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Electrochemical study of Si/C composites with particulate and fibrous morphology as negative electrodes for lithium-ion batteries

Juan Luis Gómez-Cámer*, Heidi Thuv, Petr Novák

Paul Scherrer Institute, Electrochemistry Laboratory, CH-5232, Villigen PSI, Switzerland

HIGHLIGHTS

- Si/C composites with different Si content and morphologies have been prepared.
- Lower Si content leads to lower initial specific charge but better cycling stability.
- Morphology of the Si/C composites affects their cycling stability for all the studied compositions.

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ABSTRACT

Silicon–carbon composites with two different morphologies, particulate and fibrous, prepared by NaOH catalyzed polymerization of resorcinol and formaldehyde in presence of Si nanoparticles and co-surfactants, are examined as negative electrodes in lithium-ion batteries. The composites prepared with ca. 33, 50, and 66% Si deliver around 1000, 1500, and 2000 mAh g^{-1}, respectively. Higher silicon content results in higher initial specific charge, but also faster fading during cycling. The composites with the lowest silicon content exhibit the most stable specific charges. The differences in electrochemical behavior for the optimized compositions are investigated by means of microscopy and electrochemical impedance analysis and are discussed in terms of morphology of the different composites.

1. Introduction

Lithium ion batteries (LIB) are common in portable consumer electronics such as smartphones, computers, and power tools. However, there is a growing interest for LIBs for transportation applications, such as electric vehicles [1]. These applications require higher specific energy, energy density, and long cycle life, while the cost, safety, and environmental issues also must be considered. Silicon is a promising anode material for new LIBs as it has the highest theoretical specific charge of all lithium anode materials, it is abundant, environmentally friendly, and non-toxic [2]. At a fully lithiated state at room temperature, Si has a theoretical specific charge of 3579 mAh g^{-1}, which is almost ten times higher than that of graphite (372 mAh g^{-1}). In contrast to graphite, Si does not have layered structure, and the Li is instead alloyed into the Si. This results in dramatic structural changes in the electrode during lithiation, and the volume can expand up to ~400% [3]. The extreme volume expansion/contraction upon lithiation/delithiation causes mechanical stress followed by cracking of the material, which in turn will give rise to loss of electrical contact or even isolating some parts of the material from the current collector [3]. Si also shows a large irreversible charge consumption in the first cycle, which is mainly caused by reduction of electrolyte resulting in the formation of solid electrolyte interphase (SEI) on the surface of the active particles and/or from irreversible Li insertion into Si [4]. When subsequent particle cracking exposes new Si surfaces, more SEI will be formed, and lead to further irreversible charge consumption [3].

To circumvent the problems with repeated volume changes and subsequent mechanical degradation of the electrode, several strategies have been employed. These include using Si nano-powder, creating porous structures with buffer space, dispersing Si in a

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* Corresponding author. Present address: CIC Energigune, C/Albert Einstein 48, Parque Tecnológico de Álava, Miñano, Spain.

E-mail address: jlgomez@cicenergigune.com (J.L. Gómez-Cámer).

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matrix of active or inactive material that can withstand the mechanical stresses, and making composites or coating with carbon [5]. Due to high surface area, Si nano-particles tend to aggregate during repetitive cycling, giving an increase in the Si particle size, and thereby reducing the lithiation/delithiation kinetics [3]. This may also be hindered by the carbon network throughout the material. Moreover, carbon coated Si or Si/C composites replace the Si-electrolyte interphase by a carbon-electrolyte interphase, which gives the advantage of forming a more stable SEI film, apart from increasing the materials' electronic conductivity and helping to buffer the volume changes.

Si/C composites can be prepared following many different procedures [3], however carbon gels have been considered promising materials because Si can be easily dispersed in the solution, gels can be easily shaped, and their structure and porosity can be controlled so they successfully encapsulate Si particles. Resorcinol-formaldehyde or phenol-formaldehyde gels are widely used to prepare Si/C composite particles with a wide range of Si content [6–12]. These materials present compact and porous structures, reaching high surface areas – varying from 200 to 500 m^2 g^{-1} – due to the microporosity. On the other hand one can find in the literature that the most common approach to prepare Si/C-fiber composites is the use of a dissolved polymer mixed in solution with Si particles. Typically, Si/C-fiber composites are prepared by electrospraying PAN (polyacrylonitrile) [13–17] or other polymers [18–20] with dispersed Si nanoparticles, to obtain fibers which are then carbonized. These materials are low density, open structures with Si content also in a wide range between 5 and 75 wt%.

Herein, we report the synthesis of Si/C composites with spherical and fibrous morphology by the polymerization of resorcinol and formaldehyde in the presence of a surfactant. Several syntheses with different amounts of surfactant and silicon were studied, both with and without the directing agent to form the two different morphologies. The differences in electrochemical behavior are discussed in terms of synthesis conditions, Si content, and morphology.

2. Experimental

All reagents, resorcinol (98%, Acros Organics), formaldehyde (37% in H_2O, 10–12 % methanol, Sigma–Aldrich), hexadecyltrimethylammonium bromide (CTAB, > 98%, Sigma–Aldrich), 1,2,4-trichlorobenzene (TCB, 98%, Merck), sodium hydroxide (NaOH, 96%, Merck), hydrochloric acid (HCl, 32%, VWR), ethanol (>99.8%, VWR), and silicon nanopowder (n-Si, 30–50 nm, 98%, Nanostructured & Amorphous Materials, Inc.) were used as received.

A mixture of H_2O, NaOH, TCB, CTAB, resorcinol, and Si was heated to 50 °C under stirring to form a micellar solution. Formaldehyde was then added, and the mixture was kept at 50 °C and under continuous stirring for 2 h, and subsequently heated to 90 °C for 24 h in order to polymerize. The resulting powder was filtered and washed in water and ethanol and dried at 60 °C. After drying, the powder was washed in HCl/ethanol solution (1 mL HCl and 40 mL ethanol per 1 g of powder) for 4 h under stirring. The powder was then filtered and washed in ethanol and dried at 60 °C. The dried precursor material was then calcined by heating to 1000 °C, with a heating rate of 10 °C min^{-1} and keeping at this temperature for 4h under argon atmosphere.

The morphology of the synthesized powders and the n-Si powder were studied by scanning electron microscopy using a Carl Zeiss UltraTM 55 scanning electron microscope operated at 5 kV in the in-lens secondary electron detection mode. Thermogravimetric analysis (Perkin Elmer DSC 8000) was used to obtain the carbon content of the powders. The electrodes were prepared by mixing 80% of active material, 10% conductive carbon black (Super C65, Imerys), and 10% binder (50% sodium alginate (FMC BioPolymer) and 50% polyacrylic acid (PAA, 25% in water, average M.W. 240.000, Alfa Aesar) dissolved in water. The slurry was then coated onto a copper foil current collector and dried under vacuum at 80 °C, and subsequently dried at 120 °C for a minimum of 12 h. Lithium foil served as both counter and reference electrode, and glass fiber separator soaked in electrolyte solution 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed in a 1:1 w/w ratio (Novolyte) were used. The electrochemical measurements were carried out with a standard battery cycler (Astrol Electronics AG, Switzerland). The electrodes were cycled between 5 mV and 1.5 V (vs. Li) with a constant specific current of 100 mA per gram of active material. At the minimum and maximum potentials, a potentiostatic step was included until the specific current decreased to 50 mA g^{-1}. Electrochemical impedance measurements (EIS) were carried out with a VMP3 potentiostat (Biologic) in the frequency range 0.1 MHz–10 mHz and a potential perturbation of 10 mV. A three-electrode cell was used for these measurements with Li foil as counter and reference electrodes an glass fiber soaked in electrolyte solution 1 M $LiPF_6$ in ethylene carbonate (EC) and diethyl carbonate (DEC) mixed in a 1:1 w/w ratio (Novolyte) as separator. The EIS data were analyzed and fitted with the Zview software (Version 2.2, Schribner Associates, Inc. USA).

3. Results and discussion

A procedure for synthesizing carbon nanostructures with either spherical or fibrous morphology was first reported by Fujikawa [21,22], and adapted by Gómez-Cámer et al. [18] to produce fibrous silicon carbon composites. The molar ratio of resorcinol, formaldehyde, NaOH, CTAB, TCB, and H_2O was 2:4:0.2:x:y:360, where x was either 1 or 2, and y either 0 or 2. CTAB and TCB were used as cosurfactants for the NaOH catalyzed polymerization of resorcinol and formaldehyde. Kijima et al. discussed the modification of the vesicular assemblies by altering the CTAB/1,3,5-trimethylbenzene/tert-butanol templating system [22], but the CTAB template synthesis in absence of trimethylbenzene [21] was also found to lead to nanospherical vesicular assemblies. In our synthesis, multi-spherical or multi-cylindrical vesicles are formed in the presence of Si nanoparticles, CTAB, and, in the latter case, TCB. The TCB amount used in the syntheses were doubled compared to the modified syntheses by Gómez-Cámer et al. [18]. The amount of n-Si was 2.0, 1.0, or 0.5 g added to a mixture with 45 mL H_2O. Two samples without Si were also synthesized as carbon reference material with the two different morphologies, nanospheres and nanowires. In the discussion, we refer to the composites regarding the morphology of the reference carbonaceous material. Thus, the composites prepared without TCB ($y = 0$) are referred to as particulate morphology, as the synthesis should result in spherical vesicular assemblies. On the other hand, the composites prepared with TCB ($y = 2$) are referred to as fibrous morphology. Nevertheless, both kinds of composites show macroscopically similar morphology as micrometer sized agglomerates of primary particles or fibers, however with different structure and internal porosity.

The results from thermogravimetric analysis are summarized in Table 1. The TGA showed that the materials with three different initial Si content had final carbon compositions of 1/3, 1/2, and 2/3, respectively. As the temperature could not be increased to more than approximately 1050 °C, it could not be determined how much of the remaining material was Si or SiO_x. However, it can be expected that approximately 30% of the remaining material is SiO_x, oxidized during the carbonization of the polymer due to oxygen traces or direct interaction between Si and gases released by the polymer during calcination [18].

The carbon reference sample without TCB (composite 4)