Novel Phenazine Derivatives as Anolytes for Aqueous Redox Flow Batteries

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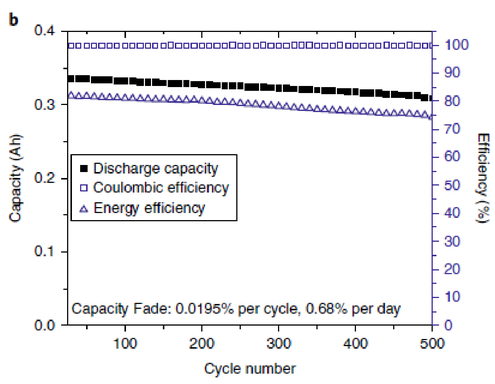
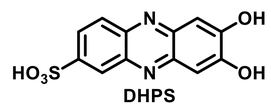
Introduction: The redox flow batteries (RFB) are promising candidate in grid energy storage due to high safety, independent tuning of energy and power and scalability.

➢All Vanadium RFB
- ✧High energy capacity
- ✧Long term stability
- ✧High cost

➢Organic RFB
- ✧Easy functionalization
- ✧Low cost

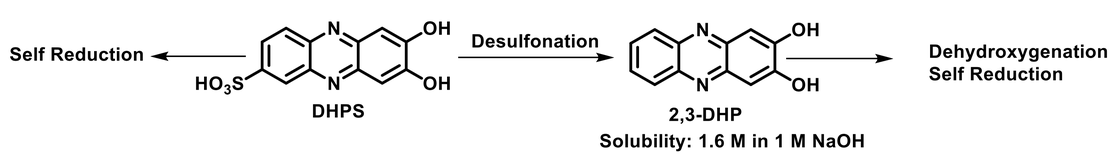
➢7,8-Dihydroxyphenazine-2-sulfonic acid (DHPS)





- ✧High solubility (1.4 M in 1 M NaOH and 1.8 M in 1M KOH)
- ✧High reversible anolyte capacity 65 Ahl^{-1}
- ✧Energy efficiency >75%
- ✧Capacity retention 90% after 500 cycles

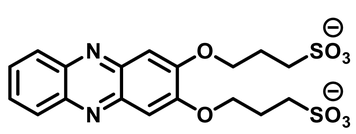
➢Decomposition of DHPS



Objective: Discover how various substitution groups in phenazine derivatives affect solubility and stability

Results and Discussion:

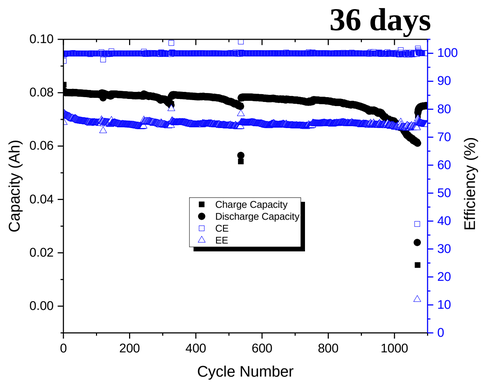
➢ Phenazine Derivative I



2,3-Dihydroxyphenazine-bis(propylsulfonate) (**DHP-bis-propyl-SO_3^{2-}**)

➢ Redox Flow Battery Performance

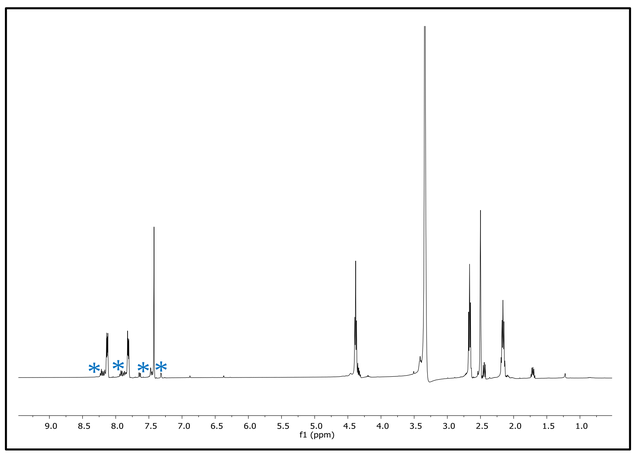
✧DHP-bis-propyl-SO_3^{2-} (0.30 M)



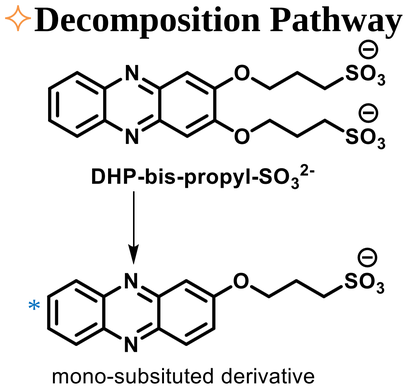
- ✧Significant capacity loss is due to precipitation of decomposed anolyte
- ✧DHP-bis-propyl-SO_3^{2-} decomposes to its mono-substituted derivative

Condition: Anolyte; DHP-bis-propyl-SO_3^{2-} in 0.8 M KH_2PO_4/0.2 M K_2HPO_4
Catholyte; excess $K_4Fe(CN)_6/K_3Fe(CN)_6$ in same buffer solution.

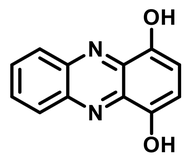
➢ NMR Study on Capacity Loss (^{1}H NMR in DMSO-d_6)



✧Decomposition Pathway



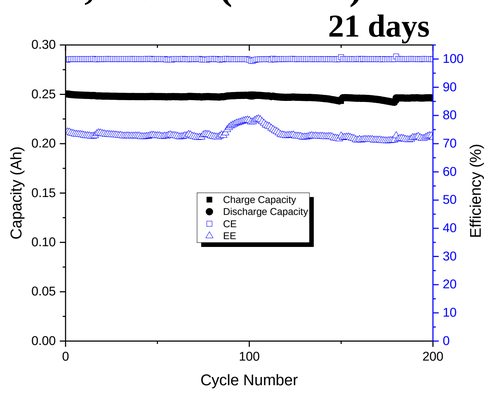
➢ Phenazine Derivative II



1,4-Dihydroxyphenazine **(1,4-DHP)**

➢ Redox Flow Battery Performance

✧1,4-DHP (0.42 M)



- ✧Solubility of deprotonated 1,4-DHP is 0.36 M in 1 M NaOH and 0.53 M in 2 M KOH
- ✧1.6% capacity decay after 200 cycles (0.008% per cycle, 0.076% per day)

Condition; Anolyte; 1,4-DHP in 2 M KOH
Catholyte; excess $K_4Fe(CN)_6/K_3Fe(CN)_6$ in 2 M KOH.

Summary:

- ✧Capping of phenoxy groups of 2,3-DHP with propyl sulfonate groups does not protect from self reduction
- ✧1,4-DHP has low solubility but higher cycling stability compare to DHPS

Future Work:

- ✧Develop new phenazine derivatives to further study effect of substitution pattern on solubility and stability
- ✧Study the decomposition pathways of the new phenazine derivatives
- ✧ Modify the stable phenazine derivatives to improve their solubility

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References:
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