



The relationship between the electrochemical performance and the composition of Si–O–C materials prepared from a phenyl-substituted polysiloxane utilizing various processing methods

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ABSTRACT

Si–O–C composite materials with various compositions are prepared from a phenyl-substituted polysiloxane. The pyrolyzing temperature and atmosphere is varied to determine the effect that these parameters have on the final composition. The compositional effect of using a divinylbenzene (DVB) as an alternative carbon source is also investigated. Materials prepared at either 800 or 1000 °C under a hydrogen atmosphere have a significantly larger reversible capacity than those prepared at the same temperature under an argon atmosphere. Utilizing DVB as the carbon source further increases the reversible capacity of the Si–O–C material. The specific capacity increases with an increase of the C/Si ratio and with a decrease of O/Si ratio of the source materials when the O/Si ratio is in the range of 1.0–2.0. A model based on the nanostructure of the Si–O–C material is employed to express the relationship between the specific reversible capacity and the structure of the Si–O–C phase. According to the utilized model, the reversible capacity of lithium in the Si–O–C phase is much greater than that in carbon, and the capacity increases with the increase of the p value in $\text{SiO}_{2(1-p)}\text{C}_p$. The “free carbon” in the synthesized materials was found to store twice as many lithium ions as the same amount of graphite.

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1. Introduction

Rechargeable lithium-ion batteries are a promising power source for consumer electronic devices. The theoretical capacity of graphite, a conventional anode material, has almost been reached. Therefore, significant efforts to identify new anode materials to replace graphite have been made. Among several identified alternatives, silicon oxycarbide (Si–O–C) composites are potentially viable anode materials [1–14]. In the literature, Si–O–C materials have been shown to have higher capacities than graphite.

An Si–O–C composite material usually includes three elements: silicon, oxygen, and carbon. The composite material also consists of two phases: free carbon and an Si–O–C glass phase. In the free carbon phase, the carbon mostly exists in the form of sp^2 graphene. In the Si–O–C glass phase, the carbon, silicon, and oxygen exist as $\text{SiO}_{2(1-p)}\text{C}_p$ (where $0 \leq p \leq 1$). The sp^2 graphene carbon forms a continuous network as “free carbon” and regions of Si–O–C glass are embedded in the carbon matrix [15]. The “free carbon” is believed to be electrochemically active in the presence of lithium. However, the effect that the composition of Si–O–C materials, particularly

the composition of the Si–O–C phase, has on the electrochemical performance is still unknown.

The present paper focuses on the relationship between the electrochemical performance and the composition of Si–O–C materials. A phenyl-substituted polysiloxane was employed as the silicon source [16,17]. The polysiloxane was transformed into Si–O–C composite materials with various elemental compositions by varying the pyrolyzing temperature and the pyrolyzing gas as well as by the addition of divinylbenzene (DVB) as an additional carbon source. The effect of the elemental composition on the electrochemical performance was tested. A model based on the nanostructures of the Si–O–C material was also established to illustrate the relationship between the reversible capacity and the structure of the Si–O–C glass phase.

2. Experimental

2.1. Synthesis of anode powder

Polysiloxane $\text{Si}(\text{CH}_3)_3(\text{Si}(\text{OH})(\text{CH}_3)\text{O})_i(\text{Si}(\text{C}_6\text{H}_5)(\text{CH}_3)\text{O})_j(\text{Si}(\text{CH}_3)(\text{H})\text{O})_k(\text{Si}(\text{CH}_3)\text{Si}(\text{C}_3\text{H}_7)_2\text{O})_l\text{Si}(\text{CH}_3)_3$ (where, $i, j, k, l > 1$) was employed as a silicon source. This polysiloxane contains multiple phenyl groups, which means it can also be used as a carbon source. If an extra carbon source was utilized, the polysiloxane and carbon source were first dissolved in toluene at 100 °C and

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then gently mixed with a rotary evaporator for 60 min. After the evaporation of toluene, the polysiloxane and carbon source were crosslinked in air. The crosslinked product was then used as a precursor. If no extra carbon was added, the polysiloxane was directly used as a precursor after it was crosslinked in air. The general pyrolyzing method utilized was as follows. The precursor was placed in an alumina boat and pyrolyzed in an alumina tube furnace under a controlled atmosphere. The flush rate was maintained at 200 mL min^{-1} , which is sufficient to prevent the decomposition and redeposition of vapors released during polymer decomposition. The temperature was raised at a rate of $5^\circ \text{C min}^{-1}$ to the maximum temperature, and the maximum temperature was maintained for 60 min.

Si–O–C materials with various compositions were produced by changing the pyrolyzing atmosphere, altering the maximum temperature, or by the addition of an extra carbon source in the following ways:

- (1) The polysiloxane was used as the silicon and carbon source. The Si–O–C materials were prepared under an argon atmosphere at a temperature of either 800 or 1000 °C. The resulting samples were named SA800 and SA1000.
- (2) The polysiloxane was used as the silicon and carbon source. The Si–O–C materials were prepared under a hydrogen atmosphere at a temperature of either 800 or 1000 °C. The resulting samples were named SH800 and SH1000.
- (3) The polysiloxane was used as the silicon source. DVB was used as the carbon source. The copolymer of the two reagents (1:1 in weight) was transformed to Si–O–C materials by pyrolyzing under a hydrogen atmosphere at a temperature of either 800 or 1000 °C. The resulting samples were named DSH800 and DSH1000.

In order to significantly decrease the carbon content, some samples were heat treated in air for a period of time. During exposure to air, the temperature was maintained at 600 °C in order to prevent significant destruction to the structure of the material. Two methods to decrease the carbon content were used:

- (1) The sample SH800 was exposed to air for either 1 or 2.5 h at 600 °C. The resulting products were named SHA1h and SHA2.5h.
- (2) The sample DSH800 was heat treated in a similar way to SH800 as detailed in method (1). The resulting products were named DSHA1h and DSHA2.5h.

The silicon content of the pyrolysis product was determined by a fusion technique that consisted of converting the solid to a soluble form and then analyzing the solute for total silicon with a Varian 715-ES. Carbon content was measured in a FlashEA1112 elemental analyzer (Thermo Electron SPA, Italy). The amount of oxygen present in the sample was calculated by subtracting the measured values of carbon and silicon from 100% using the assumption that the samples have less than 1 wt% of H in the material.

Powder X-ray diffraction (XRD) patterns were measured on a RINT 2200 (Rigaku, Japan) in the range of $2\theta = 10\text{--}90^\circ$. Cu K α radiation (1.5418 Å) was used as an X-ray source.

2.2. Half-cell preparation

Si–O–C composite anodes approximately 25 μm thick and 4 mg in weight were prepared by coating copper foil substrates with a mixture of the pyrolyzed powders (80% by weight), acetylene black (10% by weight), and polyvinylidene fluoride (PVDF) dissolved in *N*-methyl pyrrolidinone. After coating, the electrodes were dried overnight at 110 °C in air and then pressed between flat plates using

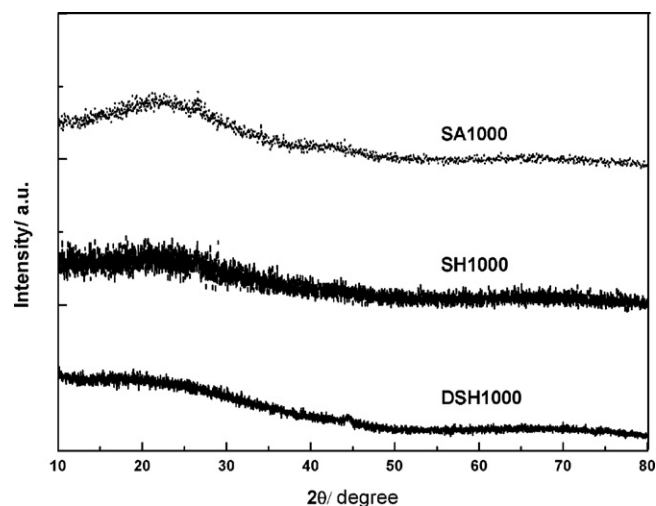


Fig. 1. XRD patterns of the model Si–O–C composite materials.

approximately 15000 kPa of pressure. Coin-type test cells (four for each sample) were constructed from the electrodes. The electrolyte used was a 1 M LiPF₆ solution in a 50/50 (% v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). A microporous film (Celgard 2400) wetted with the electrolyte was sandwiched between the active electrode and a Li metal foil anode. Cells were assembled in a glove box under an argon atmosphere. Electrochemical testing of the cells was performed using constant current cyclers, the currents of which are stable to $\pm 1\%$. The cells were placed in thermostats at 30 °C. Cells were discharged first with a constant current of 18.6 mA g^{-1} . When the cell discharge potential reached 0.001 V, the current direction was reversed and the cells were in charge mode. Upon current reversal, Li was removed from the active anode. Cell charging was considered complete when the cell potential reached 3.0 V. The reversible capacity is defined as the average of the first charge and second discharge capacity.

3. Results and discussion

3.1. XRD analysis

Fig. 1 presents the XRD patterns of the samples SA1000, SH1000, and DSH1000. A broad diffraction peak at $2\theta = 21\text{--}23^\circ$ is associated with the Si–O–C glass phase (amorphous SiO₂) and the parallel stacking of the graphene sheets. The patterns show that the materials prepared in different conditions have similar amorphous structures.

3.2. Electrochemical performance

The elemental content and reversible capacity of all the Si–O–C materials prepared using different conditions are listed in Table 1. The data for the reversible capacity per gram (in units of mAh g^{-1}) are normalized with respect to the atoms per gram of the total composition (in units of mAh g atom^{-1}) to relate the capacity with the molecular network of the materials. The general normalizing method used is as follows: assuming the average composition of the material is Si_xC_yO_z, the specific capacity per gram-atom is equal to the capacity per gram multiplied by the molecular weight ($28x + 12y + 16z$) and divided by the number of atoms in the unit cell ($x + y + z$). The details of this approach have been previously published in [8]. The typical discharge/charge profiles of the samples prepared at 1000 °C are shown in Fig. 2. The sample SA1000 shows approximately 400 mAh g^{-1} of irreversible capacity and 35% for the first coulombic efficiency. The samples SH1000 and DSH1000

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