Supplementary Information

Fine-Tuning the Indirect Electrochemical Reaction in Redox-Mediated Flow Batteries

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Section 1: Experimental and Simulated UV-VIS spectra of VBH^{2-} oxidation

The UV-VIS spectra of the change in the oxidation state of the VBH^{2-} spectra was taken by measuring the change in epsilon value of each wavelength of the VBH^{2-} upon addition of the equivalent amount of the CoHCF and gradual addition of K^+ ion as KPF_6 salt from 0, 0.25, 0.5, 0.75 and 1 equivalent (see Fig. S1). For VBH^{2-} , ε(825 nm)=25.0mol^{-1} cm^{-1}, and that for VBH^{-1} , ε(485nm)=245mol^{-1} cm^{-1} was used.[1]

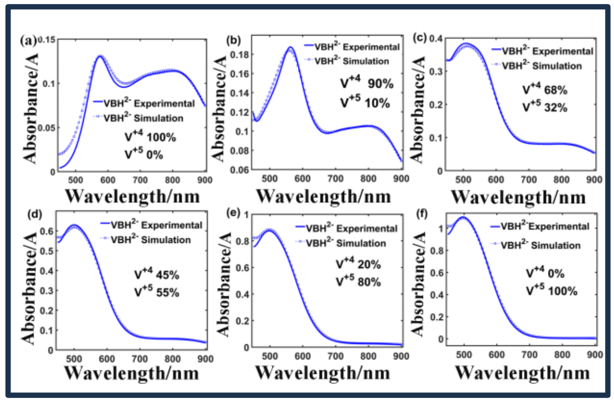

Figure S1. $VBH^{2-}/^{1-}$ Oxidation. **(a)**. UV-vis spectra of VBH^{2-} **(b)**. After addition of full equivalent of CoHCF with no KPF_6. **(c).** 0.25 KPF_6 **(d).** 0.5 KPF_6 **(e).** 0.75 KPF_6 **(f).** 1 KPF_6

Similarly, the UV-VIS spectra of the change in the oxidation state of the VBH^{2-} was taken by measuring the change in epsilon value of each wavelength of the VBH^{2-} upon addition of the same equivalent of the CoHCF and the cations (TBA^+, TMA^+, & K^+) corresponding to its PF_6 salts (see Fig. S2)

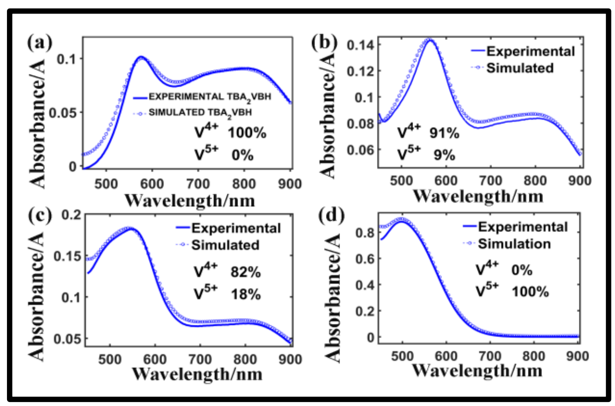

Figure S2. $VBH^{2-}/^{1-}$ Oxidation. **(a).** UV-vis spectra of VBH^{2-} **(b)**. After addition of full equivalent of CoHCF and $TBAPF_6$. **(c).** Adding Full equivalents of CoHCF and $TMAPF_6$ **(d).** After addition of full equivalents of CoHCF and KPF_6

Section 2: CV Analysis of CoHCF following addition of 0.2M $TBAPF_6$+ 0.2M KPF_6 Addition in MeCN

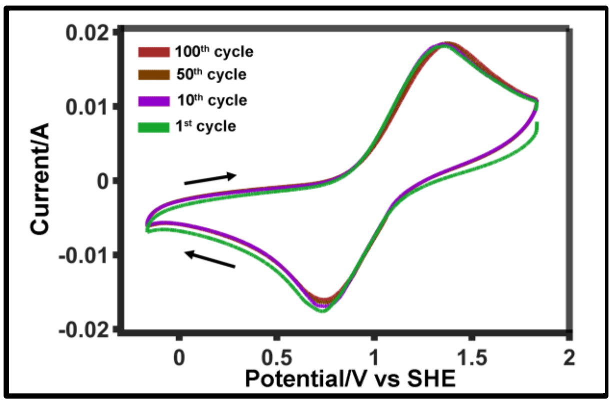

Figure S3. a) CV of CoHCF done for 100 cycles coated on carbon rod in 6:1:3 ratio of CoHCF, MWCNT, & PVDF in NMP. 0.2M $TBAPF_6$ and 0.2M KPF_6 were used as electrolyte solution in MeCN. Scan rate was 0.05 V/s.

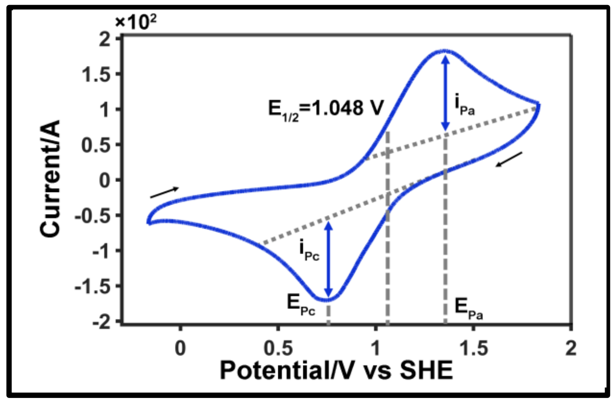

Figure S3. b) CV of CoHCF coated on carbon rod in 6:1:3 ratio of CoHCF, MWCNT, & PVDF in NMP. 0.2M $TBAPF_6$ and 0.2M KPF_6 were used as electrolyte solution in MeCN. Scan rate was 0.05 V/s. dEp value calculated as 0.60 V and the anodic to cathodic peak current ratio as 0.97.

REFERENCE

(1) Pahari, S. K.; Gokoglan, T. C.; Chaurasia, S.; Bolibok, J. N.; Golen, J. A.; Agar, E.; Cappillino, P. J. Toward High-Performance Nonaqueous Redox Flow Batteries through Electrolyte Design. *ACS Appl. Energy Mater.* **2023**, *6* (14), 7521–7534. https://doi.org/10.1021/acsaem.3c00910.