Electronic Supplementary Information for

Nonaqueous Redox-Flow Batteries: Organic Solvents, Supporting Electrolytes, and Redox Pairs

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1. Materials and methods

1.1. Cyclic voltammetry (CV)

Cyclic voltammetry (CV) was conducted in a 25 mL three-neck flask equipped with three electrodes under inert atmosphere. Before CV measurement, the nonaqueous electrolyte was prepared by the following procedure. Firstly, 0.01 mol redox compound (biphenyl, BP; or octafluoronaphthalene, OFN), 0.01 mol supporting electrolyte (tetrabutyl ammonium, Bu_4NClO_4), and 2.5 g alumina power (desiccant) were added into the flask, then the flask was repeatedly charged with nitrogen and degassed for three times; and at last, a 10 mL anhydrous organic solvent (N,N-dimethylformamide, DMF, for BP; or propylene carbonate, PC, for OFN) was injected into the flask to dissolve the redox compound and supporting electrolyte. A micro-platinum disk electrode (0.2 mm in diameter) was used as working electrode, and a platinum wire (0.5 mm in diameter) and a silver wire (1 mm in diameter) were used as counter electrode and reference electrode, respectively. CV test was carried out by a Solartron Analytical 1287 Electrochemical Interface coupled with a Solartron 1260A Impedance/Gain-Phase Analyzer. The cell resistance was measured by AC impedance method and all CV curves were IR-corrected.

1.2. Measurement of diffusion coefficient (*D*)

The diffusion coefficient of BP in DMF was obtained by using the Randles-Sevcik equation for reversible systems.[1] Specially, the relationship between the cathodic peak current density, $i_{p,c}$, and the diffusion coefficient of BP, D_O, is as follows:

$$i_{p,c} = (2.69 \times 10^5)n^{3/2} \cdot D_O^{1/2} \cdot C_O^* \cdot v^{1/2}$$

Eq. S1

where, $i_{p,c}$ is the cathodic peak current density in A cm^{-2}, D_O is the diffusion coefficient of oxidative specie (BP) in cm^2 s^{-1}, C_O^* is the bulk concentration of oxidative specie (BP) in mol cm^{-3}, v is scan rate in V s^{-1}.

Similarly, the diffusion coefficient of ONF in PC was obtained. Specially, the relationship between the anodic peak current density, $i_{p,a}$, and the diffusion coefficient of OFN, D_R, is as follows:

$$i_{\mathrm{p,a}} = (2.69 \times 10^5) n^{3/2} \cdot D_R^{1/2} \cdot C_R^* \cdot v^{1/2}$$

Eq. S2

where, $i_{\mathrm{p,a}}$ is the anodic peak current density in A cm^{-2}, D_R is the diffusion coefficient of reductive specie (OFN) in cm^2 s^{-1}, C_R^* is the bulk concentration of reductive specie (OFN) in mol cm^{-3}, v is scan rate in V s^{-1}.

1.3. Estimate of standard rate constant (k_0)

The standard rate constant, k_0, was obtained by using the Nicolson method.[2] For a cathodic CV process (like the CV of BP), the relationship between the standard rate constant and the Nicolson dimensionless number (Ψ) is given by the **Eq. S3**:

$$k_0 = [\frac{(\pi \cdot D_O \cdot f \cdot v)^{1/2}}{(D_O / D_R)^{\alpha/2}}] \cdot \psi$$

Eq. S3

where, k_0 is the standard rate constant in cm s^{-1}; π is the mathematical constant; Ψ is the Nicolson dimensionless number, which is a function of the peak potential separation (ΔE_p) from CV curve. Note that the value of Ψ is obtained from the **Figure 3** in the Nicolson's classic paper;[2] D_O is the diffusion coefficient of oxidative specie (e.g., BP) and D_R is the diffusion coefficient of reductive specie (e.g., BP•$^-$), both in cm^2 s^{-1}; and v is scan rate in V s^{-1}; α is the charge transfer coefficient, dimensionless; and $f = (n \cdot F)/(R \cdot T)$, in which n is the number of electrons transferred in redox reaction, F is the Faraday constant (96485 C mol^{-1}), R is the ideal gas constant (8.314 J mol K^{-1}), T is the absolute temperature in K.

Note that the measurement of the diffusion coefficient of BP•$^-$ is rather complicated, and it is beyond the scope of this work. Well, it can be assumed that the diffusion coefficient of BP•$^-$ is reasonably close to that of BP, since they have the same molecular weight. Then the **Eq. S3** can be further simplified as follows:

$$k_0 = (\pi \cdot D_O \cdot f \cdot v)^{1/2} \cdot \psi$$

Eq. S4

where, k_0 is the standard rate constant in cm s^{-1}; π is the mathematical constant; D_O is the diffusion coefficient of BP; v is scan rate in V s^{-1}; $f = (n \cdot F)/(R \cdot T)$; and Ψ is the Nicolson dimensionless number.

The k_0 results of the BP/BP•$^-$ redox pair are listed in the **Table S1**.

For an anodic CV process (like the CV of OFN), the relationship between the standard rate constant and the Nicolson dimensionless number (Ψ) is given by the **Eq. S5**:

$$k_0 = [\frac{(\pi \cdot D_R \cdot f \cdot v)^{1/2}}{(D_R / D_O)^{\alpha/2}}] \cdot \psi$$

Eq. S5

where, k_0 is the standard rate constant in cm s^{-1}; π is the mathematical constant; Ψ is the Nicolson dimensionless number; D_R is the diffusion coefficient of reductive specie (e.g., OFN) and D_O is the diffusion coefficient of oxidative specie (e.g., OFN•$^+$), both in cm^2 s^{-1}; and v is scan rate in V s^{-1}; α is the charge transfer coefficient, dimensionless; and $f = (n \cdot F)/(R \cdot T)$, in which n is the number of electrons transferred in redox reaction, F is the Faraday constant (96485 C mol^{-1}), R is the ideal gas constant (8.314 J mol K^{-1}), T is the absolute temperature in K.

Similarly, by assuming the diffusion coefficient of OFN$^{\bullet+}$ is reasonably close to that of OFN, the **Eq. S5** can be simplified as follows:

$$k_0 = (\pi \cdot D_R \cdot f \cdot v)^{1/2} \cdot \psi \qquad\qquad \textbf{Eq. S6}$$

where, k_0 is the standard rate constant in cm s^{-1}; π is the mathematical constant; D_R is the diffusion coefficient of OFN; v is scan rate in V s^{-1}; $f = (n \cdot F)/(R \cdot T)$; and Ψ is the Nicolson dimensionless number.

The k_0 results of the OFN$^{\bullet+}$/OFN redox pair are listed in the **Table S2**.

2. Tables

Table S1. Calculation of k_0 for the BP/BP$^{\bullet-}$ redox pair

v[a] (mV s^{-1})	ΔE_p[b] (mV)	Ψ[c] (dimensionless)	k_0[d] ($\times 10^{-3}$ cm s^{-1})	Average k_0 (cm s^{-1})	Standard deviation (cm s^{-1})
25	90	0.809	4.71		
36	94	0.711	4.97		
49	96	0.665	5.43	4.8×10^{-3}	0.4×10^{-3}
64	108	0.473	4.41		
81	114	0.421	4.41		
100	115	0.405	4.72		

[a] v: scan rate.
[b] ΔE_p: peak potential separation in CV curve.
[c] Ψ: Nicholson dimensionless number. The value was obtained from the **Figure 3** in the Nicolson's classic paper.[2]
[d] k_0: standard rate constant of the BP/BP$^{\bullet-}$ redox pair.

Table S2. Calculation of k_0 for the OFN$^{\bullet+}$/OFN redox pair

v (mV s^{-1})	ΔE_p (mV)	Ψ (dimensionless)	k_0 ($\times 10^{-3}$ cm s^{-1})	Average k_0 (cm s^{-1})	Standard deviation (cm s^{-1})
400	98	0.632	0.97		
900	98	0.628	1.44		
1600	99	0.622	1.90	1.7×10^{-3}	0.4×10^{-3}
2,500	104	0.521	1.99		
3,000	108	0.476	1.99		
3,600	111	0.446	2.05		

[a] v: scan rate.
[b] ΔE_p: peak potential separation in CV curve.
[c] Ψ: Nicholson dimensionless number. The value was obtained from the **Figure 3** in the Nicolson's classic paper.[2]
[d] k_0: standard rate constant of the OFN$^{\bullet+}$/OFN redox pair.

3. Figures

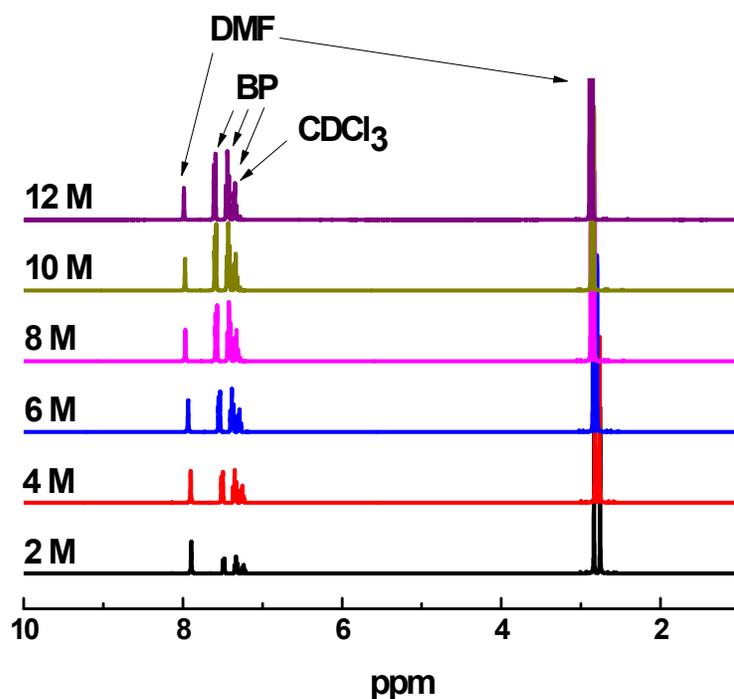**Figure S1**. ^{1}H NMR spectra of BP solution in DMF with different apparent concentrations of added BP (CDCl$_3$ as NMR solvent). The detected BP concentration can be calculated by comparing the BP peak areas and DMF peak areas.
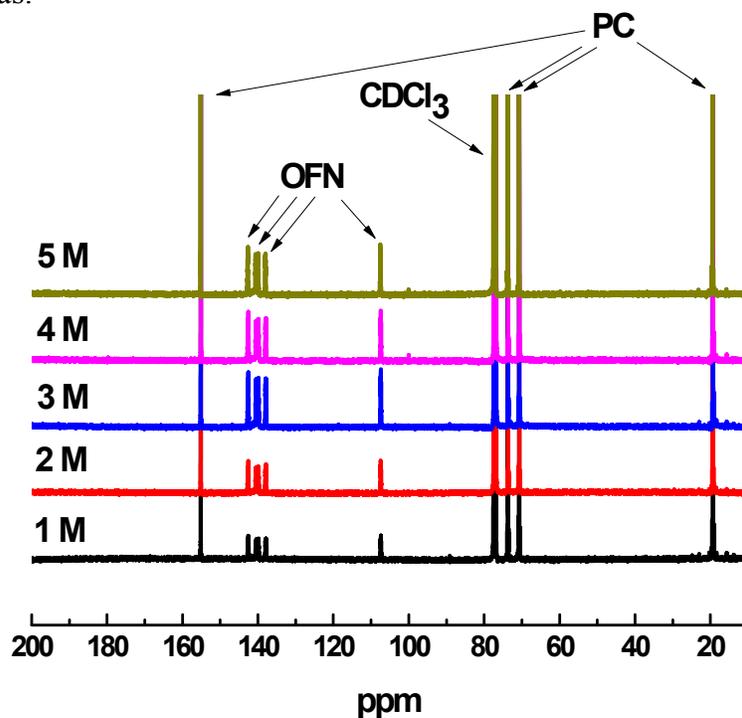

Figure S2. ^{13}C NMR spectra of OFN solution in PC with different apparent concentrations of added OFN (CDCl$_3$ as NMR solvent). The detected OFN concentration can be calculated by comparing the OFN peak areas and PC peak areas. Note: ^{1}H NMR spectroscopy is not appropriate for OFN, because the absence of protons in OFN molecule.

4. References

1. L. R. F. Allen J. Bard, *Electrochemical Methods: Fundamentals and Applications*, 2000.
2. R. S. Nicholson, *Anal. Chem.*, 1965, **37**, 1351-1355.