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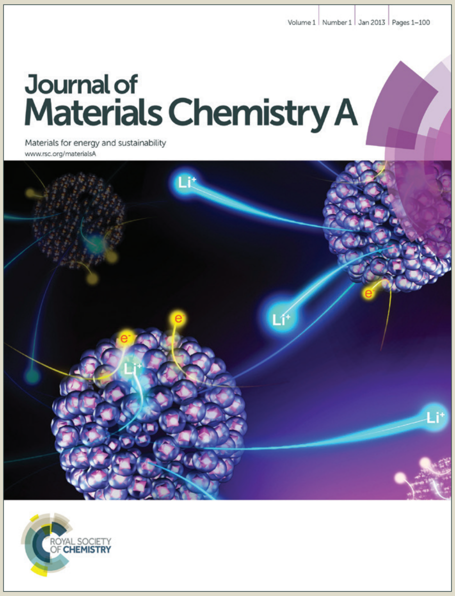

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PolyTCAQ in organic batteries: Enhanced capacity at constant cell potential using two-electron-redox-reactions

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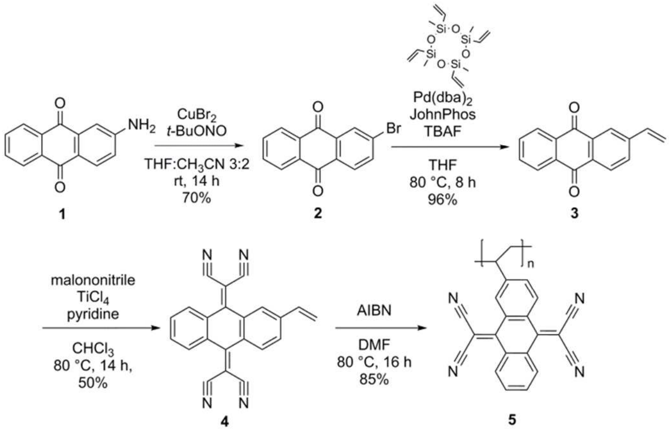
The application of polymers bearing tetracyano-9,10-anthraquinonedimethane (TCAQ) units as electrode materials in organic batteries enables one narrow charge discharge plateau due to the one two-electron-redox-reaction of the TCAQ core. Li-organic batteries manufactured with this polymer display a repeatable charge/discharge characteristics associated with a capacity of 156 mAh/g and a material activity of 97%.

Polymers with pendant redox-active groups have been employed in different organic electronic devices such as solar cells, organic LEDs and, recently, in organic batteries.[1-2] The utilization of redox-active polymers instead of heavy metals as battery electrodes is highly attractive with regard to recyclability and sustainability.[3] Additionally, polymeric materials for organic batteries have received much attention because of their beneficial properties such as flexibility, lightweight and their cycling performance.[4] A large number of polymers with different redox-active groups have been employed as active material in lithium and/or all organic batteries. From an electrochemical point of view, these polymers can be divided into two main groups, depending on the number of electrons being involved in the electrochemical reaction: (I): A significant number of polymers bear redox-active groups performing only a one-electron-reaction. They mainly consist of persistent organic radicals, like nitroxyls,[5-12] galvinoxyls[13] and redox-active molecules such as carbazoles,[14] triarylamines[15] or phthalimides.[16] Batteries manufactured from these polymers display a privileged charge/discharge behavior with only one plateau, but their theoretical capacity is limited in consequence to their one electron redox process and the molar mass of the repeating unit. For example poly(2,2,6,6-tetramethylpeperidine-N-oxyl-4-vinyl ether) (PTVE) features a theoretical capacity of 135 mAh/g,[17] poly(galvinoxylstyrene) of (51 mAh/g) and poly(N-vinylcarbazole) as well as poly(triphenylamine) both exhibit a theoretical capacity of 111 mAh/g. (II): The second group consists of polymers with redox-active groups whose redox reaction involves two or more electrons. These polymers feature higher capacities, but their redox reactions are dependent on each other and, therefore, can occur at different potentials, often leading to one broad respectivly (*resp.*) multiple charge-discharge plateaus. This behavior is adverse in electric devices that ask for a stable cell-voltage. Polymers bearing carbonyl compounds,[18] poly(imides)[[16] or tailor-made radicals are examples for the second group of polymers.[10,19] For instance, polymer-bound pyrene-4,5,9,10-tetraone features a high theoretical capacity of 263 mAh/g, but the charge-discharge plateau is spread over 1.5 V.[20] Exceptions are polymers with pendant anthraquinone groups like poly(2-vinylanthraquinone).[21] The redox reaction of the anthraquinone occurs in a two-electron-wave.

To provide an alternative to overcome these shortcomings we designed poly(2-vinyl-11,11,12,12-tetracyano-9,10-anthraquinone-dimethane (polyTCAQ) as novel redox-active polymer bearing TCAQs units as pendant groups.[22] These redox-active units feature, due to their special molecular design, one reversible two-electron-redox-reaction.[23] Combining this electrochemical feature with the



Scheme 1: Schematic representation of the synthesis of polyTCAQ **5**.

introduction of a low molar mass polymerizable vinyl group into the TCAQ system, a new monomer with a theoretical charge-discharge capacity of 160 mAh/g and one charge/discharge plateau was created.

Monomer **4** was obtained in a straightforward three step synthesis (Scheme 1). The amino group of commercially available 2-aminoanthraquinone **1** was transformed into 2-bromoanthraquinone **2** applying a modified Sandmeyer reaction.[24] The vinyl group was introduced by the application of the Hiyama reaction in excellent yields applying Pd(dba)$_2$ as palladium source and JohnPhos as ligand. The carbonyl functionalities of the 2-vinylanthraquinone **3** were transformed to dicyanomethane groups under Knoevenagel conditions to yield monomer **4**. PolyTCAQ **5** with a molar mass of M_n = 26,400 g/mol (M_w/M_n = 1.87) was prepared by free radical polymerization by which the molar mass can be adjusted by the choice of the appropriate solvent. AIBN was used as initiator and DMF as solvent.

The solubility of polymers in an electrolyte is, besides the redox behavior, one of the decisive factors for their application as active electrode material in organic batteries. Too short polymer chains may dissolve in the electrolyte either in the charged or the discharged state and, thereby, lead to capacity loss. In consequence of the low monomer solubility in a large range of common solvents, the polymerization in benzene, toluene or THF lead either to precipitation of the polymer and/or to low yields (see supporting information). Polymer **5** obtained from polymerization with DMF as solvent is soluble in *N*-methylpyrrolidone and insoluble in propylene carbonate. A cyclic voltammogram obtained for monomer **4** in propylene carbonate solution features only one reversible redox wave. As shown in Figure 1a the expected two one-electron-redox-reactions coincide as one two-electron-redox-reaction, because the structure of the radical anion is twisted and therefore destabilized. The gain of the second electron leads to rearomatization and a planar structure. Hence, the redox potential of the first reduction is lower and both reductions occur at the same potential.[23] Monomer **4** exhibits one two-electron redox reaction wave at □0.64 V *vs.* Fc/Fc$^+$ (Figure 1b), which is in good agreement with published literature derivates (□ 0.58 V).[26]

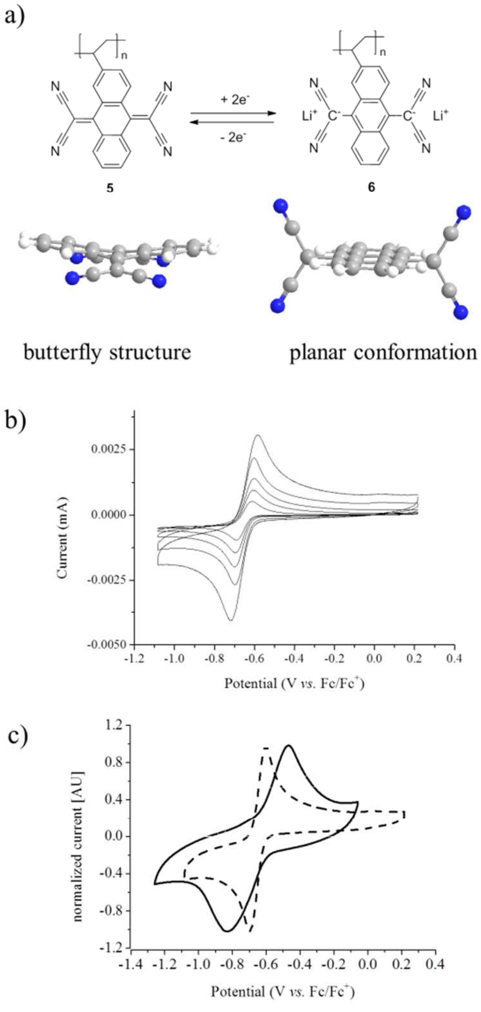


Figure 1: a) Schematic representation of the redox couple of polyTCAQ (**5**). b) Cyclic voltammogram of monomer **4** in propylene carbonate, 0.1 M lithium perchlorate at different scan rates (10, 25, 50, 100 and 250 mV/s, respectively). c) Normalized cyclic voltammograms of the monomer **4** in solution (dashed line) and a polymer-composite electrode (solid line) (10/80/10 wt% **5**/VGCF/PVdF) in propylene carbonate, 0.1 M lithium perchlorate.

Since most redox-active polymers feature low intrinsic conductivities, the electrochemical behavior of polymer **5** was investigated as composite layer with carbon nanofibers (VGCF) as conducting and polyvinyldene fluoride (PVdF) as binding additive. This composite electrode was prepared by adding a solution of polymer **5** in NMP (10 mg/mL) to the additives (10/80/10 wt% **5**/VGCF/PVdF). The resulting slurry was mixed, spread onto graphite foil and dried under vacuum. A cyclic voltammogram obtained from these electrodes displayed a reduction at □ 0.83 V and reoxidation at □ 0.47 V *vs.* Fc/Fc$^+$ (Figure 1c). The redox behavior is in good agreement with that of monomer **4** indicating that the polymer backbone does not influence the redox behavior. The small shift compared to the values of **4** is caused by hindered kinetics due to the high viscosity of propylene carbonate and the thickness of the electrode. Importantly, the intensities of the oxidation and the reduction peaks are constant for over 100 cycles (see supporting information), indicating the stability of the polymer in the electrolyte (Figure 1c).

A coin type cell battery was manufactured under inert atmosphere with a lithium metal anode and the polymer composite electrode (20/40/30/10 wt% **5**/Super P®/VGCF/PVdF) as cathode. A 0.1 M solution of lithium perchlorate in propylene carbonate served as electrolyte. The battery exhibits a highly reversible charge/discharge behavior featuring an average cell voltage of 3.05 V for charging and 2.25 V for discharging vs. Li/Li$^+$. (Figure 2) This behaviour is consistent with the redox waves observed in the cyclic voltammogram of the electrode. The cell was charged and discharged at a charging speed of 1 C. The rate of n C corresponds to

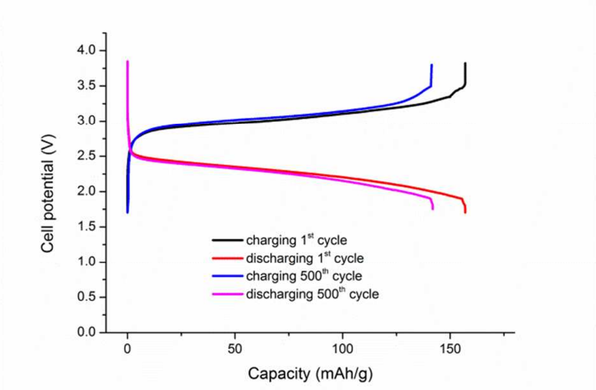


Figure 2: Charge/discharging curves (capacity *vs.* potential) of the Li-organic battery of the 1st and the 500th cycle (solid line). The anode is lithium metal, the cathode is a composite with polyTCAQ **5** as active material.

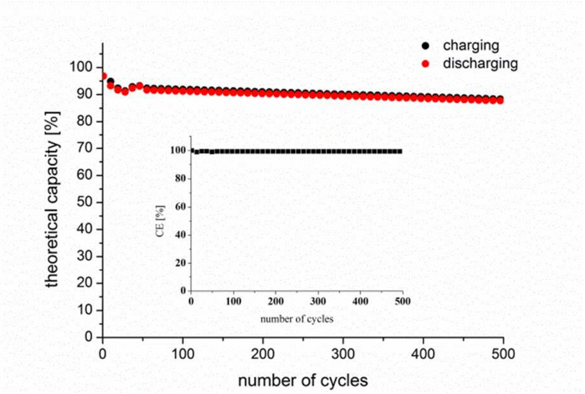


Figure 3: Extended charge/discharge cycling of **5** in propylene carbonate, 0.1 M lithium perchlorate (500 cycles, 1 C). Coulombic efficiency (CE%) of 500 charge/discharge cycles (black squares).

a full charge/discharge in 1/n hours. After the 1st cycle a material activity of 97% *resp.* 156 mAh/g was observed (Figure 3). The prototype device features a good cyclability: After 500 charge/discharge cycles, the battery maintains 88% of the initial capacity (141 mAh/g) at a consistently high coulombic efficiency of 99%. Coin type cells with a larger amount of active material like 30*wt%* led to lower material activity of 68% (see Figure S2).

Conclusions

In conclusion, tetracyano-9,10-anthraquinonedimethanes (TCAQ) represent a promising core structures for active electrode materials in organic batteries. Their interesting redox behavior consisting of one two-electron-reduction/oxidation-wave leads to one charge/discharge plateau associated with a good charge storage capacity. To maintain the theoretical capacity of the polymer as high as possible, poly(TCAQ) **5** was synthesized within four straightforward steps. Comparison of the cyclic voltammograms of the monomer in solution and the polymer as composite electrode indicate that both the polymer backbone and the conducting and binding additives have no influence on the redox behavior. A Li-organic prototype battery applying poly(TCAQ) as active electrode material displays a high material activity of 97%, high rechargability of 500 cycles with 12% loss, as well as excellent coulombic efficiency (99%), which shows that poly(TCAQ) as an interesting candidate as active electrode material in organic batteries.

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Notes and references

Electronic Supplementary Information (ESI) available: [Experimental details, size exclusion chromatograms, cyclic voltamograms]. See DOI: 10.1039/c000000x/

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