Facile electrochemical synthesis of heterostructured amorphous-Sn@Cu$_x$O nanowire anode for Li-ion batteries with high stability and rate-performance

Myeongho Kim$^a$, Insoo Choi$^{b,**}$, Jae Jeong Kim$^{a,**}$

$^a$ School of Chemical and Biological Engineering, Institute of Chemical Process, Seoul National University, 1 Gwanak-ro, Gwanak-gu, Seoul 08826, Republic of Korea

$^b$ Division of Energy Engineering, Kangwon National University, 346 Jangang-ro, Samcheok, Gangwon-do 25913, Republic of Korea

Abstract

Herein, we fabricate heterostructured copper oxide nanowires decorated with amorphous Sn by Cu anodization and Sn electrodeposition for a potential application as anode in Li-ion battery. In general, Sn experiences a pulverization caused by the stress from a severe volume change during the reaction with Li-ion. Therefore, the stress should be certainly mitigated. A nanowire with 1-D structure could be a candidate anode material because it accommodates the volume change and enlarges the surface area of electrode. Yet Sn nanowire still suffers the harsh stress, copper oxide is employed as an active anode material as well as a structural framework in the present study. By virtue of the Li-conversion mechanism of copper oxide, the as-prepared Sn-decorated copper oxide nanowires exhibits an improved discharge capacity and maintains it as high as 633.0 mAh g$^{-1}$ at extended cycles (77.7% of initial capacity at 150$^{th}$ cycle). From a rate capability experiment, the nanowire electrode presents the capacity of 424 mAh g$^{-1}$ at 16 C, and shows a moderate recovering ability. The 1-D heterogeneous structure and Cu nodes that are intentionally formed during electrochemical fabrication helps realizing a cell configuration without a binder and a conducting agent, which ultimately contributes to increase energy and power density of Li-ion battery.

1. Introduction

Much effort has been expended in search of suitable materials from which to how construct the anode of high power and energy density for Li-ion batteries (LIBs) [1,2]. Graphite exhibits a stable cycle performance during charge and discharge (C/D), however, the relatively low specific capacity (372 mAh g$^{-1}$) negates its commercial availability. Anodes made from the material which follows an alloying mechanism, e.g. Si or Sn, have much higher theoretical specific capacities compared to the conventional graphite electrode (4200 mAh g$^{-1}$ for Li$_{4.4}$Si, 994 mAh g$^{-1}$ for Li$_{4.4}$Sn) [3–9]. Unfortunately, such anodes undergo a severe volume change upon reaction with Li-ion, resulting in an exfoliation of the active material from a current collector. Accordingly, methods that allow the stable operation of the alloying anode material are highly sought after.

Among the high-capacity alloying anode materials, Sn is environmentally benign, cheap, and easy to deal with. However, Sn metal anode is prone to expand to 300% of its initial volume during the insertion of Li-ion, which leads to a pulverization and thereby the electrode exfoliates. Accordingly, the Sn-embedded battery would eventually fade. There have been many attempts to resolve the fading issues, including a nanoscale modification; nanoparticles [10–14] and nanowires [15–21]. Wu et al. fabricated a 3-D nano-architecture that was composed of Sn nanoparticles with porous graphene matrix [12]. The nanosized pores of the graphene network housed the extreme volume change of Sn nanoparticles, and facilitated a rapid access of Li-ion into the Sn particles, enabling the architecture to deliver stable electrochemical performance with high rate capability. However, the Sn nanoparticles required a large amount of conducting agent to maintain the electrical conductivity, restricting the ratio of active materials in the electrode and resulting in a poor energy density. On the other hand, Park et al. synthesized 1-D SnO$_2$ nanowires by thermal evaporation, combined with a self-catalyzed growth, to provide more reaction sites and to enhance the charge transfer in electrochemical reactions [19]. Sn particles at the tips of the nanowires contributed to the Li-ion storage, and prevented the capacity loss. However, single SnO$_2$ crystalline...
disturbed smooth Li-ion insertion into nanowires, resulting in a slow lithiation and low initial efficiency (46.9%). Moreover, such nanostructures generally suffer from the self-aggregation induced by high surface energy, and thus possess a limited electrical conductivity originating from inter-particle resistance [10–12]. Therefore, it is necessary to find a way to solve these problems that are consistently interrupting the cycle life of Sn-based anodes.

In this present study, we propose a new form of Sn-based anode that has a heterogeneous nanostructure; amorphous Sn-decorated copper oxide nanowires (a-Sn/CuO NWs, where 1 < x < 2). Copper oxide has been highlighted as a potential anode material because of its moderate theoretical specific capacity (675 mAh g\(^{-1}\)), low price and non-toxicity [22–28]. Unlike Sn or Sn oxide, copper oxide reacts with Li-ion via conversion mechanism, and therefore it is far less vulnerable to the drastic volume change. Moreover, it is expected that the charge transfer within the nanowire is efficient because the 1-D nanomaterial could intrinsically provide a direct electronic pathway. In addition, the heterogeneous nanostructure could demonstrate an additive-free and binder-free electrode, which achieves a high active material ratio and thus enhances the energy density of battery. Lastly, the heterogeneous structure contributes to decrease in electrical resistance by forming Cu nodes between CuO NWs and a-Sn. The mechanism is reliable because CuO at the marginal area of the nanowire is simultaneously reduced to Cu during the electrochemical deposition of Sn. For the reasons above, we employ CuO NWs as a structural framework as well as active material for LIBs [29]. In summary, an effective fabrication of a-Sn/CuO NWs and their use in the electrode should provide higher capacity with moderate rate capability, by reducing the over-potential and accelerating reaction kinetics at the electrode surface.

Here, we develop a facile method for preparing a-Sn/CuO NWs. To be specific, the as-prepared CuO NWs are directly grown onto Cu foil substrate by an electrochemical method. The electrochemical method proceeds at ambient temperature, while conventional thermal oxidation or solution-based methods for forming NWs require relatively high temperature [30,31]. Moreover, the electrochemical fabrication is simple and is easily controlled by adjusting the deposition parameters such as potential, current, and time [32,33].

2. Materials and methods

2.1. Preparation of a-Sn/CuO NWs electrode

a-Sn/CuO NWs were electrochemically fabricated using a three-electrode system, consisting of Ag/AgCl (sat. with KCl) and Pt as a reference and a counter electrode, respectively. To form the nanowire structure, Cu foil (thickness = 10 μm) was used as a working electrode, and was galvanostatically anodized by the following steps. First, 2 M of sodium hydroxide(aq) (NaOH(aq), Daejung, 98%) was de-aerated with \(N_2\) at 1 h at 5 °C. Then, three galvanostatic steps were sequentially applied to produce Cu(OH)\(_2\) NWs on the Cu foil; 5 mA cm\(^{-2}\) for 10 s (oxidation), –5 mA cm\(^{-2}\) for 20 s (reduction) and 5 mA cm\(^{-2}\) for 300 s. Finally, the Cu(OH)\(_2\) NWs on the Cu foil were rinsed with de-ionized water for 15 s. After being treated at high temperature in Ar atmosphere (250 °C, 1 h), the Cu(OH)\(_2\) NWs were transformed into CuO NWs. At last, Sn was electrochemically deposited on the CuO NWs by applying –10 mA cm\(^{-2}\) for 50 s in a mixture solution of 0.07 M of tin(II) pyrophosphate(aq) (SnP\(_2\)O\(_7\)-aq, Sigma Aldrich, 98%) and 0.36 M of potassium pyrophosphate(aq) (K\(_2\)P\(_2\)O\(_7\)-aq, Sigma Aldrich, 97%) to obtain a-Sn/CuO NWs. The detail fabricating process of the a-Sn/CuO NWs is depicted in Fig. S1.

The reference Sn film electrode was fabricated by electrodeposition as well. First, a commercial Cu foil was treated with 0.5 M of sulfuric acid(aq) (H\(_2\)SO\(_4\)-aq, Daejung, 95%) for 1 min to eliminate the naturally-formed oxide layer. Then, Sn was electrodeposited on Cu foil in an electrolyte of 0.07 M of SnP\(_2\)O\(_7\)-aq and 0.36 M of K\(_2\)P\(_2\)O\(_7\)-aq; –10 mA cm\(^{-2}\) for 50 s. The electrode was cut in circle (d = 11 mm) and was vacuum-dried (120 °C, 12 h) before it was placed in a glove box.

2.2. Physical and chemical characterization

The relative amount of Sn and copper oxide in the as-prepared a-Sn/CuO NWs electrode was quantitatively measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-8100). The crystallographic information of the fabricated electrode was obtained by using X-ray diffractometer (XRD, D8-Advance, Cu K\(_\alpha\), where \(\lambda = 0.15406\) nm). The step rate (20) for diffraction was 5° min\(^{-1}\) during the measurement. A field-emission scanning electron microscope (FESEM, JSM-6701F, accelerating voltage = 10 kV) and an energy-dispersive X-ray spectroscopy (EDX, INCA Energy) were employed to characterize the morphology and the elemental composition of the electrode, respectively. To picture the transmitted image with high magnification and the lattice structures of the specimen, we utilized a transmission electron microscope (TEM, JEM-ARM200F, accelerating voltage = 200 kV). X-ray photoelectron spectroscopy (XPS, Sigma probe, Al K\(_\alpha\) anode, where \(E_{\text{photo}} = 1486.6\) eV) analysis was conducted at constant power of 100 W to investigate the composition and the chemical state of the electrode surface. The specific surface area of a-Sn/CuO NWs was measured by Brunauer-Emmett-Teller (BET) method (Micromeritics ASAP 2010, USA).

2.3. Electrochemical measurement

In order to evaluate the electrochemical performance of the a-Sn/CuO NWs electrode in LIB, the electrode was assembled with 2032 coin-type cell in a protected atmosphere; a glove box filled with Ar. The cell also consisted of a commercial Li metal (Cyprus Co.) counter electrode and a polypropylene-polyethylene-polypropylene (PP-PE-PP) tri-layer separator (Celgard\(^\text{™}\)). An electrolyte was composed of 3:7 (v/v) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) with 1.3 M of lithium hexafluorophosphate (LiPF\(_6\)) salt. The galvanostatic cycling test of the cell was performed by using a cyclic (Wonatech, WBCS-3000) at 25 °C, after the electrode being impregnated in the electrolyte for additional 24 h. The cells was cycled at 0.1 C (74.68 mA g\(^{-1}\)) during the formation step, and was followed by cycling at 1 C (746.8 mA g\(^{-1}\)) at voltages ranging from 0.01 to 3.0 V (vs. Li/ Li\(^+\)). The electrochemical response of the electrode toward Li-ion was monitored by carrying out a cyclic voltammetry (CV) at the same voltage window with a scan rate of 0.1 mV s\(^{-1}\). An electrochemical impedance spectroscopy (EIS, Parstat 2273) was used to measure a total and an individual resistance applied to the electrode in a discharged state. The alternating current passes through the electrode at frequency from 0.01 to 100 kHz with amplitude of 5 mV. The data obtained by EIS was graphically expressed in a Nyquist plot. The rate capability of the manufactured cell was test by varying the C/D rate from 0.1 to 16 C. When the electrochemical measurement was completed, the cell was disassembled to collect the electrode for further ex-operando analysis. The operation was conducted in a glove box to keep the electrode from being contaminated by oxygen or water in the atmosphere. The electrode was cleaned with dimethyl carbonate (DMC) to remove the electrolyte and the lithium salt, remaining on the surface of electrode.

3. Results and discussion

3.1. Characterization of materials for electrode

The surface images of the Cu(OH)\(_2\), CuO and a-Sn/CuO NWs obtained from FE-SEM analysis were presented in Fig. 1a–c, respectively. Firstly, the anodic current was applied to Cu foil to diminish an uneven native copper oxide layer; Cu oxidation. Afterwards the copper oxide was removed by applying reduction current. Finally, the substrate was once more anodized in NaOH(aq) in order to form Cu(OH)\(_2\) NWs:
The Cu foil was covered by a layer of the Cu(OH)₂ NWs with a diameter of below 300 nm. After heat treatment, the Cu(OH)₂ NWs (light blue) turned into CuₓO NWs (black) with a rough surface in a slightly curved structure.

The curved morphology of CuₓO NWs is ascribed to the stress caused by the dehydration of Cu(OH)₂. The Cu(OH)₂ retains an orthorhombic crystal structure, where Cu²⁺ has a pentahedral geometry surrounded by five OH⁻ ions, forming a square pyramid. When temperature is elevated, the relatively long Cu–O bond becomes weak and loose, and thus the square planar entities of Cu(OH)₄ are linked together in a reversible way [34]. By doing so, a feasible shift of CuO₄ or Cu takes place. In short, when the temperature reaches 250 °C, the dehydration of Cu(OH)₂ proceeds via an oxolation mechanism. The as-prepared CuₓO NWs has an approximate length of 5 μm, and a diameter of 218.4 (± 27.9) nm, reflecting the shrinkage due to dehydration. After Sn electrodeposition, the CuₓO NWs were entirely covered by Sn. The optimal deposition time was found to be 50 s (Fig. S2). After 75 s, the nanowires were found to adhere to each other, and Sn nanoparticles were agglomerated via surface migration through nearby connected nanowires. The diameter of the as-prepared a-Sn/CuₓO NWs was approximately 227.6 (± 26.2) nm. As shown in Fig. 1d–h, the bright-field TEM image and subsequent EDS elemental mapping of consisting elements in a-Sn/CuₓO NWs evidenced the successful loading of Sn with its uniform distribution on the CuₓO NWs, and clearly identified the hybrid structure. In addition, the BET surface area of as-prepared a-Sn/CuₓO NWs was found to be 51.85 m² g⁻¹, showing a mesoporous structure, due to a combination of nanoparticle and nanowire (Fig. S3).

The crystal structures of the Sn film, Cu(OH)₂, CuₓO, and a-Sn/CuₓO NWs were investigated by X-ray diffraction, and the results were shown in Fig. 2. There appeared three characteristic peaks in all samples: 43.3°, 50.4° and 74.1° that corresponded to Cu(111), (200) and (220) (JCPDS no. 04-0836) from the Cu foil substrate. The Sn film electrode exhibited the diffraction pattern of both tetragonal Sn (JCPDS no. 04-0673) and monoclinic Cu₅Sn₅ (JCPDS no. 45-1488). The result suggested that Sn became alloyed with Cu at the initial state of Sn electrodeposition on Cu substrate. The diffraction peaks indexed to the Cu(OH)₂ NWs were proved to be an orthorhombic structure JCPDS no. 6 broad diffraction peaks at 35.5° and 38.9° observed in both CuₓO NWs and a-Sn/CuₓO NWs were identified to be (111) and (200) lattice plane of a monoclinic Cu₅O (JCPDS 48-1548). In addition, the peaks appeared at 36.4°, 42.3° and 61.3° and they corresponded to (111), (200) and (220) of cubic Cu₂O (JCPDS no. 05-0667), respectively. The result provided a basis for assigning the fabricated copper oxide to CuₓO. It was presumed that the Cu₂O was formed owing to an incomplete dehydration or a partial reduction of Cu(OH)₂ by X-ray exposure [35]. The broad diffraction peaks of CuO and Cu₂O suggested that the size of crystalline would be relatively small. Meanwhile, both CuO and Cu₂O peaks became less notable in a-Sn/CuₓO than in CuₓO NWs. It was ascribed to the reduction of copper oxides during electrodeposition of Sn onto CuₓO NWs. It was supported by the potential profile of Cu₂O reduction without Sn source, being similar to that of Sn deposition on CuₓO (Fig. S4). The diffraction peak that should be assigned for

\[ \text{Cu}^{2+} + 2\text{OH}^- \rightarrow \text{Cu(OH)}_2 \]
crystalline Sn was not observed from the a-Sn/CuxO NWs, which indicated that the electrodeposited Sn nanoparticle was amorphous. Moreover, it was notable that the diffraction peak for Cu6Sn5 alloy was not observed either. This was attributed to the reduction in the effective current density consumed during the electrodeposition of Sn, in which the surface area was enlarged and CuxO was electrochemically reduced simultaneously.

The surface composition and chemical state of Cu(OH)2, CuxO and a-Sn/CuxO NWs were analyzed by XPS. All peaks were adjusted and calibrated with respect to C 1s peak (284.8 eV). The peaks at 932.9 and 934.8 eV corresponded to Cu 2p3/2 and Cu2+ 2p3/2, respectively (Fig. 3a) [36]. Even though Cu+ 2p3/2 signal may possibly appear near Cu 2p3/2, it is not possible that Cu+ exists in Cu(OH)2 NWs. Therefore, the peak at 932.9 eV must have only come from Cu 2p3/2 out of Cu substrate. Additional peaks near at 942 and 944.5 eV could be assigned to the shake-up satellite peaks that were derived from Cu2+. Meanwhile, the peak observed at 932.9 eV from the CuxO NWs and a-Sn/CuxO NWs included both Cu 2p3/2 and Cu+ 2p3/2 from Cu2O as previously depicted in Fig. 2 (Fig. 3b and c). The atomic percentage of Cu, Cu ″, and Cu2+ elements derived from the characteristic peak area of Cu(OH)2, CuxO, and a-Sn/CuxO NWs were summarized in Table S1. The percentage of Cu ″ at CuxO NWs electrode was measured to be 7.4%, confirming that the copper oxide mainly presented as CuO. Such result becomes a basis for calculating the theoretical capacity of the electrode in the next chapter. Speaking of oxygenated species on the surface, it was presented that the oxygen strongly bound with H at 531.1 eV in the lattice of Cu(OH)2 NW (Fig. 3d). However, the CuxO NW retained two O 1s peaks; oxygen in CuO lattice and the one in the surface-bound OH-group in CuO, a leftover from the Cu(OH)2 NW (Fig. 3e). Finally, a-Sn/ CuxO NWs contained peaks for Sn 3d5/2 and Sn 3d3/2, indicating that amorphous Sn and partially-oxidized Sn existed (Fig. 3f) [37,38].

Fig. 4 depicted the transmitted morphological images of a-Sn/CuxO NWs with different degrees of magnification. The bright field images clearly showed spherical Sn grains with an approximate size of 8 nm on the surface of CuxO (Fig. 4b–c). Highly-resolved images of the marginal area of the a-Sn/CuxO NWs (region α, β, γ) were provided in Fig. 4d–f. Lattice plane was absent in the Sn-deposited area, indicative of the as-deposited Sn being amorphous, which further supplemented the previous findings from XRD analysis (Fig. 4d). On the other hand, the Cu (111) and CuO (111) lattices were prominent in the region β and γ, respectively (Fig. 4e–f), which coincided with the results in Figs. 2, 3, and Table S1. Fig. 4g depicted the part of the copper oxide near the electrode surface, being reduced to metallic Cu during the electrodeposition of Sn. Accordingly, the reduced metallic Cu should become a node between CuxO nanowire and Sn, enhancing the electrical conductivity of the material. Fig. 4h described the preferred pathway for

---

**Fig. 3.** High resolution X-ray photoelectron spectra of Cu(OH)2, CuxO and a-Sn/CuxO NWs electrode; (a–c) Cu 2p, (d–f) O 1s and (g) Sn 3d.
electronic conduction within the a-Sn/Cu_xO NW. The existence of Cu node should ensure the restricted use of carbonaceous conducting agent, which will provide a room for improvement in the energy density of LIBs.

3.2. Electrochemical investigation

The electrochemical behavior of Sn and Cu_xO in the a-Sn/Cu_xO NWs with Li-ion was investigated by performing CV. The voltammograms of Sn film, Cu_xO, and a-Sn/Cu_xO NWs at 1st – 5th cycles were provided in Fig. 5. The voltammograms of Sn film (Fig. 5a) showed a number of cathodic and anodic peaks, suggesting a multi-step reaction with Li-ion [39–41]. The cathodic peaks from 0.4 to 0.01 V matched to the Li-alloying processes of Sn (Sn → Li_{x}Sn) and Cu_{6}Sn_{5} (Cu_{6}Sn_{5} → Cu). The anodic peaks appearing from 0.4 to 0.8 V corresponded to the restoration of Cu to Cu_{6}Sn_{5} [14]. The existence of Cu_{6}Sn_{5} was previously confirmed by X-ray diffraction (Fig. 2). Fig. 5b presented the voltammograms of Cu_xO NWs. Three peaks were noticeable at 2.11 V, 1.09 V and 0.85 V from the 1st cathodic scan. It was acknowledged that the peak at 2.11 V was ascribed to the formation of LixCuO solid solution. In addition, the peaks at 1.09 V and 0.85 V were associated with Cu_{2}O formation, followed by its further reduction to Cu and Li_{2}O. In the 2nd cycle voltammogram, however, a slight peak shift by 0.16 V was observed (from 1.09 V to 1.25 V). This was a common feature, normally

![Fig. 4. Transmitted electron images of (a–c) a-Sn/Cu_xO NWs and Sn-deposited area on Cu_xO NWs, and high-resolution image of (d) Sn (region α), (e) Cu (region β) and (f) Cu_xO (region γ). (g) The schematic diagram of Cu_xO NW before and after Sn deposition and (h) preferred pathway for electron conduction within the a-Sn/Cu_xO NW.](image-url)
seen in metal oxide material that elucidated a textural modification.
The result referred to a good structural stability and redox reversibility
of the electrode [25, 42]. The broad anodic peak approximating at
2.48 V was applied to the regeneration of Cu₂O and its further oxidation
into CuO [28, 43]. The CV of a-Sn/CuxO NWs manifested a combination
of the voltammogram of Sn film and that of CuxO NWs (Fig. 5c). The
slight cathodic peak at around 0.5 V arose from the reduction reaction
depicted in Eq. (2); and the peak at 0.15 V was associated to the Li-
alloying with Sn as equated in Eq. (3).

\[
\begin{align*}
\text{SnO}_x + x \text{Li}^+ + x e^- & \rightarrow \text{Sn} + 2\text{Li}_x\text{O} & \text{(2)} \\
\text{Sn} + x \text{Li}^+ + x e^- & \rightarrow \text{Li}_x\text{Sn} & \text{(3)}
\end{align*}
\]

The peak at 0.5 V in the anodic curve corresponded to the de-al-
alloying process of Li₅Sn. Sn oxidized to SnO and even further to SnO₂
approximately at 1.25 V and 1.9 V, respectively [20, 44]. It was likely
that SnO₂ was formed in oxygen-generating atmosphere, where CuO
was reduced to Cu and released oxygen. The claim could be supple-
mented by the fact that the Sn deposition potential approximated to the
electrochemical reduction potential of CuO (Fig. S4). SnO₂ could be
also formed during de-lithiation process via reaction of Sn with Li₂O
that originated from the lithiation of CuO. During the prolonged cy-
cling of a-Sn/CuxO NWs, the voltammograms became stable (inset).
The result suggested that nanowire structure successfully relieved the stress
resulted from the volume change and alleviated a fading of the elec-

3.3. LIB performance

The specific capacity and Coulombic efficiency of the electrode were
measured in order to investigate how much effective the nanowire
structure was on improving the cycle performance of LIB. The specific
capacity of a-Sn/CuxO NW was theoretically derived as follows:

\[
C_{\text{Sn/CuxO NW}} = C_{\text{Sn}} X_{\text{Sn}} + C_{\text{CuxO}} X_{\text{CuxO}}
\]

\(C_{\text{i}}\) is a theoretical capacity of element; Sn (994 mAh g⁻¹) and CuO
(675 mAh g⁻¹) [22, 23], while \(X_{\text{i}}\) is a mass ratio of component. The loading of Sn and CuO in a-Sn/CuxO NWs was measured to be 0.079
and 0.273 mg cm⁻² respectively. The detail in determination of relative
content of Sn and CuO and their loading amounts was explained in the
electronic supporting information. Consequently, the theoretical capa-
city of a-Sn/CuxO NWs (\(C_{\text{Sn/CuxO NW}}\)) was 746.8 mAh g⁻¹. The specific
C/D capacity and Coulombic efficiency of Sn film and a-Sn/CuxO NWs
were compared in Fig. 6. Sn film exhibited an initial discharge capacity
of 296.4 mAh g⁻¹ with Coulombic efficiency of 82.7%. The capacity
was considerably lower than the theoretical value, due to the relatively
thick Sn layer [45]. It was known that Sn film severely deteriorated and
the capacity faded, as the film thickness increased. Based on the charge
consumed for electrodeposition and the density of Sn, the thickness of
Sn film reached approximately 1 μm. The a-Sn/CuxO NWs electrode,
however, showed greater initial discharge capacity (929.1 mAh g⁻¹)
with Coulombic efficiency of 87.9%. The little higher efficiency of a-Sn/
CuO NWs than Sn film meant that irreversible process took place at

![Fig. 5. Potentiodynamic CV measurement of (a) Sn film, (b) CuxO and (c) a-Sn/
CuxO NWs electrodes.](image)

![Fig. 6. Specific charge (vacant) and discharge (filled) capacity and Coulombic
efficiency (dot) of Sn film (circle) and a-Sn/CuxO NWs (square) electrodes.](image)
less extent. In general, the capacity loss seen in the initial C/D process is related with the formation of a solid electrolyte interface (SEI). The result suggested that electrolyte was less prone to decompose on the surface of a-Sn/CuxO NWs electrode. The nanowire structure also resulted in the discharge capacity of a-Sn/CuxO NWs being greater than the calculated theoretical value, due to the small size of crystalline structure of CuxO nanowire. The grain boundary between the crystalline structures could react with Li-ions by intercalation mechanism. After the formation cycle, the Coulombic efficiency was recovered up to 98%. a-Sn/CuxO NWs possessed a discharge capacity of 772.5 and 633.0 mAh g⁻¹ at 100th and 150th cycle, referring to 94.8% and 77.7% of cycle retention (1 C-rate), respectively. The value is quite similar and comparable to the Sn-based anodes for LIB, recently reported by other research groups as shown in Fig. S5 and Table S2 [11-13,18,21]. Meanwhile, the capacities suddenly decreased after 105th cycle and became stabilized. It was presumed that the structure of current heterostructure electrode changed and therefore could not relieve the stress at extended cycle. The capacity fading should be resolved by further research. The initial efficiency is commonly low when the surface area of electrode increases in pursuit of relaxing the applied stress during Li-ion reaction because the irreversible capacity from the formation of SEI arises accordingly. Therefore, it is hard to achieve both high initial Coulombic efficiency and moderate discharge capacity at extended cycle. The as-prepared a-Sn/CuxO NWs clearly demonstrated superiority in both criteria to the others as described in Fig. S5.

It is noteworthy to see that the capacity of the Sn film electrode increased until the 50th cycle, and further cycling resulted in a decrease in capacity. This was related with Sn activation in the early cycles, and a deterioration of the Sn film in the later cycles, in which the latter overwhelmed as cycles proceeded, causing a global capacity fading of the electrode. The fading was mainly attributed to the stress caused by the repeated lithiation and de-lithiation that accompanied a pulverization. On the other hand, a-Sn/CuxO NWs retained higher capacity and efficiency than Sn film over cycles. It was concluded that the nanowire structure promised an efficient charge transport, and the enlarged surface accommodated the volume change, relieving the stress during cycling.

In order to investigate the individual resistance applied to the electrode, EIS analysis was performed. Fig. 7 showed the EIS results of Sn film, CuxO and a-Sn/CuxO NWs electrode at the 1st and the 50th cycle. The resistance values of three electrodes were presented in Table 1. In contrast with Sn film electrode, the Cu₂O NWs and a-Sn/CuxO NWs electrodes had short diffusion length of the Li-ion due to a 1-D nanostructure, thereby having intrinsically low charge transfer resistance (RCT). It was notable that a-Sn/CuxO NWs possessed much lower RCT than Cu₂O did, owing to Cu nodes between the CuxO and Sn in a-Sn/CuxO NWs that enhanced the electrical conductivity. The formation of Cu nodes was already confirmed in XPS and TEM results. In speaking of change of resistance over cycles, the RCT of Sn film considerably increased after the 50th cycle because Sn film pulverized, and thus the formation of SEI was unstoppable on the fresh surface exposed to the electrolyte. However, the change of RCT in the a-Sn/CuxO NWs electrode increased at lesser extent.

Fig. S6a-d provided the electron microscopic surface images of Sn film and a-Sn/CuxO NWs electrodes before and after cycling. It was observed that the Sn film was pulverized after the 70th cycle with the rough surface of the Sn and cracked area (Fig. S6c). The a-Sn/CuxO NWs electrode, however, maintained its morphology even after the 70th cycle (Fig. S6d), even though the diameter of the a-Sn/CuxO NWs increased to about 415.1 (±3.1) nm, 182% of their initial value. In conclusion, implementing the nanowire structure contributed to relieve the stress applied to the electrode, and to prevent the nano-sized Sn from agglomerating.

The 1-D structure embedded to the a-Sn/CuxO electrode greatly affects their rate capability by increasing the active site of Li-ion insertion. The rate capability test was conducted by varying the C-rate from 0.1 C to 16 C, and the result was given in Fig. 8. The low internal resistance, revealed by EIS analysis helped the electrode retaining the capacity during C/D with high current. In specific, the a-Sn/CuxO NWs electrode presented a discharge capacity of 424 mAh g⁻¹ at 16 C, approximating to 51% of the discharge capacity measured at 1C. Moreover, the capacity was recovered nearly to 909 mAh g⁻¹ when the charging rate became back to 0.1 C (91% retention).

Table 1 Individual resistance values (RSEI, RCT, RCT) of Sn film, CuxO and a-Sn/CuxO NWs electrode at 1st and 50th cycle.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Cycle</th>
<th>RSEI (Ω)</th>
<th>RCT (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn film</td>
<td>1st</td>
<td>4.92</td>
<td>1.85</td>
</tr>
<tr>
<td>Sn film</td>
<td>50th</td>
<td>3.53</td>
<td>48.51</td>
</tr>
<tr>
<td>Cu₂O NWs</td>
<td>1st</td>
<td>5.08</td>
<td>6.98</td>
</tr>
<tr>
<td>Cu₂O NWs</td>
<td>50th</td>
<td>3.44</td>
<td>26.66</td>
</tr>
<tr>
<td>a-Sn/CuxO NWs</td>
<td>1st</td>
<td>4.88</td>
<td>7.5</td>
</tr>
<tr>
<td>a-Sn/CuxO NWs</td>
<td>50th</td>
<td>3.27</td>
<td>13.43</td>
</tr>
</tbody>
</table>

In summary, we have prepared the heterostructured a-Sn/CuxO nanowires electrode by facile electrochemical techniques; anodization and electrochemical deposition. The condition for fabricating the nanowires was optimized by precisely controlling deposition potential and time. The FE-SEM analysis showed the well-defined morphology and structure of the nanowires. The bulk and surface composition of the nanowires were investigated by XRD and XPS, respectively. Furthermore, quantitative XPS analysis confirmed the presence of Cu node that was expected to increase the conductivity of the nanowire electrode. The increased conductivity was reflected by the reduction in resistance by EIS analysis. From the CV result, both Sn and CuxO were proved to participate in the reaction with Li-ion. The a-Sn/CuxO nanowires electrode showed the stable cycle retention during 100 cycles, exhibiting a reversible discharge capacity of 772.5 mAh g⁻¹. CuxO nanowires contributed not only to increase the discharge capacity, but also to alleviate the stress applied to the electrode, retaining the electrode structure even after multiple cycles. Ultimately, we could achieve...
high initial Coulombic efficiency and discharge capacity at prolonged cycle. The a-Sn/CuO nanowires electrode exhibits a moderate rate capability and recovering ability. This work validates the a-Sn/CuO nanowires electrode for use as an anode in high performance lithium-ion batteries.

Acknowledgments

The research was financially supported by the MOTIE (Ministry of Trade, Industry and Energy) (10048778) and KSRC (Korea Semiconductor Research Consortium) support program for the development of the future semiconductor device, and also supported by the Basic Science Research Program through the NRF (National Research Fund) funded by the Ministry of Science, ICT and Future Planning (2016R1C1B1013053) and 2015 Research Grant from Kangwon National University.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.apsusc.2019.02.081.

References

[29] M. Kim, Structural Reﬁnement Using Nanowire and Micro-patterned Substrate for Si- or Sn-based Li-alloying Material in Li-ion Batteries (Thesis for Ph.D.), Seoul


