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Studies of Lithium Diffusivity of Silicon-Based Film Electrodes for Rechargeable Lithium Batteries

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ABSTRACT :

Lithium diffusivity of the silicon (Si)-based materials of Si-Cu and SiO_x ($x = 0.4$, 0.85) with improved interfacial stability to electrolyte have been determined, using variable rate cyclic voltammetry with film model electrodes. Lithium diffusivity is found to depend on the intrinsic properties of anode material and electrolyte; the fraction of oxygen for SiO_x ($x = 0.4$, 0.85), which is directly related to electrical conductivity, and the electrolyte type with different ionic conductivity and viscosity, carbonate-based liquid electrolyte or ionic liquid-based electrolyte, affect the lithium diffusivity.

Keywords : Rechargeable lithium batteries, Si-based anode, Lithium diffusivity, Film model electrode

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1. Introduction

There is an increasing need of high-energy rechargeable lithium batteries for their applications to electric vehicles and stationary energy storage grid systems. This represents the development need of higher capacity anode materials, and higher capacity and higher voltage cathode materials with a stable cycling ability and safer characteristics than the conventional ones.[1] Silicon (Si)-based materials are attractive anode materials because of superior theoretical capacity of Si: 3579 $mAhg^{-1}$ ($Li_{15}Si_4$) at room temperature compared to 372 $mAhg^{-1}$ of graphite anode.[2,3] Si-based anode materials, however, suffer from a rapid performance fade due to a severe volume change during lithiation/delithiation followed by particle cracking and the loss of electrical contact between individual particles and particles and current collector.[2,3] It has been established that interfacial instability of Si electrode with electrolyte, *i.e.*, the attack of $LiPF_6$-derived acidic species (PF_5, PF_3O, HF) additionally deteriorate the particle cracking event.[4-6] Our earlier work showed that for amorphous silicon suboxides, SiO_x (x = 0.4, 0.85, 1.0 and 1.3), higher oxygen content induces to decrease initial electrolyte reduction but larger fraction of oxides is subjected to dissolution by acid (*e.g.*, HF)-etching.[7] The control of anode-electrolyte interfacial reaction and the formation and composition of solid electrolyte interphase (SEI) has been suggested as an effective approach for enhancing the cycling performance of Si-based anodes for rechargeable lithium batteries.[4-10]

Lithium diffusivity is an intrinsic property of lithium ion-conducting electrode material. It is generally proposed that the rate of lithiation process of anode and cathode material is controlled by lithium diffusion. Thus, lithium diffusivity finds its importance in obtaining a good cycling performance of rechargeable lithium batteries, in particular, rate capability and cycling stability. Various methods have been used to determine the lithium diffusivity in Si anode such as electrochemical impedance spectroscopy (EIS),[11-13] cyclic voltammetry (CV),[11,14-17] galvanostatic intermittent titration technique (GITT)[16] and potentiostatic intermittent titration technique (PITT).[12,16]

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However, the reported diffusivities are not consistent with each other, since the measurements were conducted while having the occurrence of volume change and particle cracking, and interfacial instability with electrolyte. Accommodation of volume change and formation of a stable SEI layer are premises for determining lithium diffusivity of Si-based electrodes. Also different measurement techniques were applied to the lithium cells consisting of different electrode formulation and electrolyte composition, which lead to a different surface chemistry. Tasaki *et al.* showed that the SEI composition may affect to lithium diffusivity of Si. Inorganic compounds such as Li_2O and Li_2CO_3 have very low diffusivity compared to that of organic compounds such as lithium alkyl carbonate ($LiOCO_2R$, R: alkyl group) and lithium carboxylate ($LiCO_2R$).[17)]

Studies of dense film model electrode can give a clearer insight into the intrinsic properties of electrode material without complications from the carbon and polymeric binder additives that are necessary in bulk electrodes for enhanced electric conductivity and particle connection.[4-10,18)] Our earlier work showed that interfacial stabilization of pulsed laser deposited (PLD) Si film model electrode on Cu substrate by constructing the surface protective siloxane network at the electrode surface using dimethoxydimethylsilane (DMMS, $(CH_3)_2(CH_3O)_2Si$) provides lithium diffusivity of 2.35×10^{13} cm^2/s which is approximately three orders lower than ~1.12×10^{10} cm^2/s of graphite powder electrode.[5,19)] Nanometer-scale film electrode deposited homogeneously on a conductive substrate can have a robustness to structural and mechanical changes with cycling before disintegration and strong adherence to the substrate, yielding a good model system for the study of lithium diffusion kinetics during electrochemical cycling. There is no prior record of lithium diffusivity study for Si-based film model electrodes prepared by PLD.

In the present work, we report the determination of lithium diffusivity of Si-Cu and SiO_x (x = 0.4, 0.85) PLD film model electrodes in carbonate-based organic liquid electrolyte and ionic liquid electrolyte employing variable rate CV. The influences of electrolyte type and oxygen in SiO_x on lithium diffusivity are discussed.

2. Experimental

The 60 - 80 nm thick film model electrodes of Si-Cu (89:11 in mole%), and $SiO_{0.4}$ and $SiO_{0.85}$ were prepared on copper or stainless steel substrates by PLD at 400°C in 5 mtorr of O_2 or Ar back pressure, using a KrF excimer laser with an energy density of ~3-4 mJ cm^{-2} at 10 Hz impinging on the targets that consisted of the corresponding powder components, *i.e.*, Si-Cu, and Si-SiO or Si-SiO_2, respectively. The relative atomic ratio of Si/Cu and Si/O were determined using X-ray photoelectron spectroscopy depth profile (Thermo, MultiLab 2000) with Al Kα X-ray source and Ar-ion sputtering at 2 kV.[7,8)] The thickness and surface morphology of the film model electrodes were examined using field emission scanning electron microscopy (SEM, JEOL JSM-7000F) imaging at 5 kV. The structure of the electrodes was determined as amorphous by X-ray diffraction (Rigaku D/MAX-2200) and Raman spectroscopy (Tokyo instrument Co., Nanofinder 30).

Variable rate cyclic voltammetry (CV) was carried out at a sweep rate from 100 to 0.01 mV/s between 0.1 and 1.5 V *vs.* Li/Li^+ using a potentiostat (CHI660). Three-electrodes lithium cells includes the Si, Si-Cu, $SiO_{0.4}$ and $SiO_{0.85}$ film model electrodes as working electrodes, and lithium counter and reference electrodes. Three types of electrolytes of 1M $LiPF_6$/EC:DEC (1:1 volume ratio, Soulbrain) with and without 5 wt% tris(2-methoxyethoxy)vinylsilane (TMVS, Aldrich), ionic liquid electrolyte of 1M LiTFSI/$Py_{1,3}$TFSI, and diluted ionic liquid with dimethyl carbonate (DMC) of 0.5 M LiTFSI/$Py_{1,3}$TFSI:DMC (1:1volume ratio) were used. Lithium cell assembly and electrochemical measurement were made in Ar-filled glove box at room temperature.

3. Results and Discussion

Fig. 1a shows the CVs of the Si-Cu film in 1 M $LiPF_6$/ ethylene carbonate (EC): diethyl carbonate (DEC) (1:1 volume ratio) with tris(2-methoxyethoxy)vinylsilane (TMVS) additive. The y axis is expressed as pseudo capacitance (I/ν) by normalizing the current I with sweep rate ν that varied from 100 to 0.01 mV/s. With decreasing the sweep rate, the pseudo capacitance of anodic peaks increases and becomes sharper, then, they are separated into individual ones. At the slowest sweep rate of 0.01 mV/s, the cathodic peaks at 0.26 and 0.13 V correspond to the formation of $Li_{1.71}Si$ and $Li_{2.33}Si$-$Li_{3.25}Si$, respectively.[20,21)] The anodic peaks located at about 0.32 and 0.48 V are characteristic of delithiation from $Li_{3.25}Si$ subsequently regenerating $Li_{2.33}Si$, $Li_{1.71}Si$ and amorphous

Si,[20,21] respectively. In this work, we take the anodic peak at approximately 0.48 V for determining the lithium diffusivity as it is observed in common regardless of sweep rate, which corresponds to the removal of 2.33 Li from Li_7Si_3 ($Li_{2.33}Si$).[22]

Fig. 1b-c reveal that the anodic peak current (I_p) at 0.48 V is linearly proportional to the square root of the sweep rate ($\nu^{1/2}$) rather than ν, in the sweep rate region of 0.02 - 10 mV/s. This is characteristic of semi-infinite lithium diffusion process.[23] Lithium diffusion may undergo consequently through siloxane network layer, the SEI layer and Si electrode. The slope of I_p *vs.* $\nu^{1/2}$ is used for the calculation of lithium diffusivity.[23] The determined diffusivity is 2.51×10^{-13} cm^2s^{-1}.

Applying the same method to the CVs of Si-Cu electrodes in ionic liquid electrolyte of 1M lithium bis(trifluoromethylsulfonyl)imide (LiTFSI)/1-methyl-1-propylpyrrolidinium ($Py_{1,3}$)TFSI (Fig. 2a) and the diluted ionic liquid (Fig. 2b) electrolyte of 0.5 M LiTFSI/$Py_{1,3}$TFSI: DMC, and the electrodes of $SiO_{0.4}$ (Fig. 3a) and $SiO_{0.85}$ (Fig. 3b) in carbonate-based liquid electrolyte with TMVS additive, their lithium diffusivities were determined and compared in Table 1 and Table 2. Lithium diffusion at Si-Cu electrode becomes five times sluggish in ionic liquid electrolyte, as shown in Table 1. Abe et al. reported that the desolvation process of Li cation at the surface of graphite is a rate-determining step since the activation energy depends on the Li^+-solvation ability of solvent.[24] Borodin *et al.* suggested using molecular dynamics simulation that the interaction between Li cation and TFSI anions is depicted as the coordination of Li cation by about four oxygens from different TFSI

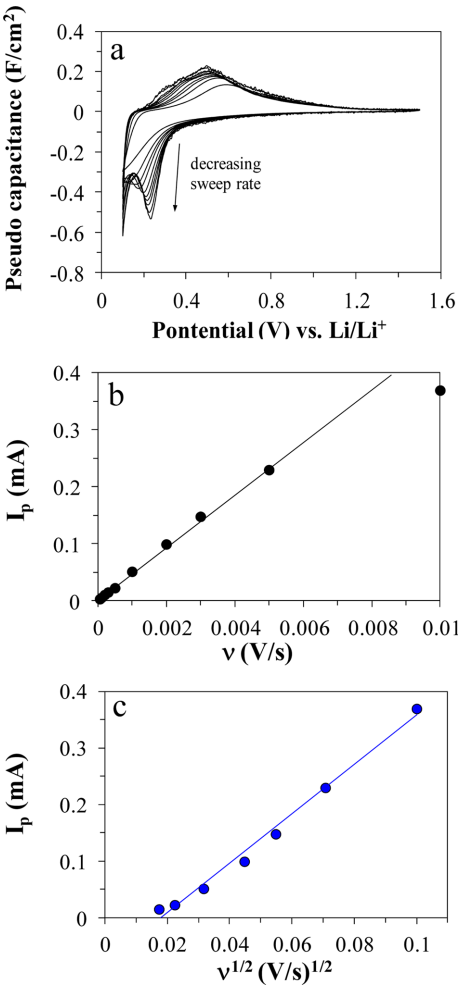

Fig. 1. Cyclic voltammograms of the lithium cell with Si-Cu film electrode in the liquid electrolyte of 1M $LiPF_6$/EC:DEC with 5wt% TMVS additive at a variable sweep rate (ν) from 100 to 0.1 mV/s (a), and the dependence of peak current (I_p) on the square-root of sweep rate $\nu^{1/2}$ (b).

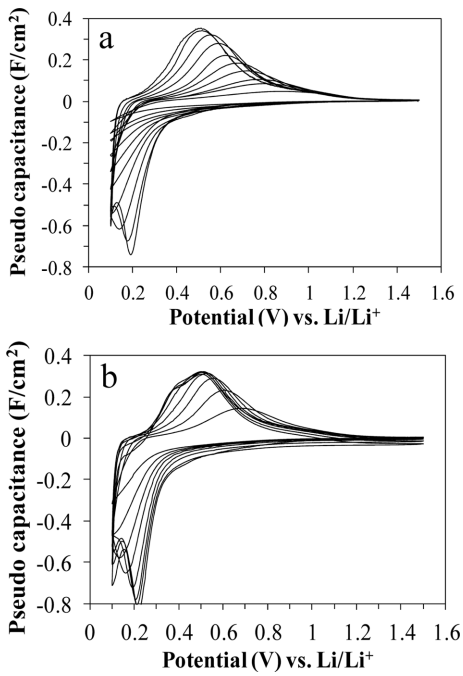

Fig. 2. Cyclic voltammograms of the lithium cell with Si-Cu film electrodes in the ionic liquid electrolyte of 1M LiTFSI/$Py_{1,3}$TFSI (a) and diluted ionic liquid electrolyte of 0.5M LiTFSI/$Py_{1,3}$TFSI:DMC (b) at a variable sweep rate from 100 to 0.1 mV/s.

Table 1. Lithium diffusivity of Si-Cu film electrodes in carbonate-based liquid electrolyte and ionic liquid-based electrolytes.

Electrolyte	*Si in 1M $LiPF_6$/ EC:DEC (1:1) + 5%wt. DMMS[5,19)]	1M $LiPF_6$/EC:DEC (1:1) + 5%wt. TMVS	1M LiTFSI/ $Py_{1,3}$TFSI	0.5M LiTFSI/ $Py_{1,3}$TFSI: DMC (1:1)
Lithium diffusivity (cm^2/s)	2.35×10^{-13}	2.51×10^{-13}	6.70×10^{-14}	3.35×10^{-13}

Table 2. Lithium diffusivity of Si-Cu and SiO_x film electrodes in 1 M $LiPF_6$ in EC:DEC with 5 wt % TMVS additive.

Electrode	Si–Cu	$SiO_{0.4}$	$SiO_{0.85}$
Lithium diffusivity (cm^2/s)	2.51×10^{-13}	1.86×10^{-13}	6.74×10^{-14}

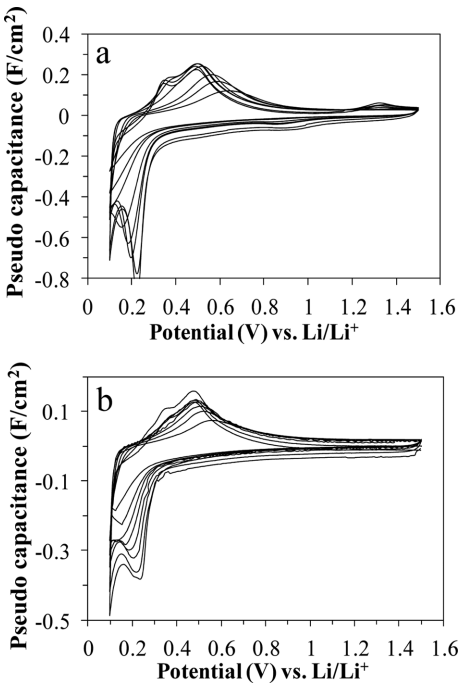

Fig. 3. Cyclic voltammograms of the lithium cells with (a) $SiO_{0.4}$ and (b) $SiO_{0.85}$ film electrodes in the electrolyte of 1M $LiPF_6$/EC:DEC with 5 wt% TMVS additive at a variable sweep rate from 100 to 0.1 mV/s.

anions.[25)] As the TFSI anion is well stabilized by electron withdrawing functionalities, the interaction between Li cation and TFSI anions might be weaker than that for solvated Li cation by polar carbonate solvent molecules in liquid electrolyte.[26,27)] Although Li cation is relatively freer in ionic liquid electrolyte than that of liquid electrolyte and the SEI layer produced in ionic liquid electrolyte is thinner and composed of relatively higher concentration of $Py_{1,3}$ decomposition products than TFSI anion,[8)] the lithium diffusivity of Si-Cu electrode in ionic liquid electrolyte is lower than that of liquid electrolyte (Table 1). This indicates that the lithium diffusivity of Si-Cu electrode in ionic liquid electrolyte is strongly affected not by dissociation of ions but by its low ionic conductivity and high viscosity. This is consistent with the conclusion from Yamada et al. that the charge-transfer kinetics at silicon monoxide (SiO) is not influenced by the desolvation of Li cation from solvent molecules, which was determined using ac impedance spectroscopy.[28)]

Fig. 3 and Table 2 show CVs and lithium diffusivity of SiO_x (x = 0.4 and 0.85) electrodes in the electrolyte of 1 M $LiPF_6$/EC:DEC + 5wt% TMVS, respectively, and compared with that of Si-Cu electrode. The $SiO_{0.4}$ electrode shows similar lithium diffusivity to Si-Cu. However, with higher oxygen content, the lithium diffusivity of $SiO_{0.85}$ electrode is lowered. Note that insulating Li_2O and lithium silicates form in the course of initial lithation of SiO_x. For the SiO_x with higher oxygen content, higher concentration of those insulating materials might form. Lithium diffusivity is known to be dependent on its electrical conductivity.[29] It is thus determined that the lower lithium diffusivity of $SiO_{0.85}$ than that of $Si_{0.4}$ is due to its lower electrical conductivity.

4. Conclusions

The lithium diffusivity of Si, Si-Cu, $SiO_{0.4}$ and $Si_{0.85}$ electrodes in the liquid electrolyte of 1 M $LiPF_6$/EC:EMC, and ionic liquid electrolyte of 1 M LiTFSI/ $Py_{1,3}$TFSI and diluted ionic liquid with DMC, respectively, has been determined using cyclic voltammetry and compared. Lithium diffusivity of Si, Si-Cu and $SiO_{0.4}$ electrodes in carbonate-based liquid electrolyte is all in the order of 10^{-13} cm^2/s. The presence of small fraction of oxygen in $SiO_{0.4}$ does not affect the diffusivity, whereas relatively higher fraction oxygen of $SiO_{0.85}$ lowers down lithium diffusivity due to lowered electrical conductivity by the formation of higher concentration of insulating Li_2O and lithium silicates. The use of

ionic liquid electrolyte also lowers down lithium diffusivity compared to liquid electrolyte due to its relatively low ionic conductivity and high viscosity.

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