

Supporting Information for:

**Dalton Transactions Tutorial Review: Assessment Methods for Screening
Electrolytes in Non-aqueous Redox Flow Batteries**

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Identification of redox couples for symmetric RFBs. The first step in identifying electrolytes for symmetric RFBs involve selecting an appropriate potential window based on the stability of both the solvent and the redox-active species. The potential is then scanned at various scan rates, typically ranging from 10 to 500 mV s^{-1} , to observe the electrochemical behavior of the redox-active species. As the potential is swept forward and reversed, the resulting current response is recorded and a voltammogram is generated that reveals the oxidation and reduction peaks. The half-wave potential ($E_{1/2}$) for a redox couple is determined as the average of the anodic ($E_{p,a}$) and cathodic ($E_{p,c}$) peak potentials. To assess the reversibility of the redox process, the peak-to-peak separation (ΔE_p) is examined, with a value close to $59/n$ mV (n = number of electrons) for a one-electron transfer indicating an electrochemically reversible reaction. Additionally, the peak currents for oxidation and reduction should be nearly equal, suggesting efficient electron transfer ($i_{p,c}/i_{p,a} \sim 1$). If the system exhibits stable peak positions at variable scan rates, minimal peak separation across multiple cycles, and a separation of at least 1 V between the anodic and cathodic $E_{1/2}$ values, it confirms the suitability of the redox couples for use in a symmetric non-aqueous redox flow battery.

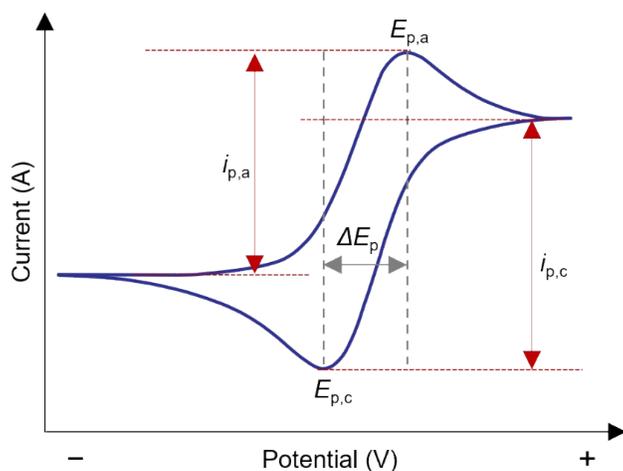


Figure S1. Schematic illustration of key electrochemical parameters used to determine reversibility of redox couples of a charge carrier – $\Delta E_p \sim 59$ mV, $i_{p,c}/i_{p,a} \sim 1$ across multiple scan rates.

Capacity units. The capacity of a redox flow battery is typically expressed in either ampere-hours (Ah) or watt-hours (Wh). The unit Ah indicates the amount of electrical charge (Amperes) that a battery can store over a period of time (hours). The unit Wh is the measure of the amount of work (Watts = Volts \times Amperes) that a battery can do over a period of time (hours).

Solubility measurements using electronic absorption spectroscopy. The first step is to create a calibration curve of concentration versus absorbance for at least 5 solutions of known concentrations of the charge carrier. Additionally, the concentration of the supporting salt should be kept the same as those used in the actual H-cell or RFB setup to simulate the electrochemical conditions of the cell and samples should be referenced against a baseline of this concentration of supporting electrolyte in the desired solvent. The wavelength for the absorbance should be selected based on the peak with the maximum absorbance of the charge carrier. To abide by the Beer's law, all absorbances must be between 0.1 and 1.0 for all samples (Figure S2, top). A linear fit between absorbance and concentration gives the slope as the molar absorptivity of the complex (Figure S2, bottom).

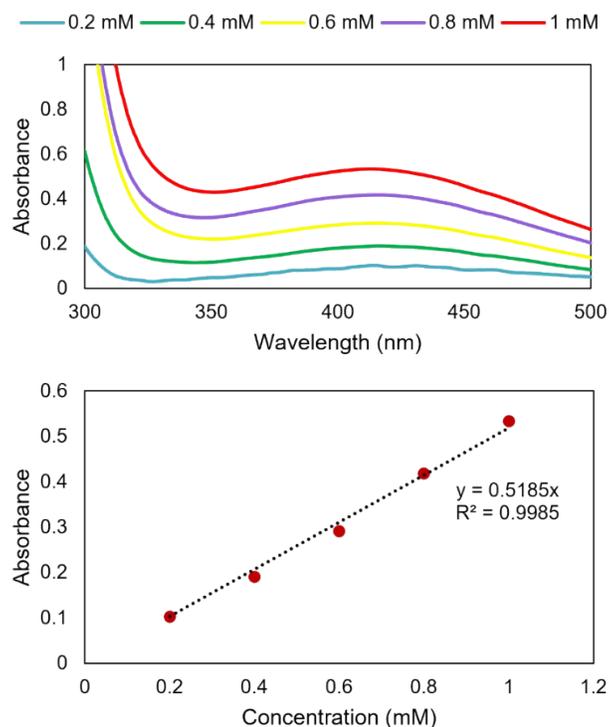


Figure S2. Representative calibration curve for solubility measurements. The linear fit (bottom plot) of absorbance versus concentration yields the molar absorptivity value through the slope.

Post molar absorptivity measurements, create a saturated solution of the charge carrier by adding an excess of the solute until no more complex can be dissolved in the given amount of solvent and supporting salt mixture. Let this solution stir overnight and filter excess material to get a stock solution. Dilute this solution until an absorbance value between 0.1 and 1.0 can be recorded. Use the absorbance at the wavelength selected while making the calibration curve to calculate the concentration using the Beer's Law calibration plot (Table S1). Repeat this procedure three times to get a precise solubility value.

Table S1. Measured solubility of a polyoxovanadate charge carrier using electronic absorption spectroscopy shown in Figure S2. Peak absorbance values at 415 nm were used to generate a calibration curve, with molar absorptivity, $\epsilon = 877 \text{ M}^{-1} \text{ cm}^{-1}$.

Trials	Absorbance at 415 nm	Diluted concentration (mM)	Saturated concentration (mM)
1	0.8385	6.46	646.86
2	0.8347	6.43	643.92
3	0.8791	6.78	678.18

Polarization curve for an electrolyte system. To create a polarization curve for an electrolyte system, start by assembling an electrochemical cell with three electrodes: a working electrode (the material of interest), a reference electrode (commonly Ag/AgNO₃ for non-aqueous systems), and a counter electrode (usually platinum). Using the potentiostat's software, configure a linear sweep voltammetry (LSV) or potentiodynamic polarization scan by setting the initial and final potentials (e.g., from -0.5 V to +1.0 V), a suitable scan rate (typically 1-10 mV/s), and step size (usually in mV). Our recommendation is to use LSV rather than potentiodynamic polarization as the latter is more suited to assess the corrosion resistance of materials. If the system is sensitive to oxygen, purge the electrolyte with an inert gas like nitrogen or argon for 15-30 minutes before starting the scan. After ensuring an inert atmosphere during the test, start the scan and the potentiostat will measure the current response (I) as the potential (V) is swept. The output I-V curve will typically show three regions: 1) Activation 2) Ohmic 3) Mass transport limitation. Calculate current density by dividing the measured current by the surface area of the working electrode. Plot the current density versus potential to generate the polarization curve.

For deeper insight, especially in kinetic regions, a Tafel plot (logarithmic current density vs. potential) can be constructed. The resulting plots can yield information about important parameters such as onset potential (where current starts to rise), Tafel slopes (kinetics), exchange current density (rate of electron transfer at equilibrium), and overpotential. To conclusively differentiate between the individual processes occurring at the electrode-electrolyte interface, consider complementing the obtained results with electrochemical impedance spectroscopy (EIS). While polarization curves reveal the overall current response to potential changes, EIS offers a frequency-dependent analysis that helps disentangle the contributions of various electrochemical reactions and transport phenomena.

Evaluation of diffusion coefficients using PFG NMR spectroscopy. To estimate diffusion coefficients using Diffusion-Ordered Spectroscopy (DOSY), first prepare a well-solubilized sample in the deuterated version of the solvent in which the battery experiments are desired to be performed. For example, use CD₃CN as the solvent if the RFB experiments are run in acetonitrile. Subsequently, acquire a standard ¹H NMR spectrum to confirm the sample's purity and concentration. Once a clean spectrum is obtained, perform a DOSY experiment by applying a pulsed-field gradient NMR sequence while systematically varying the gradient strength (Figure S3). Ensure that the gradient strengths are properly calibrated and that the signal attenuation covers a broad range for accurate diffusion coefficient estimation. After data acquisition, use the Stejskal-Tanner equation (Eq. S1) to extract the corresponding D_0 values.

$$I = I_0 \exp[-\gamma^2 g^2 \delta^2 (\Delta - (\delta/3)) D_0] \quad (\text{Eq. S1})$$

The Stejskal-Tanner equation describes the attenuation of NMR signal intensity due to molecular diffusion in the presence of pulsed field gradients. In Eq. S1, I is the observed signal intensity at a given gradient strength, I_0 is the signal intensity at zero gradient, γ is the gyromagnetic ratio of the nucleus being observed, g is the applied gradient strength, δ is the duration of the gradient pulse, and Δ is the time between gradient pulses. To extract the diffusion coefficient, the signal decay is plotted as $\ln(I/I_0)$ versus g^2 and the slope of the linear fit yields D_0 values. Several software, such as TopSpin, JEOL Delta, and Mestrelab, are available to easily calculate D_0 values accurately using the curve fitting tools based on the Stejskal-Tanner equation. A representative example of the curve fitting tool using Version 6.4 of the Delta NMR software on the polyoxovanadate-alkoxide cluster, [V₆O₇(OMe)₁₂], reported as a competitive charge carrier by our team is illustrated in Figure S4. Note that the D_0 value calculated via the DOSY experiment (8.53

$\times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) closely resemble to those reported by our team using Randles–Ševčík analysis ($7.82 \pm 0.33 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$).

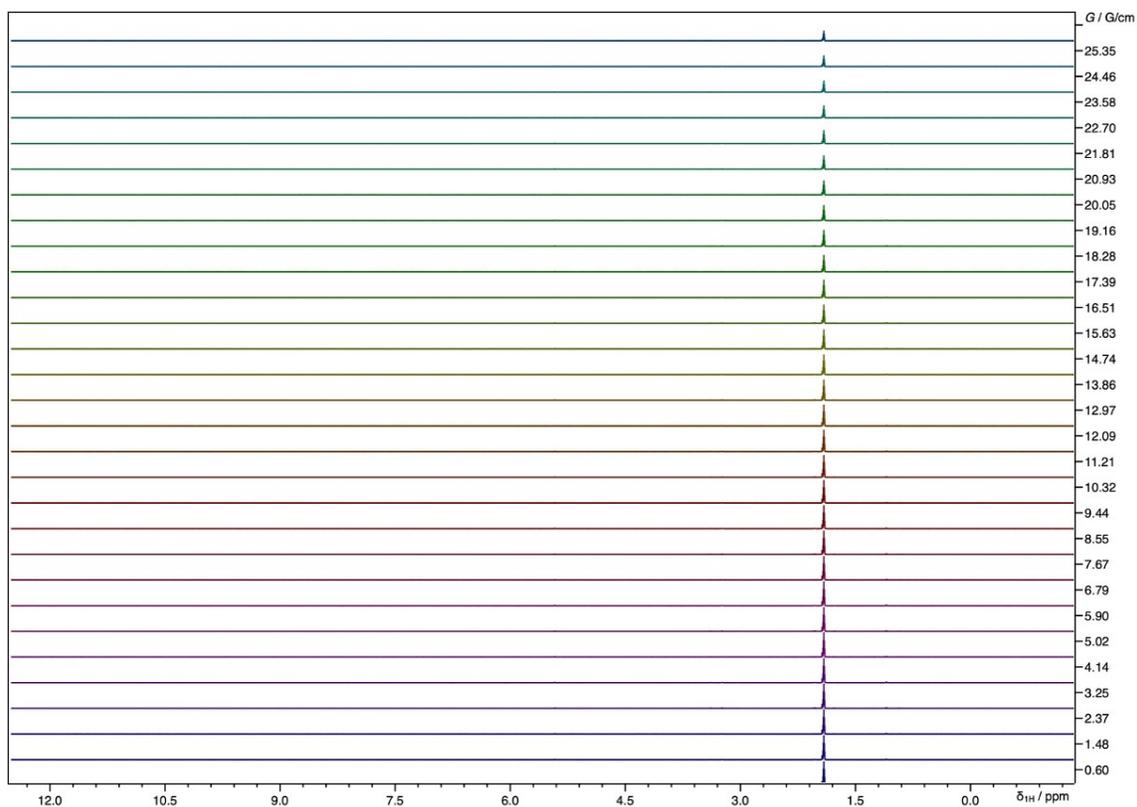


Figure S3. Decay curves obtained from a pulsed gradient echo experiment using the one-electron oxidized $[\text{V}_6\text{O}_7(\text{OMe})_{12}]$ cluster (in CD_3CN) demonstrated as a charge carrier by our research team. The x-axis denotes the chemical shift in ppm, whereas the y-axis represents the stacked spectra at different pulse-field gradient values ranging from 0.6 to 25.35 cm. Note that while only CD_3CN signal is evident in the stacked spectra due to low concentration of the charge carrier, individual peaks corresponding to the cluster are clearly visible at individual gradient strength.

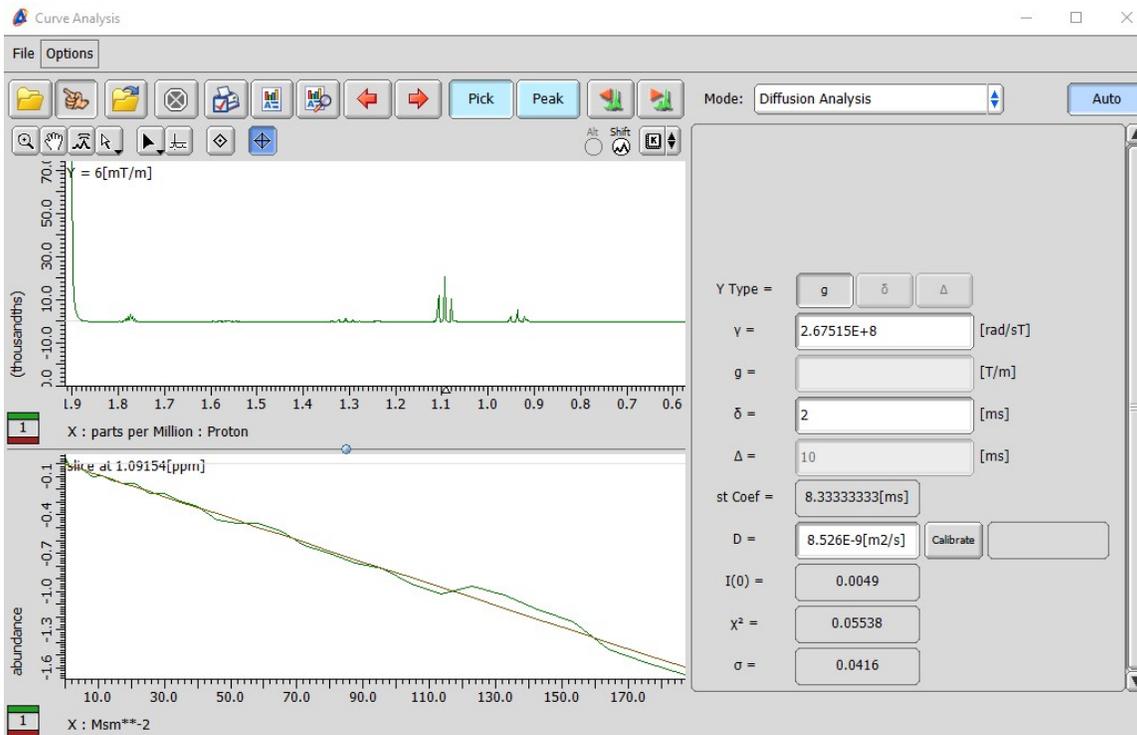


Figure S4. Diffusion coefficient estimation using the PFG NMR experimental performed on $[\text{V}_6\text{O}_7(\text{OME})_{12}]$ cluster in CD_3CN . The green line in the bottom curve is the recorded data, whereas the brown line represents the linear fit based on the model used by the software to calculate the diffusion coefficient value (reported as D on the right panel).

Evaluation of diffusion coefficients of quasi-reversible redox couples using cyclic voltammetry. In Randles–Ševčík analysis, the diffusion coefficients for the cathodic and anodic redox waves are estimated using the slopes of linear fits to the plots of peak current i_p ($i_{p,c}$ and $i_{p,a}$ for the cathodic and anodic waves, respectively) vs the square root of scan rate ($v^{1/2}$). For an electrochemically reversible redox couple at room temperature, the peak current is given by Eq. S2.

$$i_p = 2.69 \times 10^5 \times n^{3/2} \times A \times C \times D_0^{1/2} \times v^{1/2} \quad (\text{Eq. S2})$$

In Eq. S2, n is the number of electrons transferred in the reaction, A is the geometric electrode surface area, C is the bulk concentration of the redox-active species, D_0 is the diffusion coefficient of the redox-active species, and v is the scan rate. For an electrochemically irreversible redox couple, the peak current is given by Eq. S3.

$$i_p = 2.99 \times 10^5 \times n^{3/2} \times A \times \alpha \times C \times D_0^{1/2} \times v^{1/2} \quad (\text{Eq. S3})$$

In Eq. S3, α is the charge-transfer coefficient. α is generally assumed to be 0.5 when the investigated redox couples exhibit electrochemical symmetry i.e., well-defined peaks with ratio of anodic to cathodic peak currents ($i_{p,a}/i_{p,c}$) equal to unity. For redox couples that show quasi-reversible kinetics, relationships for both reversible and irreversible redox reaction are often employed to determine the diffusion coefficients. Therefore, an average value of diffusion coefficients from Eqs. S2 and S3 is approximated for the quasi-reversible redox couples and further employed for the estimation of the electron-transfer rate constants.

***iR*-free extrapolation.** Most voltammetric experiments apply a potential to the electrochemical cell and record the corresponding current, which is affected by the solution resistance and the cell geometry effects which are not accounted for by a potentiostat's internal circuitry. This resistance, known as uncompensated resistance, can be accounted for by applying a correction factor as mentioned in Eq. S4.

$$E_{true} = E_{app} - UI \quad (\text{Eq. S4})$$

In Eq. S4, E_{app} is the potential after the software's internal correction, U is the percent uncompensated resistance left after the instrumental *iR* correction, and I is the current response. For example, the polyoxovanadate-alkoxide cluster, $[V_6O_7(OMe)_{12}]$, has been demonstrated by our team to be a promising candidate for applications in non-aqueous RFBs. It exhibits reversible redox chemistries and is stable across multiple charge-discharge cycles. However, if the uncompensated resistance is not accurately accounted for, it results in erroneous values of peak separation as demonstrated in Table S2.

Table S2. Calculated values for peak separation for one electron oxidation of $[V_6O_7(OMe)_{12}]$ at different instrument *iR* compensation values and the corresponding peak separation values with and without accounting for the uncompensated resistance value derived from using Eq. S4.

Instrument compensation	$E_{p,a}$	$E_{p,c}$	ΔE_p (without external correction)	ΔE_p (with external correction)
85%	0.3862 V	0.2991 V	87.1 mV	80.4 mV
95%	0.3563 V	0.2948 V	61.5 mV	61.4 mV

Nicholson's method for electrokinetic analysis. The electron transfer kinetics can be directly estimated from the variable scan rate cyclic voltammetry data by using the Nicholson method for quasi-reversible redox reactions. First, the "true" potential difference (ΔE_{true}) of oxidation and reduction peaks after iR correction is obtained at different scan rates by using Eq. S4 (see above). The transfer parameter (ψ) is subsequently extracted from the working curve constructed by Nicholson using the obtained ΔE_{true} values as shown in Figure S5.

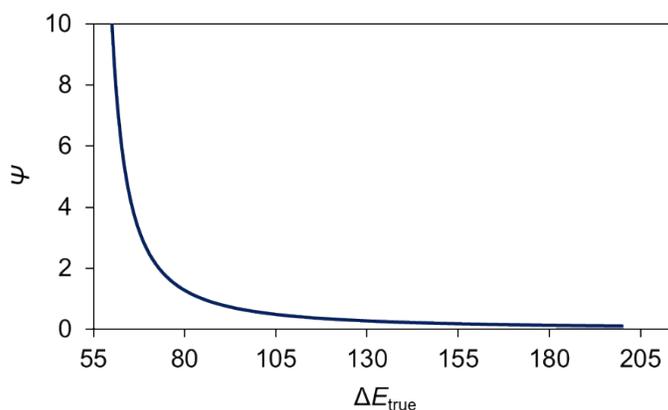


Figure S5. Working curve obtained from Nicholson's empirical relationship.

The standard heterogeneous charge-transfer rate constant, k_0 , for a given electron transfer process can be then determined using Eq. S5.

$$k_0 = \Psi(\pi n F D_o \nu / RT)^{1/2} \quad (\text{Eq. S5})$$

In Eq. S5, n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, ν is the scan rate, R is the ideal gas constant and T is the temperature. For example, for the one electron oxidation of $[\text{V}_6\text{O}_7(\text{OMe})_{12}]$, the ΔE_{true} increases with $\nu^{1/2}$ ranging between 500 mV s^{-1} to 10000 mV s^{-1} (Figure S6). Plotting the corresponding values of ψ versus $\nu^{1/2}$ then yields a slope proportional to the rate of electron transfer to the electrode surface (Figure S7).

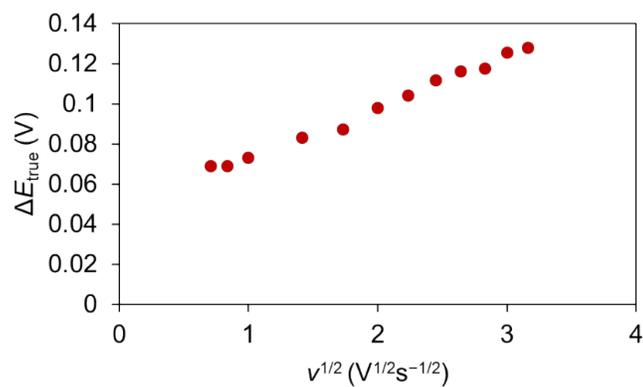


Figure S6. Plot of ΔE_{true} vs $(\text{scan rate})^{1/2}$ for $[\text{V}_6\text{O}_7(\text{OMe})_{12}]$.

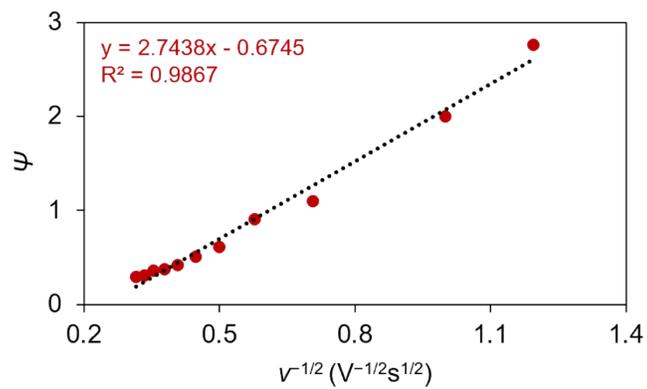


Figure S7. Plot of ψ vs $(\text{scan rate})^{1/2}$ for $[\text{V}_6\text{O}_7(\text{OMe})_{12}]$.