Quinone pending groups on polypyrrole affect the backbone doping behavior

1 Introduction

Quinones have been investigated as the active material in environmentally friendly lithium ion battery cathodes.1 Many studied compounds dissolve in the electrolyte, and exhibit slow kinetics due to the poor electron transport between individual molecules. We have suggested that functionalizing a conducting polymer with quinone moieties would prevent dissolution, while also providing a conductive matrix that enables faster kinetics, solving both these problems.2 We present a series of polymers with hydroquinone pending groups on a polypyrrole (PPy) backbone. These polymers function both as conducting polymers and as redox polymers, depending on the potential region. The linker unit between the two systems was varied in order to investigate its influence on the electrochemical properties. The pending groups have some interaction with the PPy backbone, and the redox reactions of each system influence the other. Some observed properties, such as a doping reversal phenomenon, have to our knowledge not been reported before. The nature of these properties was investigated in some detail using in situ spectroscopic and EQCM methods during electrochemical cycling.

2 Results

• Pyrrole monomers attached to hydroquinone via various linkers were synthesized, and polymerized by cyclic voltammetry (CV) into conducting redox polymers P1 - P4 (Scheme 1).
• All polymers were electrically conducting and exhibited capacitive charging of the PPy backbone, as well as a reversible redox reaction of the quinone pending groups (Figure 1).
• The linker unit affected the PPy doping onset potential, but not significantly the quinone redox potential (E°), see Table.
• In situ UV/vis/NIR spectroscopy during redox cycling revealed that the doping of the PPy backbone is halted at E°, during the pending group redox reaction, for P1, P3 and P4. For P2, with a larger quinone concentration, the doping rate was even reversed (Figure 2).
• Electrochemical quartz microbalance (EQCM) experiments reveal that, in addition to the counter ion incorporation into the film during PPy backbone oxidation, there is a large decrease in mass during the quinone oxidation (Figure 2). The decrease is dependent on the solvent polarity and the charge drawn in the CV.
• Scanning electron microscopy (SEM) shows a homogeneous and flat morphology of the polymer films, with some typical PPy “cauliflower” structures (Figure 3).

3 Discussion

In situ techniques gave some insights into the properties of quinone-substituted polypyrrole derivatives with different linker units, during redox cycling. Oxidation of the pending groups decreases the polarity of the matrix, increasing the energy of the charged bipolarons, which leads to an interesting doping reversal phenomenon. Another consequence is a mass decrease during quinone oxidation, due to the expulsion of polar electrolyte, which varies with the polarity of the solvent. It is also possible that the quinone moieties pack when oxidized, leading to a contraction of the film, and torsion of the PPy backbone. The doping reversal cannot be an effect of the electron affinity of the pending groups, since no big differences are observed with different linker units. The polymerizability and PPy onset doping potential vary within the series, however, and are likely due to different levels of torsion in the monomers and polymers, respectively.

4 Conclusions

• A series of novel pyrrole-quinone polymers behave as conducting redox polymers, with remarkable little influence of the linker unit on their properties during redox cycling.
• The rate of PPy backbone doping was halted or reversed during the quinone conversion, leading to the possibility of utilization of the quinone charge while keeping the doping level constant.
• We attribute this, previously unknown, phenomenon to a polarity decrease upon hydroquinone oxidation, which increases the energy of the charged bipolarons. This is supported by the fact that observed mass changes are dependent on the solvent polarity.

References

Scheme 1. Synthesis routes for the pyrrole-quinone polymer series. P2 has a higher degree of quinone functionalization than P1. TIPS = Pyridyl; THF = Me2CO; R = Me (P1) or H (P2); a) Pd(PPh3)4, KCOC, Toluene, H2O, b) TBAF, THF (P2: AcOD; c) 1) CV; MeCN: P1; 2) BBr3, DCM; d) BBr3 (AcOD; e) Pd(PPh3)4, NO2, 2-methylimidazole, MeCN; Toluene; f) TBAF, THF; g) 1) CV; MeCN; 2) BBr3, DCM; h) Me3SiCl, Cu, THF; i) Pd(Ph3P)4, K2CO3, THF; j) Pd(Ph3P)4, 2-chloro-2-methyl-3-pentanone, i-BuLi, Et2O; k) Cu, THF; l) 1) CV; MeCN; 2) BBr3, DCM.

Figure 3. SEM micrographs of P2. Most of the surface is flat features < 100 nm) with some “cauliflower” elements overlayed on this homogeneous morphology.

Figure 2. Top: Absorbance at 1000 nm during an oxidation sweep of unsubstituted PPy and P1-P4. At the quinone oxidation potential, the doping rate reverses (P2) or halts (other). EQCM during an oxidation sweep shows incorporation of anions at low potentials, and a large mass decrease coinciding with the quinone oxidation.

Figure 1. Cyclic voltammograms of P1-P4 in aqueous electrolyte (pH 2) showing both the PPy backbone doping and the quinone pending Group redox reaction.

Quinone pending groups on polypyrrole affect the backbone doping behavior.

Christoffer Karlsson*, Hao Huang*, Li Yang*, Maria Strömme*, Adolf Gogoll*, Martin Sjödin*
*‘Nanotechnology and Functional Materials, Department of Engineering Sciences, The Ångström Laboratory, Uppsala University, Box 534, SE-751 21 Uppsala, Sweden;’ Department of Chemistry - BMC, Biomedical Centre, Uppsala University, Box 576, SE-751 23 Uppsala, Sweden
Christoffer.Karlsson@angstrom.uu.se 247th ACS National Meeting, Dallas, TX, March 2014 - “Chemistry & Materials for Energy”