Composite cathode and anode films for rechargeable lithium batteries

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Abstract Recently the rechargeable Li and Li-ion polymer batteries have improved due to development of Li-ion conductive gel electrolytes and of high energy granting intercalation compounds. In our laboratory the composite cathodic film, the composite carbon anode film and PVC-based electrolyte film were successfully prepared by casting procedures. Cycling experiments of the cells with Li or composite carbon anode in contact with PVC-based electrolyte and composite cathode were performed. Relatively good performance of the cell with Li anode, the composite cathode and LiPF₆-EC-DEC electrolyte was achieved in that over 50 cycles were possible with minimal capacity loss upon cycling. The same cell with PVC-based electrolyte was cycled over 20 cycles. Replacing Li anode by composite carbon anode, the cell behaved like the latter. It is found that appropriate amount of carbon content is helpful to improving specific capacity.

Keywords: composite films; gel electrolyte film, poly(vinyl chloride), casting, 3-film configuration batteries.

IN recent years the most significant advances made in the field of rechargeable Li or Li-ion polymer batteries are mainly due to the development of Li-ion conductive gel electrolytes, and of high energy granting intercalation compounds used as reversible cathodes and anodes.

Considering the configuration of advanced design of multilayer cells, the advantages of composite cathode film and composite carbon anode film are obvious. This anode can prevent formation of tree-crystalline of lithium.

The use of thin-film technology for the formation of batteries offers various advantages^[1]: thin layers give a lower electrical resistance in the transverse direction; thin-film technology provides clean surface of the electrodes and electrolytes and may improve the electrode-electrolyte interface contact by reducing the interface resistance; thin-film technologies generally give very good adhesion between layers, and large areas can also be obtained with these techniques.

Remarkable progress has been achieved in developing electrolytes with both high ionic conductivity around 10^{-3} S/cm and dimensional stability. Gel electrolytes, such as polyacrylonitrile (PAN)^[2]- or poly(vinyl chloride) (PVC)^[3]-based electrolytes, are presently considered being usable as separators in rechargeable Li or Li-ion batteries.

Intercalation compounds can be characterized by layered or tunneled structures capable of providing channels for the easy access and fast mobility of the guest Li⁺. Intercalation compounds, based on vanadium oxides, such as Li_{1+x}V₃O₈^[4], Na_{1+x}V₃O₈^[5], layered lithium metal oxides, such as LiNiO₂^[6], and manganese oxides, such as LiMn₂O₄^[7], have been tested as cathodes with satisfactory results. And also, intercalation compounds, such as carbonaceous materials, can be used as anodes, capable of intercalating and deintercalating large quantity of Li⁺.

Herein are reported the preparations of 3 kinds of free-standing, thin films and cycling of cells with Li or composite carbon anode in contact with PVC-based electrolyte and composite cathode.

1 Experimental

1.1 Preparation of composite cathodic films

Details of the preparations of cathode materials (such as Li_{1+x}V₃O₈, Na_{1+x}V₃O₈ and LiMn₂O₄) synthesized at room temperature have already been reported^[4, 5, 7].

In our laboratory the composite cathodic film (46% (w) LiMn₂O₄ + 22% (w) PVC-based electrolyte + 23% (w) PVC + 9% (w) acetylene black) was prepared by casting^[8], and the general procedures included the dissolution/dispersion of the components in purified tetrahydrofuran (THF), the mixing of the solutions and the slow evaporation of the solvent in a teflon container. The composite cathodic film was

cut to proper size (diameter: 1.3 cm) for later use.

1.2 Preparation of composite carbon films

Composite carbon films were prepared by casting mixtures each consisting of 53 % (ω) carbon + 26 % (ω) PVC-based electrolyte + 21 % (ω) PVC. The casting procedure is the same as that for the preparation of composite cathode films.

1.3 Preparation of PVC-based electrolytes

PVC-based electrolytes were obtained by casting a mixture consisting of 15 % (ω) PVC + 40 % (ω) ethylene carbonate (EC) + 40 % (ω) propylene carbonate (PC) + 5 % (ω) lithium perchlorate (LiClO_4). A mixture of the components was dissolved in THF and the resulting solution was poured into a teflon container. When the THF was evaporated at room temperature, a free-standing gel electrolyte film was formed.

The casting and drying procedures for all the film preparations were performed in an argon-filled glove-box to avoid moisture contamination.

1.4 Impedance spectroscopy

Impedance spectroscopy tests were carried out on two well-polished stainless steel (SS) electrodes (blocking contacts) with a Solartron 1255 frequency response analyzer coupled with a 1286 Solartron electrochemical interface. A computer program set the experimental conditions and processed the data to obtain the relevant features from the impedance plots.

1.5 Cell preparation

Metallic cases endowed with a spring to provide tight packing of the electrodes were used. They had an internal configuration like button cells. For the Li cell: the Li anode was separated from the composite cathodic film by two layers of glass wool separator soaked with $\text{LiPF}_6/\text{EC-DEC}$ (diethyl carbonate) electrolyte or the Li anode was separated from the composite cathodic film by PVC-based electrolyte film. For the Li-ion cell: the composite carbon film was separated from the composite cathodic film by PVC-based electrolyte film. The cells were sealed in a moisture resistant package so that the test was permitted outside the glove-box. Cycling experiments were performed under galvanostatic conditions with the charge and discharge cut-off of 4.3 and 3.2 or 3.3 V, respectively.

2 Results and discussion

The above procedure gave homogeneous and mechanically stable PVC-based electrolyte film, 100–200 μm thick, without observable evidence of agglomeration, and the composite cathodic films, 50–150 μm thick, both having satisfactory mechanical strength. They are homogeneous and do not react with moisture in air. The composite carbon films, 200–300 μm thick, with moderate mechanical strength, do not react with moisture in air either. But the homogeneity of the composite carbon film is not so good as the composite cathodic films (figure 1).

PVC-based electrolyte film was cut to the size of 2.01 cm^2 and sandwiched between two electrodes for a-c measurement. The a-c measurement was made in the frequency range of 1.0 – 1.0×10^6 Hz. Fig. 2 shows the typical impedance plot of PVC-based electrolyte. The X-axis intercept gives the bulk resistance (R_b) of electrolyte. The conductivity at room temperature can be easily calculated to be $\sigma \sim 2 \times 10^{-3}$ S/cm. The near perpendicular plot indicates that there is no measurable charge transfer at the interfaces.

To compose the electrodes besides the essential electrode components, such as the active material, electronic conductor and binder, a proper proportion of polymer electrolyte has to be incorporated in both the anode and cathode in order to facilitate Li^+ migration.

The experimental cell with Li anode, the composite cathode (a film of geometric surface area 1.3 cm^2) and $\text{LiPF}_6\text{-EC-DEC}$ electrolyte was cycled under galvanostatic conditions. Fig. 3 shows the specific capacity for a Li/ LiMn_2O_4 cell as a function of cycle number. It shows that the cell cycled over 50 times with minimal capacity loss. This result means that the composite cathodic film performed well in the batteries.

The experimental cell with Li anode, composite cathode (a film of geometric surface area 1.3 cm^2)

Fig. 1. SEM pictures of (a) 46% (w) LiMn_2O_4 + 22% (w) PVC-based electrolyte + 23% (w) PVC + 9% (w) acetylene black; (b) 53% (w) C + 26% (w) PVC-based electrolyte + 21% (w) PVC.

Fig. 2. Typical impedance plot of the PVC-EC/PC-Li- ClO_4 electrolyte.

Fig. 3. Cycling behavior of the cell: Li/LiPF₆-EC-DEC/composite cathode. Cycling conditions: (1) current density: 0.08 mA/cm² in a; 0.15 mA/cm² in b; 0.23 mA/cm² in c; 0.31 mA/cm² in d; 0.38 mA/cm² in e; 0.54 mA/cm² in f; (2) voltage limit: 3.3–4.3 V in a–f.

and PVC-based electrolyte was fabricated and cycled at room temperature. Fig. 4 provides a plot of capacity vs. cycle number. The cell was cycled over 20 cycles. Following the fall off in capacity over the early few cycles a stage of capacity gradual decline was reached. It means that PVC-based electrolyte can be used in Li rechargeable batteries.

Replacement of Li anode by composite carbon anode in combination with a high voltage intercalation composite cathode and a gel electrolyte should permit the development of a new type of Li-ion rechargeable batteries.

The experimental cell with the composite carbon anode (a film of geometric surface area 0.6 cm²), the composite cathode and PVC-based electrolyte were fabricated and cycled at room temperature. The specific capacity of the composite carbon anode as a function of cycle number is illustrated in fig. 5. The behavior is like that of the cells with Li anode, composite cathode and PVC-based electrolyte. This result means that the composite carbon anode can be also performed in Li-ion rechargeable batteries. Without doubt, the specific capacity is dependent upon the parameters such as electrode composition and current density. This clearly demonstrates that it is possible to construct a composite carbon anode which functions in combination with a gel electrolyte.

In order to optimize the performance of the composite carbon anode, the effect of various carbon contents was studied. It was found that appropriate carbon content is needed in order to cast easily and to improve high specific capacity, because the specific capacity was strongly dependent on the amount of carbon

Fig. 4. Cycling behavior of the cell; Li/PVC-based electrolyte/composite cathode. Cycling conditions: (1) current density: 0.04 mA/cm² in a; 0.08 mA/cm² in b; 0.06 mA/cm² in c; (2) voltage limit: 3.2–4.3 V in a–c.

Fig. 5. Cycling behavior of the cell; composite carbon anode/PVC-based electrolyte/composite cathode. Cycling conditions: (1) current density: 0.08 mA/cm²; (2) voltage limit: 3.2–4.3 V.

content. A likely explanation is that the increasing carbon content improves electronic conductivity, which enhances the specific capacity^[9].

3 Conclusions

The composite cathodic film, the composite carbon film and PVC-based electrolyte film were successfully prepared by casting procedures. The preliminary results show that they are suitable for the rechargeable solid-state Li or Li-ion batteries. The composite carbon anode performs comparatively well, but the capacity of the Li-ion cell is not so good as the Li cell. The further work on improving the performance of the composite carbon anode is in progress.

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