

Electrochemical characteristics of LiMn_2O_4 -polypyrrole composite cathode for lithium polymer batteries

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Abstract

A LiMn_2O_4 -PPy composite cathode for lithium polymer battery was developed. We investigated temperature dependence of ionic conductivity of PVDF-PC-EC- LiClO_4 and PVDF-EC-DEC- LiClO_4 electrolytes, AC impedance response and charge/discharge characteristics of LiMn_2O_4 -PPy/MCMB in PVDF-based electrolyte. The ionic conductivity of PVDF-PC₁₀EC₁₀ LiClO_4 and PVDF-EC₁₀DEC₁₀ LiClO_4 with 25 wt.% PVDF electrolyte was 2.3 and 1.8×10^{-3} S/cm at room temperature. The first discharge capacity of LiMn_2O_4 added 15 wt.% SP270 was 123 mAh/g, while that of LiMn_2O_4 -PPy composite with 7 wt.% PPy and 10 wt.% SP270 was 135 mAh/g. The charge/discharge efficiency was above 98% after the 2nd cycle. The LiMn_2O_4 -PPy composite cathode with 7 wt.% PPy–10 wt.% SP270 in PVDF-EC-DEC- LiClO_4 electrolyte showed good capacity with cycling. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: PVDF-based electrolyte; Lithium polymer battery; LiMn_2O_4 ; Chemically synthesised PPy; LiMn_2O_4 -PPy composite

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 the attractive alternative to MnO_2 for use in lithium rechargeable batteries [2]. The lithium manganese oxide used as the active material is prepared by mixing with conductive agents such as acetylene black. Electronic conducting polymers have been taken notice of since redox reaction of polyacetylene was reported by Negrey et al. [3]. Diaz et al. [4] first reported the electrical properties of conducting polymer polypyrrole (PPy). Remarkable progress for processing the electronic conducting polymer was achieved by Murata et al. [5].

Polymer electrolytes were discovered by Fenton et al. in 1973. Wright et al., showed that complexes formed with PEO and alkali metal salts deliver high ionic conductivity [6]. Subsequently, these complexes were proposed by Abraham [7] as polymer electrolyte for solid-state battery and electrochemical device applications. Polymer electrolyte has provided the attractive possibility of developing new type of lithium battery, the so-called lithium polymer battery

(LPB) with thin layers [8]. 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 levelling batteries [9]. Chemically, LiMn_2O_4 -PPy composite has been reported by Yoneyama and co-workers in liquid electrolytes [10]. We have studied new attempts of LiMn_2O_4 -PPy-carbon composite with polymer electrolyte.

In this work, we investigated ionic conductivity of PVDF-based electrolyte and then, characteristics of charge/discharge cycling of LiMn_2O_4 , LiMn_2O_4 -PPy composite and LiMn_2O_4 -PPy/MCMB cell with polymer electrolyte.

2. Experimental

Polyvinylidene-hexafluoropropylene (PVDF-HFP, Eif Atochem, Kynar 2801) was dried under vacuum at 60°C for 20 h. LiClO_4 (Aldrich Company) was dried under vacuum at 110°C for 20 h before use. Propylene carbonate (PC), ethylene carbonate (EC) and diethylene carbonate (DEC) were purchased from Aldrich Company. LiClO_4 was dissolved in PC-EC and EC-DEC solutions. The PC-EC- LiClO_4 and EC-DEC- LiClO_4 was added 25 wt.%

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PVDF-HFP. The liquid electrolyte solution was homogeneously mixed by stirring. The polymer electrolyte film was prepared by casting and quick heating technique [11] at 110°C for 10 min. The thickness of electrolyte film was 100 μm .

The conductivity of the electrolyte films was determined at 25, 40, 50, 60 and 70°C, after equilibrium time of 30 min at each temperature. The symmetrical SUS/SUS cell was 2 cm \times 2 cm in size. The complex impedance of the polymer electrolyte was measured by the AC two-electrode method using IM6 Impedance Measurement System (Zahner Elektrik Company). The AC signal was applied across the cells and its frequency range was from 10 mHz to 2 MHz. The ionic conductivity of electrolyte films was calculated from Nyquist plot of complex impedance and the cell factor (film thickness/electrode area). PPy was obtained from chemical polymerisation and oxidation of pyrrole by Fe(III) oxidants such as FeCl_3 [12].

Composite cathode slurry was prepared by mixing LiMn_2O_4 powder with carbon black (SP270), PPy and PVDF 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 cm². 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 Company). Preparation and test of cells were carried out in argon-filled glove box.

3. Results and discussion

Fig. 1 shows variation of conductivity of PVDF-PC₁₀EC₁₀LiClO₄ electrolyte as a function of the amount of added PVDF. The PVDF-PC₁₀EC₁₀LiClO₄ electrolyte delivered lower conductivity with increasing amount of added PVDF. The PVDF-PC₁₀EC₁₀LiClO₄ with 15 wt.% PVDF was like a weak film. The ionic conductivity of PVDF-PC₁₀EC₁₀LiClO₄ electrolytes was higher than that of PEO elasticised electrolyte at room temperature [13]. The variation of conductivity of PVDF-PC₁₀EC₁₀LiClO₄ as a function of temperature was lower than that of PEO electrolyte. The ionic conductivity of PVDF-LiClO₄PC₅EC₅ with 25 wt.% PVDF electrolyte was 2.3×10^{-3} S/cm at room temperature. The electrolyte film with 25 wt.% PVDF had flexible and good mechanical property.

Fig. 2 exhibits temperature dependence of conductivity of PVDF-EC-DEC-LiClO₄ electrolytes as a function of mole ratios of plasticizer. Four different mole ratios of electrolytes were prepared. The conductivity of PVDF-EC₁₀DEC₁₀LiClO₄ electrolyte was higher than those of others. The ionic conductivity of PVDF-EC₁₀DEC₁₀LiClO₄ was 1.86×10^{-3} S/cm at room temperature. Hence, we suggest that adding

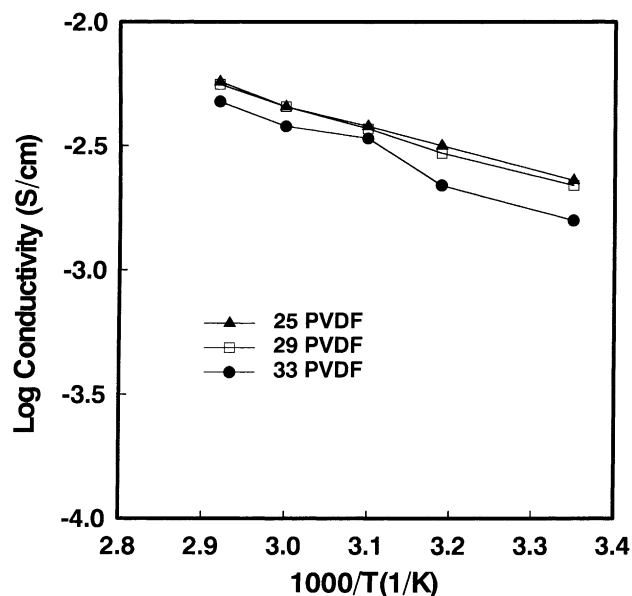


Fig. 1. Conductivity of PVDF-PC₁₀EC₁₀LiClO₄ as a function of PVDF addition ratio.

PVDF of 25 wt.% to PC₁₀EC₁₀LiClO₄ and EC₁₀DEC₁₀LiClO₄ electrolyte effectively could control high conductivity and flexibility of polymer electrolyte film.

The specific capacity of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells as a function of electrolytes in the LiMn_2O_4 added 15 wt.% SP270 cathode is shown in Fig. 3. The initial open circuit voltage (OCV) of $\text{LiMn}_2\text{O}_4/\text{Li}$ cell was 3.4 V. The charge/discharge cycling was carried out between 3.0 and 4.3 V with a current density of 0.1 mA/cm². The discharge capacity of LiMn_2O_4 with PVDF-PC₁₀EC₁₀LiClO₄ and PVDF-EC₁₀DEC₁₀LiClO₄ were 125 and 123 mAh/g at room temperature, respectively. In addition, the capacity based on LiMn_2O_4 with PVDF-PC₁₀EC₁₀LiClO₄ electrolyte was 125 and 120 mAh/g at 1 and 15 cycles, respectively. The difference of the discharge

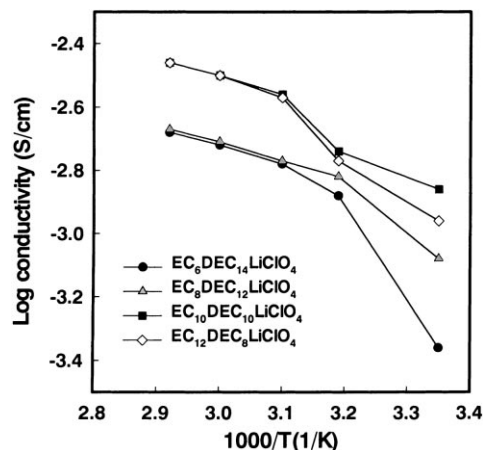


Fig. 2. Conductivity of PVDF-EC_xEC_yLiClO₄ as a function of mole ratio of plasticizer.

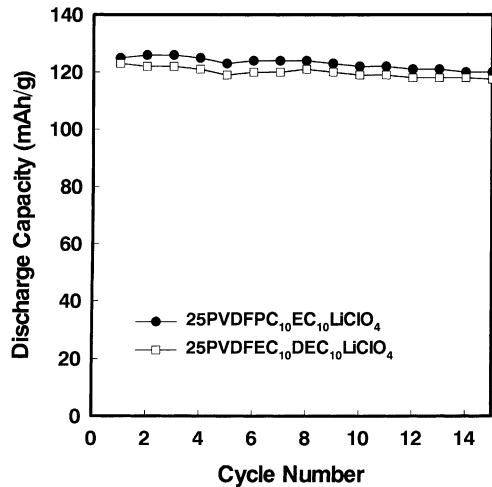


Fig. 3. Specific capacity of $\text{LiMn}_2\text{O}_4/\text{Li}$ cells with PVDF based polymer electrolytes.

capacity was 4%. The charge/discharge efficiency was above 96% at all cycles.

Fig. 4 shows the specific capacity of $\text{LiMn}_2\text{O}_4\text{-PPy/Li}$ cells with $\text{PVDF-EC}_{10}\text{DEC}_{10}\text{LiClO}_4$ as a function of addition ratio of PPy. The discharge capacity decreased with charge/discharge cycling from the 1st cycle to the 5th cycle. However, capacity of LiMn_2O_4 with 7 wt.% PPy–10 wt.% SP270 was higher than that of LiMn_2O_4 with 15 wt.% SP270. The fading-in-capacity of LiMn_2O_4 composite with 10 and 7 wt.% PPy was 7% during 10 cycles. Also, the charge/discharge efficiency was above 98% after the 5th cycle. The discharge capacity of $\text{LiMn}_2\text{O}_4\text{-PPy}$ with 7 wt.% PPy was 135 and 125 mAh/g at 1 and 10 cycles. We suggest that the capacity increase is due to doping/undoping of anions in PPy.

Fig. 5 shows impedance spectra of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell with $\text{PVDF-EC}_{10}\text{DEC}_{10}\text{LiClO}_4$ as a function of charge/

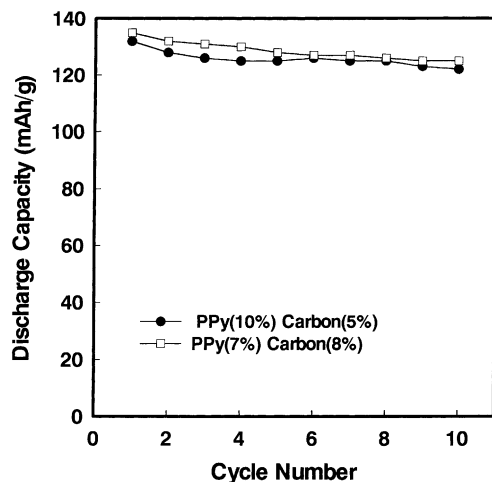


Fig. 4. Specific capacity of $\text{LiMn}_2\text{O}_4\text{-PPy/Li}$ cells with $\text{PVDF-EC}_{10}\text{DEC}_{10}\text{LiClO}_4$.

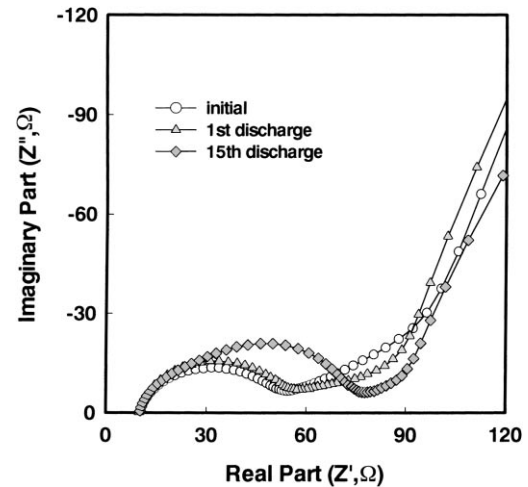


Fig. 5. Impedance spectra of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell with $\text{PVDF-EC}_{10}\text{DEC}_{10}\text{LiClO}_4$ during cycling.

discharge cycling at 25°C , indicating that the radius of the semicircle is associated with the electrodes resistance of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell increases with increasing cycling. The AC impedance response of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell forms a broad semicircle in the frequency range of $64\text{ kHz} \sim 1\text{ Hz}$, and a gradual line to the real axis in the frequency range of $1\text{ Hz} \sim 10\text{ mHz}$. The bulk resistance of $\text{PVDFEC}_{10}\text{DEC}_{10}\text{LiClO}_4$ electrolyte was $10\ \Omega$. The cell resistance was 58 and $85\ \Omega$ at the initial state and 15th discharge, respectively. As shown in previous research, the increase in cell resistance is due to the increment of the electrode's resistance. The discharge capacity of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell was 60 and 49 mAh/g at 1st and 15th cycle, respectively. The optimisation of $\text{LiMn}_2\text{O}_4\text{-PPy}$ composite in polymer electrolyte is on test in our laboratory now. In these results, we suggest that the $\text{LiMn}_2\text{O}_4\text{-PPy}$ composite cathode with 7 wt.% PPy 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 ionic conductivity of $\text{PVDF-PC}_{10}\text{EC}_{10}\text{LiClO}_4$ and $\text{PVDF-EC}_{10}\text{DEC}_{10}\text{LiClO}_4$ with 25 wt.% PVDF electrolyte was 2.3 and $1.8 \times 10^{-3}\text{ S/cm}$ at room temperature. The cathode resistance of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell increased with increasing cycling. The discharge capacity of $\text{LiMn}_2\text{O}_4\text{-PPy}$ with 7 wt.% PPy was 135 and 125 mAh/g at 1 and 10 cycles. The cell resistance was 58 and $85\ \Omega$ at the initial state and 15th discharge, respectively. The discharge capacity of $\text{LiMn}_2\text{O}_4\text{-PPy/MCMB}$ cell was 60 and 49 mAh/g at 1st and 15th cycle, respectively. The $\text{LiMn}_2\text{O}_4\text{-PPy}$ composite cathode with 7 wt.% PPy–10 wt.% SP270 with $\text{PVDF-EC-DEC-LiClO}_4$ electrolyte showed good capacity with cycling.

Acknowledgements

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