



Vertical graphene nanowalls coating of copper current collector for enhancing rate performance of graphite anode of Li ion battery: The merit of optimized interface architecture

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ABSTRACT

Carbon coating has been attracting wide interests as optimum protection technology for Li ion batteries. Recently, carbon-coating has been considered as effective modification for copper/aluminum current collector. Although rate performance and lifetime of electrodes have been widely investigated, interfacial insight remains very superficial, hampering considerable improvement of electrode performance. Here we propose mechanistic models of double interfaces: one interface locates between Cu and active materials, and the other is referred to as solid electrolyte interphase (SEI) film coating on the current collector. Then vertical graphene nanowalls coated copper (VG) was prepared to reduce interfacial resistance of SEI film derived from an amorphous carbon coating layer. As a result, it exhibited a good rate performance with ~190 mAh/g at 3 C, in contrast with ~160 mAh/g for commercial carbon-coated copper (CC) and ~90 mAh/g for traditional bare copper (BC).

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1. Introduction

Tailoring ionic diffusion/electronic resistances of active materials is one of the most practical ways in order to obtain high-performance electrochemical electrode. Thus, more attention has been paid to optimize the interface between active materials and electrolyte [1–3]. For example, solid electrolyte interphase (SEI) films affect highly rate performance and lifetime of Li-ion batteries (LIBs), because it can control Li ion diffusion and protect electrode

from co-intercalation of impurities [4–7]. In addition, as another important interfacial phenomenon during continuous charging and discharging cycles, the interfaces of substrate/active materials can also affect electrochemical performance of a battery, where electron transport occurs [8,9].

Electrons firstly transport from current collector into anode in charging process. Then they are delivered to active materials via conductive medias. More importance has been thereof attached to electron transport between active and conductive materials towards affording more industrial recipes of slurry [10,11]. However, the current collector/electrode interfaces have been less focused, as a choice of current collector lies usually at metal-based materials, such as copper foil, aluminum foil, three dimensional nickel foam and etc. As an indispensable part of a battery, however, this interface has been crucial and responsible for direct electron transport. For instance, since the slurry of Li-ion anode is coated on Cu current collector, the interfaces include active materials/Cu, conductive

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materials/Cu and binder/Cu. During the first several cycles, local SEI films are formed. So the derived effective contact areas may be inferior to the area of Cu foil. Carbon-coated copper/aluminum has been commercially applied, such as Showa Denko K.K. (SDK), Showa Denko Packaging Co., Ltd. (SPA), and Linyi Gelon Lib Co., Ltd [12–14]. It has been found that in LIBs, carbon-coated current collector contributes to prolonging of lifetime, increase of rate performance, reduction of polarization and enhancement of battery stability. However, carbon coating for current collector lies mainly at painting conductive carbon slurry or in situ growing conductive carbon layer by using CVD. Therefore, coating layers are usually composed of nanocrystalline conductive graphite and amorphous carbon.

Graphene is promising for utilization in batteries due to high ion/electronic conductivity and stable chemical surface [15]. Hence using graphene as coating layer may yield higher electrochemical performance. Specifically, vertical graphene nanowalls anchored on a current collector has been treated as active materials of electric double layer capacitors and one functional protection layer [7,16]. In this work, stimulated by such excellence, we attempted to utilize vertical graphene anchored on copper to improve the performance of current collector. Using this layer coating for Li ion anode, higher rate performance was obtained and superior to those commercial carbon-coated coppers.

2. Experimental

A bare copper foil, vertical graphene nanowalls anchored on copper foil and carbon-coated copper foil (Hefei Kejing Materials Technology Co., LTD.) were used as the current collector of graphite anode, simply named BC, VG and CC, respectively. The VG sample was prepared by using PECVD (plasma enhanced chemical vapor deposition) equipped with 13.56 MHz radio-frequency (RF) and CCP (capacity couple plasma) modes. The parameters were 200 W (power), 890 °C (temperature), 30 min (time) and 1000 Pa (pressure), and the gas employed was CH₄:Ar = 20:80 (sccm). Then the vertical graphene nanowalls were grown on this BC substrate using RF-PECVD while the BC and CC samples were commercially available.

The graphite powder (Hefei Kejing Materials Technology Co., LTD.) was combined with conductive carbon and poly(vinylidene fluoride) (PVDF) as a binder with a mass ratio of 6:1:3 and milled into a slurry with N-methylpyrrolidone (NMP). The slurry was then blade cast onto different current collectors and dried at 60 °C for overnight in a vacuum oven.

The coin battery was assembled in a glove box filled with Ar gas (>99.99%) and the O₂ and H₂O contents of less than 0.1 ppm. The CR2032 coin battery, the Celgard 2325 membrane and the electrolyte (1 M LiPF₆ in EC/DMC/DEC = 1:1:1) were selected in this work, using MSK-110 for cell assembly and MSK-110D for cell separation (Hefei Kejing Materials Technology Co., LTD.). The BC, VG and CC samples were putted on one side as work electrode, meanwhile the Li foil on another side as counter electrode and reference electrode. The electrochemical impedance spectroscopy (EIS) of each battery was characterized by using PARSTAT 2273. The parameter of EIS was set as follows: high frequency is at 1 MHz and low frequency is at 0.1 Hz. The open circuit voltage of battery was applied. Every EIS spectrum was tested after shelving for more than 30 min. The battery cycling performance was characterized by using Neware battery testing system.

Raman spectrometer (Renishaw inVia) equipped with a 667 nm laser was used to characterize the surface carbon bonding in CC and VG. The electrode surface was investigated by using FE-SEM (Field emission scanning electron microscope, HITACHI, SU8010). To obtain the surface information in CC and VG, the surface chemical

element and bonding for SEI film characterization were analyzed by using X-ray photoelectron spectroscopy (Thermo Scientific Escalab 250Xi). The contact angle was tested by a video based contact angle measuring device (KRUS DSA40). The microstructural characterization was performed by using a FEI TECNAI G2-F20 transmission electron microscope, operated at 200 kV.

3. Results and discussion

3.1. Characterization of morphology, structure and contact angle

Fig. 1a–f shows morphology of BC, VG and CC by using SEM. VG was prepared via PECVD, in which active hydrocarbon-based gas was deposited onto copper for formation of vertical graphene in Fig. S1. As shown in Fig. 1a/d, the surface of copper is smooth in BC. Fig. 1b/e shows mazy-like walls in VG. The nanoscale accumulated fragments exist in CC (Fig. 1c/f). Fig. S2 suggests that the thickness of carbon layer is below 1 μm for both CC and VG. The contact angles of BC, VG and CC were illustrated in Fig. 1g/h/i, respectively. The highest contact angle is 128° for VG, in comparison with 63° and 109° for BC and CC. Obviously, an aqueous system is not suitable for coating slurry of electrode. As shown in Fig. S3, VG can offer a higher affinity of slurry, probably enhancing the interfacial binding force. The C1s fitting data of VG and CC in Fig. 1j/k, suggest that VG is dominated by sp²C–C with a ratio of sp²C/sp³C 1.18. In CC sp³C–C is the major form with the ratio 0.442 [17]. Such difference is attributed to the abundance of sp²C–C in graphene. Meanwhile, CC holds more oxygen groups (25%) on the carbon surface, different from 13.2% for VG. Judged from the different I_D/I_G in Fig. 1l/m, VG (1.8) holds smaller graphite crystallites and more disordered integration than CC (0.8). The G peak position of VG and CC is 1584 and 1576 cm⁻¹; it suggests that carbon in VG is favorable for nanocrystalline sp²C–C, and CC consists partially of amorphous carbon [18]. An additional peak occurred at 1620 cm⁻¹ in the Raman of VG, i.e., D' peak. The appearance of D' peak implies that sp² carbon material is abundant in small crystallites. Specifically, it indicates the peak of vertical graphene edges in this material, which was also commonly found in these vertical graphenes [19–22]. Fig. S4a shows that the thickness of graphene walls is ~5 nm. Fig. S4b/d suggests that CC consists mainly of amorphous carbon. Crystalline carbon is abundant in VG, in good agreement with the analysis of XPS and Raman. Meanwhile, the 2D peak of VG at ~2700 cm⁻¹ in Fig. S5 also indicates 3D stacking of hexagonal carbon networks [22].

3.2. Electrochemical lithium storage with graphite anode as current collectors

Fig. 2a–f shows the properties of electrochemical lithium storage for three samples with graphite anode as current collectors. The current collectors coated with carbon hold the best rate capability. The worst case is BC. Such differences among these three samples are not obvious at low charge–discharge rate. All their capacities are ~360 ± 4 mAh/g at 0.1 C. The increase of current density can lead to more obvious difference. For example, the discharge capacity of BC VG and CC are ~150, 220 and 250 mAh/g at 1 C, respectively. The capacity of BC is much lower than the other two. At the initial cycles, CC as current collectors has better rate capability than the graphene modified copper foils, which is not consistent with our proposed rate capability. Probably vertical graphene directly anchored on copper induces inhomogeneous interfaces, which consist of amorphous carbon and imperfect graphene. However, one can find that the VG capacity has been obviously enhanced after 15 cycles at 3 C. As shown in Fig. 2b/c, the capacities fading of

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