Composite anode containing nano-$SiO_{1.1}$ and $Li_{2.6}Co_{0.4}N$ with solid PEO electrolytes for lithium-ion batteries

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Abstract

Electrochemical behavior of the composite electrodes containing $Li_{2.6}Co_{0.4}N$ and nano-size $SiO_{1.1}$ has been investigated with the solid poly (ethylene oxide) electrolytes at various temperatures. The composite electrodes have a high first cycle efficiency of ca. 100% and a large reversible capacity of ca. 500 mAh g^{-1}. Result reveals that the operating temperature and the electrode composition dominate the cycling performance. Dispersing a certain amount of sub-micro ceramic $BaTiO_3$ within the electrodes is favorable for improving the morphology stability of the composite electrodes at the elevated temperature. Some factors influencing the electrode properties are presented and discussed in detail.
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1. Introduction

PEO electrolyte formed by dissolving a lithium salt in a host poly (ethylene oxide) (PEO) shows high ionic conductivity at the elevated temperature. All solid rechargeable lithium batteries based on above electrolyte appear to be ideal power sources for electric vehicles and hybrid electric vehicles (EV & HEV) due to high energy density and feasible design [1]. Previously developed PEO lithium batteries contain lithium metal anodes; thereby they have a safety problem arising from surface lithium dendrites on the anode surface [2,3]. An effective way to overcome this detriment is to use insertion hosts. However, the layered graphite as in the commercial Li-ion batteries with the PEO electrolytes seems unacceptable because of a poor interfacial compatibility. Some Li–M–O materials, e.g., spinel $Li_4Ti_5O_{12}$, have zero-strain effects upon Li-insertion/extraction and long cycling life with the solid PEO electrolytes, but they suffer from low capacities and high reactive potentials [4,5]. On the other hand, silicon and some

metals that could alloy with lithium, such as Sn, Sb and Al, show promising prospects due to high Li storage capacities [6]. In particular, silicon is most attractive for the largest theoretical capacity of ca. 4000 mAh g^{-1} among all known host materials. The major hindrance with respect to the Li alloy anodes is the rapid capacity fade upon cycling caused by the morphology deteriorates during Li insertion and extraction [7–10]. In general, creating a composite microstructure comprising active hosts uniformly dispersed in an inert matrix can tackle this problem [11]. For example, SiO_x nano-composites consisting of nano-size silicon highly distributed in the inert SiO_2–Li_2O matrix were found to show good cycling stability [12]. However, these nano-composites have no practical application. This is attributed to an extremely high capacity loss in the first cycle. Recently, we found that the introducing of a certain amount of Li-rich $Li_{2.6}Co_{0.4}N$ into above active hosts based electrodes can provide a compensation for the irreversible capacity that results in a high initial coulombic efficiency [13]. This is because that Li rich $Li_{2.6}Co_{0.4}N$ has a very low insertion capacity and high extraction capacity. The $SiO_{1.1}$–$Li_{2.6}Co_{0.4}N$ composite demonstrated a good cycling stability with a large reversible capacity above 600 mAh g^{-1}

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and a high first cycle efficiency of 100% with the liquid electrolytes. Whether such composite electrode can fulfill the requirements to enable use as anode with the solid PEO electrolytes is the purpose of this research. Some factors influencing the electrode properties are presented and discussed in detail.

2. Experimental

Nano-size $SiO_{1.1}$ (ca. 50 nm) was obtained from Denki Kagaku Kogyo, Japan. $Li_{2.6}Co_{0.4}N$ powder (typical particle size, 1–6 μm) was synthesized by solid-state reaction using Li_3N and Co as precursors [14]. The $SiO_{1.1}$–$Li_{2.6}Co_{0.4}N$ composite electrode was prepared in a glove box. The electrode components were homogeneously mixed in an agate mortar by the aid of hexane and further pressed onto a 300-mesh stainless steel grid, which served as a current collector. The geometric area of the electrodes was 0.55 cm^2, and the typical thickness was 100–160 μm.

The preparation of the solid PEO electrolyte was as follows: a given weight of $LiN(CF_3SO_2)_2$ and poly (ethylene oxide) (MW = 6×10^5) (O/Li = 18) were dissolved in anhydrous acetonitrile. $BaTiO_3$ (ca. 0.1 μm) was homogeneously dispersed in the solution as a filler. The viscous composite solution was cast onto a Teflon dish. After acetonitrile solvent was slowly and completely evaporated with a N_2 flow, the resulted electrolyte film was dried at 90 °C under vacuum for 10 h. The film thickness was about 300 μm.

To evaluate the electrochemical properties of the electrodes, lithium metal was utilized as the counter electrode and the PEO film was used as electrolyte and separator. All the three layers, including test electrode, PEO film and lithium metal, were stacked in a 2025 coin type cell. Unless stated elsewhere, cycling was carried out at a constant current density of 0.15 mA cm^{-2} and a voltage cutoff at 1.5/0.02 V versus Li/Li$^+$. Before experiments, the cell was preheated for 2 h at a temperature of 10 °C higher than the operating temperature, when the cell working temperature was lower than 70 °C. Charge and discharge of the cell refer, respectively, to lithium extraction from, and insertion into, the active hosts. The electrode capacity was calculated according to the weight of active materials.

3. Result and discussion

To suppress the morphology instability upon Li insertion and extraction, nano-silicon can be dispersed within an inert matrix containing Li_2O and SiO_2. By this way, the mechanical stress from silicon can be alleviated under a reasonable level. A decrease of oxygen content in SiO_x enhances the reversible capacity and the first cycle efficiency, but reduces the capacity retention upon cycling [12]. The $SiO_{1.1}$ powders are in an average size of ∼50 nm with some particle agglomerates, as shown in Fig. 1. The observation from XRD and
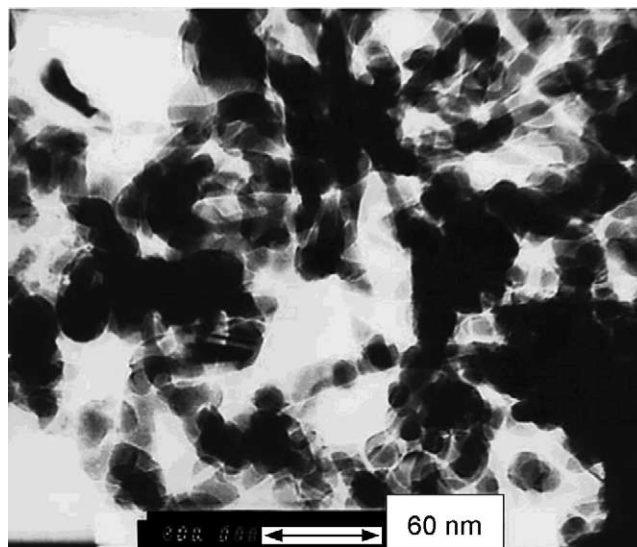

Fig. 1. TEM image of the $SiO_{1.1}$ powders.

elemental analysis indicates that the $SiO_{1.1}$ contains a small amount of SiO_2 besides SiO and elemental silicon. With the first Li-intercalation, SiO undergoes an irreversible transformation to form Si and Li_2O. This, in turn, results in a large capacity loss in the first cycle. Li-rich $Li_{2.6}Co_{0.4}N$ was found to bring capacity compensation for the nano-$SiO_{1.1}$ in the first cycle that leads to a high initial coulombic efficiency [13].

Fig. 2 shows charge and discharge profiles of the $SiO_{1.1}$–$Li_{2.6}Co_{0.4}N$ composite electrode in the PEO electrolytes at different cycles. The electrode has an obvious shift in the potential plateaus from the first cycle to the subsequent cycles that could relate to a phase transformation of silicon and $Li_{2.6}Co_{0.4}N$ from crystalline to amorphous state in the discharge and charge, respectively. The insertion ca-
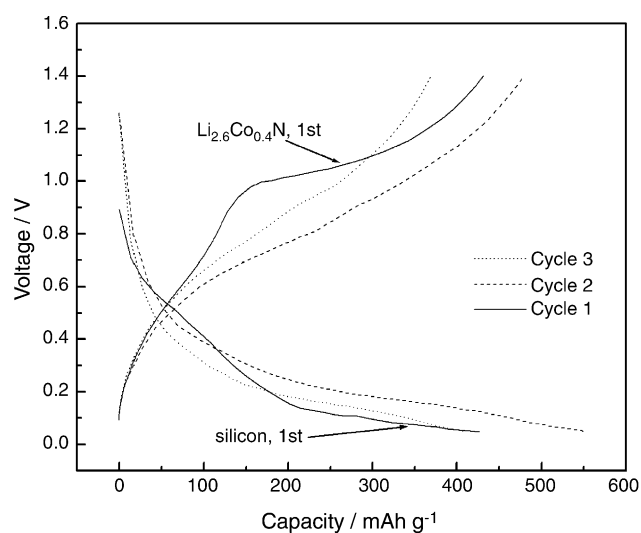

Fig. 2. Charge and discharge curves of the $SiO_{1.1}$–$Li_{2.6}Co_{0.4}N$ composite electrode at different cycles, electrode composition (wt.%): 10% PVDF–HFP, 15% PEO, 5% $LiN(CF_3SO_3)_2$, 20% AB, 30% $Li_{2.6}Co_{0.4}N$, 20% $SiO_{1.1}$, operating temperature: 75 °C.
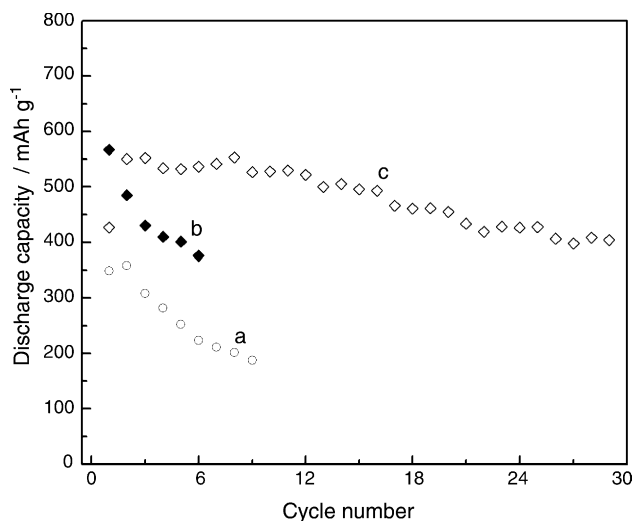
Fig. 3. Cycling performance of the electrodes with different components, electrode compositions (wt.%): (a) 30% Ni, 30% $Li_{2.6}Co_{0.4}N$, 40% $SiO_{1.1}$; (b) 21% PEO, 7% $LiN(CF_3SO_3)_2$, 20% Ni, 29% $Li_{2.6}Co_{0.4}N$, 23% $SiO_{1.1}$; (c) 10% PVDF–HFP, 15% PEO, 5% $LiN(CF_3SO_3)_2$, 20% Ni, 30% $Li_{2.6}Co_{0.4}N$, 20% $SiO_{1.1}$, operating temperature: 75 °C.

Fig. 4. Cycling performance of the composite electrodes at different temperature, the electrode compositions are the same as Fig. 2.

pacity was increased to about $550\,mAh\,g^{-1}$ at the second cycle, versus $420\,mAh\,g^{-1}$ at the first cycle. It is probably attributed to a reduced polarization caused by the improved electrochemical kinetics at the electrode interface compatibility. The voltage trends of the composite reflect mixing potential characteristics of these two types of active materials. In fact, the capacity above 0.8 V from $Li_{2.6}Co_{0.4}N$ plays an important role for the compensation for the irreversible capacity. As a result, a high first cycle efficiency of ca. 100% was obtained.

The electrode compositions have an apparent influence upon the electrochemical behavior of the electrode, as shown in Fig. 3. The composite electrode without any electrolyte component and polymer binder suffers from a low capacity and a poor capacity retention (see (a)). This is due to poor interface compatibility between the active particles and the electrolyte, as well as the lack of the lithium ionic channels among the active hosts. An introducing of the PEO-based electrolyte component within the electrode brings an obvious improvement in the capacities (see (b)). However, the PEO–$LiN(CF_3SO_2)_2$ composite within the electrode above 65 °C (the melting point of PEO) possesses a viscous characteristic that can hardly stabilize the electrode morphology for Li insertion. As a result, rapid capacity fading occurs. The capacity decline was significantly suppressed by using poly (vinylidene fluoride)-hexafluoropropylene as a framework within the composite electrode (see (c)). The fluorinated polymer is a popular binder for anode in Li-ion batteries and has a stable electrochemical window as wide as 0–5 versus Li/Li$^+$. These polymers appear to be dispersed easily within the electrode and can improve the adhesion between the active material and the current collector that can maintain a stable mechanical strength.
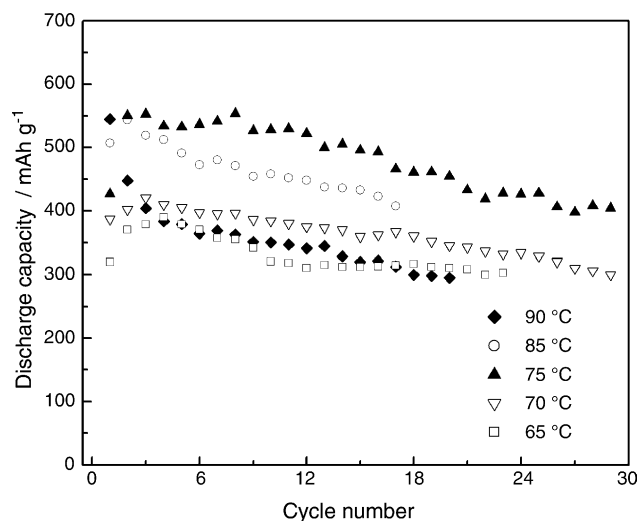
It is well known that the ionic conductivity predominates in the amorphous rather than crystalline regions of PEO electrolytes, the local relaxation and segmental motion of the polymer chains appears to be a requirement for lithium ion transport. The effect of operating temperature on mechanical strength and ionic movement of the PEO–$LiN(CF_3SO_2)_2$ electrolytes is contradictory. Fig. 4 shows the capacity change as a function upon the cycle number of the $SiO_{1.1}$–$Li_{2.6}Co_{0.4}N$ composite electrodes at various environment temperatures. The reversible capacity in the cycling beginning was improved with increasing the temperature due to the adhesive interface contact and high ionic conductivity. However, high temperature fast the capacity fading. It indicates that an aggravated decay in the mechanical strength of the PEO electrolytes can hardly endure the morphology instability arising from silicon. By contrast, PEO electrolyte at low temperature possesses a high mechanical stability with a low ionic conductivity that leads to a small capacity with good capacity retention.

Dispersing sub-micro ceramic $BaTiO_3$ within the electrode was found to show improvement in the cycling behavior of the composite electrode, as shown in Fig. 5. Ceramic fillers, such as $BaTiO_3$ and Al_2O_3, can improve the mechanical performance of the flexible PEO electrolyte and stabilize the interfacial properties at elevated temperature. Furthermore, it can reduce the crystallizing tendency of the polymer electrolyte; thereby it enhances the ionic conductivity. With temperature increasing, the solid PEO–$LiN(CF_3SO_2)_2$ composite turns into be serious sticky and fluid. The function of $BaTiO_3$ is to enhance the mechanical strength of the electrolyte components within the composite electrode that could maintain the electrode integrity.

Fig. 6 shows cycling performance of the composite electrode upon current density. A decrease in the current density is favorable for reducing kinetic hinder and depressing the
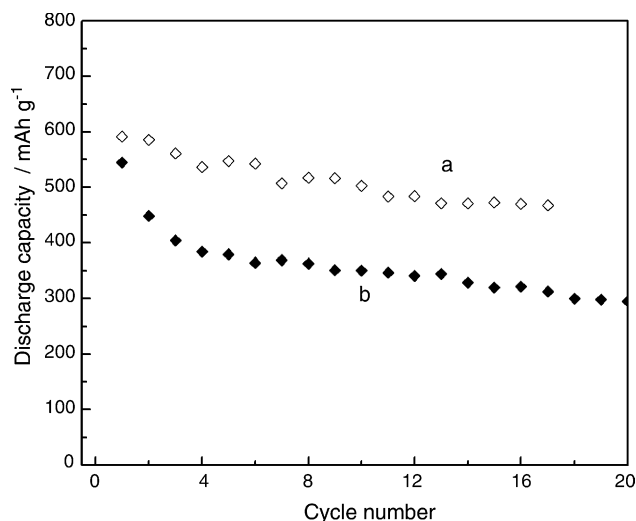
Fig. 5. Effects of the ceramic BaTiO$_3$ upon the cycling performance of the composite electrodes. Electrode compositions (wt.%): (a) 6% BaTiO$_3$, 10% PVDF–HFP, 18% PEO, 6% LiN(CF$_3$SO$_3$)$_2$, 20% AB, 24% Li$_{2.6}$Co$_{0.4}$N, 16% SiO$_{1.1}$; (b) 10% PVDF–HFP, 15% PEO, 5% LiN(CF$_3$SO$_3$)$_2$, 20% AB, 30% Li$_{2.6}$Co$_{0.4}$N, 20% SiO$_{1.1}$, operating temperature: 85 °C.
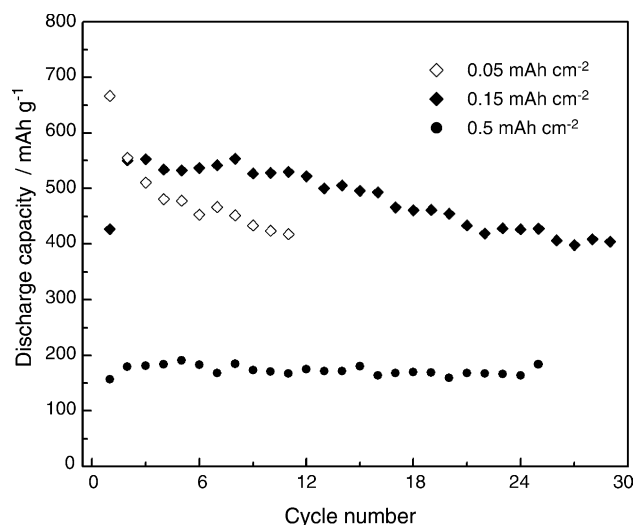

Fig. 6. Effects of the current density upon the cycling performance of the composite electrodes. The electrode compositions are the same as Fig. 2 operating temperature: 75 °C.

polarization within the composite electrodes that results in a comparable capacity. However, low current density costs more time to fulfill one cycle. Thus, a rapid electrode self-discharge rate caused by the possible interfacial reaction, such as reducing oxide impurity or electrolytes decomposition, could lead to a rapid capacity decline. By contrast, high current density, e.g., above 0.5 mA cm^{-2}, obviously cuts the reversible capacity with a good charge recovery. It is attributed to a server polarization associated with relatively slow lithium diffusion within the solid electrolyte and electrode system. The suitable current density for this composite electrode in the solid PEO electrolytes is between

0.1 and 0.5 mA cm^{-2} after trade off capacity and capacity retention.

4. Conclusions

We reported studies upon the electrochemical behavior of the SiO$_{1.1}$–Li$_{2.6}$Co$_{0.4}$N composite electrode with the solid PEO electrolytes. The operating temperature, electrode composition and current density have been investigated as function upon the electrode properties. The electrode has a reversible capacity of ca. 500 mAh g^{-1} within 30 cycles and an initial efficiency of ca. 100% at an appropriate temperature. A certain amount of the electrolyte components and PVDF–HFP within the electrode is favorable for the electrochemical performance. Dispersing of sub-micro BaTiO$_3$ as an electrode component can greatly enhance the mechanical stability of the electrolyte component that results in an improvement in the capacity retention at the elevated temperature. We expect that further optimization of the composite anodes might lead to an all solid-state lithium-ion battery with an improved safety over the metallic lithium based PEO batteries.

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