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Effect of radical polymer cathode thickness on the electrochemical performance of organic radical battery

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Abstract

The influence of cathode thickness on the electrochemical performance of an organic radical battery (ORB) with the radical polymer poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate) (PTMA) as the cathode active material is presented. The ORB consists of lithium metal anode and PTMA cathode with an active material content of 40 wt.%. An increase in cathode thickness results in a decrease in specific capacity and discharge voltage of the cell and an increase in electrode/electrolyte interfacial resistance. The best performance is achieved with a thin cathode of 17 µm that shows nearly 100% utilization of the active material (~ 111 mAh/g) at current densities up to 1.0 mA/cm^2. The cell exhibits excellent high-rate capability and cycle characteristics with a stable impedance behavior and an intact cathode structure on cycling. The results demonstrate that high performance can be achieved from the non-conductive PTMA cathode with higher active material content by using a thin and properly prepared cathode consisting of a uniform, nanometer range coating of the polymer layer on the conductive carbon particles.

Keywords: Organic radical battery; Cathode materials; Lithium secondary batteries; PTMA; Electrochemical property

1. Introduction

Organic radical batteries (ORBs) are emerging as promising, environmentally benign, high-rate capable power sources. An ORB is composed of at least one of its electrodes based on an organic radical as the active material. The first report on the use of an organic radical as an electrode-active or charge-storage material in lithium battery was by Nakahara et al. in 2002 [1]. They employed the radical polymer PTMA, poly(2,2,6,6-tetramethylpiperidinyloxy-4-yl methacrylate), as the cathode active material in lithium battery. Since then, a few more studies were reported that demonstrate the vast potential of ORBs, especially high-rate capability [2–7]. PTMA is a derivative of polymethacrylate with a 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) radical in the repeating unit. Compounds containing TEMPO radical are known to show redox behavior in aprotic solvents in the range of 3.69–4.04 V vs. Li/Li$^+$, independent of their structure [8,9]. TEMPO-based compounds have attracted interest as subjects of electron spin resonance [10] and molecular motion studies [11]. They find applications as polymeric stabilizer [12], oxidants of alcohols [13] and charge-storage materials [1,2]. Polyacetylene and polynorbonene derivatives carrying TEMPO also were synthesized recently and evaluated as materials for ORBs [14].

The nitroxide radical in TEMPO is characterized by good chemical stability [15] contributed by its resonance structures. Two redox couples can be exhibited by nitroxide radical: the anodic oxidation resulting in oxoammonium cation (p-type doping) and the cathodic reduction resulting in aminoxyl anion (n-type doping) [15]. The anodic oxidation of nitroxide radical in PTMA has been utilized in employing it as the cathode active

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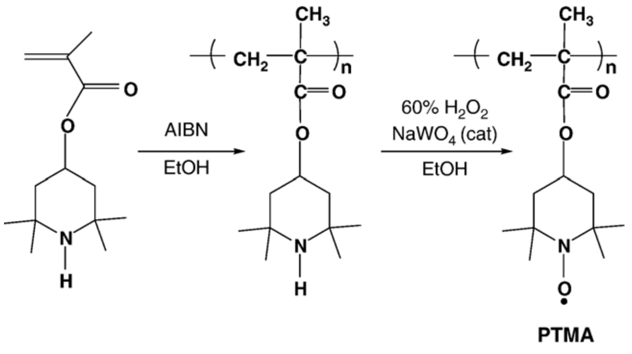
material of rechargeable ORBs [1–7]. A significantly small molecular weight of 30 per radical moiety, nearly 100% localized density of the unpaired electron in the radical and the extremely rapid electron transfer rate are important advantages of PTMA as a battery material. The fast reaction kinetics of PTMA during the charge–discharge operations, with an estimated electron transfer rate constant of $>10^{-2}$ cm/s, leads to high power-rate capability for the battery [2,3].

Since PTMA is an insulator, the cathode composition usually consists of only a small proportion of the active material; the major portion being the conductive agent like carbon. Thus, many of the earlier studies have employed only 10 wt.% of PTMA with high amount (about 80 wt.%) of carbon [1,2,4]. For practical applications of ORB, it is essential to increase the active material content of cathode and attain higher specific energy from the battery. A few recent studies employ 30–50 wt.% of PTMA in the cathode [5–7]. The thickness of PTMA cathode needs to be optimized for deriving the maximum performance from the non-conductive active material. In this article we present the results of our evaluation of the influence of cathode thickness on the performance of a room temperature Li/PTMA cell with a relatively high PTMA content of 40 wt.%.

2. Experimental

PTMA was synthesized by the radical polymerization method, similar to the one reported by Nakahara et al. [1]. The synthesis steps followed are shown in Scheme 1. 2,2,6,6-tetramethylpiperidine methacrylate monomer is polymerized first using 2,2'-azobisisobutyronitrile radical initiator and then oxidized with H_2O_2 in the presence of $NaWO_4$ catalyst to get PTMA. For preparing the cathode, 40 parts by weight (pbw) of PTMA was mixed with 50 pbw of conductive, Super-P carbon and 10 pbw of poly(vinylidene fluoride) binder in *N*-methyl pyrrolidone solvent. The ingredients were mixed uniformly by ball milling at room temperature for 30 min and the slurry was cast on an aluminum foil and dried at 70 °C for 12 h. The film so obtained was cut into circular discs of 1.01 cm diameter for use as cathode. Cathode films of thicknesses varying between 17 and 64 μm were prepared using different spacers. The mass of cathode discs varied between 2.0 to 2.6 mg for these thicknesses.

The surface morphology examination was performed with scanning electron microscope (SEM) (JEOL JSM 5600). The glass transition temperature (T_g) of PTMA was determined by differential scanning calorimetry (DSC: TA 2040) at a heating rate of 5 °C/min. The thermal stability was analyzed by thermogravimetric analysis (TGA: SDT Q600 TA, USA) in nitrogen atmosphere at a heating rate of 10 °C/min from 20 °C to 400 °C.



Scheme 1. Synthesis of PTMA.

The Swagelok® type Li/PTMA coin cell was fabricated by stacking lithium metal (300 μm thickness, Cyprus Foote Mineral Co.) anode and PTMA-based cathode with Celgard 2200 separator film. 1 M $LiPF_6$ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by vol) was used as the liquid electrolyte. The lithium salt and organic solvents were supplied by Aldrich. The cell assembly was performed under argon atmosphere in a glove box ($H_2O < 10$ ppm). The charge–discharge and cycling properties of the cell were evaluated between 3.0 and 4.0 V at different current densities using an automatic galvanostatic charge–discharge unit, WBCS-3000 battery cycler (WonA Tech. Co.) at room temperature. Cyclic voltammetry measurement of the cell was conducted at a scan rate of 5 mV/s between 2.5 and 4.4 V and AC impedance of the cell was measured using IM6 frequency analyzer over a frequency range of 100 mHz to 2 MHz.

3. Results and discussion

The radical polymer PTMA has a glass transition temperature of 74 °C that is convenient enough for easy processing, and good thermal stability with an initial decomposition temperature (corresponding to 10 wt.% decomposition) of 270 °C and peak decomposition temperature of 300 °C. The radical centers in PTMA are reported to be stable up to the decomposition temperature of the polymer and the storage stability of PTMA under ambient conditions is also good with no change in radical concentration for more than a year [3]. The SEM image of PTMA is shown in Fig. 1 (a). It reveals that at room temperature, the amorphous, glassy polymer has a homogenous, flake-like morphology. Fig. 1 (b) shows the morphology of PTMA-based cathode fabricated by blending PTMA, carbon powder (of average particle size 40 nm) and PVdF binder. Well-defined, uniform particle morphology is observed with an average particle size of 80 nm. This shows that the carbon particles have been coated with a very thin layer (thickness of ~40 nm) of the polymer. During the cathode preparation by the solution process of ball mill blending of ingredients, the carbon particles with high surface area adsorb the polymer solution and get impregnated with it. Subsequent removal of solvent by evaporation leaves the thin coating (nanometer thick) of the active material on the conductive carbon particles. The uniform morphology of the electrode so obtained is highly beneficial in realizing good electrochemical performance for the Li/PTMA cell.

Fig. 2 shows the CV of Li/PTMA cell with PTMA cathode of 17 μm thickness. A sharp, single redox couple with a redox half-wave potential at 3.6 V vs. Li^+/Li is obtained. The peak separation between the anodic peak (at 3.75 V) and cathodic peak (at 3.45 V) is only 300 mV. Such low redox peak separation has been reported in earlier studies employing PTMA cathodes as well [1,2] and has been attributed to the fast