Thermodynamic analysis and effect of crystallinity for silicon monoxide negative electrode for lithium ion batteries

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HIGHLIGHTS

- Thermodynamic analysis of SiO electrodes.
- Highest discharge capacity and relatively high coulombic efficiency for SiO anode.
- Superior characters of amourphous SiO than disproportionated SiO.

ARTICLE INFO

ABSTRACT

The electrochemical behavior of SiO negative electrodes for lithium ion batteries is thermodynamically and experimentally investigated. The analysis of the reaction pathway and the calculation of the reaction potentials during the Li insertion/extraction reactions are carried out by the construction of the ternary phase diagram for the Li–Si–O system. In the initial reaction of Li insertion, metallic Si and lithium silicates are formed above 0.37 V vs. Li/Li$^+$ as a conversion reaction of the SiO negative electrode. Further Li insertion produces Li–Si alloys as reversible reaction phases. The decomposition of the Li$_4$SiO$_4$ phase begins before the formation of the Li–Si alloy is completed. The measured electrode behavior of the SiO negative electrode basically agrees with the thermodynamic calculations, especially at a low reaction rate; deviations can be ascribed to kinetic factors and electrode resistance. The values of over 1898 mA h g^{-1} and 71.0% were obtained for the discharge capacity and the coulombic efficiency, respectively. Furthermore, the overvoltage for an amorphous SiO electrode was smaller than that for a disproportionated SiO electrode into Si and SiO$_2$ phases.

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1. Introduction

Lithium ion batteries (LIBs) are widely utilized as efficient storage devices for mobile systems such as laptop computers and cell phones. The large operational voltage derives from the redox reactions for lithium (Li) species both at the positive and negative electrodes. One major concern surrounding LIBs is the insufficient capacity of the graphite negative electrode in the context of long-distance driving for electric vehicles (EVs) and hybrid electric vehicles (HEVs). The development of alloying-dealloying processes

with Li by using alloying materials such as silicon (Si) and tin (Sn) as well as conversion-type materials of metal oxides, nitrides, and phosphides constitutes a crucial task toward achieving large capacities [1–3]. Among the various candidates, silicon monoxide (SiO) is expected to have a high capacity and impressive cyclability by overcoming the drawbacks of a large volume expansion and a large irreversible capacity for alloying materials and conversion-type materials, respectively.

In the Si–oxygen (O) binary system [4], silicon dioxide (SiO$_2$) is the only stable oxide at ambient pressure and temperature. Silicon oxides with lower oxygen content, SiO$_x$ – where x is the atomic ratio of oxygen with respect to silicon, and falls between 0 (Si) and 2 (SiO$_2$) – have no stable crystalline structure including SiO [5–11]. Among silicon lower oxides, solid SiO is the only commercially

available variety, and is usually manufactured with a vapor deposition technique from the gaseous SiO produced by the reaction of Si and SiO_2 at high temperatures [11–13]. The notable characteristic of solid SiO is its disproportionation into solid nanocrystalline Si particles and solid SiO_2 matrix above ~1123 K [14,15]. The crystallinity of the SiO materials changes with the thermal history during the production processes. Accordingly, both the amorphous and disproportionated varieties of SiO are sometimes referred to as "commercial SiO." Nevertheless, it should be emphasized that the characteristics of amorphous SiO and disproportionated SiO are different. For instance, the Si valence states for amorphous SiO are evaluated using X-ray photoelectron spectroscopy (XPS) analysis as Si(0), Si(1+), Si(2+), Si(3+), and Si(4+), depending on the number of bonds coordinated with oxygen; on the other hand, the valence states are evaluated as Si(0) and Si(4+) for disproportionated SiO [16–18].

The characteristics of SiO negative electrodes for LIBs have already been reported by many researchers for the case of both amorphous SiO and disproportionated SiO [19–32]. In addition to SiO negative electrodes, the electrochemical characteristics of (SiO + carbon) composite electrodes [33–44] and SiO_2 electrodes [28,45–50] have also been reported. Table 1 summarizes the results for the SiO phase (amorphous or disproportionated), the intermediate phase during Li insertion/extraction, the initial charge and discharge capacities, the initial coulombic efficiency, and the analysis methods, where the charge/discharge rates and cut-off voltages are irrelevant.

In this paper, we use the phrases "charge" and "discharge" for Li insertion and extraction reactions, respectively. The Li insertion reaction is reported to proceed with the formation of Li–Si alloys, lithium silicates (Li–Si–O), and/or Li_2O [21,33,34]; moreover, the alloying-dealloying of Si contributes to the reversible capacity. Whereas the formed silicates and Li_2O lead to the irreversible capacity, the silicates play the role of a matrix of nano Si (2–10 nm diameter) for the fast diffusion of Li atoms and the mitigation of structural collapse [24]. The formation of these oxide phases has been evaluated by various techniques such as XPS, nuclear magnetic resonance (NMR), high-resolution transmission electron microscopy (HR-TEM), and electrochemical dilatometry.

The theoretical reaction of a SiO negative electrode was reported as follows [28,29,51]:

$$20\,SiO + 86\,Li \rightarrow 3\,Li_{22}Si_5 + 5\,Li_4SiO_4. \tag{1}$$

According to Eq. (1), the initial charge and discharge capacities and initial coulombic efficiency are theoretically calculated as 2615 mA h g^{-1}, 2007 mA h g^{-1}, and 76.7%, respectively. However, as understood from Table 1, the reported values for SiO negative electrodes differ among researchers. In addition, the reaction potentials observed as potential plateaus in the potential-charge curves and capacity peaks in voltammograms also differ between reports [34,52]. Consequently, the nature of the electrochemical characteristics of SiO has not yet been sufficiently clarified. Although Yang et al. have provided a thermodynamic analysis of the reaction potentials of a SiO electrode [53], their calculations are not entirely reliable because they do not take into account the Gibbs phase rule that is indispensable for the evaluation of the equilibrium.

In this paper, the reactions for a SiO negative electrode are thermodynamically evaluated. Firstly, the Li–Si–O system is investigated on the basis of the construction of the ternary phase diagram according to the Gibbs phase rule, in which the number of degrees of freedom at a fixed temperature can be expressed as:

$$f = C - P + 1, \tag{2}$$

where f stands for the number of degrees of freedom, C is the number of components, and P is the number of equilibrated phases. Secondly, the formation potentials of Li–Si alloys, lithium silicates,

Table 1
Representative reports on battery and electrode characteristics of the SiO negative electrode.

Author, Ref.	Year	SiO phase	Intermediate phase	Initial charge capacity (mAh g^{-1})	Initial discharge capacity (mAh g^{-1})	Initial coulombic efficiency (%)	Note
Yang et al. [19]	2002	Amor.	–	ca. 2250	ca. 1300	ca. 57.8	–
Nagao et al. [20]	2004	Amor.	SiO_2	1594	–	–	Neutron elastic scattering
Miyachi et al. [21]	2005	Amor.	Li–Si–O, Li_2O	2404	598	24.9	XPS
Miyachi et al. [22]	2007	–	Li–Si–O, Li_2O	2520	1260	50.0	Metal-doped SiO, XPS
Kim et al. [23]	2007	–	Li–Si–O, Li_2O	2680	1470	54.9	NMR, HR-TEM, electrochemical dilatometry. Plateau at 0.8 V vs. Li$^+$/Li in 1st discharge
Yamada et al. [24]	2007	–	–	–	–	–	Kinetics evaluation by AC impedance spectroscopy
Park et al. [25]	2010	Amor./ dispro.	SiO_x	2216/185	1104/94	49.8/50.8	TEM, Disproportionated at 800, 1000, and 1200 °C.
Komaba et al. [26]	2011	–	–	ca. 1800	826	45.9	–
Kim et al. [27]	2011	Amor./ dispro.	Li–Si–O, Li_2O	2410	1300	53.9	NMR, HR-TEM, Differential capacity peaks at 0.08 and 0.24 V vs. Li$^+$/Li
Yamamura et al. [28]	2011	Dispro.	Li–Si–O	2548	1791	70.3	Plateau at 0.2 and 0.5 V vs. Li$^+$/Li in 1st discharge. First principles calculation. SiO_2 was also reacted.
Miyuki et al. [29]	2011	Amor./ dispro.	–	–	–	–	$LiFePO_4$/SiO full cell.
Jeong et al. [30]	2012	Dispro.	–	1757	1265	72.0	TiO_2 coated SiO
Kim et al. [31]	2013	Dispro.	–	1958	1413	72.2	Carbon coated SiO. Differential capacity peaks at 0.06, 0.21, 0.31 and 0.48 V vs. Li$^+$/Li after 5th cycle
Takezawa et al. [32]	2013	Amor.	Li–Si–O, Li_2O	2418	1306	54.0	SiO_x (0.17 < x < 1.34) was used. XPS

–: Not given.