The confinement of SnO$_2$ nanocrystals into 3D RGO architectures for improved rate and cyclic performance of LIB anode†

S. K. Park,‡a H.-K. Kim,†bc K. C. Roh,‡d K.-B. Kim,*b and H. S. Park*a

In this study, we demonstrate the synthesis of a composite with SnO$_2$ nanoparticles anchored on three-dimensional (3D) reduced graphene oxide (RGO) as an anode for Li ion batteries (LIBs). SnO$_2$ nanoparticles were uniformly deposited on the surface of RGO sheets and the resulting RGO–SnO$_2$ architecture had an interconnected hierarchical structure. This hierarchical RGO–SnO$_2$ architecture exhibited outstanding electrochemical performance with a high reversible capacity of 810 mAh g$^{-1}$ at 0.1 A g$^{-1}$ and a high rate capacity of 210 mAh g$^{-1}$ at 2 A g$^{-1}$. Moreover, this architecture achieves 99% capacity retention even after 150 cycles at 0.1 A g$^{-1}$. The improved performance of the RGO–SnO$_2$ architecture is attributed to the uniform dispersion of SnO$_2$ nanoparticles and the 3D macroporous continuity, which afford a highly accessible area, easy ion accessibility, a short ion diffusion length, and rapid mass and charge transport. The composite described here is practically useful in the development of high-energy-density anode materials for LIBs.

1. Introduction

Li ion batteries (LIBs) are important for energy storage in portable electronic devices, power tools, and electrical vehicles,1–3 all of which require a high energy density. In order to meet the increasing demand for high energy density batteries, it is essential to develop high-capacity electrode materials. Although graphite has been used as a commercial anode material, it has a limited theoretical capacity of 372 mAh g$^{-1}$.4–7 In order to resolve the capacity bottlenecks of LIB anodes, it is important to develop high-capacity anode materials with high rate performance and cycle stability.

Recently, metal- and metal oxide-based anode materials have been reported to exhibit higher Li storage capacities than graphite through the formation of alloys with Li or by undergoing conversion reactions with Li ions.4–7 Especially, Sn oxide (SnO$_2$) has attracted attention because its theoretical reversible capacity (~790 mAh g$^{-1}$) based on the conversion reaction is almost twice that of graphite-based anodes.6,7 However, the reversible charging and discharging process is accompanied by large volume variation, which can result in the pulverization of SnO$_2$ and loss of electrical contact, causing rapid capacity decay upon extended cycling.6–8 Thus, the development of SnO$_2$-based anodes with enhanced cycling stability and high capacity is becoming important.

One promising solution is the use of nanostructured SnO$_2$, such as nanoparticles, nanowires, and nanosheets, to suppress volume variation.9–12 The nanostructuring of the electrode materials can overcome the kinetic limitation due to a short diffusion length, thereby enhancing the rate performance arising from a lower polarization.11,12 However, nanoscaling tends to invoke agglomeration, which reduces the electrochemically active surface area. Another approach involves the integration of SnO$_2$ with carbonaceous materials, which offer the benefits of high surface area, excellent electrical conductivity, and electrochemical and mechanical stability. Such an integrative approach inspires the nanoscale architecturing of SnO$_2$-based composites using different carbonaceous materials, such as amorphous carbon, carbon nanotubes, and graphene or reduced graphene oxide (RGO).13–19 Especially, RGO mitigates volume expansion for enhanced cyclic capability as well as improves the electrical conductivity of the composite for improved rate performance.17,18

The combination of SnO$_2$ nanoparticles and high-conductivity RGO could yield advanced anode materials; motivated by this possibility, several groups reported various synthetic methods for fabricating RGO–SnO$_2$.
nanocomposites.13,14,20,21 These strategies have improved the electrochemical performance of SnO2-based anode materials. However, improving the cycling and rate performances of RGO–SnO2 nanocomposites is still challenging because of the reduced surface area and long tortuous diffusion pathway originating from the restacking of RGO nanosheets. Thus, the confinement of SnO2 into three-dimensional (3D) RGO architectures through a favorable interplay is postulated to be a viable solution because of the synergistic effects of interconnected 3D internetworked connectivity and the inherent properties of the constituent RGO.22–24 3D macroscopic structures provide high surface areas, easy accessibility of ions to storage sites, short ion diffusion lengths to redox sites, and rapid charge and mass transport.22–26

With this in mind, we herein report a facile strategy for fabricating a 3D RGO–SnO2 architecture that encompasses the merits of both SnO2 nanostructures and carbonaceous materials with the aim of improving energy storage in LIBs, especially in terms of cycling performance. The fabricated 3D RGO–SnO2 architecture has a hierarchically interconnected porous structure, making it a suitable template for directly growing SnO2 nanoparticles without aggregation using a wet chemistry process in water. The as-synthesized 3D RGO–SnO2 architecture shows high specific capacity, rate capability and good cycling stability without drastic volume expansion.

2. Experimental

2.1 Synthesis of 3D RGO–SnO2

Graphene oxide (GO) was prepared using Hummers’ method following the procedure described in the literature.1 Subsequently, GO (40 mg) and DI water (7.6 mL) were uniformly dispersed by sonication. The GO dispersion was mixed with hypophosphorous acid (H3PO2) and iodine (I2) in a vial. This mixture was thermally treated at 90 °C for 12 h, and RGO was produced after gel formation. The RGO was then washed with an aqueous solution until the pH became 7, followed by freeze-drying to produce 3D RGO. To prepare the 3D RGO–SnO2, 3D RGO was simply immersed in SnCl2 solution (25 mg SnCl2 powder (98%, Aldrich) in 10 mL DI water) for 4 h at 25 °C.

2.2 Characterization

The structure and morphology of the resulting samples were characterized using scanning electron microscopy (SEM; JSM-7001F, JEOL Ltd.), transmission electron microscopy (TEM; 200 kV; CM200, Philips), X-ray diffraction (XRD; Cu Kα, 40 kV, 20 mA; Rigaku), and Raman spectroscopy (LabRam, Jobin Yvon-Spex). In addition, the surface of all the samples was analyzed using Fourier transform infrared spectroscopy (FTIR; Vertex 70, Bruker) and X-ray photoelectron spectroscopy (XPS; 15 kV, 150 W; ESCALAB 250, Thermo Electron Corporation). Thermal data for the samples were collected using DSC and TGA (NETZSCH) operating in air from room temperature (25 °C) to 700 °C at a heating rate of 10 °C min⁻¹. N2 adsorption–desorption isotherms of the samples were obtained at 77 K using a Micromeritics ASAP 2010 instrument.

2.3 Electrochemical measurements

The room temperature (25 °C) electrochemical properties of the samples were investigated using a CR2032 coin cell with metallic Li as the cathode and 3D RGO–SnO2 electrode as the working electrode. The electrolyte was a 1 M solution of LiPF6 dissolved in equal weights of ethylene carbonate and dimethyl carbonate. The charge–discharge tests and cyclic voltammetry were performed using a potentiostat/galvanostat (VMP3, Princeton Applied Research).

3. Results and discussion

Fig. 1 shows the 3D RGO–SnO2 architecture synthesized in two simple steps along with a schematic illustration of the synthetic protocol. In the formation of the 3D RGO–SnO2 architecture, GO agglomerate was first formed and then transformed into a partially reduced GO hydrogel by HI. According to the mechanism proposed based on the following reaction (1), the oxygen-containing groups on the GO surface were reduced by hydriodic acid (HI) to produce the reduced GO hydrogel.27

\[
\begin{align*}
H_3PO_2 + I_2 + H_2O &\rightarrow H_2PO_2 + HI \\
C &= O + HI &\rightarrow C - I - H_2O &\rightarrow RGO \text{ hydrogel}
\end{align*}
\] (1)

Next, Sn ions were introduced by adding SnCl2 precursors, as shown in reaction (2).28,29 Sn2+ ions were first bonded with the functional groups through electrostatic force and then anchored on the reduced GO surface to nucleate and grow 2–3 nm SnO2 nanoparticles in situ.30,31 Finally, these nanoparticles were loaded uniformly on RGO sheets.

\[
4Sn^{2+} + 2H_2O + O_2(g) \rightarrow 2SnO_2(s) + 4H^+ (aq)
\] (2)

The fabricated 3D RGO–SnO2 architecture was mechanically strong enough to support a load of 25 g without noticeable deformation. The macroporous connectivity of the 3D RGO–SnO2 architecture was well maintained even after several washing treatments with water. This result indicated that a final product could secure the benefits of 3D architecture such as a highly accessible surface area and short Li diffusion length for high-capacity LIBs.25,26

The 3D RGO–SnO2 architecture exhibits a well-defined interconnected microstructure with uniformly dispersed macropores that are several micrometers in size with a wall thickness of tens of nanometers and SnO2 nanoparticles in the composite, as evidenced by the SEM image in Fig. 2(a). Although SnO2 nanoparticles are not identified by a low magnification SEM image, their existence is distinguished from RGO due to a high contrast discrepancy as shown in a high
magnification SEM image in Fig. 2(b). Moreover, the SnO$_2$ nanoparticles are clearly observed and homogenously anchored on the RGO sheets, as indicated by energy-dispersive X-ray elemental analysis (Fig. S1 in the ESI†). The TEM image in Fig. 2(c) also shows that all the SnO$_2$ nanocrystals even with 2–3 nm size are anchored on the 3D RGO surfaces and stabilized as discrete particles by means of the confinement onto the 3D architecture and the interaction between them.
The interaction will be discussed below. In particular, the SnO₂ nanoparticles covered the entire surface of the 3D RGO structure.

Further investigation using high-resolution TEM further confirmed the highly crystalline nature of the SnO₂ nanoparticles, as shown in Fig. 2(d). Moreover, selected area electron diffraction (SAED) patterns corresponding to the (101), (110), and (220) planes shown in the inset further demonstrate the high degree of crystallinity.²⁰,²¹ The actual mass ratio of SnO₂ particles in the 3D RGO–SnO₂ architecture is determined by TGA to be about 51% (Fig. S2 in the ESI†).

Representative XRD patterns of the 3D RGO–SnO₂ composite and the standard XRD pattern for SnO₂ (JCPDS card no. 72-1147) are shown in Fig. 3(a).²⁰ The (002) peak of graphite at 26.5° has an interplanar distance, 20,21 2θ, of 0.334 nm, as shown in Fig. S3 in the ESI, which implies that graphite is a highly oriented carbon material. Meanwhile, for the GO powder, the sharp diffraction peak at 10.3° is characteristic of GO and corresponds to a d-spacing of ~0.83 nm.²¹ This measured distance could be attributed to an approximately one-molecule-thick layer of water that is hydrogen-bonded between the GO sheets. The 3D RGO–SnO₂ architecture does not exhibit this GO peak; instead, it shows a broadened peak at 25° corresponding to the (002) plane of graphite.²⁰,²¹ The broadening and shift of the characteristic diffraction peak of graphite from 26.5° to 25° was due to the short-range order in stacked graphene sheets. The interlayer spacing of the 3D RGO-SnO₂ architecture was slightly larger than that of graphite, which was because of the slight expansion of graphene sheet layers distorted by the presence of a small amount of residual oxygen-containing functional groups or other structural defects during the process. The major peak intensities corresponding to (110), (101) and (220) are in good agreement with the observation from the SAED patterns. The fringe lattice distance of 0.335 nm corresponds to the (110) plane as confirmed by the diffraction patterns. The size of the crystalline domain along the (110) plane observed from the high resolution TEM image was almost consistent with the particle size calculated using the Scherrer equation from the (110) plane in XRD data. These results support the highly crystalline structure of SnO₂ nanoparticles which is close to that of a single crystal. The ring patterns might be attributed to the small crystal size below the instrument resolution.

The chemical properties of GO and 3D RGO–SnO₂ were characterized by XPS, as shown in Fig. 3(b). From the C 1s XPS spectra, it is clear that the proportion of C–C bonds increases when GO is reduced in the 3D RGO–SnO₂ architecture.²²–²⁴ As shown in Fig. 3(b) left one, the Sn 3d₃/₂ and Sn 3d₅/₂ peaks associated with the SnO₂ nanoparticles are located at 487.4 and 495.8 eV, respectively, further suggesting the formation of SnO₂ nanoparticles coupled with RGO sheets. Moreover, the amount of C–OH and C–O–C groups in the composite was significantly lower than that expected based on the intensity of the peak at 533.4 eV in the O 1s spectrum for pristine GO (Fig. S4 in the ESI†). This suggests that the hydrogen in the hydroxyl groups or possibly the Sn 3d₃/₂ electrons in SnO₂ were replaced to form an O–Sn⁴⁺ connection accompanied by the opening of the epoxy rings.²⁰,²¹,²² Thus, the extra peak at 530.2 eV was attributed to the formation of an O–Sn⁴⁺ bond. It is worth noting that the Sn 3d₅/₂ electrons may bind with oxygen-containing functional groups on the RGO surface.²²,²³ Such a favorable interaction led to the stabilization of small sized, discrete SnO₂
nanocrystals confined in 3D architectures, which is associated with improved rate and cyclic performances.

The Raman spectra of GO and 3D RGO-SnO$_2$ in the selected ranges of 120 to 1000 cm$^{-1}$ and 1200 to 2000 cm$^{-1}$ are shown in Fig. 3(c). The Raman peaks in the 1200 to 2000 cm$^{-1}$ range were examined to confirm the formation of the RGO–SnO$_2$ architecture. For both materials, disordered (D) and graphitic (G) carbonaceous Raman bands were observed at 1350 and 1580 cm$^{-1}$, respectively. The spectrum of the 3D RGO–SnO$_2$ architecture exhibited a higher D/G intensity ratio than that of GO. This may be attributed to the reduction of GO into graphene during the 3D RGO–SnO$_2$ synthesis process and the presence of SnO$_2$ nanoparticles on 3D RGO. Moreover, the bands observed at ~630, 688, and 770 cm$^{-1}$ are related to the A$_{1g}$, A$_{2u}$, and B$_{2g}$ vibrational modes of SnO$_2$,$^{10,11}$ respectively, as shown in the inset of Fig. 3(c).

Finally, the electrochemical performance of 3D RGO–SnO$_2$ was investigated using Li metal as the counter electrode. Fig. 4(a) shows the dQ/dV curves of 3D RGO–SnO$_2$ in the voltage window of 0.01–3.0 V at a current density of 0.1 A g$^{-1}$. The dQ/dV curves clearly show that there is a substantial difference between the first and subsequent cycles. In the first cycle, reduction peaks were observed at about 0.8 and 0.6 V, which corresponded to the electrochemical formation of amorphous Li$_2$O and the formation of a partially irreversible SEI layer.$^{17,18}$ From the second cycle, a cathodic peak is observed at 0.75 V, which can be ascribed to the formation of SEI layers on the surface of the active material, the reduction of SnO$_2$ to Sn, and the synchronous formation of Li$_2$O. The peak near 0 V is attributed to the intercalation of Li into graphene to form LiC$_6$, whereas other relatively weak peaks located between 0.75 and 0 V can be ascribed to the formation of Li$_x$Sn$_y$ compounds. In the anodic curve, peaks at 0.2, 0.5, and 1.26 V are attributed to Li deintercalation from LiC$_6$, Li dealloying from Li$_x$Sn, and the partially reversible conversion of Sn to SnO$_2$, respectively.$^{20,21}$ High capacities of 810 and ~210 mAh g$^{-1}$ even at 0.1 and 2 A g$^{-1}$ (Fig. 4(b) and (c)) are made possible by the highly conductive 3D RGO sheets in the electrode, which serve as electrically conductive porous channels for the SnO$_2$ nanoparticles. Moreover, this architecture demonstrated a capacity retention of 99% after 150 cycles at 0.1 A g$^{-1}$ and 200 cycles at 0.5 A g$^{-1}$, while the volumetric efficiency remained at approximately 99% after the first cycle, which indicates an improvement in the cycle performance compared to the pure SnO$_2$ electrode prepared without the 3D RGO template (Fig. S5 in the ESI†).

These results indicate the existence of synergy between SnO$_2$ nanoparticles and 3D RGO in the hybrid composite.

---

Fig. 4  a) dQ/dV curves of the 3D RGO–SnO$_2$ architecture at a current density of 0.05 A g$^{-1}$. (b) Galvanostatic discharge/charge voltage profiles of the 3D RGO–SnO$_2$ architecture. (c) Rate performance of the 3D RGO–SnO$_2$ architecture at varying current densities from 0.1 to 2 A g$^{-1}$. (d) Cycling performance of 3D RGO–SnO$_2$ architecture at a current density of 0.1 (150 cycles) and 1 A g$^{-1}$ (200 cycles).
The hierarchical architecture prevents the aggregation of SnO$_2$ nanoparticles and RGO sheets during the charge-discharge process and improves the utilization of SnO$_2$ supported on the highly conductive RGO matrix. In addition, the 3D macroporous structure affords a highly accessible redox surface area and fast transport pathways for the electrolyte ions.

4. Conclusions

In this study, we demonstrated the synthesis of a 3D RGO-SnO$_2$ architecture consisting of SnO$_2$ nanoparticles anchored onto 3D RGO aerogels as an anode for LIBs. Mechanically stable 3D RGO–SnO$_2$ having a hybrid structure was electrochemically superior, showing high capacities of 810 and 210 mAh g$^{-1}$ even at 0.1 and 2 A g$^{-1}$ along with a good cyclability of 99% over 150 cycles at 0.1 A g$^{-1}$. The improved performance of 3D RGO–SnO$_2$ is attributed to the following factors: i) the 3D architecture affords the advantages of macroporous continuity and high surface area, which produces a large contact area between the active material and the electrolyte; moreover, the architecture provides fast transport pathways for the electrolyte ions. ii) RGO nanosheets provide a highly conductive matrix for electron transfer during lithiation and delithiation. iii) The intimate interaction between SnO$_2$ nanoparticles and RGO nanosheets, combined with uniform mixing, prevents the aggregation of SnO$_2$ nanoparticles and the restacking of RGO nanosheets.

Acknowledgements

This work was supported by the Energy Efficiency & Resources program of the Korea Institute of Energy Technology Evaluation Planning (KETEP) granted financial resources from the Ministry of Trade, Industry & Energy, Republic of Korea (No. 20122010100140), by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (NRF-2015R1A1A05027727 and 2015R1A6A3A03018844), and by the National Research Foundation of Korea Grant funded by the Korean Government (MSIP) (NRF-2011-0030542).

Notes and references

8 J. S. Chen and X. W. Lou, Small, 2013, 9, 1877.