Electrophoretically deposited carbon nanotube anchor layer to improve areal capacity of Si-O-C composite anode for lithium secondary batteries

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Abstract

In this study, we report the preparation of carbon nanotubes (CNTs) anchor layer on a Cu substrate (CNTs/Cu) by using electrophoretic deposition technique. The CNTs anchor layer increases adhesion strength between Si-O-C composites and Cu substrate, as a result, it is possible to improve deposited Si amounts and areal capacity. The electrodeposited Si-O-C composites on CNTs/Cu (Si-O-C/CNTs/Cu) show homogenously coated surface morphology without cracks even large passing charge for electrodeposition of 15 coulomb cm^{-2} , resulting in 0.21 mg cm^{-2} of deposited Si amounts. On the other hand, Si-O-C composites deposited on as-received Cu substrate (Si-O-C/Cu) begin to peel off from substrate at 8 coulomb cm^{-2} of passing charge, resulting in 0.13 mg cm^{-2} of deposited Si amounts, and decrease down to 0.10 mg cm^{-2} at 15 coulomb cm^{-2} of passing charge. As a results, the improved Si amounts deposited on CNTs/Cu substrate achieve higher areal capacity, delivering 0.24 mA h cm^{-2} , which attains increase in 84.6 % in comparison to Si-O-C/Cu, which has areal capacity of 0.13 mA g cm^{-2} at 8 coulomb cm^{-2} of passing charge. Moreover, the Si-O-C/CNTs/Cu shows improved anode performances including discharge capacity and C-rate performance of the Si-O-C composites than Si-O-C/Cu without CNTs anchor layer.

Keywords: Electrophoretic deposition, Electrodeposition, Carbon nanotubes, Si-O-C composites, CNTs anchor layer, Li secondary battery.

1. Introduction

Energy conversion system such as solar cell, fuel cell [1,2] and energy storage devices such as capacitor, lithium ion batteries (LIBs) [3,4] have been researched and developed to solve environmental problems such as global warming, severe climate change, and exhaustion of fossil fuel [5-7]. Among them, the LIBs have attracted as next generation energy storage devices because of their outstanding physical and chemical properties like high energy density, no memory effect, and high working voltage. Researches and developments on materials of LIB components, such as cathode and anode active material, electrolyte, separator and so on, have been vigorously carried out to improve their energy and power density, stable cycle ability, low cost, and safety as well for their application on electric vehicles, medical devices, home appliances, and industrial machines in near future [8-10].

Graphite has been widely used as an anode active material due to its low cost, natural abundance, easy handling, eco-friend, and stable intercalation/de-intercalation with Li at low potential (~ 0.1 V vs. Li/Li⁺) [11]. For enhanced capacity of anode, carbon nano fiber, carbon nano tubes (CNTs), and graphene have been researched [12-16].

Recently, silicon-based materials have been attracted as a promising anode active material instead of carbon materials because of their light weight, abundance in the nature, and it can alloying/de-alloying with Li at low working potential (~ 0.5 V vs. Li/Li⁺) [17-19]. Moreover, it has higher theoretical capacity than graphite (silicon: 4200 mA h g^{-1} , graphite: 372 mA h g^{-1}). In spite of these advantages, silicon suffered from volume change up to 400 % during charge/discharge cycling, which lead to severe pulverization of silicon particle, and it lead to loss of electronic contact with active materials and current collector, resulting in fading anode performance.

Many researches have been studied to overcome above problems by nano-scale silicon size [20, 21], combination with carbon materials [22], surface modification of substrate [23, 24]. For instance, Y. Zhao, et al. synthesized the hierarchical micro/nano porous silicon anode by wet-chemical etching method, which has porous anode material, and it can be endure the large volume change during charge/discharge process, showing good cycle ability over 50 cycles with good discharge capacity (1500 mA h g⁻¹ with the current density of 100 mA h g⁻¹). In addition, large scale production of silicon-based anode material could be obtained from wet-chemical etching method for industrial fields [25]. B. Liu, et al. reported the nanowires-carbon textiles matrix anode without binder materials by spray-coating method. The obtained silicon and carbon composite delivered a high reversible specific capacity (2950 mA h g⁻¹ at 0.2 C), good coulombic efficiency of 92% at 1st cycle, and stable cycle ability for 200 cycles. Moreover, the nanowires-carbon textiles matrix anode can apply to flexible devices due to its flexibility of carbon textiles. The full-cell assembled with nanowires-carbon textiles matrix anode and commercial LiCoO₂ cathode shows enhanced reversible discharge capacity (1580 mA h g⁻¹ at 1 C) with high coulomb efficiency (ca. 99.7%). In addition, the designed full-cell demonstrates the stable voltage profile of 3.24 V under several situation such as curvature, temperature, and humidity [26]. Furthermore, S. Komaba, et al. researched the sodium polyacrylate (PAANa) as polymer binder for silicon-graphite anode, and its electrochemical properties were compared with Polyvinylidene fluoride (PVdF) binder. The anode prepared with PVdF binder was peeled off from the current collector after charge/discharge. On the other hand, the silicon-graphite anode synthesized with PAANa binder shows stronger adhesion strength even after charge/discharge, which can deliver around 800 mA h g⁻¹ with good capacity retention [27].

In our previous studies, a novel Si-O-C composites was deposited directly onto copper substrate without binder and conductive additive by electrodeposition from an organic solvent, resulting in high discharge capacity around of 1045 mA h (g of Si)⁻¹ at 2000th cycle and 842

$\text{mA h (g of Si)}^{-1}$ with the current density of $250 \mu\text{A cm}^{-2}$ (1.0 C) with outstanding stability over 7200 cycles [28]. Despite the high discharge capacity of Si-O-C composites as anode, it is not easy to obtain the high areal capacity, which is thicker Si-O-C composite film, by Si-O-C electrodeposition because of weak adhesion strength between Si-O-C composites and Cu substrate, leading the Si-O-C composite to peel off from substrate due to its stress during the electrodeposition. In order to increase the adhesion strength between Si-O-C composites with current collector, new type surface modified substrate, namely nickel micro-nanocones hierarchical structured substrate (NMS), was prepared as current collector via electrodeposition method for Si-O-C electrodeposition. The Si-O-C composites deposited on NMS/Cu substrate achieved improved anode performance, showing high reversible discharge capacity of around $800 \text{ mA h (g of Si)}^{-1}$ ($600 \mu\text{A h cm}^{-2}$) with 88% capacity retention for 100 cycles [29]. Herein, we introduce other way to enhance adhesion strength between Si-O-C composites and Cu substrate by surface modification of Cu substrate using CNTs, which have high electric conductivity ($5 \times 10^5 \text{ S m}^{-1}$) with lightweight [30-34]. The CNTs deposited Cu substrate was prepared by electrophoretic deposition with CoCl_2 in isopropyl alcohol (IPA) [ref 35]. Electrophoretic deposition method is widely used useful way to synthesize thin layer because it is easy to control the thickness of deposited film and loading amounts by time, voltage, and so on. In addition, surface charge of CNTs can be controlled by various additives such as $\text{Mg}(\text{NO}_3)_2$, NaOH , CuCl_2 , and $\text{Al}(\text{NO}_3)_3$, and these kinds of materials can effect on their stability of suspension [36-40]. The Si-O-C composites deposited on CNTs anchor layer on a Cu substrate (Si-O-C/CNTs/Cu) exhibits increased deposition amounts of Si, resulting in improved areal capacity. Furthermore, it shows high discharge capacity of $1696 \text{ mA h (g of Si)}^{-1}$ at 1st cycle with good cycle ability for 100th cycle and enhanced C-rate performance compared to Si-O-C composites deposited on Cu substrate (Si-O-C/Cu) without CNTs anchor layer. This research propose a valuable new method to increase the stability of Si-O-C composites without

cracks and detachment during electrodeposition by introducing CNTs anchor layer prepared via electrophoretic deposition.

2. Experimental

2.1 Preparation of CNTs/Cu substrate for Si-O-C composites

Commercial thin multi-walled CNTs, which has carbon purity around 90% with diameter around 10nm, were purchased from nanocyl (NC7000). As-received CNTs were oxidized in concentrated $\text{H}_2\text{SO}_4/\text{HNO}_3$ (3:1; v/v, purity of 96.0 % and 60.0 %, respectively) for 4 hours at 45 °C by sonication to functionalize surface of CNTs, and washed until pH 7. After washing process, the oxidized CNTs were dried in vacuum oven at 80 °C for 4 hours. The oxidized CNTs (0.05 mg ml^{-1}) and cobalt dichloride (CoCl_2) are sonicated in IPA for 30 min by sonication, separately, followed by both of dispersed samples were sonicated together in same bottle for 30 min again. The parallel copper substrates with an exposed area of $1 \times 1 \text{ cm}^2$ and a gap of 0.7 cm were soaked in CNTs and CoCl_2 suspension with glass cell. For electrophoretic deposition, a direct current power supply was used as power resource with a voltage of -120 V for 5 minutes. After that, prepared CNTs/Cu substrate was washed with distilled water and ethanol to remove aggregated CNTs particles and impurities of their surface. Afterward, the CNTs/Cu substrate was dried at room temperature for overnight.

2.2 Electrodeposition of Si-O-C composites

For the electrodeposition of Si-O-C, as-received Cu and CNTs/Cu substrate, lithium metal, and platinum plate were used as working, reference, and counter electrode, respectively. The propylene carbonate solvent (Kishida), which contain $0.5 \text{ mol dm}^{-3} \text{ SiCl}_4$ (Sigma-aldrich) and 0.5 mol dm^{-3} tetrabutylammonium perchlorate (Kanto Chemical) was employed as electrolyte for electrodeposition, and the Si-O-C electrodeposition was carried out in argon-filled globe box with dew point lower than -90 °C. A constant cathodic current of -1.0 mA cm^{-2} was applied to pass a charge of 2, 4, 8, and 15 coulomb cm^{-2} for the electrodeposition.

2.3 Measurement of Si-O-C composites

The morphological properties of Si-O-C/CNTs/Cu were characterized by field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) with energy dispersive X-ray spectroscopy (SEM, Hitachi TM-3000). The surface properties of Si-O-C/CNTs/Cu, which was moved into transfer vessel to prevent oxidization of silicon, were measured by X-ray photoelectron spectroscopy (XPS, JEOL, JPS-9010TR). The deposited Si amounts were measured by inductively coupled plasma (ICP, Thermo Scientific, iCAP6500 Duo) analysis.

2.4 Electrochemical analysis of Si-O-C/Cu and Si-O-C/CNTs/Cu

The electrochemical cell of Si-O-C composites deposited on as-received Cu substrate and CNTs anchor layer on Cu substrate was equipped containing 1.0 mol dm^{-3} lithium perchlorate (LiClO_4) in propylene carbonate-ethylene carbonate (PC:EC = 1:1, v/v) as electrolyte (Kishida) in a glove box with dew point below -110°C , using coin type cell (2032 type). Cyclic voltammograms (CV) of as-receive Cu, CNTs/Cu substrate and Si-O-C/CNTs/Cu was measured in the potential range of 0.01-1.20 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} (Hokuto Denko, HZ-5000). Electrochemical properties of Si-O-C/Cu and Si-O-C/CNTs/Cu were investigated by a constant current charge/discharge measurement with 0.1 C-rate in the potential range between 0.01-1.20 V vs. Li/Li^+ , and the C-rate was calculated depending on deposited Si amounts by ICP measurement.

3. Results and discussion

Figure 1. Schematic figures explaining Si-O-C composites deposition process on CNTs/Cu Substrate; (a) as-received Cu substrate, (b) electrophoretically deposited CNTs anchor layer on Cu substrate, (c) electrodeposited Si-O-C on CNTs/Cu substrate, and (d) Si-O-C/CNTs/Cu anode with cross-section view.

Figure 1 illustrates a preparation process of CNTs/Cu substrate supporting Si-O-C composites. The CNTs anchor layer was deposited on as-received Cu substrate by electrophoretic deposition as presented in Fig. 1 (b). Subsequently, Si-O-C electrodeposition was carried out on the obtained CNTs/Cu substrate in Fig. 1 (c). The Si-O-C composites are deposited on CNTs anchor layer which might contribute to improve deposited Si amounts. It is supposed that the Si-O-C composites were electrodeposited by filling inside of CNT layer, lead to increase adhesion between Si-O-C with Cu substrate (see Fig. 1 (d)).

Figure 2. Plane view FE-SEM images of (a) as-received Cu substrate, and Si-O-C composites deposited on as-received Cu substrate at (b) 2, (c) 8, and (d) 15 coulomb cm^{-2} passing charge. The plane view of (e) CNTs/Cu substrate, Si-O-C composites deposited on CNTs/Cu substrate at (f) 2, (g) 8, and (h) 15 coulomb cm^{-2} of passing charge.

Figure 2 shows plane view FE-SEM images of as-received Cu substrate, CNTs/Cu substrate, and after Si-O-C deposition on them depending on quantity of electricity for electrodeposition from 2 to 15 coulomb cm^{-2} of passing charge. Figure 2 (a) shows a typical surface morphologies of as-received Cu substrate, which is smooth without any grainy and with marks caused by rolling Cu plate through rolls. **By contrast**, it is shown that the CNTs are densely covering Cu substrate via electrophoretic deposition and the CNTs/Cu substrate formed three-dimensional (3D) structure in Fig.2 (e). The unique surface morphologies of CNTs/Cu substrate may have many features such as higher surface area than as-received Cu substrate and higher adhesion strength between Si-O-C composites with Cu substrate, resulting in enhanced deposited Si amount without peeling off and electrochemical properties. After Si-O-C electrodeposition, surface morphologies of Si-O-C/Cu and Si-O-C/CNTs/Cu are remarkably different as shown in Fig. 2 (b)-(d) and Fig. 2 (f)-(h), respectively. In Fig. 2 (b), Si-O-C composites deposited on as-received Cu substrate at 2 coulomb cm^{-2} of passing charge shows cracked surface. In

addition, after electrodeposition at 8 and 15 coulomb cm^{-2} of passing charge, the plane view of both samples depicts the peeled off Si-O-C composites from Cu substrate because of its stress and weak adhesion strength between Si-O-C composites and Cu substrate. On the other hand, Si-O-C/CNTs/Cu have homogeneous surface without any cracks at 2, 8, and even 15 coulomb cm^{-2} of passing charge owing to increased adhesion strength. It reveals that the CNTs layer is related to adhesion strength, resulting in non-cracked surface of Si-O-C/CNTs/Cu as shown in Fig. 2 (f)-(h). From these results, we suggest that CNTs anchor layer can hold and sustain each Si-O-C composite particles during electrodeposition, resulting in enhanced adhesion strength and improved structural stability.

Figure 3. (a) Comparison of deposited Si amounts of Si-O-C composites deposited onto as-received Cu substrate and CNTs/Cu substrate at 2 coulomb cm⁻² of passing charge, and (b) depending on various quantity of electricity for electrodeposition from 2 to 15 coulomb cm⁻² of passing charge.

The deposited Si amounts of Si-O-C/Cu and Si-O-C/CNTs/Cu prepared by 2 coulomb cm⁻² of passing charge were measured by ICP analysis. The average deposited Si amounts of Si-O-C/Cu and Si-O-C/CNTs/Cu are 0.048 and 0.056 mg cm⁻², respectively (see in Fig. 3 (a)). The Si-O-C/CNTs/Cu has higher deposited Si amount than Si-O-C/Cu up to 16.7 % because the CNTs/Cu substrate is able to maintain the high electric conductivity during electrodeposition, resulting in higher electrodeposition efficiency than as-receive Cu substrate. In addition, it can be expected that increasing of deposited Si amounts shows increased areal capacity. Table S1 shows the deposited Si amounts of Si-O-C/Cu and Si-O-C/CNTs/Cu synthesized at 2 coulomb cm⁻² of passing charge. Electrodeposition of the Si-O-C composites on either as-received Cu or CNTs/Cu substrate was prepared and their ICP measurements were carried out to test the reproducibility of Si-O-C electrodeposition. From these results, we could confirm that the method of Si-O-C electrodeposition from organic solvent has good reproducibility. Figure 3 (b) shows the deposited Si amounts of Si-O-C/Cu and Si-O-C/CNTs/Cu depending on quantity of electricity for electrodeposition at 2, 4, 8, and 15 coulomb cm⁻². At 2 and 4 coulomb cm⁻² of

passing charge, each samples show almost same deposited Si amounts of 0.05 and 0.10 mg cm⁻², respectively. However, Si-O-C/Cu has highest deposited Si amounts of 0.13 mg cm⁻² at 8 coulomb cm⁻² of passing charge and started to decrease until 0.10 mg cm⁻² at 15 coulomb cm⁻² of passing charge because deposited Si-O-C composites begin to peel off from as-received Cu substrate. By contrast, deposited Si amounts of Si-O-C/CNTs/Cu continued to increase and the deposited Si amounts are 0.18 and 0.21 mg cm⁻² at 8 and 15 coulomb cm⁻² of passing charge, respectively. It reveals that the adhesion strength between Si-O-C composites and Cu substrate was enhanced by introducing of CNTs anchor layer. Moreover, we can suppose that CNTs layer increased structural stability of Si-O-C composites as well, resulting in non-cracked surface of Si-O-C composites, which is corresponding to Fig. 2.

Figure 4. Plane view SEM image of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge with elemental mapping of silicon, oxygen, carbon and cobalt.

Figure 4 shows plane view SEM image of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge with elemental mapping of Si, O, C, and Co. The results of elemental mapping depict that Si, O, and C were homogenously deposited on CNTs/Cu substrate. However, cobalt was not detected clearly from surface of Si-O-C/CNTs/Cu because of their very small quantity, which has around of 0.525 $\mu\text{g cm}^{-2}$. The detail information of deposited Co amounts and their effectiveness related to CNTs electrophoretic deposition is shown in Fig. S1, S2 and Table S2. From these results, we suppose that the small amounts of Co cannot interfere in electrochemical performance of Si-O-C composites as anode for LIB. In addition, it is important to find the appropriate amounts of Co because exceed amounts of cobalt might be a resistance material, which can effect on electrochemical properties of Si-O-C composites. Therefore, we confirmed that the appropriate amounts of Co were used to impart positive charge on surface of CNTs during electrophoretic deposition.

Figure 5. SEM images of cross-section of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge (a) before and (b) after charge/discharge with elemental mapping of silicon, oxygen, and carbon.

The cross-section SEM images of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge before and after charge/discharge process for 100 cycles with EDX elemental mapping of Si, O, and C are shown in Fig. 5 (a) and (b), respectively. The homogenous dispersion of each elemental, i.e. Si, O, and C are also observed before and after charge/discharge. However, EDX elemental mapping of Co was not detected because of their very small quantity (not shown here), which is corresponding to that of Fig. 4. Figure 5 (a) shows the cross-section image of Si-O-C/CNTs/Cu before charge/discharge process, which has thickness of 6.3 μm . After charge/discharge process for 100 cycles, the thickness of Si-O-C/CNTs layer (discharge state) was increased up to 14.9 μm because of volume expansion of Si during lithiation at 1st cycle, and this behavior is corresponding in our previous report (shown in Fig. 5 (b)) [28]. In addition, we confirmed that the elementals of Si, O, and C were homogeneously dispersed before and after charge/discharge process for 100 cycles, and it means that Si-O-C composites deposited on CNTs/Cu substrate has good stability even after volume change.

Additional result related existence of Co was measured by XPS analysis before and after charge/discharge process for 100 cycles and presented in Fig. S3. The peak change of Co_{2p3}

was not detected in the narrow peak before and after charge/discharge (in Fig. S3 (a)). Therefore, we suppose that the very small quantities of cobalt, which deposited on to CNTs surface, cannot influence electrochemical reaction with Si-O-C composites, and it is corresponding to results of elemental mapping in Fig. 4. As seen the spectrum of C_{1s} in Fig. S3 (b), only one peak was observed before charge/discharge cycling at the around 284.4 eV. After charge/discharge for 100 cycles, the peak located at the around 284.4 eV was decreased, and a new peak was detected at the around 289.8 eV, attributed to carbonate peak including Li₂CO₃ and R-CH₂OCO₂Li. Moreover, the peak located at the around 284.4 eV has lower intensity than our previously study [28]. We suggest that the reason for lower intensity of C_{1s} peak after charge/discharge is concentration change of each elemental of Si, O, and C because of change of electric conductivity by existence of CNTs layer. Figure S4 shows the glow discharge optical emission spectroscopy (GDOES) results of Si-O-C/Cu and Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm⁻² of passing charge. The concentration of Si, O, and C of Si-O-C/Cu and Si-O-C/CNTs/Cu was different because of differential electric conductivity of as-received Cu substrate and CNTs/Cu substrate during electrodeposition. For more specific reasons, related research should to be focused in our future study.

Figure 6. CV results of (a) as-receive Cu and CNTs/Cu substrate and (b) Si-O-C/CNTs/Cu for 5 cycles synthesized by electrodeposition with 2 coulomb cm^{-2} of passing charge. The potential range is between 1.2 and 0.01 V vs. Li/Li^+ at a scan rate of 0.1 mV s^{-1} . The inset in (b) indicates the enlarged CV results of Si-O-C/CNTs/Cu from 2nd to 5th cycle.

CV measurements were carried out to compare the surface area of as-received Cu and CNTs/Cu substrate in the potential range between 0.01 and 1.2 V at a scan rate of 0.1 mV s^{-1} in Fig. 6 (a). These both substrates show the electric double layer capacitor behavior without any peaks related to lithiation. As can be seen in Fig. 6 (a), it is clear that the CNTs/Cu substrate shows higher capacitance of 7.54 mF cm^{-2} than as-received Cu substrate, which has capacitance of 0.57 mF cm^{-2} owing to their higher surface area by 3D structured CNTs anchor layer. These results mean that the surface area of Cu substrate was increased by CNTs anchor layer and implies that the CNTs/Cu substrate can react more with electrolyte containing SiCl_4 during electrodeposition. The CV results of Si-O-C composites deposited onto CNTs/Cu substrate prepared at 2 coulomb cm^{-2} of passing charge are shown in Fig. 6 (b) for 5 cycles. At 1st cycle, a huge cathodic peak was started at ca. 0.1 V vs. Li/Li^+ due to conversation reaction of SiO_x and formation of SEI on surface on Si-O-C composites, which lead to huge irreversible capacity at 1st cycle [29]. After 2nd cycle, the lithiation with Si was started at the around 0.2 V vs. Li/Li^+ , resulting in formation of amorphous- Li_xSi_y phase. In addition, the reaction peaks of delithiation of Li_xSi_y forward to amorphous-Si was detected at 0.37 and 0.50 V vs. Li/Li^+ . From CV results

of Si-O-C composites for 5th cycle, it reveal that irreversible capacity at 1st cycle was disappeared after 2nd cycle because almost reactions related to formation of SEI on Si-O-C composites surface and conversion or lithiation of SiO_x are finished at 1st cycle.

Figure 7. (a) Charge/discharge profiles of Si-O-C/CNTs/Cu from 1st to 100th cycle, the potential range is 0.01-1.2 V vs. Li/Li⁺ at 0.1 C-rate, (b) comparison of cycle abilities with Si-O-C/Cu and Si-O-C/CNTs/Cu for 100 cycles, (c) discharge areal capacity of both samples, (d) areal capacity depending on quantity of electricity from 2 to 15 coulomb cm⁻² of passing charge at 1st cycle, (e) C-rate performance, and (f) discharge capacity retention rate at various C-rate from 0.1 to 1 C and 0.1 C again for 25 cycles. (a) - (d) were tested at 0.1 C-rate. The discharge capacity values of Si-O-C/Cu and Si-O-C/CNTs/Cu were normalized with the calculated Si amounts from ICP results. The all Si-O-C composites were synthesized by electrodeposition with 2 coulomb cm⁻² of passing charge except to (d).

The charge/discharge potential profiles of Si-O-C/CNTs/Cu at 1st, 2nd, 10th, 50th and 100th cycle are shown in Fig. 7 (a). At the 1st cycle, the charge and discharge capacity are 7375 and

1696 mA h (g of Si)⁻¹, respectively, and this irreversible capacity is attributed to **conversion reaction** of SiO_x to Li_xSi_y and Li₂O, and consumption of Li ion to form SEI on surface of Si-O-C composite, which is corresponding to in Fig. 6 (b). **In addition, it reveals that the charge process was carried out at a potential below 0.4V vs. Li/Li⁺ after 2nd cycle, and discharge process began at a potential below 0.6 V vs. Li/Li⁺ which corresponding to reaction of amorphous Si to amorphous Li_xSi phase and delithiation of amorphous Li_xSi to amorphous Si. These behaviors are corresponding to cathodic peak around 0.2 V vs. Li/Li⁺ and anodic peak below 0.6 V vs. Li/Li⁺ in CV results.**

Figure 7 (b) indicates the cycle abilities of Si-O-C/Cu and Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm⁻² of passing charge for 100 cycles with their coulomb efficiency. **As mentioned above, irreversible capacity of Si-O-C/Cu and Si-O-C/CNTs/Cu substrate was observed at 1st cycle, resulting in low coulomb efficiency (discharge capacity/charge capacity) of 24.1 and 25.3 % at 1st cycle, respectively. However, the coulomb efficiency of Si-O-C/Cu and Si-O-C/CNTs/Cu was increase up to 86.7 and 87.1 % after 2nd cycle. It means that the Si-O-C composites deposited on both substrates suffer from coulomb efficiency fading because of lithiation and formation of SEI at 1st cycle.**

The discharge capacity of Si-O-C/Cu is 1173, 934 and 840 mA h (g of Si)⁻¹ at 1st, 50th and 100th cycle, respectively. However Si-O-C composites deposited onto CNTs/Cu substrate show higher discharge capacity of 1696, 1268 and 1078 mA h (g of Si)⁻¹ at same cycles. From this research, as mentioned above, we can surmise that the high electric conductivity of CNTs layer might lead to different Si concentration of Si-O-C/CNTs/Cu and Si-O-C/Cu during electrodeposition. For this reason, Si-O-C/CNTs/Cu can have increased deposited Si amounts than Si-O-C/Cu with higher discharge capacity for 100 cycles.

The discharge areal capacity of Si-O-C/Cu and Si-O-C/CNTs/Cu was compared and presented

in Fig. 7 (c). This results demonstrate that the Si-O-C composites deposited on CNTs/Cu substrate delivered a higher discharge areal capacity of 0.10 and 0.06 mA h cm⁻² at 1st and 100th cycle, respectively, than Si-O-C/Cu which has discharge areal capacity of 0.08 and 0.05 mA h cm⁻² at 1st and 100th cycle, respectively. The discharge areal capacity of both Si-O-C composites deposited on as-received Cu and CNTs/Cu substrate depending on quantity of electricity for electrodeposition were compared in Fig. 7 (d). As mentioned in Fig. 7 (c), the Si-O-C composites deposited on CNTs/Cu substrate delivered a higher areal capacity than Si-O-C/Cu but that is not much different, only 0.02 mA h cm⁻² at 1st cycle. However, as increase the quantity of electricity for electrodeposition, the differences of areal capacity from both samples are gradually increasing until 15 coulomb cm⁻² of passing charge. At 8 coulomb cm⁻² of passing charge, the Si-O-C/Cu has highest discharge areal capacity of 0.13 mA h cm⁻² at 1st cycle and it began to decline until 0.03 mA h cm⁻² at 15 coulomb cm⁻² of passing charge at 1st cycle. On the other hand, Si-O-C composites deposited on CNTs/Cu substrate show increased discharge areal capacity even at 15 coulomb cm⁻² of 0.49 mA h cm⁻² at 1st cycle due to its enhanced adhesion strength between Si-O-C composites and Cu substrate which is corresponding to Fig. 2. From areal capacity results, we could identify that the Si-O-C composites deposited on CNTs/Cu substrate show higher areal capacity because Si-O-C/CNTs/Cu has increased deposited Si amounts than Si-O-C/Cu owing to enhanced adhesion strength by introducing of CNTs layer via high voltage electrophoretic deposition. In addition, we could confirm that Si-O-C/CNTs/Cu prepared 15 coulomb cm⁻² of passing charge shows higher areal capacity than our previous report (Si-O-C/CNTs/Cu: 0.49 mA h cm⁻², Si-O-C/NMS composites: 0.18 mA h cm⁻² at 1st cycle) [29].

To identify the influence of introduced CNTs layer during charge/discharge process, C-rate performance was measured depending on various C-rate values from 0.1, 0.2, 0.5, and 1.0 C and 0.1 C again for 25 cycles in Fig. 7 (e). In general, Si-O-C/CNTs/Cu has higher discharge

capacity than Si-O-C/Cu, and these two samples show almost same reduction rate of discharge capacity depending on various loading current. For more detail analysis, the C-rate results was converted to discharge capacity retention ratio, which is shown in Fig. 7 (f). From 1st to 5th cycle, the discharge capacity retention ratio of Si-O-C/Cu and Si-O-C/CNTs/Cu show similar values around of 97.9 and 95.5 %, respectively. However, discharge capacity decreasing rate of Si-O-C/Cu have been decreased rapidly around 20.6, 18.4, and 19.7 % per 5 cycles for 20 cycles. **By contrast**, discharge capacity decreasing rate of Si-O-C/CNTs/Cu shows slight decreasing rate of 9.3, 9.6, and 8.5 % per 5 cycles for 20 cycles. Furthermore, the discharge capacity retention ratio of Si-O-C/Cu was decreased around 18.9 % from 21st-25th cycle compared to initial value. On the other hand, Si-O-C/CNTs/Cu shows decreasing rate around of only 7.3% from 21st-25th cycle in comparison with 1st cycle. **For an easier understanding, discharge capacity retention rate of both samples are presented in Fig. S5 with one cycle per each C-rate.** From C-rate performance results, we suppose that the high conductivity of the CNTs reduces the internal strain from volume change of Si during charge/discharge cycling, resulting in good C-rate performance at high C-rate values. In addition, we suggest that the CNTs layer employed as electric pathway, lead to enhanced electrochemical properties such as higher discharge capacity and good recovery rate at high C-rate values. Besides, the electric path way could play a role to decrease the internal resistance in Si-O-C composites during charge/discharge process. As seen the charge/discharge profile at 100th cycle (in Fig. S6), it is believed that Si-O-C/CNTs/Cu exhibits the lower internal resistance voltage drop (IR drop) than Si-O-C/Cu, results in higher discharge capacity with good retention ratio of Si-O-C/CNTs/Cu.

Figure 8. Plane view FE-SEM images of (a) Si-O-C/Cu and (b) Si-O-C/CNTs/Cu synthesized by electrodeposition with 2 coulomb cm^{-2} of passing charge after charge/ discharge process for 100 cycles at 0.1 C-rate.

The morphological characteristics of Si-O-C/Cu and Si-O-C/CNTs/Cu after 100 cycles were measured by FE-SEM analysis and presented in Fig. 8. The Si-O-C/Cu shows the cracked surface due to volume change during charge/discharge cycling, lead to occur isolated Si particles from current collector and it is a critical reason of discharge capacity fading. However, Fig. 8 (b) depicts non-cracked surface of Si-O-C/CNTs/Cu even after charge/discharge cycling for 100 cycles. In addition, we could confirm that Si-O-C composites were deposited onto CNTs and entangled together. To summarize, Si-O-C particles were intertwined with CNTs anchor layer to prevent cracks on their surface, lead to enhanced adhesion strength between Si-O-C composites with Cu substrate. Moreover, the CNTs anchor layer electrophoretic deposited Cu substrate can withstand the much amounts of Si-O-C composite at large passing charge of electrodeposition even at 15 coulomb cm^{-2} , resulting in enhanced deposited Si amounts compared to as-received Cu substrate without CNTs anchor layer. In other words, CNTs layer could play a role to bind Si-O-C composites and space of CNTs layer can be endurable the volume change during charge/discharge cycling, resulting in enhanced deposited Si amounts and higher discharge capacity for 100 cycles.

4. Conclusion

We have prepared the CNTs/Cu substrate by high voltage electrophoretic deposition in IPA for improving adhesion strength between Si-O-C composites and Cu substrate, and Si-O-C composites deposited onto obtained CNTs/Cu substrate by electrodeposition from reduction of SiCl_4 . The Si-O-C/CNTs/Cu shows the higher discharge capacity than Si-O-C/Cu of ca. 1078 and 840 mA h (g of Si)⁻¹ at 100th cycle, respectively. Furthermore, Si-O-C/CNTs/Cu shows the good cycle ability for 100 cycles, and increased discharge areal capacity of 0.49 mA h cm⁻² at 15 coulomb cm⁻² of passing charge at 1st cycle, it is higher than our previous report (Si-O-C/NMS composites: 0.18 mA h cm⁻² at 15 coulomb cm⁻² of passing charge at 1st cycle). In addition, CNTs anchor layer on Cu substrate achieves higher discharge capacity retention at various C-rate values than as-received Cu substrate because of enhanced adhesion strength and high electric conductivity of CNTs. The discharge capacity retention of Si-O-C/Cu is 49.94 % at 1.0 C-rate, whereas the Si-O-C/CNTs/Cu shows improved discharge capacity retention of 69.81 % at 1.0 C-rate. The reasons of these superb results are enhanced adhesion strength between Si-O-C and CNTs/Cu substrate and good electric conductivity of CNTs, and it can complement the deterioration of cell performance. From these results, it is clear that CNTs layer can perform as not only additive for increasing adhesion strength but also electron transfer pathway for high performance Si-O-C composites as anode for LIBs.

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Figure 1. Schematic figures explaining Si-O-C composites deposition process on CNTs/Cu Substrate; (a) as-received Cu substrate, (b) electrophoretically deposited CNTs anchor layer on Cu substrate, (c) electrodeposited Si-O-C on CNTs/Cu substrate, and (d) Si-O-C/CNTs/Cu anode with cross-section view.

Figure 2. Plane view FE-SEM images of (a) as-received Cu substrate, and Si-O-C composites deposited on as-received Cu substrate at (b) 2, (c) 8, and (d) 15 coulomb cm⁻² passing charge. The plane view of (e) CNTs/Cu substrate, Si-O-C composites deposited on CNTs/Cu substrate at (f) 2, (g) 8, and (h) 15 coulomb cm⁻² of passing charge.

Figure 3. (a) Comparison of deposited Si amounts of Si-O-C composites deposited on to as-received Cu substrate and CNTs/Cu substrate at 2 coulomb cm⁻² of passing charge, and (b) depending on various quantity of electricity for electrodeposition from 2 to 15 coulomb cm⁻² of passing charge.

Figure 4. Plane view SEM image of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge with elemental mapping of silicon, oxygen, carbon and cobalt.

Figure 5. SEM images of cross-section of Si-O-C/CNTs/Cu prepared by electrodeposition at 2 coulomb cm^{-2} of passing charge (a) before and (b) after charge/discharge with elemental mapping of silicon, oxygen, and carbon.

Figure 6. CV results of (a) as-receive Cu and CNTs/Cu substrate and (b) Si-O-C/CNTs/Cu for 5 cycles synthesized by electrodeposition with 2 coulomb cm⁻² of passing charge. The potential range is between 1.2 and 0.01 V vs. Li/Li⁺ at a scan rate of 0.1 mV s⁻¹. The inset in (b) indicates the CV results of Si-O-C/CNTs/Cu from 2nd to 5th cycle.

Figure 7. (a) Charge/discharge profiles of Si-O-C/CNTs/Cu from 1st to 100th cycle, the potential range is 0.01-1.2 V vs. Li/Li⁺ at 0.1 C-rate, (b) comparison of cycle abilities with Si-O-C/Cu and Si-O-C/CNTs/Cu for 100 cycles, (c) discharge areal capacity of both samples, (d) areal capacity depending on quantity of electricity from 2 to 15 coulomb cm⁻² of passing charge at 1st cycle, (e) C-rate performance, and (f) discharge capacity retention rate at various C-rate from 0.1 to 1 C and 0.1 C again for 25 cycles. (a) - (d) were tested at 0.1 C-rate. The discharge capacity values of Si-O-C/Cu and Si-O-C/CNTs/Cu were normalized with the calculated Si amounts from ICP results. The all Si-O-C composites were synthesized by electrodeposition with 2 coulomb cm⁻² of passing charge except to (d).

Figure 8. Plane view FE-SEM images of (a) Si-O-C/Cu and (b) Si-O-C/CNTs/Cu synthesized by electrodeposition with 2 coulomb cm^{-2} of passing charge after charge/ discharge process for 100 cycles at 0.1 C-rate.

Graphical abstract