Supporting Information for:

High Capacity Organic Radical Mediated Phosphorus Anode for Sodium Based Redox Flow Batteries

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Experimental Methods

In all experiments, diglyme (anhydrous, 99.5%, Sigma-Aldrich) was distilled under Ar using a Schlenk line before use. All solutions not containing anion radicals were stored over 4A zeolite and dispensed in an Ar-filled glovebox with < 0.1 ppm O₂ and H₂O.

Cyclic Voltammetry Experiments

A three electrode cell was used to collect cyclic voltammograms with electrolytes containing: (i) 0.02 m biphenyl (99.5%, Sigma-Aldrich), (ii) 0.02 m pyrene (98%, Sigma-Aldrich), and (iii) 0.01 m biphenyl + 0.01 m pyrene with 0.9 m sodium trifluoromethanesulfonate (NaTFS, 98%, Sigma-Aldrich) dissolved in diglyme. Na metal (ACS reagent grade, Sigma-Aldrich) was added to the solutions such that the molar ratio of the anion radical/neutral species was 1/1. Cyclic voltammograms were collected using a Au working electrode (1.6 mm diameter, polished to 0.050 µm), Ti counter electrode (6.4 mm diameter), and Na reference electrode. The reference electrode contained Na metal submerged in a solution of 1 m NaTFS in tetraglyme (99%, Sigma-Aldrich) and was separated from the cell’s electrolyte by a poly(ethylene oxide)/NaTFS/tetraglyme membrane. Voltammograms were acquired by polarizing the working electrode between 0.05 – 1.50 V vs. Na/Na⁺ at a scan rate of 10 – 100 mV/s using a Biologic SP-200 potentiostat. The solution resistance between the working and reference electrodes was estimated using a current interruption method in which a -5 µA pulse current was applied for 0.05 s, and the potential response was measured. The calculated solution resistance (867 ± 55 Ω for each electrolyte) during the cyclic voltammograms was automatically compensated in the EC-Lab software. At least 5 scans were conducted with each system to ensure collection of stable and reproducible voltammograms.
Redox Flow Cell Experiments

Figure S1a shows a photograph of the flow cell. Flow cell experiments were conducted in an Ar-filled glovebox using a custom stainless steel electrochemical cell. Ni foam electrodes (2.54 x 2.54 cm$^2$ footprint, 0.125 - 0.130 cm thick, MTI Corp) were spot welded over serpentine flow channels (shown in Figure S1b). A Na-$\beta”$ Al$_2$O$_3$ membrane (4.5 x 4.5 cm$^2$ footprint, 1.5 mm thick, Ionotec Ltd.) was placed between Celgard 2325 separator layers and butyl rubber gaskets, and the cell was torqued to 10 in-lbs. Syringe pumps were used to intermittently circulate electrolyte at 5 mL/min back-and-forth through each side of the cell via polypropylene Luer fittings and polypropylene tubing. Ultra-high purity Ar (passed through a ppb gas scrubber) flowed over the headspace of the solution reservoirs to avoid side reactions of the anion radical solutions with trace impurities (e.g., CO$_2$) in the glovebox. The electrolyte added to the working and auxiliary electrode compartments (approximately 10 and 35 mL, respectively) contained NaTFS, biphenyl, and pyrene dissolved in diglyme. Species concentrations in the electrolyte are listed in Table S1. For the mediated RFB tests, red P powder (98.9%, 100 mesh, Alfa-Aesar) was added directly to the electrolyte in the working compartment (i.e., the powder was not placed in a packed bed reactor).

Table S1. Species concentration in the working and auxiliary compartments for the electrochemical cells evaluated in this study.

<table>
<thead>
<tr>
<th>Cell Configuration</th>
<th>Species</th>
<th>Concentration (mol/kg$_{\text{diglyme}}$)</th>
<th>Theoretical Capacity* (mAh)</th>
<th>Concentration (mol/kg$_{\text{diglyme}}$)</th>
<th>Theoretical Capacity* (mAh)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flow Cell (see Figure S1)</td>
<td>NaTFS</td>
<td>0.728</td>
<td>N/A</td>
<td>0.372</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Biphenyl</td>
<td>0.0768</td>
<td>22.1</td>
<td>0.234</td>
<td>210</td>
</tr>
<tr>
<td></td>
<td>Pyrene</td>
<td>0.0768</td>
<td>22.1</td>
<td>0.235</td>
<td>211</td>
</tr>
<tr>
<td>Cylindrical Cell (see Figure S7)</td>
<td>NaTFS</td>
<td>0.608</td>
<td>N/A</td>
<td>0.376</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td>Biphenyl</td>
<td>0.0327</td>
<td>11.2</td>
<td>0.234</td>
<td>212</td>
</tr>
<tr>
<td></td>
<td>Pyrene</td>
<td>0.0320</td>
<td>11.0</td>
<td>0.233</td>
<td>211</td>
</tr>
</tbody>
</table>

* Theoretical capacities calculated assuming a 1 e$^-$ transfer.
A Biologic SP-200 potentiostat was used to perform galvanostatic charge/discharge experiments in which the working electrode was cycled between 0.10 – 1.4 V vs. Na/Na\(^+\) at currents of 1 and 5 mA (corresponding to 0.16 and 0.78 mA/cm\(^2\), respectively, based on the active surface area of the Na-\(\beta\)” Al\(_2\)O\(_3\) membrane). A Na reference electrode (Na metal submerged in a 1m NaTFS/tetraglyme solution separated by a polyethylene oxide/NaTFS/tetraglyme membrane) was used to monitor the potential of the working electrode as indicated in Figure S1a.

**Cylindrical Cell Experiments**

A symmetric cylindrical cell was also designed (see Figure S7) to study the electrochemical properties of biphenyl and pyrene dissolved in the NaTFS/diglyme electrolyte. In this configuration, a Na-\(\beta\)” Al\(_2\)O\(_3\) tube (18 mm inner diameter, 1 mm wall thickness, and 80 mm length, Ionotec, Ltd.) separated the inner and outer solution compartments (compositions listed in Table S1) which were covered with a Delrin cap. Each compartment contained magnetic stir bars to ensure uniform mixing of the solutions during cycling. Ni foam electrodes were placed on both sides of the Na-\(\beta\)” Al\(_2\)O\(_3\) tube. Galvanostatic charge/discharge experiments were performed at 2.5 mA (corresponding to 0.24 mA/cm\(^2\)) over several voltage windows (0.1 – 1.1, 0.5 – 1.1, and 0.1 – 0.5 V vs. Na/Na\(^+\)) using a Biologic SP-200 potentiostat. The potential of the working electrode was monitored using a Na reference electrode (Na metal submerged in a 1m NaTFS/tetraglyme solution separated by a polyethylene oxide/NaTFS/tetraglyme membrane) positioned in the inner solution compartment as shown in Figure S7.
Chemical Titrations of Phosphorus

A 2 m biphenyl (β) titrant solution was prepared by dissolving biphenyl in diglyme followed by addition of Na metal such that the molar ratio of Na⁺β⁻/β⁰ was 2/1. Titrant was added dropwise to red P powder until the blue color associated with Na⁺β⁻ persisted for at least 12 h. The resulting Naₓ⁺P powder was rinsed with diglyme and dried at 70 °C under vacuum overnight. Naₓ⁺P was then oxidized to NaₓP using 0.5 m pyrene dissolved in diglyme. A 1.5 molar excess of pyrene was added to the Naₓ⁺P powder and periodically swirled over several days to obtain the final product. In addition to the fully titrated compounds, several Na-P binary compounds (NaP₁₅, NaP₇, Na₃P₁₁, Na₃P₇, and NaP) were prepared by adding a stoichiometric amount of Na⁺β⁻ titrant to red P powder. The solutions were periodically swirled until the blue color associated with the presence of Na⁺β⁻ dissipated, indicating the anion radical had fully reacted to form the desired sodiated P compound. All powders were rinsed with diglyme and dried at 70 °C under vacuum before performing structural characterization.

Structural Characterization

Commercial red P and sodiated P powders were characterized using X-ray diffraction (XRD) and Raman spectroscopy. Samples for XRD were placed on a glass slide and covered with Kapton tape in an Ar glovebox to avoid air exposure. XRD was conducted on a Scintag XDS 2000 powder diffractometer with Cu Kα radiation (λ = 1.540562 Å) in the 2θ range of 25 - 80° with a step size of 0.02 ° and count time of 1 s. The operating voltage and current of the X-ray generator were 45 kV and 35 mA, respectively. Samples for Raman spectroscopy were hermetically sealed in an optical cell in the glovebox. Raman spectra were acquired with an Alpha 300 confocal Raman microscope (WITec, GmbH) using a solid-state 532 nm excitation laser, a 20x objective, and a
grating with 600 grooves/mm. The laser spot size was approximately 1 µm, and the laser power was attenuated to 100 µW to prevent sample damage from laser-induced heating. Raman spectra were analyzed using WITec Project Plus software. After performing a background subtraction, the reported XRD and Raman data were smoothed using a Savitzky-Golay filter.

Fourier-transform infrared spectroscopy (FTIR) was performed on RFB electrolyte solutions using a Bruker Alpha instrument housed in an Ar-filled glovebox. Spectra were acquired in attenuated total reflectance (ATR) mode using a diamond window. No background corrections were performed on the spectra.

Figure S1. Digital photographs showing (a) the redox flow cell and (b) one side of the cell stack which contained serpentine flow channels for electrolyte flow. Syringe pumps (not shown) on each side of the cell were used to flow electrolyte back-and-forth through the system. The compositions of the working and auxiliary solutions are given in Table S1.
Figure S2. Representative charge/discharge curves collected at currents of 1 and 5 mA (corresponding to 0.16 and 0.78 mA/cm², respectively) for a redox flow cell containing biphenyl and pyrene mediators with red P powder. The 0.78 mA/cm² curve was collected during cycle 9 of the experiment shown in Figure 3, and the current density was then lowered to 0.16 mA/cm² during the subsequent cycle.
Figure S3. Summary of the capacity and coulombic efficiency for the RFB experiments with and without red P. Experiments were conducted at a current of 5 mA (corresponding to 0.78 mA/cm$^2$). Electrolyte compositions of the working and auxiliary compartments are given in Table S1.
Figure S4. FTIR spectra of the baseline electrolyte (0.9 m NaTFS in diglyme) before and after storing over Na$_{1.99}$P powder (generated using a Na$^+$β$^-$ solution at ~0.2 V vs. Na/Na$^+$) at room temperature for 17 months. No changes were detected in the vibrational spectra after extended storage, indicating excellent chemical compatibility between the electrolyte and active material. The left panel (a) shows the entire FTIR spectra, and the right panel (b) shows a magnified region at low wavenumbers.
**Figure S5.** FTIR spectra of the RFB anode solution containing biphenyl, pyrene, NaTFS, and diglyme (a, b) before and after the cycling tests reported in Figure 3 and (c, d) the cycled electrolyte before and after storage for 14 months. Left panels (a, c) show the entire FTIR spectra, and right panels (b, d) show magnified regions at low wavenumbers.
Figure S6. (a) XRD patterns and (b) Raman spectra of red P, several Na$_{x+y}$P compounds generated with Na$^+$β$^-$, and a desodiated Na$_y$P powder generated from Na$_{2.11}$P and π$^0$ (y ≈ 0.91 as estimated from the 0.16 mA/cm$^2$ electrochemical data in Figure S2).

Evaluation of Parasitic Side Reactions Using a Cylindrical Cell Design

A symmetric cylindrical cell was designed (see Figure S7 and Table S1) to further study the electrochemical decomposition of solutions containing biphenyl and pyrene dissolved in the NaTFS/diglyme electrolyte. Each compartment contained magnetic stir bars to ensure all species were circulated over the Ni foam electrodes. When cycled between 0.1 – 1.1 V vs. Na/Na$^+$ at a current density of 0.24 mA/cm$^2$ (see Figure S8), the cell showed two voltage plateaus associated with formation of Na$^+$β$^-$ and Na$^+$π$^-$. Interestingly, the reduction and oxidation capacities of each plateau differed by ~1.5 mAh each cycle, but the overall irreversible capacity loss was low (~0.3 mAh corresponding to ~98% coulombic efficiency). These results are consistent with those shown in the RFB tests (Figure 2).

When cycled over narrower voltage windows (i.e., 0.1 – 0.5 and 0.5 – 1.1 V vs. Na/Na$^+$, see Figure S8), the cell showed improved reversibility with only 0.10 – 0.15 mAh loss each cycle.
While the capacity near 0.20 V agreed with that expected for biphenyl undergoing a 1 e⁻ transfer (10 vs. 11 mAh), the observed capacity near 0.75 V (4 mAh) was much less than expected based on the original pyrene content in the cell (11 mAh). Furthermore, the capacity near 0.75 V gradually faded when cycling over the entire voltage window (0.1 – 1.1 V). These results suggest that pyrene was decomposed at potentials < 0.5 V vs. Na/Na⁺ with possible degradation routes including: (i) reductive dearomatization and/or (ii) formation of an unstable dianion radical species.¹

**Figure S7.** Schematic of the cylindrical cell used to evaluate the electrochemical properties of biphenyl and pyrene mediators. A Na-β” Al₂O₃ tube separated the inner and outer electrolyte solutions which were homogenized using a magnetic stirrer. The compositions of the inner and outer solutions are given in Table S1.
Figure S8. Electrochemical results for the symmetric cylindrical cell showing (top) oxidation and reduction capacities of plateaus near 0.20 and 0.75 V vs. Na/Na\(^+\) and (bottom, i-iv) representative voltage profiles. A cell schematic is given in Figure S7, and compositions of the inner and outer electrolyte solutions are listed in Table S1.
Projected Energy Density of a Mediated Phosphorus-Sulfur RFB

The mediated phosphorus anode had a desodiation capacity up to 1,120 mAh/g\(_P\) at an operating potential \(~0.75\) V vs. Na/Na\(^+\). A sulfur cathode in which reversible Na storage occurs via \(S + 2 Na^+ + 2 e^- \leftrightarrow Na_2S\) has a theoretical capacity of 687 mAh/g\(_{Na_2S}\) and operating potential \(~1.8\) V vs. Na/Na\(^+\).\(^2\) Na storage in a sulfur cathode can, in principle, also be driven by appropriate redox mediators. Assuming complete sulfur utilization, the maximum specific capacity \(Q_{\text{theoretical}}\) and energy density \(E_{\text{theoretical}}\) of a mediated phosphorus-sulfur battery are 426 mAh/g\(_{P+Na_2S}\) and 447 Wh/kg\(_{P+Na_2S}\) as shown below:

\[
Q_{\text{theoretical}} = \frac{1}{Q_{\text{anode}}} + \frac{1}{Q_{\text{cathode}}} = \frac{1}{1,120 \text{ mAh}} + \frac{1}{687 \text{ mAh}} = \frac{426 \text{ mAh}}{g_P + g_{Na_2S}}
\]

\[
E_{\text{theoretical}} = Q_{\text{theoretical}} \times V_{\text{average}} = \frac{(426 \text{ mAh})}{g_{P+Na_2S}} (1.8 - 0.75)V = 447 \text{ Wh/kg}_{P+Na_2S}
\]

Figure S5 shows the computed energy density of such a battery (including the mass of the active powder and mediator solutions) asymptotically approaches 447 Wh/kg as the mass ratio of the active powder to the mediator solutions increases. For a situation in which the weights of the powder and solutions are equal, the projected energy density of the system (including only the weight of the active components and electrolyte) is 224 Wh/kg.
Figure S9. Projected energy density of a mediated P-S RFB as a function of the mass ratio of the active material powders (P and Na₂S) to the mediator solutions.

References
