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Lithiation and Delithiation of Silicon Oxycarbide Single Particles with a Unique Microstructure

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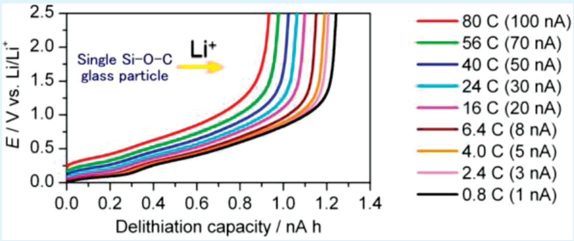

ABSTRACT: Single particles (11 and 13 μm diameter) of a silicon oxycarbide (Si—O—C) glass were electrochemically analyzed using a microelectrode technique. A micromanipulator-guided nickel-plated rhodium—platinum microfilament (25 μm diameter, 13 wt % rhodium) was used to maintain electrical contact to a single Si—O—C glass particle in an organic solution containing 1 mol dm^{-3} $LiClO_4$. The cyclic voltammograms of a single Si—O—C glass particle (11 μm diameter) featured a characteristic sharp peak at ca. 0.1 V vs Li/Li$^+$, along with a broad peak and a shoulder, in the anodic reaction. This result indicates that there are several electrochemically active sites for lithium storage in the single Si—O—C glass particle. The first lithiation and delithiation capacities of a single Si—O—C glass particle (13 μm diameter) were 1.67 nA h and 1.12 nA h, respectively, at 5 nA (4C rate) in the potential range 0.01—2.5 V vs Li/Li$^+$, leading to a Coulombic efficiency of 67%. These results are in good agreement with those observed in typical porous composite electrodes. The 13 μm diameter particle gives 75% of the full-delithiation capacity even at 100 nA (80C rate), demonstrating that its intrinsic delithiation rate capability is suitable for practical purposes. Assuming that the Tafel equation is applicable to the delithiation of the single Si—O—C glass particle, the charge-transfer resistance tended to increase as lithium was released.

KEYWORDS: rechargeable lithium batteries, anode material, micropore, high-rate performance, charge-transfer resistance

INTRODUCTION

Rechargeable lithium-ion batteries have become the most important power source for portable applications such as notebook computers and cell phones. In addition, emerging applications, such as electric vehicles, also need rechargeable lithium-ion batteries for both vehicle utility and environmental protection. In both portable applications and electric vehicles, attention has focused on developing more advanced lithium-ion batteries with higher energy and power densities, longer cycle life, and higher safety levels.[1] Both anode and cathode materials are significant in improving the performance of rechargeable lithium-ion batteries. Anode materials that can be alloyed with lithium are known to provide much higher capacities than those provided by commercially successful graphite ($\leq$372 mA h g^{-1}).[2] However, such high-capacity anode materials may not necessarily be required in practical lithium-ion batteries unless cathode materials are drastically improved.[3]

Recently, a silicon oxycarbide (Si—O—C) glass prepared from a blend of a phenyl-substituted branched polysilane, $(Ph_2Si)_{0.85}$-$(PhSi)_{0.15}$, and polystyrene (1:1 by weight) was reported as an anode material of great potential.[4] The Si—O—C glass achieved a reversible capacity of more than 600 mA h g^{-1} and excellent cyclability. One of the attributes of the Si—O—C glass is that micropores are present in its host framework, which are minor but thought to act as electrochemically active sites. In the previous study, electrochemical measurements were conducted, using typical porous composite electrodes, to evaluate the lithium storage capability of the Si—O—C glass. The porous composite electrodes used in battery research usually consist of an active material such as Si—O—C glass, a conductive additive, and an organic binder, in certain ratios. Difficulties are, however, encountered in understanding the underlying electrochemical lithium storage capability of the active material because of the complexities, such as potential/current distributions and electrolyte penetration into the porous architecture, associated with porous composite electrodes.[5] It is also known that additives in the porous composite electrodes have an influence on electrochemical lithium storage.[6] It is therefore very important to simplify the method used to evaluate the active material, particularly at high current densities.

In this study, we investigate a microelectrode technique, which uses a single particle of the Si—O—C glass. It has been recognized that microelectrode techniques are very powerful methods for investigating the underlying electrochemical lithium storage capability

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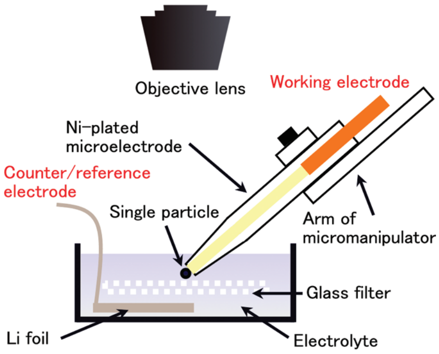

Figure 1. Schematic representation of an electrochemical cell used in this study.

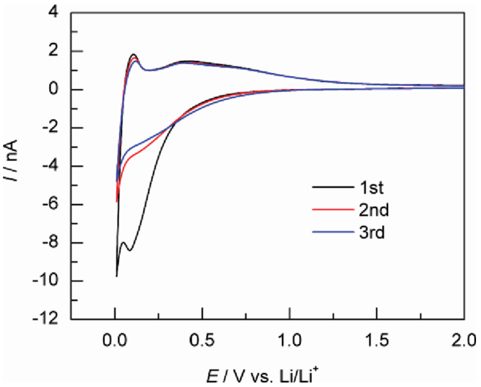

Figure 2. Cyclic voltammograms of a single Si−O−C glass particle (11 μm diameter) measured at a scan rate of 0.5 mV s^{-1}.

of microsized single particles.[7,8] A single particle electrode produces only a very small *iR* potential drop because the current flowing is at the nanoampere level. In addition, an almost uniform potential/current distribution can be attained at the surface of a single particle electrode. Microelectrode techniques enable us to obtain far more valuable information about the active material itself than typical porous composite electrodes and to find an ideal combination of anode and cathode materials. The purpose of this study is therefore to understand the underlying lithiation and delithiation of the Si−O−C glass using a microelectrode technique. To leverage the strength of a microelectrode technique, we focus on measuring cyclic voltammetry and high-rate delithiation which is unattainable without a single particle. Comparison of a single Si−O−C glass particle and the porous composite electrodes is also given.

EXPERIMENTAL METHODS

The details of the Si−O−C glass production have been reported elsewhere.[4] Electrochemical measurements were performed in an argon-filled glovebox at ambient temperature, using the same experimental setup as already reported elsewhere.[9] A glass-sealed, rhodium-containing (13 wt % rhodium) platinum microfilament (25 μm diameter) was plated with nickel in a Watts bath, prior to the measurements, using a potentiostat/galvanostat (HSV-100; Hokuto Denko).[10] The detailed procedure for preparing a typical glass-sealed microfilament has been described elsewhere.[11] The Si−O−C glass particles were placed on a glass filter and an electrochemical cell with the glass filter was filled with a 1 mol dm^{-3} $LiClO_4$/ethylene carbonate and propylene carbonate solution (1:1 by volume; Kishida Chemical). In the electrolyte, electrical contact was ensured with a micromanipulator and an optical microscope between the glass-sealed microfilament and a single Si−O−C glass particle, as shown in Figure 1. The glass-sealed microfilament was used to minimize the background current. In this study, we chose to adopt a two-electrode system with lithium foil (area 1 cm^2) as the counter and reference electrode. The potentials in this study were referenced to Li/Li$^+$. All electrochemical measurements were carried out with an ALS model 660A. Cyclic voltammetry was performed for a single Si−O−C glass particle (11 μm diameter) at a scan rate of 0.5 mV s^{-1} in the potential range 0.01−3.0 V. Galvanostatic lithiation and delithiation were undertaken for a single Si−O−C glass particle (13 μm diameter) in the potential range 0.01−2.5 V.

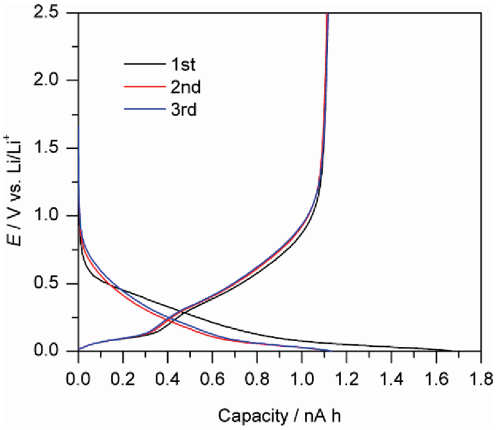

Figure 3. Initial three lithiation and delithiation curves of a single Si−O−C glass particle (13 μm diameter) measured at 5 nA.

RESULTS AND DISCUSSION

Figure 2 shows the cyclic voltammograms of the single Si−O−C glass particle (11-μm diameter). The currents observed were of the order of nanoamperes because of the particle size. A significant difference can be clearly seen between the first lithiation and the following lithiation. In particular, major irreversible reactions take place in the potential range 0.01−0.3 V, where two cathodic peaks were observed upon the first lithiation. After the second lithiation, a cathodic peak observed at *ca.* 0.1 V during the first lithiation was hardly discernible. It has been reported that irreversible capacities are observed near 0.25 V in the case of hard carbon, associated with reactions of lithium and surface functional groups.[12] Given that the Si−O−C glass is structurally related to hard carbon to some extent, similar irreversible reactions may occur in the potential range 0.01−0.3 V. Some active sites inside the single Si−O−C glass particle may also cause part of the irreversible capacity, as seen in the case of carbon materials.[13] As discussed in a previous report,[4] in addition, it remains possible that the Si−O−C glass phase reacts with lithium during the first lithiation.

Surface films, such as a solid electrolyte interface (SEI) film, are known to be formed in hard carbon during lithium insertion.[14] In the case of this single Si−O−C glass particle, a similar SEI film formation will also occur but became less pronounced in the cyclic voltammograms. This may be because of a particle-to-particle variation in surface states.

A peak was observed at ca. 0.1 V upon the first delithiation, which slightly shifted to higher potentials with a decrease in current

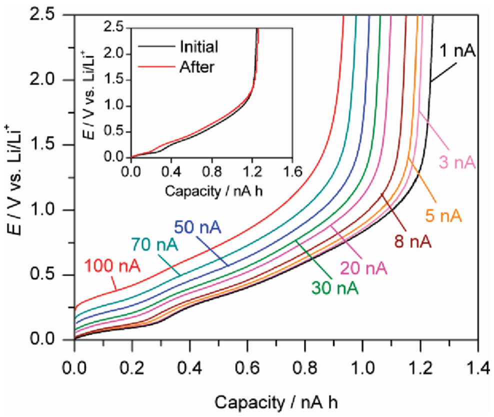

Figure 4. Delithiation curves of a single Si−O−C glass particle (13 μm diameter) measured at various currents. The single Si−O−C glass particle was lithiated at 1 nA before every delithiation. The inset compares delithiation curves measured at 1 nA: the initial curve and the curve subsequently recorded after delithiation at 100 nA.

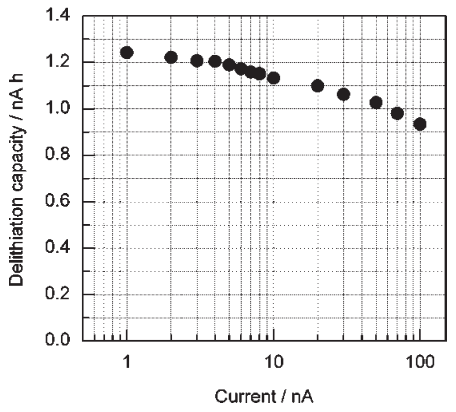

Figure 5. Delithiation capacities of a single Si−O−C glass particle (13 μm diameter) measured at various currents.

over three cycles. This anodic peak is attributed to the presence of a characteristic pseudo-voltage plateau in the delithiation curves discussed later. At higher potentials, there was no clearly visible peak in the anodic reaction, but a slight broad peak and a shoulder can be seen in the potential range 0.25−1.0 V. This is consistent with the presence of several active sites for lithium storage proposed in a previous report.[4]

Figure 3 presents the lithiation and delithiation curves of the single Si−O−C glass particle (13 μm diameter) at 5 nA in the potential range 0.01−2.5 V for the initial three cycles. A short pseudo-voltage plateau can be clearly seen below ca. 0.1 V upon delithiation. This characteristic voltage plateau was also observed for the porous composite electrodes,[4] indicating the presence of less-ionic lithium species in micropores of the single Si−O−C glass particle. The first lithiation and delithiation capacities were 1.67 nA h and 1.12 nA h, respectively, giving a Coulombic efficiency of 67%. The initial irreversible reaction was found to occur at <0.5 V. After the first cycle, lithiation and delithiation reversibilities were excellent, with Coulombic efficiencies of more than 98%. As previously reported,[4] the porous composite electrodes gave the first delithiation capacity of more than 600 mA h g^{-1} and Coulombic efficiency of about 70%. Assuming that the particle is spherical, and that its true density and theoretical capacity are 1.8 g cm^{-3} and 600 mA h g^{-1}, respectively, the delithiation capacity should be 1.24 nA h. Of course, it is not easy to determine the theoretical capacity of a single Si−O−C glass particle because of its amorphous nature. Furthermore, the single particle is not strictly spherical and there should therefore be some errors in its volume. However, the delithiation capacity and the Coulombic efficiency of the single Si−O−C glass particle agreed quite well with those observed in the porous composite electrodes (see the delithiation capacity at 1 nA in the following section). Use of a single particle therefore allows us to demonstrate the underlying lithiation and delithiation of the Si−O−C glass.

The rate capability of active materials is vital in broadening the range of applications of rechargeable lithium-ion batteries. We therefore focused on evaluating the delithiation rate capability of the single Si−O−C glass particle (13 μm diameter). Figures 4 and 5 show the delithiation curves and capacities, respectively, of the single Si−O−C glass particle at different currents in the range 1−100 nA. To ensure that the single Si−O−C glass particle was as fully lithiated as possible, we always performed electrochemical lithiation at 1 nA. Given the above theoretical capacity, a rate of 1*C* represents a gravimetric current density of 600 mA g^{-1}. A current of 1 nA corresponds to a 0.8*C* rate for the single Si−O−C glass particle. In the current range 1−8 nA, the delithiation curves showed that a small shift in the operating potential occurred because of an increase in the overpotential, and that the capacities decreased mainly above 0.5 V. At 100 nA, corresponding to an 80*C* rate, which means a time of 45 s to attain full delithiation, the delithiation capacity of the single Si−O−C glass particle was 0.93 nA h. Although the overpotential obviously became larger as the current was increased above 8 nA, 75% of the delithiation capacity obtained at 1 nA was retained at 100 nA. Thus, it can be said that the single Si−O−C glass particle intrinsically has good delithiation rate capability and can respond well to release lithium under practical operating conditions. As previously reported, a single mesocarbon microbead (MCMB) particle heat-treated at 2800 °C showed excellent deintercalation at high rates,[10] but the capacity of graphite is limited by the lithiated form of LiC_6. These results confirm difficulties to satisfy all performance requirements for active materials.

When the current was increased, the characteristic voltage plateau appeared to become slightly shorter (Figure 4). One may infer from this observation that release of lithium in the micropores is limited at currents higher than 8 nA. In fact, it is possible that the solid-state diffusion of quasi-metal lithium is slower than that of intercalated lithium in hard carbon.[15] As shown in the inset in Figure 4, however, the single Si−O−C glass particle unambiguously exhibited shortening of the voltage plateau in the delithiation curve at 1 nA after measurement at 100 nA, while maintaining the full-delithiation capacity. Kinetically limited release of lithium cannot therefore completely explain the striking changes in the delithiation curves at higher currents. This phenomenon was also observed with the porous composite electrodes,[4] and so it is likely that some structural changes (irreversible) also occur in the single Si−O−C glass particle during repeated lithiation and delithiation. In addition, the fact that the full-delithiation capacity was maintained supports the idea that the Si−O−C glass has excellent cyclability.

Several processes are thought to control electrochemical lithiation and delithiation in the single Si−O−C glass particle. It is important to understand the rate-determining step of electrochemical

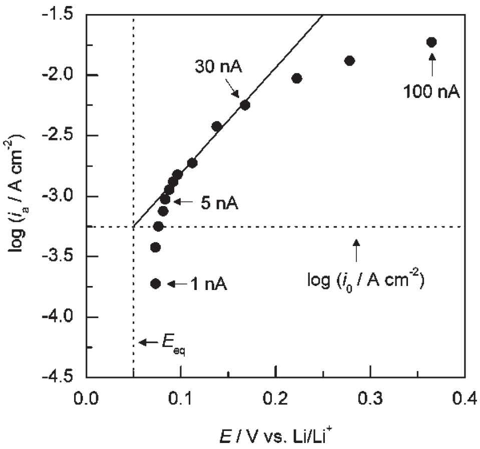

Figure 6. Tafel plot of a single Si−O−C glass particle (13 μm diameter) at DOD = 10%.

lithiation and delithiation in order to improve this type of composite material. As shown in Figures 4 and 5, the single Si−O−C glass particle suffered a 7% capacity loss at 8 nA and a 25% capacity loss at 100 nA. For example, if a large lithium concentration gradient is formed in the single Si−O−C glass particle, the electrode potential will rapidly increase to 2.5 V upon delithiation with a lithium content of zero at the particle surface. In this case, the lithium content at the center of the particle will not become zero. It is therefore thought that the single Si−O−C glass particle no longer generates the full-delithiation capacity of 1.24 nA h. The capacity loss was observed even at currents lower than 20 nA, which shows that the solid-state diffusion of lithium affects the delithiation rate of the single Si−O−C glass particle to some extent. The capacity loss at currents below 20 nA appears to mainly occur at higher potentials. Given that there are several electrochemically active sites for lithium storage in the single Si−O−C glass particle, the solid-state diffusion of lithium may be relatively slow at higher potentials, as is observed in a single MCMB particle heat-treated at 1000 °C.[16]

According to Figure 4, less-ionic lithium species associated with part of the voltage plateau (0.2 nA h, 16% of the full-delithiation capacity) should be stored in and released from the micropores upon repeated lithiation and delithiation, even at higher currents. Normally, the diffusion coefficient of lithium ions solvated in an electrolyte is higher than that of lithium ions in a solid. Here, we also eliminate crystallographic structural changes, which may influence the delithiation rate, because the single Si−O−C glass particle is amorphous. The delithiation capacities were apparently governed by a charge-transfer process, not by a mass-transfer process, even at relatively high currents in the capacity range ≤ca. 0.2 nA h.

If the mass-transfer process is negligible, the Butler−Volmer equation can be used to describe the delithiation current−overpotential relationship.[17] When the applied current is small, the departure from the equilibrium potential E_{eq} during electrochemical lithiation and delithiation is also small. We thus treat the midpoint potential, $[E(\text{lithiation}) + E(\text{delithiation})]/2$, measured at 1 nA, as E_{eq} for electrochemical lithiation and delithiation in the single Si−O−C glass particle. At large overpotentials, the kinetic parameters can be evaluated by the Tafel equation as follows[17]

$$\log i_a = \log i_0 + \frac{\alpha F}{2.303RT}\eta \qquad (1)$$

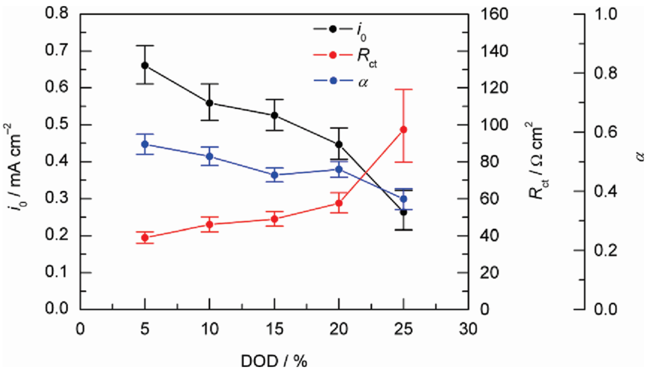

Figure 7. Exchange current density (i_0), charge-transfer resistance (R_{ct}), and transfer coefficient (α) for delithiation of a single Si−O−C glass particle (13 μm diameter) evaluated at various DODs.

where i_a is the applied current density, i_0 is the exchange current density, α is the transfer coefficient for the anodic reaction, F is the Faraday constant, R is the gas constant, T is the temperature, and η (= $E - E_{eq}$) is the overpotential for the anodic reaction. In this study, the current densities represent the currents normalized by the geometric surface area of the single Si−O−C glass particle (5.3×10^{-6} cm^2).

Figure 6 shows the Tafel plot of the single Si−O−C glass particle at a depth of delithiation (DOD) of 10%, where the "irreversible" structural changes over repeated lithiation and delithiation appear to be vanishingly small, as mentioned above. There is a linear segment in the capacity range 6−30 nA, but the linearity can no longer be seen above 30 nA owing to limited mass transfer in the single Si−O−C glass particle.

According to the Tafel equation, the slope of the linear segment is $\alpha F/2.303RT = 8.76$, and thus the transfer coefficient α is 0.52 at DOD = 10%. In addition, the exchange current density $i_0 = 0.56$ mA cm^{-2} can be obtained from the intercept of the linear segment. Using the following correlation for a one-electron process,[17] we can obtain the charge-transfer resistance, R_{ct}, at the interface.

$$R_{ct} = \frac{RT}{Fi_0} \qquad (2)$$

As a result, the charge-transfer resistance R_{ct} was estimated to be 46 Ω cm^2, which is comparable to that observed in a single MCMB particle heat-treated at 2800 °C,[10] but higher than that observed in a single MCMB particle heat-treated at 1000 °C.[16] It should be noted that the SEI film is formed upon the initial lithiation on the particle surface. Therefore, the charge-transfer resistance obtained in this study may include some contributions from the surface film resistance.

If we employ the same method as that used for DOD = 10%, the exchange current density, charge-transfer resistance, and transfer coefficient of the single Si−O−C glass particle at different DODs can be obtained, as shown in Figure 7. The transfer coefficient of the single Si−O−C glass particle varied depending on DODs and was in the range 0.37−0.56. The estimated exchange current density decreased with increasing DODs, and the estimated charge-transfer resistance reasonably increased; for example, the charge-transfer resistances were 49 Ω cm^2 at DOD = 15% and 57 Ω cm^2 at DOD = 20%, respectively. These values are still close to those reported for a single MCMB particle heat-treated at 2800 °C[10] but higher than those reported for a single MCMB particle heat-treated at 1000 °C.[16] At DOD = 25%, the charge-transfer resistance further increased for the single Si−O−C glass particle. Other than the surface film resistance, we cannot ignore here the electrical conductivity of the single Si−O−C glass particle itself; it may also contribute greatly to the overpotentials. However, we have confirmed that the Si−O−C glass has electrical conductivity on the order of 10^{-1} S cm^{-1} (see the Supporting Information). In this study, it would appear that the electrical conductivity of the single Si−O−C glass particle itself has no significant influence on the charge-transfer resistance discussed above. As previously reported, a single MCMB particle heat-treated at 1000 °C showed that the apparent chemical diffusion coefficient of lithium ions decreased with increasing DODs.[16] In our case, likewise, the mass transfer in the single Si−O−C glass particle cannot be completely ignored, in particular, at higher DODs. Further studies, such as electrochemical impedance analysis, need to be performed to understand the kinetic parameters in more detail. Our result, however, suggests that the charge-transfer resistance tends to increase as the lithium content of the single Si−O−C glass particle becomes low, as seen in the case of a single MCMB particle heat-treated at 1000 °C.[16] Because a single MCMB particle heat-treated at 2800 °C shows no large variation in R_{ct} in the range DOD = 10−90%,[10] this behavior is thought to be characteristic of the single Si−O−C glass particle. These results should be considered to be the first fundamental indication of kinetic parameters for this type of composite material.

■ CONCLUSIONS

A microelectrode was employed to evaluate the underlying lithiation and delithiation of single particles (11 and 13 μm diameter) of a silicon oxycarbide (Si−O−C) glass prepared by pyrolysis of a phenyl-substituted branched polysilane-polystyrene polymer blend. The cyclic voltammetry of a single Si−O−C glass particle (11 μm diameter) showed that major irreversible reactions occurred in the potential range 0.01−0.3 V. This may partly be explained by reactions of lithium and surface functional groups during the first lithiation, as seen in the case of hard carbon. In the anodic reaction, a clearly discernible peak was observed, along with a broad peak and a shoulder, for this glass particle. This result supports the idea that the Si−O−C glass has several electrochemically active sites for lithium storage. Upon the first lithiation and delithiation, a single Si−O−C glass particle (13 μm diameter) achieved the electrochemical performance consistent with that of typical porous composite electrodes. A characteristic pseudo-voltage plateau was clearly visible in the delithiation curve, indicating the existence of less-ionic lithium species in micropores of the glass particle. The single Si−O−C glass particle still generated 75% of the full capacity at 100 nA, corresponding to an 80C rate. Our study therefore shows that the single Si−O−C glass particle has good delithiation rate capability from the practical point of view. In the capacity range ≤ca. 0.2 nA h, the charge-transfer resistance at the interface apparently controls electrochemical delithiation of the single Si−O−C glass particle even at relatively high currents. Interestingly, the charge-transfer resistance tended to increase as the DOD was increased. At higher potentials, that is, higher DODs, the mass-transfer process should be included in the delithiation kinetics of the single Si−O−C glass particle. The thermodynamic factors associated with "irreversible" structural changes should also be considered to obtain an exact picture. However, these results probably reflect the electrochemical characteristics of the single Si−O−C glass particle.

■ ASSOCIATED CONTENT

Ⓢ **Supporting Information.** The electrical conductivity of the Si−O−C glass discussed in this paper. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ NOTE ADDED AFTER ASAP PUBLICATION

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