Supporting Information

Impact of Electrolyte Composition on the Reactivity of a Redox Active Polymer

Studied through Surface Interrogation and Ion-Sensitive Scanning Electrochemical Microscopy

Mark Burgess\textsuperscript{a,b}, Kenneth Hernández-Burgos\textsuperscript{a,b}, Kevin J. Cheng\textsuperscript{a,b}, Jeffrey S. Moore\textsuperscript{a,b,c}, and Joaquín Rodríguez-Lopez\textsuperscript{a,b,*}

\textsuperscript{a} Joint Center for Energy Storage Research

\textsuperscript{b} Department of Chemistry, University of Illinois at Urbana-Champaign, Urbana, Illinois, 61801, USA

\textsuperscript{c} Beckman Institute for Advanced Science and Technology
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1.0 General Information

$^1$H spectra were recorded on a UNITY INOVA™ 500 NB High-Resolution NMR. UV-Vis absorption spectra were recorded on Shimadzu instruments. Elemental analyses were performed on the following instruments: CHN analysis - Exeter Analytical CE 440 and Perkin Elmer 2440, Series II

Unless otherwise stated, all starting materials and reagents were purchased from Sigma-Aldrich or Matrix Scientific and used without further purification. Polystyrene of 190 kDa (PDI: 1.01) was purchased from Polymer Source.

**Polynitrostyrene (PNS)** – Synthesis based on work by Philippides et. al. A flask was charged with 4-nitrotoluene (100 mL) and polystyrene (5.0 g). Then nitric acid (80 mL) was added to the flask and stirred vigorously while cooled to 0 °C in an ice bath. Sulfuric acid (20 mL) was added slowly to the flask under vigorous stirring. The mixture was allowed to return to room temperature and stirred for 16 hours. The resultant emulsion product was precipitated into isopropanol and then redissolved into dimethylformamide. The precipitation was repeated three times and placed under high vacuum for 24 hours. Functionalization was found to be 78% by UV-Vis spectroscopy.

The molecular weight of the PNS RAP was calculated using the degree of polymerization of the polystyrene multiplied by the monomer molecular weight. The degree of polymerization of the polystyrene is the molecular weight of polystyrene ($M_n$) /104.15. The calculated molecular weight for PNS was 270 kDa.
1.1 Redox Active Polymer Characterization

1.1 Elemental Analysis

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<td><strong>PNS RAP</strong></td>
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<tr>
<td></td>
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<tr>
<td></td>
<td>Difference</td>
<td>6.43</td>
<td>-0.24</td>
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Table S1: Elemental analysis data from mass spectrometry measurements. The theoretical percentage of carbon (C), hydrogen (H), and nitrogen (N) are shown in the table, as well as the experimentally derived amounts.
1.2 UV-Vis Absorption Spectrum

Figure S1: UV-Vis absorption spectrum of 0.5 mM PNS in DMF using a quartz cuvette with a 1 cm path length.
1.3 UV-Vis Absorption Calibration

Figure S2: UV-Vis calibration curve using 4-nitrotoluene as the PNS standard in DMF.

Table S2: Molar extinction coefficients of 260 kDa PNS in DMF

<table>
<thead>
<tr>
<th>Molecular Weight of PNS</th>
<th>Molar Extinction Coefficient $\varepsilon$ (M$^{-1}$·cm$^{-1}$)</th>
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<tbody>
<tr>
<td>270 kDa</td>
<td>2523.9</td>
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</table>
1.5 $^1$H NMR of 270 kDa PNS

Figure S3: $^1$H NMR spectra of 0.5 mM PNS in d-DMF.
2.0 Cyclic Voltammetry of PNS with Li⁺ Electrolyte

Figure S4: Cyclic voltammetry with a 1.15 mm Pt disk electrode in the presence of 5 mM PNS in DMF with 0.1 M TBA.PF₆ and 17 mM LiPF₆ electrolytes. The black voltammogram is the same voltammogram shown in the main article in Figure 3, scanned at 20 mV/s demonstrating the irreversibility of PNS in the presence of Li⁺. The red voltammogram is the same electrode scanned between the same potentials at the fourth cycle. There is a significant decrease in current from the first cycle due to irreversibility of the PNS with Li⁺. The blue voltammogram is the same electrode and same solution scanned more positively to show the potential at which the oxidation of PNS in Li⁺ electrolyte can be finally be seen, ~0.2 V, after which the reduction the reduction peak is now restored to its initial current magnitude. The seventh cycle shows the reduction peak is maintaining its peak current magnitude, but the oxidation peak is decreased because there has not been a buildup of reduced PNS as was the case in cycles 1-4.

2.1 Macrodisk Voltammetry of PNS with Li⁺ Electrolyte
2.2 Microelectrode Voltammetry with PNS

Figure S5: Voltammetry of 33 mM PNS at 100 mV/s using a 12.5 μm radius microelectrode in 0.1 M TBAPF6. The diffusion coefficient (D) was calculated using the steady state current at -2.3 V, ~18 nA, and using the equation $i_{\text{steady state}} = 4nFaC^*$, in which $F$ is Faraday’s constant (96,485 C/mol) $a$ is the radius of the microelectrode, and $C^*$ is the bulk concentration (mol/cm$^3$). The calculated value of the diffusion coefficient for PNS in TBA$^+$ electrolyte was $1.1 \times 10^{-6}$ cm$^2$/s.
3.0 Scanning Electrochemical Microscopy with Hg Capped UME

3.1 Deposition of Hg onto the Pt UME Surface

Figure S6: Electrodeposition of Hg onto the Pt UME surface. Deposition solution was 10 mM Hg(NO$_3$)$_2$ with 0.1 M tetramethylammonium nitrate electrolyte, with 0.1% HNO$_3$ (by volume) in distilled water. The UME was poised at -0.4 V vs. a tungsten wire quasi-reference electrode for 400 seconds. The current blips in the chronoamperometric step are indicative of the growth and subsequent combination of micro-Hg droplets. Deposited charge was 48 nC, which after accounting for 2 electrons passing per molecule to reduce Hg$^{2+}$ to Hg metal, the Hg droplet was found to be 11.75 microns tall, which to one significant figure gives ratio of the height of the Hg droplet to the radius of the UME is 1.
3.2 UME Aligning with a Hg Capped UME

Figure S7: Aligning of the microelectrodes via the feedback mode of SECM. The tip UME is generating TMPD$^+$ and the PNS filmed substrate is reducing it to neutral TMPD. When feedback is sensed (~100 µm position in Figure S6) the tips are aligned in that particular dimension. Both of the UMEs had a radius of 12.5 µm. The solution contained 10 mM TMPD, 0.1 M TBAPF$_6$, 17 mM KBF$_4$, and 17 mM LiPF$_6$. 
3.3 Approach Curve with a Hg Capped UME to the Coaligned Substrate UME

Figure S8: Approach curve of a Hg capped UME using the first oxidation of TMPD to the PNS filmed substrate UME that was placed at open circuit. The motor speed was 36 microns per second. The theoretical fitting of the experimental data was made using an RG of 2 for the Hg capped UME and used fitting protocol from Lindsey et. al. After accounting for the height of the droplet, the final placement of the Hg capped UME was found to be 5 microns above the PNS filmed substrate UME, as measured from the top of the Hg droplet.
3.4 Deposition of PNS onto Substrate UME

Figure 59: Deposition of a PNS film onto the substrate UME by a chronoamperometric step at -2 V from a solution of 33 mM PNS in 0.1 M TBA.PF$_6$ supporting electrolyte for 400 seconds. The total charge passed was 3.35 µC.
3.5 Determination of the Amount of Nitro Groups on the Substrate UME Surface

Figure S10: Voltammetry with the PNS filmed UME in a solution only containing 0.1 M \( \text{TBA.PF}_6 \) in DMF at 10 mV/s. The voltammogram was integrated in the region shown by the red lines to determine the amount of accessible nitro groups on the UME surface. The integrated charge was 45.7 nC, which equates to \( 2.85 \times 10^{11} \) accessible nitro groups.
Figure S11: Voltammetry with the Hg capped tip UME before and after the SECM experiments. The electrode was scanned at 0.5 V/s in the presence of 10 mM TMPD, 17 mM LiPF$_6$, 17 mM KBF$_4$, and 0.1 M TBA.PF$_6$. The current levels for the oxidation of TMPD and the stripping of K$^+$ and Li$^+$ are nearly identical before and SECM experiments, demonstrating that the size of the Hg droplet electrode had not been perturbed in any significant amount.
4.0 Surface Interrogation Scanning Electrochemical Microscopy

4.1 Coaligning Two Pt UMEs via Collection Mode of SECM

Figure S12: The coaligning of the two UMEs used in the surface interrogation SECM experiments using the collection mode of SECM. The substrate UME was generating TMPD$^+$ and the tip UME was collecting it and reducing the species back to neutral TMPD. The solution contained 1 mM TMPD in 0.1 M TBA.PF$_6$. The large spike in currents for both UMEs at approximately the 150 µm position is from the collection and subsequent regeneration of the redox mediator between the tips when aligned.
4.2 Collection Cyclic Voltammograms of TMPD between Coaligned UMEs

Figure S13: Collection voltammograms between the tip UME and a Pt substrate UME. The tip UME generates TMPD$^+$ via voltammetry and the substrate UME is poised at -1.9 V during this process. The collection efficiency between the tips for the redox mediator is approximated as 100%, due to the same order of magnitude of current being measured between both tips. This high collection efficiency of the species between the SECM tips is only possible when the tips are properly aligned and placed very near each other (< 6 µm for the size of the UMEs used here).
4.4 Approach Curve with a Pt UME to a Pt Substrate UME

Figure S15: Approach curve in the feedback mode of SECM of a Pt UME to a Pt UME substrate after alignment of the tips. The tip UME is generating TMPD$^+$ and the substrate is reducing this species back to neutral TMPD. The distance between the tips at the approached position was estimated by fitting the approach curve to theory for SECM feedback reported by Cornut and Lefrou. The fitting program used an RG of 2 for the tip UME. Fitting of the approach curve finds that the tips were separated by less than 6 microns at the approached position. The solution contained 1 mM TMPD with 0.1 M TBA.PF$_6$. 
4.5 Approach Curve with a Pt UME to a PNS Filmed UME in TBA⁺ Electrolyte

Figure S16: Approach curve in the feedback mode of SECM of a Pt UME to a PNS filmed Pt UME substrate after alignment of the tips. The tip UME is generating TMPD⁺ and the substrate is reducing this species back to neutral TMPD. The distance between the tips at the approached position was estimated by fitting the approach curve to theory for SECM feedback reported by Cornut and Lefrou. The fitting program used an RG of 2 for the tip UME. Fitting of the approach curve finds that the tips were separated by less than 6 microns at the approached position. The solution contained 1 mM TMPD with 0.1 M TBAPF₆.
4.6 Approach Curve with a Pt UME to a PNS Filmed UME in TBA$^+$ and Li$^+$ Electrolyte

Figure S17: Approach curve in the feedback mode of SECM of a Pt UME to a PNS filmed Pt UME substrate after alignment of the tips. The tip UME is generating TMPD$^+$ and the substrate is reducing this species back to neutral TMPD. The distance between the tips at the approached position was estimated by fitting the approach curve to theory for SECM feedback reported by Cornut and Lefrou. The fitting program used an RG of 2 for the tip UME. Fitting of the approach curve finds that the tips were separated by less than 6 microns at the approached position. The solution contained 1 mM TMPD with 0.1 M TBA.PF$_6$ and 17 mM LiPF$_6$. 
4.7 Approach Curve with a Pt UME to a PNS Filmed UME in TBA⁺ and K⁺ Electrolyte

Figure S18: Approach curve in the feedback mode of SECM of a Pt UME to a PNS filmed Pt UME substrate after alignment of the tips. The tip UME is generating TMPD⁺ and the substrate is reducing this species back to neutral TMPD. The distance between the tips at the approached position was estimated by fitting the approach curve to theory for SECM feedback reported by Cornut and Lefrou. The fitting program used an RG of 2 for the tip UME. Fitting of the approach curve finds that the tips were separated by less than 6 microns at the approached position. The solution contained 1 mM TMPD with 0.1 M TBAPF₆ and 17 mM KBF₄.
5.0 Calculation of Polymer Film Thickness

**Figure S19:** The PNS film voltammogram at 100 mV/s in the presence of 0.1 M TBA⁺, shown in Figure 3B of the main text, is integrated to find the total amount of charge corresponding to the reduction of PNS. The voltammogram is integrated in the region shown by the red lines. The calculation of the film properties was as follows. The integrated charge was found to be 1.56 x 10⁻⁶ C. The surface coverage would be 37.6 µC/cm². Dividing the integrated charge by Faraday’s constant (96,485 C/mol) finds that there were 1.62 x 10⁻¹¹ mol of PNS on the electrode surface. Multiplying the amount of PNS in mol by the molecular weight of the polymer repeat unit (149 g/mol) finds that there was 2.40 x 10⁻⁹ g of PNS on the surface. Dividing the amount of PNS in grams by the density of the precursor polymer (1.05 g/mol) shows that there was a volume of PNS on the surface of 2.29 x 10⁻⁹ cm³. Dividing the PNS volume by the macrodisk electrode area (0.0415 cm²) finds that the polymer film was 0.6 nm thick.

5.1 Macrodisk Polymer Film Thickness
5.2 UME Polymer Film Thickness for Hg Stripping SECM Experiments

Figure S20: Voltammetry with the PNS filmed UME in a solution only containing 0.1 M TBA.PF$_6$ in DMF at 10 mV/s. The voltammogram was integrated in the region shown by the red lines to determine the amount of accessible nitro groups on the UME surface and the polymer film thickness. The integrated charge was found to be 45.7 nC. The surface coverage would be 9,300 µC/cm$^2$. Dividing the integrated charge by Faraday’s constant (96,485 C/mol) finds that there were 4.74 x 10$^{-13}$ mol of PNS on the electrode surface. Multiplying the amount of PNS in mol by the molecular weight of the polymer repeat unit (149 g/mol) finds that there was 7.06 x 10$^{-11}$ g of PNS on the surface. Dividing the amount of PNS in grams by the density of the precursor polymer (1.05 g/mol) shows that there was a volume of PNS on the surface of 6.72 x 10$^{-11}$ cm$^3$. Dividing the PNS volume by the UME electrode area (4.91 x 10$^{-6}$ cm$^2$) finds that the polymer film was 136 nm thick.
5.3 UME Polymer Film Thickness for Surface Interrogation SECM Experiments

Integrating the interrogation currents, shown in Figure 7A of the main text, from the surface interrogation SECM experiments in the TBA$^+$, TBA$^+$ + K$^+$, and TBA$^+$ + Li$^+$, containing electrolytes from 0 to 100 seconds finds that there was a surface coverage of 17 ± 5 nmol/cm$^2$. This value in terms of charge per area would be equal to 1,700 µC/cm$^2$. Taking this value and multiplying by the molecular weight of the polymer repeat unit (149 g/mol), it was found there was a mass per area of the electrode ratio of 2.53 x 10$^{-6}$ g/cm$^2$. Dividing this value by the density of the precursor polymer (1.05 g/cm$^3$) finds that the film thickness was 24 ± 7 nm.

5.4 Summary of Polymer Film Calculated Properties

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Film Charge/Area (µC/cm$^2$)</th>
<th>Approximate Film Thickness (nm)</th>
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<tr>
<td>Macrodisk Film</td>
<td>37.6</td>
<td>0.6</td>
</tr>
<tr>
<td>UME Film Used in Hg Stripping SECM</td>
<td>9,300</td>
<td>136</td>
</tr>
<tr>
<td>UME Film Used in SI-SECM</td>
<td>1,700</td>
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