Polymer-Bound Pyrene-4,5,9,10-Tetraone for Fast-Charge and -Discharge Lithium-ion Batteries with High Capacity

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Organic rechargeable batteries[1] have received significant research interest from the viewpoints of structural diversity, flexibility[2] and sustainability[3,4] of electrode materials. Although extensive studies have been made for the development of organic cathode materials,[5,6,7] there is still a great demand for organic materials with high cyclability for the storage of electrical energy in practical use.

We designed core structures of organic cathode materials for lithium-ion (Li-ion) batteries based on density functional theory (DFT) calculations, which indicated that six-membered cyclic 1,2-diketones serve as excellent core structures cathode materials. Here we show that the Li-ion battery composed of pyrene-4,5,9,10-tetraone (PYT), which contains two six-membered-ring 1,2-diketone units, bound to polymethacrylate exhibits remarkable charge–discharge properties.

Synthesis of polymer-bound PYT is shown in Figure 1. Nitration of PYT using HNO_3 gave 2-nitropyrene-4,5,9,10-tetraone (PYT-NO_2). Reduction of PYT-NO_2 with $Na_2S_2O_4$ followed by treatment with 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (DDQ) gave 2-aminopyrene-4,5,9,10-tetraone (PYT-NH_2). The reaction of PYT-NH_2 with PMAC in the presence of a catalytic amount DMAP in pyridine followed by treatment with methanol gave the target Polymer-Bound Pyrene-4,5,9,10-tetraone (PPYT).

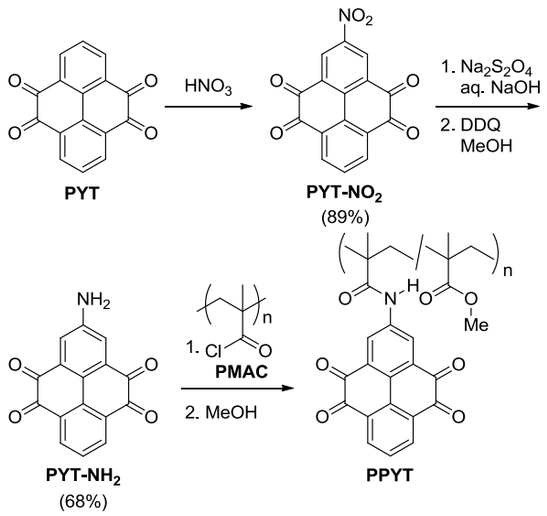

Figure 1. Synthesis of PPYT.

The charge–discharge behavior of PPYT was studied using a coin-type cell equipped with the cathode prepared by PPYT, AB, and PVDF. Cells were imbibed with $LiPF_6$/propylene carbonate ($LiPF_6$/PC) or an equimolar complex $LiN(SO_2CF_3)_2$/tetraglyme ($LiNTf_2$/G4). The battery exhibited reversible two-stage discharge–charge behavior with average discharge voltage of circa 2.8 V and 2.2 V vs. Li/Li^+ (Figure 2),corresponding to two two-electron redox processes. The battery exhibited excellent rechargeability (Figure 3). Even after 500 charge–discharge cycles at the rate of 1 C (0.2 C every 20 times), 83% (first cycle: 231 mAh/g, 500th cycle: 193 mAh/g) of the capacity of the material was retained.

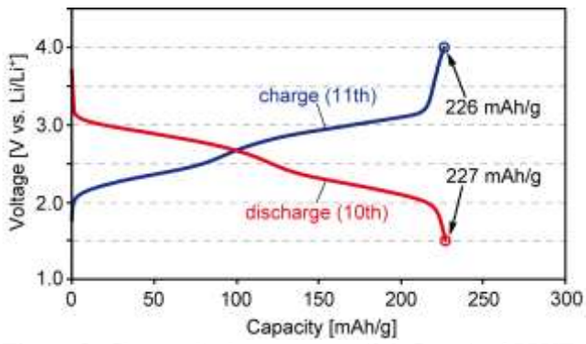

Figure 2. Charge–discharge curves (0.2 C rate) of PPYT in $LiNTf_2$/G4 at 45 °C.

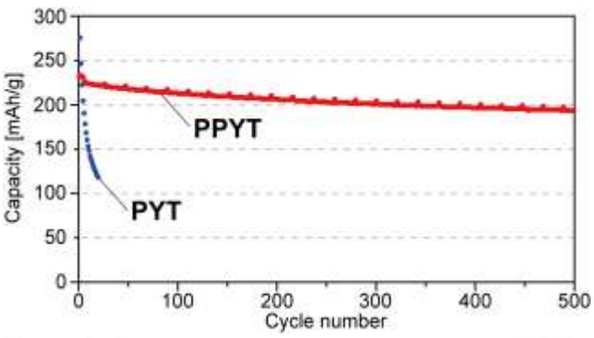

Figure 3. Extended charge–discharge cycling of PPYT and PYT in $LiNTf_2$/G4 at 45 °C. PPYT (500 cycles, 1 C rate), PYT (20 cycles, 0.2 C rate).

In conclusion, the battery using PPYT exhibited excellent charge−discharge ability. High capacity and excellent cyclability speak well for the high potential of organic materials for Li-ion batteries, and open a new aspect of energy storage. Details of the charge−discharge behaviors of PPYT such as rate dependence will be discussed in the presentation.

Reference

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