Supporting Information

Unlocking High-Potential Non-Persistent Radical Chemistry for Semi-Aqueous Redox Batteries

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Experimental Procedures

Materials: *N*-Hydroxyphthalimide (NHPI) was purchased from TCI Chemicals. Nafion 117 and Toray carbon paper 120 were purchased from FuelCellStore. Anthraquinone-2-sulfonic acid (AQS) sodium salt monohydrate, poly(acrylic acid) (PAA) solution with 35 wt% , poly(vinyl alcohol) (PVA), polyethylene glycol (PEG) and other reagents including acetonitrile (ACN), 2,2,6,6-tetramethylpiperidine-*N*-oxyl (TEMPO) and methyl viologen dichloride hydrate (MV) were purchased from Sigma Aldrich. All reagents were used without further purification.

Characterizations: *In-situ* UV-Vis spectroscopy for NHPI and PINO was conducted from 250 nm to 800 nm by direct injection of catholyte outlet into a quartz cuvette upon charging the battery (up to 1.4 V) on a Shimadzu UV-3600 spectrophotometer. The flammability test was done by soaking a piece of cellulose filter paper into a pure ACN solvent or a W-ACN binary solvent (x_{ACN} = 0.5). EPR was carried out on a Bruker EMX X-Band ESR Spectrometer at a temperature of 120 K, with a microwave frequency at 9.44 GHz. The PINO-containing solutions were obtained by charging the AQS-NHPI battery in a range of binary solvent electrolytes to 1.4 V, followed by freezing the solution in liquid N_2 to capture the labile radicals.

Electrochemical measurements: Electrochemical experiments were conducted on a CHI 760e potentiostat in a three-electrode setup, which comprises of a glassy carbon (GC) working electrode, a graphite counter electrode and a Hg/Hg_2SO_4 reference electrode (in a saturated K_2SO_4). W-ACN binary solvents at different volume ratios (containing 10 mM NHPI in 1.0 M H_2SO_4) were used as the electrolyte for voltammetry experiments. Typically, CV was performed at 200 mV s^{-1} across the 0.0 to +1.0 V potential window (vs. Hg/Hg_2SO_4).

Scan rate dependence was conducted at 10, 20, 50, 100, 150, 200 mV s^{-1}. Linear sweep voltammetry (LSV) under electrode rotation (using a ALS RRDE-3A rotator) at 10 mV s^{-1} with rotation speeds of 400, 900, 1600, 2500 and 3000 rpm was used to examine the charge transfer (Tafel analysis) and mass transport (Koutécky−Levich analysis) properties of redox-active materials. For K–L analysis, Eq.1 (K–L equation) was used with following system parameters: $n = 1$, $F = 96{,}485$ C mol^{-1}, $A_G = 0.1257$ cm^2, $C_0 = 0.01$ M and $v = 0.01$ cm^2 s^{-1}, where n is electron-transfer number, F is Faradaic constant (C mol^{-1}), A_G is the electrode geometrical area (cm^2), D is diffusion coefficient (cm^2 s^{-1}), C_0 is the bulk analyte concentration (M) and ω is the electrode rotation rate (rpm).

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{0.2nFAC_0D^{2/3}v^{-1/6}\omega^{1/2}} \quad (1)$$

***NHPI/AQS battery test*:** Nafion 117 membranes were pretreated prior to battery assembly by the following procedure. A Nafion 117 membrane was soaked in deionized water at 80 °C for 20 min and then in 5% hydrogen peroxide solution for 35 minutes. The membranes were then stored in the binary solvent electrolyte of $x_{ACN} = 0.5$ at ambient condition for overnight. Also, carbon paper (size: 3×3 cm) was pertreated by storing in the same binary solvent electrolyte at ambient condition for overnight. 5mL 0.05 M AQS in W-ACN electrolyte ($x_{ACN} = 0.5$) and 5 mL 0.1 M NHPI in the same electrolyte were taken as anolyte and catholyte, respectively. N_2 was purged into the solution for 20 min for deaeration. The deaerated solutions were pumped into the battery to circulate the electrolyte and ensure electrode wetting before OCV or GCD tests (LAND). Open-circuit voltage (OCV) measurements were carried out to assess the stability of PINO in a given electrolyte by examining the voltage drop profile on resting after charged up to 1.6 V. The GCD tests was performed in a voltage range of 0.2 V to 1.6 V at 3−5 mA cm^{-2} at room or ice temperature. Polymer additives (PAA, PVA and PEG) were applied to the electrolyte solution to further stabilize PINO radicals and the PAA was further studied at 2, 4 and 8 wt% in the electrolyte solution.

Supplementary Figures and Tables

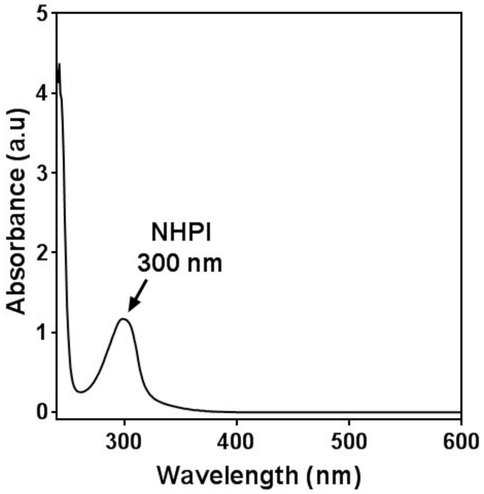

Figure S1. UV-Vis spectrum of 0.5 mM NHPI in 1.0 M H_2SO_4 W-ACN electrolyte at x_{ACN} = 0.5.

Table S1. List of full names of the abbreviations used in Figure 1a.

Abbreviation	**Full Name**
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy
4−HO-TEMPO	4-Hydroxy-2,2,6,6-tetramethylpiperidine 1-oxyl
FcNCl	(ferrocenylmethyl)trimethylammonium chloride
BQDS	1,2-benzoquinone- 3,5-disulfonic acid
HQ	Hydroquinone
$K_3Fe(CN)_6$	Potassium hexacyanoferrate(III)

AQS	anthraquinone-2-sulfonic acid
MV	Methyl viologen
EV	Ethyl viologen
DHAQ	2,6-dihydroxyanthraquinone
ACA	alloxazine 7/8-carboxylic acid
Na_2S_4	Sodium polysulfide

Note: Prices of all chemicals in Figure 1a (manuscript) were based on Sigma Aldrich as by Sep. 2018. The energy densities (Wh/g) were calculated by multiplying the theorectical specific capacity by the cell voltage (E_{cell}). The E_{cell}'s of catholytes were determined by taking AQS as the reference anolyte and the E_{cell}'s of anolytes were determined by using NHPI as the reference catholyte.

Table S2. Comparison of aqueous metal-free battery systems.

Systems	Redox Couples	E_{cell}^0 (V)	*Price per Wh*
1	4-OH TEMPO/MV	1.25[a]	416.10
2	**NHPI/AQS**	**1.15**	**3.14**
3	**NHPI/MV**	**1.65**	**273.09**

[a] The value is obtained from T. Liu, X. Wei, Z. Nie, V. Sprenkle, W. Wang, *Adv. Energy Mater.* **2016**, *6*, 1501449.

The price per Wh of each system is calculated by Eq. 2, assuming one-electrode transfer, where the prices are in US dollars per gram from Sigma-Aldrich, M_{wt} is molecular weight, F is Faradaic constant and E_{cell}^0 is cell voltage.

$$US\$\ (Wh)^{-1} = \frac{\sum (Price \times M_{wt}) \times 3600}{F \times E_{cell}{}^{0}} \tag{2}$$

Clearly, the battery system of 4-OH TEMPO/MV is 132.5 times more expensive than that of NHPI/AQS.

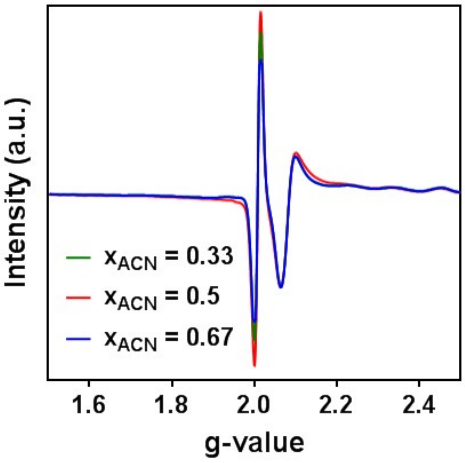

Figure S2. EPR meausrements of oxidation of 10 mM NHPI in 1.0 M H_2SO_4 W-ACN electrolyte at x_{ACN} = 0.33, 0.5 and 0.67.

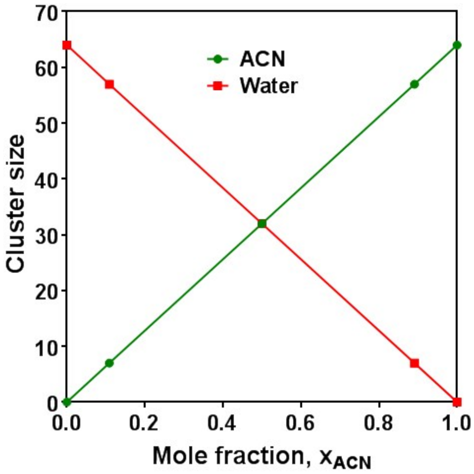

Figure S3. Cluster size of water and ACN in different mole fractions of ACN.[1]

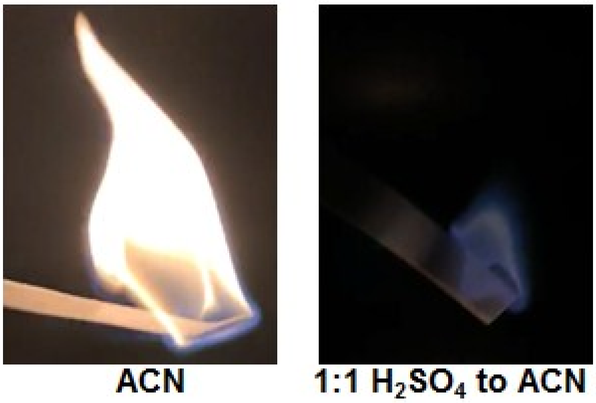

Figure S4. Flammablity test of pure ACN solution and binary solvent at x_{ACN}=0.5.

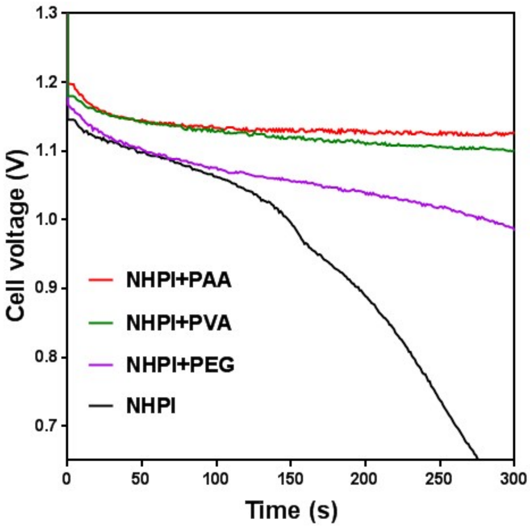

Figure S5. Effects of difference polymer additives on the stabilization of PINO.

PAA shows the best stabilizing ability among the additives. Since NHPI-PINO reaction is an oxidation reaction at high potential, a stable additive that can stay inert to PINO while can act as a soft anchor for the ACN clusters is necessary. It is noted that carboxylic acid functional group in PAA is at the highest oxidation state for a carbonaceous functional group before decomposing into CO_2. Thus, due to the good chemical stability, PAA can work as a stabilizing additive to PINO radicals, even at a low temperature.

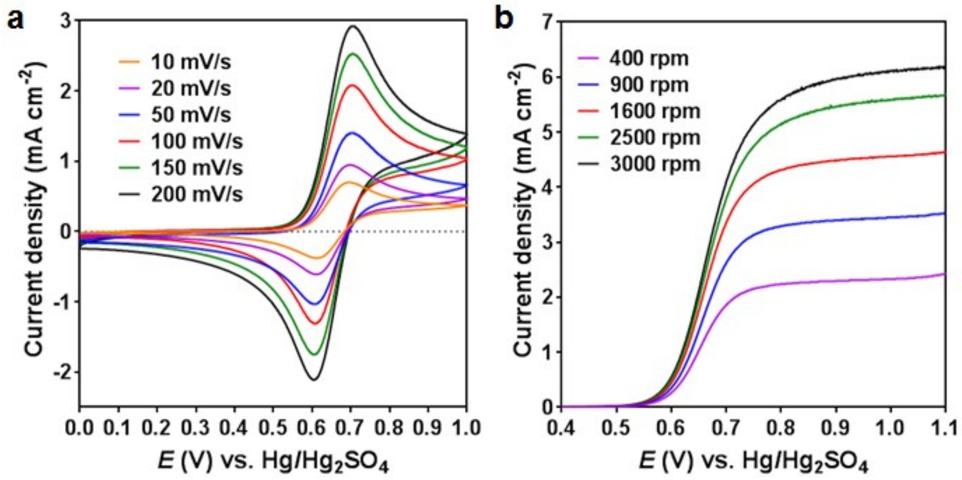

Figure S6. (a) CV (at different scan rates) and (b) LSV-RDE profiles (at different electrode rotation rates) of 10 mM NHPI in 1.0 M H_2SO_4 W-ACN electrolyte at x_{ACN} = 0.5 in the presence of 4 wt% PAA.

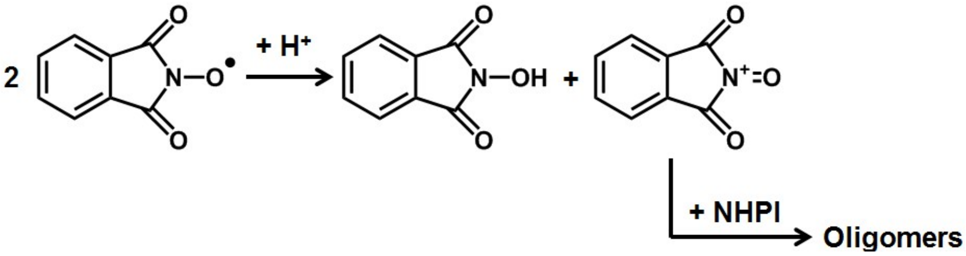

Figure S7. Self-decomposition reaction of PINO radical.[2–4]

As shown in Figure S6, PINO radicals can self-react and the oxoammonium product can further consume the NHPI to generate oligomers. This could severely reduce the utilization of active materials, deteriorating the battery rechargeability.

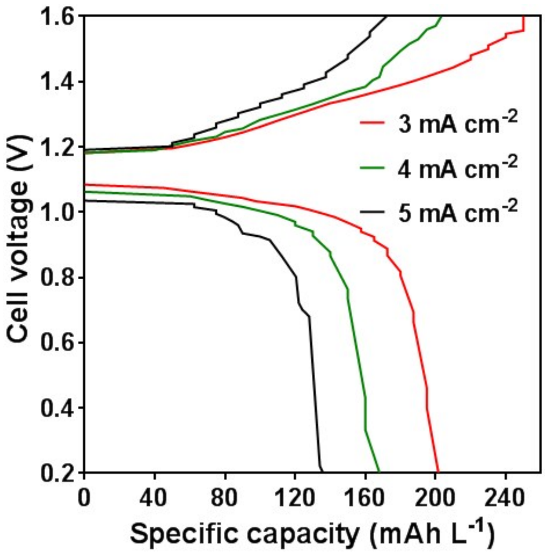

Figure S8. GCD profiles of the NHPI/AQS aqueous redox battery in the presence of 4 wt% PAA at different current densities.

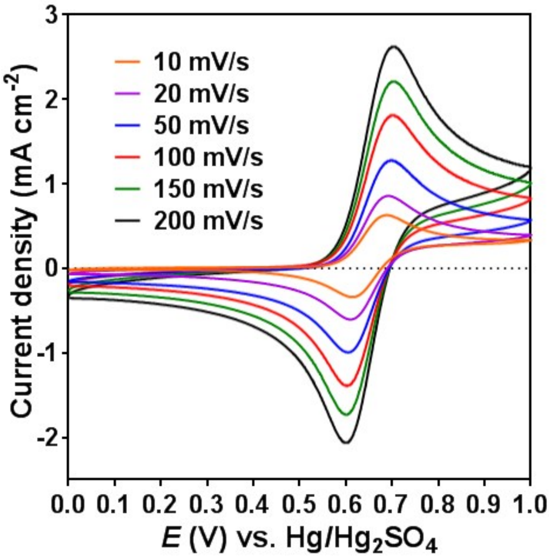

Figure S9. Scan rate dependence of 10 mM NHPI in 1.0 M H_2SO_4 W-ACN electrolyte at x_{ACN} = 0.5 in the presence of 4 wt% PAA in the ice bath.

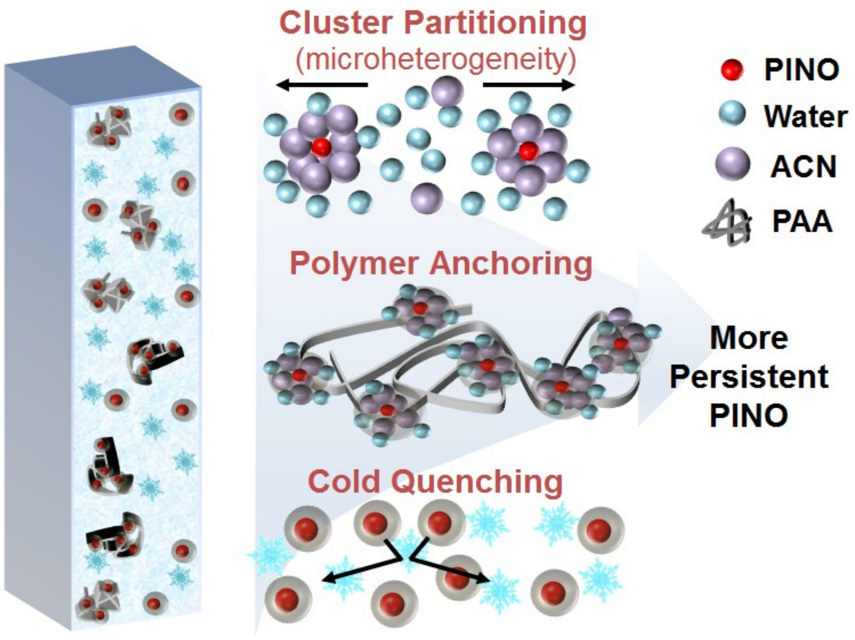

Figure S10. Schematic illustration of the radical-stabilizing effects in the PAA-containing binary solvent electrolyte.

References

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