Novel Solid-State Cells LiNi$_{0.8}$Co$_{0.2}$O$_2$/PEO/SnSb–Li$_{2.6}$Co$_{0.4}$N Without Metallic Lithium

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Novel solid-state PEO rechargeable lithium cells based on the LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode and the SnSb–Li$_{2.6}$Co$_{0.4}$N composite anode have been developed for the high reliability exclusive of metallic lithium and the large energy density at 110 Wh kg$^{-1}$. Electrochemical behavior of the cells demonstrates strong reliance dependent on the anode preparations. In view of the relatively low lithium ion diffusion, current density plays a significantly role upon the capacity and the retention of the composite anode. A cell design with good sealing and compacting configuration, as well as an appropriate thickness of electrolyte and electrode, results in a comparable cycling performance.

Key-words: SnSb–Li$_{2.6}$Co$_{0.4}$N composite anode, Solid polymer electrolytes, Lithium-ion batteries, Current density

1. Introduction

Since the discovery of ionic conductivity in the Poly (ethylene oxide) (PEO)-lithium salt composites, lithium-ion batteries based on such category of electrolytes has attracted worldwide attentions. In view of the high energy density and feasible design, all solid-state PEO rechargeable lithium batteries could be considered as an ideal power source for EV & HEV$^{1,2}$. So far, research has been extensively concentrated on two major points: the improvement of ionic conductivity of PEO–LiX complex at the relatively low temperature as well as the modification of interfacial characteristics between lithium anode and polymer electrolytes. It is generally accepted that there is some instable issue between metallic lithium and PEO electrolytes caused by lithium dendrite grown$^{3,4}$. Insertion hosts such as carbon, Li-alloy and Li–M–O, in place of lithium, present the promising alternative anodes$^{5,6}$. Unfortunately carbon still cannot be adopted successfully in the PEO electrolytes due to the interfacial incompatibility, regardless of its wonderful electrochemical manners in the liquid system. On the other hand, some Li–M–O materials, e.g., spinel LiTi$_4$O$_4$, demonstrate zero-strain effects for Li-insertion, resulting in long cycling life in the solid PEO electrolytes. Relatively low capacity and high Li-insertion potential of lithium titanates suffers loss of the comparable energy density. In contrast, for the large lithium storage capacity and low operating voltage close to lithium, Li-alloy could be considered as the appropriate candidate. It is believed that the morphology instability, which caused by the volume change of active host in association with lithium insertion, severely hinders the development of Li-alloy in both solid and liquid electrolytes. Decreasing particle size and adopting of multi-phase structure is favor for greatly enhancing the cyclability. Some positive results have been obtained, such as Li–Al electrode and interfacial layers of Li–Bi and Li–Pb alloys between lithium metal and solid polymer electrolytes$^{7,8}$. However the cycling performance of Li-alloy as anode in the solid PEO electrolytes is still poor.

Recently we developed a novel lithium ion cell consisting of the composite anode base on SnSb–Li$_{2.6}$Co$_{0.4}$N and the LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode in the solid PEO-LiN(CF$_3$SO$_2$)$_2$ electrolytes$^{9,10}$. It offers the large reversible anode capacity at 450 mAh g$^{-1}$ and the high working voltage at ca. 2.7 V, as well as an ensure safety without metallic lithium. Rapid capacity can hardly be avoided upon long cycles due to the volume effects of SnSb alloy. In this paper, the factors strongly affecting the electrochemical performance of the all solid-state cells were optimized and discussed.

2. Experimental

2.1 Active materials

LiCoO$_2$/Ni$_2$O$_3$ (typical particle size is 10 μm) was prepared by the normal solid state reaction. Ultrafine SnSb alloy powder (ca. 0.2 μm) was produced by chemical precipitation from aqueous solutions$^{10}$ and Li$_2$Co$_{0.4}$N powder (typical particle size, 1–6 μm) was synthesized by the traditional ceramic method$^{11}$. Nickel powder (99.9%, ca. 0.03 μm), PEO (MW = 6 × 10$^5$), LiN(CF$_3$SO$_2$)$_2$, BaTiO$_3$ (typical particle size, ca. 0.1 μm), PVDF (MW = 534000) were commercially purchased.

2.2 Polymer electrolyte and cathode film

PEO electrolytes (Li/O ratio: 1/18) were prepared under the casting technique. All the procedure was protected by Ar atmosphere in the glove box. A given weight of PEO (MW = 6 × 10$^5$) and LiN(CF$_3$SO$_2$)$_2$ was dissolved completely in anhydrous acetonitrile (AN). BaTiO$_3$ was dispersed homogeneously in the solution as filler. After strong stirring overnight the viscous solution was cast into a Teflon dish. After AN was slowly and completely evaporated under N$_2$ flow, obtained film was further dried at 90°C under vacuum at least 8 h. Cathode films consisting of 52 wt% LiNi$_{0.8}$Co$_{0.2}$O$_2$, 10 wt% acetylene black (AB) and 38 wt% PEO–LiN(CF$_3$SO$_2$)$_2$ were prepared by the normal casting method similar to PEO film and the thickness was about 200 μm.

2.3 Anode preparations

Different preparations were adopted and nominated as (a) dry mixing, (b) wet mixing, (c) hot pressing and (d) casting, respectively. For the dry mixing way, the electrode components were mechanically mixed in agate mortar. In the case of method (b), the components were homogeneously mixed by the aid of Hexane as disperser. Polymer binder was added and mixed after Hexane was entirely evicted. Mixtures prepared by (a) and (b) were pressed onto 280-mesh stainless steel grid. Normally area and thickness of the composite anodes were 0.55 cm$^2$ and 50–60 μm, correspondingly. Anode prepared by...
hot pressing was described as follows: PEO powders were carefully sieved and only the smallest particles were used. Before hot pressing, the electrode components were homogeneously mixed and pressed directly onto Cu-foil (20 μm) in a steel mold at temperature of 70–90°C and pressure of 10–60 MPa. The press time was 0.5 h–6 h. The thickness of obtained film was 60–90 μm (including Cu-foil). The procedure of method (d) was similar to the PEO film preparation. PEO and LiNi(CF₂SO₄)₂ (Li/O ratio: 1:18) were dissolved in AN entirely. SnSb and Ni powders were added following strong stirring. At last Liₓ₂C₀ₓ,N was added at 10 min before casting. The viscous solution was cast onto a 280-mesh stainless steel grid and further dried at 90°C under vacuum for 2 h.

2.4 Cell assembling and electrochemical measurement

To examine the cycling performance of the composite anode, half-cell was used and metallic lithium was utilized as counter electrode. The full cells were composed of the LiNiₓ₂C₀ₓ,N cathode and the SnSb–Liₓ₂C₀ₓ,N composite anode. Basically all the three layers, including composite anode, PEO electrolyte and cathode film (or lithium counter electrode), were stacked in coin type cells. A small constant pressure was kept inside cells by the means of the Ni foam as filler. Considering the corrosion instability of Al foil with LiNi(CF₂SO₄)₂, stainless plate was used as cathode current collector. Thickness ratio of cathode film and current collector was about 1/3. Before assembly, the cathode film was tightly press on the current collector under slightly heat and pressure. Unless state elsewhere, cycling properties tests were performed at a current density of 0.15 mA cm⁻² and the working temperature was 65°C. The voltage cutoff is 1.4–0.1 V vs Li/Li⁺ and 2.1–3.6 V for half cell and full cell respectively. Before electrochemical test, the cells were preheated for 2 hrs at a temperature of 75°C. The discharge capacity was adopted for all figs, corresponding to Li-insertion into the SnSb–Liₓ₂C₀ₓ,N composite in half-cell and Li-extraction from the SnSb–Liₓ₂C₀ₓ,N composite in full cell, respectively.

3. Results and discussion

3.1 Anode preparations

Considering the drastic volume effects in association with lithium insertion into and extraction from SnSb hosts, the anode morphology stability, as well as the interfacial compatibility between the composite anode and the solid PEO electrolytes, dominate the cycling performance of the all solid-state cells²,³,¹⁰. Although it is believed that the increased area of electrode is favorable for improving the electrochemical properties by decreasing the bulk resistance of the solid-state cells, the non-uniform dispersion of anode components prepared by dry mixing method may turn into aggravation along with the enlarged electrode area. Non-uniform dispersion of lithium salt and nano-Ni powder with electron-conductivity will lead to the relatively low coulombic efficiency at the first cycle and the slightly increased voltage polarization. In addition, ultrafine SnSb particles with non-uniform distribution will form the large aggregation region and easily cause to the local volume mismatch during charging and discharging. At last rapid capacity decline is inevitable. It is hopeful to obtain the relatively homogeneous distribution for anode components by adopting the casting and hot pressing methods. The cycling performance of the composite anode upon different preparations is compared in Fig. 1. The cycling stability of the composite anode prepared by hot pressing and casting way demonstrates severe deterioration compared to dry mixing way. In the case of casting way, the observed data may be attributed to the high sensitivity of Liₓ₂C₀ₓ,N against acetoni-trile (AN), which cause to the possible electrochemical instability. The further confirm is still in the present work. For hot pressing method, it is noted that the capacity lessen in the lithium extraction process is mainly corresponding to the shortness of the voltage plateau near 1.1 V, which is related to the Liₓ₂C₀ₓ,N active material, as shown in Fig. 2. This result indicates that the hexagonal Liₓ₂C₀ₓ,N may lose some electrochemical activity at relatively high pressure and temperature in the coexistence of PEO and LiNi(CF₂SO₄)₂ salt, resulting in the reduced charge recovery upon cycling. From above points of view, a solution stirring preparation by the aid of dispersant was introduced to achieve the homogeneous distribution of electrode components. Considering the chemical stability with Liₓ₂C₀ₓ,N and the low boiling point, hexane was selected as a dispersant. The cycling stability of the composite electrode prepared by the aid of solvent dispersion was obviously superior to other preparations. The obtained result suggests that the appropriate anode preparation shows the apparent effects upon the electrochemical behavior of the SnSb–Liₓ₂C₀ₓ,N composite anode in the solid PEO electrolytes.

![Fig. 1. The cycling performance of the composite anode prepared by different methods.](image1)

![Fig. 2. The first charge and discharge profiles of the electrodes prepared by different methods.](image2)
3.2 The applied current density

In view of the fact that the PEO–LiN\(_{(CF\text{S}_2)\text{O}}\)\(_3\) system will turn into viscous and show poor mechanical strength above 65°C (the melting point of PEO), the drastic volume changes of SnSb host in association with lithium insertion and extraction will easily cause to the serious interfacial deteriorates between the composite anode and the PEO electrolytes. This holds true especially for the high Li-utilization state of the SnSb hosts. Decreasing current density is favorable for reducing the electrochemical kinetic hinder and depressing the polarization within composite anodes, as shown in Fig. 3. It will lead to a comparable large reversible capacity. In the case of high current density, e.g., above 0.4 mA cm\(^{-2}\), low Li-ion diffusion rate will bring about the server polarization in accompany with the low utilization of the Li-alloy. Lot amounts of charge do not really intercalation into the active hosts, but accumulating on the surface of the active particles. Although the increased reversible charge recovery at the subsequent cycles could be obtained at the relatively high current density, significantly reduced capacity is inevitable. After optimizing the tradeoff between the large reversible capacity and the better capacity retention, the suitable current density in the scale of 0.1–0.4 mA cm\(^{-2}\) should be adopted in the charge and discharge tests for this system.

3.3 Cell designs

Figure 4 shows the effects of active amount in the composite anode upon the electrochemical performance. The cycling stability of low active amount of the composite anode is obviously superior to that of the comparably high one. This phenomenon appears to be related to a time-dependent process such as electrolyte decomposition on the surface of the active hosts and self-discharge of the SnSb–Li\(_{2.6}\)Co\(_{0.4}\)N system. The improving cycling behavior in the case of low active amount may be attributed to the shorter time to complete one cycle. Thus the discharge capacity lose during cycling will be lessen and the charge recovery at the subsequent cycle may be increased. Moreover the relatively non-uniform dispersion of electrode components may take part consequence while the active material amount is increased. The low ion-conductivity and lithium diffusion in the solid PEO system can be partly suppressed by decreasing the thickness of electrode and electrolyte as thinner as possible. Besides it is reasonable that thin thickness of the composite anode is helpful for reducing the volume effects when the path of lithium diffusion is shorten. It clearly observed in Fig. 5 that the capacity and cycling performance is obviously improved when the thickness of electrolytes is decreased. On the other hand, the PEO electrolytes should possess enough mechanical strength to restrain the volume effects of the SnSb–Li\(_{2.6}\)Co\(_{0.4}\)N anode especially at deep lithium insertion stage. Relatively small but secure pressure within cells, as well as a good sealing condition can maintain the morphology stability of the PEO electrolyte and improve the interfacial behavior between anode and electrolyte, resulting in a comparable cycling performance.

Figure 6 shows the typical charge and discharge profiles of the solid-state PEO cells based on the LiNi\(_{0.5}\)Co\(_{0.5}\)O\(_2\) cathode and the SnSb–Li\(_{2.6}\)Co\(_{0.4}\)N composite anode at 65°C. For full utilization of lithium storage capacity of the composite anode, the weight of cathode has to be much over that of anode at about 4–5 times. A slight increasing of voltage plateau from the first cycle to the following ones can be remarkable and it is
mainly linked to the phase transformation of Li$_{2.4}$Co$_{0.6}$N from crystal to amorphous along with Li-extraction. High initial coulombic efficiency over 95% and the large reversible anode capacity above 450 mAh g$^{-1}$ can be obtained within 30 cycles. It indicates that a rather high energy density could be realized by adopting such system and it is could be considered as an ideal power source for HEV & EV. However, with cycling increase deeply, the capacity decline inevitably takes place. A further improvement of the solid-state cells focusing on the cycling stability is still on the progress.

4. Conclusions

In this work a novel all-solid-state rechargeable lithium-ion battery consisting of the composite SnSb–Li$_{2.4}$Co$_{0.6}$N anode and the LiNi$_{0.8}$Co$_{0.2}$O$_2$ cathode in the PEO-LiN(CF$_3$SO$_2$)$_2$ electrolytes has been developed. It shows high reliability by adopting insertion hosts in place of metallic lithium as negative electrode. Large anode reversible capacity at ca. 450 mAh g$^{-1}$ can be obtained within 30 cycles. The electrochemical behavior of the cells is strongly dependent on the anode prepreparations. Considering the relatively low ionic conductivity within the solid system, the suitable current density is found in the scale of 0.1–0.4 mA cm$^{-2}$. A cell design with good sealing and compacting configuration, as well as an appropriate thickness of electrolytes and electrode, is favorable for greatly improving the cycling performance.

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