Rikard Emanuelsson

Proton batteries – Final report for 17-344

Summary:

In this project all-organic proton batteries have been studied targeting stable charge/discharge at 1 V cell voltage. A number of conducting redox polymers carrying different quinone redox units have been synthesized, electrochemically characterized, and studied as such proton batteries. The approach presented in this report show which chemical features are required and what other considerations are important to achieve both high stability (rechargeability) and cell voltage for such proton batteries. Both aqueous (water) and organic containing proton electrolytes have been studied to explore its effect on the battery characteristics which revealed markedly different results.

Background:

Assembling rechargeable batteries where the capacity carrying electrode material consists of organic redox active molecules is an attractive route towards clean, sustainable and inexpensive electrochemical energy storage.[1-2] Unlike the metal-ion batteries that presently power most of our everyday life, organic batteries would be produced from renewable sources, provide competitive electrochemical characteristics whilst being safer and easier to recycle at end-of-life.[3-4] The above benefits, along with the vast possibility to tailor properties through organic synthesis, fuel research on organic matter based batteries.[5] However, the huge success and continuous progress in Li-ion battery (LIB) technology makes this a formidable challenge.[6] Likely this is not an either-or proposition as energy storage is needed on multiple scales, ranging from minute, to small electronic devices, up to grid facilities the size of warehouses. Some can be rigid, like the LIBs of today, while others would need to be flexible or even wearable. For example, the rapid development of "internet-of-things", where more and more of our everyday items becomes "smart" will require energy storage where in many cases LIBs are unwanted or unsuitable. Until now the most successful examples of all-organic battery systems are found in flow-batteries, these are aimed for large grid applications and involves pumping large volumes of electrolyte. Most research into conventional rechargeable organic batteries primarily utilizes metal-ions and form mixed organic/inorganic batteries.

Results and discussion:

The starting point for this study reported herein is our results from 2017 where we presented a proof-of-concept for such a proton battery (Figure 1)[7]. The study involved using a conducting polymer base to which quinones as capacity carriers are attached.
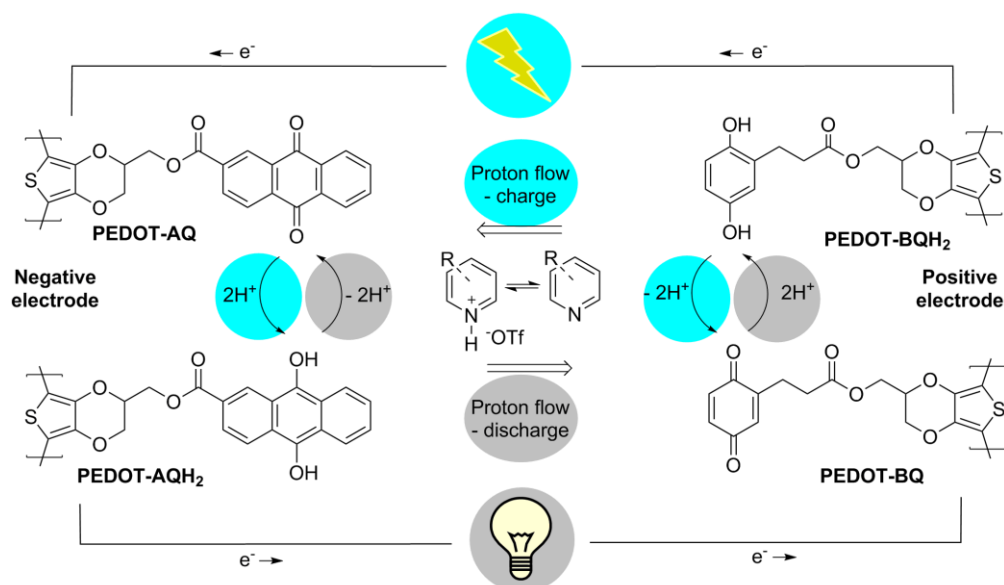

Figure 1. Schematically depicting the conducting redox polymers (electrode materials), the pyridine based proton donors and acceptors (electrolyte), and displaying the redox chemistries which occur during charge (cyan) and discharge (grey). The chemical structures of the negative electrode material **PEDOT-AQ** (top left) and positive electrode **PEDOT-BQH₂** (top right) set in the initial discharged state. The redox reactions during charging are shown in cyan as the AQ form is reduced to AQH$_2$ (bottom left) while simultaneously BQH$_2$ is oxidized to BQ (bottom right) ending in the charged state. The pyridinium/pyridine electrolyte, seen in the middle, enables 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.

The initial challenge addressed in the present study was to increase the cell voltage of such a battery. In chemical terms this means increasing the difference between the redox reaction of the anode and the cathode (Figure 2). The thermodynamic stability of water and protons and the conductive potential region of the polymer backbone are the limiting factors.
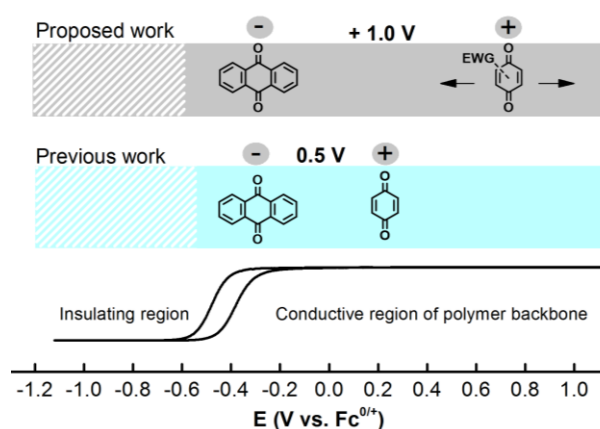

Figure 2. Showing the potential region where the polymer backbone is insulating or conductive (bottom) and where the AQ and BQ redox reactions of our original study are located (cyan). The grey area show the present study with an increased cathode formal potential.

Thus, according to Figure 2 there is more design space on the cathode side and this is where the most effort has been made. We have however also investigated alterative anodes to minimize unwanted proton reduction side reactions which compromises the battery stability. These materials have been synthesised, characterized and electrochemically tested to compare their redox potential relative to our previously report benzoquinone (**1**). These include quinone derivatives of flouro (**2**), difluoro (**3**), bis(trifluoromethyl) (**4**), nitro (**5**), dinitro (**6**) phthalimide (**7**), naphthazarin (**8**) and quinizarin (**9**) as potential cathodes, and methylnaphtquinone (**10**) aminenaphtquione (**11**), indole (**12**) and tert-butylhydroquinone (**13**). All attached through different chemical linkers (ether, thio, ester, alkyne etc) to **EDOT** unit which upon polymerization form the conducting polymer (Figure 3).
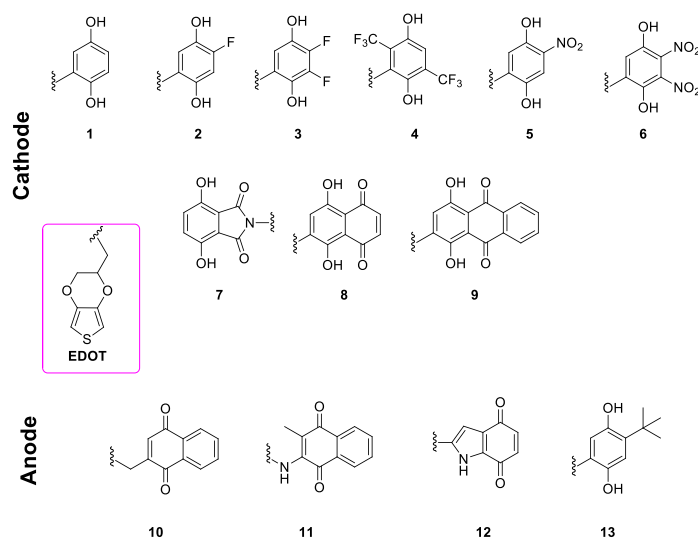

Figure 3. The capacity carriers investigated, top cathode materials and bottom anode materials.

Scheme 1 display a selection of the synthetic procedures employed to attach the redox active charge carrier to the polymerizable EDOT unit. We have developed reliable synthetic protocols to produce the EDOT unit with a range of suitable functional groups for attachment of the tailored quinone. Thus, much effort has been spent on synthesising different capacity carriers. In order to increase the oxidation potential (top panel of Figure 2) of the quinone a range of quinones with electron withdrawing groups have been targeted. Sonogashira type palladium/copper catalysed coupling reactions (top left in Scheme 1) as well as classical polar reactions such as esterification and etherification (top right in Scheme 1) were combined with alkylations of thiols and amines as well as amide formations (bottom in Scheme 1). These compounds have been characterized using standard organic chemistry techniques such as NMR, IR and MS to confirm their structure.
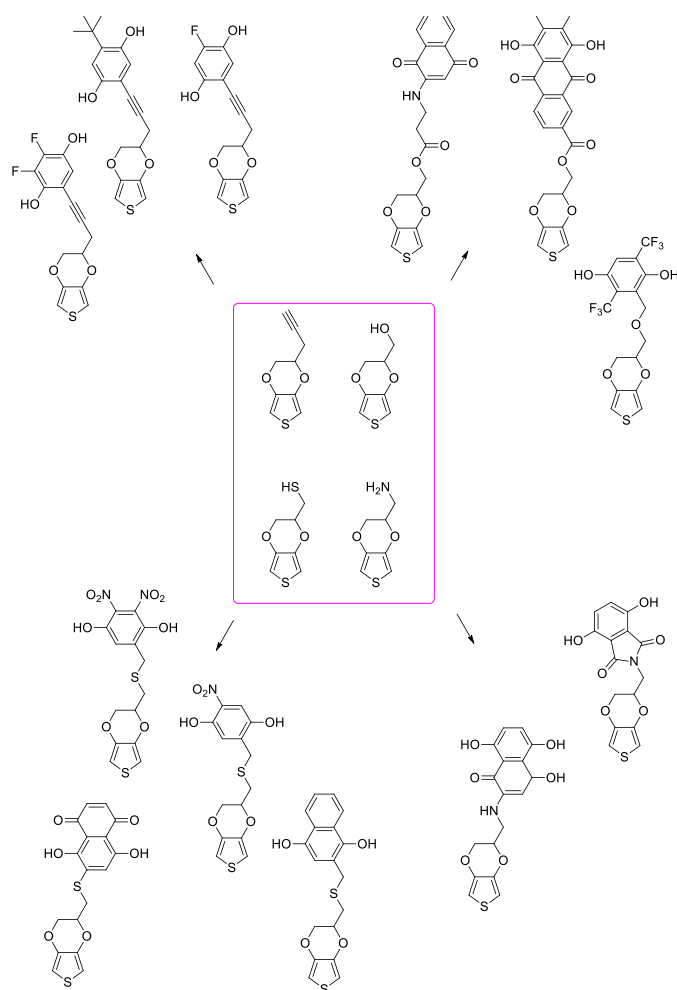
Scheme 1. The different derivatives of EDOT (centre) and examples of the diverse reactions employed to couple the polymerizable unit to the capacity carrier.

The compounds were then subject to standard electrochemical techniques to determine their electrochemical characteristics in both aqueous and organic electrolytes. I.e., we tested the compounds individually to determine stability and formal potential of the redox reaction. Surprisingly, in acidic aqueous electrolyte there is almost no potential difference between our previously reported **1** and these of **2**, **3** and **4** carrying increasingly number of strongly electron withdrawing fluorine atoms (Figure 4). The difference is a maximum of 100 mV which is insufficient to achieve the targeted 1 V battery. Capacity carriers **2-4** all rely on electronic sigma-withdrawing effects, i.e. electrons are withdrawn through sigma bonds. Compounds **5-9** instead incorporates functional groups that also withdraws electrons through the pi-system. This seems to be the key to achieve higher oxidation potentials. Still, these compounds only achieve an approximately 250 mV increase in aqueous electrolytes, much lower than expected. On the other hand, tuning the oxidation potential to lower potentials (relative to **1**) is straightforward and the reported structures **10-14** covers the entire range between our previous reported compounds. In organic protic electrolytes, the same system used as in our previous study, a larger potential difference is found and gradual increase of oxidation potential in found across all compounds. Close to 500 mV for the most electron withdrawing **8** and **9** and derivatives thereof. We have initiated a computational study to try to understand these differences between water and organic electrolytes. Initial results from these studies reproduce this difference, however, the origin needs further

investigations. If this effect can be understood and combated it would allow assemble of truly high-powered water based batteries, something which increase the environmental value of these batteries even further.
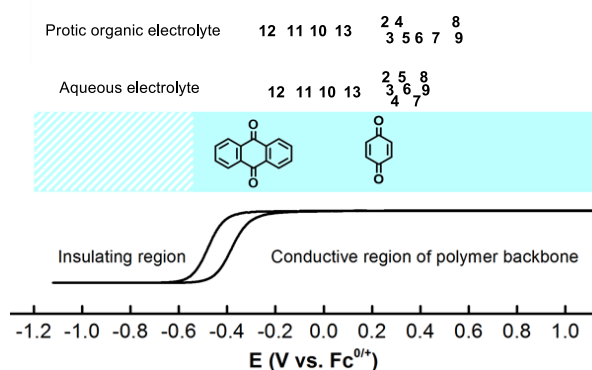

Figure 4. A schematic summary of the formal potential of the investigated quinones relative our previous studies, in aqueous and protic organic electrolyte. The formal potential of compound **2**-**13** is placed on a potential scale relative to our previously studied compounds.

Next, selected quinones were chosen to assemble a range of all-organic batteries. While maximum cell voltage, i.e. as large difference between the formal potential of the redox reactions of the anode and cathode is of course always desirable, we choose to study a range of batteries to find the optimum mix of power and stability. Figure 5 display the characteristics of such a battery while the inset show the flexible nature of the device. We are currently testing these batteries and the results are not yet final, however, as can been seen from Figure 5 we can achieve a quite remarkable 800 cycles with only a 6 % drop in capacity. This battery consists of compound **11** as anode and **5** as cathode. Different combinations of cathodes and anodes are currently in testing employing both aqueous and organic electrolytes. The cell voltage of these batteries ranges from 0.4 up to 1.0 V. Stability is excellent in the lower range while presently being somewhat lower in the high voltage range, however, we are currently assembling batteries excluding even traces of oxygen as oxygen is detrimental to stability. The nitro group (**5** and **6**) so far seems unstable under these conditions while particularly compounds **8** and **9** are very promising.
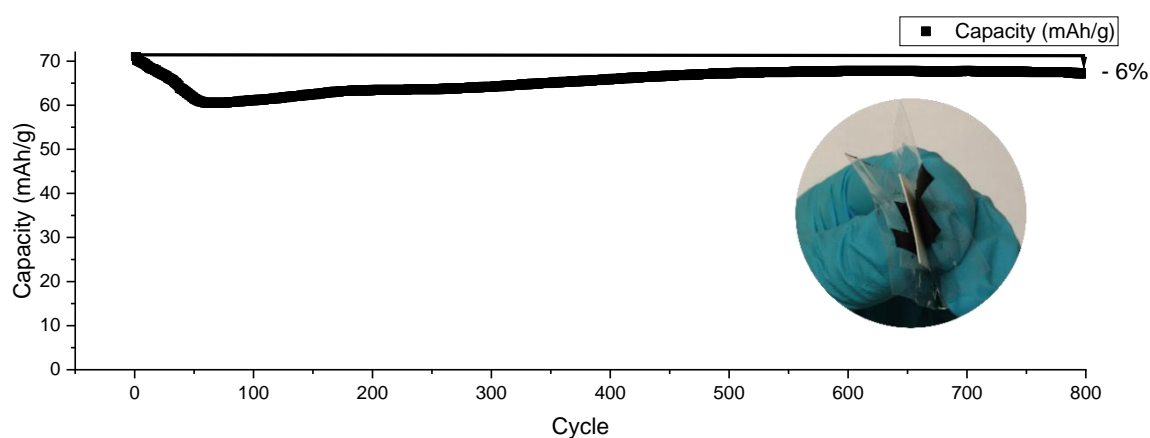

Figure 5. The characteristics of a 0.5 V battery in aqueous electrolyte and a photo (inset) of the electrodes used.

An interesting finding during these studies is the realization of how fast these batteries can be charged. There is practically no difference in the capacity of the battery using ten times the standard current density (Figure 6). Furthermore, it is also possible to apply a set potential and charge the batteries this way. Such charging allow a battery that is discharged over several hours to be fully charged in less than 10 min. This will be one of the main points in the coming articles covering this project. Charging time is one of the significant downsides of Li-ion batteries which is very difficult to improve as it involves intercalation of ions into the anode and cathode. The flexible and wholly organic nature of these batteries could make them ideal for energy applications in packaging, clothes or other materials where inorganic batteries currently are unsuitable. We are currently investigating how to scale these systems so that the energy density reaches commercially interesting values rather than laboratory scale. Thus, we are currently testing batteries in the 1-5 mAh range which would be enough to power simple devices for a considerable time. However, these results are not yet final and likely some work will be needed in the nano-structuring of these materials to reach 100% of all capacity carriers. In total this project and related studies will generate one patent and five publications in the coming months. [8-13]
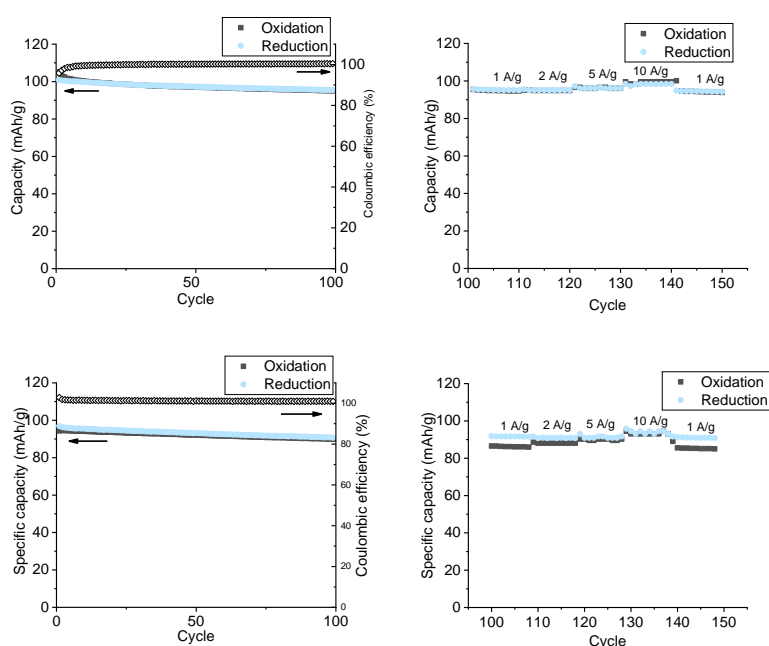

Figure 6. Cycling stability for two further batteries (0.4 and 0.7 V) and the capacity during different current densities (so called C-rate study). Note, first the battery is charged/discharged 100 times, then the C-rate study is performed for the next 50 cycles.

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