High Rate Charge and Discharge Characteristics of Graphite/SiO_x Composite Electrodes

Shuhei YOSHIDA,^{a,b,*} Takashi OKUBO,^b Yuta MASUO,^b Yasuyuki OBA,^a
Daisuke SHIBATA,^a Masakazu HARUTA,^b Takayuki DOI,^b and Minoru INABA^b

^a DENSO CORPORATION, 1-1 Showa, Kariya, Aichi 448-8661, Japan

^b Department of Molecular Chemistry and Biochemistry, Doshisha University,
1-3 Tatara-Miyakodani, Kyotanabe, Kyoto 610-0321, Japan

* Corresponding author: SYUHEI_YOSHIDA@denso.co.jp

ABSTRACT

Charge and discharge properties of a graphite/SiO_x composite electrode were studied over a wide range of charge/discharge rates (1/20 to 5 C) for use in automotive applications. The graphite/SiO_x (90/10 by weight) composite electrode gave a high reversible capacity (453 mAh·g⁻¹), and showed a good capacity retention at a low rate of 1/20 C. However, the capacity decreased significantly on cycling at a high rate of 2 C. From the analysis of the charging and discharging processes, it was found that the charging reaction occurs predominantly at SiO_x particles initially at higher potentials and then proceeds at graphite particles at lower potentials to be fully charged. This tendency was also supported by a dependence of the activation energy of the charge transfer reaction on the state of charge (SOC) estimated by ac impedance analysis. Because the composite electrode contains only 10% SiO_x, the current was excessively concentrated to the SiO_x particles at the initial state when charged at high rates. This caused crack formation in SiO_x particles, and the resulting contact loss between particles was considered as the reason for the observed poor cycleability at 2 C.

© The Electrochemical Society of Japan, All rights reserved.

Keywords : Graphite/SiO_x Composite Electrode, High Rate Charge and Discharge, Crack Formation, Ac Impedance Spectroscopy

1. Introduction

Silicon has been developed as a promising anode material in the next generation lithium-ion batteries due to its high gravimetric specific capacity of 4200 mAh·g⁻¹. However, the lithiation and de-lithiation reactions are accompanied by large volume changes, resulting in crack formation and pulverization of Si particles and leading to a loss of electrical contacts.¹ To overcome these problems, nano-sized Si and its composite materials (Si/C, SiO_x, etc.) have been proposed for relaxation of the large volume changes.^{2–4} Of these, silicon oxide (SiO_x) consisting of Si nanoparticles embedded in a SiO₂ matrix has received attention in recent years,^{4,5} which gives an improved cycle performance than pure Si materials.^{6–9} However, numerous issues (i.e., irreversible capacity, Coulombic efficiency, and rate capability) still remain to be solved for practical use.

Guerfi et al. prepared graphite/SiO_x composite electrodes using a flexible polyimide binder, and showed its promising cycle life.¹⁰ The graphite/SiO_x composite electrode, a compromise between energy density and cycleability, might be one of solutions for practical use, and has been already used as anodes in some lithium-ion batteries for portable electronic devices. However there are few reports on their electrochemical properties at high rates aiming at their use in batteries for automotive applications such as idling-stop systems (ISS), hybrid and electric vehicles. In these systems, high-power rechargeable lithium-ion battery cells, which have a higher energy density and can be charged and discharged more quickly than lead-acid batteries, can efficiently store more regenerated power and deliver electricity quickly to vehicle's electronic and electrical components.

In the present study, charge and discharge characteristics of a graphite/SiO_x composite electrode were studied over a wide range of charge and discharge rates (1/20 to 5 C) to clarify the issues for

automotive applications. The capacities from graphite and SiO_x were separated from the total capacity using the difference in their working potential ranges, and the reaction mechanism for lithiation and de-lithiation in the composite electrode was elucidated in detail. In addition, the kinetic aspects of the graphite/SiO_x electrode were analyzed using ac impedance spectroscopy.

2. Experimental

A slurry was prepared by mixing 87.1 wt% graphite (Alfa Aesar, <200 mesh) and 9.7 wt% SiO_x (Shin-Etsu, 5 μm, composed by dispersion of nano-crystalline Si particles within amorphous SiO₂¹¹) as active materials, 1 wt% carbon nanofiber (Showa Denko, VGCF) as a conductive agent, 1 wt% carboxymethyl cellulose sodium salt (Na-CMC, Nippon Paper Industries) and 1.2 wt% styrene-butadiene rubber (SBR, JSR Corp.) as binders using water as a solvent. The slurry was coated on a copper foil (10 μm in thickness, UACJ Corp.), dried overnight at 100°C under vacuum and pressed. The loading and the density of the electrode were 4.6 mg cm⁻² and 1.45 g cm⁻³, respectively. For comparison, graphite electrode and SiO_x electrode were prepared separately in a similar manner. For the graphite electrodes, a slurry of 96.8 wt% graphite, 1.0 wt% VGCF, 1.0 wt% Na-CMC, and 1.2 wt% SBR was used. For the SiO_x electrodes, acetylene black (Denka, HS-100) was added to ensure good electronic conductivity (50 wt% SiO_x, 40 wt% AB, 5 wt% Na-CMC and 5 wt% SBR).

Electrochemical measurements were carried out with coin-type two-electrode half cells with a Li foil counter electrode (Honjo Metal) and a separator (Celgard®2400). The electrolyte solution was 1 M LiPF₆ dissolved in ethylene carbonate (EC) and diethyl carbonate (DEC) (1:1 by volume, Mitsubishi Chemical). The cells were assembled in an Ar-filled glove box (Miwa, MDB-1NKP-DS) with a dew point lower than -80°C. The electrochemical properties

were measured at 30°C using a battery test system (Toyo System, TOSCAT-3100) in the constant current-constant voltage (CC-CV) mode between 1.5 and 0.01 V unless otherwise noted. The charge and discharge rates were varied in the range of 1/20 to 5 C, where 1 C denotes of 337, 453 and 1371 mAh·g⁻¹ for graphite, graphite/SiO_x (9:1) and SiO_x electrode, respectively.

The cross sections of the graphite/SiO_x composite electrodes in the fully charged state were observed with a field emission scanning electron microscope (FE-SEM, Hitachi, S4800). The composite electrodes were charged to 0.01 V at different C rates (1/20 and 2 C) and washed with dimethyl carbonate, dried in the argon-filled glove box. The cross sections of the electrodes were obtained with an ion milling system (Hitachi, IM4000), and the samples were transferred to the FE-SEM using a transfer-vessel without exposure to the air.

The AC impedance spectroscopy was performed using a frequency response analyzer (Solartron, 1260) coupled with a potentiostat (Solartron, 1287) over the frequency range of 100 kHz to 10 mHz with an applied ac voltage of 10 mV. Prior to measurements, the cell was charged to a given state of charge (SOC 20% and 60%) and held for 24 h at 30°C. AC impedance was then measured at different temperatures (in the order of 30, 15, 0, 45 and 60°C).

3. Results and Discussion

3.1 Charge/discharge characteristics and high rate cycleability

Figure 1 shows charge and discharge profiles of the graphite, SiO_x, and graphite/SiO_x composite electrodes at 1/20 C. The charge and discharge capacity and Coulombic efficiency for each electrode are summarized in Table 1. The discharge capacity of the graphite/SiO_x composite electrode was 453 mAh·g⁻¹, which was by 34% higher than that of the graphite electrode (337 mAh·g⁻¹). On the discharge profiles of the graphite and graphite/SiO_x electrode (Fig. 1(b)), three plateaus, which are characteristic to the stage trans-

Table 1. Charge/discharge capacities and Coulombic efficiencies of graphite, graphite/SiO_x and SiO_x electrodes at 1/20 C in the first cycle.

Electrode	Charge capacity (mAh·g ⁻¹)	Discharge capacity (mAh·g ⁻¹)			Coulombic efficiency (%)
		Total	<0.24 V	>0.24 V	
Graphite	365	337	306	31	92.4
SiO _x	2129	1371	219	1252	64.4
Graphite/SiO _x (90/10)	555	453	281	172	81.6
Graphite/SiO _x (90/10) calculated*	541	440	297	153	81.3

*Estimated from the weight ratio (90/10 in weight) and the discharge capacities of the graphite and SiO_x in the potential ranges of 0.01 to 0.24 V and of 0.24 to 1.5 V.

formations from stage 1 to 2, stage 2 to 2L, and stage 4 to random stage 1 (stage-1') of graphite intercalation compounds (GICs) were observed clearly at 0.09, 0.14, and 0.24 V, respectively.¹²

The discharge capacities in the potential ranges of 0.01 to 0.24 V and 0.24 to 1.5 V of each electrode were estimated from Fig. 1, and are shown in Table 1. The SiO_x electrode had a major capacity (84% of the total discharge capacity) in the potential range of 0.24 to 1.5 V, whereas the graphite had a major capacity (91% of the total discharge capacity) in the potential range from 0.01 to 0.24 V. This is due to a difference in their working potentials as anodes. We also calculated the discharge capacity of the graphite/SiO_x electrode using the weight ratio (90/10) and the discharge capacities of the graphite and SiO_x in the potential ranges of 0.01 to 0.24 V and of 0.24 to 1.5 V as shown in Table 1. The calculated values agree reasonably with the values obtained experimentally including the charge capacity and Coulombic efficiency. This fact clearly shows that the lithiation and de-lithiation reactions proceed separately at graphite and SiO_x particles during charging and discharging without remarkable synergy effects.

Figure 2 compares the cycleability of the graphite and graphite/SiO_x composite electrode at 1/20 and 2 C. The graphite electrode showed a good cycleability at both 1/20 to 2 C rates and only slight drops in discharge capacity were observed when the rate was increased from 1/20 to 2 C. The discharge capacity of the graphite/SiO_x electrode was higher than the graphite electrode at 1/20 C with a good cycleability. However the capacity decreased significantly at 2 C (~400 mAh·g⁻¹), and the capacity retention was poor

Figure 1. (Color online) (a) Charge/discharge curves against specific capacity and (b) Discharge curves against the depth of discharge (DOD) of graphite and graphite/SiO_x electrodes at 1/20 C in 1 M LiPF₆ dissolved in EC/DEC (1:1 by volume).

Figure 2. (Color online) Capacity retention of graphite and graphite/SiO_x electrodes at 1/20 and 2 C in 1 M LiPF₆ dissolved in EC/DEC (1:1 by volume). Potential range: 0.01–1.5 V vs. Li/Li⁺.

Figure 3. (Color online) Cross-sectional FE-SEM images of (a, b, c) electrode composites and (d, e, f) SiO_x particles. (a, d) as prepared, and after charged to 0.01 V at (b, e) 1/20 C and (c, f) 2 C to 0.01 V.

(98 $\text{mAh}\cdot\text{g}^{-1}$ in the 11th cycle). This fact implies that the graphite/ SiO_x electrode was damaged during cycling at a high rate of 2 C.

Figure 3 shows the cross-sectional FE-SEM images of the graphite/ SiO_x electrodes as prepared and after fully charged to 0.01 V at 1/20 and 2 C. The thickness of the electrode increased from 45 μm (before charged) to 48 and 56 μm after charged at 1/20 and 2 C, respectively. While the expansion in the thickness at 1/20 C (7%) was comparable to that of the graphite ($\sim 10\%$), the expansion at 2 C was as large as 24%. In addition, crack formation was found in some SiO_x particles after charged to 0.01 V at 2 C. This fact indicates that charging current was concentrated to SiO_x particles in the charging (lithiation) reaction at 2 C, which caused the crack formation and resulted in the poor cycleability in Fig. 2 owing to contact loss between particles.

3.2 Effects of lower cut-off potential

To investigate the charge process of the graphite/ SiO_x composite electrode in more detail, they were charged to different lower cut-off potentials (LCPs) and then discharged to 1.5 V at 1/20 C as shown in Fig. 4. Table 2 summarizes the charge and discharge capacities, and Coulombic efficiencies when charged to different LCPs. The Coulombic efficiency increased with lowering a LCP. A SiO_x particle consists of Si nanoparticles dispersed in a SiO_2 matrix. It is widely known that SiO_x has a large irreversible capacity on cycling because the SiO_2 matrix irreversibly reacts to form lithium silicate upon the initial charging.^{13,14} The increasing tendency of the Coulombic efficiency in Table 2 indicates that SiO_x was first charged at high potentials and then graphite was charged at lower potentials.

We divided the total discharge capacity of the composite electrode into the contributions from graphite and SiO_x using the potential of 0.24 V as a border, because the discharge capacity in the range 0.01 to 0.24 V at 1/20 C was originated mostly from the graphite particles, while that in the range 0.24 to 1.5 V mostly from the SiO_x particles as shown in Fig. 1 and Table 2. Figure 5 shows the calculated discharge capacities from graphite and SiO_x when charged to different LCPs. Even though the weight ratio of SiO_x in the composite electrode was only 10%, the discharge capacity from SiO_x was predominant when charged to higher LCPs (i.e., 0.3 and 0.2 V). SiO_x was charged by 80% at 0.1 V, while graphite was

Figure 4. (Color online) Charge/discharge curves of graphite/ SiO_x electrode when charged to different lower cut-off potentials (0.01, 0.04, 0.06, 0.1, 0.2, and 0.3 V) at 1/20 C, and then discharged to 1.5 V at 1/20 C.

Table 2. Charge/discharge capacities and Coulombic efficiencies of graphite/ SiO_x electrode when charged to different lower cut-off potentials and discharged to 1.5 V at 1/20 C.

Lower cut-off potential (E/V vs. Li/Li^+)	Charge capacity ($\text{mAh}\cdot\text{g}^{-1}$)	Discharge capacity ($\text{mAh}\cdot\text{g}^{-1}$)	Coulombic efficiency (%)
0.3	52	14	26.8
0.2	90	27	30.0
0.1	344	260	75.7
0.06	516	439	85.1
0.04	539	435	80.8
0.01	555	453	81.7

charged only by less than 50%. These results indicate that the charging reaction started at SiO_x particles and they were fully charged at around 0.1 V before graphite particles were fully charged at around 0.06 V.

Figure 5. (Color online) (a) Contributions of discharge capacity (mAh·g⁻¹) and (b) ratio of discharge capacity (%) from graphite and SiO_x in graphite/SiO_x composite electrode when charged to different lower cut-off potentials at 1/20 C and then discharged to 1.5 V at 1/20 C. The discharge capacity of graphite and SiO_x were estimated from the discharge curves in Fig. 4 using 0.24 V as a border (graphite: <0.24 V, SiO_x: >0.24 V).

3.3 Effects of charge and discharge rate

To investigate the effect of charging rate, the graphite/SiO_x electrode was charged to 0.01 V at different C rates (1/20, 1/3, 2 and 3 C) and discharged at a slow rate of 1/20 C as shown in Fig. 6 Table 3 summarizes the charge and discharge capacities, and Coulombic efficiencies obtained at different C rates on charging. Here we employed the data in the 2nd cycle to eliminate the effect of the irreversible loss owing to solvent decomposition. The total discharge capacity gradually decreased with increasing the charge rate up to 2 C. The discharge capacity at potentials > 0.24 V, which is mainly originated from SiO_x, was nearly equal to the full capacity of SiO_x in the composite electrode (~153 mAh·g⁻¹), whereas that at potentials < 0.24 V, which is mainly originated from graphite, decreased significantly with increasing the charge rate. These results indicate that SiO_x is more preferably charged than graphite at high rates. The discharge capacity was significantly dropped at 3 C, mainly because of high overpotentials.

To investigate the effect of the discharge rate, the composite electrode was charged to 0.01 V at a slow rate of 1/20 C and discharged at different C rates (1/20, 1/3, 2 and 5 C) to 1.5 V. Figure 7 shows the discharge curves plotted against the specific capacity and the depth of discharge (DOD). Though the overpotential increased with increasing the discharge rate, the specific capacity was almost unchanged (> 430 mAh·g⁻¹) up to 5 C. In these experiments, we were not able to divide the discharge capacities to those from graphite and SiO_x because the overpotential increased remarkably with discharge rate. Nevertheless the results in Fig. 7 show that when the graphite/SiO_x electrode is fully charged, the de-lithiation reactions from graphite and SiO_x are facile so that they can keep up with a high rate of 5 C.

Figure 6. (Color online) (a) Charge/discharge curves in the 2nd cycle against specific capacity and (b) Discharge curves against the depth of discharge (DOD) of graphite and graphite/SiO_x electrodes when charged to 0.01 V at different rates (1/20, 1/3, 2, and 3 C) and then discharged to 1.5 V at 1/20 C.

Table 3. Charge/discharge capacities and Coulombic efficiencies of graphite/SiO_x electrode in the 2nd cycle when charged to 0.01 V at different rates and then discharge to 1.5 V at 1/20 C.

Charging rate (C)	Charge capacity (mAh·g ⁻¹)	Discharge capacity (mAh·g ⁻¹)*			Coulombic efficiency (%)
		Total	<0.24 V	>0.24 V	
1/20	472 (100%)	447 (100%)	294 (100%)	153 (100%)	94.7
1/3	415 (87.9%)	398 (89.0%)	252 (86.3%)	146 (95.4%)	95.8
2	392 (83.1%)	279 (62.4%)	120 (40.8%)	159 (104%)	71.1
3	47 (10.1%)	19 (4.2%)	2 (0.7%)	17 (11.1%)	40.9

*Values in parentheses are the ratio to the capacities when charged at 1/20 C.

From these results, it was found that the charge and discharge processes of the graphite/SiO_x electrode are significantly affected by the state of charge (SOC). At low SOC's where both graphite and SiO_x are charged little, lithiation starts from SiO_x and the charging current is concentrated mainly to SiO_x particles. For example, when the composite electrode was charged at 2 C, the current corresponds to 6 C rate for SiO_x particles considering the current (2 C = 900 mA/g) and the capacity of SiO_x in the composite (ca. 150 mAh (g-composite)⁻¹). On the other hand, at high SOC's where both graphite and SiO_x are almost fully charged, de-lithiation proceeds at both graphite and SiO_x, and a high discharge capacity is obtained even at high C rates. It is therefore concluded that the

Figure 7. (Color online) Discharge curves in the 2nd cycle against (a) specific capacity and (b) the depth of discharge (DOD) of graphite and graphite/SiO_x electrodes when charged to 0.01 V at 1/20 C and then discharged to 1.5 V at different rates (1/20, 1/3, 2, and 5 C).

excessive current concentration to SiO_x particles upon charging process at high potentials is the reason for the crack formation in SiO_x particles observed in Fig. 3, which resulted in the poor capacity retention at 2 C as shown in Fig. 2.

3.4 AC impedance analysis

The intrinsic kinetics of graphite and SiO_x also should affect the charge and discharge properties of the composite electrode. Yamada et al. reported that the activation energy for the charge (lithium ion) transfer reaction at SiO_x thin film prepared by vapor deposition was lower than graphite.¹⁵ This fact implies that lithiation and de-lithiation kinetics of Li-alloy anodes such as SiO_x is faster than that of insertion anodes like graphite. To investigate the reaction kinetics of the graphite/SiO_x composite electrode, ac impedance was measured at different SOC. Here the graphite/SiO_x electrode was cycled once between 1.5 and 0.01 V, charged to SOC 20% (ca. 0.20 V) or to SOC 60% (ca. 0.07 V), and ac impedance was measured under open-circuit conditions.

Figure 8 shows the Nyquist plots of the composite electrode measured at SOC 20% and 60%. The semicircle at around 1 Hz is assigned to the charge transfer reaction. In general, the charge transfer resistance decreases with the degree of lithiation for both graphite and SiO_x anodes.^{15–17} However this was not the case for the graphite/SiO_x electrode in the present study; that is, the semicircle at SOC 60% was larger than that at SOC 20%. The impedance spectra were fitted with an equivalent circuit shown in Fig. 8(b), where R_e denotes the electronic resistance in the electrode and at the electrode/current collector interface, R_{sol} the ionic resistance in the electrolyte, R_{SEI} the resistance of SEI, and R_{ct} the charge transfer resistance.

Figure 8. (Color online) (a) Nyquist plots of graphite/SiO_x composite electrode measured at SOC 20% and 60%, (b) Equivalent circuit used for analysis.

Figure 9. (Color online) Arrhenius plots of $\ln(R_{ct})^{-1}$ for graphite/SiO_x composite electrode at SOC 20% and 60%.

Figure 9 shows Arrhenius-type plots of the reciprocal of the charge transfer resistance ($1/R_{ct}$) in the range of 0 to 40°C. The values of R_{ct} at different temperatures and the activation energies (E_a) estimated from the Arrhenius-type plots at SOC 20% and 60% are shown in Table 4. R_{ct} 's and E_a 's of the graphite electrode at SOC 20% (ca. 0.16 V) and 60% (ca. 0.09 V) were obtained at different temperatures in a similar manner, and their values are also shown in Table 4. Abe et al. reported that R_{ct} 's of graphite and SiO_x electrodes are 53–59 kJ mol^{−1}^{16,17} and 29–32 kJ mol^{−1},¹⁵ respectively. In the present study, E_a 's of the graphite electrode were 56.2 and 55.3 kJ mol^{−1} at SOC 20% and 60%, respectively, both of which were very close to the reported value for graphite electrode. On the other hand, E_a 's of the graphite/SiO_x electrode were 45.6 and 58.5 kJ mol^{−1} at SOC 20% and 60%, respectively. The value at SOC 60% was close to the reported value for graphite, which indicates that lithiation and de-lithiation reactions proceed predominantly at graphite particles at SOC 60% (ca. 0.09 V). On the other hand, the value at SOC 20% was much lower and was between the reported values of graphite and SiO_x electrodes. This clearly shows that the utilization of SiO_x is higher at SOC 20% (ca. 0.16 V), which supports our discussion in Sections 3.3 and 3.4.

Table 4. Charge transfer resistances (R_{ct} 's) and activation energies (E_a 's) of graphite and graphite/SiO_x electrodes at SOC 20% and SOC 60% measured at different temperatures.

SOC (%)	Graphite		Graphite/SiO _x (90/10)	
	20	60	20	60
OCV (E/V vs. Li/Li ⁺)	0.16	0.09	0.2	0.07
0°C (Ω)	55.2	14.3	32.6	125
15°C (Ω)	13.6	11.4	12.4	39.1
R_{ct} 30°C (Ω)	6.36	3.02	6.29	10.9
45°C (Ω)	3.15	0.63	1.25	2.87
60°C (Ω)	0.42	0.24	1.13	1.41
E_a (kJ·mol ⁻¹)	56.2	55.3	45.6	58.4

4. Conclusions

The graphite/SiO_x (90/10) composite electrode gave a high reversible capacity (453 mAh·g⁻¹), and showed a good capacity retention at a low rate of 1/20 C. However, the capacity decreased significantly upon cycling at a high rate of 2 C. From the analysis of the charging and discharging processes, it was found that the charging reaction occurs predominantly at SiO_x particles initially at higher potentials and then proceeds at graphite particles at lower potentials to be fully charged. This tendency was also supported by a dependence of E_a of the charge transfer reaction on SOC estimated by ac impedance analysis. Because the composite electrode contains only 10% SiO_x, the current was excessively concentrated to the SiO_x particles at the initial state when charged at high rates. This caused crack formation in SiO_x particles, and the resulting contact loss between particles is considered as the reason for the observed poor cycleability at 2 C.

These results suggests that charge and discharge reactions of SiO_x are exceptionally fast in the graphite/SiO_x composite electrodes and these intensive reactions of SiO_x may cause the contact loss failure in the graphite/SiO_x composite electrodes upon cycling. In other words, graphite/SiO_x composite electrodes with a small amount of SiO_x have to be carefully designed for use as anodes in which high rate charging is essential such as idling-stop systems (ISS), hybrid and electric vehicles, etc.

Acknowledgment

The authors are grateful to Shin-Etsu Chemical Corporation (Japan) for providing SiO_x sample.

References

1. B. A. Boukamp, G. C. Lesh, and R. A. Huggins, *J. Electrochem. Soc.*, **128**, 725 (1981).
2. I. Kim and N. Kumta, *J. Power Sources*, **136**, 145 (2004).
3. M. Saito, T. Yamada, C. Yodoya, A. Kamei, M. Hirota, T. Takenaka, A. Tasaka, and M. Inaba, *Solid State Ionics*, **225**, 506 (2012).
4. Y. Nagao, H. Sakaguchi, H. Honda, T. Fukunaga, and T. Esaka, *J. Electrochem. Soc.*, **151**, A1572 (2004).
5. K. Yasuda, Y. Kashitani, S. Kizaki, K. Takeshita, T. Fujita, and S. Shimosaki, *J. Power Sources*, **329**, 462 (2016).
6. M. Mamiya, H. Takei, M. Kikuchi, and C. Ueda, *J. Cryst. Growth*, **229**, 457 (2001).
7. M. Miyachi, H. Yamamoto, H. Kawai, T. Ohta, and M. Shirakata, *J. Electrochem. Soc.*, **152**, A2089 (2005).
8. T. Tabuchi, H. Yasuda, and M. Yamachi, *J. Power Sources*, **146**, 507 (2005).
9. H. Huijun, G. Han, J. Xie, and Q. Zhang, *Int. J. Electrochem. Sci.*, **11**, 8697 (2016).
10. A. Guerfi, P. Charest, M. Dontigny, J. Trottier, M. Lagacé, P. Hovington, A. Vijh, and K. Zaghib, *J. Power Sources*, **196**, 5667 (2011).
11. J. Park, S. S. Park, and Y. S. Won, *Electrochim. Acta*, **107**, 467 (2013).
12. J. R. Dahn, *Phys. Rev. B*, **44**, 9170 (1991).
13. T. Kim, S. Park, and S. M. Oh, *J. Electrochem. Soc.*, **154**, A1112 (2007).
14. Y. Liu, Z. Y. Wen, X. L. Yang, A. Hirano, N. Imanishi, and Y. Takeeda, *J. Power Sources*, **189**, 480 (2009).
15. Y. Yamada, Y. Iriyama, T. Abe, and Z. Ogumi, *J. Electrochem. Soc.*, **157**, A26 (2010).
16. Y. Yamada, Y. Iriyama, T. Abe, and Z. Ogumi, *Langmuir*, **25**, 12766 (2009).
17. T. Abe, H. Fukuda, Y. Iriyama, and Z. Ogumi, *J. Electrochem. Soc.*, **151**, A1120 (2004).