Discharge Properties of Stable Radical Cathodes at High Current Density

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Introduction
We have investigated the discharge properties of poly 2,2,6,6-tetramethylpiperidinoxyl-4-y1 methacrylate (PTMA) cathodes at high current density for the purpose of creating batteries with high power density.

Some organic radicals are stable in air with respect to steric hindrance or reactivity. We recently demonstrated that a stable nitroxy radical, (PTMA) could be used as a cathode for lithium rechargeable batteries. [Refs. 1 & 2]. PTMA is preferred as a cathode material because of its high voltage and excellent cycle performance. [Refs. 3 & 4]

Experimental and Results
We synthesized PTMA from 2,2,6,6-tetramethylpiperidyl methacrylate by radical polymerization followed by oxidation in m-chloroperbenzoic acid. We confirmed 72% of all units of the polymer have radical structures by measuring their ESR spectra. The PTMA cathodes were prepared from 55% synthesized PTMA powder, 35% carbon black, and 10% polyvinylidene fluoride binder (Daiken Industries, #1300) by casting N-methyl-pyrrolidone slurry onto Al foil in thicknesses from 20 – 30 µm. The prepared cathodes were dried at 125°C. We used lithium foil as the anode. The electrolyte was LiPF6 in a 3:7 (by volume) EC and DEC mixture (Ube Industries). We fabricated coin cells using these electrodes and electrolyte.

We then carried out charge-discharge experiments on the fabricated cells at 20°C, at a constant current density, with a cut-off voltage of 2.5 – 3.9 V. The discharge curves of a Li/PTMA coin cell at variable current densities are shown in Figure 1. We can see a very flat plateau at about 3.75 Volts (Li vs. Li+) at 0.1 mA/cm2 (0.7 C). The specific capacity of PTMA was 62 mAh/g at this rate. This value corresponds to 78% of the theoretical capacity of PTMA. The fabricated cells showed excellent discharge properties at high currents. At a discharge current density of 10 mA/cm2 (70 C), the cell discharge capacity retained 94% of that at a current density of 0.1 mA/cm2 and the discharge curve is very flat.

The dependence of the PTMA specific capacities on discharge current densities is shown in Figure 2. The PTMA specific capacity decreases rapidly with an increase in current density at 0 - 2.5 mA/cm², but at 2.5 – 10 mA/cm², the specific capacity maintained almost the same value of 60mAh/g. Above 10 mA/cm², the specific capacity decreased linearly with increasing current density. At a discharge current density of 10 mA/cm² (280 C), the cell discharge capacity maintained 65% of that at a current density of 0.1 mA/cm². The discharge process took only 8 seconds at 280 C.

The newly developed cathodes have excellent discharge properties at high currents. The stable radical cathodes show promise for new fields of high power application for polymer batteries.

Acknowledgments
This work was performed using the high power density organic radical battery project for data-backup and was supported by the New Energy and Industrial Technology Development Organization (NEDO).

References