

# High-capacity composite anodes with SnSb and $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ for solid polymer electrolyte cells

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## Abstract

Composite anodes based on SnSb alloy and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  compound can provide a reversible capacity more than 650 mAh/g in solid polymer electrolyte. However, the capacity retention on cycling is poor at a high-capacity level. Limited lithium insertion (<500 mAh/g) is favorable for the cyclability. Cyclic voltammetry of the composite electrode exhibits good electrochemical reversibility. Because the nano-sized  $\text{SiO}_{1.1}$  host has a relatively small volume change effect and different insertion potential from SnSb and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ , its addition in a small amount into the composite electrode can improve the mechanical and cycling stability.

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## 1. Introduction

The Li-ion battery containing organic liquid electrolytes has been widely used in our daily life. However, its application range has not been expanded into large-scale power sources for electric vehicle, home-use load leveling system and others. This is because some unsafe factors associated with this battery system, such as leakage of flammable electrolyte, gas formation and consequent explosion, cannot be eliminated. In recent years, attention has turned to solid polymer electrolyte battery using lithium metal anode for its advantage of enhanced safety, high energy density and flexibility [1–4]. At this stage, the main problems related to this type of battery seem to be the low ionic conductivity of the polymer electrolyte at ambient temperature and the interface instability between lithium and polymer electrolyte under high lithium utilization. The use of insertion anodes with reduced reactivity, in place of metallic lithium, may improve the interface characteristics and provide a higher safety. Unfortunately, conventional carbonaceous materials that are widely applied in liquid electrolyte systems have not shown a good performance in solid polymer electrolyte [5]. On the other hand,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  exhibited excellent cycling stability in a solvent-free polymer electrolyte, but its capacity was less than 160 mAh/g and the voltage loss (1.5 V versus Li) was remarkable for anode purpose [6]. We have

developed new  $\text{SnSb}_x/\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  composite anodes for Li-ion batteries. This electrode system demonstrated a reversible capacity more than 500 mAh/g and the initial cycle efficiency close to 100% in liquid electrolyte [7]. In the present work, we investigate key factors influencing electrochemical performance of the composite electrodes in contact with polyethylene oxide (PEO)-based polymer electrolyte.

## 2. Experimental

### 2.1. Preparation of electrode and electrolyte

Ultrafine SnSb alloy powder (<0.2  $\mu\text{m}$ ) and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  were synthesized as described previously [7].  $\text{SiO}_{1.1}$  (particle size: ca. 50 nm) and Ni conducting additive (ca. 30 nm) were obtained, respectively from Denki Kagaku Kogyo and Nilaco, Japan. High-density polyethylene (mp 144 °C) and polyethylene oxide (PEO, MW =  $6 \times 10^5$ ) were from Aldrich. Electrodes were fabricated by a solvent-free method. All the electrode components were homogeneously mixed in agate mortar in glove box and the mixture was then directly pressed onto 300-mesh stainless steel grid. The electrode area was 0.55  $\text{cm}^2$  for cycling tests and 0.65  $\text{cm}^2$  for impedance measurements. The cathode film, which contained 54%  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ , 10% acetylene black and 36%  $(\text{PEO})_{18}\text{-LiN}(\text{CF}_3\text{SO}_2)_2$ , was prepared by normal casting methods.

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Solid polymer electrolyte films were prepared by a casting method. BaTiO<sub>3</sub> ceramic powder (0.1 μm) in 10 wt.% was dispersed in (PEO)<sub>18</sub>–LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub> solution via magnetic stirring. The homogeneous gel solution was cast on a Teflon dish under Ar atmosphere. Acetonitrile solvent was slowly evaporated by controlled N<sub>2</sub> gas flow. Finally, the casting film (ca. 130 μm in thickness) was dried at 90 °C under vacuum for 8 h.

## 2.2. Electrochemical measurements

Half cells with lithium counter electrode and full cells with LiNi<sub>0.8</sub>Co<sub>0.2</sub>O<sub>2</sub> cathode were assembled for electrochemical measurements. Three films, anode, polymer electrolyte, and cathode (or lithium), were stacked and compacted in stainless steel test cell, where a certain pressure was exerted via a stainless steel spring. The cell operation temperature was 65 °C and current density for charge and discharge was 0.15 mA/cm<sup>2</sup>. Before cycling test, the cells were preheated at 70 °C (above PEO melting point) for 3 h and then kept at 65 °C for 1 h. The impedance response was measured by Solartron SI 1260 (impedance/gain-phase analyzer) in a frequency range over 0.1 Hz and 100 KHz at open-circuit voltage. A Solartron 1286 coupled with electrochemical interface was used for cyclic voltammogram.

## 3. Results and discussion

Previous study on solid polymer electrolyte cells revealed that the SnSb/Li<sub>2.6</sub>Co<sub>0.4</sub>N composite electrode had a high efficiency at the first cycle and large cycling capacity using PEO as binder [8]. However, lithium salt is easy to diffuse from polymer electrolyte into the PEO-containing electrode at elevated temperature. As a consequence, lithium salt content and ionic conductivity of the polymer electrolyte will decline with the time. For this reason, lithium salt as an electrode component is necessary, if PEO is used as binder. Another possibility is adopting binders that do not absorb lithium salt. Fig. 1 shows cycling behavior of the composite anodes containing different binders. The dispersion of the active particles in polymer electrolyte can increase the interfacial area and improve ionic conductivity within the electrode. Owing to faster electrochemical kinetics, the reversible capacity of the electrode becomes apparently larger. On the other hand, more lithium insertion and extraction causes a larger volume change of the hosts, leading to mechanical instability. The electrode faces a rapid capacity fade in the initial cycles. Rigid high-density polyethylene as binder (in part or all) seems to be favorable for morphological stability of the electrode.

In view of that the large volume change of SnSb alloy for lithium insertion and extraction may cause mechanical and conducting instability, nano-sized SiO<sub>1.1</sub>, which

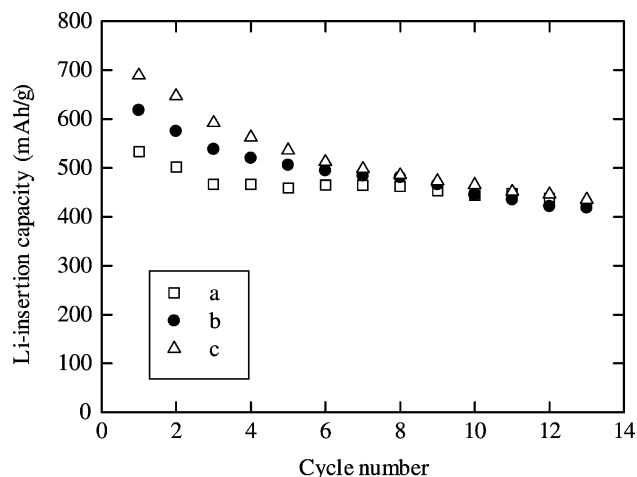


Fig. 1. Cycling stability of the composite electrodes with different binders. (a) 10% PE, 8% Ni, 33% Li<sub>2.6</sub>Co<sub>0.4</sub>N and 49% SnSb. (b) 8% PE, 10% Ni, 9% PEO, 3% LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 26% Li<sub>2.6</sub>Co<sub>0.4</sub>N and 44% SnSb. (c) 15% PEO, 5% LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 10% Ni, 18% Li<sub>2.6</sub>Co<sub>0.4</sub>N and 52% SnSb. Voltage cut-off: 0.05/1.4 V vs. Li.

demonstrated good cyclability in liquid electrolyte [9], is chosen for active component. Fig. 2 displays lithium insertion capacity based on total weight of active components versus cycle number for composite electrodes with different SiO<sub>1.1</sub> contents. The electrode containing SiO<sub>1.1</sub> and Li<sub>2.6</sub>Co<sub>0.4</sub>N shows rapid capacity fade on cycling in the polymer electrolyte. Similarly, a poor cycling result was also obtained with an electrode based on SnO and Li<sub>2.6</sub>Co<sub>0.4</sub>N, even when a sufficient amount of inert conductor (nickel or acetylene black) was added. The reason for it is not clear. Nevertheless, the addition of a small amount of SiO<sub>1.1</sub> into the composite electrode based on SnSb and Li<sub>2.6</sub>Co<sub>0.4</sub>N improves the cycling stability. Relatively weak volume effect of SiO<sub>1.1</sub> (5–7 wt.%) and stepwise lithium insertion into different hosts may stabilize the mechanical and conducting property of the electrode.

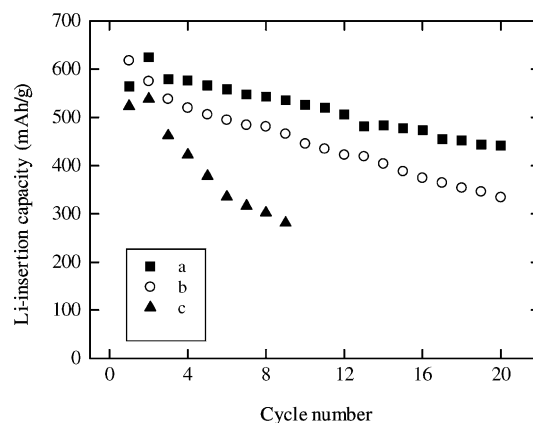


Fig. 2. Li-insertion capacity versus cycle number for three composite electrodes. (a) 8% PE, 10% Ni, 9% PEO, 3% LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 32% Li<sub>2.6</sub>Co<sub>0.4</sub>N, 33% SnSb and 5% SiO<sub>1.1</sub>. (b) 8% PE, 10% Ni, 9% PEO, 3% LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 26% Li<sub>2.6</sub>Co<sub>0.4</sub>N and 44% SnSb. (c) 21% PEO, 7% LiN(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>, 20% Ni, 29% Li<sub>2.6</sub>Co<sub>0.4</sub>N and 23% SiO<sub>1.1</sub>.

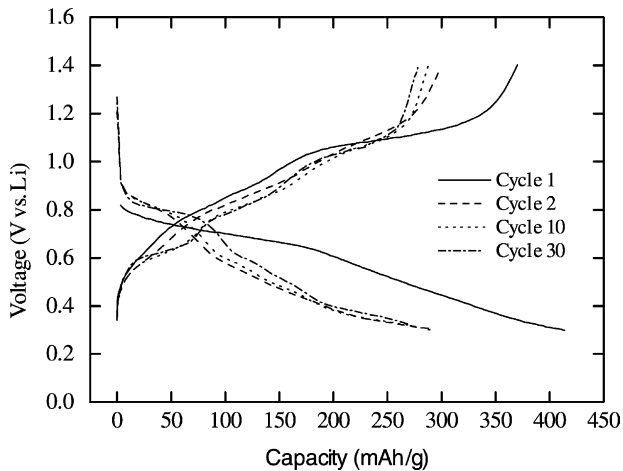


Fig. 3. Discharge and charge profile of an electrode containing 12% PE, 6% Ni, 29%  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  and 53% SnSb under limited lithium insertion.

The cycling stability can be also enhanced, when the volume expansion of SnSb alloy is controlled at a low level via limited lithium insertion. As shown in Fig. 3, the capacity loss during cycling is relatively small with cut-off of 0.3/1.4 V. In this experiment, three layers of polymer electrolyte films were used to prevent shunting effect arising from lithium micro-dendrites on the surface of lithium counter electrode. Although the good cyclability can be obtained under limited lithium insertion, the capacity below 300 mAh/g is not competitive with some carbonaceous materials. But this result may give us such information: the interface between the electrode and solid polymer electrolyte is chemically and electrochemically stable. The argument here is if a higher voltage lower-limit (0.3 V, instead of 0.05 V versus Li) is favorable for the interface stability. The results of impedance experiments seem to deny it. In both the cases, impedance change with the time does not show a significant difference. From this

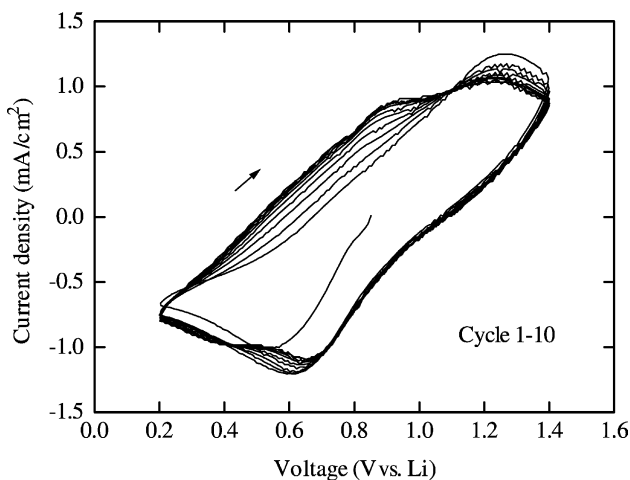


Fig. 4. Cyclic voltammogram for an electrode containing 10% PE, 8% Ni, 33%  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  and 49% SnSb.

point of view, the poor cyclability by more lithium insertion at 0.05/1.4 V is mainly caused by mechanical and structural instability of the electrode.

Fig. 4 presents cyclic voltammogram for a composite anode. After five cycles, the curves become overlapping, indicating good electrochemical reversibility. An obvious curve shift in the first several lithium extraction processes is attributed to the phase change of  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  compound from crystalline to amorphous state [10].

A full cell using  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode and composite anode was assembled to examine the charge and discharge behavior in the voltage range of 2.1/3.6 V. As shown in Fig. 5, a sloping cell voltage is advantageous as an indicator for the state-of-charge of the cell. The initial capacity is about 500 mAh/g. However, the large capacity cannot be maintained during cycling. After six cycles, the capacity fading takes place. One of the unstable factors may be related to the present cell configuration. The dimension of the polymer electrolyte film in the test cell will gradually change at elevated temperature by a spring pressure. It seems that a clever cell design with good sealing condition and compacting configuration without free space is necessary for a long-term cycling. A preliminary test indicates that the cyclability can be obviously improved by adopting 2015 type coin cell with nickel foam as filler, with a capacity of 300–400 mAh/g. The Ni foam support may be favorable for structural stability of the system.

Fig. 6 exhibits impedance spectrums for cells in different charge states. A larger second semicircle in the discharge state suggests that the interface layer resistance increases after discharging. When the anode contains polymer electrolyte, lithium diffusion in the interface layer becomes quicker, which may be due to increased interface area. Half-cell tests confirm that the change of the second semicircle at the different charge state is dominated by anode side. It appears that lithium extraction from the anode will result in a larger interface layer resistance.

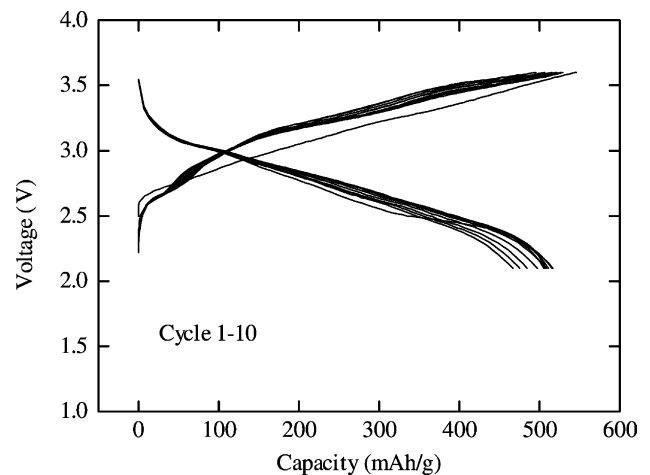


Fig. 5. Charge and discharge profile of a cell using  $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$  cathode and composite anode containing 8% PE, 10% Ni, 9% PEO, 3%  $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ , 32%  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$ , 33% SnSb and 5%  $\text{SiO}_{1.1}$ .

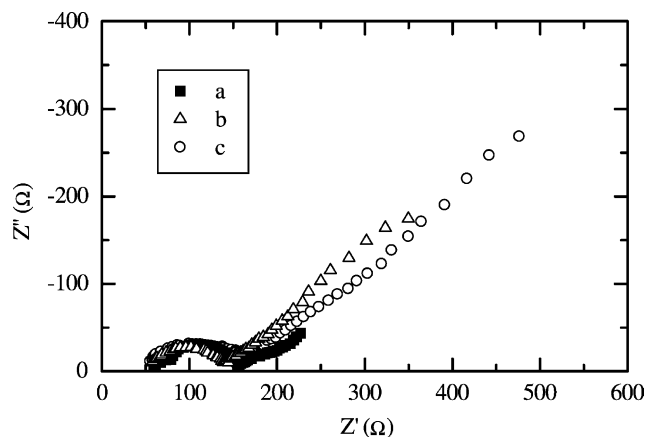


Fig. 6. Impedance spectrums of full cells at charge and discharge states. (a) 8% PE, 10% Ni, 9% PEO, 3%  $\text{Li}(\text{CF}_3\text{SO}_2)_2$ , 26%  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  and 44% SnSb. Charge state at 3.3 V. (b) the same composition as in (a). Discharge state at 2.4 V. (c) 10% PE, 8% Ni, 33%  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  and 49% SnSb. Discharge state at 2.4 V.

#### 4. Conclusions

For composite anode in solid polymer electrolyte cell, a combination of SnSb alloy and  $\text{Li}_{2.6}\text{Co}_{0.4}\text{N}$  can supply a large reversible capacity and high faradic yield above 90% at the first cycle. The composite anode containing polymer electrolyte demonstrates an initial capacity of more than 650 mAh/g. However, the soft PEO at elevated temperature seems unable to stabilize the morphology of the electrode, in which the SnSb alloy undergoes a big volume expansion for lithium insertion. Rigid high-density polyethylene as binder (in part or all) can improve the mechanical and cycling stability, especially in the initial cycles. Nano-sized  $\text{SiO}_{1.1}$  as the third active component also

shows a positive effect on the electrode performance. Relatively small volume change of  $\text{SiO}_{1.1}$  and stepwise lithium insertion and extraction from host to host may be an important reason for it. A long cycle life appears to require a more suitable cell design and a controlled depth of discharge.

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