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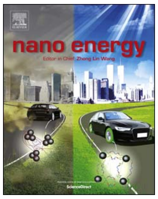

Full paper

Enabling high performance lithium storage in aluminum: The double edged surface oxide

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ABSTRACT

Aluminum is an attractive anode material for lithium ion batteries due to its low cost, high capacity and low equilibrium potential for lithiation/delithiation. The compact surface oxide layer is usually considered to be detrimental for lithium storage in Al due to its poor conductivity for Li^+. Here we show that the Al oxide layer, which is positively charged, can be utilized to assist the homogeneous loading of the Al nanoparticles on to the negatively charged graphene oxide (GO) sheets. During the thermal reduction of GO to reduced GO (rGO), anhydrous HCl is introduced to selectively remove the surface oxide on the Al particles. The vitalized Al/rGO composite exhibits high lithium storage capacity of 1041 mAh g^{-1} after 500 cycles at current density of 500 mA g^{-1}. The results demonstrate how the double edged surface oxide layer on Al nanoparticles can be manipulated to enable high performance lithium storage in Al, which is illuminating for the application of Al as a high performance, low cost anode material for lithium ion batteries.

1. Introduction

There is a continuous pursuit for lithium ion batteries (LIBs) with higher energy and power density. Currently, the energy density of LIBs is mainly limited by the cathode. However, capacity improvement of the cathode even by only a few percentage without significantly lowering the potential and stability is already extremely challenging. On the other hand, there have been many anode candidates with capacity several times higher than that of the graphite anode in commercial LIBs. Therefore, application of high capacity anode materials in commercial LIBs is essential to fulfil the requirement of high energy density LIBs.

Metals or metalloids forming Li rich alloys, such as Si, Ge and Sn are promising high capacity anode materials and have been extensively studied in the past two decades [1–6]. However, it is somehow surprising that aluminum is significantly less studied as the anode material for LIBs. Aluminum is the third most abundant element in the earth crust and the second most produced metal in the modern world. It forms the intermetallic compound LiAl at low equilibrium potential of 0.4 V vs. Li/Li^+, corresponding to high capacity of 993 mAh g^{-1}. Even higher lithium storage capacity is also achievable at lower potential. The low cost, high capacity and low lithiation potential make aluminum an ideal candidate for anode materials in LIBs.

Unfortunately, Al based anode materials with high capacity and good cyclic stability is rarely reported. A primary obstacle is the very compact and stable oxide layer of Al, which is a very good insulating barrier for both electrons and Li^+. For comparison, the oxide of Si, Ge and Sn can readily react with Li and can even be directly used for lithium storage [7–11]. Due to its high chemical reactivity, it is very difficult to obtain oxide free Al particles.

Al also suffers from the poor reversibility due to the huge volume change during lithiation/delithiation, which is a common issue for all the high capacity alloy type anode materials. Strategically, this issue can be readily solved by reducing the particle size together with using carbon based conductive buffer, as demonstrated by many successful examples for Si, Ge and Sn based anode materials [12–16]. However, similar composite structure of Al is much more difficult to obtain, as the high chemical reactivity of Al significantly limits the application of soft chemistry based techniques.

In this work, we show that high performance lithium storage in Al can be achieved by properly manipulating the surface oxide layer. The surface oxide layer enables homogeneous Al loading onto graphene oxide (GO) sheets by simple sonication in tetrahydrofuran through an electrostatic interaction based self-assembly process, leading to a stable composite structure during charge/discharge. Then the oxide layer is removed by anhydrous HCl etching when GO is thermally converted to reduced GO (rGO), which effectively vitalizes the lithium storage capacity of Al. The combined efforts result in high lithium storage performance, featured for a high capacity of 1041 mAh g^{-1} after 500

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cycles at current density of 500 mA g^{-1}. The results clearly demonstrate the critical importance to manipulate the double edged surface oxide layer to achieve high performance lithium storage in Al.

2. Material and methods

2.1. Material synthesis and characterization

Al nanoparticles are prepared by thermal plasma evaporation and condensation according to our previous publications [17–19]. Graphene oxide is prepared by a modified Hummer's method [20,21].

To prepare the Al/GO composite, Al nanoparticles and GO are dispersed in tetrahydrofuran (THF) by sonication to give a concentration of 1.0 g L^{-1}. The two suspension is rapidly mixed with desire proportion and further sonicated for 4 h. Solid precipitates rapidly form when the sonication stops, which can be easily collected by filtration (Fig. S1).

To obtain the Al/rGO composite, Al/GO sample 500 mg is thermal etched by anhydrous HCl at 300 °C for 2 h. Anhydrous HCl is generated by feeding concentrated aqueous HCl solution (37 wt%) at 0.050 mL min^{-1} into solid P_2O_5 powder by an injection pump, corresponding to flow rate of anhydrous HCl gas of 36 standard cubic centimeter per minute (sccm). The generated HCl is introduced into the tube furnace by high purity Ar flow of 50 sccm. The setup for HCl thermal etching is schematically illustrated in Fig. S2. The cooling process is carried out in pure Ar flow by stopping HCl feeding.

The structure of the composites is characterized by X-ray diffraction (XRD, Rigaku D/max 2000 diffractometer, Cu Kα), scanning electron microscopy (SEM, Hitachi S4800, 10 kV) with an energy dispersive X-ray spectroscopy (EDS) analyzer, transmission electron microscopy (TEM, JEOL JEM-2100F, 200 kV) and X-ray photoelectron spectroscopy (XPS, Kratos Analytical, Ultra Axis, monochromatic Al Kα radiation). The composition is determined by thermogravimetric analysis (TGA) and energy dispersive spectroscopy (EDS) in SEM.

2.2. Electrochemical measurement

The electrodes used in electrochemical performance measurements are composed of the active material, super P carbon black and a polyvinylidene fluoride (PVDF) binder with weight ratio of 8:1:1 smeared on copper foils. The mass loading (0.35–0.40 mg cm^{-2}) is determined by a high accuracy microbalance (Mettler Tole36do, accuracy 1 μg). Coin type half cells are assembled in an argon-filled glove-box. A lithium foil is utilized as the counter electrode. 1 M $LiPF_6$ in ethylene carbonate/dimethyl carbonate = 1/1 in volume with the addition of 5 wt% fluoroethylene carbonate (FEC) is used as the electrolyte. Polypropylene films (Celgard 2400) are used as the separators. Galvanostatic charge/discharge measurements are performed on a multichannel battery testing system (Wuhan LAND, China). The cells are tested at current density from 100 to 5000 mA g^{-1} for both charge and discharge at room temperature in the voltage range of 0.05–3.0 V (versus Li/Li^+). Cyclic voltammetric measurements are performed in the voltage range of 3.0–0 V (versus Li/Li^+) at a scan rate of 0.1 mV/s. Electrochemical impedance spectra (EIS) is obtained by applying a sine wave with amplitude of 5.0 mV over the frequency range from 100 kHz to 0.1 Hz.

3. Results and discussion

The preparation process of the Al/rGO composite is illustrated in Fig. 1. Aluminum nanoparticles are prepared by thermal plasma evaporation and condensation as described in our previous study [17–19]. As shown by the TEM image, the average diameter of the obtained Al nanoparticles is about 100 nm (Fig. 2b). XRD suggests that the obtained Al nanoparticles are highly crystallized without any crystalline impurity (JCPDS No. 04–0787, Fig. 2a). The graphene oxide (GO) sheets are prepared by a modified Hummers' method, which exhibits 2D thin layer structure characteristic of chemically exfoliated GO (Fig. 2c). The XRD pattern of GO nanosheets features a broad peak centered at 10.9° (Fig. 2a), corresponding to the (002) plane of GO.

Both the Al nanoparticles and the GO sheets can be easily dispersed in tetrahydrofuran (THF) by sonication. However, when the THF dispersion of the Al nanoparticles and GO is mixed and further sonicated, the obtained solid rapidly precipitates from THF when sonication is stopped, leaving a very clear supernatant (Fig. S1). The solid is separated by filtration and dried at 60 °C under vacuum for 1 h, which is further treated in a Ar flow with anhydrous HCl gas at 300 °C for 1 h to remove the surface oxide layer on the Al particles. Here anhydrous HCl is generated by dehydration of aqueous HCl solution using P_2O_5, which is very convenient to prepare small amount of anhydrous HCl in laboratories. The thermal etching setup is schematically illustrated in Fig. S2. Thermogravimetric analysis (TGA) suggests that the Al content is about 50% in mass percentage (Fig. S3).

The obtained Al/rGO composite exhibits highly interesting morphology. As shown in the SEM image (Fig. 2d), the characteristic 2D sheet morphology of rGO is absent in the Al/rGO composites. Instead, the composite appears in the form of 3D quasi-spherical assembly of several tens of micrometers. Magnified SEM images clearly show that these 3D quasi-spherical assembly are composed of rGO sheets on which the Al nanoparticles are homogeneously loaded (Fig. 2h, i). Elemental mapping again implies very uniform distribution of aluminum and carbon in the Al/rGO sample (Fig. 2e-g). The XRD pattern of Al/rGO retains the sharp diffraction peaks correspond to cubic metallic Al (Fig. 2a). In addition, there is a broad peak between 20° and 30° which is corresponding to rGO. The TEM image more clearly reveals homogeneous distribution of the Al nanoparticle loaded on the 2D rGO sheets (Fig. 2j). In the HRTEM image, clear lattice fringes are observed with inter-planar spacing of 0.23 nm, corresponding to the (111) planes of cubic aluminum (Fig. 3c). In addition, the thermal etching process also effectively convert GO into rGO. As shown by the Raman spectrum (Fig. 2k), the characteristic G and D bands of rGO at 1593 and 1356 cm^{-1} can be identified [22].

The formation mechanism of the 3D quasi-spherical assembly is highly intriguing. In fact, the 3D quasi-spherical assembly is already formed the sonication step, as shown in Fig. S4. It is remarkable that the Al nanoparticles can be homogeneously loaded onto the GO sheets with such a simple process. A possible mechanism for this effective self-assembly is due to the electrostatic interaction. Aluminum oxide carries positive surface charge in neutral solution. Organic solvents such as THF does not affect the surface positive charge [23]. On the other hand, the GO sheets are negatively charged due to the oxygen containing functional groups (e.g. carboxylate groups) generated during chemical exfoliation [24]. Driven by the opposite surface charge, the Al nanoparticles will spontaneously attached to the GO sheets during the sonication process. It has been reported that amino group functionalized silica and Co_3O_4 nanoparticles with positive surface charge can be wrapped by GO sheets in aqueous solution through a similar electrostatic interaction mechanism [25]. However, formation of the quasi-spherical 3D assembly is quite surprising. It has been shown that aprotic solvents such as THF have weaker solvation effect for the negatively charged GO sheets [26]. Therefore, formation of the quasi-spherical 3D assembly might be driven by minimizing the total interface energy in aprotic solvents such as THF.

Although there is no crystalline oxide phase detected by XRD, the Al nanoparticles are covered by an amorphous native oxide layer around 5 nm, as shown in Fig. 3a. As will be shown later, the surface oxide layer on the Al nanoparticles is highly detrimental for lithium storage. Thus, it is critical to remove the surface oxide layer to achieve good lithium storage performance of the Al nanoparticles. The main challenge is to remove the surface oxide layer without introducing new impurities or over etching the metallic Al. In this work, we propose a thermal etching method using anhydrous HCl to selectively remove the