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Journal of Power Sources 97–98 (2001) 779–781

JOURNAL OF  
POWER  
SOURCES

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# Solid polymer electrolyte cells using SnSb/Li<sub>2.6</sub>Co<sub>0.4</sub>N composite anodes

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Received 21 June 2000; received in revised form 1 November 2000; accepted 28 December 2000

## Abstract

This work involves the use of a new type of composite anode system containing SnSb alloy and Li<sub>2.6</sub>Co<sub>0.4</sub>N for lithium secondary batteries based on solid polymer electrolytes. The composite electrode shows a high coulombic efficiency (close to 100% even in the first cycle) and a cycle capacity more than 500 mAh/g. An addition of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> salt into the electrode by direct powder-mixing will decrease its efficiency and capacity. The cycle performance of a cell, using the composite anode and LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode, can be greatly enhanced by modifying the PEO-based polymer electrolyte with BaTiO<sub>3</sub> as filler. © 2001 Elsevier Science B.V. All rights reserved.

**Keywords:** Li-alloy composite anode; Li<sub>2.6</sub>Co<sub>0.4</sub>N; Solid polymer electrolyte; Lithium-ion battery

## 1. Introduction

Considerable effort has been devoted towards the development of lithium rechargeable batteries based on solid polymer electrolytes [1–4]. The use of the solid polymer electrolytes can avoid the problems related to liquid electrolytes, such as leakage and gas formation arisen from solvent decomposition, leading to an improvement in battery design and safety. Although metallic lithium as anode will achieve the highest energy density, its high reactivity to polymer electrolytes can lead to uncontrolled passivation phenomena in the presence of a trace amount of water and impurity. For this reason, it is significant to search high-capacity insertion anodes in place of metallic lithium for large scale Li-ion batteries using solid polymer electrolytes. In this work, we examine charge and discharge behaviors of a new composite anode based on SnSb alloy and Li<sub>2.6</sub>Co<sub>0.4</sub>N compound in solid polymer electrolytes.

## 2. Experimental

Ultrafine SnSb alloy powder (<0.2 μm) and Li<sub>2.6</sub>Co<sub>0.4</sub>N were synthesized as described previously [5,6]. A given weight of polyethylene oxide ( $M_w = 9 \times 10^5$ ), Ni (particle size ca. 0.03 μm), and active host powders were homogeneously mixed in agate mortar in glove box. The powder

mixture was then directly pressed onto 280-mesh stainless steel grid to form an anode film (0.55 cm<sup>2</sup>). Unless stated otherwise, the anode is composed of 15 wt.% PEO, 10 wt.% Ni, 22 wt.% Li<sub>2.6</sub>Co<sub>0.4</sub>N, and 53 wt.% SnSb. Cathode film, which contains 54% LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub>, 10% acetylene black, and 36% PEO–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, was prepared by normal casting method.

Several ceramic powders (BaTiO<sub>3</sub>, 0.1 μm; TiO<sub>2</sub>, 0.07 μm; LiAlO<sub>2</sub>, 0.1–0.3 μm) were used as filler of polymer electrolytes. They were homogeneously dispersed in (PEO)<sub>18</sub>–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> solution via magnetic stirring and ultrasonic treatment. After acetonitrile solvent evaporation, the casting film (ca. 110 μm in thickness) was dried at 95°C under vacuum. For each cell, two pieces of the electrolyte films were used.

Cycling tests were performed at a current density of 0.15 mA/cm<sup>2</sup> for cells with the composite anode and the LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode at 75°C. The impedance response was measured by Solartron SI 1260 (impedance/gain-phase analyzer) in a frequency range over 0.05 Hz and 100 kHz under open-circuit condition.

## 3. Results and discussion

Generally, active materials are dispersed in lithium salt/polymer composite to form anodes and cathodes for polymer electrolyte cells. However, it is found that an addition of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> into an electrode based on ultrafine SnSb powder and Li<sub>2.6</sub>Co<sub>0.4</sub>N causes a slightly higher voltage

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polarization, and decreases the coulombic efficiency in the first cycle. Moreover, the electrode capacity is also relatively low during cycling. We assume that highly dispersed SnSb and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  hosts and compact electrode structure can ensure interparticle contacts and a rapid Li diffusion within the electrode at elevated temperature. On the other hand, direct powder-mixing for electrode preparation appears to be unable to ensure a homogenous salt dispersion in the electrode. Besides non-uniform salt dispersion, the surface passivation of the active particles caused by salt-participating decomposition reactions may also be responsible for the above result.

In order to improve the cell performance, the PEO-based polymer electrolyte is modified by ceramic fillers. As has been reported [7], dispersing ceramic powders, especially nano-sized powders, in polymer electrolytes can improve cycling and storage performance of lithium polymer batteries. It appears that ceramic fillers have two major functions: improving the mechanical performance of the soft polymer electrolyte films and stabilizing the interfacial properties. It is believed that finely dispersed ceramic additives in the polymer structure can capture the electrolyte impurities, and thus ensure their removal from the interface with the final result of decreasing and stabilizing the interfacial resistance. Our test results show the addition of ceramic additive such as ultrafine  $\text{BaTiO}_3$  powder into  $(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte can obviously enhance the cycle efficiency and capacity retention of a cell composed of the SnSb/ $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  composite electrode and lithium counter electrode.

Complete cells with the composite anode and the  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode have been cycled to evaluate the function of the ceramic additives. As shown in Fig. 1, fine ceramic fillers more or less improve the cycle stability, and barium titanate is superior to the other fillers. Fig. 2 presents a typical test result of the first three cycles for a cell with 10%  $\text{BaTiO}_3$  in

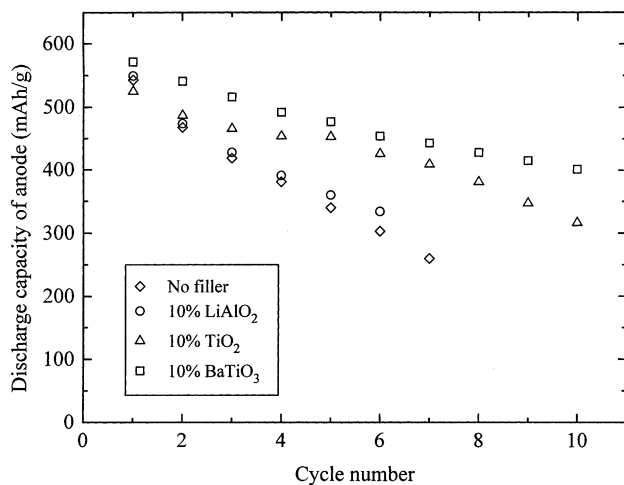


Fig. 1. Effect of ceramic fillers in  $(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolytes on the cycle performance under cut-off of 2.1/3.7 V. The cell was composed of the composite anode and  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode.

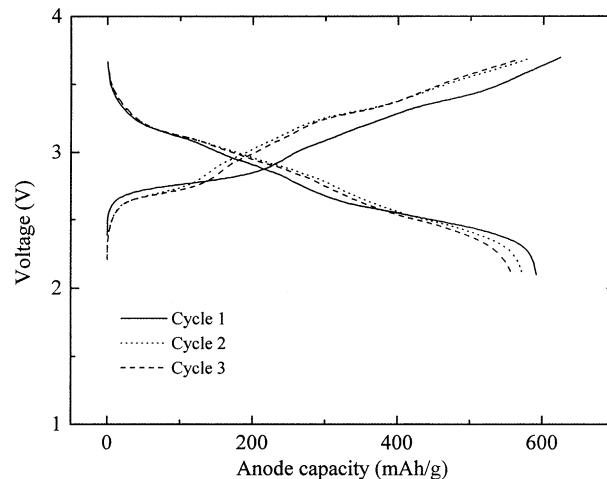


Fig. 2. The first three cycle profiles for a cell using 10%  $\text{BaTiO}_3/(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$  electrolyte. The weight ratio of cathode to anode active material = 4.4.

the polymer electrolyte. The cell gives not only a high efficiency, but also a high cycle capacity. A measurement of time dependence of the cell impedance shows that the addition of  $\text{BaTiO}_3$  into the polymer electrolyte can suppress the growth of the second semicircle related to the interface films (Fig. 3). This could be an important reason why the cell based on  $\text{BaTiO}_3$ -modified polymer electrolyte has a better performance.

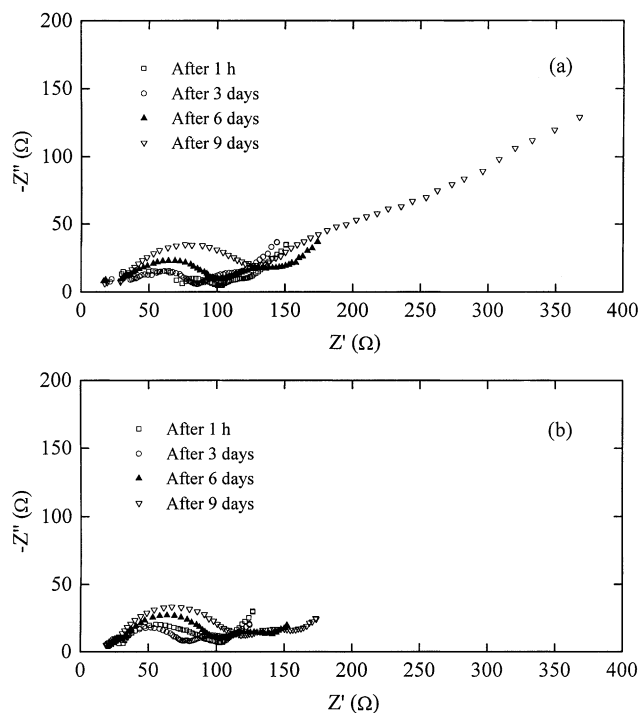


Fig. 3. Time dependence of the impedance of cells with different polymer electrolytes: (a)  $(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ ; (b) 10%  $\text{BaTiO}_3/(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ . Before storage, the cells were charged to 3.6 V. Electrode areas =  $0.65 \text{ cm}^2$ .

#### 4. Conclusions

Highly dispersed active materials and compact electrode structure can ensure interparticle contacts and a rapid Li diffusion within the SnSb/Li<sub>2.6</sub>Co<sub>0.4</sub>N composite electrodes. The use of LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> salt as an electrode component leads to a degradation of the electrode performance. The modified polymer electrolyte with BaTiO<sub>3</sub> as filler significantly improves the cell performance.

#### Acknowledgements

This research work was carried out under a collaboration program of Mie University and Genesis Research Institute, Nagoya, Japan.

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