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# An All-Organic Proton Battery

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#### Abstract

Rechargeable batteries that use organic matter as the capacity-carrying material have previously been considered a technology for the future. Earlier batteries in which both the anode and cathode consisted of organic material required significant amounts of conductive additives and were often based on metal-ion electrolytes containing Li<sup>+</sup> or Na<sup>+</sup>. However, we have used conducting poly(3,4-ethylenedioxythiophene) (PEDOT), functionalized with anthraquinone (PEDOT-AQ) or benzonquinone (PEDOT-BQ) pendant groups as the negative and positive electrode materials, respectively, to make an all-organic proton battery devoid of metals. The electrolyte consists of a proton donor and acceptor slurry containing substituted pyridinium triflates and the corresponding pyridine base. This slurry allows the  $2e^{-}/2H^{+}$ quinone/hydroquinone redox reactions while suppressing proton reduction in the battery cell. By using strong (acidic) proton donors, the formal potential of the quinone redox reactions is tuned into the potential region in which the PEDOT backbone is conductive, thus eliminating the need for conducting additives. In this all-organic proton battery cell, PEDOT-AO and PEDOT-BQ deliver 103 and 120 mAh g<sup>-1</sup> which correspond to 78 % and 75 %, respectively, of the theoretical specific capacity of the materials at an average cell potential of 0.5 V. We show that PEDOT-BQ determines the cycling stability of the device whilst PEDOT-AQ provides excellent reversibility for at least 1000 cycles. This proof-of-concept shows the feasibility of assembling all-organic proton batteries which require no conductive additives, and also reveals where the challenges and opportunities lie on the path to producing plastic batteries.

### Introduction

Assembling batteries in which the capacity-carrying electrode material consists of organic redox-active molecules is an attractive route towards clean, sustainable, inexpensive electrochemical energy storage.<sup>1-2</sup> Unlike metal-containing batteries that presently power most of everyday life, organic batteries could be produced from renewable sources, and could provide competitive electrochemical characteristics while being safer and easier to recycle at end-of-life.<sup>3-4</sup> The above benefits, together with the vast potential for tailoring properties through organic synthesis, are fueling research on organic matter-based batteries.<sup>5</sup> However, the huge success of and continuous progress in metal-ion battery technology make this a formidable challenge.<sup>6</sup> It is unlikely that this will be an either-or proposition, as energy storage is needed on multiple scales ranging from minute to small electronic devices, up to storage facilities the size of warehouses; of these, some can be stiff while others need to be flexible and even wearable.<sup>7-9</sup> So far, the primary approach to organic battery research has been to replace the inorganic metal oxides used for the cathode in metal-ion batteries with redox-active organic molecules, which are often polymeric to avoid dissolution, while keeping the metal-containing anode and electrolyte.<sup>10-11</sup> Quinones and other carbonyl derivatives and sulphur and organic radicals are primarily used as the redox-active organic compounds.<sup>12</sup> Of these, quinones are particularly attractive because of their high specific capacity, fast 2e<sup>-</sup> redox reactions and structural diversity.<sup>13</sup> Using a metal as the anode maximizes the operating window of the device. However, it also requires the electrolyte to be tailored for metal-ion cycling reactions to avoid side reactions at the anode.<sup>14</sup> and thus it is not necessarily optimal for the organic cathode. All-organic batteries, where the capacity-carrying materials for both the anode and the cathode are organic redox-active molecules, are much rarer. Nishide pioneered this field by using polymeric organic radicals based on N-oxides and phenoxyls to assemble dual-ion-type batteries in which both cations and anions are needed to

charge-compensate the redox reactions at the electrodes.<sup>15</sup> His group also assembled bipolar (i.e. the same material in the cathode and anode) all-organic batteries using organic radicals; they produced dual-ion batteries as well as conventional single-ion batteries in which one ion, tetrabutylammonium, moves between the electrodes in a rocking-chair motion to compensate the charge.<sup>16</sup> Yang and co-workers have constructed bipolar dual-ion batteries based on polyparaphenylene,<sup>17</sup> as well as all-organic Na-ion batteries with polytriphenylamine and poly(anthraquinonyl sulphide) as the positive and negative electrodes, respectively.<sup>18</sup> Yao and co-workers designed a molecular ion battery that shuttled hexafluorophosphate ions (PF<sub>6</sub>) between two redox polymer electrodes.<sup>19</sup> A number of di- and tetra-anionic organic salts based on quinones balanced by Li ions and employed as both anode and cathode material have been investigated, first by Poziot, Tarascon, Dolhem and co-workers,<sup>20-21</sup> and recently by several other groups employing similar strategies and using Li or Na salts of terephthalic acids,<sup>22-23</sup> quinones,<sup>24</sup> and imides.<sup>25-26</sup> Generally, organic molecules are insulators, and all of the above studies used large amounts of conductive additives, often different forms of carbon, e.g., carbon black or carbon nanotubes, ranging from 20 to 80 % by weight. The use of use Li or Na ions as charge-compensating electrolyte ions is prevalent in these studies, with research into the more abundant Na ion gaining prominence. However, there is one ion that is even more abundant, that is lighter and smaller than these, and that binds covalently to anionic organic functional groups: the proton (H<sup>+</sup>). Armand and Tarascon predicted the future development of entirely metal-free all-organic proton batteries,<sup>1</sup> whilst Song and Zhou suggested that a proton battery could consist of a conjugated carbonyl anode (denoted N) and a conjugated carbonyl cathode  $(N'H^+)$ .<sup>5</sup> We have now realized this concept; we have created an all-organic proton battery using the envisioned carbonyl compounds and developed a proton-containing organic electrolyte, in addition to assembling a battery with a conductive polymeric backbone. The all-organic battery has a well-defined charge/discharge potential,

provides discharge capacities close to the theoretical limit, and has excellent rate capability without any conductive additives.

#### **Results and discussion**

The design of the all-organic proton battery in the discharged (1a - top half) and charged (1a bottom half) states is depicted in Figure 1 together with illustrations of the redox reactions and how these processes are followed by different electrochemical techniques (1b, c and d). The capacity-carrying material is based on the two electron/two proton (2e<sup>-</sup>/2H<sup>+</sup>) quinone/hydroquinone (O/OH<sub>2</sub>) redox couple and we used an anthraquinone (discharged/oxidized form: AQ, charged/reduced form: AQH<sub>2</sub>), and a benzoquinone (charged/oxidized form: BQ, discharged/reduced form: BQH<sub>2</sub>) as the negative and positive electrode materials, respectively. The AQ and BQ moieties were attached as pendant groups to a conducting polymer backbone, poly(3.4-ethylenedioxythiophene) (PEDOT), to form the conducting redox polymers (CRPs)<sup>27</sup> **PEDOT-AO** and **PEDOT-BO** (Figure 1a). The conducting backbone ensures facile electron transport throughout the material without any conducting additives while also anchoring the redox group to avoid its dissolution into the electrolyte. Finally, the electrolyte consisted of a slurry of proton donors and acceptors in the form of protonated pyridinium triflate derivates and the corresponding pyridines (Figure 1a – centre). This slurry allows the AQ and BQ  $2e^{-2}/2H^{+}$  redox reaction to occur, with the quinones switching between a carbonyl and an alcohol form, while the charge balance is maintained by shuttling protons between the electrodes in a rocking-chair motion, precisely as in metal-ion batteries.



**Figure 1.** Depiction of the conducting redox polymers (electrode materials), the pyridinebased proton donors and acceptors (electrolyte), and the redox reactions which occur during charge (cyan) and discharge (grey). **a)** The chemical structures of the negative electrode material **PEDOT-AQ** (top left) and positive electrode **PEDOT-BQH**<sub>2</sub> (top right) in the initial discharged state. The redox reactions during charging are shown in cyan as the AQ form is reduced to AQH<sub>2</sub> (bottom left) while, simultaneously, BQH<sub>2</sub> is oxidized to BQ (bottom right), ending in the charged state. The pyridinium and pyridine electrolyte, seen in the middle, enable the transfer of protons from the positive to the negative electrode while the electrons are transported in the external circuit. During discharge the opposite reactions occur, as shown

in grey, resulting in a net flow of protons towards the positive electrode. **b**) The threeelectrode voltammograms of **PEDOT-AQ** (left) and **PEDOT-BQ** (right) showing the redox reactions depicted as charging (cyan) and discharging (grey) as they occur in a battery. The potential difference between the peaks in the voltammograms is the expected cell potential of the battery. **c**) The charge and discharge processes shown as the output from a constantcurrent, two-electrode, galvanostatic, charge-discharge experiment showing plateaus at cell potentials where the redox reactions occur. **d**) A differential capacity plot using the galvanostatic data from c) to illustrate these processes in a way that resembles a voltammetric two-electrode experiment.

Behind this straightforward design lie several challenges. First: conducting polymers are only conductive in certain potential regions, otherwise they are insulators.<sup>28</sup> Thus, to take advantage of the conductivity of the backbone and avoid the use of conductive additives, the redox reaction of the pendant groups, in this case AQ/AQH<sub>2</sub> and BQ/BQH<sub>2</sub>, needs to occur in the conductive region of the backbone. Second: the system requires an electrolyte that allows the pendant group redox reaction to happen reversibly, quickly, and without side reactions within the conducting region of the polymer backbone. We have previously shown that the 2e<sup>-</sup>/2H<sup>+</sup> redox reaction involving BQ attached to a polypyrrole backbone is sustained by using an organic donor (acid) and acceptor (base) as the electrolyte.<sup>29</sup> The resultant quinone redox potential was controlled or tuned by the organic donor/acceptor strength. With a 1:1 ratio of acid to base, the quinone potential could be shifted 0.5 V by varying the pyridinium pK<sub>a</sub> value. PEDOT, which has been shown to provide an accessible and stable fundament in other CRP investigations on organic energy storage, was chosen as the conductive backbone.<sup>30-31</sup> First, we synthesized two functionalized monomers based on 3,4-ethylenedioxythiophene (EDOT), one carrying an AQ pendant group (**EDOT-AQ**) and one a BQH<sub>2</sub> (**EDOT-BQH<sub>2</sub>**)

(see the Supporting Information [SI] for synthetic procedures and full characterization). These were subsequently either electropolymerized onto glassy carbon- (for three-electrode characterization) or graphite current collectors, or chemically polymerized and deposited onto a graphite current collector (see the Methods section for the polymerization conditions and details of the electrochemical investigations). Figures 2a and b show the three-electrode cyclic voltammetry of PEDOT-AQ and PEDOT-BQ in MeCN solutions of different pyridinium triflates and the corresponding free pyridines (0.1 M each) with pK<sub>a</sub> values of: -0.43 (2fluoropyridine), 2.76 (3-chloropyridine), 5.23 (pyridine) and 7.46 (2,4,6-trimethylpyridine). The expected Q/QH<sub>2</sub> redox peak was evident for **PEDOT-BQ** in all electrolytes and, similar to our previous study, the formal potential of the  $Q/QH_2$  reaction decreased by about 60 meV per pK<sub>a</sub> (Figure 2c). A scan rate study revealed mixed diffusion-kinetic behavior for thicker films of both polymers (SI section S5). Interestingly, for **PEDOT-AQ**, there was a significant Q/QH<sub>2</sub> redox peak only in the 2-fluoropyridine electrolyte (Figure 2b). This is in contrast to the monomers in solution where the AQ redox reaction is evident and follows a shift of -58 meV/pK<sub>a</sub> in different pyridine electrolytes.<sup>29</sup> Transferring the polymer-covered electrode from any of the other pyridine electrolytes to cells containing the 2-fluoropyridine electrolyte revealed that the AQ functionality was still active; its redox chemistry was essentially silent in the less acidic electrolytes (see SI section S6 for results from experiments on the monomers and a discussion about charge-trapping phenomena on the oxidation sweep of these polymer films). Monitoring the potential dependence of the conductance on the polymers *in situ* during electrochemical redox conversion using interdigitated array (IDA) microelectrodes (Figures 2d and e)<sup>32</sup> provided the answer to why the AQ redox reaction was silent in the less acidic electrolytes. In the 2-fluoropyridine electrolyte, the conductance onset potential, which coincided with the onset of oxidation of the PEDOT backbone of **PEDOT-AQ**, was just below the formal potential of the AQ/AQH<sub>2</sub> redox reaction. The data obtained from the

EDOT-AQ monomer in solution shows that in the less acidic electrolytes the AQ/AQH<sub>2</sub> redox reaction was well outside the conductive region of the polymer backbone (Figure 2c), In contrast, even the least acidic 2,4,6-trimethylpyridine electrolyte was still not enough to shift the BQ/BQH<sub>2</sub> redox reaction outside the polymer conductivity window. In comparison, there were no peaks associated with the quinone redox reaction in the voltammograms for Li ionand Na ion-containing electrolytes. The reason for this is as discussed above; in a CRP, a redox match between the pendant group redox reaction and the conductive potential region of the conductive polymer backbone is an absolute requirement for successful polymer-pendant group combinations. In Li ion- and Na ion-based electrolytes and with the less acidic pyridinium ions, the BQ/BQLi<sub>2</sub>, BQ/BQNa<sub>2</sub>, AQ/AQLi<sub>2</sub>, AQ/AQNa<sub>2</sub>, and AQ/AQH<sub>2</sub> redox reactions, respectively, occur outside the conductive potential window and the requirement above is not met (Figure 2c). The IDA measurement also revealed that the doping/dedoping process of both polymers was relatively unaffected by the choice of pyridine electrolyte. The attachment of the large AQ pendant groups to the PEDOT backbone caused the doping onset to occur at a higher potential than for the smaller BO, where the doping onset was close to that of unsubstituted PEDOT (SI section S7). Presumably, this variance between the polymers was due to the dissimilar steric bulks of the pendants, resulting in subtle differences in the polymer ordering. Electrochemical quartz crystal microbalance (EQCM) experiments on both polymers revealed a complex uptake and expulsion of pyridinium ions, triflate ions and ion pairs during the doping/de-doping processes. However, during the  $Q/QH_2$  redox reactions, the mass change per charge was very close to one, indicating only uptake or expulsion of protons (see SI section S8). Redox conversion of the pendant group was thus only associated with charge compensation by protons and the mass transport relied only on the diffusion and migration of the small, mobile proton. Unfortunately, like protons in water, pyridinium ions undergo reduction and this process is dependent on the proton activity (Figure 2f). The

 process somewhat overlaps with the AQ to AQH<sub>2</sub> reduction and is detrimental to a battery cell (SI section S9). Recent research into electrolytes for electrochemical energy storage has revealed that it is possible to expand the potential window in which aqueous electrolytes are stable and to suppress proton reduction by employing very concentrated electrolyte slurries.<sup>33-34</sup> We employed a similar technique and utilized an equimolar (1:1) slurry of 2-fluoropyridinium triflate and 2-fluoropyridine without any additional solvent, which significantly shifted the proton reduction to lower potentials (Figure 2f).



**Figure 2**. The three-electrode electrochemical characterization of **PEDOT-AQ** and **PEDOT-BQ**, including *in situ* conductance measurements and galvanostatic reduction of the electrolyte. The different colors indicate the electrolyte used: 0.1 M 2-fluoropyridinium triflate - 2-fluoropyridine in MeCN (black), 3-chloropyridinium triflate - 3-chloropyridine (grey), pyridinium triflate - pyridine (orange), 2,4,6-trimethylpyridinium triflate - 2,4,6-trimethylpyridine (yellow), and 1:1 slurry of M 2-fluoropyridinium triflate / 2-fluoropyridine

without solvent (brown). **a)** and **b)** The voltammograms from **PEDOT-BQ** and **PEDOT-AQ** in the different pyridine electrolytes. **c)** The formal potentials vs. pK<sub>a</sub> of the pyridium ion and its linear dependence on **PEDOT-BQ** (squares) and **PEDOT-AQ** (circles). The half-filled circles and dotted line indicate where the AQ/AQH<sub>2</sub> reaction occurs in the **EDOT-AQ** monomer. The pK<sub>a</sub>-independent formal potentials of the first (filled) and second (empty) BQ/BQLi<sub>2</sub> (stars) and AQ/AQLi<sub>2</sub> (triangle) redox reactions are also shown as references<sup>35-36</sup> The colored regions indicate the conductive potential region for **PEDOT-BQ** (grey) and **PEDOT-AQ** (dashed grey) obtained from IDA measurements. **d)** and **e)** IDA measurements showing the conductance at different potentials from the same polymer film in different electrolytes for **PEDOT-BQ** and **PEDOT-AQ**. **f)** The galvanostatic reduction of the 0.1 M electrolyte solutions and, for comparison, the 1:1 electrolyte slurry (brown) using a graphite working electrode and a similar current density to that used in the battery tests.

Based on the potential difference between the AQ/AQH<sub>2</sub> and BQ/BQH<sub>2</sub> reactions, a cell potential of approximately 0.5 V can be expected from the redox reactions in the threeelectrode setup. We assembled the all-organic batteries in the discharged state, i.e. with **PEDOT-AQ** as the negative electrode (anode) and **PEDOT-BQH<sub>2</sub>** as the positive electrode (cathode) (Figure 1a - top). A swagelok cell was used for the battery tests and a glass microfiber filter wetted with the 2-fluoropyridine electrolyte slurry served as separator (see the Experimental section and SI section S10 for full information and pictures). In order to investigate the properties of each polymer type separately, we assembled cells with significantly more of one of the polymers (n/p ratio 2:1 or 1:2 determined from the peak area of the Q/QH<sub>2</sub> redox reaction in three-electrode cyclic voltammetry of the electrode; see SI section S11 for examples of pre and post voltammograms of the electrodes), which allowed characterization of the limiting material. Constant-current galvanostatic charge-discharge

cycles using different current densities for PEDOT-AQ as the limiting material gave a discharge capacity of 103 mAh g<sup>-1</sup> (78% of the theoretical specific capacity) for the  $AQ/AQH_2$  2e<sup>-</sup>/2H<sup>+</sup> redox reaction at a current density of 70 mA g<sup>-1</sup>, approximately corresponding to a C-rate of C/2 (Figure 3a and b). Note, that the mass used is based on the total deposited mass and energy dispersive X-ray spectroscopy experiments (see the experimental section) indicate remaining electrolyte from polymerization. The discharge capacity remained above 90 mAh g<sup>-1</sup> at current densities up to 400 mA g<sup>-1</sup> (3C) and then gradually decreased to 25 mAh g<sup>-1</sup> at 20 000 mA g<sup>-1</sup> (160 C). A plateau centered at 0.5 V, consistent with the Q/QH<sub>2</sub> redox reaction, was apparent, contributing to most of the capacity (see Figure 3b and SI section S12 for differential capacity plots). Figure 3a shows a competing, irreversible process at low current densities during the charging; the majority drew close to the cut-off potential (0.8 V in this case, SI section S13), indicating that it occurred at lower potentials than the reduction of AQ to  $AQH_2$ . We attribute this to proton reduction partly caused by the electrode imbalance, as a large capacity excess on the positive cathode forced the potential of the anode into the proton reduction potential region (Figure 2f). However, this process did not adversely influence the stability of the anode and, at higher current densities; the coulombic efficiency was close to 100%. PEDOT-AQ was very stable up to some 100 cycles at 400 mA g<sup>-1</sup>, giving a discharge capacity of 88 mAh g<sup>-1</sup> (66 % of theoretical) with a constant cell potential before it dropped off and reached 70 mhA  $g^{-1}$  after 150 cycles (Figure 3c). Differential capacity plots of these results effectively demonstrate the electrochemical process occurring and show the capacity associated with the  $Q/QH_2$  redox reaction centered at 0.5 V and how it changes during cycling (Figure 3d). Post-battery threeelectrode cyclic voltammetry of the electrode revealed that primarily PEDOT capacity remained on the positive electrode while PEDOT-AQ was more or less unaffected. PEDOT-BQ was thus responsible for the loss of capacity (SI Figure S17). In fact, the same PEDOT-

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AQ electrode could be used repeatedly in several battery cells, exchanging the cathode, and was stable for at least 1000 cycles (SI Figure S18). For PEDOT-BQ it was possible to achieve a capacity of 120 mAh g<sup>-1</sup> (75%, at 140 mA g<sup>-1</sup>, 1C), gradually decreasing to about 40 mAh  $g^{-1}$  at 14000 mA  $g^{-1}$  (100 C). In the stability test performed at 600 mA  $g^{-1}$ , the battery delivered an initial capacity of 90 mAh g<sup>-1</sup> (56%), subsequently decreasing steadily to 40 mAh g<sup>-1</sup> over the next 125 cycles (Figure 3g and h). At lower current densities, the drop-off was faster and post-battery three-electrode investigation of the electrode showed an essentially unchanged PEDOT capacity with a minor broad O/OH<sub>2</sub> peak (SI Figure S19). However, when PEDOT-BQ was used as the limiting material, the coulombic efficiency improved at low current densities; this strengthened our belief that reduction of protons mainly occurs at lower potentials reached after completing the AQ to AQH<sub>2</sub> reduction. To summarize, high coulombic efficiencies for the all-organic proton battery with concentrated acid-base electrolytes can be achieved by avoiding depletion of the negative electrode. The cause of capacity fading during cycling has been associated with processes occurring at the positive electrode, and stabilizing the BQ group is expected to improve cyclability. Finally, the battery device without conductive additives, as presented in this work, demonstrated good rate performance that could be traced to fast proton cycling and the synergy between the pendant group redox chemistry and the conducting polymer backbone, accomplished by redox matching.



**Figure 3**. Battery cell characteristics measured in a two-electrode setup with **PEDOT-AQ** as limiting material (top panels) and **PEDOT-BQ** as limiting material (bottom panels). a) Specific capacity for the charge (cyan) and discharge (grey) processes at different current densities for **PEDOT-AQ**. b) Selected discharge curves, 2<sup>nd</sup> cycle in the set of 4, from a). The dashed cyan curve was the 38<sup>th</sup> cycle. c) Stability cycling at 400 mA g<sup>-1</sup> showing the specific capacity (left axis) for the charge (cyan) and discharge (grey) processes as well as the coulombic efficiency (black, right axis). d) The corresponding differential capacity plots from c) for the 2<sup>nd</sup>, 50<sup>th</sup>, 100<sup>th</sup> and 150<sup>th</sup> cycles. e) Specific capacity at different current densities for **PEDOT-BQ**. f) Selected discharge curves, 2<sup>nd</sup> cycle in the set of 4, from e). The dashed cyan curve is the 28<sup>th</sup> cycle. g) Stability cycling at 600 mA g<sup>-1</sup> showing the specific capacity (left axis) for the charge (grey) processes as well as the curve is the 28<sup>th</sup> cycle. g) Stability cycling at 600 mA g<sup>-1</sup> showing the specific capacity (left axis) for the charge (cyan) and discharge (grey) processes as well as the coulombic efficiency (black, right axis). h) The corresponding the specific capacity (left axis) for the charge (cyan) and discharge (grey) processes as well as the coulombic efficiency (black, right axis). h) The corresponding differential capacity form g) for the 2<sup>nd</sup>, 25<sup>th</sup>, 75<sup>th</sup> and 125<sup>th</sup> cycles.

#### Conclusions and further perspectives

In this proof-of-principle study, we have shown how two quinone-based CRPs can be used as positive and negative electrode materials to assemble a proton battery by employing a slurry of organic acids and bases as an ionic liquid-type electrolyte. While an aqueous electrolyte could theoretically also function with these electrode materials, the redox reaction of **PEDOT-AQ** becomes very slow in an acidic aqueous electrolyte. We speculate that the large hydrophobic AQ unit was causing this problem (SI section S14), and are working to solve this issue. Importantly, in the presented batteries, no conductive additive was needed when the redox reaction of the capacity-carrying pendant groups overlapped with the conductive potential region of the polymer backbone (Figure 4). This is in stark contrast to previous metal-organic and all-organic batteries in which it has not been unusual for the organic electrode material to consist of at least 50 wt% conductive additives. Much work remains to be done to realize industrializable devices; the cell potential is limited, the electrolyte can likely be developed further, and the stability of the cathode material needs to be improved. On the other hand, the stability and rate capability of **PEDOT-AO** show the potential of this concept. Importantly, the presented battery technology is highly versatile (Figure 4 - panels a, b, and c). First, the developed electrolyte system makes it possible to shift the formal potential of the pendant redox group without significantly affecting the conductive region of the polymer by varying the donor/acceptor strength of the pyridine electrolyte through substitution. Second, quinones can function as either anode or cathode Third, there is wide structural diversity in, and many commercially available, guinone derivatives. Fourth, any combination of a conductive polymer backbone and a capacity-carrying group is, in theory, possible. These factors allow for a high degree of tailoring and a large design space with opportunities to increase the conductive region, and to find suitable, stable combinations of capacity-carrying units for the desired application and for maximal cell potential. Indeed,

quinones substituted with electron-withdrawing groups have significantly higher redox potentials than their unsubstituted analogs.<sup>37-39</sup> Utilizing such materials as the cathode and keeping the AQ anode could theoretically create a proton battery with a cell potential well above 1 V, bringing us closer to competitive and truly plastic electrochemical energy storage (Figure 4 – panel c).



 **Figure 4**. Depiction of the versatile nature of the CRP and electrolyte concept presented herein. The formal potential of the quinone redox reaction is approximately marked by its chemical structure while the conductive and insulating regions of PEDOT are depicted below (also marked with a dashed line). The different background colors correspond to the electrolyte slurry used and show the approximate point at which the potential pyridinium reduction occurs (cyan – 2-fluoropyridine, purple – pyridine). The plus and minus signs indicate the use of Q as the positive or negative electrode. **a)** Shows the conditions we used to provide a cell potential of ~0.5 V. **b)** Shows how BQ can be used as anode in a pyridine-based battery and how the undesired proton reduction shifts to lower potentials. Note that the AQ moiety is outside of the conductive region, thus demonstrating that there is design space both below and above the BQ redox reaction which can be accessed through substituents could increase stability and/or cell potential. **c)** Shows how electron-withdrawing substituents could

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be used to allow batteries with cell potential above 1 V. Note also that there are opportunities to extend the cell potential even further if the conductive polymer region can be extended to more negative potentials.

#### Experimental

#### **General considerations**

Both three- and two-electrode experiments were performed under ambient conditions. MeCN was of anhydrous quality and stored over activated 4 Å molecular sieves. Electrolyte solutions were purged with N<sub>2</sub> before measurement. A Pt wire was used as counter electrode and in organic solutions the reference electrode consisted of an Ag wire submerged in an AgNO<sub>3</sub> solution of the electrolyte which was kept in a separate compartment. Three-electrode potentials were measured and referenced against the ferrocene redox couple (vs.  $Fc^{0/+}$ ) which is at 3.25 V vs.  $Li^{0/+40}$ .

#### Three-electrode investigations

Electropolymerization onto glassy carbon disk electrodes ( $\emptyset = 3 \text{ mm}$ ) was achieved by cyclic voltammetry on 10 mM solutions of **EDOT-AQ** or **EDOT-BQH<sub>2</sub>** (up to 1.0 V) at 50 mV/s or 100 mV/s in 0.1 M TBAPF<sub>6</sub>/MeCN. Polymerization was also achieved with the same result using 0.1 M pyridinium triflate/MeCN. Note that, in the presence of an electrolyte containing the free pyridine, no polymerization occurred. Polymerization onto the IDA microelectrode was performed with a 1 mV bias. Conductivity was subsequently measured using a 10 mV bias at 10 mV/s. Monomers where investigated using a 2 mM solution of **EDOT-AQ** or **EDOT-BQH<sub>2</sub>** using square wave voltammetry. Both forward and backward scans were recorded and the mean of these are reported (SI section S6).

#### Two-electrode battery cells

Circular current collectors ( $\emptyset = 13 \text{ mm}$ ) were cut from a graphite sheet and the back side was covered with a polyamide tape (Kapton) under which a rectangular piece of graphite was attached to allow connection to the electrode holder during electropolymerization (see SI section S10 for pictures). Electropolymerization was achieved using the same three-electrode setup as above at 25 mV/s and 10 mM EDOT-AQ (up to 1.0 V) whilst EDOT-BQH<sub>2</sub> needed slightly higher potentials (up to 1.15 V). Subsequently, the electrodes were cycled in the 2fluoropyridine electrolyte and stopped in the discharged state, rinsed with MeCN and dried at 50°C under vacuum overnight. Chemical polymerization of EDOT-AQ was achieved using a 10 mM monomer solution in MeCN with slow addition of 3 eq of FeCl<sub>3</sub> (anh) dissolved in a minimal amount of MeCN. After stirring for 1 h, EtOH was added, followed by centrifugation and repeated washing with water and EtOH to yield a black powder. The powder was mixed with carboxymethylcellulose (CMC) and styrene-butadiene rubber (SBR) binders (90:5:5 by weight) in water, ground, and applied to the current collectors before drying at 50 °C under vacuum overnight. The electrodes were then characterized and put in the discharged state before drying again. Under these conditions, EDOT-BQH<sub>2</sub> produced only short polymers that were poorly conducting; electropolymerized material was used for the positive electrode. Electrochemically and chemically polymerized **EDOT-AO** were completely interchangeable, producing the same electrochemical response. The electrode loading (for the limiting electrode) was between 0.5 - 1.5 mg with an n/p ratio of approximately 1:2 (negative limiting) or 2:1 (positive limiting). Scanning electron microscopy (SEM) on electrode cross sections of the electropolymerized material gives a thickness of between 5-10 µm for **PEDOT-BO** while **PEDOT-AO** is denser at 2-4  $\mu$ m. Energy dispersive X-ray spectroscopy (EDX) indicate that  $TBAPF_6$  electrolyte remains in the electrode even after complete dedoping of the polymer film and extensive washing and constitutes between 10-20 wt% (SI

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section S15). The battery cells were assembled using a swagelok cell and the electrodes were separated by a glass microfiber filter paper (grade GF/A) wetted with the equimolar 2-fluoropyridinium triflate – 2-fluoropyridine electrolyte slurry. The cut-off potentials for the galvanostatic cycles ranged from 0 V to 0.8 V.

#### Associated content

#### **Supporting information**

The Supporting Information is available free of charge on the ACS Publications website at DOI:

Synthetic details and full characterization, further electrochemical results from the scan rate study, charge trapping data, EQCM data, full description of the battery setup, pre- and post-battery cyclic voltammograms of the electrodes, and differential capacity plots of the organic battery are supplied.

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#### Notes

The authors declare no competing financial interests.

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