



# Facile synthesis and stable cycling ability of hollow submicron silicon oxide–carbon composite anode material for Li-ion battery



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## ARTICLE INFO

### Article history:

Received 6 November 2014

Received in revised form 26 January 2015

Accepted 31 January 2015

Available online 7 February 2015

### Keywords:

Lithium-ion battery

Silicon oxide–carbon composite

Chelation

Hollow microstructure

Submicron

## ABSTRACT

Advanced SiO<sub>2</sub>–carbon composite anode active material for lithium-ion battery has been synthesized through a simple chelation of silicon cation with citrate in a glyme-based solvent. The resultant composite material demonstrates a homogeneous distribution of constituents over the submicron particles and a unique hollow spherical microstructure, which provides an enhanced electrical conductivity and better accommodation of volume change of silicon during electrochemical charge–discharge cycling, respectively. As a result, the composite electrode exhibits a high cycling stability delivering the capacity retention of 91% at the 100th cycle and discharge capacities of 662–602 mAh/g and coulombic efficiencies of 99.8%. This material synthesis is scalable and cost-effective in preparing various submicron or micron composite electrode materials.

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## 1. Introduction

Recent technological progress in lithium-ion batteries has achieved a remarkable performance improvement but critical challenges regarding energy density and cycle life remain for their applications to electric vehicles and energy storage systems. Increasing the energy density and cycle life requires the development of advanced electrode materials that offer a higher capacity, cycling stability and safety.

Carbon composites of silicon (Si) [1–4] and silicon oxides (e.g., SiO, SiO<sub>x</sub>) [5–8] have been actively researched in recent years because of about ten-fold large theoretical specific capacity (3579 mAh/g) of Si [9] compared to that (370 mAh/g) of graphite, which is currently used in commercial lithium-ion batteries. The structure, particle morphology and performance of Si-based anodes are well known to degrade rapidly during electrochemical charge (lithiation)–discharge (delithiation) cycling, due to a large volume change followed by particle cracking and electrochemical and mechanical disintegration [9]. Silicon oxide (SiO) is favored in industry with respect to cycling stability despite sacrificing the

capacity, as lithium oxide (Li<sub>2</sub>O) and lithium silicates formed during initial lithiation helps accommodate better the volume change [10,11]. Nanostructured SiO<sub>2</sub> materials were recently reported for their applications to battery anode materials [5,8]. Generally, silicon oxides however have a low electrical conductivity that deleteriously affects electron transport kinetics. Composites of nano-silicon oxides with carbon are efficient to overcome this conductivity issue [12–15]. Nano-sized silicon oxide can be advantageous for a shorter Li<sup>+</sup>-diffusion path and a better accommodation of strain caused by large volume change, with a reduced tendency of particle cracking [13,16]. Nonetheless, nano-material is limited in industrial applications due to high cost, uneasy handling, low packing density in the electrode and complicated synthesis processes. In fact, micron- or submicron-scale material is preferred for scalable industrial processing. For a composite synthesis, a homogeneous mixing of different materials is essential in attaining a homogeneous current distribution. Otherwise, the significant volume change during repeated lithiation and delithiation drives silicon oxide and carbon not to remain intact.

Here we report a designed synthetic strategy for submicron SiO<sub>2</sub>–carbon composite anode material for lithium-ion batteries; a chelation of Si<sup>4+</sup> by citrate ligand for the preparation of precursor and subsequent calcination for the conversion of citrate to carbon. Citric acid plays as both a chelating agent and a carbon source, providing a molecular-level distribution of silicon oxide with carbon.

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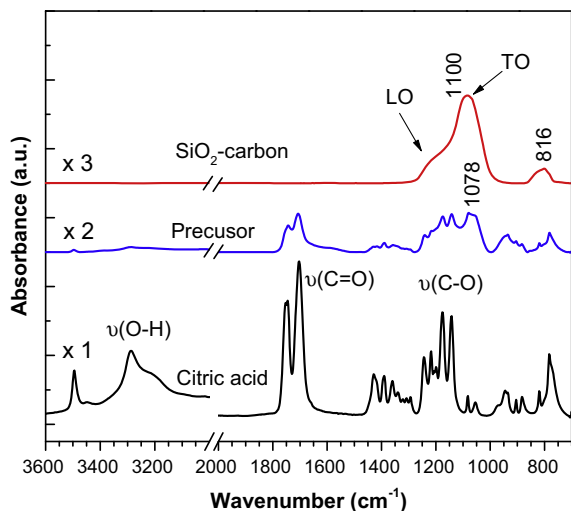


Fig. 1. FTIR spectra for citric acid, precursor and synthesized composite material.

## 2. Experimental

Silicon tetrachloride ( $\text{SiCl}_4$ , 99%, Sigma–Aldrich) and citric acid (Anhydrous, Junsei Chemical) were dissolved in 1,2-dimethoxyethane (Glyme, 99.5%, Sigma–Aldrich) and then stirred for 10 min at room temperature in the Ar filled-glove box. Although various molar ratio of  $\text{SiCl}_4$  to citric acid was tested, the optimized ratio was 1:0.08. To evaporate the residual glyme solvent, the mixed solution was dried at 50 °C for 24 h in the vacuum oven. White powder was obtained (denoted as precursor). Then, the precursor was calcined at the optimized temperature and time of 900 °C for 1 h in 4.0%  $\text{H}_2/\text{Ar}$  atmosphere. Finally, black powder of composite (denoted as composite) was obtained.

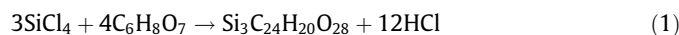
The formation of composite was monitored using attenuated total reflectance (ATR) FTIR spectroscopy (Thermo Nicolet 670) equipped with a mercury-cadmium telluride (MCT) detector. The mid-IR spectra were collected with 512 scans and the spectra resolution of  $4\text{ cm}^{-1}$ . Crystal structure of the composite was characterized using powder X-ray diffraction (XRD) analysis with X-ray diffractometer (Rigaku D/MAX-2200) with Ni-filtered  $\text{Cu K}\alpha$  radiation, measured from  $10^\circ$  to  $70^\circ$   $2\theta$  at the scan rate of  $2^\circ/\text{min}$  at 40 kV and 40 mA. Carbon structure of the composite was examined using Raman spectroscopy (Tokyo instrument, Nanofinder 30) with the 632 nm line of He–Ne laser at 3mW. The size of the laser beam at the sample was less than 200 nm in diameter. The content of carbon in the composite was determined using automatic elemental analyzer (Thermo Flash EA 1112). Particle morphology and micro-structure of the composite was examined using field-emission scanning electron microscopy (FESEM, Sirion) at 10 kV and high-resolution transmission electron microscopy (HRTEM, JEOL JEM-2100F) at 200 kV, respectively. The atomic ratio of silicon and oxygen in the composite material was measured by SEM-energy dispersive X-ray (EDX) spectral analysis.

Composite electrode was fabricated by casting a slurry, consisting of 70 wt% active material, 15 wt% carbon black, and 15 wt% polyacrylic acid (PAA, MW 450,000, Aldrich) binder in N-methyl-2-pyrrolidone (NMP, Aldrich) solvent onto a 10  $\mu\text{m}$  thick copper foil to the loading level of 1.2  $\text{mg}/\text{cm}^2$ . The coated electrode was dried in a vacuum oven at 110 °C for 24 h. 2016 coin half-cells, which consisted of composite electrode as a working electrode, a lithium foil as a counter electrode, the electrolyte of 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC): ethyl methyl carbonate (EMC) (3:7 volume ratio, Panax E-tech) containing 3 wt% trimethylphosphite (Aldrich, denoted as TMP) as an acid scavenging agent [17], and a separator (Celgard 2400), were assembled in Ar-filled glove box with the contents of water and oxygen less than 1 ppm. Galvanostatic charge (lithiation)–discharge (delithiation) cycling test was conducted in the voltage window of 0.01–2.0 V at a current density of 70 mA/g (corresponding to the rate of C/10) using a multichannel cycler (WBCS3000, Wonatech). For comparison, a reference electrode, consisting of 50 wt% commercial nano- $\text{SiO}_2$  (10–20 nm, Aldrich), 35 wt% carbon black, and 15 wt% PAA binder, was prepared and tested for its cycling ability in 1 M  $\text{LiPF}_6/\text{EC}:\text{EMC}$  with 3 wt% TMP additive.

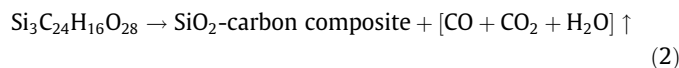
## 3. Results and discussion

Fig. 1 compares IR spectra of precursor and synthesized composite powders, and citric acid as a reference. The precursor shows prominent peaks at 3289, 1744–1708 and 1176–1142  $\text{cm}^{-1}$  attributed to  $\nu_{\text{sym}}(\text{O–H})$ ,  $\nu_{\text{sym}}(\text{C=O})$  and  $\nu_{\text{sym}}(\text{C–O})$ , respectively,

of citrate ligand [18]. A significant decrease in the peak absorbance of  $\nu_{\text{sym}}(\text{O–H})$  at 3289  $\text{cm}^{-1}$  indicates a lowered concentration of OH functionality of citric acid by the chelation of citrate ligand to  $\text{Si}^{4+}$  in the precursor. Also observed is a weak absorbance peak at 1079  $\text{cm}^{-1}$  due to Si–O bond. Chelation reaction between  $\text{Si}^{4+}$  and citric acid thus occurs as the following, producing the precursor precipitate. This reaction might favorably occur in terms of an increase in the entropy.



After calcination at 900 °C, the peaks of citrate disappear but a broad band ranged from 1300 to 900  $\text{cm}^{-1}$  appears, which is of the LO and TO phonon modes of  $\nu_{\text{asym}}(\text{Si–O–Si})$  from silicon oxide. The blue-shift of TO band from 1079  $\text{cm}^{-1}$  of the precursor to 1100  $\text{cm}^{-1}$  of the silicon oxide of composite is ascribed to an increase in the Si–O bond strength [19,20]. Calcination of the precursor brings out the decomposition of citrate to carbon and gases (e.g., CO,  $\text{CO}_2$ ) and formation of  $\text{SiO}_2$ –carbon composite. The composition of  $\text{SiO}_2$  would be determined in the TEM-EDX section.



Powder XRD pattern of the composite (Fig. 2a) shows a very broad feature, characteristic of amorphous  $\text{SiO}_2$ . Amorphous silicon oxide can provide the benefits of lower activation energy barrier

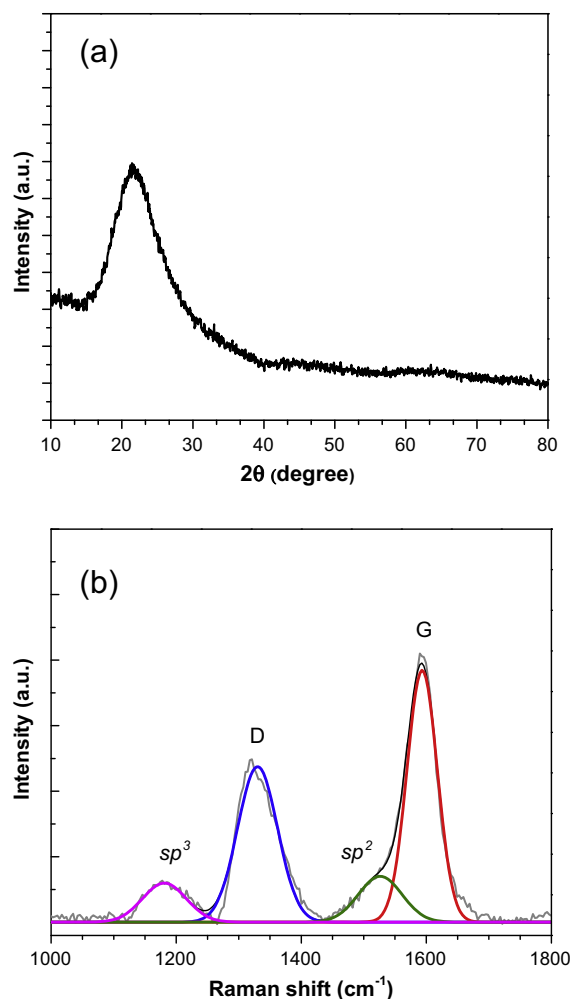


Fig. 2. Powder XRD pattern (a) and Raman spectrum (b) of synthesized composite material.

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