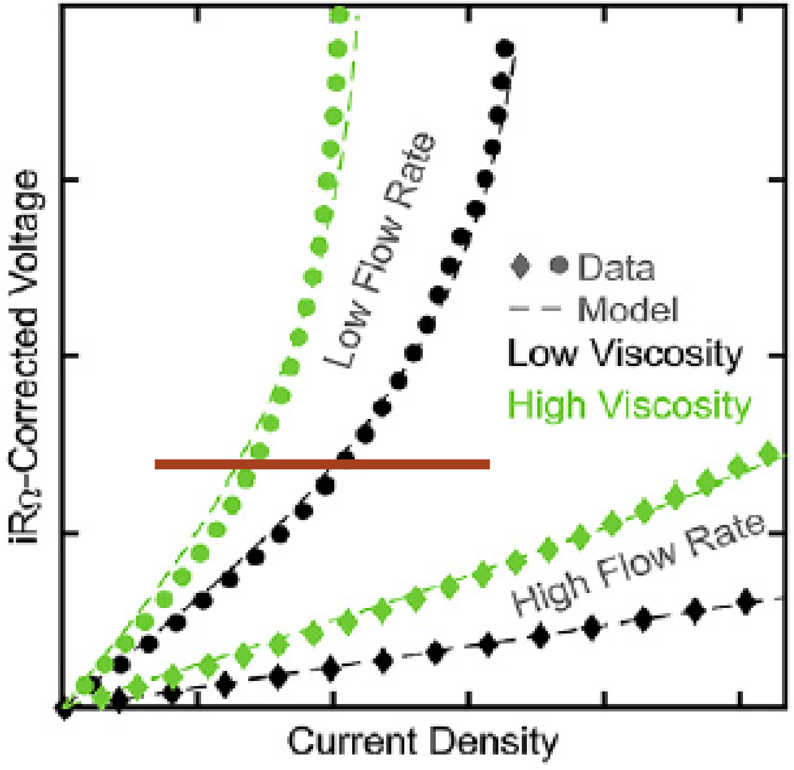
"pKa equalization principle"

$$\Delta pKa = pK_{AH}(D\text{–}H) - pK_{BH+}(A\text{–}H^{+})$$

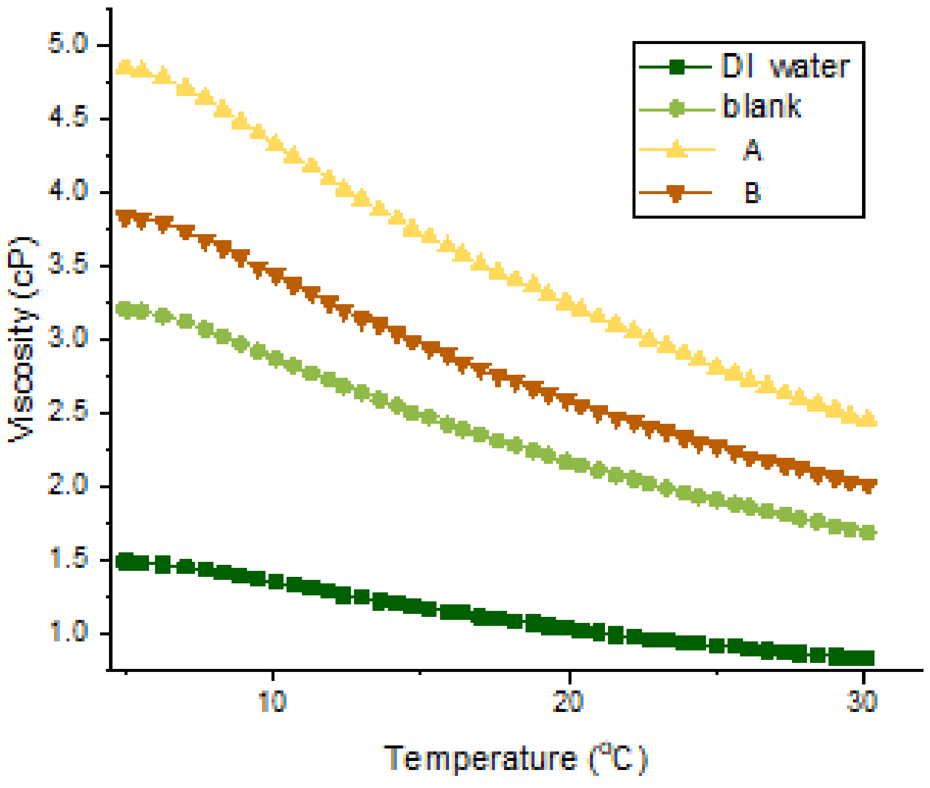
Smaller ΔpKa, stronger H-bonding

Gilli, P.; Gilli, G. Hydrogen Bond Models and Theories: The Dual Hydrogen Bond Model and Its Consequences. J. Mol. Struct. 2010, 972 (1), 2–10.

viscosity influence on flow battery

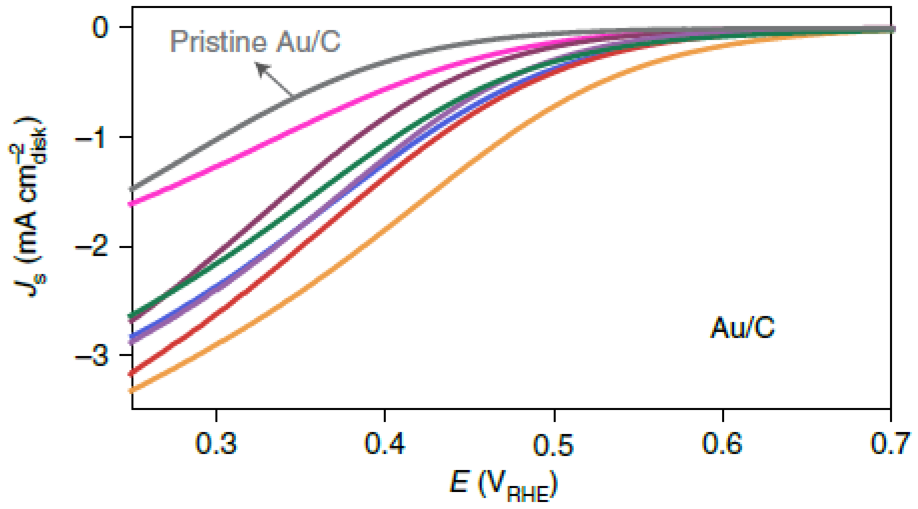


J. Power Sources **2018** ,*399*, 133-143



Unpublished result

Validation in a flow cell? Constant Potential vs Constant Voltage



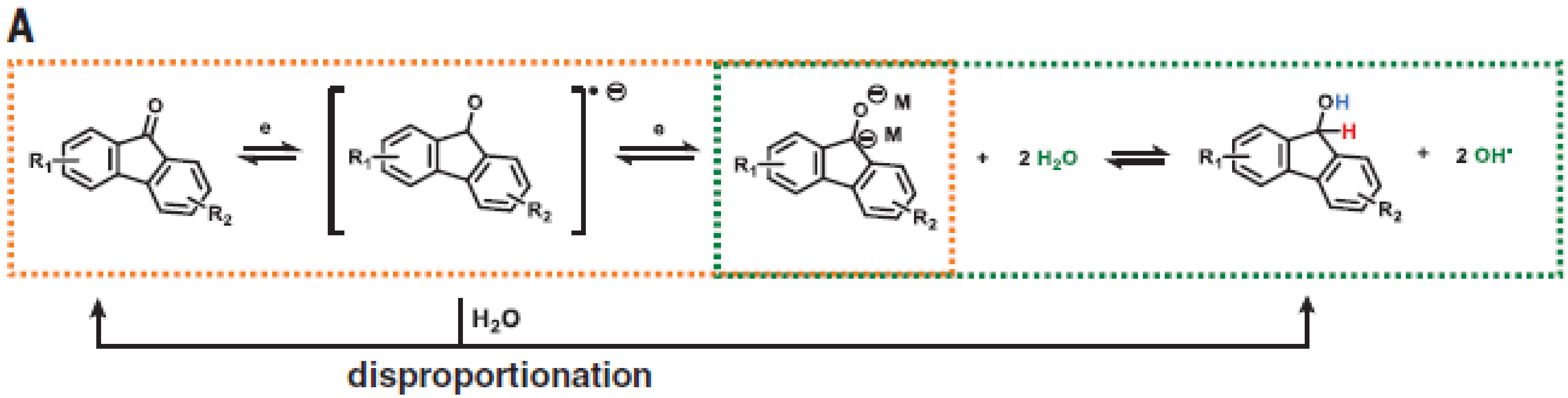
Compare current density at certain *applied potential vs ref*

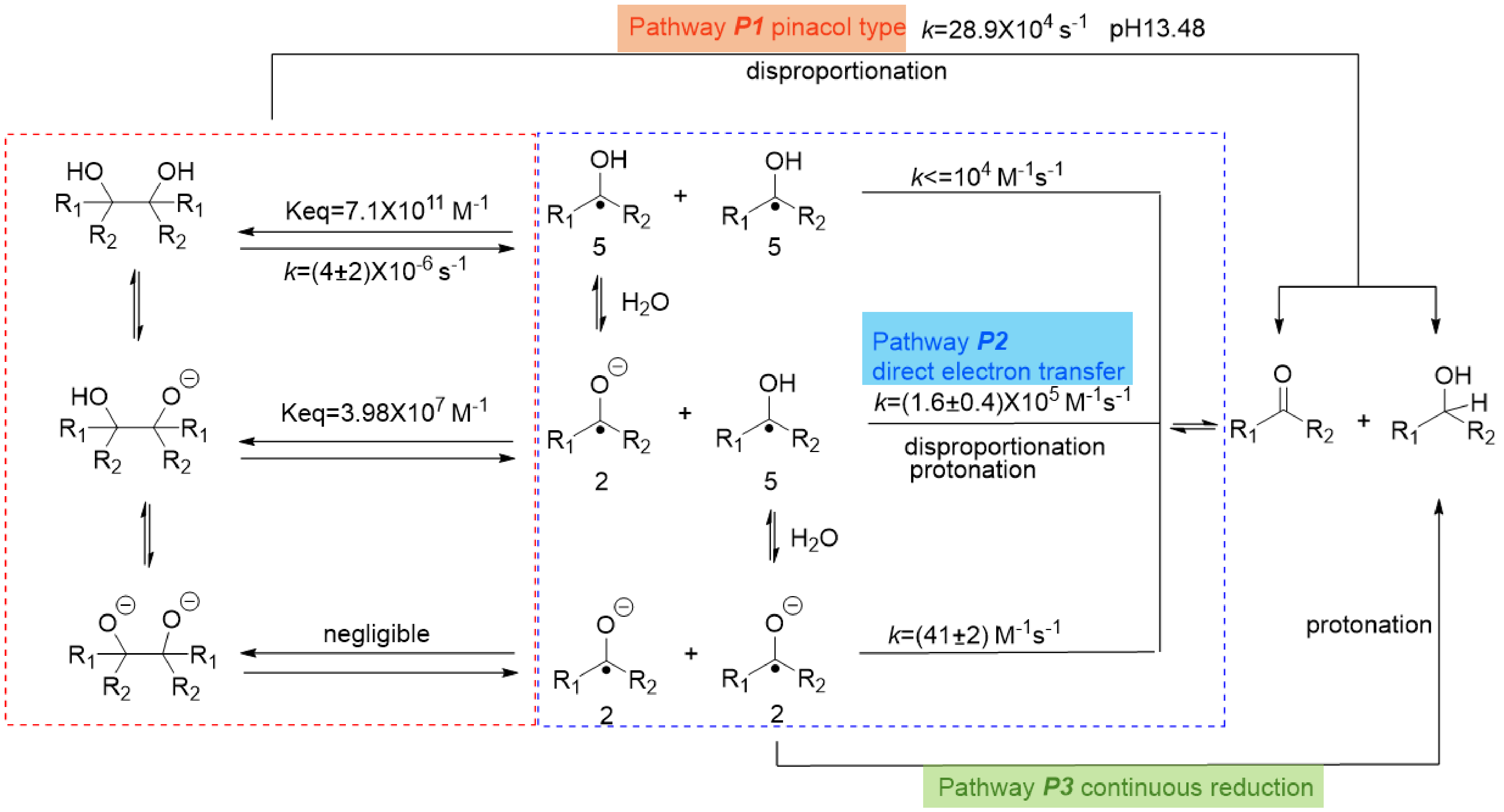
higher current density, faster kinetics

Pseudo reference in flow battery

-Large excess catholyte
-Relative constant SOC for catholyte side during cycling
-Constant voltage ≈ constant potential

Coupled chemical electrochemical process




Pathway P1 pinacol type
k=28.9X10^4 s^-1 pH13.48
disproportionation
Keq=7.1X10^11 M^-1
k=(4±2)X10^-6 s^-1
Keq=3.98X10^7 M^-1
negligible
k<=10^4 M^-1s^-1
H2O
Pathway P2
direct electron transfer
k=(1.6±0.4)X10^5 M^-1s^-1
disproportionation
protonation
H2O
k=(41±2) M^-1s^-1
protonation
Pathway P3 continuous reduction