Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl19

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Version of record first published: 24 Sep 2006

To cite this article: Jin On Kim, Min-Kyu Song, Seung Won Lee, Byung Won Cho, Kyung Suk Yun & Hee-Woo Rhee (2000): Structural and Electrochemical Properties of ICP/$LiMn_2O_4$ Composite Cathodes, Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals, 349:1, 287-290

To link to this article: http://dx.doi.org/10.1080/10587250008024921

Mol. Cryst. and Liq. Cryst., 2000, Vol. 349, pp. 287-290
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PPy/$LiMn_2O_4$ composites were prepared by chemical synthesis of pyrrole monomer onto $LiMn_2O_4$ powder in the presence of dodecyl bezenesufonic acid (DBSA) dopant. Thermogravimetric analysis showed that the content of $LiMn_2O_4$ in the composite increased with increasing the amount of manganese oxide powder. The battery performance of PPy/$LiMn_2O_4$ composite cathodes initially charged was compared with the physical mixture of both materials. Li/(PPy/$LiMn_2O_4$) ion cell with EC/DMC/1M $LiPF_6$ electrolyte showed that cycle performance was enhanced by the redox reactivity of PPy as well as the enhanced conductivity of composite electrode. The reversibility of Li cation was proven by electrochemical voltage spectroscopy (EVS).

Keywords: PPy/$LiMn_2O_4$ composite; Li ion cell; active material; electrochemical voltage spectroscopy (EVS)

INTRODUCTION

Many attempts to develop manganese oxides for cathode materials have been tried but there has been no commercial success yet. In this study composite cathode based on intrinsically conductive polymers (ICP) and manganese spinel, $LiMn_2O_4$, were prepared to minimize severe capacity fading of $LiMn_2O_4$ during cycling [1]. Conducting polymers have been known to play key roles on stabilizing the structure with enhanced conductivity of composite electrodes.

In the composite electrodes the structural property of conducting polymer layer is an important factor for high energy density because ionic species diffuse into and out of polymer layer during cell operation.

If the polymers possess a channel-like or layered structure, they should allow reversible intercalation/deintercalation of Li cation without any considerable changes in the structure. Therefore, we chemically synthesized PPy onto $LiMn_2O_4$ composite (CS) using a series of alkylbenzenesulfonic acid as dopants. The discharge capacity of Li/(PPy/$LiMn_2O_4$) ion cell was monitored as a function of cycle number. It was compared with pure $LiMn_2O_4$ powder and physical mixture of PPy and $LiMn_2O_4$ (PM).

EXPERIMENTAL

PPy powder was chemically prepared by the method as described elsewhere. The standard 4-probe method was used to measure the electrical conductivity of PPy pellets and films. XRD studies were performed with a Rigaku Rad-C 4037A1 diffractometer (Cu Kα). PPy/$LiMn_2O_4$ powder was prepared by adding 10 g pyrrole monomer into 0.28 M DBSA aqueous solution containing various amounts of $LiMn_2O_4$. The resultant powders were dispersed in 6 wt% Kynar761/NMP solution with auxiliary graphite conductor. The slurry was dip-coated onto extended Al grid and dried at 80 °C in vacuum oven for 24 hrs. The weight of active material was ca. 0.1 g in 2x2 cm^2. The laminate of Li/(PPy/$LiMn_2O_4$) ion cells with EC/DMC/1M $LiPF_6$ was enclosed in a metallized plastic bag by vacuum sealer in drying room. A layer of microporous polyethylene membrane electrically separated both electrodes. Electrochemical voltage spectroscopy (EVS) and charge/discharge test were carried out with WBCS 3000 Battery cycler ($I_{threshold}$ = 800 μA, potential step = 10 mV).

RESULTS AND DISCUSSION

The structure of PPy chain was well characterized by XRD. Figure 1 confirmed highly ordered and layered structure of PPy/DBSA at parallel direction to film surface. The layered structure resulted from the separation of the polymer backbone by the long alkyl side chain of surfactant dopant [2]. PPy/DBSA could have large space between polymer chains for liquid solvent molecules. Thus, DBSA was used as a dopant to prepare PPy/$LiMn_2O_4$ composite.

Figure 2 showed TGA curves for PPy/$LiMn_2O_4$ powders. The thermograms showed the onset of PPy decomposition around 270 °C.

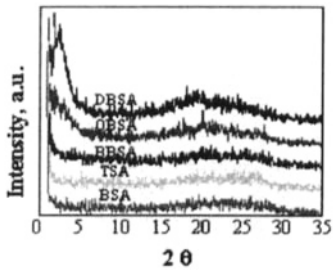

FIGURE 1 XRD spectra of PPy powders.

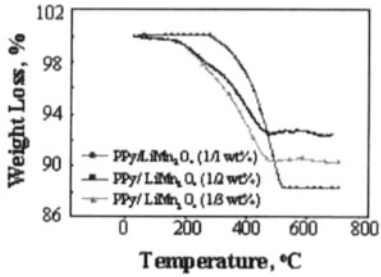

FIGURE 2 TGA curves of PPy/$LiMn_2O_4$ composite powders.

The amount of PPy on $LiMn_2O_4$ was successfully controlled from 6 to 14% by varying the initial weight ratio of PPy/$LiMn_2O_4$. PPy coating onto $LiMn_2O_4$ increased the conductivity of Mn spinel and their conductivities were compared with that of physically mixed powders in Figure 3. The battery performances for the different battery systems are compared in Figure 4.

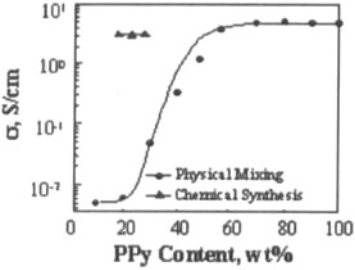

FIGURE 3 Electrical conductivity of PPy/$LiMn_2O_4$ composite powder

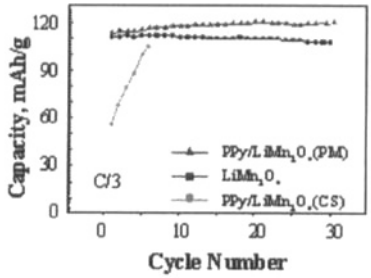

FIGURE 4 Discharging capacity of Li/(PPy/$LiMn_2O_4$) cells.

The physically mixed system (PM) showed the higher capacity and better cyclability than pure $LiMn_2O_4$ system. The redox reactivity and good electrical conductivity of PPy enhanced the capacity of $LiMn_2O_4$. Even if the initial capacity of PPy/$LiMn_2O_4$ (CS, 1/9) was quite low, it

increased with increasing cycle number and approached the capacity of pure $LiMn_2O_4$. The initial low capacity of PPy/$LiMn_2O_4$ (CS, 1/9) may be related to the delithiation of $LiMn_2O_4$ during polymerization and the delithiation resulted in electrochemically inactive λ-MnO_2 in aqueous acid solution [3]. To prove the conversion of λ-MnO_2 to $LiMn_2O_4$, EVS was employed in Figure 5. Two sharp redox peaks appeared at 3.95 and 4.11 V [4], whose sharpness indicates the reversibility of Li ion diffusion. PM system has the sharpest peaks with the latter much sharper. However, for CS system initial peaks are much smaller than PM system but peaks are growing with cycling. This is the reason why the capacity of CS battery system approached the pure $LiMn_2O_4$ battery with cycling. EVS result also supports the conversion of $LiMn_2O_4$ to λ-MnO_2 during the chemical polymerization of PPy in the acid solution.

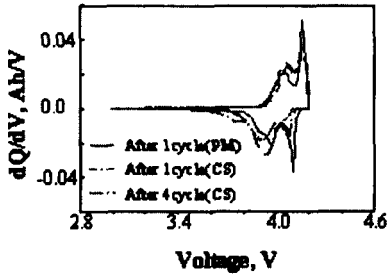

FIGURE 5 EVS curves of Li/(PPy/$LiMn_2O_4$) cell.

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