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New Approach for Enhancing Electrical Conductivity of Electrodeposited Si-Based Anode Material for Li Secondary Batteries: Self-Incorporation of Nano Cu Metal in Si-O-C Composite

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Abstract

The poor electrical conductivity of Si-based anode materials is a critical challenge for the development of high-performance Li secondary batteries. We propose a new approach for enhancing the electrical conductivity of an electrodeposited Si-O-C composite anode via self-incorporation of nano Cu metal (*n*-Cu) using a facile and inexpensive electrochemical synthetic method. The Si-O-C composite with *n*-Cu (Cu/Si-O-C composite) shows stable cycle performance with a fairly high specific capacity. Since Cu precursor ions for the electrodeposition of *n*-Cu are directly dissolved from a Cu substrate used as the current collector for the anode, electrical conducting additives that causes increase in the weight and volume of the electrode are not unnecessarily supplemented. In the synthesis process, the *n*-Cu metal and Si-O-C composite are electrodeposited simultaneously. The *n*-Cu/Si-O-C composite anode results in improved electrochemical performance, including enhancement of areal and specific capacity; coulombic efficiency; and rate capability. Electrochemical impedance spectroscopy suggests that such improvements in performance are due to the enhanced electrical conductivity resulting from the conductive network of the incorporated *n*-Cu. Moreover, the electrical conductive properties of the incorporated *n*-Cu suppress electrochemical degradation of the *n*-Cu/Si-O-C composite anode.

Keywords: Electrodeposition, Anode, Si-O-C composite, Li secondary battery, Nano copper metal

Introduction

Recently, improvements to battery performance have been researched through the emergence of Si-based anodes, which undergo reversible alloying/dealloying reaction with Li ions and show significantly larger theoretical capacity ($\text{Li}_{4.4}\text{Si}$: 4200 mA h g^{-1}) as compared to graphite (LiC_6 : 372 mA h g^{-1}).^{1, 2} However, severe obstacles of the Si-based anode materials are encountered in their practical application for the high-performance Li secondary batteries. The first issue is the large volume change of Si resulting from its ionic character in the Li alloying reaction, which leads to the formation of the “Zintl phase,” $\text{Li}_x^{\times+}\text{M}^{\times-}$. Such volume change manifests during charge/discharge cycles when large internal mechanical stresses occur between the active material particles.¹ Consequently, the Si-based active materials are detached from the current collector, causing rapid capacity fade and deterioration of the cycle life.³ Previously, it was reported that nano-sized Si structures show outstanding improvement in cycle life because volume changes could be accommodated by minimizing the Si structures.⁴⁻⁷ Core-shell and porous structures were also considered to effectively endure the volume change during cycling by introducing robust shell or void space for enlarged Si particles and achieved stable cycle life with high capacity.⁸⁻¹⁰ Another serious problem associated with the Si-based anode is the poor electrical conductivity of Si itself. Si has fairly low electrical conductivity ($2.3 \times 10^3 \Omega \cdot \text{m}$ at 20°C) relative to other Li-alloying anode materials such as tin ($115 \text{ n}\Omega \cdot \text{m}$ at 20°C), antimony ($417 \text{ n}\Omega \cdot \text{m}$ at 20°C), and aluminum ($28.2 \text{ n}\Omega \cdot \text{m}$ at 20°C). The low electrical conductivity of Si causes issues such as limited areal capacity, poor-rate capability, and low power density. Therefore, various conductive additives such as metallic and carbonaceous materials, i.e., carbon nanotubes (CNTs) and graphene, have been strongly suggested to improve electrical conductivity of the Si-based anode materials.¹¹⁻¹⁶ Published works have indicated that the conductive additives enhance the electron path by improving electrical contacting between the active material particles,

resulting in the improved electrochemical performance of Si as anode materials for Li secondary batteries.

In our previous report, a Si layer was synthesized via an electrochemical method from an organic carbonate solvent.¹⁷⁻¹⁹ Electrodeposition is regarded as an inexpensive synthetic process to form metal and semiconductor film layers on a conducting substrate.²⁰ In general, Si electrodeposition has been performed in non-aqueous solvents including organic solvents,^{21, 22} molten salts,²⁰ and ionic liquids,^{23, 24} which have been researched for over 30 years. In our previous work we have reported that the reduction process of Si precursors occurs with decomposition of the organic carbonate solvent molecules, resulting in SiO_x deposition combined with decomposed product of organic carbonate molecules. The weight ratio of Si, O, and C determined by glow discharge optical emission spectroscopy was 61.6 : 21.8 : 16.6 at the depth of 1.0 to 1.5 μm . SEM images with elemental mapping also confirmed homogeneous composition of Si, O, and C elements, designated as Si-O-C composite.¹⁸ We revealed that the unique composite was preferable for use as an anode of Li secondary batteries because of its durable cycle life and relatively high specific capacity delivering delithiation capacity of 1045 mA h g⁻¹ of Si at the 2000th cycle and even 842 mA h g⁻¹ of Si at the 7200th cycle.^{17, 18} The composite's volume change and chemical structure were thoroughly explored in another study to determine how the cycle stability was achieved.²⁵ Volume change of the Si-O-C composite was mitigated with further charge/discharge cycles followed by a constant volume after the 100th cycle. The formation of the organic phase, i.e., the decomposition products of organic solvent, Li₂O, Li₂CO₃, and lithium silicates such as Li₄SiO₄, resulted in buffer effects of the composite during charge/discharge cycles. Additionally, we introduced a nickel micro-nanocones hierarchical structure (MHS) current collector for the Si-O-C electrodeposition to improve its areal capacity.²⁶ The MHS current collector created a complex conductive substrate with a high surface area and enhanced the interfacial strength between active materials, achieving ca. 4-5 times larger areal capacity for

the anode material compared to conventional flat Cu substrate. The anode material's impedance analysis was also thoroughly explored.²⁷

In this study, nano Cu metal was incorporated into the Si-O-C composite to improve internal electrical conductivity of the active material composite. As mentioned above, fundamental and applicative studies of CNTs or graphene for Li secondary batteries have seen many advances because of these materials' excellent mechanical and electrical properties. Huang et al. reported the one-step aerosol assisted capillary assembly technique for crumpled graphene-encapsulated Si nanoparticles.¹⁵ The Si nanoparticles can accommodate the volume change during cycling by graphene encapsulating and also protect the Si from solid electrolyte interphase (SEI) deposition. This approach achieved good cycle stability with relatively high discharge capacity showing 940 mA h g⁻¹ at the 250th cycle. Guan et al. has also reported graphene coating on Si nanoparticle for high performance anode material for Li-ion batteries.¹⁶ The researchers introduced graphene/carbon coated Si nanoparticle hybrids and compared them to graphene coated Si nanoparticles resulting in enhanced anode performance delivering 902 mA h g⁻¹ at the 100th cycle with a current density of 300 mA g⁻¹. Although these graphene/carbon coated Si nanoparticles performed well, challenges associated with their mass production, handling, and purity limited their practical application. Moreover, these materials increase the total volume of the active material composite causing reduced volumetric energy density. Herein, we selected copper as a conductive additive to improve electrical conductivity of the Si-O-C composite due to its outstanding electrical property (16.78 nΩ·m at 20 °C). Its ductility and inactivity with Li⁺ were also considered favorably in its use as a conductive additive in Si active material composite as copper buffers the volume change of the Li-alloying anode during cycling as previously reported.²⁸⁻³¹ Furthermore, another merit of the copper incorporation is that the copper precursor ions could be easily provided by the copper substrate used as the current collector of the preparing anode. To explain the concept of this work, Scheme 1 outlines the stepwise preparation process. For *n*-

Cu incorporation in the Si-O-C composite via an electrochemical synthetic method, it is essential to introduce Cu precursor ions to the electrolyte bath in order to co-deposit the *n*-Cu metal and the Si-O-C composite during the electrodeposition process. As shown in Scheme 1, Cu ions were directly released from the Cu plate by applying an anodic current to the electrochemical reaction cell. The existence of SiCl₄ in the electrolyte bath enhanced dissolution of Cu ions due to its highly corrosive property to most metals, in particular copper. As a result, a Cu plate with a highly roughened surface, which was designated as a modified Cu substrate, was simultaneously prepared by deposition of CuCl particles on the Cu substrate. Afterwards, co-deposition of the *n*-Cu metal and the Si-O-C composite was carried out by applying a cathodic current, resulting in the synthesis of the Cu/Si-O-C composite, designated as *n*-Cu/Si-O-C composite. The *n*-Cu/Si-O-C composite anode exhibited ca. 30 % improved capacity compared to the Si-O-C composite without *n*-Cu incorporation, despite the two composites containing the same amount of silicon.

There have been many reports on the electrodeposition of Si on Cu substrate and vice versa.^{14, 32, 33} Additionally, the use of ion assisted oblique angle deposition technique,^{34, 35} polyol reduction method,¹¹ or rapid physical vapor deposition method³⁶ for the preparation of a Cu-Si mixture phase or copper coating on Si-based materials have been reported. Yet, to the best of our knowledge, an electrochemical synthetic method for simultaneous and homogenous deposition of both Cu and Si and the resulting composite's application for Li secondary batteries have not been reported. This study proposes a valuable new approach for enhancing electrical conductivity via a simple and economical synthesis of the electrodeposited *n*-Cu/Si-O-C composite.

Experimental Section

Preparation of electrolyte bath and Cu substrate: All chemicals including SiCl₄ (Sigma-Aldrich), tetrabutylammonium perchlorate (TBAP, Kanto Chemical), and propylene

carbonate (PC, Kishida, H₂O < 30 ppm) were used as-received and prepared in a super dry air room with a dew point lower than -50 °C.

For the dissolution of Cu ions and the co-deposition of *n*-Cu and Si-O-C composite, anodic and cathodic currents were applied, respectively. Then in each case, an electrolyte bath was prepared by dissolving 0.5 M of SiCl₄ and 0.5 M of TBAP into PC. The SiCl₄ and TBAP were used as the Si precursor and the supporting electrolyte, respectively.

A Cu plate was firstly rinsed in trichloroethylene and then ethanol by ultra-sonication for 20 min each. The rinsed Cu plate was further treated by electrolytic degreasing for 30 sec at 1 mA cm⁻² in degreasing bath, which was prepared by dissolving 40 g L⁻¹ of NaOH, 20 g L⁻¹ of Na₂CO₃, and 1 g L⁻¹ of sodium dodecyl sulfate in deionized water. Afterwards, an acid treatment of the Cu plate was carried out with 10 % H₂SO₄ followed by rinsing with deionized water and drying with N₂ gas. The Cu plate's dimensions were 10 mm x 10 mm.

Cu-dissolution and n-Cu/Si-O-C deposition by electrochemical reactions: The dissolution process of Cu ions was carried out using a three-electrode system that was composed of the pretreated Cu plate, a Pt wire, and a Li metal as working, counter and reference electrodes, respectively. The potentiostatic technique was performed for passing a charge of 1 C cm⁻² at 3.6 V vs. Li/Li⁺ using a potentiostat (Bio-Logic, VSP). The modified Cu plate was pulled out from the electrolyte bath following the anodic reaction, rinsed with dimethyl carbonate (DMC, Kanto Chemical), and vacuum dried for 2 hr. The electrolyte bath was preserved for the cathodic reaction.

After being fully dried, the modified Cu plate was brought back to an electrodeposition cell (having the same three-electrode system configuration as during the anodic reaction) for the co-deposition process of the *n*-Cu and the Si-O-C composite. The cathodic reaction was also performed by the potentiostatic technique at 1.3 V vs. Li/Li⁺ for passing a charge of either 5 or 15 C cm⁻² to deposit 0.06 or 0.18 mg cm⁻² of Si, respectively. To verify the effect of *n*-Cu incorporation on anode performance, the Si-O-C composite

anodes without *n*-Cu were also prepared as reported previously.³⁷ Briefly, the Si-O-C composites were electrodeposited by the galvanostatic technique using -1 mA cm^{-2} of current density for the passing charge of either 2 or 10 C cm^{-2} in electrolytic bath containing 0.5 M of SiCl_4 and TBAP dissolved in PC solvent to deposit 0.06 or 0.18 mg cm^{-2} of Si, respectively. The electrodeposition conditions and deposition profiles for the Si-O-C composite are summarized in Supporting Information Table S1 and Figure S5.

The potentials for both the anodic and cathodic reactions were selected by linear sweeping voltammetry (LSV, Hokuto Denko, HZ-5000), cyclic voltammetry (CV, Hokuto Denko, HZ-5000), and X-ray photoelectron spectroscopy (XPS, ULVAC-PHI Inc., PHI 5000 VersaProbe) measurements. All the processes for electrochemical treatment were carried out in an Ar filled glove box (dew point less than -110°C). The weight of electrodeposited Si was measured by inductively coupled plasma (ICP-AES, Thermo, iCAP6500) analysis.

Analysis of the anodic and cathodic reaction: Analysis of chemical species composed in the electrolyte bath caused by the anodic process was completed using UV-Visible spectra (UV-Vis spectra, JASCO, V 630) in the range of 200 – 550 nm. CV measurements were performed with a scan rate of 10 mV s^{-1} . The detailed measurement conditions will be explained in the Results and Discussion section. XPS analysis was performed to explore the surface chemistry after both anodic and cathodic reactions. The binding energies were corrected by setting the C 1s hydrocarbon peak to 284.8 eV. Morphology changes after both the anodic and cathodic reactions were observed by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4500). Elemental mapping images were observed by scanning transmission electron microscopy (STEM, Hitach, HF-2200, accelerating voltage = 200 kV) equipped with an energy-dispersive X-ray spectrometer (EDS). The STEM sample was prepared as follows. Firstly, the electrodeposited active material was dispersed in dehydrated ethanol (purity > 95.5 %, Kanto chemical). Subsequently, the dispersed active material was carefully mounted on a TEM-grid followed by vacuum drying overnight. Depth

profile scans of XPS were performed at intervals of 30 sec for 3 min by using 5 kV of Ar ion beam voltage. The crystalline structures after both anodic and cathodic reactions were characterized by grazing incidence X-ray diffraction (GIXRD, Rigaku, Rint-Ultima III).

Electrochemical characterizations of the n -Cu/Si-O-C composite anode: For the electrochemical test, coin-type (2032) half cells of the electrodeposited n -Cu/Si-O-C or the Si-O-C composites were assembled with Li metals and glass microfiber filters (Whatman, GF/A) soaked in 1 M of LiClO₄ in EC : PC (1 : 1 v/v, Tomiyama Pure Chemical, H₂O content < 20 ppm) in an Ar filled glove-box (dew point less than -110 °C). The electrolyte was selected because of its stable cycle performance as reported previously.³⁸ The electrochemical cycling test was carried out using a galvanostatic charge/discharge unit (Toyo system, TOSCAT-3100) using potentials between 0.01 and 1.20 V vs. Li/Li⁺ with a various loading current. Electrochemical impedance spectroscopy (EIS) was performed using a Biologic VSP potentiostat with impedance spectroscopy function over a frequency range of 100 kHz – 0.1 Hz with an AC amplitude of 10 mV.

Results and Discussion

As explained in the introduction, synthesis of the n -Cu/Si-O-C composite was carried out after dissolution of Cu ions from the Cu plate by means of an electrochemical method. Both anodic and cathodic reactions were performed via the potentiostatic technique at 3.6 and 1.3 V vs Li/Li⁺, respectively. To determine the applying potential points, LSV, CV and XPS, measurements were closely carried out. As shown in Figure 1a and b, the Cu plate was either negatively or positively swept from an open circuit potential (OCP). Supporting Information Table S2 summarized the LVS and CV measurement conditions including potentials on initiation, termination, and reversal points. Each Cu plate swept under various LSV and CV conditions was analyzed by wide scan of XPS to determine its surface state resulting from its electrochemical reaction. Sample A shown in Figure 1a was negatively swept from OCP to

1.4 V vs Li/Li^+ , resulting in no specific peaks. The XPS result of sample A in Figure 1c indicates strong peaks assigned to O 1s and C 1s with a weak peak assigned to Si 2p; this weak peak is likely the result of partially reduced or absorbed Si ion and organic carbonate molecule, herein PC. Sample B shown in Figure 1a was negatively swept from OCP to 0.0 V vs Li/Li^+ , showing a drastic increase in the reduction current from ca. 1.4 V vs Li/Li^+ . The XPS result of sample B in Figure 1c indicates strong peaks assigned to O 1s, C 1s, and Si 2p. In particular, a clear increase in peak intensity for Si 2p is observed, implying that deposition of the Si-O-C composite began at ca. 1.4 V vs Li/Li^+ . This result agrees with our previous results.¹⁸ Sample C shown in Figure 1b was positively swept from OCP to 3.6 V vs Li/Li^+ , showing an oxidation peak at ca. 3.4 V vs Li/Li^+ . The XPS result of sample C in Figure 1c presents strong peaks assigned to different core levels of the Cu element. This XPS result is in agreement with that of pure Cu substrate indicated by the black plot in Figure 1c. Sample D shown in Figure 1b was positively swept from OCP to 4.0 V vs Li/Li^+ , showing a sharp increase in the oxidation current at 3.6 V vs Li/Li^+ . Sample D in Figure 1c has a similar XPS result to that of sample C. Additionally, peaks assigned to the core level of Cl element were also observed for sample D. An unknown anodic reaction occurred at ca. 3.4 V vs Li/Li^+ and an electrochemical reaction between Cu and Cl elements were induced with further sweeping, which will be discussed in detail later. Sample E shown in Figure 1b was positively swept from OCP and reversed at 4.0 V vs Li/Li^+ followed by negative sweeping to 0.0 V vs Li/Li^+ . The CV measurement resulted in two cathodic peaks at ca. 1.6 and 2.7 V vs Li/Li^+ , which were not obtained with sample A. The XPS result of sample E in Figure 1c clearly shows peaks assigned to not only the Si-O-C composite but to the Cu element as well. Thus, the potential for the co-deposition of Cu and the Si-O-C composite was determined as ca. 1.3 V vs Li/Li^+ . To summarize, the LSV, CV, and XPS results suggested the anodic process for the dissolution of Cu ions at 3.6 V vs Li/Li^+ and the cathodic process for the co-deposition of Cu and the Si-O-C composite at 1.3 V vs Li/Li^+ .

Figure 2 displays (a) current transient curve, (b) UV-Vis spectra of the electrolyte bath and (c) morphological changes of the Cu plate as increases in passing charge are applied during the anodic process for dissolution of Cu ions. Points i, ii and iii in Figure 2a-c represent the termination points of the anodic process where charge passed on 0.1, 0.5 and 1 C cm⁻², respectively. In Figure 2a, the current density initially increased up to a maximum value showing ca. 2.4 mA cm⁻² at 0.1 C cm⁻², followed by a gradual decrease with further processes indicating ca. 1.7 mA cm⁻² at 1 C cm⁻². In Figure 2b, the UV-Vis spectra for the electrolyte baths containing 0.5 M of both SiCl₄ and TBAP dissolved in PC solvent following the anodic process with different passing charges are presented to determine the chemical species introduced by the anodic electrochemical reaction. Four distinctive peaks were obtained at 225, 253, 315, and 470 nm. The peaks at 253, 315 and 470 nm are ascribed to the complex ion, CuCl₃⁻, in PC solvent.³⁹ The peak at 225 nm is ascribed to d-d transition bands of the copper-chloro complex, in particular, trichloro complex in PC medium.³⁹ Pictures of the electrolyte baths are presented next to the UV-Vis spectra, showing the enrichment of the yellow color as the amount of passing charge increases, which is also in proportion to increases in intensities of the UV-Vis peaks. Hence, Cu ions directly dissolved from the Cu plate via the anodic reaction, leading to the release of trichlorocuprate ions to the electrolyte bath, whose concentration proportionally increased to the amount of passing charge. Herein, quantitative analysis of the trichlorocuprate ions in electrolyte bath was not performed. Figure 2c shows SEM images for the modified Cu substrate with different amounts of passing charge during the anodic process. In order to compare morphology changes, an as-received Cu substrate without any electrochemical treatment and subsequently fairly clear surface morphology is presented in Supporting Information Figure S1a. On the other hand, following the anodic process, highly roughened surfaces were observed, as shown in Figure 2c. The insets present surface images with high magnification where particles varied from several hundred nm to ca. 1 μm as increase in the amount of passing charge for the anodic process. The images clearly

show the particles densely covering the Cu substrate. In reference to the current density transient curve in Figure 2a and the SEM observation image in Figure 2c-i, it is assumed that the nucleation process of the particles was carried out up to point i where the current density has increased. Subsequently, the growth of crystals has occurred with further anodic reaction. GIXRD results shown in Supporting Information Figure S1b also validate the nucleation and growth of crystals seen in Figure 2c. GIXRD patterns of the as-received Cu plate and the samples obtained from point i, ii, and iii were compared to each other. The as-received Cu plate has strong peaks at $2\theta = 43.3, 50.4,$ and 74.1° ascribed to (111), (200), and (220) crystal plans, respectively. In sample i, strong peaks assigned to (111), (200), and (220) crystal plan of the as-received Cu plate were prominently obtained. Other peaks with weak peak intensities appeared at $2\theta = 28.5, 33.0, 47.4, 56.2, 69.3,$ and 76.5° ascribed to (111), (200), (220), (311), (400), and (331) crystal planes of a CuCl (nantokite, PDF-# 00-006-0344), respectively. Stronger intensity of the diffraction pattern representing CuCl was attained for sample ii with weakened-peak intensity of the Cu plate. Finally, sample iii predominantly shows a diffraction pattern assigned to CuCl without the Cu plate, which implies that CuCl crystals were considerably grown, completely covering the Cu plate. To summarize, Cu ions were dissolved from the Cu substrate by the anodic reaction. Afterwards, a deposit layer of CuCl was formed on the Cu substrate by the reaction of Cu (I) ions with chloride ions, which caused a decrease in the current density during the anodic process. At the same time, a complex CuCl_3^- ion was generated within the electrolyte bath via the reaction between Cu (II) ions and chloride ions. The relevant electrochemical reactions are indicated below.

A current transient curve for the cathodic co-deposition of Cu and the Si-O-C composite is presented in Figure 3a, showing a high reduction current at the initial stage followed by a rapid decrease until it was stabilized at ca. -1 mA cm^{-2} . The point where the current density began to be constant was designated as iv. XPS results of the point iv was compared to the point iii in Figure 2a to clarify the cathodic current dependent change of the modified-Cu substrate chemical state. The XPS spectra in Figure 3c were obtained following Ar ion etching for 1 min. As already discussed with XRD results in Supporting Information Figure S1b, CuCl particles were deposited on the Cu substrate after anodic treatment, which was derived from simultaneous reactions of dissolution of Cu ions and generation of trichlorocuprate ions in the electrolyte bath. In Cu 2p3 spectra, both iii and iv showed strong peaks assigned to ca. 933.0 eV. In general, Cu (0) and Cu (I) are not definitely distinguished by the Cu 2p3 core level since their spectra are widely overlapped in the ca. 932 – 933 eV region.⁴⁰ Therefore, $L_{3}M_{4,5}M_{4,5}$ Auger peak and Cu 3d spectra were also measured to elucidate their oxidation states. $L_{3}M_{4,5}M_{4,5}$ Auger peaks of Cu were obtained at 572.5 and 568.1 eV with samples iii and iv, respectively. The binding energy of samples iii and iv were obtained where they were defined as Cu (I) and Cu (0).^{41, 42} In particular, that of sample iv was in agreement with as-received Cu plate shown in Supporting Information Figure S2a. A small satellite peak at ca. 7 eV was obtained with sample iii in the Cu 3d spectra, ascribing it to the oxidized state of Cu.⁴³ In sample iv, the small satellite peak disappeared and a broad peak at ca. 3 eV was observed, which was in agreement with metallic Cu (see Supporting Information Figure S2b). A strong peak was obtained with sample iii in the Cl 2p3 spectra, which was derived from the CuCl particles after the anodic process. However, the peak disappeared in sample iv. To summarize the results of the XPS investigation, CuCl particles caused by the anodic process were reduced during the initial stage of the cathodic process, which was verified from the high reduction current as indicated in Figure 3a. Consequently,

the modified-Cu plate with metallic Cu particles was formed when the cathodic current became constant.

After the entire deposition process was completed, XPS and GIXRD were performed to explore the changes of the deposit. The XPS was performed with Ar ion etching for 3 min as shown in Figure 3d. The intensities of spectra were normalized to the highlighted peak. In Cu 2p3 spectra, the spectrum at the surface without Ar ion etching showed no specific peaks. However, in the inner part following Ar ion etching, strong peaks assigned to 933 eV were continuously obtained. In O 1s and C 1s spectra, strong peaks assigned to ca. 533 eV and 284.8 eV were obtained from the surface to inner part for 3 min of Ar ion etching. For the O 1s spectra, these peaks represented oxygen bonded to carbon in the state of C-O-C.^{18, 44} For the C 1s spectra, the strong peaks were ascribed to C-C bonding, which was derived from decomposition of organic carbonate solvent.^{18, 44} For Si 2p spectra, strong peak assigned to ca. 103 eV was obtained at the surface without Ar ion etching, indicating that the chemical state of Si existed as SiO_x in this composite. Small shoulders on the peaks at ca. 99.8 eV ascribed to Cu-silicide began to appear after 1 min of Ar ion etching. Appearance of the Cu 2p3 peak after 1 min of Ar ion etching is in agreement with the existence of the Cu-silicide peaks in the Si 2p core level. Hence, the XPS results verified that the cathodic reaction resulted in co-deposition of Cu and Si-O-C composite. The depth profile of Cu 2p3 and Si 2p core levels was summarized and the weight ratio calculated for the two elements as shown in Supporting Information Figure S3a. The weight % of Cu and Si at the surface was calculated as 45.9 and 54.1 %, respectively. The weight % and atomic % of each element including oxygen and carbon was also calculated and shown in Supporting Information Figure S3b.

The profile shows different values following Ar ion etching for 3 min. The average weight % value for Cu and Si was calculated as 81.0 and 19.0 %, respectively. The Cu content in the inner part significantly increased compared to its surface. It is assumed that the XPS initially detected the surface layer, in general less than 10 nm, where the Cu/Si-O-C

composite mostly existed. Afterwards, the Cu particles which consisted of the modified Cu substrate were predominantly measured in the inner part, causing a significant increase in the weight % value for Cu (see scheme in Supporting Information Figure S3e, which presents Cu particles on Cu substrate prepared during the anodic process and the electrodeposited Cu/Si-O-C composite). The thickness was ~ 35 μm as observed from the cross section view in Supporting Information Figure S3d. Furthermore, the depth profile measured by XPS verified homogeneity of each element, i.e. Cu, Si, O, and C, following a given time of Ar ion etching as shown in Supporting Information Figure S3c. Meanwhile, Cu 2p_{3/2} and Si 2p spectra of the Si-O-C composite without Cu incorporation are also displayed for comparison (in Supporting Information Figure S4a and b). Cu 2p_{3/2} spectra were not detected following 3 min of Ar ion etching. Moreover, Si 2p spectra indicated only SiO_x peaks assigned to ca. 103 eV without any peaks Cu-silicide peaks at 99.8 eV.

Changes in the GIXRD patterns following the anodic and cathodic processes are summarized in Figure 3b. The as-received Cu plate is also shown for comparison. As already discussed, the GIXRD pattern of the CuCl crystal was obtained with the modified Cu substrate after the anodic process. However, the strong CuCl pattern evidently disappeared after the cathodic process was completed. In its GIXRD pattern, two peaks at $2\theta = 50.4$ and 74.1° ascribed to (200) and (220) crystal planes of metallic Cu were prominent. Average crystallite size of the incorporated Cu was estimated by the *Debye-Scherrer formula*, equation (5):

$$D = \frac{k\lambda}{\beta \cos\theta} \quad (5)$$

where k is Scherrer constant, λ is the X-ray wavelength, β is full width at half maximum, and θ is the scattering angle. From this equation, average crystallite size of the incorporated Cu metal was calculated as less than ca. 21 nm (Supporting Information Table S3). Moreover, it was confirmed that Si existed as the amorphous phase due a lack of crystal planes in the

GIXRD pattern. To summarize, the amorphous Si-O-C composite was deposited with the incorporation of nano-sized Cu particles.

SEM images of the *n*-Cu/Si-O-C composite were observed and indicated in Figure 4a showing different magnifications. In the low magnification image, it was observed that the *n*-Cu/Si-O-C composite was densely deposited. In comparison to the modified Cu substrate, causing highly roughened surface morphology (See Figure 4a inset), the morphology was clearly changed, i.e., the highly roughened surface changed to a film-like flat surface. In a higher magnification image, small particles with sizes of 50-100 nm were aggregated and formed the flat surface. EDS elemental mapping results for copper, silicon, oxygen, and carbon are shown in yellow, red, white, and green, respectively, in the high-angle annular dark field STEM (HAADF-STEM) and SEM images in Figure 4b and c. As discussed for SEM images, small particles formed aggregation of large clusters and the clusters homogeneously contained each element, i.e., Cu, Si, O, and C. The weight % of Cu and Si was calculated as 43.8 and 56.2 %, respectively, which are similar to the values calculated from the XPS measurements of the surface elements (Supporting Information Figure S3). The weight % of each element was calculated as 25.5, 32.7, 20.8, and 21.0 with Cu, Si, O, and C, respectively. The HAADF-STEM image indicates well-dispersed aggregation of nano particles of sizes less than ca. 40 nm. This homogeneous incorporation of *n*-Cu was expected to effectively improve electrical conductivity of the Si-O-C composite.

Electrochemical performance of the *n*-Cu/Si-O-C composite was carefully tested. Potential profiles of the *n*-Cu/Si-O-C composite anode are presented in Figure 5a with the 20th, 40th, 60th, 80th, and 100th cycle, which were obtained with a loading current of C/2. Insets of Figure 5a display the profile at the 1st cycle, showing significantly low coulombic efficiencies, i.e., 28.8 %. This poor coulombic efficiency increased up to 88.2 % for the 2nd cycle. The large irreversible capacity at the 1st cycle is attributed to the conversion reaction of SiO_x to Li_ySi and Li₂O.^{18, 45} The Si-O-C composite was made of a unique structure consisting

an active material SiO_x phase combined with decomposed product of organic carbonate solvent. Oxidized Si phase mainly consisted of the composition of SiO_x active material with partial metallic Si as revealed by XPS measurement in our previous work.¹⁸ Therefore, the conversion reaction of the SiO_x phase to Li_ySi and Li_2O to activate oxidized Si phase was dominantly carried out at the 1st lithiation process along with SEI formation, causing poor coulombic efficiency. Furthermore, a plateau at ca. 1.3 V vs Li/Li^+ demonstrated that the irreversible capacity was derived from SEI formation as well. Potential profiles indicating a typical amorphous SiO_x anode were obtained from the subsequent cycles.⁴⁵ These results were further investigated with differential capacity (dQ/dV) plots (DCPs) as shown in Figure 5b. During the lithiation process, DCPs indicated broad cathodic peaks at ca. 0.19 and 0.07 V vs Li/Li^+ attributed to phase transition between amorphous Si to Li_xSi phases.⁴⁶ Broad anodic peaks at ca. 0.33 and 0.45 V vs Li/Li^+ ascribed to a phase transition during the delithiation process of amorphous Si electrodes were also obtained.⁴⁷ Meanwhile, in the potential profiles, a small plateau at ca. 0.34 V vs Li/Li^+ was obtained at the 20th cycle, which gradually diminished with further cycles and disappeared from the 80th cycle onward. DCPs more clearly showed this behavior via the irreversible peak at ca. 0.34 V vs Li/Li^+ . The peak gradually increased from the 20th to the 40th cycle followed by gradual diminution and final disappearance from the 80th cycle. These observations were likely due to the structural breakdown of the Li ternary silicides (Li-M-Si ; M = metal, herein Cu) into Cu and Li-Si phase.⁴⁸

Figure 6a and b indicate cycle performance carried out under a C/2 loading current, delivering specific and areal delithiation capacity for the $n\text{-Cu/Si-O-C}$ composite anodes. For the cycling test, the $n\text{-Cu/Si-O-C}$ composite anodes containing either 0.06 or 0.18 mg cm^{-2} of Si were prepared. To verify the effect of $n\text{-Cu}$ incorporation on anode performance, the Si-O-C composite anodes without $n\text{-Cu}$ were also prepared to contain either 0.06 or 0.18 mg cm^{-2} of Si for comparison of the effects of $n\text{-Cu}$ incorporation. (Their electrodeposition profiles

and as-electrodeposited SEM images are presented in Supporting Information Figure S5a-c.) The opened-circle plot in blue shows the Si-O-C composite with 0.06 mg cm^{-2} of Si. Its areal delithiation capacity delivered $0.088 \text{ mA h cm}^{-2}$ at the 1st cycle, which slightly decreased with further cycles delivering $0.060 \text{ mA h cm}^{-2}$ at the 125th cycle, as shown in Figure 6a. The opened-square plot in red shows the *n*-Cu/Si-O-C composite with 0.06 mg cm^{-2} of Si for comparison. The *n*-Cu/Si-O-C composite achieved areal delithiation capacities of 0.102 and $0.084 \text{ mA h cm}^{-2}$ at the 1st cycle and the 92nd cycle, respectively, causing ca. 30 % improvement relative to the Si-O-C composite. Two other anodes, with and without *n*-Cu incorporation, containing 0.18 mg cm^{-2} of Si were prepared by the same deposition method. The blue solid-circle shows the Si-O-C composite with 0.18 mg cm^{-2} of Si. This composite attained areal delithiation capacity of $0.270 \text{ mA h cm}^{-2}$ at the 1st cycle and the capacity gradually decreased delivering $0.189 \text{ mA h cm}^{-2}$ at the 125th cycle. The *n*-Cu/Si-O-C composite anode containing 0.18 mg cm^{-2} of Si is shown as red solid-square; this composite delivered areal delithiation capacities of 0.315 and $0.247 \text{ mA h cm}^{-2}$ at the 1st cycle and the 125th cycle, respectively. The areal delithiation capacity for the 0.18 mg cm^{-2} of Si composites also improved by 30 % upon the incorporation of *n*-Cu.

The areal delithiation capacities were converted to specific delithiation capacities calculated per gram of deposited Si and shown in Figure 6b. (See Supporting Information Figure S6a indicating specific capacity calculated per gram of elements with either “Si, O, and C”, i.e. 0.46 mg cm^{-2} , or “Cu, Si, O and C”, i.e., 0.61 mg cm^{-2} . The total weight loadings of the active layer were calculated based on XPS and ICP measurements.) Herein, all plots were equally represented as explained in Figure 6a. The Si-O-C composite anodes attained specific delithiation capacities delivering approximately 1280 and 1000 mA h g^{-1} of Si at the 5th and the 125th cycle, respectively. The *n*-Cu/Si-O-C composite anodes achieved specific delithiation capacities delivering approximately $1520 - 1600$ and 1390 mA h g^{-1} of Si at the 5th and the 92nd cycle, respectively. Approximately 30 % improvement of the specific

delithiation capacities was attained with the *n*-Cu/Si-O-C composite anodes compared to the Si-O-C composite anodes. It was assumed that the active material utilization is improved by enhancing electric conductivity in the electrode. Further analysis for the enhanced electric conductivity in the electrode will be discussed in detail with the EIS results.

Coulombic efficiencies of the *n*-Cu/Si-O-C and the Si-O-C composite anodes containing 0.18 mg cm^{-2} of Si were measured and are shown in Figure 6c. Both anodes achieved high coulombic efficiencies over 99.8 % at the end of the cycle test. However, the coulombic efficiencies during initial cycles were significantly distinguished. The coulombic efficiency over 99 % was obtained at the 9th cycle with the *n*-Cu/Si-O-C composite anode in spite of the 22nd cycle with the Si-O-C composite anode. Moreover, a high coulombic efficiency over 99.5 % was consistently obtained after the 13th cycle for the *n*-Cu/Si-O-C composite anode but after the 51st cycle for the Si-O-C composite anode.

Figure 6d presents rate capabilities for the *n*-Cu/Si-O-C and the Si-O-C composite anodes containing 0.18 mg cm^{-2} of Si. The loading current was varied from C/5 to 10 C. Evidently, *n*-Cu/Si-O-C composite obtained greater specific delithiation capacity values than did the Si-O-C composite anode from all loading currents. The *n*-Cu/Si-O-C composite anode attained ca. $1659 \text{ mA h g}^{-1}_{\text{of Si}}$ at the 1st cycle with a loading current of C/5. The specific delithiation capacity value gradually decreased with a higher loading current delivering ca. 1424, 1315, and $1114 \text{ mA h g}^{-1}_{\text{of Si}}$ at the 11st, 21st, and 31st cycle with C/2, 1 C, and 2 C, respectively. Although the specific delithiation capacity value steeply decreased down to 696 and $337 \text{ mA h g}^{-1}_{\text{of Si}}$ at the 41st and 51st cycle with 5 C and 10 C, respectively, the *n*-Cu/Si-O-C composite anode showed a far higher value than that of the commercial graphite anode, whose theoretical capacity is $372 \text{ mA h g}^{-1} (\text{LiC}_6)$.^{1,2} Meanwhile, the rate capability of the Si-O-C composite attained ca. $1530 \text{ mA h g}^{-1}_{\text{of Si}}$ at the 1st cycle with a loading current of C/5. The Si-O-C composite also showed a gradual decrease in the specific delithiation capacity value as the loading current increased, i.e., ca. 1229 and $1092 \text{ mA h g}^{-1}_{\text{of Si}}$ at the 11st and

21st cycle with C/2 and 1 C, respectively. However, the specific delithiation capacity value decreased down to less than 1000 mA h g⁻¹_{of Si} with 2, 5, and 10 C, delivering 874, 485 and 142 mA h g⁻¹_{of Si} at the 31st, 41st, and 51st cycle. Furthermore, the rate capabilities for each anode were plotted as capacity retention against the 1st cycle and shown in Supporting Information Figure S6b. The *n*-Cu/Si-O-C composite anode attained stable capacity retention delivering 93.4 % at the 10th cycle with C/5 of loading current. Afterwards, it achieved stable and high capacity retention delivering over 60 % up to the 40th cycle, i.e., 85.5, 78.2 and 66.2 % with a loading current of C/2, 1 C, and 2 C, respectively. The Si-O-C composite anode also obtained stable capacity retention delivering 91.8 % at the 10th cycle with C/5 of loading current. On the other hand, the capacity retention rapidly decreased as the loading current increased, resulting in 80.4, 70.0, and 55.8 % with C/2, 1 C, and 2 C of loading current, respectively. Both anodes indicated low capacity retention values with high loading current such as 5 C and 10 C delivering only 40.9 and 16.8 % for the *n*-Cu/Si-O-C composite anode and 30.8 and 7.4 % for the Si-O-C composite anode, respectively. However, the *n*-Cu/Si-O-C composite anode gave fairly stable cycle performance even with a loading current of 10 C compared to that of the Si-O-C composite anode. This improvement in cycle stability also indicates enhanced rate capability for the *n*-Cu/Si-O-C composite anodes. Based on these improved electrochemical features including a higher specific delithiation capacity value and more stable capacity retention, the incorporated *n*-Cu was expected to enhance the electrical connections among the active materials (the Si-O-C composite), forming a conductive network.

To further examine the improved electrochemical performances of the *n*-Cu/Si-O-C composite and validate the electrical connection of *n*-Cu incorporation, Nyquist plots for both composite anodes were compared and are shown in Figure 7a and b for the 1st, 10th, 30th, and 50th cycle. Both anodes were tested at 100 % state of charge at 0.01 V vs Li/Li⁺ with a loading current of C/10. All spectra for both electrodes indicated similar features containing

suppressed semi-circles from high to mid frequency regions and an inclined line at the low frequency region, in agreement with other works on Si anode material.^{27, 34, 49, 50} These features represented the charge transfer resistance (R_{ct}) and Li^+ diffusion in solid active material, respectively. Moreover, the semi-circle contained R_{ct} and electric conductivity of the entire electrode. The larger magnitudes of the semicircle were clearly illustrated with the comparison of the Si-O-C composite anode to the *n*-Cu/Si-O-C composite anode from all of the measured cycles. The findings implied that the R_{ct} was remarkably reduced by *n*-Cu incorporation, which plays a role in enhancing the electrical conductivity of the entire Si-O-C composite electrode. Moreover, R_{ct} of the *n*-Cu/Si-O-C composite anode at the 50th cycle resulted in the same magnitude of the semicircle with that of 30th cycle in spite of an enlarged semicircle at the 50th cycle with the Si-O-C composite anode. This implied that degradation of the anode active material occurred more with the Si-O-C composite relative to the *n*-Cu/Si-O-C composite. Generally speaking, there are mainly two types of electrode degradation for the Si anode: mechanical and electrochemical degradation. The former is a well-known phenomenon deteriorating the Si anode by large volume changes.⁵¹ According to the literature, electrochemical degradation is derived from continuous SEI formation on the Si active site. The continuous SEI formation accompanies low coulombic efficiency because electrons are consumed by the decomposition of the electrolyte other than the alloying reaction between Li^+ and Si active materials, which is accelerated by low electrical conductivity of the active materials. Juchuan Li et al. demonstrated that the electrochemical degradation was significantly mitigated by not only enhancements to Li^+ conductivity but also by electric conductivity.⁵¹ Hence, it was deduced that the enhanced electrical conductivity by *n*-Cu incorporation realized suppression of further electrochemical degradation on the electrode resulting in an R_{ct} increase. The results of improved coulombic efficiency with *n*-Cu/Si-O-C composite (in Figure 6c) also validated the suppressed electrochemical degradation. Furthermore, total irreversible capacities between the 1st and 100th cycle were obtained as

5158.5 and 4906.2 mA h g⁻¹ with the *n*-Cu/Si-O-C and the Si-O-C composite anodes, respectively. These values correspond to 2.8 and 3.5 % relative to total delithiation capacity, and suggest more stable electrochemical degradation for the *n*-Cu/Si-O-C composite anodes. Additionally, the enhanced electrical conductivity also effects initial irreversible capacity related to the SEI formation reaction at the initial cycle. The percentage changes for irreversible capacities at the 2nd cycle and subsequent cycles were clearly different for the two anodes. Higher percentage of irreversible capacity was obtained with the *n*-Cu/Si-O-C composite anodes at the 2nd cycle, i.e., 11.8 and 10.4 % with the *n*-Cu/Si-O-C and the Si-O-C composite anodes, respectively. However, a lower percentage for irreversible capacity was obtained with the *n*-Cu/Si-O-C composite anodes from the 3rd cycle onward (see Supporting Information Table S4). These results indicate the difference for the *n*-Cu/Si-O-C composite compared to the Si-O-C composite at the 2nd cycle following the vigorous SEI formation reaction. The higher electrical conductivity from *n*-Cu incorporation possibly enhanced the lithiation/delithiation reaction with more active material such that the intensive SEI formation reaction was obtained at the initial cycle. On the other hand, further SEI formation on the Si-O-C composite continued during subsequent cycles in comparison to the *n*-Cu/Si-O-C composite.

Morphological changes at initial cycle, i.e., after lithiation and delithiation states of the 1st cycle, and after 120th cycle were closely observed to figure out ductile property for buffering effect of the *n*-Cu incorporation in Figure 8a and b. After lithiation of the 1st cycle, the *n*-Cu/Si-O-C composite anode shows volume change with perpendicular expansion at local site of the flat surface (Figure 8a-ii). After delithiation of the 1st cycle, the swelled volume was shrunk back showing flat surface with cracks consisting of domains with sized of several μm (Figure 8a-iii). On the other hand, the Si-O-C composite showed volume expansion toward all direction on entire surface after lithiation of the 1st cycle (Figure 8b-ii). Even after delithiation, the expanded structure did not revert to its original structure observed

in as-prepared sample, showing film-like surface morphology (Figure 8b-iii). After long cycling of 120 cycles (Figure 8a and b-iv), they show almost similar morphologies with pulverized particle and their aggregation with cracks on the surface in spite of the obvious morphological differences between both anodes at the initial cycle. From these SEM observation, it is considered that mechanical degradation was suppressed by *n*-Cu incorporation at the initial cycle buffering volume expansion toward perpendicular at local site of the flat surface. However, the effective suppression of volume expansion was not significantly observed after long cycles. This behavior is well corresponding to cycle retention of both anodes. Their cycle retentions (delithiation) are plotted against capacity of the 1st and 20th cycle and shown in Supporting Information Figure S7a and b, respectively. First of all, the tendency of decrease in capacity shows similar slope with both anodes. The cycle retentions against capacity of the 1st cycle obtained 95 and 90 % at the 2nd cycle and gradually decreased down to 83 and 75 % at 50th cycle with *n*-Cu/Si-O-C composite and Si-O-C composite anode, respectively. Finally, they show 77 and 70 % at 120th cycle with *n*-Cu/Si-O-C composite and Si-O-C composite anode, respectively. However, the cycle retentions against capacity of 10th cycle show 96 and 95 % at 50th cycle 90 and 89 % at 120th cycle with *n*-Cu/Si-O-C composite and Si-O-C composite anode, respectively. This results indicate that initial capacity fading was severe with Si-O-C composite compared to *n*-Cu incorporation. It is considered that the improved capacity retention during the initial cycles is due to buffering effect and ductility of *n*-Cu, which was observed from SEM images taken at the initial cycle as discussed in Figure 8.

Conclusion

In summary, the *n*-Cu/Si-O-C composite was electrochemically synthesized by *n*-Cu incorporation into the Si-O-C composite and its electrochemical performance as an anode

material for Li secondary battery was thoroughly examined. Cu ions that were directly dissolved from a Cu substrate by anodic current were co-deposited with Si, resulting in a nano-sized metallic conductive network within the Si-O-C composite. The prepared *n*-Cu/Si-O-C composite achieved improvements in electrochemical performance as an anode material due to its enhancements in the electron path and electrical contact between the active materials. As a result, electrochemical degradation was stably suppressed with the *n*-Cu/Si-O-C composite. Furthermore, buffering effect and ductility of *n*-Cu was effected during initial cycles, causing improved capacity retention at initial cycles.

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Captions of figures

Scheme 1. Schematic illustration of the novel stepwise approach for electrochemical synthesis of *n*-Cu/Si-O-C composite. Cu ions were directly dissolved from the Cu substrate by anodic current and CuCl was simultaneously deposited on the Cu substrate. Afterward, the *n*-Cu/Si-O-C composite was synthesized by co-deposition of the dissolved Cu ion and the Si-O-C composite by cathodic current. (① reference electrode; Li metal, ②, ④ working electrode; Cu plate and modified Cu plate, respectively, ③ counter electrode; Pt wire).

Figure 1. LSV (a) and CV (b) of the Cu plate swept in 0.5 M of SiCl₄ and TBAP dissolved in PC solvent under 5 different measured conditions and (c) their XPS spectra with wide scan.

Figure 2. (a) Current transient curve during the anodic process, (b) UV-Vis spectra for the change of the electrolyte bath and (c) morphological changes of the Cu plate, respectively, at point i, ii and iii (as increase in passing charge during the anodic process, i.e., i: 0.1 C cm⁻², ii: 0.5 C cm⁻², iii: 1 C cm⁻²).

Figure 3. (a) Current transient curve during the cathodic co-deposition of Cu and the Si-O-C composite, (b) GIXRD patterns of the *n*-Cu/Si-O-C composite, the modified Cu substrate, as-received Cu substrate and CuCl (PDF-# 00-006-0344), (c) XPS spectra of Cu and Cl elements at the point iv indicated in Fig. 3(a), (d) XPS spectra of Cu, O, C, and Si elements of the *n*-Cu/Si-O-C composite (Ar ion etching was performed for 3 min).

Figure 4. (a) SEM images, (b) EDS element mapping of copper, silicon, oxygen and carbon shown as yellow, red, white and green color, respectively with SEM image and (c) high-angle annular dark field STEM (HAADF-STEM) of the *n*-Cu/Si-O-C composite.

Figure 5. (a) Potential profiles and (b) DCPs of the *n*-Cu/Si-O-C composite anode.

Figure 6. (a) Areal, (b) specific delithiation capacity, (c) coulombic efficiency of the *n*-Cu/Si-O-C and the Si-O-C composite anodes carried out under C/2 of loading current and (d) rate capabilities of the *n*-Cu/Si-O-C and the Si-O-C composite anodes.

Figure 7. Nyquist plots for the *n*-Cu/Si-O-C and the Si-O-C composite anodes tested at 100 % state of charge where fully charged (lithiation) down to 0.01 V vs Li/Li⁺ with loading current of C/10.

Figure 8. SEM images of (a) *n*-Cu/Si-O-C composite and (b) Si-O-C composite at different SOC state and cycle number (i) as-prepared, (ii) fully lithiated state at the 1st cycle, (iii) fully delithiated state at the 1st cycle, and (iv) after 120th cycle.

Biosketch

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Tokihiko Yokoshima is a researcher (associate professor) in Faculty of Science and Engineering, Waseda University. He worked as a Post-doctoral Research Scientist in National Institute of Advanced Industrial Science and Technology (AIST). His research area is in the field of material chemistry for thin film and electrochemical energy devices. He is working on thin film materials design of high functional materials for rechargeable batteries and electronics devices. He also interested in the development and improvement of the electrochemical impedance spectroscopy for the rechargeable batteries as non-destructive diagnosis of the devices.

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Toshiyuki Momma

Toshiyuki Momma is a Professor of Department of Applied Chemistry and Department of Nanoscience and Nanoengineering, Faculty of Science and Engineering, Waseda University. He worked at University of Minnesota, USA. His research area is in the field of electrochemical energy devices. He is working on materials design of electrodes for rechargeable batteries and fuel cells, including anode and electrolyte for future batteries. He also interested in the development and improvement of electrochemical impedance spectroscopy. He is currently working on the in-situ electrochemical impedance analysis of rechargeable batteries and fuel cells as non-destructive diagnosis of the devices.

Tetsuya Osaka

Tetsuya Osaka is a Professor Emeritus of the Department of Applied Chemistry, Waseda University, Tokyo, Japan. He was President of the Electrochemical Society (ECS) after serving as Vice President of the International Society of Electrochemistry (ISE), etc.

The recent works focus on a newly “electrochemical nanotechnology”. His technical contributions have been recognized by many awards including Medal with Purple Ribbon bestowed from the Decoration Bureau of the Cabinet Office, Japan, Pergamon Electrochimica Acta Gold Medal of ISE in 1998, etc. He has been elected as a Fellow of IEEE (2002), ECS (2002), IUPAC (2004) and ISE (2006).

Figure1

Figure2

Figure3

Figure4

Figure 5

Figure 6

Figure7

Figure8

scheme1

Graphical Abstract