# Preparation of Microporous Si–O–C Composite Material and Its Lithium Storage Capability

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A microporous Si–O–C composite material was prepared by pyrolysis of a blend of polysilane, $(Ph_2Si)_{0.85}(PhSi)_{0.15}$ (**1**) and polystyrene (1:1 in weight) at 1000 °C. This material electrochemically performed well, offering a capacity of more than 600 mA h g$^{-1}$ and a good cycle life. Our $^7$Li NMR analysis confirmed the possibility of several electrochemical active sites for lithium storage in this new composite material.

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Much effort has been devoted in high-temperature chemistry for a wide variety of prechar polymers to produce silicon oxycarbide (Si–O–C) glasses (so-called black glasses), minutely dealing with pyrolysis of sol/gel precursors, polysiloxanes, and polysilanes throughout polymer-to-ceramic conversion processes.[1] The color of their black is attributed to a free aromatic carbon phase. Its content depends largely on the architecture of the prechar polymers.[2]

A potential application of the Si–O–C glasses is of use as anode materials for rechargeable lithium ion batteries. Many reports have demonstrated that the Si–O–C glasses are capable of delivering high capacities of more than 372 mA h g$^{-1}$ (the theoretical capacity of graphite commercially used).[3] However, further efforts have been needed to attain a long charge/discharge cycle life for the Si–O–C glasses from a practical aspect. To overcome this disadvantage, in the present study we prepared a microporous Si–O–C composite material consisting of (1) Si–O–C glasses, (2) free aromatic carbon, and (3) micropores, by pyrolyzing a blend of polysilane, $(Ph_2Si)_{0.85}(PhSi)_{0.15}$ (**1**)[4] and polystyrene with a weight ratio of 1:1. It was believed that the incorporation of micropores contributed to both increasing capacity (active site for lithium storage) and prolonging cycle life (alleviative site for volume change). To prove the advantage of this material, the lithium storage capability was electrochemically evaluated. Furthermore, $^7$Li NMR analysis was also conducted to gain insight into its lithium storage mechanism.

The prechar polymer, polystyrene, was purchased from Wako Pure Chemical Industries. Polysilane **1** and polystyrene were dissolved in toluene at 100 °C and then gently mixed with a rotary evaporator for 60 min. After evaporation of toluene, the polymer blend was further heated at 100 °C under vacuum. The resulting powdery sample (ca. 10 g) was placed in an alumina boat and then degreased to remove any possible decomposed by-products, such as benzene and silane compounds, in a muffle furnace at 600 °C under a nitrogen atmosphere. After degreasing, the isolated char intermediate was milled with a zirconia ball in air, and then it was sieved (below 300 mesh). Finally, the char intermediate (ca. 1 g) was placed in an alumina boat and then pyrolyzed in an alumina tube furnace at 1000 °C under an argon atmosphere. The chemical composition of the pyrolysis product was determined by elemental analysis ($SiO_{0.51}C_{7.78}H_{0.49}$).[5] The pyrolysis product was further characterized using scanning electron microscopy (SEM, JSM-6490A, JEOL), X-ray diffraction with Cu K$\alpha$ radiation (XRD, RINT-2000, Rigaku), and $N_2$ sorption isotherm (BELSORP-mini II, BEL JAPAN) measurements.[5]

The lithium storage capability of the Si–O–C composite material was evaluated using a 2016 coin-type cell fabricated with a composite electrode (14-mm diameter), a lithium foil (15-mm diameter) as a counter electrode, and 1.0 mol dm$^{-3}$ $LiPF_6$/ethylene carbonate (EC) and diethylcarbonate (DEC) (1:1 in volume) as electrolyte. Prior to the cell fabrication, the composite electrode was prepared by mixing the active material, Ketjen black, and poly(vinylidene fluoride) with a weight ratio of 85:7.5:7.5 (galvanostatic charge/discharge testing) or 85:5:10 ($^7$Li NMR analysis) in *N*-methylpyrrolidone. The galvanostatic charge/discharge testing was performed at 30 °C with an HJ1010mSM8A (Hokuto Denko) in the range of 0–3 V at 37.2 mA g$^{-1}$. The Si–O–C composite material was washed with dimethylcarbonate (DMC) after short circuiting overnight. After removal of DMC, a $^7$Li NMR spectrum was recorded on a CMX-300 spectrometer (Chemagnetics) at room temperature. A 1.0 mol dm$^{-3}$ aqueous LiCl solution was used as an external standard ($\delta$ 0).

Figure 1 presents the SEM images of the Si–O–C composite material. The SEM images confirm that the particles are irregular in shape and that the small particles adhere to the larger ones. Surface micropores, unfortunately, are so small that they cannot be verified in the SEM images.

The XRD pattern of the Si–O–C composite material is shown in Figure 2. No sharp peak was observed, but two broad peaks were visible at $2\theta =$ ca. 21 and 44°. Considering the XRD pattern, this material has an amorphous nature. To characterize the surface porous character of the Si–O–C composite material, the $N_2$ sorption isotherm was measured at 77 K (Figure 2). A rapid growth of $N_2$ molecules adsorbed ($V_a$) was verified at low relative pressures ($p/p_0 = <0.1$). Until $p/p_0 = \approx 0.9$, the amount of $N_2$ molecules adsorbed showed little increase. According to this behavior, the $N_2$ sorption isotherm can be assigned to IUPAC type I, characteristic of microporous materials.[6] This

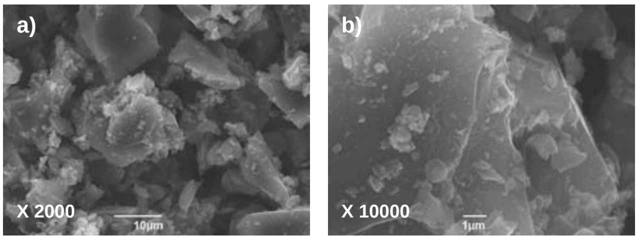

**Figure 1.** SEM images of the microporous Si–O–C composite material.

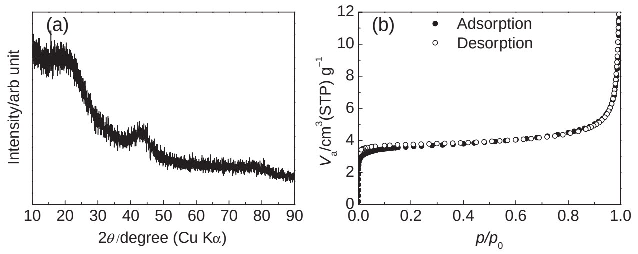

**Figure 2.** XRD pattern (a) and $N_2$ sorption isotherm (b) of the microporous Si–O–C composite material.

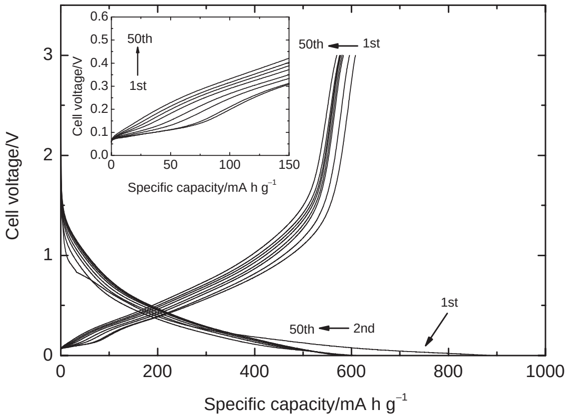

**Figure 3.** Selected charge/discharge curves of the microporous Si–O–C composite material at the 1st, 2nd, 5th, and 10–50th (every ten cycles) cycles. The charge represents a direction where lithium species are inserted into the Si–O–C composite material. An inset figure is the enlarged view of the discharge curves in the range of 0–150 mA h g$^{-1}$.

means that the Si–O–C composite material possesses a microporous nature. Nevertheless, unlike typical activated carbon, its specific surface area (SSA) is not high. In fact, the SSA of the Si–O–C composite material was 14 m$^2$ g$^{-1}$, calculated from the Brunauer–Emmett–Teller (BET) method.

Figure 3 exhibits typical charge/discharge curves of the Si–O–C composite material. Upon the 1st cycle, the charge and discharge capacities became 888 and 608 mA h g$^{-1}$, respectively, thus yielding the 1st Coulombic efficiency of 68.5%. Although the efficiency should still be improved, this material held 94% of the 1st discharge capacity even after 50 cycles, thus demonstrating much potential as an anode material. In the first few discharge profiles, interestingly, a short plateau was clearly seen in the range of <ca. 0.1 V. This plateau suggests that at least two different electrochemical active sites are present in the Si–O–C composite material.

As shown in Figure 4, the $^7$Li NMR spectrum also supports the possibility of multi-active sites for lithium storage. Considering that hard carbon presents a similar broad peak at a relatively low field as well as a voltage plateau,[7] less ionic lithium species could also be stored in closed micropores of the Si–O–C composite material. Furthermore, it has been known that the peak ascribed to the less ionic lithium species shifts to considerably lower fields at low temperatures.[8] Therefore, the lower field peak in Figure 4 could represent a mean of two or more different active sites for lithium storage. Since the plateau tends to fade over cycling, some structural changes are likely to occur in the Si–O–C composite framework. If the micropores gradually collapse, further studies will be made to determine their benefit.

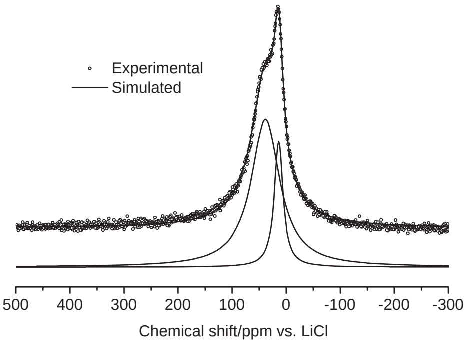

**Figure 4.** $^7$Li NMR spectrum of the microporous Si–O–C composite material in a fully lithiated state. Top: Experimental and simulated spectra. Bottom: Deconvoluted spectra of a lower field peak at $\delta$ 38 and a higher field one at $\delta$ 14. When polysilane **1** itself was pyrolyzed, the resulting product exhibited a peak at $\delta$ ca. 20.

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## References and Notes

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4 Polysilane **1** was kindly supplied by Dow Corning Corporation. Neither a product name nor a product number is available for **1** because of being a test sample.
5 The unique polymer architecture made precise control of the characters in the pyrolysis product difficult. But we have confirmed little influence on lithium storage capability.
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