

Rechargeable Li/LiMn₂O₄ batteries with a polymeric solid electrolyte

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Abstract

The discharge/charge characteristics of Li/polymeric solid electrolyte/LiMn₂O₄ batteries at room temperature were investigated. The battery exhibited a large realizable capacity and long cycle life. The reaction of the interface between lithium electrode and polymeric solid electrolyte is controlled by both the ionic diffusion and the electrochemical reaction, but that of spinel LiMn₂O₄/polymeric solid electrolyte interface is only limited by the diffusion of lithium cation in the crystal lattice of spinel LiMn₂O₄, and the diffusion coefficient is 2.1×10^{-12} cm²/s.

Introduction

In the last decade, a lot of work has been done to find suitable rechargeable positive materials for lithium batteries. Among those materials investigated, spinel-related Li_xMn₂O₄ ($0 \leq x \leq 2$) is a very promising candidate positive material since its spinel structure during both Li cation insertion and extraction is maintained over a wide range of Li composition. The use of manganese oxide in rechargeable Li batteries offers a number of advantages such as high voltage and low cost as compared with other transition-metal compounds. The materials were already utilized as positive materials for rechargeable Li batteries with organic liquid electrolytes [1, 2].

Recent emphasis has been on investigations of all-solid Li batteries with polymeric solid electrolytes (PSE). Since Fendon *et al.* [3] developed the complexes of poly(oxyethylene)/alkali-metal salts as PSE in which polyether is taken as the matrix, the research on PSE has been widely expanded. Some of the PSE studied exhibit high conductivity at room temperature (higher than 6×10^{-5} S/cm) as well as good mechanical strength [4]. Room temperature all-solid Li batteries with PSE are very attractive because of the benefits of the thin film, but most of the batteries investigated are moderate temperature cells because of their low ionic conductivity in the PSE.

In this paper, we report the discharge/charge behavior of the room temperature all-solid Li batteries with comb-like copolyether/dimethoxyl oligo(oxyethylene)/LiClO₄ electrolyte, and the limitations at the electrode/PSE interface.

Experimental

Materials

Spinel LiMn₂O₄ was prepared by mixing appropriate amounts of Li₂CO₃ and MnO₂, and heating at 850 °C for 24 h in air. The resultant material is a blue-black

powder. Its X-ray diffraction pattern agreed with that of the spinel LiMn_2O_4 standard (ASTM 18-736).

Poly(oligo(oxyethylene)methacrylate-co-acrylamide) (P(MEO₁₆-AM)) and dimethoxyl oligo(oxyethylene) (DMEO₁₆) (where 16 represents the number of oxyethylene units) were prepared by the method described in our previous paper [5]. The polymeric solid electrolyte (Li/EO=0.056) was prepared by dissociating the calculated amount of LiClO_4 , DMEO₁₆ and P(MEO₁₆-AM) in methanol, and then evaporating slowly the methanol. The conductivity of the PSE reached 4×10^{-4} S/cm at room temperature.

The composite cathode material was made of 60 wt.% spinel LiMn_2O_4 , 30 wt.% PSE and 10 wt.% carbon black. Both the PSE film and the composite cathode film were prepared by the hot-press method at 80 to 120 °C in vacuum for 24 h (the film thickness is about 100 μm).

Measurements

A galvanostatic technique was employed to perform the discharge/charge tests of the batteries at 30 °C. The three-electrode cell was employed to study the electrochemical properties on the electrode/PSE interface. The electrochemical measurements were completed by means of WDZ-1 electrochemical measurement system with microcomputer. In all the tests, the ohmic potential drop of the PSE was compensated. All the procedures dealing with the cells were carried out in a moistureless glove box. X-ray powder diffractogram was taken by using Cu K α radiation with a graphite monochromator.

Results and discussion

Li/PSE/spinel LiMn_2O_4 batteries

The open-circuit voltage of Li/PSE/ LiMn_2O_4 cells was 3.15 V and stabilized at this value after 6 months storage. The discharge behavior of stored batteries showed no difference from new batteries. The batteries exhibited a long shelf life.

The discharge/charge curves of the batteries under different current density are shown in Fig. 1. When the batteries were discharged at 25, 50 and 100 $\mu\text{A}/\text{cm}^2$ to

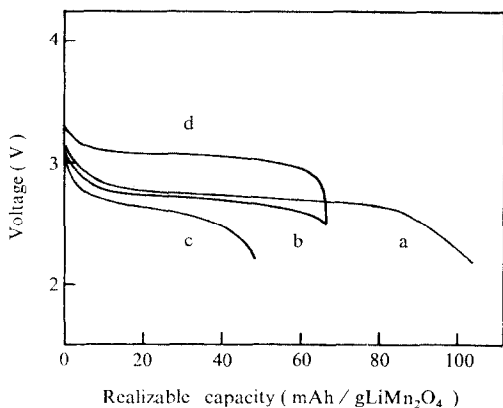


Fig. 1. Discharge/charge curve of Li/PSE/spinel LiMn_2O_4 cells; discharge: (a) 25 $\mu\text{A}/\text{cm}^2$, (b) 50 $\mu\text{A}/\text{cm}^2$, (c) 100 $\mu\text{A}/\text{cm}^2$, and charge: (d) 25 $\mu\text{A}/\text{cm}^2$.

2.5 V, respectively, the stable voltage plateaus appeared at about 2.75, 2.7 and 2.6 V, respectively, and the realizable discharge capacities were about 81, 68 and 38 mA h/g LiMn_2O_4 , respectively. With the increase of the discharge current, the voltage fell and the realizable capacity decreased. After they were discharged at $50 \mu\text{A}/\text{cm}^2$ to 2.5 V, the batteries were charged immediately at $25 \mu\text{A}/\text{cm}^2$. The charge voltage plateau was about 3.2 V. When the charge current density increased, the charge voltage plateau rose, and the discharge/charge efficiency lessened. The cause of the above phenomenon was the lower ionic conductivity in the PSE and the higher electrode/PSE interface resistance. Up to now, this is the largest shortcoming about Li batteries with the PSEs. We are studying the single-cation electrolyte and the plasticized-ion electrolyte further.

Figure 2 shows the cyclic voltammograms of the LiMn_2O_4 material between 2.0 and 3.8 V (versus Li) in the PSE. At 30°C , the voltammogram of the spinel was not symmetrical, but stable with increasing scan times. At 60°C , the voltammogram illustrates that the lithiation process of the spinel is reversible and similar almost to that in $\text{PC} + \text{LiClO}_4$ [2] but the difference in redox peak potentials is larger and there are a pair of shoulder peaks. The main reduction and oxidation peaks represent the insertion and extraction of Li cation, respectively. The reactions can be regarded as:



The voltammogram showed a pair of the shoulder peaks at 3.0 V during reduction and at 2.6 V during oxidation. We suspect that the migration of the polarized anion caused them when the current direction through the cell was reversed. The anionic polarization is larger in polymeric solid electrolytes than in liquid electrolytes. The polymeric single-cation electrolyte, in which only the cation is mobile and the anion is fixed on the polymer's chain, could overcome the defect [5].

Even if Li/PSE/spinel LiMn_2O_4 cells are overdischarged, the voltage plateau of about 1.4 V did not appear in contrast with Li/1 M LiClO_4 -PC/ λ - MnO_2 cells [6]. The result might prove that the reduction of propylene carbonate causes the voltage plateau

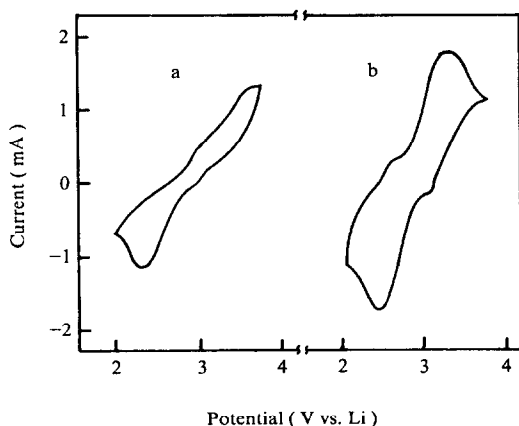


Fig. 2. Cyclic voltammogram of the spinel LiMn_2O_4 in the PSE; scan rate: 5 mV/s (a) at 30°C , and (b) at 60°C .

of 1.4 V [7]. The PSE is a more stable electrolyte than propylene carbonate (PC) under overdischarge.

The discharge/charge cycling test of Li/PSE/spinel LiMn_2O_4 cells was performed only in the voltage interval 3.3 to 2.5 V. The cycling dependence of the discharge/charge efficiency and the realizable capacity of the batteries are shown in Fig. 3. With the increase of the cycling number, the discharge/charge efficiency stabilized around 90%, but the realizable capacity dropped at first, then reduced slowly after the 100th cycle, and was about 60% of the initial capacity at the 150th cycle. Hitherto, it is still not clear what is the cause of the decreasing realizable capacity. Among the room temperature all-solid Li batteries investigated [8, 9], the discharge/charge properties of the Li/spinel LiMn_2O_4 battery are the best.

Limitations at the electrode/PSE interface

Figure 4 shows the polarization measurement curves of the Li electrode or the spinel LiMn_2O_4 electrode in the PSE. The result showed that the reaction of Li

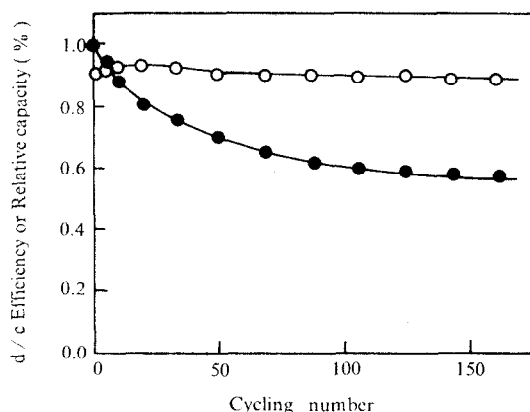


Fig. 3. Variation of (○) the discharge/charge efficiency and (●) the realizable capacity of Li/PSE/spinel LiMn_2O_4 cells with cycling number; discharge: $50 \mu\text{A}/\text{cm}^2$, and charge: $25 \mu\text{A}/\text{cm}^2$.

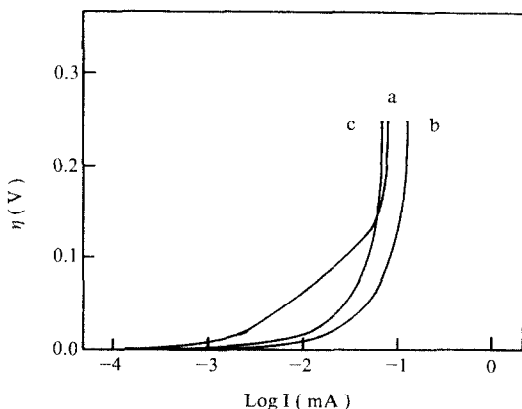


Fig. 4. Polarization measurement curves: (a) Li electrode in the PSE, (b) Li electrode in the PSE containing 10% PC, and (c) spinel LiMn_2O_4 electrode in the PSE at 30°C .

electrode/PSE interface (curve a) was controlled by both the diffusion of Li^+ in the PSE and the electrochemical reaction of Li^+/Li , the limit diffusion current density (i_d) and the exchange current density (i^0) of Li electrode/PSE interface were 0.76 and 1.2×10^{-2} mA/cm², respectively. When the plasticizer, PC, was added into the PSE, the polarization test (curve b) showed that the reaction of Li electrode/PSE interface was limited only by the diffusion of Li^+ in the PSE containing 10% PC, and that i_d was 1.2 mA/cm². But the reaction of spinel LiMn_2O_4 electrode/PSE interface (curve c) was limited only by the diffusion of Li^+ ; its i_d is 0.71 mA/cm². When PC was added into the PSE, the polarization curve of spinel LiMn_2O_4 electrode in the PSE was not significantly changed. The above results might suggest that the reaction of spinel LiMn_2O_4 electrode/PSE interface is limited by the diffusion of Li^+ in the crystal lattice of spinel LiMn_2O_4 .

Diffusion coefficient of Li^+ in spinel LiMn_2O_4

On the basis of the method suggested by Atlung *et al.* [10], we used the potential step test. The working electrode is the composite spinel LiMn_2O_4 electrode. Both the reference electrode and the counter electrode are Li metal. The electrolyte is the PSE. Figure 5 shows that the time ($t^{-1/2}$)-dependence of current (I) obtained from the potential step test is given as a straight line. The average diameter of a spinel LiMn_2O_4 grain used was about 1 μm . In the potential step test, the variation of the current with time may be expressed by the following equation:

$$I = zFS\Delta cD((1/D\pi t)^{1/2} - 1/r) \quad (3)$$

where z is the charge of Li cation, F is the Faraday constant, S is the effective area of spinel LiMn_2O_4 electrode, Δc is the different amount of the concentration of Li^+ on the surface of spinel LiMn_2O_4 grain during the potential step, D is the diffusion coefficient and r is the radius of spinel LiMn_2O_4 grain. According to above eqn., the diffusion coefficient of Li^+ in the crystal lattice of spinel LiMn_2O_4 was estimated as 2.1×10^{-12} cm²/s. This value is the identical order with that of the tunnel compounds such as Li_xWO_3 and Li_xTiO_2 [11], and smaller than that of the lamellar compounds [12]. The result is consistent with the structural characteristic of spinel LiMn_2O_4 .

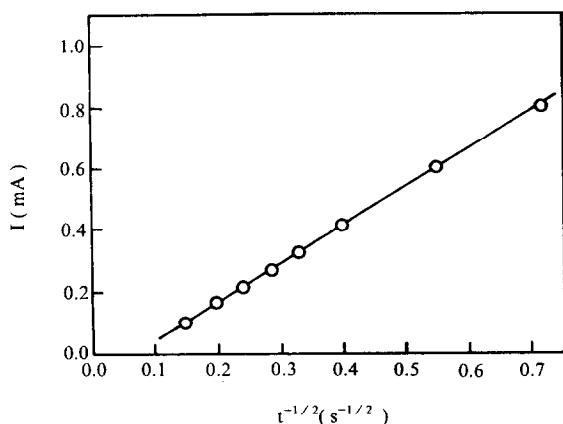


Fig. 5. Time ($t^{-1/2}$)-dependence of the current (I) obtained from the potential step test at 30 °C.

References

- 1 D. Guyomard and J. M. Taroscon, *J. Electrochem. Soc.*, **139** (1992) 937.
- 2 A. de Kock, M. H. Rossouw, L. A. de Picciotto and M. M. Thackeray, *Mater. Res. Bull.*, **25** (1990) 657.
- 3 D. E. Fendon, J. M. Parker and P. V. Wright, *Polymer*, **14** (1973) 589.
- 4 Z. Deng, K. Xu and G. Wan, *Chin. J. Polym. Sci.*, **10** (1992) 218.
- 5 Z. Deng, Q. Xu, Y. Zheng, K. Xu and G. Wan, *J. Functional Mater. (Gongneng Cailiao)*, **22** (1991) 267.
- 6 H. Yang, S. Li and Z. Wu, *Ext. Abstr. 5th Int. Meet. Lithium Batteries, Beijing, China, May 1990*, p. 287.
- 7 J. O. Besenhard and H. P. Fritz, *J. Electroanal. Chem.*, **53** (1974) 329.
- 8 F. Bonino, M. Ottariani, B. Scrosati and G. Pistoia, *J. Electrochem. Soc.*, **135** (1988) 12.
- 9 Z. Ogumi, Y. Uchimoto, Z. Takehara and Y. Kanamori, *J. Electrochem. Soc.*, **135** (1988) 2649.
- 10 S. Atlung, K. West and T. Jacobasen, *J. Electrochem. Soc.*, **126** (1979) 1311.
- 11 C. Ho, I. R. Raistrick and R. A. Huggins, *J. Electrochem. Soc.*, **127** (1980) 342.
- 12 D. A. Winn, J. M. Shemilt and B. C. H. Steele, *Mater. Res. Bull.*, **11** (1976) 551.