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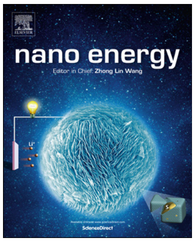

RAPID COMMUNICATION

Interfacial stabilizing effect of ZnO on Si anodes for lithium ion battery

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Abstract
Silicon nanoparticles with atomic layer deposited zinc oxide (ZnO) coating show significantly improved electrochemical performance mainly because of enhanced mechanical integrity and stablized interface. These ZnO coated Si nanoparticles demonstrate stable cycling with a reversible capacity of 1500 mAh/g over 260 cycles. With ZnO protected interface, these electrodes can achieve stable cycling with mass loading as high as 1.4 mg/cm^2. In-situ structural characterization is performed to illuminate the stabilizing mechanism of the ZnO coating during cycling. It is confirmed that the coating is mechanically robust to remain intact even though Si expands inside, and a battery electrode made of this Si/ZnO structure will undergo minimal structural damage upon cycling.

Introduction

Rechargeable lithium-ion batteries hold great promise as next generation energy storage devices [1-3]. However, the current electrode materials have limited specific charge storage capacity and cannot achieve the energy density, power density, and cycle times that all the important applications such as portable electronics and electric vehicles require [2]. Si is attracting much attention as an alloying electrode material because of its highest known theoretical charge capacity (4200 mAh/g). There are significant challenges, such as large volume changes (400% volume expansion) during Li ion insertion and extraction and unstable solid-electrolyte interphases (SEI), which can cause many issues, such as particle fracture, low Coulombic efficiency, and short cycle life [4]. Recently, many Si

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nanostructures, such as Si nanowires [5], Si/carbon spheres [6], Si nanotubes [7-9], have been intensively explored to address the issues of the fracture and unstable SEI [5,6,10-19]. Wu et al. designed a Si double wall tube through electrostatic spinning to stablize the SEI layer. Wang et al. reported that they can alleviate the fracture of Si particles through adding the self-healing binder [20]. Different from them, in this work we take the approach of surface engineering by coating Si surface with a thin layer of ZnO by atomic layer deposition (ALD). Among various Si nanostructures, silicon nanoparticles (SiNPs) are considered as a promising candidate because they are commercially available, industrially scalable, and compatible with the current slurry coating manufacturing process. However, even with the development of several novel binders [12,21,22] such as sodium carboxymethyl cellulose (CMC), sodium alginate, poly (acrylic acid) (PAA), which can help to connect the SiNPs, there are still loss of active materials. In addition, the surfaces of silicon particles are still directly exposed to the electrolyte and lead to unstable SEI formation. In this work, we use ALD ZnO to coat Si NPs, which not only can enhance the mechanical integrity of SiNPs electrode, but also stablize the SEI layer between the electrode and electrolyte.

Atomic layer deposition (ALD) coating has been used for nanoscale surface modification, which can improve the mechanical integrity and electrochemical performance of materials [23-25]. Previously, Al_2O_3 by ALD has been used to coat cathode materials such as $LiCoO_2$ [26] to improve electrochemical performance. Here we found that 3 nm ZnO ALD coating on SiNPs can improve the mechanical property, form an electrochemical stable interface, maintain good ionic and electrical pathway, and therefore lead to improved electrochemical performance (Figure 1). SiNPs with ZnO coating demonstrated high initial discharge capacity of 2600 mAh/g (charge/discharge rate of C/20) and still reached 1500 mAh/g (charge/discharge rate of C/2) after 260 deep electrochemical cycles.

Materials and methods

Si electrodes were prepared by mixing Si powders (~100 nm) with CMC (MW: 250,000) and Super-P carbon (8:1:1). Deionized water was added to the powdered mixture to make a solution with 1% CMC/w (i.e., 10 mL deionized water, 0.1 g CMC). The well-mixed slurry was spread on stainless steel disks (15 mm diameter) and allowed to dry in an oven in air at 100 °C for 8–12 h. A second drying step was performed at 150 °C in a vacuum oven for 1 h. The stainless steel disks were then transferred to ALD chamber for ZnO coating. The whole electrode materials were coated by ZnO via ALD in this study. Diethylzinc [Zn $(C_2H_5)_2$, DEZ] and H_2O were selected as the zinc precursor, and oxygen reactant sources, respectively. Here, the deposition was started with a substrate temperature of 90 °C and a background pressure of 0.2 Torr. In each cycle, a 60 ms DEZ pulse and a 70 ms H_2O pulse were alternately introduced into the ALD chamber respectively. Ar flow was employed for both precursors. The ZnO shell thickness of 3 nm was obtained through about 8 precursor/purge cycles. In addition, we also coat Si nanowire (SiNW) with ZnO by ALD to enable in-situ investigation of structural changes during cycling.

Results and discussion

Figure 2a and b shows the scanning electron microscopy (SEM) image and X-ray diffraction (XRD) patterns of the SiNPs. The diameter of these SiNPs is about 100 nm. In Figure 2b, all diffraction peaks can be indexed to crystalline silicon, confirming the high crystal quality of these Si nanoparticles before lithiation. The transmission electron microscopy (TEM) image (Figure 2c) confirms the uniformity of the ALD ZnO layer with thickness of about 3 nm on the SiNW. Furthermore, the high-resolution TEM (HRTEM) image of SiNW with ALD ZnO coating exhibits crystal planes with space of 0.24 nm, corresponding to the (101) planes of ZnO (Figure 2d).

In a Li-ion battery anode, Li is inserted during the charging process and is extracted during the discharging process. During the charging process, ZnO goes through the following conversion reaction followed by an alloying reaction. Once zinc oxide is lithiated in reaction 1, zinc nanograins are formed in a lithium oxide matrix.

$$2Li^{+}+ZnO+2e^{-}\rightarrow Li_2O+Zn \tag{1}$$

$$Zn+xLi^{+}+xe^{-}\leftrightarrow Li_xZn\ (x<3) \tag{2}$$

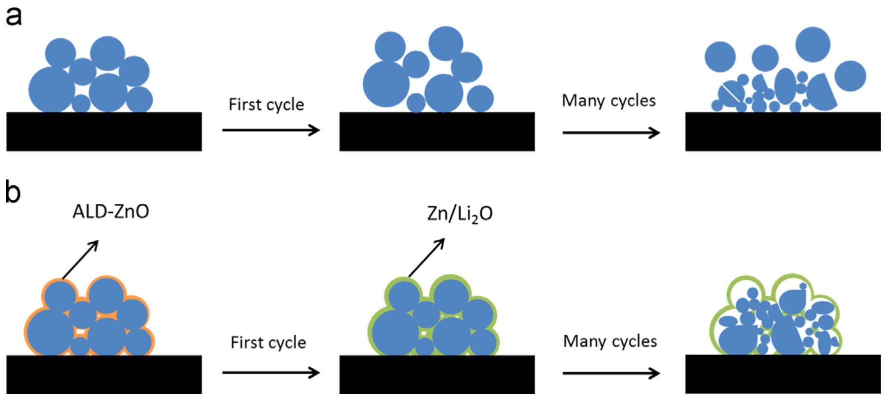

Figure 1 Schematic of the electrode materials. (a) A conventional slurry coated SiNP electrode. The expansion of each SiNP disrupts the microstructure of the electrode; (b) a novel Si/ZnO electrode. The ZnO coating layer allows Si to expand without rupturing the coating layer, which ensures that a stable and thin SEI layer. Also, the volume change of the SiNPs is accommodated and does not change the microstructure of the electrode.

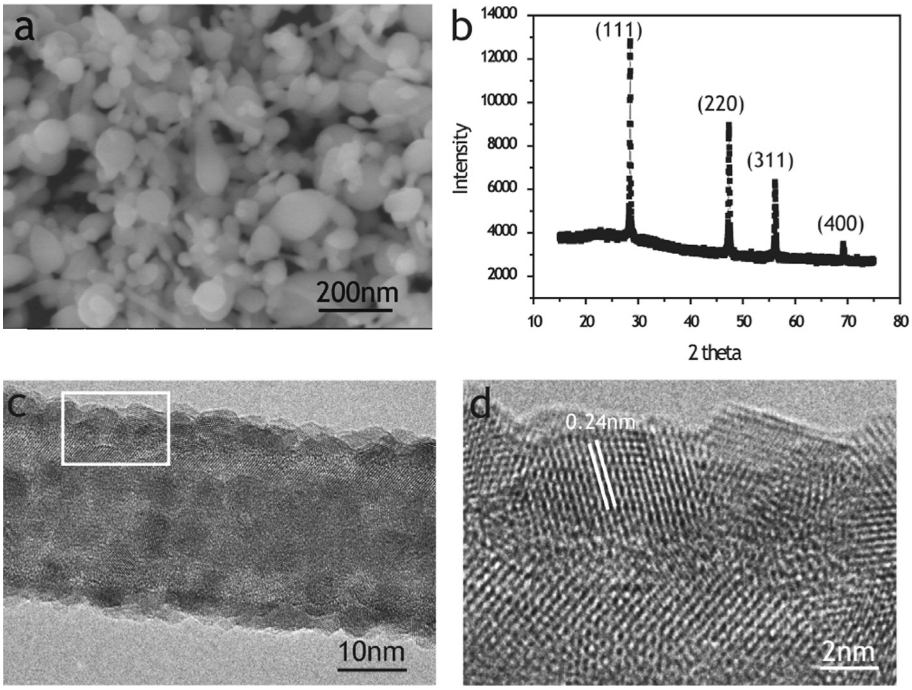

Figure 2 Characterizations of Si/ZnO electrodes. (a) SEM and (b) XRD pattern of Si nanoparticles; (c) TEM image of ZnO coated Si nanowires and (d) HRTEM image of ZnO layer on the surface of Si nanowires.

After these reactions, there is a thin layer of Zn/Li_2O coated on the surface of silicon particles. This structure has several advantages as Li-ion battery alloy anodes. First, the Zn/Li_2O shell is uniform and mostly free of pinholes, which prevents the electrolyte from reaching the SiNP surface inside the shell. Lithiation of the Si occurs by Li diffusion through the Zn/Li_2O shell into the Si core. Second, as zinc itself will experience significant volume expansion, the Zn/Li_2O shell allows each particle to expand upon lithiation without deforming the electrode microstructure. This in turn allows for the growth of a stable SEI. Third, the Zn/Li_2O shell is both electrically and ionically conductive, which allows for good kinetics.

To investigate the electrochemical performance of these ZnO coated Si nanoparticles, two-electrode 2032 coin cells with these Si/ZnO on the Cu substrate were fabricated with Li metal as the counter electrode. To understand the intrinsic properties of these Si/ZnO materials, galvanostatic cycling is used with voltage cut-offs of 0.01 and 1 V vs Li/Li+. The charge capacity reported here is the total charge inserted per unit mass of the Si materials during Li insertion, whereas the discharge capacity is the total charge removed during Li extraction.

The first discharge capacity of SiNPs with 3 nm ZnO coating was 2600 mAh/g at the C/20 rate, or 20 h per half-cycle (Figure 3a). The first cycle Coulombic efficiency (CE) was 63%, mainly due to reactions at the surface of these structures. One reason is the formation of a surface-electrolyte interphase (SEI) film due to electrolyte decomposition [4,9,27]. This has been well studied in Si electrodes. The second reason is the irreversible conversion from ZnO layer to Zn/Li_2O mixtures that forms on the Si. The low Coulombic efficiency is limited to the first cycle, after which the CE was above 90%, suggesting most side reactions occur only in the initial cycle. More studies will be done to determine the exact processes and the origin of the large initial irreversible capacity loss. In addition, the discharge capacity remains stable above 1700 mAh/g over 160 cycles at C/5 rate from the 4th cycle, indicating that the SiNP networks remain contacted to the current collector and do not pulverize. In comparison, the discharge capacity of SiNPs without ZnO coating decreases significantly to only 1000 mAh/g after 140 cycles. The voltage profiles of the different cycles are shown in Figure 3b. The lithiation potential shows a flat profile between 0.1 and 0.01 V, consistent with the behavior of crystal silicon. The large capacity between 1 and 0.1 V in the first lithiation presented in Figure 3b is partly from the irreversible reaction between Li^+ and ZnO. No obvious change in charge/discharge profile can be found after 160 cycles, indicating superior and stable cycling performance. Figure 3c shows that even cycled at C/2 rate the discharge capacity can reach 1500 mAh/g after 260 cycles, which is 4 times higher than that of conventional graphite anodes (370 mAh/g). The electrodes with active material mass loading up to 1.4 mg/cm^2 are also tested. After 100 cycles the reversible areal capacity still reached 1.1 mAh/cm^2 (Figure 3d). To confirm the stability of structure during cycling, the morpholoy of ZnO/Si electrode after 100 cycles was then examined with SEM (Figure S1, Supporting information), which shows that the ZnO/Si electrode is still intact with a thin and uniform SEI layer coating the surface.

The recent application of in situ TEM to study electrochemical reactions has provided a powerful way to monitor the structural changes of materials during electrochemical processes [28-31]. Here, we use in situ TEM to study the deformation and structural changes of the ZnO coated Si materials during cycling to gain insight into their interface stabilizing effect. SiNW with similar diameter as the SiNP is chosen for a more straightforward in situ TEM cell, which is

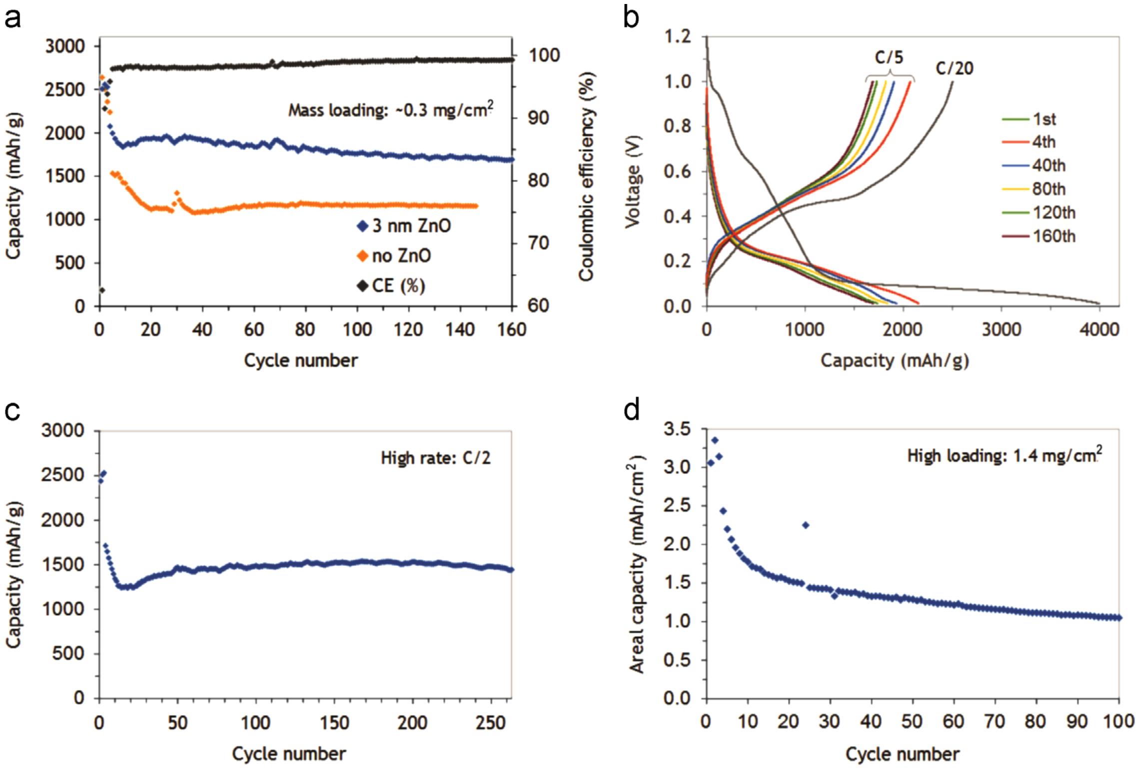

Figure 3 Electrochemical characteristics of ZnO coated Si nanoparticles tested between 1 V and 0.01 V. (a) Delithiation capacity and CE of ZnO coated Si nanoparticles at the charge/discharge rate of C/20 for the first 3 cycles, then at the charge/discharge rate of C/5 until 160 cycles; (b) voltage profiles plotted for the 1st, 4th, 40th, 80th, 120th and 160th cycles; (c) capacity of ZnO coated Si nanoparticles cycled at high rate of C/2 and (d) capacity of ZnO coated Si nanoparticles cycled with high mass loading of 1.4 mg/cm^2.

shown schematically in Figure 4a. 15 nm ZnO is coated onto Si nanowires (SiNWs) grown on a flat Si substrate. A few NWs with ZnO coating are then transferred to a metallic probe on a specialized dual-probe biasing TEM holder, as shown at the bottom of the schematic. $LiCoO_2$ particles are attached to the other metallic probe (the top of the schematic), and a drop of ionic liquid electrolyte is placed on this electrode. The ionic liquid has extremely low vapor pressure and therefore does not evaporate when exposed to the high vacuum of the TEM column. Inside the TEM, the NW is positioned so that the NW tip is immersed in the ionic liquid. In this way, a nanoscale electrochemical device is formed where the Si/ZnO electrode is the working electrode and the $LiCoO_2$ is the Li-containing counter electrode. By applying a 4 V bias to the NW side, Li^+ diffuses and is inserted into the NW. While this experimental geometry is different from what is in an actual battery, the deformation characteristics are expected to be similar, especially since fast surface diffusion causes lithiation to proceed relatively uniformly in the SiNWs. Figure 4b shows a series of images taken from a movie of the in situ lithiation of Si/ZnO (Movie S2, Supporting information). In the first image (0 s), pristine Si nanowires are visible within the conformal ZnO shell coating by ALD. In subsequent frames, the Si nanowire expands in volume as Li diffuses through the Zn/Li_2O coating and reacts with the SiNW. In the frame labeled '650s', the nanowire is partially lithiated, and an amorphous Li_xSi shell/crystalline Si core structure is readily discernible (the crystalline core is the region with darker contrast). The electron diffraction pattern of Si core is shown in Figure 4b, confirming that before the lithiation Si core is crystalline. This two-phase reaction mechanism is well-known to occur during the lithiation of crystalline Si. After complete lithiation, the diameter of the nanowires increases from 55 to 95 nm and the Si core turned to amorphous, as the electron diffraction pattern shown in Figure 4c. Fracture was not observed in the nanowire. In addition, the ZnO coating also becomes lithiated; the thickness of the shell increases from 15 to 25 nm after lithiation. Some of the shell thickness increase could also be attributed to the build-up of a thin layer of ionic liquid electrolyte at the surface. Figure 4c shows a series of images taken from a movie of the in situ delithiation of a Zn/Li_2O coated Si NW (Movie S3, Supporting information). In the first image (0s), fully lithiated Si nanowires are visible within the conformal Zn/Li_2O shell. In subsequent frames, the Si nanowire shrinks in volume as Li diffuses out of Si nanowire through the Zn/Li_2O coating. After complete delithiation, the diameter of the nanowire decreases from 95 to 55 nm. No fracture was observed either. In addition, the thickness of the shell decreases from 25 to 20 nm after delithiation.

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This in situ TEM experiment reveals important details related to the volume changes in this structure. First, in this configuration, Li must diffuse through the Zn/Li_2O shell into the nanowires for them to become lithiated. The whole Si

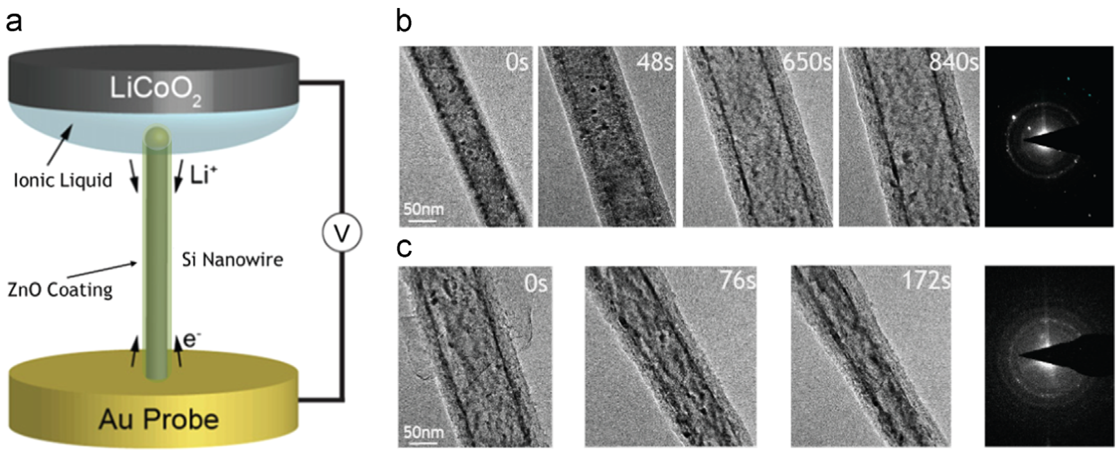

Figure 4 In-situ TEM characterization of Si/ZnO during electrochemical lithiation and delithiation. (a) Schematic of the in situ TEM device; (b) in situ TEM image series during lithiation (also see Movie S1 in Supporting information). Both Si nanowire and the ZnO shell are observed to expand, and the shell does not rupture. In addition, these data indicate that Li transport through the shell layer is sufficient for good rate capability and (c) in situ TEM image series during delithiation (also see Movie S2 in Supporting information). Both Si nanowire and the shell shrink, and the shell do not rupture.

nanowires in the observation window were lithiated (Figure 4b and Movie S2 in Supporting information). In addition, the rate of Li diffusion through the Zn/LiO_x shell seems to be fast enough for lithiation to occur in a reasonable time. Second, it is clear that the Zn/LiO_x coating is mechanically robust to remain intact even though Si expands inside. Because the overall shape of the Si/ZnO structure does not change appreciably upon lithiation, it is expected that a battery electrode made of this Si/ZnO structure will undergo minimal microstructural damage upon cycling.

Conclusion

In conclusion, we have shown that Si nanoparticles with ZnO coating have a high specific capacity and excellent cycling performance. The process is compatible with slurry process. Thus, Si nanoparticles with ZnO networks can be a promising, higher-capacity alternative for the existing graphite anode in Li ion batteries.

Acknowledgments

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.nanoen.2015.03.019.

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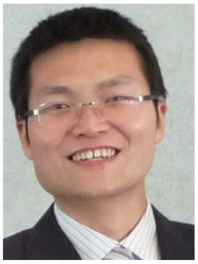

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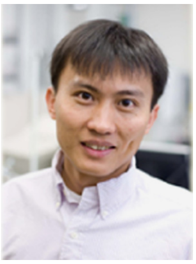

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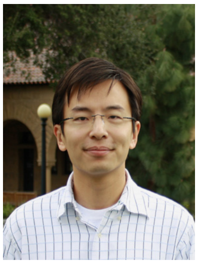

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