Particulate-reinforced Al-based composite material for anode in lithium secondary batteries

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Abstract

Particulate-reinforced Al/SiC composite materials are prepared by ball-milling technique to be used as an anode material for lithium secondary battery. The microstructure of the composite powders show that the SiC particles are embedded homogeneously in the Al matrix. This feature is distinctively different from any other active/inactive composite anode materials reported recently. The cycle performance of these composite electrodes is superior to that of an unreinforced aluminium electrode. This improved cycelability may be due to an enhanced mechanical stability of the electrode. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

Lithium-ion batteries are becoming the major power sources for modern consumer electronic devices. Although commercially available these batteries are still the subject of intense research activity aimed at the development of new high-performance electrode and electrolyte materials. Present-day commercial lithium-ion batteries employ $LiCoO_2$ as the cathode (positive electrode) material and a carbon-based intercalation compound such as graphite as the anode (negative electrode) material. The graphite anode material, however, has a capacity limited to a theoretical value of 372 mAh g^{-1} and suffers from a significant irreversible loss in capacity on the first cycle. Due to this problem, together with safety concerns and the requirement for higher energy densities, it is necessary to find alternatives to carbon-based materials. Recently, a new class of anode material based on a tin composite oxide glass has been proposed [1]. This material has higher reversible gravimetric (>600 mAh g^{-1}) and volumetric (>2200 mAh cm^{-3}) capacities than carbon-based materials. Courtney and Dahn [2,3] reported that the high specific capacity of tin-based oxide is due to an Li–Sn alloying reaction. They also showed that the oxides

exhibited large irreversible capacity on the first cycle and formation of Li_2O. Nevertheless, this research has prompted renewed interest in Li-alloy anode materials for lithium secondary batteries.

With an lithium alloy system, the mechanical stability is one of the most important parameters which affects the electrode performance. The large volume change during charge and discharge generates severe stresses which results in cracks and crumbling of the particles. This deterioration causes loss of electrical contact of Li-alloy material, which gives poor cycle life. To overcome this problem, intermetallic compounds [4–6], active/inactive nanocomposite materials [7,8] and sub-microcrystalline materials [9,10] have been studied recently.

Particulate-reinforced composites are mechanically strengthened by embedding other hard particles such as ceramics or intermetallics, and show high tensile strength and enhanced resistance to crack initiation and propagation [11–13]. Such composites have been studied extensively in the aerospace and automotive industries because of their enhanced mechanical strength. In the present study, the concept of the particulate-reinforced composite has been applied to the aluminum electrode in an attempt to enhance the mechanical stability, and thereby, the cycle performance. Among these materials, Al/SiC composites are synthesized by a ball-milling technique and their electrochemical characteristics have been investigated with a view to using the materials as anodes for lithium secondary batteries.

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2. Experimental

The Al powder (Kojundo, ~30 μm, 99.9%) and SiC powder (Aldrich, −400 mesh) were used as received. The composite powders of Al/SiC were prepared by a ball-milling technique, and the volume fraction of SiC in the composite was fixed at 20% since excellent mechanical stability of composite can generally be obtained at this composition [14,15]. The Al and SiC powders were put into a hardened steel vial (80 cm^3) with steel balls (combination of 3/8 and 3/16 in.); the ball to powder ratio was 20:1. Ball-milling was performed for up to 36 h using a laboratory-made vibratory mill. All processes prior milling were conducted inside an Ar-filled glove box and the vial was firmly sealed to prevent oxidation of the starting materials.

Slurries were prepared and consisted of 10 wt.% composite powder, 10 wt.% carbon black, and 10 wt.% polyvinylidene fluoride (PVDF) dissolved in *n*-methyl pyrrolidinone. Electrodes were made by coating the slurries on copper foil substrates. Coin-type test cells were assembled in an Ar-filled glove box using Celgard 2400 as a separator, 1 M LiPF$_6$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1:1 vol. ratio) as an electrolyte, and Li foil as a counter electrode. The charge (Li insertion)–discharge (Li removal) experiments were performed galvanostatically within the voltage window of 0.0–2.0 V or under conditions of limited charge capacity.

The phase composition of ball-milled power was characterized using X-ray diffraction (XRD, MacScience Co., MXP18A-HF). The morphology and internal microstructure of the ball-milled powder and its electrode were investigated by scanning electron microscopy (SEM, JEOL, JSM-T200). Energy dispersive X-ray spectroscopy (EDX) was used to distinguish particles of Al and SiC.

3. Results and discussion

The XRD patterns of ball-milled Al-20 vol% SiC powder after various milling times are given in Fig. 1. Obviously, the starting materials that were simply mixed contain coarse polycrystalline grains of Al and SiC, as shown by the sharp diffraction peaks. By contrast, the Bragg peaks of Al and SiC become slightly broad and appear to reach a steady state after 6 h of ball-milling. This indicates the formation of finer Al/SiC composite powders and/or stress induced by the ball-milling processes. The milled-products are still intact composites of Al and SiC, i.e. they do not coexist with any reactive products such as Al$_4$C$_3$ and Si, and this suggests the absence of any undesirable reactions at the Al and SiC interfaces.

A scanning electron micrograph of ball-milled Al-20 vol.% SiC composite powder is shown in Fig. 2. The powders at the commencement of milling are a simple mixture of Al powder of random shape (average diameter of nearly 30 μm) and SiC of square shape (average diameter
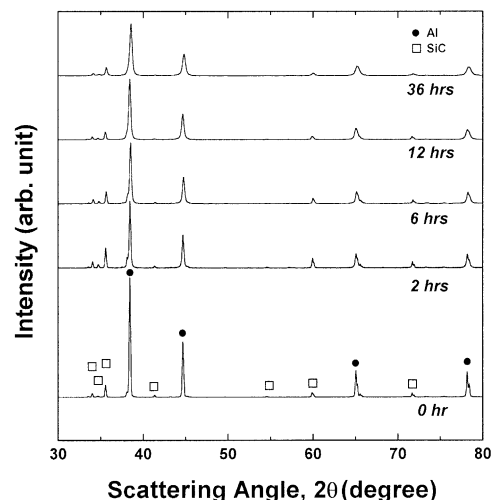

Fig. 1. XRD patterns of ball-milled Al-20 vol.% SiC composite powders after various ball-milling time.

of nearly 15 μm), see Fig. 2a. On milling, the morphology of the powder is typical of milled-powders, i.e. between ductile and brittle materials. In the next 2 h, the powder undergoes repeated flattening and fracturing as the result of collision
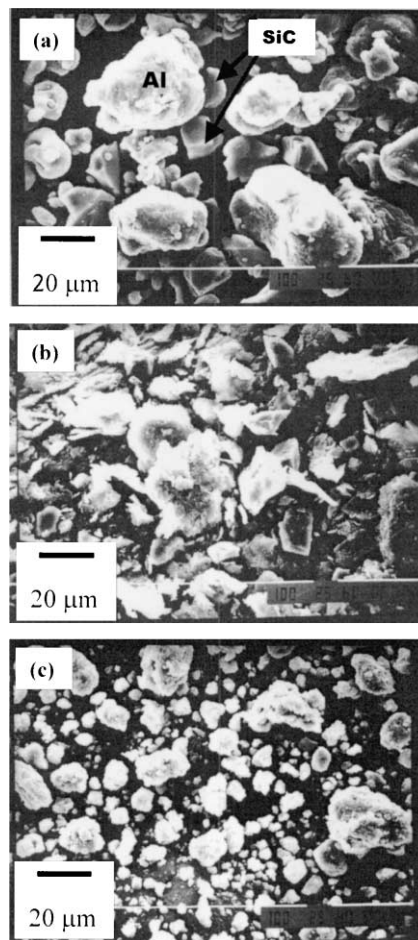

Fig. 2. Scanning electron micrographs of ball-milled Al-20 vol.% SiC composite powder after (a) 0 h, (b) 2 h and (c) 12 h of milling.
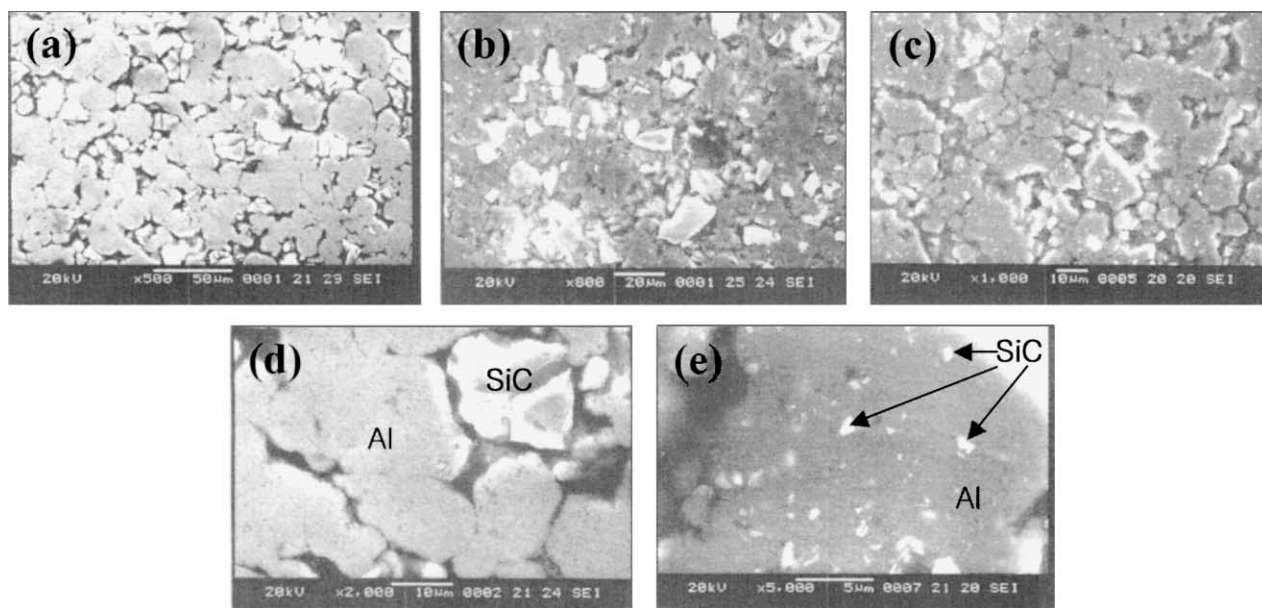
Fig. 3. Scanning electron micrographs of cross-sectional view of ball-milled Al-20 vol.% SiC composite powder at various milling times: (a) 0 h; (b) 2 h; (c) 12 h; (d) 0 h; (e) 12 h (relative light-colored portions correspond to SiC).

with the milling balls (Fig. 2b). Consequently, fine composite powders of Al and SiC are produced at 12 h (Fig. 2c). Cross-sectional images of the ball-milled Al/SiC composite powder are shown in Fig. 3. After ball-milling for 2 h (Fig. 3b), the coarse Al and SiC (relatively light-colored) powders still exist separately, i.e. a composite of Al and SiC is not accomplished completely. After 12 h of ball-milling, the size of the brittle SiC powders is dramatically reduced to form finer particle (∼1 μm) which are embedded homogeneously in the ductile Al matrix (Fig. 3e). The distinctive feature of this composite lies in its microstructure. Generally, the active/inactive composites which have been studied as anode materials have an active phase that stores lithium and expands during charge. The phase is finely dispersed within the inactive matrix which acts as an electron or lithium-ion conductor and buffers the expansion of active phase [16,17]. Compared to this concept, the microstructure of the composite in this work has dispersed reinforcement particles of SiC in an Al matrix. In addition, the reinforcement particle is not an electron or lithium-ion conductor and very brittle, i.e. difficult to buffer the volume change during charge.

Voltage profiles for the charge–discharge of a Al-20 vol.% SiC composite electrode which was ball-milled for 12 h and a SiC electrode are given in Fig. 4. The latter electrode does not react electrochemically with Li (Fig. 4b). The negligible capacity of about 15 mAh g^{-1} corresponds to the reaction between carbon black (conducting agent) and Li. By contrast, the first charge and discharge capacities of the composite electrode are 783 and 703 mAh g^{-1}, respectively, and the initial charge capacity coincides with the theoretical value of this composite in which the weight percentage of aluminum is 77% (Fig. 4a). The discharge voltage profiles

are typical of an aluminum electrode. They are very flat below 0.5 V. These are very attractive features for high-capacity anode materials for lithium secondary batteries.

The cycle performance of Al/SiC composite electrodes is presented in Fig. 5. Compared with the simply mixed one, the ball-milled composites, except that ball-milled for 2 h, show enhanced capacity retention. This improved cycle performance may be related to the enhanced mechanical stability of these particulate-reinforced composites. It is well known that the particulate-reinforced aluminum composite has a higher elastic modulus, greater tensile strength, and more resistance to crack initiation and propagation than the unreinforced one [11–13,18]. The enhanced resistance to crack initiation and propagation is known to be attributed to the mechanism of crack deflection [12,19,20]. Crack deflection induced by the particulates reduces the stress intensity
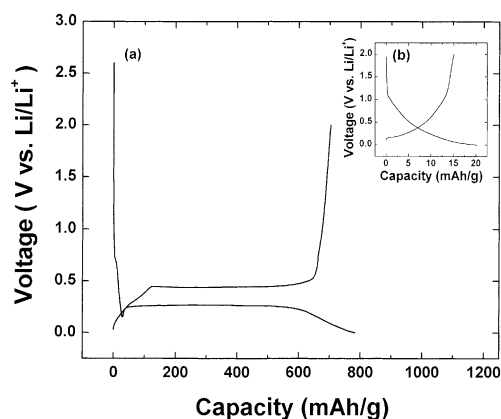

Fig. 4. Voltage profiles for: (a) ball-milled Al-20 vol.% SiC composite electrode; (b) SiC electrode.
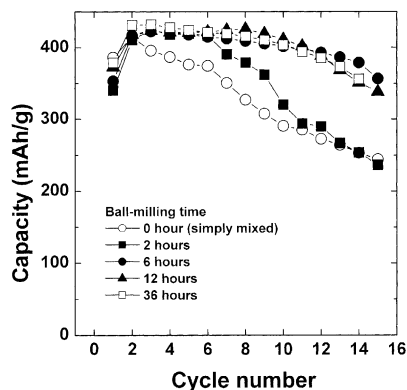
Fig. 5. Discharge (Li removal) capacity vs. cycle numbers of ball-milled Al-20 vol.% SiC composite electrode. Cut-off condition of charge process: capacity of 450 mAh g^{-1} (60% depth-of-charge capacity). If cell voltage reaches 0.0 V before 450 mAh g^{-1} of capacity condition, charge process was cut-off at 0.0 V of voltage condition.
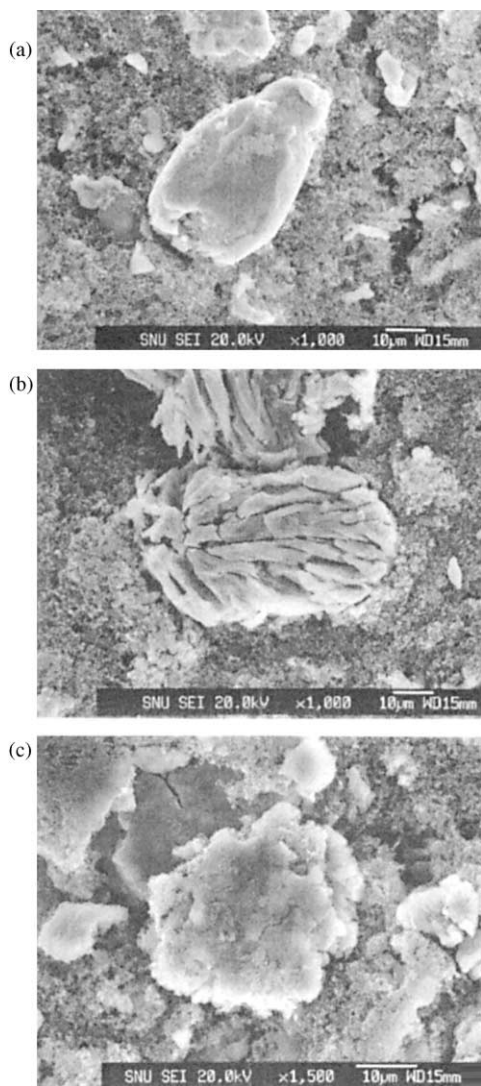

Fig. 6. Scanning electron micrographs of: (a) unreinforced pure Al electrode before cycling; (b) unreinforced Al electrode after 1 cycle; (c) SiC-reinforced Al composite electrode after 1 cycle.

experienced by the crack-tip and thus decreases the driving force for the growth of the crack. Another role of crack deflection is to increase fracture surface roughness and thus promote roughness-induced crack closure. Therefore, it is believed that these enhanced mechanical properties retard cracking and crumbling of the electrode, and thereby, improve cycle performance [12].

To confirm the mechanical stability of the particulate-reinforced composite electrode that reacted with Li, the morphology of the SiC-reinforced Al electrode and the unreinforced Al electrode was compared after 1 cycle by means of scanning electron microscopy. The unreinforced Al electrode shows severe cracks in particles after 1 cycle, cf., Fig. 6a and b. This is found not to be the case with the SiC-reinforced Al composite electrode (Fig. 6c), which indicate the enhanced mechanical stability of this composite electrode.

4. Conclusion

Particulate-reinforced Al/SiC composite materials prepared by ball milling have a distinctive microstructure, namely, the SiC particles are embedded in an Al powder matrix. These composite materials exhibit a relatively high discharge capacity, a flat voltage profile and an enhanced cyclability, which are attractive features for anode materials in lithium secondary batteries. Strengthened mechanical properties, such as high tensile strength and greater resistance to crack growth, can be obtained by synthesizing the particulate-reinforced composite. This enhanced mechanical stability may retard pulverization of the electrode, and thus, improve cycle performance.

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