

Study of the cycling performance of finely dispersed lithium alloy composite electrodes under high Li-utilization

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Abstract

The cycling behavior of lithium alloy composite electrodes in liquid electrolyte composed of 1 M LiClO₄/EC + DEC (1:1) was examined. The lithium alloys were formed by electrochemical insertion of lithium into metallic host matrices (Al, Sn and SnSb_x powders). With a wide potential cut-off between 0.1 and 1.2 V vs. Li/Li⁺, the capacity retention (ca. 550 mA h/g) of Sn-based electrodes during cycling can be remarkably improved by decreasing the particle size of the host materials to near nano-scale. Moreover, the cycle life performance and coulombic efficiency are also dependent on polymer binder and conducting additive as the other components of the electrodes. Under a similar condition, it was found that an ultra-fine Al powder was not fit for host material due to a strong passivation of the electrode after Li-insertion. © 1999 Elsevier Science S.A. All rights reserved.

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1. Introduction

Considerable safety problem with lithium metal electrodes for secondary batteries has stimulated various efforts to replace them by lithium insertion compounds. Some lithium alloys such as Li–Al, Li–Sn and Li–Pb have been chosen as negative electrode materials, owing to their high charge capacity and fast lithium mobility in the host matrices at ambient temperature [1–6]. Several rechargeable lithium cells with lithium alloy anodes (e.g., Mn-doped Li–Al) have been commercialized [7]. They are typically used for memory back-up in a ‘shallow-cycling’ mode. Long-term cycling of lithium alloy electrodes with high capacity, however, has not been achieved so far. The major problem here lies in that the substantial volume changes during insertion/removal of lithium into/from metallic host matrices cause a fast mechanical disintegration and electrical disconnection of the electrode under high Li-utilization.

In order to minimize the mechanical stress in lithium alloy electrodes caused by the volume change during cycling, the active lithium alloy phases have been dispersed in different inert mediums. The medium can be

another lithium intermetallic phase (e.g., Li_xCd in Li_{4.4}Sn [8]), plastic mixed-conducting materials [9] or Li⁺-conducting glass form material (amorphous tin-based composite oxide, ‘ATCO’) [6].

In this research, ultra-fine powders (particle size < 0.3 μm) of metallic host matrices for Li-insertion are examined as negative electrode materials in lithium ion cell. The host matrices are dispersed and encapsulated in polymer binder to form flexible composite electrodes. In such an ultra-fine particle system, even a large change of the dimensions of the metal crystal structure due to insertion and removal of lithium will not necessarily cause a further subdivision of the particles and subsequent disintegration of the electrode, as the absolute changes in particle dimensions are still small.

2. Experimental

2.1. Metal and alloy powders

Aluminum (99.9%, particle size < 0.6 μm), tin (99.8%, < 45 μm) and nickel powder (99.9%, 0.03 μm) are commercially available. Ultra-fine Sn and SnSb_x (x = 0.13–0.14) powders were obtained by chemical precipitation from aqueous solutions containing the chlorides of the

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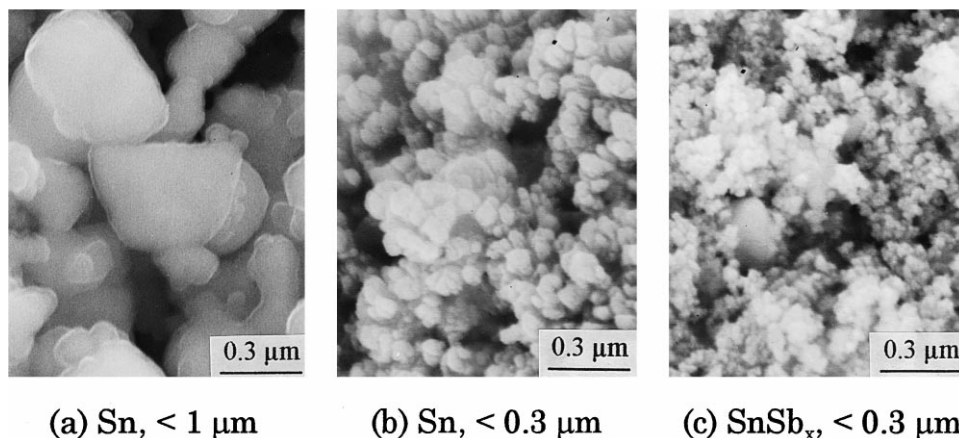


Fig. 1. The SEM micrographs of synthesized metallic powders for Li-insertion.

respective metals and complex agents with sodium borohydride as reductive agent [10]. Fig. 1 shows scanning electron microscopy (SEM) micrographs of the synthesized powders.

2.2. Fabrication of composite electrodes

Composite electrodes were prepared by following two methods.

(1) For poly(vinylidene fluoride) (PVDF) binder, metallic host matrix powder, conducting additive and PVDF dissolved in 1-methyl-2-pyrrolidinone were mixed to form slurry, which was painted on stainless steel grid as current collector. The electrode was pressed and finally dried at 130°C under vacuum. The geometric area of the electrode was 0.5 cm². The weight of composite material was 6–7 mg for Sn- and SnSb_x-based electrodes and 4–5 mg for Al-based electrodes. All electrode compositions refer to weight percentage.

(2) For polyethylene (PE) and polytetrafluoroethylene (PTFE) binder, metallic host matrices, conducting additive and polymer binder powder, were mixed in agate mortar in glove box. The powder mixture was pressed on current collector. The weight of composite material was 7–9 mg for an area of 0.5 cm².

2.3. Electrochemical measurements

Half-cell studies were performed in laboratory-type glass cells with excess of organic electrolyte (1 M LiClO₄/EC + DEC, 1:1) and battery grade lithium counter and reference electrodes. Composite electrodes were vertically placed in the electrolyte without any pressure.

Cycling tests were carried out at charge and discharge current densities of 0.4 mA/cm² with a cut-off of 0.1/1.2 V vs. Li/Li⁺ for Sn-based electrodes and 0.05/1.1 V vs. Li/Li⁺ for Al-based electrodes. The rest time between charge and discharge was 1 min. Charging and discharging of the cell refer, respectively, to insertion and extraction of

lithium into/from alloy composite electrodes. Impedance spectroscopy of cell was measured by Solartron SI 1260 (impedance/gain-phase analyzer) with a frequency range from 500 kHz to 0.05 Hz at open circuit voltage of the cell.

3. Results and discussion

3.1. The type and granulometry of metallic host material

Bulk aluminum metal as host material for accommodation of lithium has been carefully investigated. Cracks and pulverization of the electrode material during cycling were observed [11]. As ultra-fine aluminum powder (spherical, typical particle size: 0.1–0.5 μm) instead of bulk aluminum was used as the host material, the situation seemed to be worse. As shown in Fig. 2, accommodated lithium

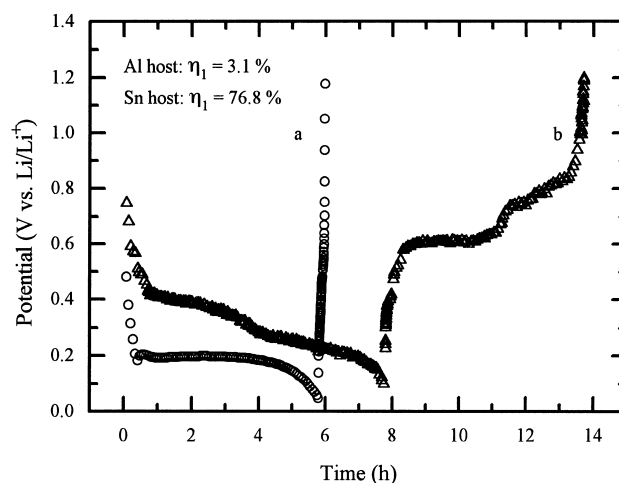


Fig. 2. The first cycle curve of Li-alloy composite electrodes. Electrode composition: (a) 20% Ni/12% PVDF/68% Al; (b) 10% Ni/8% PVDF/82% Sn.

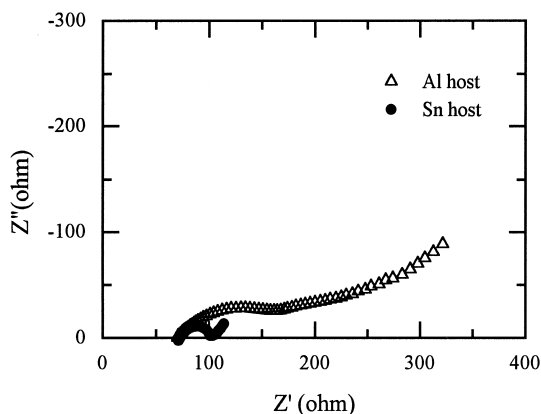


Fig. 3. Impedance spectrums of alloy composite electrodes after charging to 0.05 V vs. Li/Li^+ with current density of $0.2 \text{ mA}/\text{cm}^2$. Electrode composition: 20% Ni/12% PVDF/68% Al; 10% Ni/8% PVDF/82% Sn.

can be hardly extracted from aluminum and a further cycling is impossible; in contrast, Sn-based electrode (tin particle size $< 1 \mu\text{m}$) has much higher coulombic efficiency under a similar condition. A change in current density and electrode composition cannot improve the cycling characteristics of Li–Al alloy composite electrodes significantly. As well-known, active Al metal has great tendency towards passivation. For fine-particle-sized powder, it could be more serious. Fig. 3 exhibits impedance spectrums of the above-mentioned two composite electrodes after lithium insertion until 0.05 V vs. Li/Li^+ . The high charge transfer and Li-diffusion resistance are responsible for the poor cycling performance of Al-based electrode. The low electrode impedance indicates that fine tin powder is the more suitable host matrix.

Table 1 lists the cycling data of the initial five cycles of Li–Sn alloy composite electrode with different tin particle sizes. A comparison of the data reveals that the influence of granulometry of the tin host matrix on cycling behavior of the electrode is striking. At first, it can be noted that the charging capacity at the first cycle becomes larger with the decrease of tin particle size, but the coulombic efficiency is the highest with ‘middle’ particle size ($< 1 \mu\text{m}$). The electrode formed by fine powder (particle size $< 0.3 \mu\text{m}$) is connected with great real surface area and short Li-diffu-

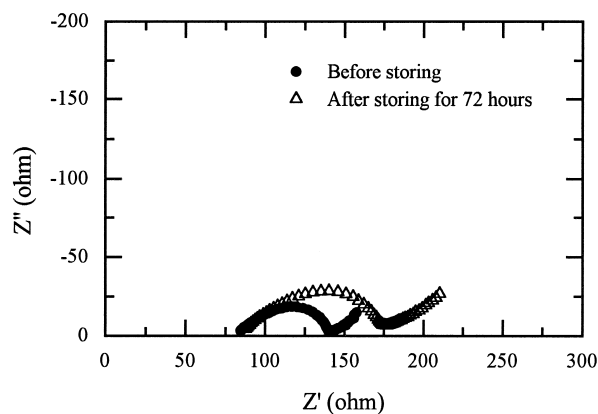


Fig. 4. Impedance spectrums of Li/Sn alloy composite electrode after charging to 0.05 V vs. Li/Li^+ with current density of $0.2 \text{ mA}/\text{cm}^2$. Electrode composition: 15% Ni/10% PE (h)/75% Sn ($< 0.3 \mu\text{m}$). Storing temperature: 30°C .

sion length in the host matrix, so the polarization of the electrode during Li-insertion is relatively small, resulting in a high charging capacity at a given potential cut-off. On the other hand, it has to be considered that, as in the case of carbon materials and metallic lithium, solid electrolyte interphase films are also formed on the lithium storage metals. An indirect evidence for it is the increase of electrode impedance with the storing time (as shown in Fig. 4). Surface filming consumes lithium and thus increases the irreversible capacity. It is the unfavorable side for fine particle host matrices. In the case of coarse metallic powder, mechanical degradation and consequent electrical disconnection caused by drastic volume change are main reason for its high irreversible capacity.

A notable phenomenon for the electrode based on coarse tin particles ($< 45 \mu\text{m}$) is that the charging capacity increased, but its coulombic efficiency declined fast with enhanced cycle number. This phenomenon could be explained by continuous subdivision of coarse tin particles, which produces new surface area, and subsequent loss of the interparticle contact. An apparent advantage of the use of fine metallic powder is its improved cycling stability. From the point of view of cyclability, it is necessary to control tin particle size, at least under $0.3 \mu\text{m}$, for Sn-based composite electrode.

Table 1

The effect of Sn particle size on cycling behavior of the composite electrode composed of 15% Ni, 10% PE (h)^a and 75% Sn

Particle size of Sn powder	Cycling data of the initial five cycles ^b				
	1	2	3	4	5
$< 45 \mu\text{m}$	577 (65%)	524 (91%)	580 (89%)	626 (85%)	647 (81%)
$< 1 \mu\text{m}$	679 (76%)	548 (98%)	574 (94%)	570 (91%)	578 (89%)
$< 0.3 \mu\text{m}$	876 (57%)	553 (97%)	561 (96%)	558 (95%)	550 (95%)

^aPE (h): polyethylene with ultra-high molecular weight (m.p. 144°C).

^bIncluding cycle number, Li-insertion capacity ($\text{mA h}/\text{g}$) and coulombic efficiency.

A finer metallic host powder than the above-mentioned has been synthesized by co-precipitation of tin and a small amount of antimony. X-ray diffraction analysis showed that SnSb_x ($x = 0.13\text{--}0.14$) powder consisted of Sn phase and intermetallic SnSb phase. It can be observed from Fig. 1c that there are some relatively large particles scattered in extremely fine powder. A measurement of ‘electron spectroscopic imaging in the transmission electron microscope’ indicated that the content of antimony was higher in these large particles than in much smaller particles. Ultra-fine particle structure at near nano-scale (typically $< 0.1 \mu\text{m}$) is the main part of the powder. Fig. 5 shows the cycling characteristics of ultra-fine tin powder and SnSb_x alloy powder as host material. The significant improvement in cycling performance by the use of multiphase SnSb_x structure instead of single-phase tin is not only attributed to a smaller particle distribution in SnSb_x , but also to ‘buffering effect’ of volume changes in the multiphase system where lithium was first inserted into SnSb phase ($> 0.66 \text{ V vs. Li/Li}^+$) around still-ductile Sn phase [12].

3.2. Polymer binder

Several polymers have been examined for the use as binder in the lithium alloy composite electrodes. PVDF is a popular binder for anode materials in lithium ion cell. The soft and weak-polar PVDF exhibits a strong swelling effect in polar organic solution. The electrolyte is easy to penetrate into the electrode, which is expected to reduce the polarization of the electrode under high charge and discharge current density. However, PVDF does not seem to be an excellent binder material, as lithium alloy electrodes are cycled under high Li-utilization. Fig. 6 exhibits a great difference between PVDF and PE (h) as binder for SnSb_x -based electrode. PVDF-containing electrode has low coulombic efficiency in the first several cycles and fast decline in charge capacity. Comparably, PE (h) is a more suitable binder. Its use not only improves the coulombic

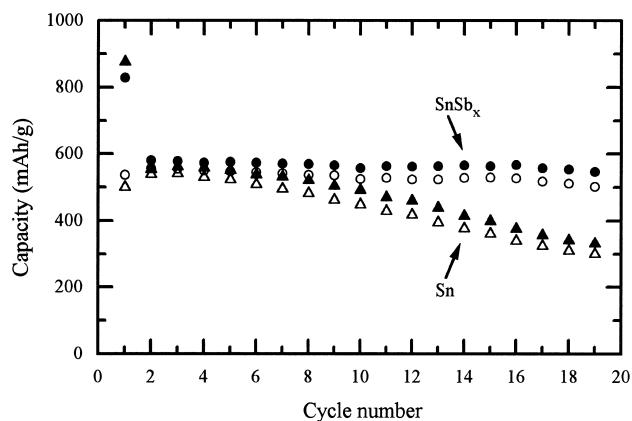


Fig. 5. Cycling performance of Sn- and SnSb_x -based electrodes. Electrode composition: 15% Ni/10% PE (h)/75% M (Sn or SnSb_x). Solid dot: charging. Hollow dot: discharging.

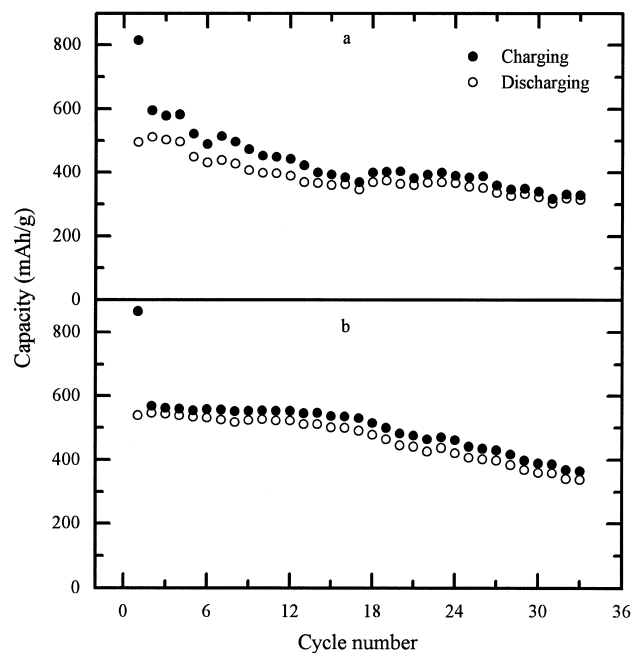


Fig. 6. Cycling performance of SnSb_x -based electrodes with different binders: (a) 10% Ni/8% PVDF/82% SnSb_x , (b) 10% Ni/10% PE (h)/80% SnSb_x .

efficiency, but also makes the Li-insertion capacity stable until 18th cycle. Unlike graphite anode and most cathode materials, the great volume change of lithium alloys during deep cycling requires some specific compatible polymer binder to keep electrical contact of the active alloy particles. Strong swelling due to interaction between solvents in the electrolyte and PVDF results in a slight expansion of the binder, therefore, a fast loss of internal contact brought about by the double actions (swelling of binder and volume change of lithium alloy) cannot be excluded.

In fact, as shown in Fig. 7, molecular weight of polymer binder also has great influence on the cycling behavior

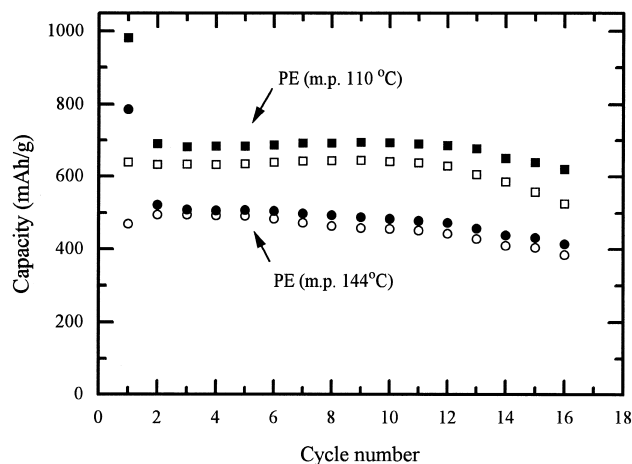


Fig. 7. The effect of binder rigidity on the cycling performance of alloy composite electrode composed of 12% PE and 88% SnSb_x . Solid dot: charging. Hollow dot: discharging.

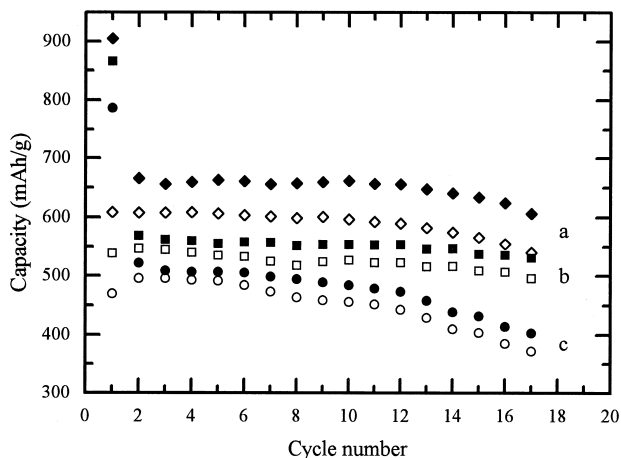


Fig. 8. The effect of inert conducting additives on the cycling behavior: (a) 6% AB/10% PE (h)/84% SnSb_x, (b) 10% Ni/10% PE (h)/80% SnSb_x, (c) 12% PE (h)/88% SnSb_x. Solid dot: charging. Hollow dot: discharging.

of metallic host materials. PE with lower molecular weight (m.p. 109–111°C) corresponds to higher charge capacity, but lower coulombic efficiency (ca. 93%). Furthermore, it was found that adding inert conducting material such as Ni powder in the electrode or decreasing its capacity to a comparable level to PE (h) by enhancing potential low-limit of cycling cannot improve its coulombic efficiency. It means that the rigidity of polymer binder is an important factor determining the coulombic efficiency.

PTFE is also a widely used binder for lithium batteries, especially for cathode materials. As binder for anode materials, lithium reacts with PTFE at approximately 1.2 V vs. Li/Li⁺ in the first charging process [13]. In the case that ultra-fine metallic host materials are used, a relatively high binder content is necessary; thus, a loss of irreversible capacity in binder is not negligible at the first cycle. With the same composition as PE (h)-containing electrode (η_1 : ca. 65%), the use of PTFE as binder corresponded to a low coulombic efficiency (η_1 : ca. 54%). On the other hand, PTFE-containing electrode had no advantage over the other electrodes in the cycling life performance.

3.3. Additional conducting material

Although metallic host materials such as Sn and SnSb_x are excellent electron conductors, their physical and chemical properties undergo some changes with the continuous insertion and extraction of lithium. The subdivision (even pulverization) and surface passivation of the alloy particles will deteriorate the electrical conductivity. For this reason, high disperse inert-conducting materials can stabilize the electrical conductivity of the electrode. Fig. 8 shows that charging and discharging are also feasible without any additional conducting material. However, an addition of Ni powder in the electrode is obviously helpful for the capacity retention. Acetylene black (AB) as conducting additive

can remarkably enhance the charge capacity of the electrode. In addition, the coulombic efficiency in the first cycle is also higher than that of the other two kinds of electrodes. Unfortunately, the efficiency is quite low (< 93%) in the whole cycling process. In point of cycling stability and coulombic efficiency, Ni powder is superior to conventional carbon additives.

4. Conclusions

The cycling performance of lithium alloy composite electrodes under high Li-utilization can be significantly improved by choosing appropriate host material and controlling its granulometry. In order to obtain a good cycling stability, decreasing the particle size of metallic host materials is necessary, but it is limited by increased irreversible capacity at the first cycle. On the other hand, an enhancement of the rigidity of polymer binder to a certain extent is favorable for the improvement of the coulombic efficiency during cycling. By the use of ultra-fine SnSb_x powder and high-density polyethylene, the electrode can be stably cycled for ca. 18 times with Li-insertion capacity of ca. 550 mA h/g; after that, the electrode gradually lost capacity on cycling.

Acknowledgements

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