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Highly Stable Silicon–Carbon–Nitrogen Composite Anodes from Silsesquiazane for Rechargeable Lithium-Ion Battery

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Herein, we developed novel silicon–carbon–nitrogen (SiCN) composites synthesized by pyrolyzing silsesquiazane polymer as an anode material for rechargeable lithium-ion batteries. Among variable pyrolysis temperatures of 700 °C, 1000 °C and 1300 °C, the SiCN composites prepared at 1000 °C showed the highest capacity with outstanding battery cycle life by cyclic voltammetry and electrochemical impedance spectroscopy. Such good battery and electrochemical performances should be attributed to a proper ratio of carbon and nitrogen or oxygen in the SiCN composites. Furthermore, our SiCN electrode possessed better lithium ion conductivity than pure silicon nanoparticles. This work demonstrates that polymer-derived composites are among the promising strategies to achieve highly stable silicon anodes for rechargeable batteries.

1. Introduction

Extensive demands for developing the lithium (Li) ion battery with high energy density have pursued alternative anode materials because of the limited capacity of graphite. Among promising candidates to replace graphite, silicon (Si) is one of the best materials owing to its high theoretical capacity of 3579 mA h g^{-1} at room temperature[1,2]. However, dramatic capacity fades are observed during repeated charging–discharging cycles as a result of large volume change and pulverization in Si by alloying and de-alloying with Li ions[3–8]. In order to overcome the issue in Si electrodes, many researchers have suggested employing additional carbon structures that can prohibit the volume expansion or pulverization. The carbon layers also increase the electrical conductivity of silicon electrodes remarkably[9–13]. However, employing additional carbonaceous materials is not suitable to achieve good battery performance due to their low Li-ion conductivity.

One possible solution to improve Li-ion conductivity would be utilizing nitrogen (N) by making silicon–carbon–nitrogen (SiCN) composite, as reported by Yamane et al.[14]. Riedel and coworkers also reported good electrochemical performance by using carbon-rich SiCN composite made from various Si-containing polymers such as polyphenylvinylsilazane or polysiloxanes[15–20]. The SiCN materials derived from polysilazane precursors possess amorphous 3D network structures, which are sure to give dimensional stability during lithiation/delithiation process[21]. The solid SiCN network makes its structure more stable during charge–discharge to attain good cycle stability. Nevertheless, the exact mechanism of Li-ion loading in the materials has not been clearly elucidated due to the difficulty in characterizing amorphous inorganic materials. There have been reports claiming that the lithiation sites would be the mixed bond configuration of the ceramics[22], the free nanocarbon clusters embedded in the network[20,23], and the free dangling bonds of Si[24]. In addition, the so-called ‘conversion electrode’ interpretation has also been presented, claiming that alloy electrode would be formed from converted precursors. For example, Suzuki and coworkers used silicon nitride thin film made by a pulsed laser deposition[25]. On the first charging for the SiN electrode, metallic Si was generated with forming Li_2N and acted as a reversible Li-ion loading sites on the following charging–discharging processes. As a result, characterizations and performance of the prepared electrode varied according to slight variations of initial materials and processing conditions. For example, Si_3N_4 has been usually regarded inactive or very low in the activity to lithium[26,27]. However, the silicon nitride thin film of Suzuki and coworkers showed clear charge–discharge behavior[25]. There has also been discrepancy in the effect of nitrogen to oxygen (N/O) ratio. In the report of Ahn and Raj[22], high capacities of 600 mA h g^{-1} can only be found for materials with an N/O ratio below 1. However, Su et al. reported that ~456 mA h g^{-1} of discharge capacity was achieved from SiCN with N/O ratio of 5.6[28]. These

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discrepancies indicate that additional studies to understand the structure–property relationship of SiCN are required to design effective polymer-derived SiCN.

In this work, we prepared novel SiCN composites by pyrolyzing silsesquiazane (SSQZ) polymer. The SSQZ would be a good precursor to form SiCN composites owing to its phenyl substituents on the Si center, which affects the physical state of SSQZ to be solid by high glass transition temperature of higher than 200 °C. Because the structure of the final inorganic material could also be affected by modifying pyrolysis conditions, we further varied the temperature from 700 to 1300 °C.

2. Experimental

2.1. Materials

Phenyl-substituted SSQZ polymer was synthesized by following the literature[29]. The prepared polymer was pyrolyzed under argon at 700 °C (SiCN–700), 1000 °C (SiCN–1000), and 1300 °C (SiCN–1300) in a quartz crucible. The heating and cooling rates were set to 100 °C h^{-1} and the dwelling time at the maximum temperature was set to 1 h. The total carbon, hydrogen, oxygen, and nitrogen contents of the samples were determined by an elemental analysis. The silicon fraction was calculated as the difference between 100% and the analyzed values of the other elements. Poly(methylphenyl silane) (PMPS) was also synthesized by the Wurtz-type reductive coupling reaction using dichloromethylphenyl silane and sodium to make SiC composite without nitrogen.

2.2. Characterization

The microstructural properties of the SiCN were characterized by scanning electron microscopy (SEM, LEO 1550) and Raman spectroscopy (Renishaw) with an excitation wavelength of 785 nm. X-ray powder diffraction was obtained in flat-sample transmission geometry on an STOE STAD1 P equipped with monochromatic Mo *K*α radiation. Fourier transform infrared (FT-IR) spectra were recorded on NaCl pellet over the range of 600–4000 cm^{-1} using a Jasco FT-IR 6300 spectrometer with a minimum of 64 co-added scans at a resolution of 4 cm^{-1}. Nitrogen was used to purge the detector and sample compartments prior to and during scans to avoid interference from gaseous water bands. The total carbon, hydrogen, oxygen, and nitrogen contents of the samples were determined by an elemental analysis (Thermo Scientific Flash 2000). Silicon fraction was calculated as the difference between 100% and the analyzed values of the other elements.

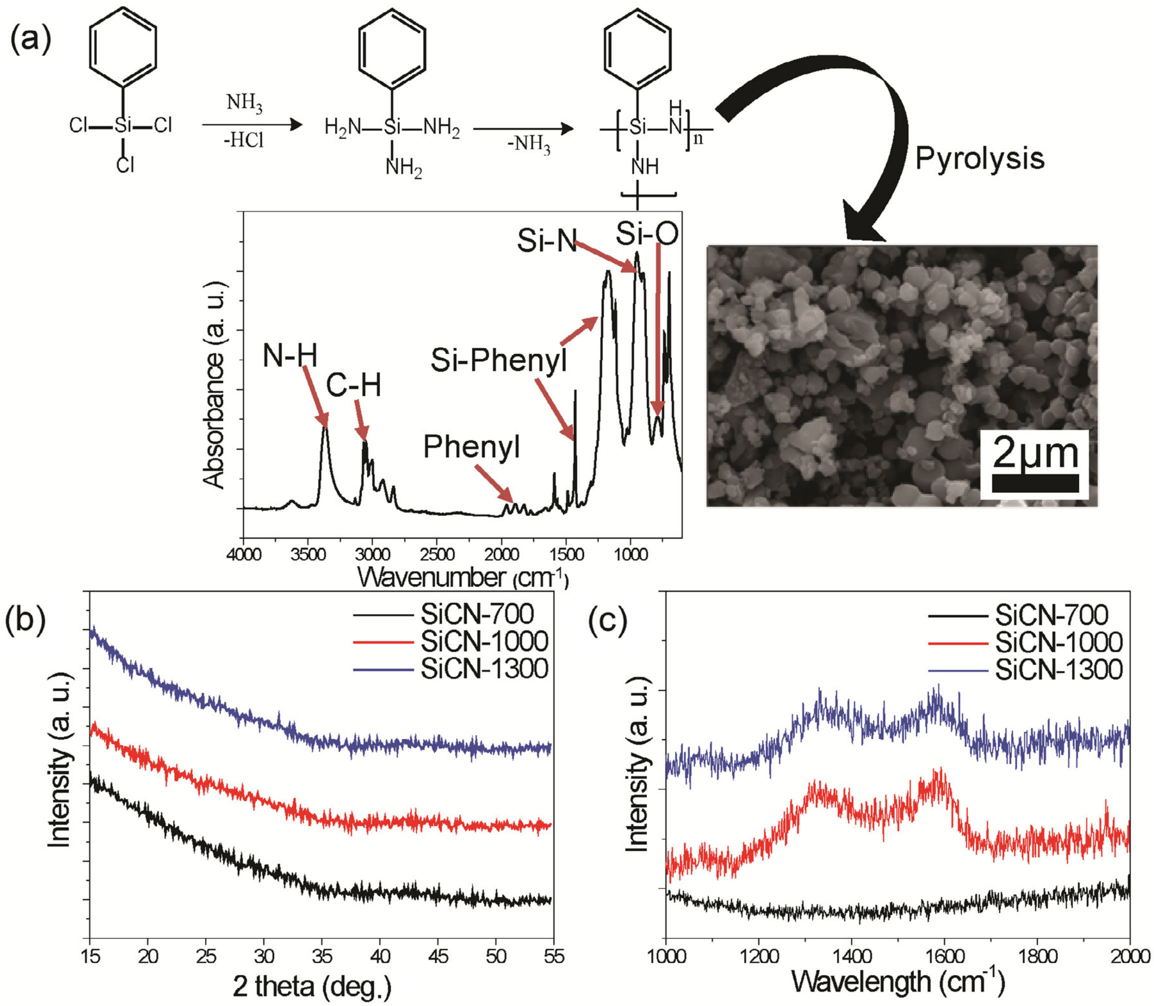

Fig. 1. (a) Overall reaction steps to synthesize SSQZ polymer, its FT-IR spectrum, and SEM image of SiCN composite made from pyrolysis of SSQZ; (b) X-ray diffraction patterns; and (c) Raman spectra of SiCN composites pyrolyzed at 700, 1000 and 1300 °C.