

Charge/discharge characteristics of LiMnO_2 composite for lithium polymer battery

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Abstract

A LiMnO_2 -PAN-DMcT composite cathode for a lithium polymer battery (LPB) was developed. We investigated impedance spectroscopy, electrochemical properties of LiMnO_2 , LiMnO_2 -PAN and LiMnO_2 -PAN-DMcT composites with polyvinylidene (PVDF)-based polymer electrolyte as a function of mixing ratio. The capacity of LiMnO_2 with 3 wt.% PAN–12 wt.% SP270 was higher than that of LiMnO_2 with 15 wt.% SP270. The discharge capacity of LiMnO_2 -PAN with 3 wt.% PPy was 119 and 121 mAh/g at 7 and 15 cycles. The capacity of LiMnO_2 with 2 wt.% PAN and 3 wt.% DMcT was higher than that of LiMnO_2 with 3 wt.% PAN and 12 wt.% SP270 with cycling. The LiMnO_2 -PAN-DMcT composite cathode with 2 wt.% PAN and 3 wt.% DMcT in PVDF-based electrolyte shows good capacity with cycling. © 2003 Elsevier Science B.V. All rights reserved.

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1. Introduction

Lithium manganese oxide is known to be one of the cathode materials for lithium rechargeable batteries [1]. In recent publications, LiMn_2O_4 and LiMnO_2 have been regarded as attractive alternatives to MnO_2 for use in lithium rechargeable batteries. The lithium manganese oxide used as the active material is prepared by mixing with conductive agent such as acetylene black. Electronic conducting polymers have been of interest since the redox reaction of polyacetylene was reported by Negrey et al. [2]. Oyama and coworkers [3,4] reported that polyaniline (PAN) organic composite shows a novel cathode active material for lithium batteries operating at room temperature.

Polymer electrolytes were discovered by Fenton et al. [5] in 1973. Wright et al. [6], and they showed that complexes formed with PEO and alkali metal salts deliver high ionic conductivity. Subsequently, these complexes were proposed by Armand et al. [7] as polymer electrolytes for solid-state battery and electrochemical device application. The polymer electrolyte has provided an attractive possibility of developing new type of lithium battery, so-called lithium polymer battery (LPB) [8] with thin layers. The LPB is an all-solid

state system, which consists of a lithium-ion-conducting polymer electrolyte and two lithium-ion reversible electrodes. The LPB can be viewed as a suitable system for wide applications, such as thin-film batteries for microelectronics, electric vehicle batteries and load leveling batteries [9]. A chemically prepared LiMn_2O_4 -PPy composite has been reported by Yoneyama et al. in liquid electrolytes [10]. Transition metal oxide-conducting polymer composite is able to increase capacity due to doping/undoping of ions in the conducting polymer. Application of DMcT-PAN composite cathode has been reported by Hatozaki and Oyama in liquid electrolytes [11]. We have studied a new approach to LiMnO_2 organic material composite with polymer electrolyte.

In this work, we investigated characteristics of charge/discharge cycling of LiMnO_2 , LiMnO_2 -PAN and LiMnO_2 -PAN-DMcT composites with PVDF-based polymer electrolyte.

2. Experimental

Polyvinylidene fluoride-hexafluoropropylene (PVDF-HFP, Eif Atochem, Kynar 2801) was dried under vacuum at 60 °C for 20 h. LiClO_4 (Aldrich) was dried under vacuum at 110 °C for 20 h before use. Propylene carbonate (PC) and ethylene carbonate (EC) were purchased from Aldrich.

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LiClO_4 was dissolved in PC–EC solutions. The PC–EC– LiClO_4 was added 25 wt.% PVDF–HFP. The liquid electrolyte solution was homogeneously mixed by stirring. The polymer electrolyte film was prepared by casting and a rapid heating technique [12] at 110 °C for 10 min. The thickness of electrolyte film was 100 μm .

Polyaniline was synthesized by polycondensation of aniline in HCl, and catalyzed by $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ammonium persulfate, Aldrich). For direct chemical deposition, we prepared 1 M HCl solution containing 0.1 M of aniline monomers and 1 M HCl solution containing 0.1 M $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (ammonium persulfate). Ammonium persulfate solution was added very slowly to prevent the warming of the solution. After completion of the addition, stirring was continued for 2 h to ensure completion of the reaction. During the polymerization, the temperature was kept around 5 °C. After filtering to obtain the polymer, PAN was washed several times with methyl alcohol and acetone to remove the oligomers and the catalyst. Then it was dried under dynamic vacuum at 60 °C for 8 h and the polymer was dried again under dynamic vacuum at 60 °C after holding overnight in 1 M HCl [13]. LiMnO_2 was synthesized by the reaction of an intimately mixed preparation of Mn_2O_3 (Aldrich) and $\text{LiOH}\cdot\text{H}_2\text{O}$ (Aldrich) with a molar ratio of $\text{Mn}/\text{Li} = 1:1.1$. The mixtures were fired at 450 °C for 5 h and then heated at 700 °C for 12 h under Ar flow [14].

Composite cathode slurry was prepared by mixing LiMnO_2 powder with carbon (SP270), PAN and DMCt in NMP solution. The mixture slurry was stirred for 3 h. The composite cathode films were prepared by coating this slurry on Al foil current collector. After solvent evaporation, the composite films were vacuum dried at 60 °C for 24 h. The size of each cell was 2 cm \times 1 cm. The current density of charge/discharge cycling was 0.1 mA/cm². The complex impedance of composite cathode/Li cells was measured by the ac two-electrode method using IM6 Impedance Measurement System (Zahner Elektrik Co.). The ac signal was applied across the cells and its frequency range was from 10 mHz to 2 MHz. Preparation and test of cells were carried out in argon-filled glove box.

3. Results and discussion

Fig. 1 shows XRD pattern of the LiMnO_2 prepared by heating a reaction mixture of Mn_2O_3 and $\text{LiOH}\cdot\text{H}_2\text{O}$ at 700 °C in Ar. Molar ratio of Li/Mn is 1.1:1. All peaks can be indexed by assuming an orthorhombic phase. The Li_2MnO_3 impurity phase was present in the LiMnO_2 powder.

The first charge/discharge cycling curves of LiMnO_2 added 3 wt.% PAN and 12 wt.% carbon (SP270) composite cathode and Li electrode in PVDF–PC₁₀EC₁₀ LiClO_4 electrolyte at room temperature shown in Fig. 2. The initial open circuit voltage (OCV) of LiMnO_2 –PAN/Li cell was 3.2 V. The charge/discharge cycling was carried out between 4.3 and 2.2 V with current density of 0.1 mA/cm². At the

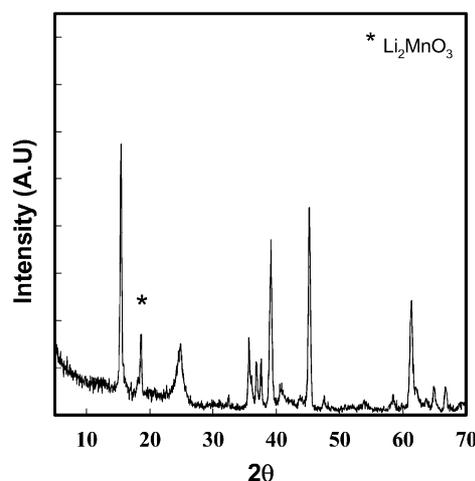


Fig. 1. XRD pattern of the LiMnO_2 prepared by heating method at 700 °C in Ar.

charging process, the plateau of charge voltage appeared at 3.8 V. The first charge capacity of LiMnO_2 with 3 wt.% PAN composite was 136 mAh/g.

The specific capacity of LiMnO_2 –PAN/Li cells as a function of addition ratio of PAN is shown in Fig. 3. The charge/discharge cycling was carried out between 2.2 and 4.3 V with current density of 0.1 mA/cm². The discharge capacity of LiMnO_2 added 15 wt.% SP270 in PVDF–PC₁₀EC₁₀ LiClO_4 electrolyte was 85 and 118 mAh/g at one and seven cycles at room temperature, respectively. Then the discharge capacity decreased with charge/discharge cycling from the 8th to the 15th cycle. However, the capacity of LiMnO_2 with 3 wt.% PAN–12 wt.% SP270 was higher than that of LiMnO_2 with 15 wt.% SP270 at 15th cycle. This different of the discharge capacity was 16%. After the eighth cycling, the capacity fading of LiMnO_2 composite with 3 and 5 wt.% PAN was less than that of LiMnO_2 with 15 wt.% SP270. Also, the charge/discharge efficiency was above 96% after the seventh cycle. The discharge capacity of LiMnO_2 –PAN with 3 wt.%

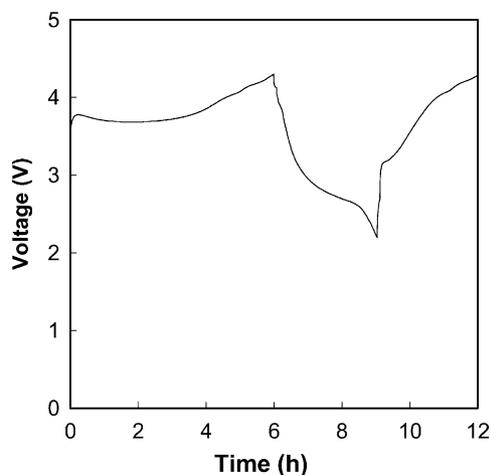


Fig. 2. Charge/discharge curve of LiMnO_2 –PAN/Li cell with PVDF–PC₁₀EC₁₀ LiClO_4 .

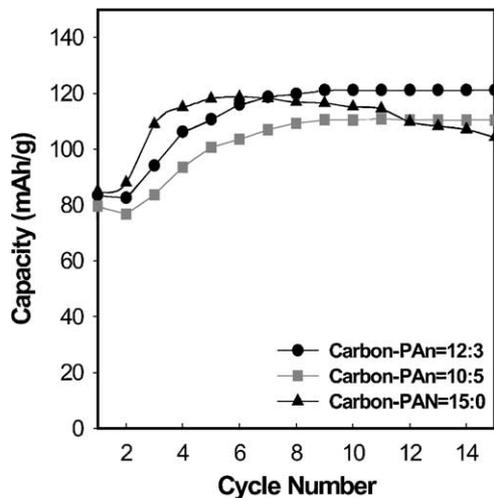


Fig. 3. Specific capacity of $\text{LiMnO}_2\text{-PAN/Li}$ cells with $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$.

PAN was 119 and 121 mAh/g at 7 and 15 cycles. We suggest that capacity increasing is due to doping/undoping of anions in PAN.

Fig. 4 shows impedance spectra of $\text{LiMnO}_2\text{-PAN/Li}$ cell with $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ as a function of charge/discharge cycling at 25°C , indicating that the radius of the semicircle is associated with the electrodes resistance of $\text{LiMnO}_2\text{-PAN/Li}$ cell increases with discharge cycling. The ac impedance response of $\text{LiMnO}_2\text{-PAN/Li}$ cell forms a broad semicircle in the frequency range of $60\text{ kHz}-1\text{ Hz}$, and a gradual line to the real axis in the frequency range of $1\text{ Hz}-10\text{ mHz}$. The bulk resistance of $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ electrolyte was $7\ \Omega$. The cell resistance was 32 and $48\ \Omega$ after first charge and discharge cycling, respectively. As shown in previous research, the increase in cell resistance is due to the increment of the electrodes resistance.

Fig. 5 shows the specific capacity of $\text{LiMnO}_2\text{-PAN-DMcT/Li}$ cells with $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ as a function

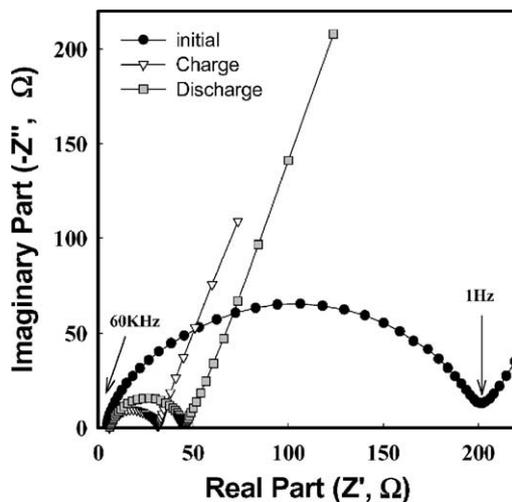


Fig. 4. Impedance spectra of $\text{LiMnO}_2\text{-PAN/Li}$ cell with $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ during cycling.

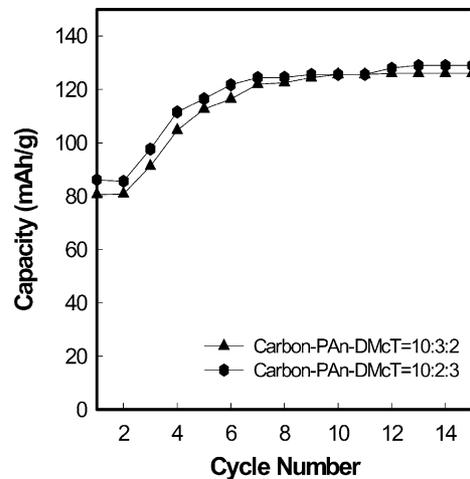


Fig. 5. Specific capacity of $\text{LiMnO}_2\text{-PAN-DMcT/Li}$ cells with $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$.

of addition ratio of PAN-DMcT. The capacity retention of LiMnO_2 with 2 wt.% PAN and 3 wt.% DMcT was higher than that of LiMnO_2 with 3 wt.% PAN and 12 wt.% SP270. The charge/discharge efficiency was above 98% after the seventh cycle. The discharge capacity of $\text{LiMnO}_2\text{-PAN-DMcT}$ composite was 121 and 126 mAh/g at 7 and 15 cycles. The optimization of $\text{LiMnO}_2\text{-PAN-DMcT}$ composite in polymer electrolyte is on test in our laboratory now. In these results, we suggest that the $\text{LiMnO}_2\text{-PAN-DMcT}$ composite cathode with 2 wt.% PAN and 3 wt.% DMcT in PVDF-based electrolyte shows good capacity with cycling.

4. Conclusions

On the basis of the results described above, we can come to the following conclusions. The discharge capacity of LiMnO_2 added 15 wt.% SP270 in $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ electrolyte was 85 and 118 mAh/g at first and seventh cycle, respectively. The capacity of LiMnO_2 with 3 wt.% PAN-12 wt.% SP270 was higher than that of LiMnO_2 with 15 wt.% SP270 at 15th cycle. The discharge capacity of $\text{LiMnO}_2\text{-PAN}$ with 3 wt.% PPy was 119 and 121 mAh/g at 7 and 15 cycles. The cell resistance of $\text{LiMnO}_2\text{-PAN/Li}$ cell was 32 and $48\ \Omega$ after first charge and discharge cycling. The capacity of LiMnO_2 with 2 wt.% PAN and 3 wt.% DMcT was higher than that of LiMnO_2 with 3 wt.% PAN and 12 wt.% SP270 with cycling. The $\text{LiMnO}_2\text{-PAN-DMcT}$ composite cathode with 2 wt.% PAN and 3 wt.% DMcT in PVDF-based electrolyte shows good capacity with cycling.

Acknowledgements

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