Journal of Power Sources 366 (2017) 226–232

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Crack-resistant polyimide coating for high-capacity battery anodes

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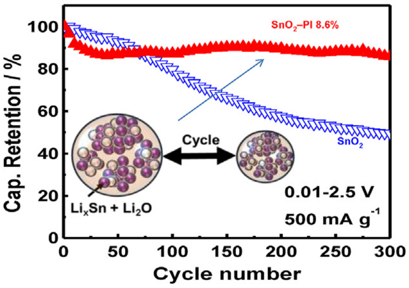
HIGHLIGHTS

- Conformal polyimide coating on SnO_2 is achieved.
- Capacity of SnO_2 during cycling is sustained with a high-modulus PI coating.
- Electrode cracking is suppressed with the PI coating.
- Volume change of the alloying and conversion processes is reduced with the coating.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 June 2017
Received in revised form
7 September 2017
Accepted 11 September 2017

Keywords:
Crack-resistant coating
Polyimide
Surface protection
Tin dioxide
Lithium-ion battery

ABSTRACT

Electrode cracking is a serious problem that hinders the application of many next-generation high-capacity anode materials for lithium-ion batteries. Even though nano-sizing the material can reduce fracturing of individual particles, capacity fading is still observed due to large volume change and loss of contact in the electrode during lithium insertion and extraction. In this study, we design a crack-resistant high-modulus polyimide coating with high compressive strength which can hold multiple particles together during charge and discharge to maintain contact. The effectiveness of the coating is demonstrated on tin dioxide, a high-capacity large-volume-change material that undergoes both alloy and conversion reactions. The polyimide coating improves capacity retention of SnO_2 from 80% to 100% after 80 cycles at 250 mA g^{-1}. Stable capacity of 585 mAh g^{-1} can be obtained even at 500 mA g^{-1} after 300 cycles. Scanning electron microscopy and in-situ dilatometry confirm that electrode cracking is suppressed and thickness change is reduced with the coating. In addition, the chemically-stable polyimide film can separate the surface from direct contact with electrolyte, improving coulombic efficiency to ~100%. We expect the novel strategy of suppressing electrode degradation with a crack-resistant coating can also be used for other alloy and conversion-based anodes.

1. Introduction

Energy storage is a key component in our quest towards sustainability. For example, electric vehicles which can reduce CO_2 emissions from the tail pipes require batteries with high energy density. Large-scale renewable energy systems such as wind turbines and solar farms which can decrease our dependency on fossil fuel also require efficient energy storage to buffer the intermittency of the sources. Lithium-ion battery (LIB) is one of the leading technologies in this area due to its high energy density and availability. Though, drastic improvements in capacity and lifetime are still needed to meet future applications.

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http://dx.doi.org/10.1016/j.jpowsour.2017.09.037
0378-7753/

Commercial LIB typically uses graphite as its anode material. To increase the energy density of the battery, numerous anode materials with higher capacity have been investigated. For example, metal oxides such as Fe_2O_3, MnO and Co_3O_4 can undergo conversion reaction with lithium, and elements such as Si, Sn, and Sb can incorporate large amount of lithium by alloying [1–8]. Initial charge-discharge capacities of more than 700 mAh g^{-1} can be readily achieved [7,8]. However, these materials undergo large volume change when they take in and release lithium. Tin (Sn), for example, has a theoretical volume change of 260% with the incorporation of 4.4 Li into the lattice [9]. This causes mechanical failures within the electrode, such as fracturing of the particles, loss of contact, and delamination from current collector, leading to poor cycle performance.

Part of the issues can be overcome with the use of nanomaterials [1,7,10]. Fracturing of the particles is suppressed with reduced size, as the internal stress within the material is smaller [11–13]. In addition, part of the volume change can be accommodated by voids between the nano-particles. This leads to some improvements in cycle performance. However, capacity fading is still often observed during long-term cycling. This is because nanostructuring cannot effectively solve two other problems within an electrode: (1) the loss of contact between adjacent particles/domains from continuous expansion and shrinkage during lithiation and delithiation, and (2) surface reactions between the material and the electrolyte [14,15]. In this study, we present our novel strategy to keep the connectivity of the particles while suppressing surface reactions, which is to incorporate a robust surface coating on multiple particles. The idea is to use the surface film to actively pull the particles back together during delithiation to ensure mechanical stability of the electrode, and to eliminate direct contact between the surface of the material and the electrolyte. Here, we show that a high-modulus polyimide (PI) with good chemical stability is an excellent material choice for this purpose.

Polymer coatings on anode material are previously reported in the literature, but for different applications. For example, Bhaskar et al. used poly(3,4-ethylenedioxythiophene) as a coating material to improve the electrical conductivity of the composite material [16]. He et al. used an alucone coating to enhance electronic and Li ion conductivity [17]. Wang et al. employed polydopamine as a soft and elastic buffer layer between the active material and the binder to accommodate the volume change of the active material [18]. We are taking a different approach in this study – to use a high-modulus PI coating that can prevent crack formation in the electrode and at the same time exert a large compressive force on the active material to pull the particles back together during particle shrinkage. Lithium diffusion through the PI layer is not a major issue, as PI has previously been reported as a binder for various electrode materials [19,20].

Here, we illustrate the effectiveness of our strategy to improve electrode stability with tin dioxide (SnO_2) nanoparticles, readily available in large quantity from Alfa Aesar. Nano-SnO_2 is an ideal model material for this study, as it undergoes both conversion and alloying reactions with a capacity of more than 850 mAh g^{-1}. The volume expansion of SnO_2 is larger than most transition metal oxides due to the Sn-Li alloying process. In addition, the conversion reaction between Li_2O and Sn requires intimate contact between the domains. Moreover, the nanoparticles have large surface to volume ratios, so surface reaction is more severe. Numerous works have been carried out on nano-SnO_2, but capacity fading is still often observed with cycling (see Table S1). In this study, we are able to significantly improve the cycle stability of SnO_2 with a PI coating. We confirm that the PI coating reduces volume change of SnO_2 electrodes, suppresses crack formation in the electrodes, increases reversibility of the alloying and conversion reactions and improves coulombic efficiency. An additional advantage is that the coating process involves simple steps – just dispersing the commercial active material with polyimide precursors and heat-treating it to get the coated material. It can therefore be applied easily on other materials.

2. Experimental section

2.1. Preparation of polyimide-coated SnO_2

SnO_2 nanoparticles (Alfa-Aesar, 99.9%) were mixed with polyimide precursors (DB100, IST Japan) in N-methyl pyrrolidinone (NMP) solvent with a weight ratio of 1:0.05, 1:0.1 and 1:0.2. The mixtures were then dried at 60 °C for 24 h in an oven to remove the NMP solvent. The powders were further annealed under nitrogen flow in a tube furnace at 350 °C for 4 h to form the polyimide coating on the surface of the SnO_2.

2.2. Characterization

The amount of PI in the sample was determined by thermogravimetric analysis in air from 30 °C to 650 °C with a ramping rate at 5 °C min^{-1} (TGA/DSC-1, Mettler-Toledo). The crystal structure of SnO_2 powders was analyzed by powder X-ray diffraction (D2 Phaser Brucker) with Cu K_α ($\lambda = 0.154184$ nm) as the X-ray source. The diffraction data were collected between 20 and 80° with an acquisition rate of 0.1° per second. Morphologies of SnO_2 and the PI-coated SnO_2 powders, as well as the electrodes before charge and discharge were investigated by scanning electron microscopy (FEG SEM XL30, Philips, 5 kV). Microstructure of the PI-coated SnO_2 powders was investigated by transmission electron microscopy (FEI CM-20, Philips).

2.3. Electrochemical analysis

Active material, acetylene black (AB) and carboxyl methyl cellulose (CMC) were mixed in water with a weight ratio of 6:2:2 to form a slurry. The slurry is then coated with a doctor blade onto roughened copper foil, which acts as the current collector. The coating was dried on a hot plate and compressed by a roll press. 16 mm diameter discs were punched, and the weight and thickness of each electrode were measured. Electrodes were further dried at 110 °C for 4 h in vacuum before they were transferred into an Ar-filled glovebox. The electrodes were made into 2032 coin cells with Li metal as the counter electrodes and Celgard 2325 membrane (Celgard Inc. USA) as the separator. 1 mol L^{-1} of $LiPF_6$ in fluorinated ethylene carbonate and diethyl carbonate (FEC/DEC) with a 1:1 ratio by volume (Soulbrain Co. Ltd.) was used as the electrolyte. The coin cells were tested at current rates of 100, 250 and 500 mA g^{-1} with a battery tester (Neware, China). All of the battery tests were performed at room temperature (23 ± 1 °C). Capacities reported in this paper are calculated with respect to the total mass of the PI-SnO_2 composite.

2.4. In-situ electrochemical dilatometry

The change in electrode thickness during charge and discharge was measured by a dilatometer (ECD-2, EL-CELL, Germany). The working electrodes were 9 mm in diameter. The cell was assembled in the Ar-filled glovebox using Li foil as counter and reference electrodes with a porous ceramic T-shape frit as separator. About 1 ml of electrolyte solution was filled into the cell with a syringe after cell assembly. The dilatometer is connected to a potentiostat (Biologic VMP3) for charge and discharge. While a current is applied, the voltage, height displacement and temperature of the