

Supplementary Information for

**Thin Layer Electrochemical Extraction of
Non-Electroactive Cations with an Anion-Exchanging
Conducting Polymer Overlaid with a Selective
Membrane**

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Experimental section

Reagents. High molecular weight poly(vinyl chloride) (PVC) (Selectophore grade), bis(2-ethylhexyl) sebacate (DOS) (Selectophore grade), sodium tetrakis [3,5-bis-(trifluoromethyl) phenyl]borate (NaTFPB) (Selectophore grade), tetradodecylammonium chloride (TDDACl) ($\geq 97\%$), 3-octylthiophene (97%), lithium perchlorate (LiClO_4 , 99.99%), potassium chloride (99.5%), tetrabutylammonium bromide (TABBr) (99%), tetrahydrofuran (THF) (99.9%) and acetonitrile (anhydrous, 99.8%) were purchased from Sigma-Aldrich. Sodium chloride (99.9%) was received from Biolab, Australia. Hydrochloric acid (32%, reagent grade) was obtained from Scharlau, Spain.

Electrochemical Polymerization of Poly (3-octylthiophene). Poly (3-octylthiophene) (POT) was electrochemically polymerized on Au as follows: 1) An Au electrode (3mm in diameter) was polished and carefully cleaned; 2) 0.1M 3-octylthiophene and 0.1M LiClO_4 in acetonitrile was purged with pure N_2 for 15 mins; 3) Electrodeposition was conducted in a three-electrode cell, where the Au electrode acted as working electrode, a home-made Ag/AgCl wire was used as reference electrode, and a coiled Pt wire was used as counter electrode. Using a potentiostat (Princeton Applied Research, PARSTAT2273), the POT film was obtained by cyclic voltammetry (0–1.5V, 100 mV/s, 3 scans) and discharging at 0 V for 120 s). The resulting POT film was immersed in pure acetonitrile for 30 min to remove the electrolyte.

PVC Membrane Preparation. The ‘cocktail’ solution of PVC membrane contained 42 mmol/kg of cation exchanger NaTFPB, 10 mmol/kg of anion exchanger TDDACl and 30.0 mg PVC plasticized with 60.0 mg DOS, which were dissolved in 2 ml THF. Using a spin-coater (Model WS-400B-6NPP/LITE, LAURELL Technologies Corp.), the PVC membrane was coated on the POT-deposited Au electrode at 1500 rpm for 2 min and dried in air at room temperature (18.2 °C) for 30 min before further testing.

Experimental setup. 0.1M NaCl, KCl and HCl solutions were made by dissolving the respective salts in pure water (18 MOhm cm). TABBr solutions with varying concentrations (10^{-7} M – 0.1 M) were prepared by adding TABBr salt to a background solution of 0.1 M NaCl. All voltammetric measurements of the thin layer were performed in a three-electrode cell system. The thin layer spin-coated PVC on the POT-deposited Au electrode behaved as a working electrode. A single-junction Ag/AgCl electrode with 3M KCl internal solution was used as reference electrode. A Pt wire acted as counter electrode. The scan potential range was -0.2V to 1.3V.

Cathodic and anodic peak analysis

Both cathodic and anodic peak areas (number of coulombs) were obtained using the software *Electrochemistry PowerSuite – PowerCV 2.44*, which are shown in figure S1 and figure S2. An overall charge of POT in 0.1 M NaCl around 1.0 V is $11.61 \mu\text{C}$. The charge for the cathodic Na^+ and Cl^- waves is 9.60 and $2.01 \mu\text{C}$, respectively. The sum of the cathodic peaks is $11.61 \mu\text{C}$. Using the same method, the sum of anodic waves, $11.64 \mu\text{C}$, is estimated. The fitting curve of anodic peak around 1.0 V could not be precisely obtained with this software.

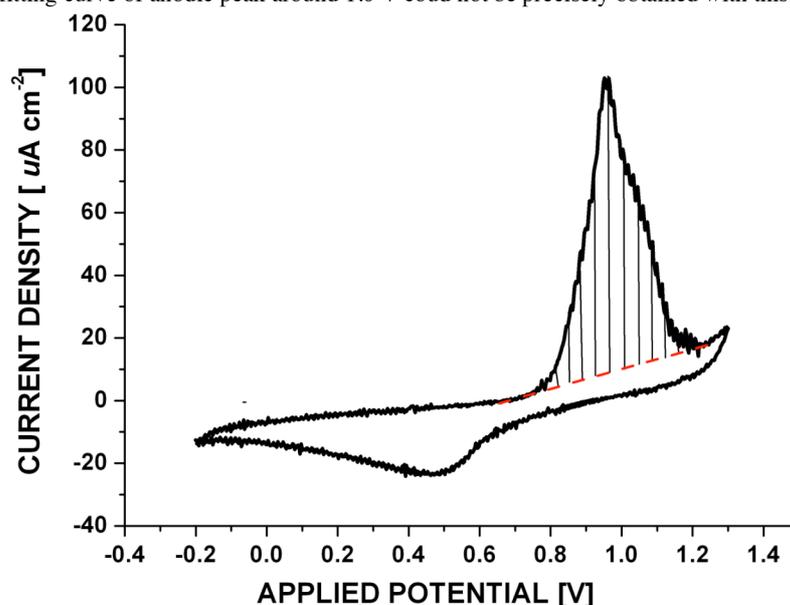


Figure S1. Cyclic voltammogram of POT film deposited on Au electrode in 0.1 M NaCl (no PVC membrane). Scan rate: 100 mV/s.

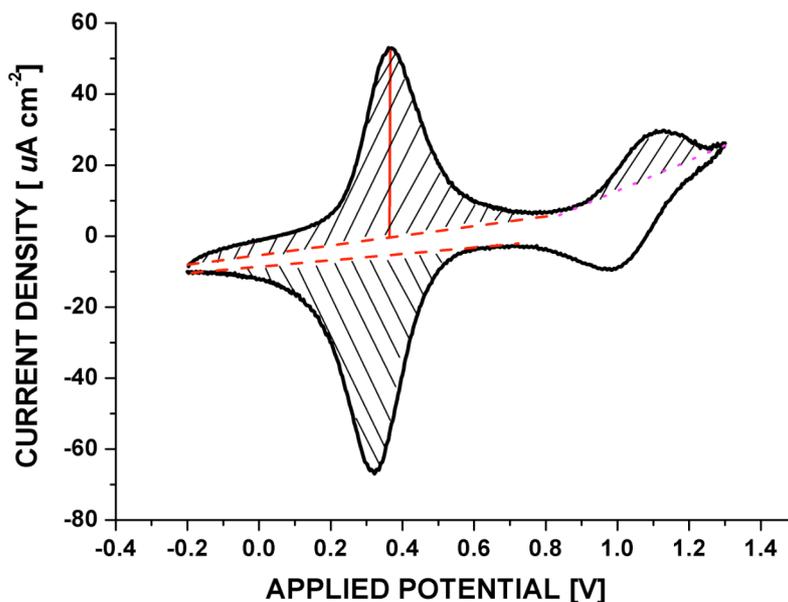


Figure S2. Cyclic voltammograms of thin layer on the PVC–POT–Au electrode in 0.1 M NaCl. Scan rate: 100 mV/s. Peak analysis performed by Electrochemistry PowerSuite – PowerCV 2.44.

Meanwhile, as shown in Figure S3, a peak analysis of the cathodic Na^+ waves gives the peak currents for different scan rates, which may be utilized for confirming thin layer behavior.¹

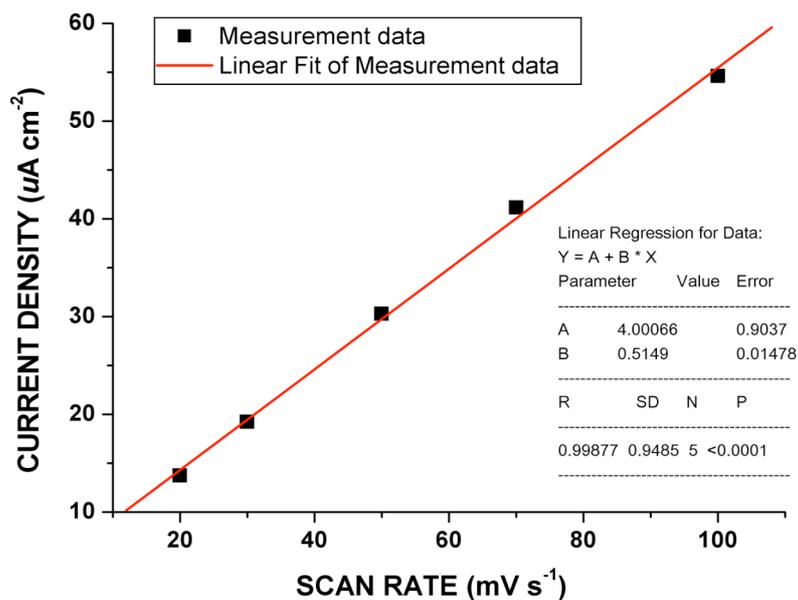


Figure S3. Linear fitting of peak currents of cathodic Na^+ peaks in **Fig.1** and **Fig.S2** as a function of scan rates.

Estimation of thickness of PVC membrane layer

The thickness of the PVC membrane can be estimated based on the known cation-exchanger concentration (42 mmol/kg) and electrode area ($\Phi=3$ mm, geometric area 0.07068 cm^2). The amount of excess cation-exchanger in the overlaid PVC membrane is calculated using the charge for the cathodic Na^+ peak ($9.60 \mu\text{C}$). Considering the concentration of excess NaTFPB (32 mmol/kg) and the approximate density of PVC membrane of 1.299 g/cm^3 ,² the thickness of the PVC membrane is calculated as $0.34 \mu\text{m}$, which is consistent with expectations (less than $0.5 \mu\text{m}$).³

O₂ dependence measurements

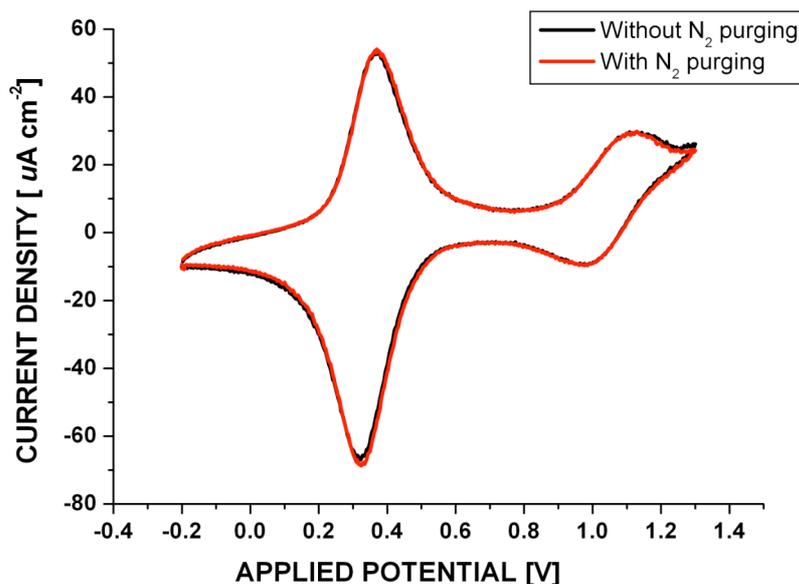


Figure S4. Cyclic voltammograms of PVC-POT-Au electrode in 0.1M NaCl without and with N₂ purging for 5 min. Potential scan: -0.2 V to 1.3V; Scan rate: 100 mV/s; Four consecutive scans are shown for each situation.

Calculation of selectivity coefficients

As described in the main text, the location of the peaks ascribed to the extraction/stripping of I⁺ ions according to Scheme 1, a and d, may be approximated based on eq 2 as follows:

$$E = E^0_I - \frac{RT}{F} \ln \frac{[P]_p [R^-]_m [I^+]_m}{[P^+]_p [R^-]_p [I^+]_{aq}} \quad (S1)$$

where E is the potential at the working electrode; $[P]$, $[R^-]$, $[I^+]$ are ion concentration (strictly: activities) of the indicated species, and R, T , and F have their established meanings. The symbols P, P^+, p, m and aq have the same meaning as given in the main text. Equation S1 is rewritten as:

$$E = E^0_I - \frac{RT}{F} \ln \frac{[P]_p [R^-]_m}{[P^+]_p [R^-]_p} + \frac{RT}{F} \ln \frac{[I^+]_{aq}}{[I^+]_m} \quad (S2)$$

For ions of the same charge and assuming dissociated electrolytes in the membrane, the ion-exchange constant, $K_{I,J}$, can be approximated by the selectivity coefficient, $K_{I,J}^{pot}$,^{3,4} and may be written as:

$$K_{I,J} = K_{I,J}^{pot} = \frac{[I^+]_{aq} [J^+]_m}{[I^+]_m [J^+]_{aq}} \quad (S3)$$

Where J^+ is the interfering ion. Equation S3 is inserted into eq S2 to describe the potential as a function of the interfering ion concentration:

$$E = E^0_I - \frac{RT}{F} \ln \frac{[P]_p [R^-]_m}{[P^+]_p [R^-]_p} + \frac{RT}{F} \ln K_{I,J}^{pot} \frac{[J^+]_{aq}}{[J^+]_m} \quad (S4)$$

It is now assumed that the peak potentials for the cation extraction processes of I⁺ and J⁺ describe separate situations where the redox state of the conducting polymer, the doping concentration of cation exchanger in both phases, and the membrane concentrations of I⁺ and J⁺ are the same. Under these conditions, eqs S2 and S4 are simplified as:

$$E_{Peak,I} = K + \frac{RT}{F} \ln[I^+]_{aq} \quad (S5)$$

$$E_{Peak,J} = K + \frac{RT}{F} \ln K_{I,J}^{pot} [J^+]_{aq} \quad (S6)$$

The selectivity coefficient is then obtained from the experimental peak potential shift as follows:

$$\log K_{I,J}^{pot} = \frac{F(E_{Peak,J} - E_{Peak,I})}{2.303RT} + \frac{RT}{F} \ln \frac{[I^+]_{aq}}{[J^+]_{aq}} \quad (S7)$$

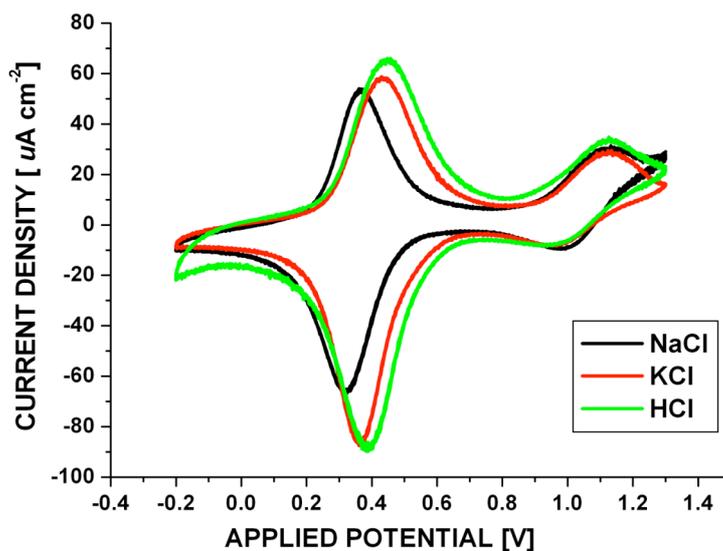


Figure S5. Cyclic voltammograms of PVC-POT-Au electrode in 0.1 M NaCl, KCl and HCl, respectively. Scan potential: -0.2 V – 1.3V; Scan rate: 100 mV/s; Four consecutive scans.

As shown in Fig. S5, the potentials of the anodic peaks for Na⁺ (0.1M), K⁺ (0.1M), and H⁺ (0.1M) are 0.322 V, 0.364V, 0.388 V, respectively.

Nernstian slope analysis for the tetrabutylammonium ion.

The broad anodic peaks observed for concentrations above 1 mM TABBr (see Figure 2) are interpreted as consisting of two contributions, the extraction of TAB⁺ ion and stripping of halide ions. After Gaussian fitting, the anodic peak potentials for 0.1M, 0.01M and 0.001M TAB⁺ are found as 0.740 V, 0.80 V, and 0.86V, see Figure S6.

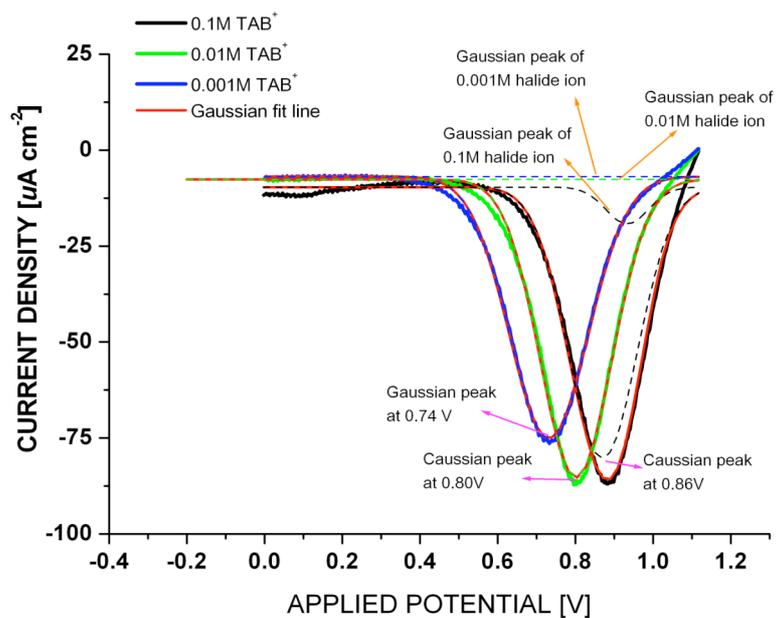


Figure S6. Gaussian fittings of anodic peaks of the bilayer electrode in 0.1 M, 0.01 M and 0.001 M TABBr in a background of 0.1 M NaCl , respectively. Data for anodic peaks is as in figure 2, main text.

References

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