

Lithium Batteries with Organic Radical Cathodes

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Polyradicals have been used as one-dimensional throw-bond organic ferromagnets, and considerable effort has been made to increase their values of spin quantum number (S) in an electronic ground state. In addition to that, many polyradicals are known to be oxidized and reduced electrochemically, and it is characteristic that radical-cation/anion is not produced in any stage of the redox process. If polymers did not have radical electrons in a charged/discharged state, they would stabilize. We initially found that these redox processes would be suitable for a reaction of cathode active materials in aprotic rechargeable batteries. The use of organic materials as an active material in cathodes appears promising to design environmentally friendly, high energy-density rechargeable batteries. We describe the electrochemical properties of a stable nitroxyl polyradical, poly (2,2,6,6-tetramethylpiperidinyloxy methacrylate) (PTMA)(Fig.1), and the performance of the prototype lithium battery using this design.

A cyclic voltammogram of PTMA electrode is shown in Figure 2. A half-wave potential ($E_{1/2}$) of PTMA is 3.58 V vs. Li/Li^+ . It is noted that the difference of ration of the anodic ($E_{a,p}$: 3.66 V) and cathodic ($E_{c,p}$: 3.50 V) peak potentials is estimated as 0.16 V at a sweep rate of 10 mV/sec, which is extremely smaller than that of the other electroactive organic materials such as disulfide compounds. The small gap of the anodic and cathodic peaks corresponds with its fast electrode reaction rate of the present polyradicals, which leads to a capability for high power rate in the charge and discharge process of the battery.

The fabricated PTMA/Li battery was charged at constant current densities of 0.1 and 1.0 mA/cm^2 until its voltage reached 4.0 V. In the charge-discharge curves, an obvious voltage plateau is evident. The found plateau voltage of nearly 3.5 V is comparable to the redox potential of PTMA. The initial discharge capacity was 77 Ah/kg of the PTMA weight at a current density of 0.1 mA/cm^2 . Assuming one electron per monomer unit in the redox process, we estimate the theoretical capacity of the PTMA to be 111 Ah/kg. The experimentally obtained discharge capacity was 70 % of the theoretical capacity. At the current density of 1.0 mA/cm^2 , the discharge capacity retained 91% of that found for the 0.1 mA/cm^2 measurement. It should be noted that a current density of 1.0 mA/cm^2 is much larger than that of conventional battery and suggests that only 5 minutes was needed to fully charge the battery. Figure 3 shows the cycle performance of the fabricated PTMA/Li battery. Charging and discharging were repeated at a current density of 1.0 mA/cm^2 for cell voltages ranging from 3.0 to 4.0 V. As shown in this figure, no significant deterioration in the capacity is observed at up to 1000 cycles. Because the capacity of the PTMA composite cathode is significantly less than that of the lithium metal

anode, its use did not result in the usual decrease in battery capacity. It should be noted, however, that the cathode contains only 10 wt % of active material, and it is necessary to increase this percentage for the practical use.

A space distribution of non-bonding molecular orbital for nitroxyl radicals is considered to be localized in the nitroxyl group. The locality of the energy storage component promises to offer a variety of molecular design possibilities for use in cathode active materials. It might be possible to produce flexible, adhesive, electroconductive, or even liquid cathode active materials. Further, because their localized nature restrains the interaction between energy storage components, these systems enable overcoming the capacity limitations, which are seen in conductive polymers.

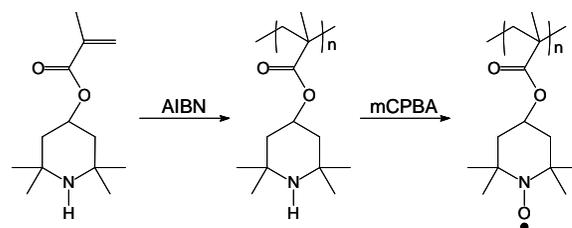


Figure 1 Synthesis procedure of PTMA

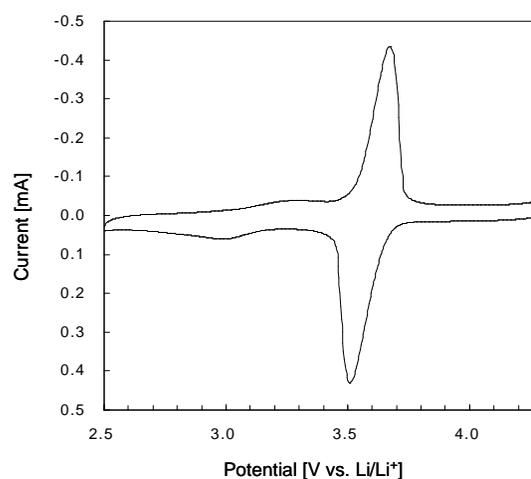


Figure 2 Cyclic Voltammogram of PTMA contained a composite electrode at sweep rate of 10 mV/s. Platinum wire counter electrode and Li/Li^+ reference electrode were used in an electrolyte mixture solution of EC/DEC, into which 1M- LiPF_6 had been dissolved.

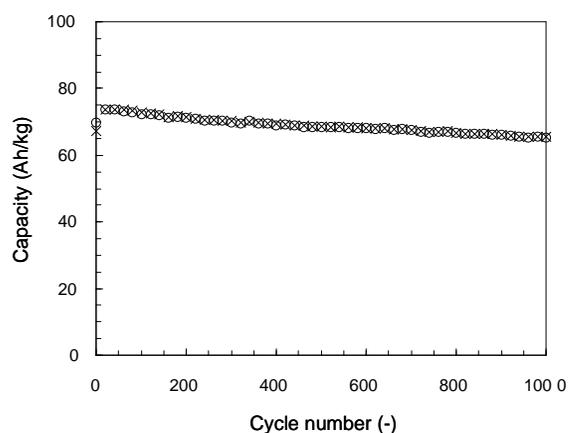


Figure 3 Changes in charge (x) and discharge capacities (o) of PTMA/Li battery during repeated cycles (1.0 mA/cm^2 , 3.0 - 4.0 V)