

리튬 폴리머 전지용 $\text{Li}_x\text{V}_3\text{O}_8$ Composite Cathode의 충방전 특성

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Charge/discharge Properties of $\text{Li}_x\text{V}_3\text{O}_8$ Composite Cathode for Lithium Polymer Batteries

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Abstract-The purpose of this study is to research and develop $\text{Li}_x\text{V}_3\text{O}_8$ composite cathode for lithium polymer battery. We investigated electrochemical, interfacial properties and charge/discharge cycling of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell.

The radius of semicircle associated with the interfacial resistance of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell increased very slowly during discharge process from 100% SOC to 90% SOC. And then the cell resistance was increased at discharge process from 10% SOC to 0% SOC. The discharge capacity based on $\text{Li}_x\text{V}_3\text{O}_8$ was 212mAh/g at 15th cycle. The $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell has a good properties.

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]. $\text{Li}_x\text{V}_3\text{O}_8$ is an interesting active material for lithium rechargeable batteries. High initial capacities were reported for low rate discharges, the maximum lithium uptake corresponding to more than three addition Li per formula unit, giving a stoichiometric energy density in excess of 650Wh/kg[6].

In this work we report the interfacial resistance variation as a function of state of charge(SOC) and discharge capacity with cycling of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cells.

2. Experimental

High molecular weight PEO(MW 2×10^6), 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-LiClO₄-PC-EC-ACN solution. The polymer electrolyte films were prepared by solution casting. After solvent evaporation, the electrolyte films were vacuum-dried for 12h, yielding films of 250μm thickness. The pre-active material Li_xV₃O₈ was prepared on the basis of sol-gel process. Li_xV₃O₈ gel was made following the procedure as described in Ref(6). V₂O₅(Aldrich Co.) was slowly added to a stirred LiOH(Aldrich Co.) water solution at 60°C and stirred for 48h. This gel was dried under vacuum at 200°C for 10h. The product was heated to 680°C and quench cooled to room temperature. Li_xV₃O₈ ground and was vacuum dried at 200°C. Powder x-ray diffraction(XRD) measurements were made with a Dmax/1200 X-ray diffractometer.

Composite cathode slurry was prepared by mixing Li_xV₃O₈ powder with acetylene black and SPE solution. The mixture slurry was stirred for 3h. 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 Li_xV₃O₈/SPE/Li cells were 2 X 1 cm².

Cyclic voltammetry was performed in the voltage range from 1.8V to 3.5V vs. Li/Li⁺ using scan rate of 0.1mV/sec at 25°C. The current density of charge/discharge cycling was 0.05 and 0.1mA/cm².

The complex impedance of Li_xV₃O₈/SPE/Li cells were measured by the AC two electrode method using IM6 Impedance Measurement System(Zahner Elektrik Co.). Preparation and tests of cells were carried out in argon-filled glove box.

3. Results and discussion

X-ray diffractograms of the sol-gel

Li_xV₃O₈ heat-treated at 80°C shown in Fig. 1. The peak positions of the Li_xV₃O₈ coincides with the peak positions observed for the conventional high-temperature material. Intensity of the (100) peak at 2

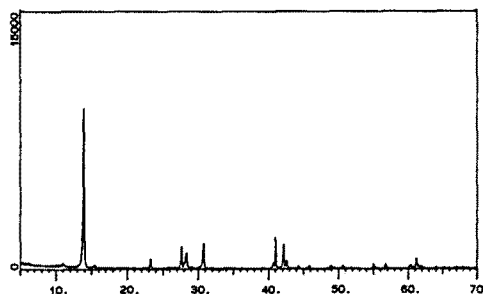


Fig. 1 X-ray diffractogram of sol-gel Li_xV₃O₈ heat-treated at 80°C.

$\theta = 14^\circ$ is higher than that of LiV₃O₈ heat-treated with starting crystal. Particle size of sol-gel Li_xV₃O₈ heat-treated is very small.

Fig. 2 shows cyclic voltammogram of Li_xV₃O₈/SPE/Li cell. In the cyclic voltammogram for Li_xV₃O₈ composite cathode film, the reduction reaction of

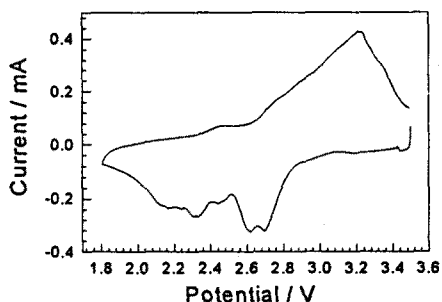


Fig. 2 Cyclic voltammogram of Li_xV₃O₈/SPE/Li cell.(Scan rate : 0.1mV/sec)

Li_{1+x}V₃O₈ showed four reduction peaks. Reduction peaks rised at 2.7, 2.6, 2.45 and 2.35V. On the other hand, the oxidation peaks rised 2.5, 2.7, 2.9 and 3.25V.

Fig. 3 exhibits impedance spectra of Li_xV₃O₈/SPE/Li cell as a function of state of charge(SOC). The resistance of Li_xV₃O₈ composite cathode during discharge process, intercalating lithium ions into Li_xV₃O₈ with various SOC was investigated. The

radius of semicircle associated with the interfacial resistance of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell increased very slowly during discharge

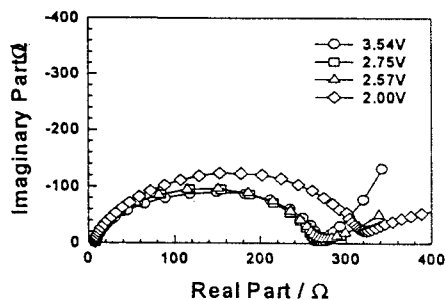


Fig. 3 Impedance spectra of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell as a function of SOC at 25°C.

process from 3.54V to 2.57V. The cell resistance was 270Ω and 280Ω at 3.54V and 2.57V, respectively. On the other hand, the cell resistance of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell at 2.00V was high. The cell resistance was increased at discharge process from 10% SOC to 0% SOC. The increment of cathode resistance is attributed to increase of cell resistance during end discharge process.

Fig. 4 shows the specific capacity of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell as a function of charge/discharge cycling. The discharge

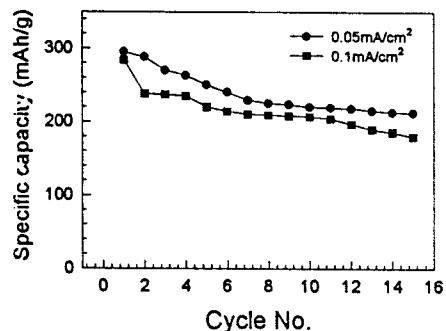


Fig. 4 Specific discharge capacity of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell at 25°C.

capacity based on $\text{Li}_x\text{V}_3\text{O}_8$ of 1st and 15th cycles was 295mAh/g and 212mAh/g at current density of $0.05\text{mA}/\text{cm}^2$, respectively. The Ah efficiency was above 98% at all cycles. The discharge capacity was decreased with charge/discharge cycling from 1st cycle to 10th cycle.

However, the capacity variation was not so clear after 10th cycle. From these results, we suggest that the sol-gel $\text{Li}_x\text{V}_3\text{O}_8$ heat-treated composite cathode showed good capacity with cycling.

4. Conclusions

On the basis of the results described above, one can reveal the following conclusions : Particle size of sol-gel $\text{Li}_x\text{V}_3\text{O}_8$ heat-treated is very small. The reduction reaction of $\text{Li}_{1+x}\text{V}_3\text{O}_8$ showed four reduction peaks. The discharge capacity based on $\text{Li}_x\text{V}_3\text{O}_8$ was 284mAh/g. The radius of semicircle associated with the interfacial resistance of $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell increased very slowly during discharge process from 3.54V to 2.57V. And then the cell resistance was increased at discharge process from 10% SOC to 0% SOC. The discharge capacity based on $\text{Li}_x\text{V}_3\text{O}_8$ of 1st and 15th cycles was 295mAh/g and 212mAh/g. The $\text{Li}_x\text{V}_3\text{O}_8/\text{SPE}/\text{Li}$ cell has a good properties.

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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. Alangir, 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.
- (6) K. West et al., J. Electrochem. SOC., Vol. 143, p.820, 1996.