



Electrochemical performance of Si anode modified with carbonized gelatin binder



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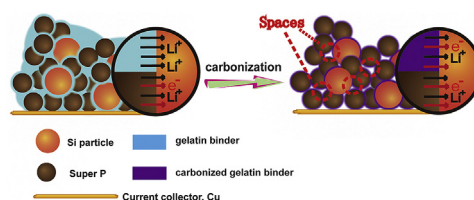
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HIGHLIGHTS

- Gelatin binder is alternatively adopted to modify Si anode.
- With a controlled heat-treatment, a carbonized gelatin binder is formed.
- The modified Si anode shows a good electrochemical performance.
- It is a simple and environmentally friendly approach for Si anode modification.

GRAPHICAL ABSTRACT



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ABSTRACT

Gelatin is alternatively adopted as the binder to modify Si anode coupling with its carbonization treatment. The binder can provide good bonding and uniform dispersion of the particles besides its environmental benignancy. Importantly, the carbonized binder containing nitrogen will be advantageous to the electrical conductivity of the electrode. In addition, some spaces are formed in the electrode due to the decomposition and shrinkage of the gelatin binder during heat-treatment, which may facilitate electrolyte penetration and accommodate volume change during cycling. All these merits make contribution to the good electrochemical performance of the modified Si electrode. It exhibits a reversible capacity of 990.3 mA h g⁻¹ after 70 cycles at a current density of 100 mA g⁻¹ and 904 mA h g⁻¹ after 100 cycles at 400 mA g⁻¹.

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1. Introduction

For the rechargeable lithium-ion batteries, graphite is the most widely used negative electrode material because of its abundant natural resource, low operating potential and excellent electrical conductivity [1]. But the demand for high capacity exceeds that it can provide (theoretical value of 372 mA h g⁻¹) [1]. Alternatively,

silicon has received significant attention as one of the most promising candidates to replace graphite [2–4] owing to its quite high theoretical capacity (about 3579 mA h g⁻¹ for Li₁₅Si₄) and moderate working potential (<0.5 V vs. Li/Li⁺) [5]. However, the volume change (~300%) of silicon during lithiation/delithiation will cause excess growth of solid electrolyte interphase (SEI), pulverization of silicon particles and exfoliation of the active material from the current collector [6,7]. As a result, the silicon anode usually shows serious capacity fading and low coulombic efficiency upon cycling [8,9].

Much efforts have been made to improve the electrochemical

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properties of Si anode. The three main methods are reducing the particle size of silicon to minimize the pulverization of Si particles [10–13], developing functional binders to enhance the adhesion and/or conductivity of Si anode [14–18], and preparing Si/carbon composites to combine the advantages of silicon and carbon [19–23]. As a commonly-used binder, Poly(vinylidene fluoride) (PVDF) is widely used in conventional lithium-ion batteries because of its acceptable adhesion and wide electrochemical window [24,25]. However, the binder can only attach to Si particles via weak van der Waals force for its non-functionalized linear chain structure. Thus the PVDF binder is hard to accommodate large volume changes of silicon [20]. So, in the view of modifying the anode using a functionalized binder [14,15], along with avoiding the toxic organic solvent N-methyl-2-pyrrolidone (NMP) for PVDF, we investigated the Si anode with carbonized gelatin binder. Gelatin is an amphoteric macromolecule, containing both acidic and basic amino groups ($-\text{COOH}$ and $-\text{NH}_2$), which makes it suitable for bonding different types of materials and widely used as a dispersing agent [26,27]. When gelatin is used as an electrode binder, it may not only promote the dispersion of active material and conductive additive, but also provide good connection among them and strong adhesion with current collector [26–29]. Gelatin is commercially available, cheap and environmentally friendly [27]. Moreover, it is water soluble, which can avoid the use of NMP. In the work, we employed gelatin as the binder of Si electrode, more importantly, we carbonized the gelatin binder to enhance the electrode conductivity. The carbonized gelatin contains nitrogen residues, which is also benefit for lithium insertion [30–32]. In addition, some spaces could be formed among particles due to the heat treatment of the electrode, allowing for silicon expansion during cycling and facilitating the penetration of the liquid electrolyte into active material [31]. The constituent and morphology of the Si anode modified with carbonized gelatin binder are examined and the electrochemical performance is also studied in detail.

2. Experimental

2.1. Preparation

Gelatin (from porcine skin-Vetec™ reagent grade, gel strength ~300 g Bloom) was dissolved in deionized water under magnetic stirring at 60 °C for 2 h. Si powder (alfa aesar, ~100 nm) and carbon black (Super P) were milled in a mortar. Then the gelatin solution was added in the mortar and the mixture was grinded. The slurry was cast onto a piece of Cu foil by using a doctor blade and dried under vacuum at 60 °C for 24 h. The obtained electrode in a diameter of 1.1 cm was named as Si-g. It consisted of 60 wt% Si, 30 wt% gelatin and 10 wt% Super P.

Then the Si-g electrode was put into a tubular furnace and pre-carbonized under argon atmosphere at 300 °C for 2 h, ramping at 2 °C min⁻¹ to different temperatures (400 °C, 500 °C and 600 °C), held for 1 h, and then cooled to room temperature. The treated electrodes were named as Si-g-4, Si-g-5 and Si-g-6, respectively. Gelatin was also carbonized at 500 °C under the same experimental conditions and the obtained sample was denoted as CG (carbonized gelatin).

The coin-type cell was assembled in an Ar-filled glovebox with a lithium sheet as counter electrode, a Celgard 2300 membrane as separator and 1 mol L⁻¹ LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 by volume ratio) as electrolyte. The loading amount of active material (silicon and carbonized gelatin) per electrode was estimated as 1 mg cm⁻². As a comparison, commercial PVDF dissolved in NMP was used as a binder for the Si electrode and it was named as Si-PV.

The electrode without conductive carbon (Super P) was also

prepared using the same process as above.

2.2. Measurements

The mass change of the carbonized electrode was characterized by thermogravimetric (TG, Seiko TG/DTA 6300) analysis, ramping at 10 °C min⁻¹. The samples were characterized by X-ray diffraction (XRD, Rigaku Ultima IV-185) with a Cu K α radiation source (scan rate: 8° min⁻¹, scan range: 10°–80°) and by Raman spectroscopy (Renishaw RM 2000) with 632.8 nm excitation from a He-Ne laser. The elemental states in the composites were analyzed with an X-ray photoelectron spectrometer (XPS), which was conducted on a PHI QUANTERA-II SXM system, using a monochromatized Mg K α radiation source. The morphology of the electrode was observed using a field-emission scanning electron microscope (FE-SEM QUANTA 6000). The details of the carbonized electrode were observed with a high-resolution transmission electron microscopy (HRTEM, JEM-2010 instrument).

The cycle performance of the cell was measured galvanostatically at the charge/discharge current density of 100 mA g⁻¹ and 400 mA g⁻¹ within the voltage range of 0.01 V–1.5 V by a cell tester (LAND CT2001A battery testing system) under a temperature of 30 °C. A CHI 608 1D electrochemical workstation was used for cyclic voltammetry (CV). The CV test of the electrode was recorded between 0.01 V and 3 V at a scan rate of 0.1 mV s⁻¹. The potentials mentioned in this study refer to the Li/Li⁺ redox couple.

3. Results and discussion

As shown in Fig. 1a, the five diffraction peaks of Si, Si-g, Si-g-4, Si-g-5 and Si-g-6 composites at the positions of 28.3°, 47.1°, 56.0°, 69.2° and 76.3° can be assigned to (111), (220), (311), (400) and (331) planes of Si crystallite (JCPDF 37-1402) [33], respectively, indicating that the crystal structure of the silicon in the composites remains intact after the carbonization process. The XRD pattern of CG is different from that of gelatin. For CG composite, two broad diffraction peaks at 24° and 43° are observed. They can be indexed as the (002) and (100) planes of amorphous carbon, showing a non-graphitized structure [34]. It is inferred that the gelatin in Si-g turns into amorphous carbon after carbonization process under 500 °C. But the two peaks cannot be detected in Si-g-4, Si-g-5 and Si-g-6 samples, this is mainly due to the low content of carbonized gelatin compared with the content of Si. It is the same reason why the peaks corresponding to gelatin cannot be detected in Si-g sample.

The Raman spectra of Si, Si-g, Si-g-4, Si-g-5 and Si-g-6 samples all exhibit a Si peak at ~518 cm⁻¹ and a broad and weak SiO₂ peak at ~943 cm⁻¹ [33], as shown in Fig. 1b. For Si-g-4, Si-g-5 and Si-g-6 composites, the characteristic carbon peaks of D-band (1343 cm⁻¹) and G-band (1581 cm⁻¹) confirm the existence of carbon [22,35]. However, the heat treatment temperature is far lower than the graphitization temperature of gelatin. Coupling with XRD pattern of CG, it is confirmed that the existence of non-graphitized carbon in Si-g-4, Si-g-5 and Si-g-6 composites. In the case of 400 °C, the curve fluctuates obviously in the Raman spectra of Si-g-4, it may reflect the existence of incomplete pyrolytic organics. When heated at 600 °C, the electrode easily peels off from the current collector, because the gelatin binder is pyrolyzed and carbonized severely leading to a weaker binding effect. While in the case of Si-g-5, the electrode keeps a good integrity. Fig. 1c shows the TG curve of gelatin, which helps to determine the heat treatment temperature. The residual carbon content of the carbonized electrode is estimated by the TG analysis for the composites (excluding Super P) and the curve for Si, as shown in Fig. 1d. The carbon content in Si-g-4, Si-g-5 and Si-g-6 electrodes (containing Super P)

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