리튬 고체전지용 $LiMn_2O_4$ Composite Cathode의 충방전 특성

김종욱°, 박계춘*, 구할본
전남대학교 전기공학과, *목포대학교 전기공학과

Charge/discharge Properties of $LiMn_2O_4$ Composite Cathode for All-solid state Rechargeable Batteris

Jong-Uk Kim°, Gye-Choon Park*, Hal-Bon Gu
Dept. of Electrical Eng., Chonnam National University
*Dept. of Electrical Eng., Mokpo National University

Abstract - The purpose of this study is to research and develop PEO/PVDF electrolytes and $LiMn_2O_4$ composite cathode for all-solid state lithium rechargeable battery. We investigated AC impedance response and charge/discharge cycling of $LiMn_2O_4$/SPE/Li cells. The cell resistance was decreased so much initial charge process from 0% SOC to 100% SOC. The radius of semicircle of $LiMn_2O_4$/SPE/Li cell was so much from initial state to 20th cycling. The discharge capacity of the $LiMn_2O_4$ composite cathode was 144mAh/g based on $LiMn_2O_4$.

1. Introduction

Polymer electrolytes were discovered by B. E. Fenton et al.[1] in 1973. P. V. Wright et al.[2] then showed that complexes formed with PEO and alkali metal salts exhibit high ionic conductivity. Subsequently these complexes were proposed by M. B. Armand et al.[3] as polymer electrolyte for solid state battery and electrochemical device applications. Polymer electrolyte have provided the interesting possibility of developing new types of lithium battery, so-called lithium polymer battery(LPB)[4], having 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, from thin film batteries for microelectronics to electric vehicle batteries and load leveling batteries.

Adding poly(vinylidene fluoride)[PVDF] to PEO-PC-EC-$LiClO_4$ electrolyte, its conductivity becomes higher than that of PEO-PC-EC-$LiClO_4$ without those[5]. $LiMn_2O_4$ is an interesting active material for lithium rechargeable batteries.

In this work we report the interfacial resistance variation as a function of state of charge(SOC) and discharge capacity with cycling of $LiMn_2O_4$/SPE/Li cells.

2. Experimental

High molecular weight PEO(MW : 5×10^6), Li salt($LiClO_4$), propylene carbonate(PC) and ethylene carbonate(EC) were purchased from Aldrich Co. PEO was dissolved in acetonitrile(ACN, Aldrich Co.) by 20wt% solution. $LiClO_4$ and PEO were dissolved in acetonitrile(Aldrich Co.), the ratio of EO/Li was 8 (EO represents repeating unit of PEO), and adding of PC and EC was followed after that. Also, poly(vinylidene fluoride)[PVDF, EIF Autochem North America Inc.] were added to the PEO-$LiClO_4$-PC-EC-ACN solution with various mole ratios. The polymer electrolyte films were prepared by solution casting. After solvent evaporation, the electrolyte films were vacuum-dried at 50°C for 12h, yielding films of 150μm thickness. The complex impedance of the polymer electrolyte was measured by the AC two electrode method using IM6 Impedance Measurement System(Zahner Electrik Co.). The AC signal was applied across the cells and its frequency range was from 100mHz to 2MHz.

Composite cathode slurry was prepared by mixing $LiMn_2O_4$ powder with acetylene black and SPE solution. The mixture slurry was stirred for 6h. 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 50°C for 4h. The area of $LiMn_2O_4$/SPE/Li cells were 2 X 2 cm^2. The current density of charge/discharge cycling was 0.05 and 0.1mA/cm^2. Preparation and tests of cells were carried out in argon-filled glove box.

3. Results and discussion

Fig. 1 shows the first charge/discharge cycling curve of $LiMn_2O_4$/SPE/Li cell at room temperature. The initial open circuit voltage(OCV) of $LiMn_2O_4$/SPE/Li cell was

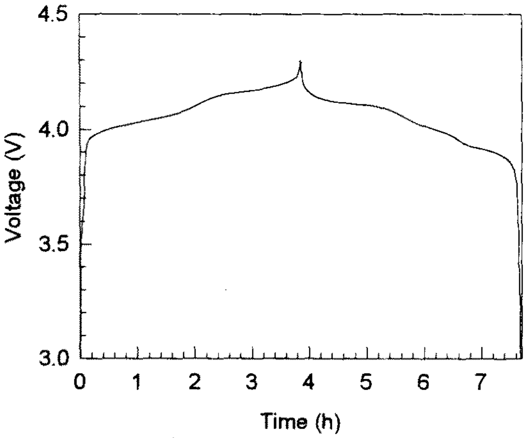

Fig. 1 Charge/discharge characteristics of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5$/ Li cell at 25℃

2.97V. The charge/discharge cycling was carried out between 3.0V and 4.3V with current density of 0.1mA/cm^2 at room temperature. The first discharge capacity based on $LiMn_2O_4$ was 133mAh/g.

Fig. 2 is impedance spectra of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5$/Li cell as a function of state of charge(SOC). The

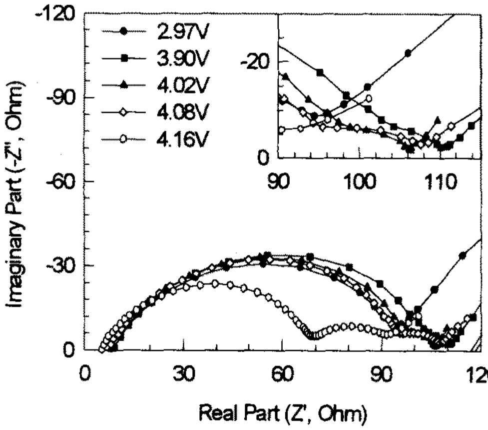

Fig.2 Impedance spectra of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5$/Li cell as a function of SOC during charge process

resistance of $LiMn_2O_4$ composite cathode during first charge process, lithium ions are deintercalated in the $LiMn_2O_4$, with various SOC was investigated. The radius of semicircle associated with the interfacial resistance and cathode resistance of $LiMn_2O_4$/SPE/Li cell increased during charge process from 2.97V to 3.90V. The cell resistance was 95Ω and 110Ω

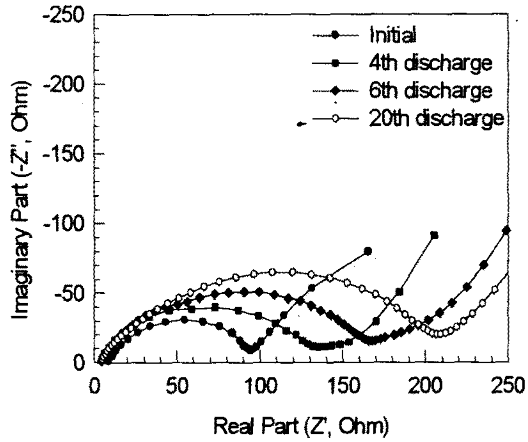

Fig. 3 Impedance spectra of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5$/Li cell with charge/discharge cycling at 25℃

at 2.97V to 3.90V, respectively. However, during charge process cell resistance was decreased slowly from 3.90V to 4.08V. The cell resistance was decreased so much initial charge process from 0% SOC to 100% SOC. The decrement of semicircle radius is attributed to decrease of cell resistance during charge process. The impedance plot of $LiMn_2O_4$/SPE/Li cell as a function of charge/discharge cycling at 25℃ is shown in Fig. 3. The impedance plot of the initial cell is compared with that obtained at the 0% SOC of the 4th, 6th and 20th discharge. As shown in Fig. 3, the radius of semicircle associated with Li/SPE interfacial resistance and cathode resistance of $LiMn_2O_4$/SPE/Li cell was so much from initial state to 20th cycling. The cell resistance was 210Ω after 20th discharge. We suggest that the increase of cell resistance is attributed to the increment of cathode resistance.

Fig. 4 exhibits the specific capacity and Ah efficiency of $LiMn_2O_4$/SPE/Li cell as a function of charge/discharge cycling with current density of 0.1mA/cm^2. The theoritical capacity of $LiMn_2O_4$ is 148mAh/g. The discharge capacity based on $LiMn_2O_4$ of

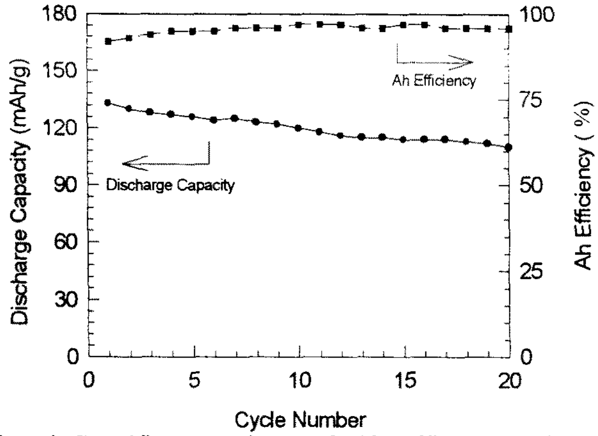

Fig. 4 Specific capacity and Ah efficiency of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5/Li$ cell with current density of $0.1mA/cm^2$

the 1st and 20th cycles was 133mAh/g and 110mAh/g, respectively. The utilization based on $LiMn_2O_4$ at 1st and 20th discharge process were 90% and 74%, respectively. The Ah efficiency was above 92% at all cycles. Fig. 5 shows specific capacity and Ah efficiency of $LiMn_2O_4$/SPE/Li cell with cycling at $0.05mA/cm^2$. The Ah efficiency was 97% at 20th cycle. The decrement of discharge capacity was very slowly during charge/discharge cycling. The discharge capacity of 1st and 20th cycles was 144mAh/g and 118mAh/g, respectively. The utilization of $LiMn_2O_4$ was above 80% until 20th cycles. From these results, we can suggest that the $LiMn_2O_4/PEO_4PVDF_4LiClO_4$ PC_5EC_5 /Li cell has a excellent cycleability at room temperature.

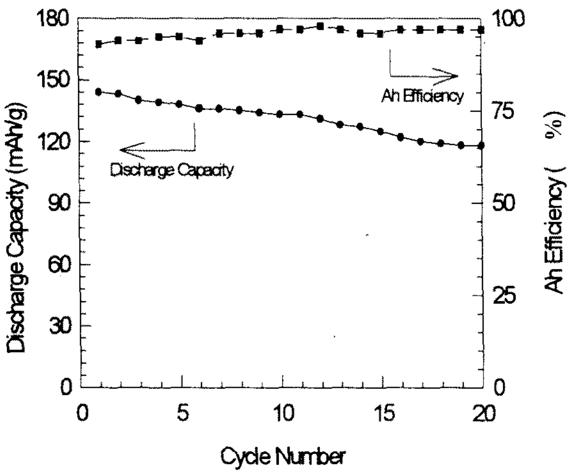

Fig. 5 Specific capacity and Ah efficiency of $LiMn_2O_4/PEO_4PVDF_4LiClO_4PC_5EC_5/Li$ cell with current density of $0.05mA/cm^2$

4. Conclusions

On the basis of the results described above, one can reveal the following conclusions. ; The cell resistance was decreased so much initial charge process from 0% SOC to 100% SOC. The decrement of semicircle radius is attributed to decrease of cell resistance during charge process. The radius of semicircle associated with Li/SPE interfacial resistance and cathode resistance of $LiMn_2O_4$/SPE/Li cell was so much from initial state to 20th cycling. The decrement of discharge capacity was very slowly during charge/discharge cycling. The discharge capacity of 1st and 20th cycles was 144mAh/g and 118mAh/g, respectively. The $LiMn_2O_4$/SPE/Li cell has a good properties.

References

[1] B. E. Fenton et al., Polymer, Vol. 14, p. 589, 1973.

[2] P. V. Wright, Brit. Polymer J., Vol. 7, p. 319, 1975.

[3] M. B. Armand et al., 2nd Int. Meeting on Solid Electrolytes, St. Andrew, Scotland, p. 20, 1978.

[4] K. M. Abraham and M. Alamgir, J. Power Source, Vol. 43-44, p. 195, 1993.

[5] J. U. Kim et al., Proceedings of 5th ICPADM on the IEEE Dielectrics and Electrical Insulation Society, Vol. 2, p. 646, 1997.