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Electrolyte Design Formulations for Aqueous Redox Flow Battery

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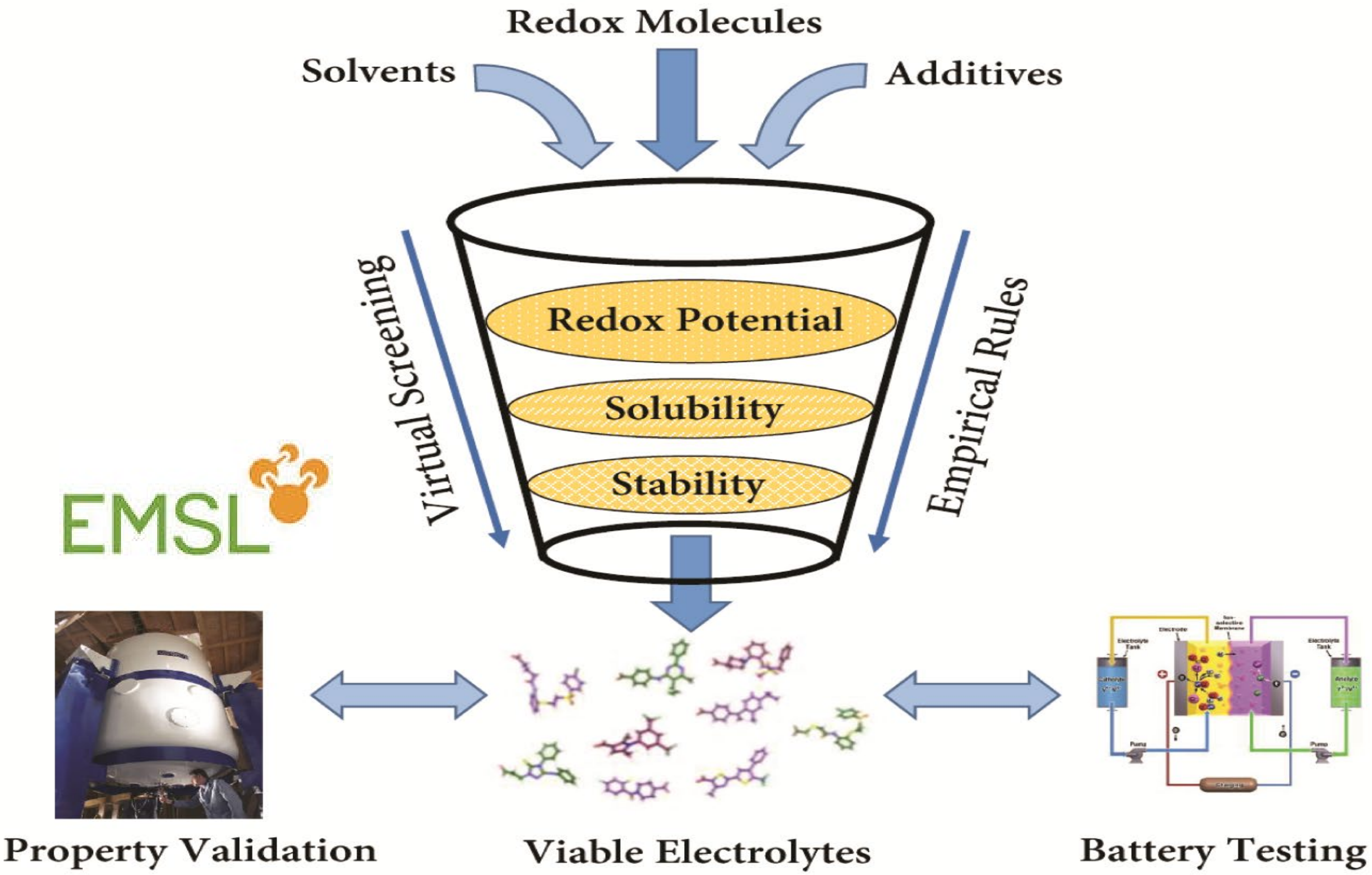
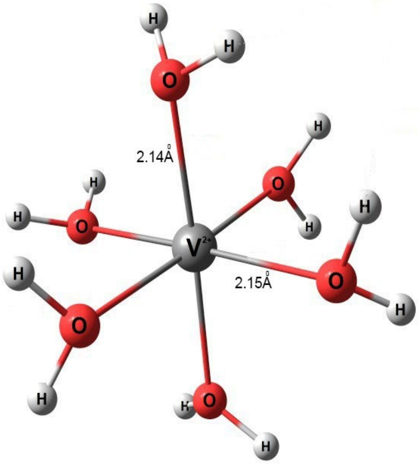
Pacific Northwest National Laboratory,
Richland, WA

Building Robust Electrolyte Design Module

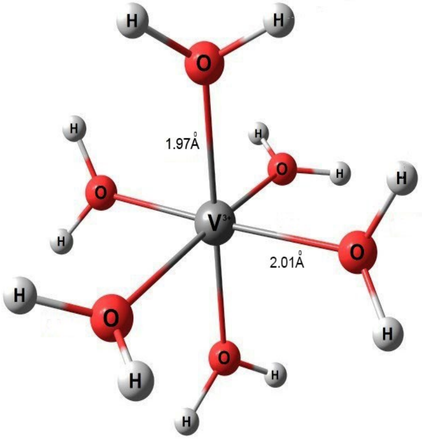


Virtual screening assisted with empirical rules to down select viable Inorganic and Organic Aqueous electrolytes and subsequent property and battery testing for model validation

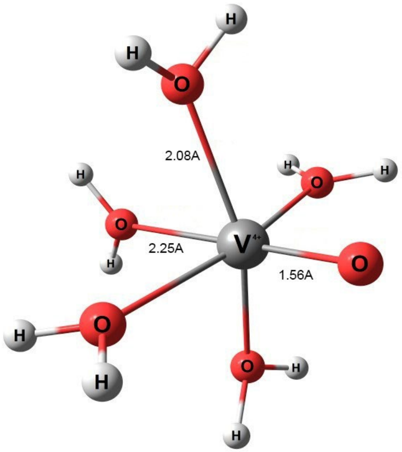
Solvation is the basis of VRFB electrolyte



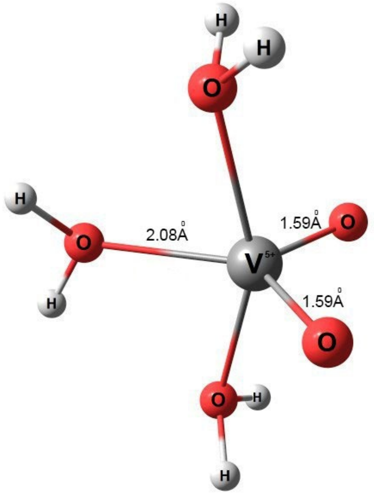
V^{2+}



V^{3+}



V^{4+}

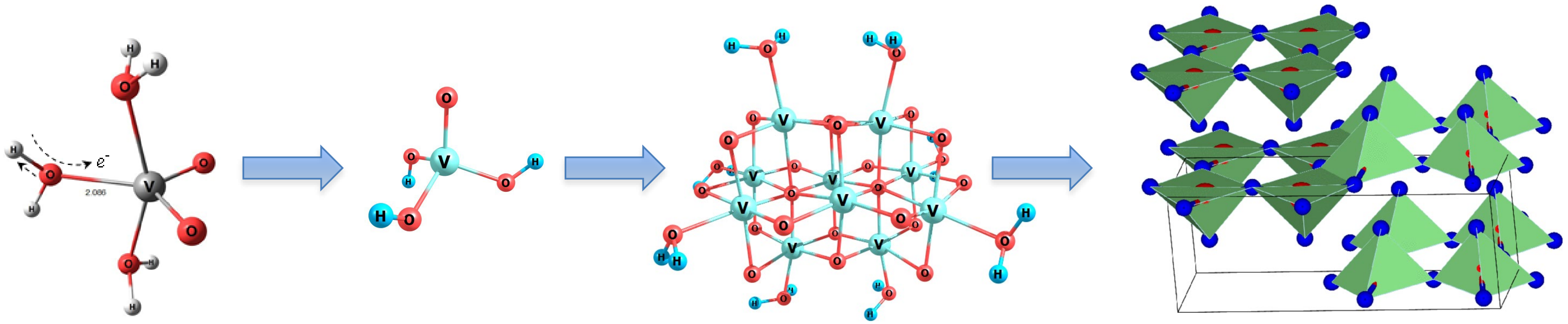


V^{5+}

Water a highly polar solvent, due to significant difference in electronegativity of hydrogen and oxygen, can actively interact with both cations and anions and established as an efficient solvent for redox flow battery technology.

ChemPlusChem 80 (2015), 428-437

Evolution of V_2O_5 solid precipitate



$$VO_2.3H_2O \rightarrow H_3VO_4 \rightarrow (V_{10}O_{28}).nH_2O \rightarrow (V_2O_5).nH_2O$$

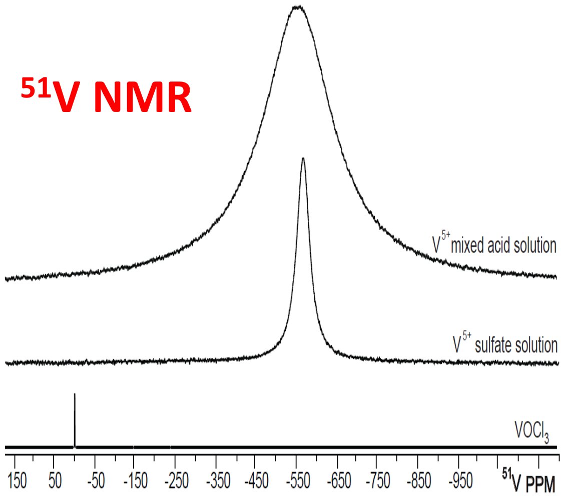
Deprotonation → Hydrolysis → Clustering → Solid precipitate

Long range network formation can act as seed for crystallization and subsequently cause solid precipitation in electrolytes

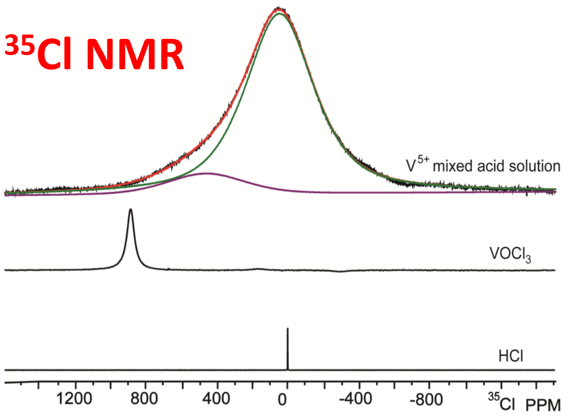
J. Power Sources 196 (2011), 3669-3672

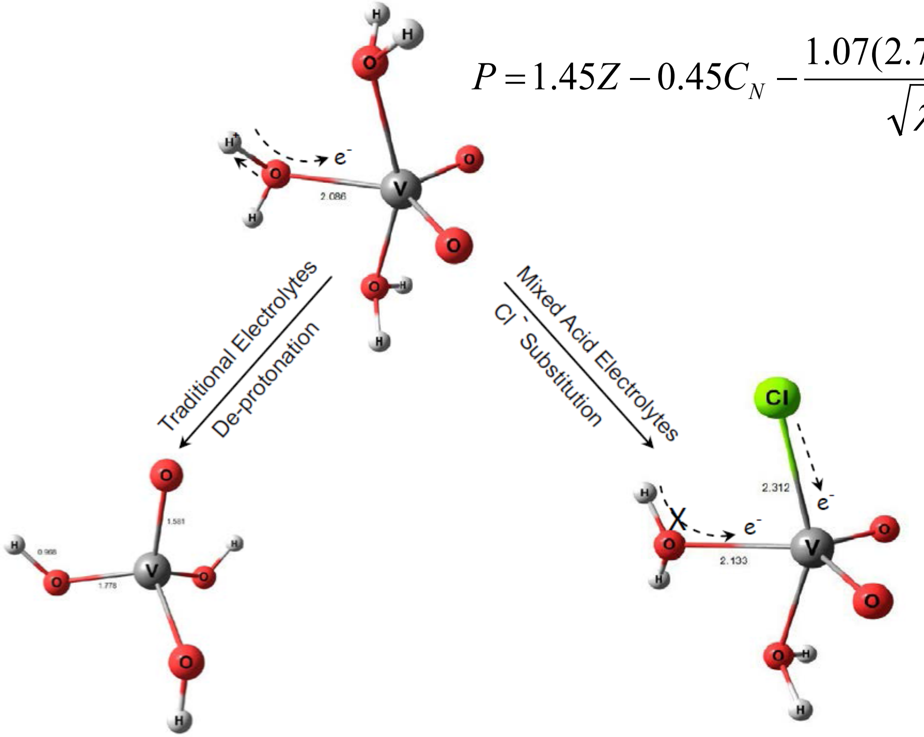
How to minimize De-protonation??

^{51}V NMR



^{35}Cl NMR





$$P = 1.45Z - 0.45C_N - \frac{1.07(2.71 - \chi_M)}{\sqrt{\chi_M}}$$

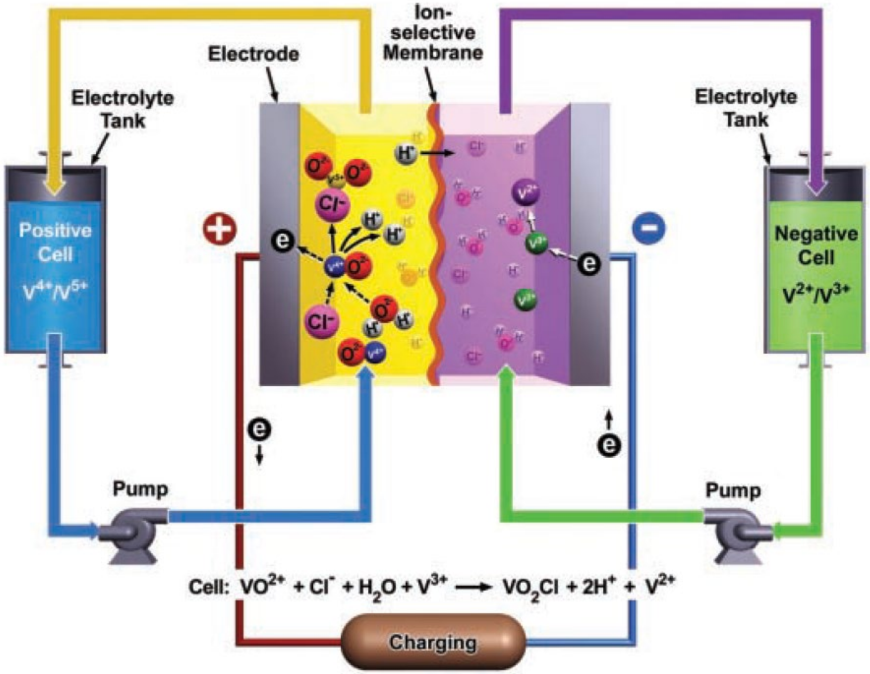
Leads to V_2O_5 Precipitation

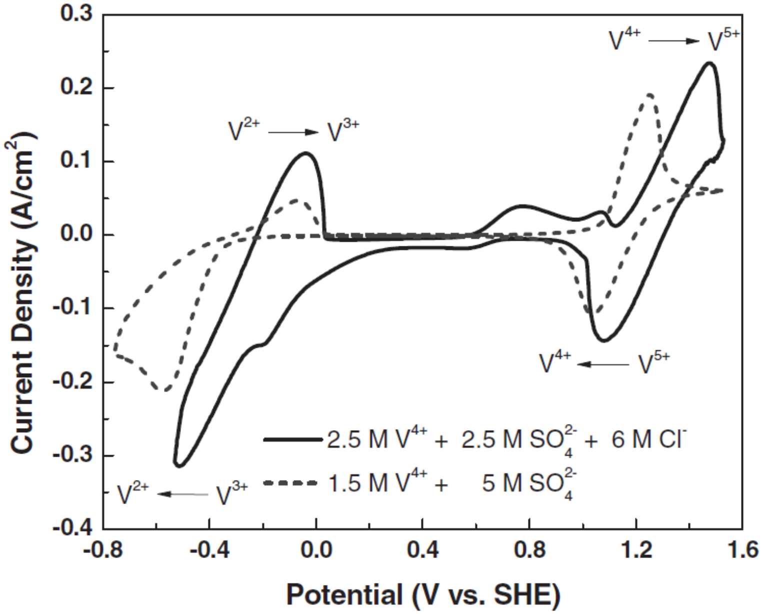
Higher Thermal Stability

$$[VO_2(H_2O)_3]^+ + HCl \leftrightarrow VO_2Cl(H_2O)_2 + [H_3O]^+ \Delta H > 0$$

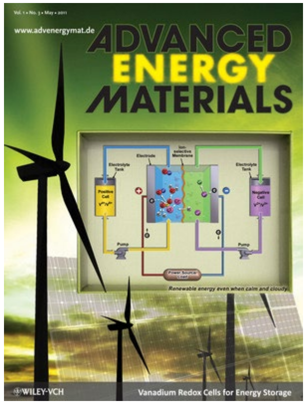
Counter anion can suppress the deprotonation and subsequent precipitation reaction

New mixed-acid based Redox Flow Battery





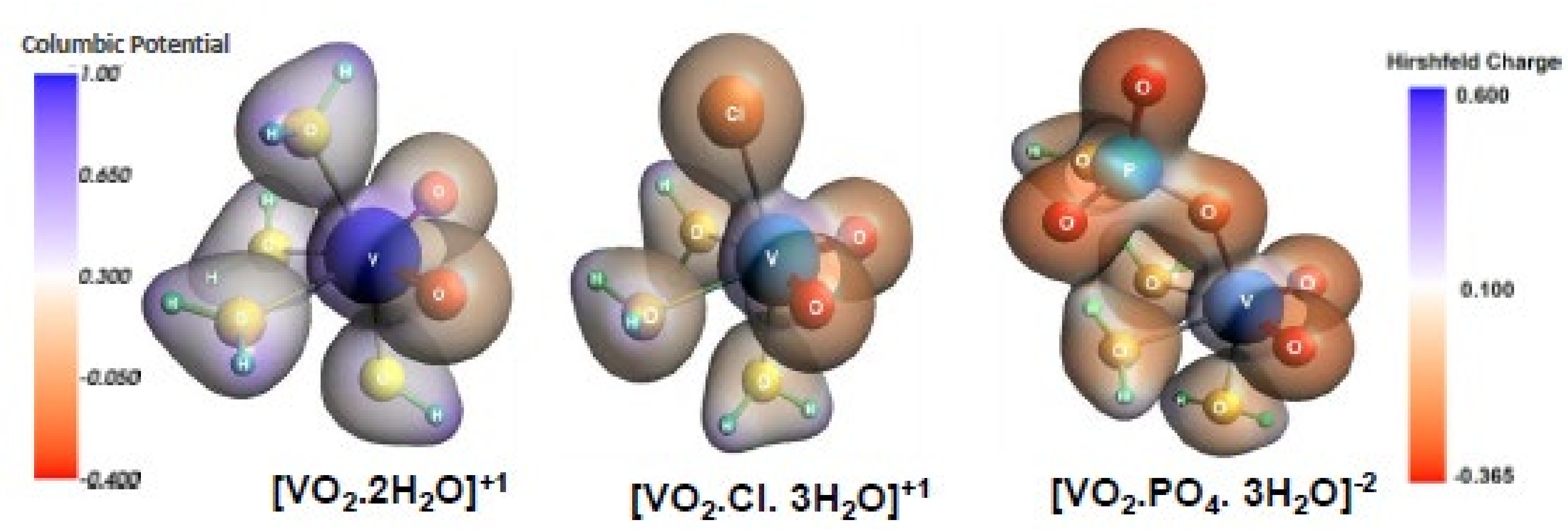
Current of Discharge, (mA.cm^2)	Energy Density (Wh.L^{-1})		
	2.5 VS 6 Cl	3 VS 6 Cl	1.6 V 4.5 S
100	36.2	39.5	22.3
75	37.5	40.8	22.4
50	38.5	41.8	22.6
25	39.2	43.1	22.6



This new RFB System is Commercialized in 2012.

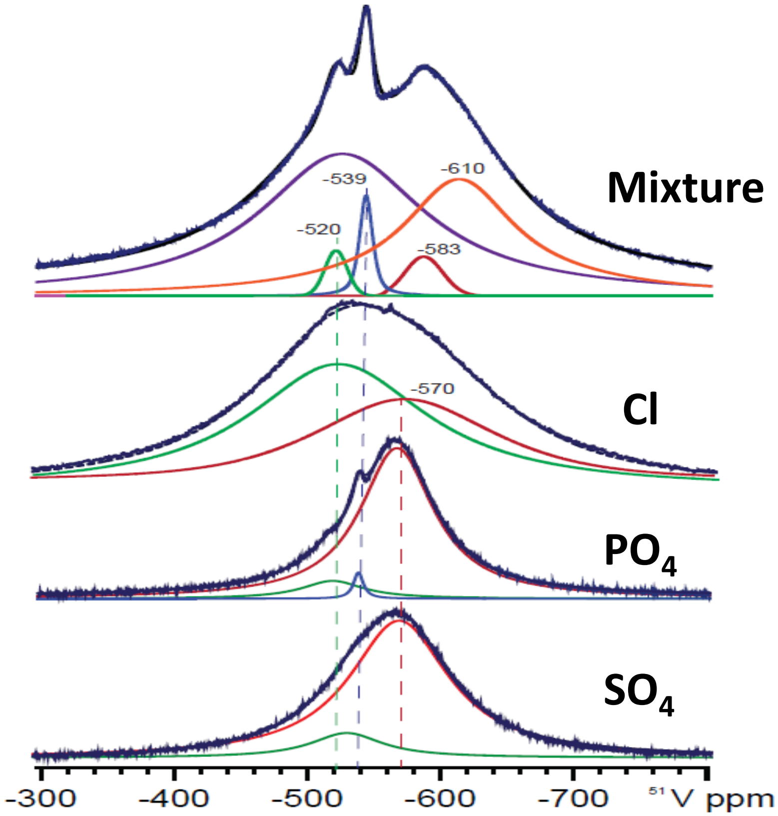
Adv. Energy Mater 1 (2011), 394-400

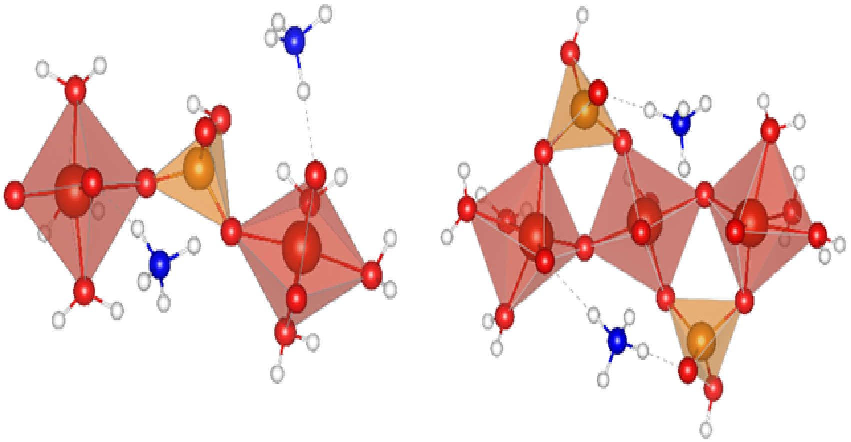
Manipulating charge density through contact ion pair formation



Counter ion provides asymmetric charge distribution and modulates the thermodynamic and kinetic aspects of extended network formation

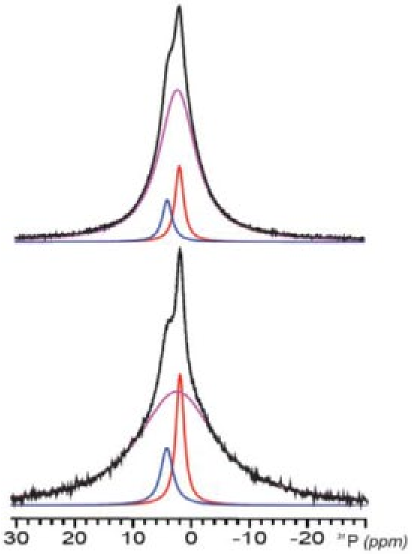
Disrupting the Extended network to prevent nucleation



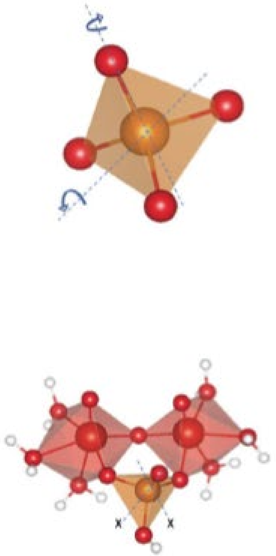


Finding optimal level of counter ion is critical, to modulate the charge density but avoid the extended network formation

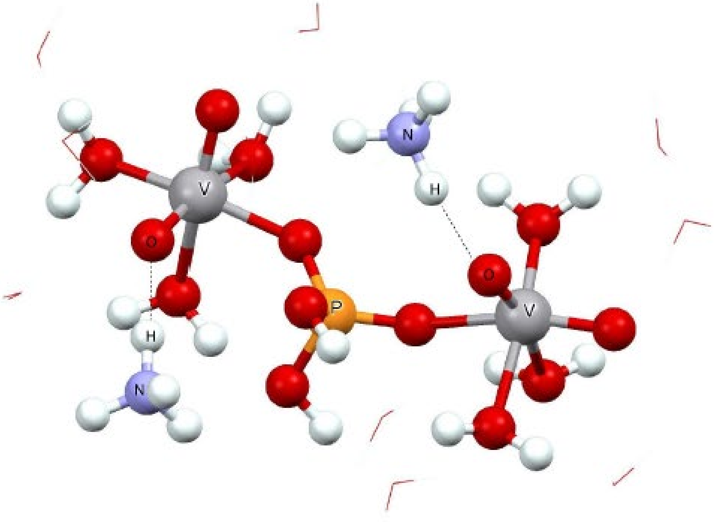
Spectroscopic signatures of solubility limit



^{31}P NMR



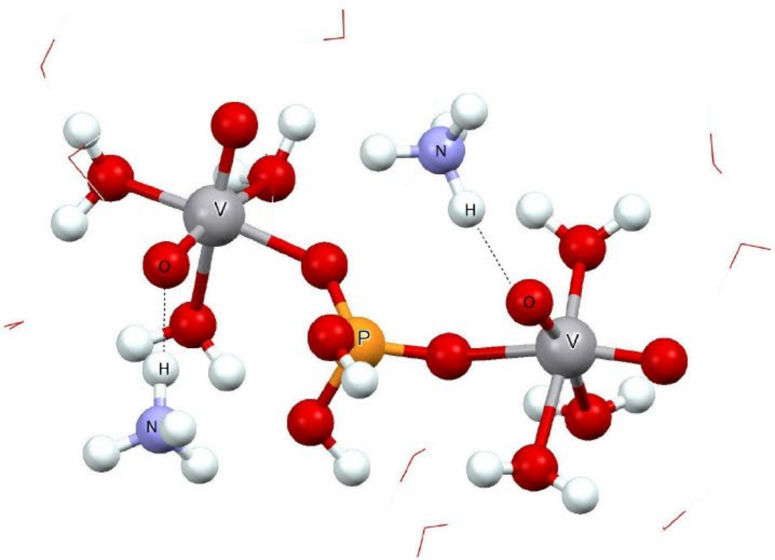
Phosphate rotation

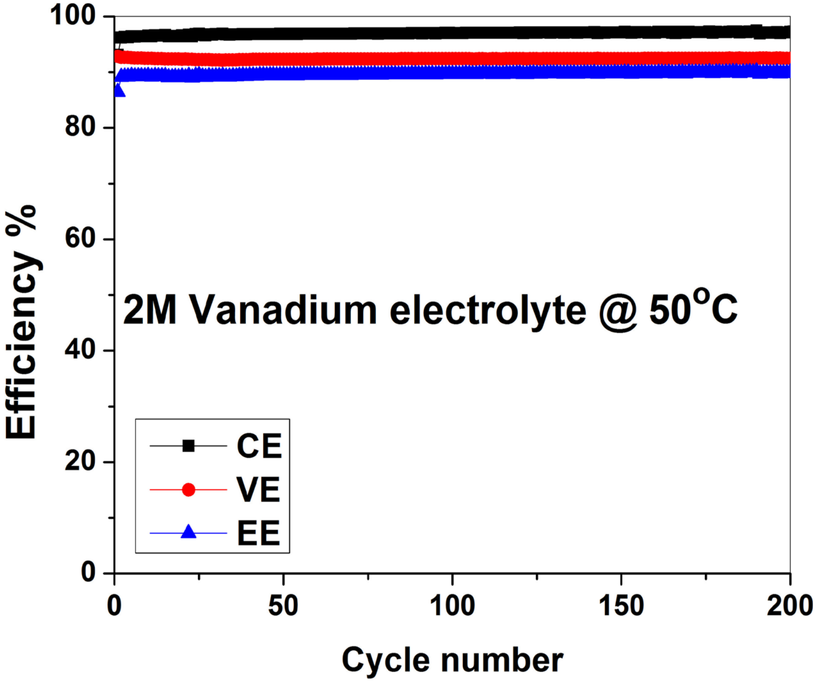


Preferential solvation of NH_4^+

Intramolecular dynamics can be used as fingerprint to monitor the extended network formation and nucleation seeds

Bi-additive for Vanadium Redox Flow Battery

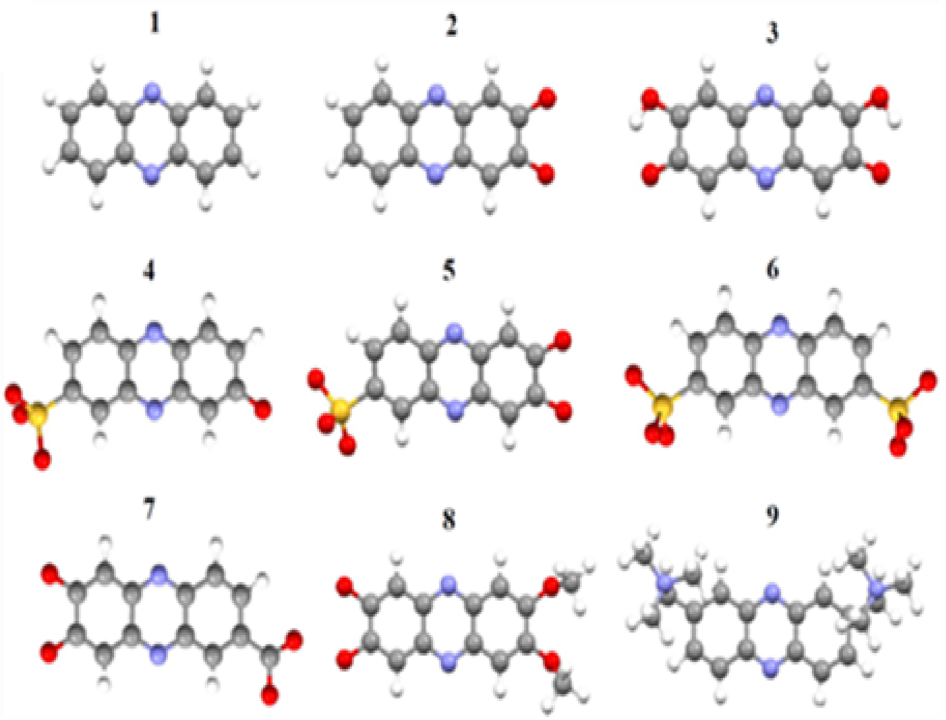




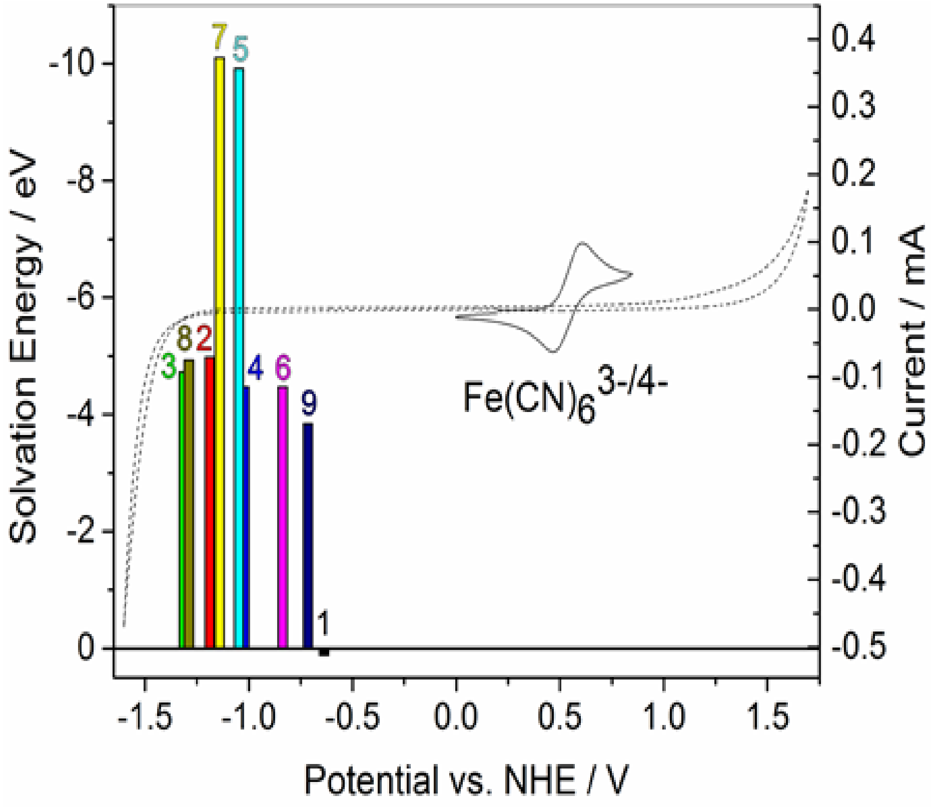
Optimal additive can be designed through our electrolyte design module using predictive understanding of electrolyte solvation phenomena

Brian Berland (ITN) Talk and Zimin Nie (PNNL) poster on 26th September

Designing phenazine derivatives as redox molecule for Aqueous organic flow battery



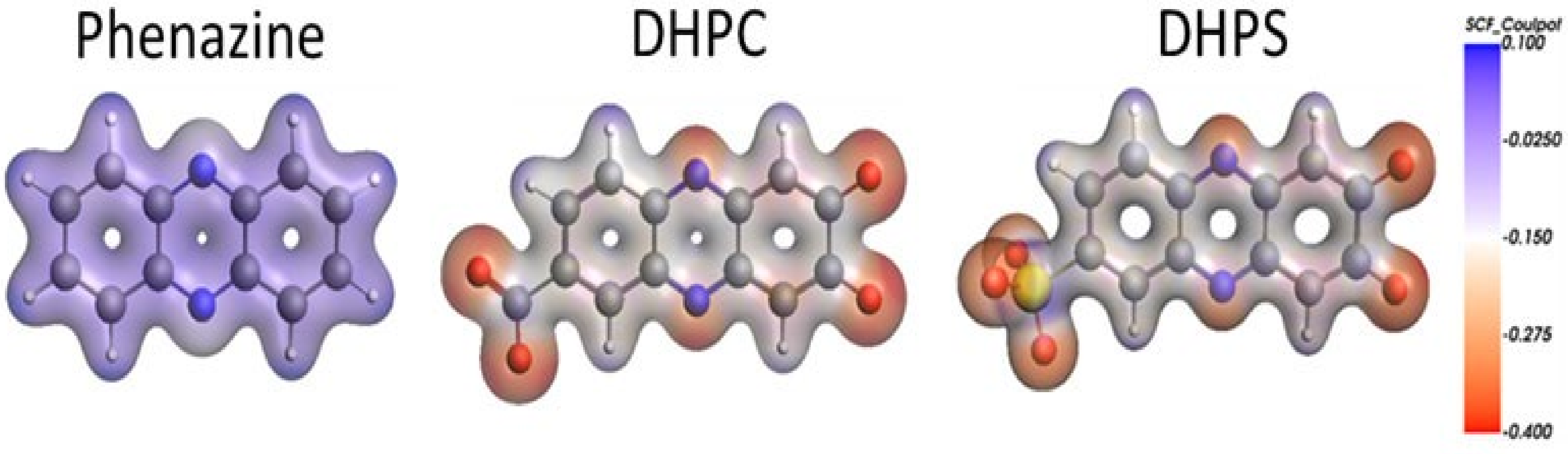
Phenazine derivatives



Solubility of phenazine can be manipulated through wide range of functional groups, the challenge is to find optimal species

Nature Energy, Vol 3, pages 508–514 (2018)

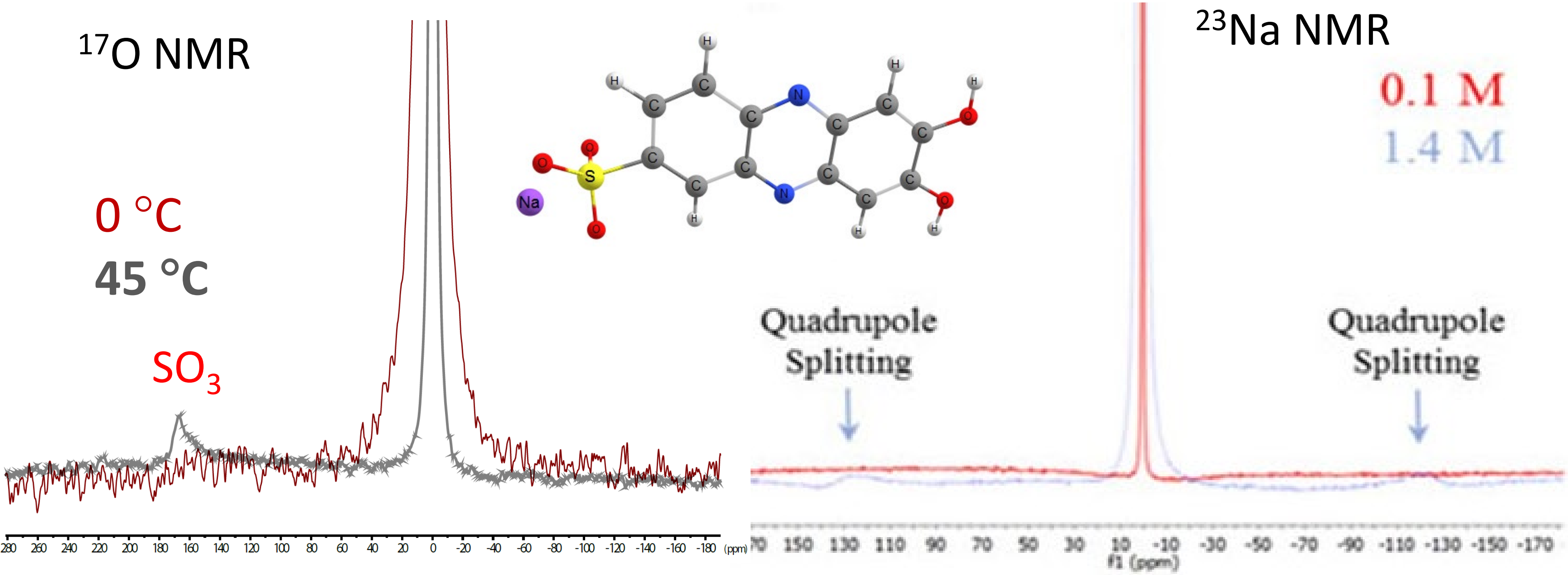
Asymmetric charge distribution can be useful



Functional moieties can introduce asymmetrical configuration and initiates location specific intensified solvation (i.e. preferential solvation) that significantly enhances the solubility from near-zero to up to 1.8 M in potassium-based supporting electrolyte

Nature Energy, Vol 3, pages 508–514 (2018)

Spectroscopic signatures of solubility limit

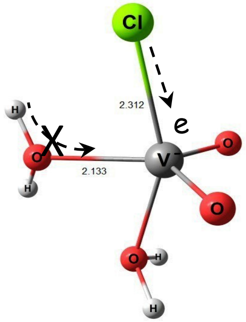


Intramolecular dynamics dictated by counter ion interaction can dictate the solubility limit by manipulating the extended network formation

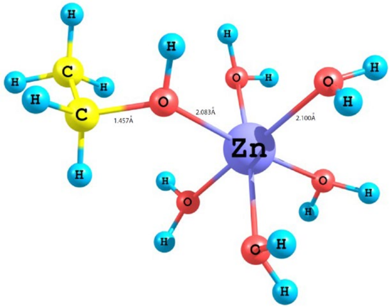
Summary

Establishing preferential solvation through, asymmetric charge distribution, contact-ion pair and intramolecular dynamics can enhance the solubility, stability and redox properties of electrolyte molecules.

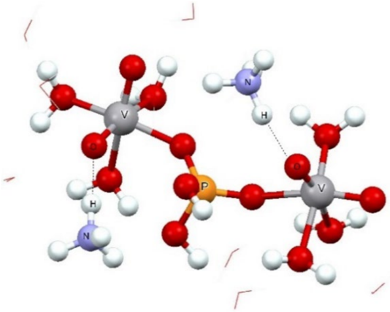
Virtual screening with these predictive understanding help us design novel electrolyte for redox flow batteries.



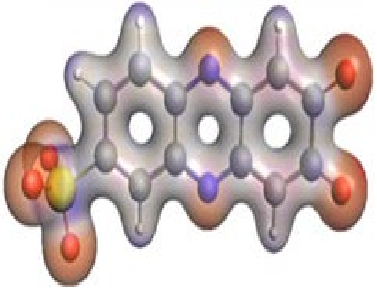
Mixed Acid



Zn-I electrolyte



Bi-additives



Organic-Flow

Optimal electrolyte design through molecular engineering

2011

2013

2016

2018

Acknowledgements

Office of
ELECTRICITY

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