Supporting Information

The Catalytic Role of Ge for Enhancing Electrochemical Performance of SnO$_2$(GeO$_2$)$_{0.13}$/G Anodes in Lithium Ion batteries

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Experimental section

Preparation of SnO$_2$/GeO$_2$, SnO$_2$/G and SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposites

Graphene oxide (GO) was synthesized via a modified Hummer’s method. $^{[1,2]}$ The as-prepared GO (43 mg) was ultrasonically dispersed in 60 mL of deionized (DI) water for 5 h and then 0.02 g GeO$_2$ (1.60 mmol) and 0.1 g SnCl$_2$ ($1.44 \times 10^{-2}$ mmol) was added into the solution. After magnetic stirring and sonication for 1 h and 20 min respectively, 0.76 mL HCl was added and stirred for 10 min. Then the mixture was transferred to a 100 mL Teflon-lined stainless steel autoclave and heated in a normal lab oven at 180 $^\circ$C for 24 h. After cooling naturally, the black precipitate was collected by centrifugation and washed with deionized water and ethanol for several times to remove the unreacted chemicals and residue, followed by drying in vacuum oven at 60 $^\circ$C for 24 h. For the control samples, SnO$_2$/G was prepared by the same method without the addition of GeO$_2$, and SnO$_2$/GeO$_2$ was prepared by mixing the commercial SnO$_2$ (0.08 g) and GeO$_2$ (0.02 g) powder through the mechanical mixing method.

Materials Characterization

The crystal structures of the as-prepared samples were characterized by X-ray diffraction (XRD) using a Siemens D5005 powder diffractometer equipped with Cu K$\alpha$ radiation ($\lambda \approx 1.54\text{Å}$). The microstructures were investigated by field-emission scanning electron microscopy (FESEM, JEOL JSM-7600F) and transmission electron microscopy (TEM JEM2100F). Raman spectra were carried out by a WITec Instruments Raman system (Germany) with a 514.5 nm Ar$^+$ laser excitation. The elemental composition of samples was characterized by an X-ray photoelectron spectrometer (SPECS, mode XP-50) with a monochromatic Al K$\alpha$ radiation ($h\nu = 1486.6$ eV).

Electrochemical measurement
The electrode slurry was made by mixing 75 wt% active materials (i.e., SnO$_2$/GeO$_2$, SnO$_2$/G, or SnO$_2$(GeO$_2$)$_{0.13}$/G), 15 wt% acetylene black and 10 wt% polyvinylidene fluoride (PVDF) in N-methyl pyrrolidone (NMP) with magnetic stirring for 5 h. The slurry was then coated onto nickel foam and dried at 110 °C in vacuum furnace for 12 h. The coin-type cells (CR 2032) were assembled in an argon filled glovebox with the slurry as the active electrodes, Li metal as the counter/reference electrode, and polypropylene micro-porous film (Celgard 2300) as the separator. The electrolyte was 1 M LiPF6 in ethylene carbonate (EC) and dimethyl carbonate (DMC) (EC/DMC, 1:1 in volume). The cells were galvanostatically charged and discharged at 50–2000 mA/g in the voltage range of 0.01–3.0 V vs Li/Li$^+$ on a NEWARE battery tester. Cyclic voltammetry (CV) measurements were carried out at 0.1 mV/s between 0.01 and 3.0 V using an electrochemical work station (VMP3, Bio-logic). The electrochemical impedance spectra (EIS) measurements were measured by applying a sinusoidal wave with amplitude of 5 mV in the frequency range of $10^5$ to 0.01 Hz. All of the electrochemical measurements were conducted at room temperature.

**Calculation of the theoretical capacity of SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposite**

The electrochemical reactions involved for the alloying-dealloying type metals as following:

$$ MO_2 + 4 Li^+ + 4e^- \xrightarrow{\text{discharge (1)}} M + 2Li_2O $$

$$ M + xLi^+ + xe^- \xrightarrow{\text{discharge (2)}} Li_xM \quad (0 \leq x \leq 4.4) $$

$$ Li_xM \xrightarrow{\text{charge (3)}} M + xLi^+ + xe^- \quad (0 \leq x \leq 4.4) $$

$$ M + 2Li_2O \xrightarrow{\text{charge (4)}} MO_2 + 4Li^+ + 4e^- $$

The theoretical capacity of SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposite can be calculated according to the
above electrochemical reaction. Thus, we could divide the calculation into the following two cases:

1) The reactions (1) and (4) are irreversible.

The content of SnO$_2$, GeO$_2$, and graphene are 72.3 wt%, 6.5 wt%, and 21.2 wt%, respectively. According to the following formula: $C = \frac{n \times F}{3600 \times m_a}$, where $C$ is the theoretical specific weight capacity of the active material, $n$ is the number of transferred electrons per molecule of active material, $F = 96485$ C/mol is the Faraday constant, $m_a$ is the molar weight of the active material. Without reaction (1) and (4), the involved electrons are 4.4. Thus, the theoretical specific weight capacity of SnO$_2$ and GeO$_2$ is 782 and 1126 mAh/g, respectively. The reversible capacity graphene obtained by the modified Hummer’s method is around 300 mAh/g. Therefore, the theoretical capacity of SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposite is calculated by:

$$782 \times 72.3\% + 1126 \times 6.5\% + 300 \times 21.2\% = 702 \text{ mAh/g}.$$ 

2) The reactions (1) and (4) are reversible.

If the reactions (1) and (4) are reversible, the involved electrons during the charge and discharge process are 8.4. Thus, according to the following formula: $C = \frac{n \times F}{3600 \times m_a}$, the theoretical capacities of SnO$_2$ and GeO$_2$ are 1493 and 2152 mAh/g, respectively. So, the theoretical capacity of SnO$_2$(GeO$_2$)$_{0.13}$/G nanocomposite is $1493 \times 72.3\% + 2152 \times 6.5\% + 300 \times 21.2\% = 1283 \text{ mAh/g}$. 
Figure S1. SEM images of the (a) commercial SnO$_2$ and (b) commercial GeO$_2$ particles.
Figure S2. TGA curves of SnO$_2$(GeO$_2$)$_{0.13}$/G (a) and SnO$_2$/G (b).
Figure S3. XPS C 1s spectrum of reduced graphene oxide (RGO).
Figure S4. The galvanostatic charge/discharge curves of 1st, 3rd, and 5th cycles of (a) SnO$_2$/G and (b) SnO$_2$/GeO$_2$ nanocomposites at a current density of 50 mA/g.
Figure S5. Electrochemical impedance spectroscopy (EIS) spectra of (a) SnO$_2$/G and (b) SnO$_2$/GeO$_2$ after 5 and 100 cycles.
Figure S6. (a) The 5th and 30th charge and discharge curves of SnO$_2$/GeO$_2$ electrode. The retention of the plateau for the electrochemical reaction of forming SnO$_2$ or GeO$_2$ is around 70%. (b) The 5th and 30th charge and discharge curves of SnO$_2$/G electrode. The retention of the plateau for the electrochemical reaction of forming SnO$_2$ is about 60%.

References

