Catalystic Role of Ge in Highly Reversible GeO₂/Ge/C Nanocomposite Anode Material for Lithium Batteries

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Experimental Methods

GeO₂ nanoparticles were prepared through hydrolysis of GeCl₄ in a water/ethanol system, as reported by us previously. ^[2e] In a typical procedure, 2 ml GeCl₄ (99.99%, Alfa Aesar) was added to 8 ml ethanol (99.9%, anhydrous, Sigma Aldrich) and left to stir for 10 minutes. In a separate beaker, 8 ml de-ionised water was added to 120 ml anhydrous ethanol and left to stir for 10 minutes. The GeCl₄ mixture was injected into the water/ethanol solution. Then, the mixture was left to stir for 3 hours. The resultant white precipitate was collected by centrifugation and washed several times with ethanol before drying at 100°C to obtain the final product.

The carbon coating process for the GeO₂ nanoparticles was carried out in a horizontal tube furnace using 10% acetylene in argon as the carbon source. The powders were placed in an alumina crucible in the central heating zone. The tube was then evacuated to eliminate air, and flowing 10% C₂H₂ in argon gas was introduced at 200 mL/min. The sample was then heated to 520°C for 30 minutes and removed from the furnace after cooling. For the synthesis of the GeO₂/Ge/C, the reaction temperature was increased to 650°C, and the reaction time remained 30 minutes. The heating rate used for both experiments was 5°C/min. At least 3 batches were prepared for each sample.

For electrochemical analysis, the samples were mixed with sodium carboxymethyl cellulose (MW = 90000; Sigma Aldrich), polyacrylic acid (MW = 100000; Sigma Aldrich), and Ketjenblack in a ratio of 70:7.5:7.5:15. De-ionised water was added to form a homogeneous slurry, which was then pasted on copper foil using a doctor blade. 2016 type coin cells were assembled in an argon filled glove box using lithium metal as counter electrode, microporous polyethylene as separator, and 1.15 M LiPF₆ in ethylene carbonate/dimethyl carbonate/diethyl

carbonate (EC/DMC/DEC; 3/4/3; PanaxStarlyte) as electrolyte. The loading amounts of active materials for all electrodes were $0.50 \pm 0.05 \text{ mg/cm}^2$ and $0.75 \pm 0.05 \text{ g/cm}^3$. The specific capacities were calculated based on the active materials only (i.e. GeO₂/Ge/C).



Figure S1. Isotherm curves of (a) GeO₂-nano, (b) GeO₂/C and (c) GeO₂/Ge/C from BET analysis. Insets are the pore-size distributions calculated using the Barrett-Joyner-Halenda (BJH) method.



Figure S2. Rietveld refinement of the $GeO_2/Ge/C$ sample, indicating a ratio of Ge to GeO_2 of 17:83. The weight percentages of the components in the composite are 64 wt% GeO_2 , 13 wt% Ge and 23 wt% C. The red line is the original XRD pattern, the blue line is the fitted profile and the short vertical lines mark the line positions of the standards. The spectrum in the bottom panel is the difference spectrum.



Figure S3. (a) Low magnification SEM image of the GeO₂-bulk sample. (b) Higher magnification image of the GeO₂-bulk sample. (c,d) SEM images of the GeO₂-nano sample. Large clusters were not observed and the individual particles were less than 100 nm in size. (e,f) SEM images of GeO₂/C sample. Clusters of up to 30 micrometers can be observed and the particle size remains similar to that of GeO₂-nano. (g,h) SEM images of the GeO₂/Ge/C sample. Clusters of up to 30 micrometers can be observed, and the individual particle size is similar to those of both GeO₂-nano and GeO₂/C.

The surface morphologies of all the samples were investigated using a field-emission scanning electron microscope (FE-SEM). Figure S3c and d shows the morphology of the GeO₂-nano sample. No large clusters can be observed at low magnification, while at high magnification, the individual particles are rather small. After carbon coating, the granulation effect from the acetylene gas can be observed. Figure S3e presents FE-SEM image of the GeO₂/C sample, which is composed of large granules up to 50 micrometres in size. At higher magnification (Figure S3f), the particle size remains relatively small, and the morphology is identical to that of GeO₂-nano. The surface morphology of the GeO₂/Ge/C shows similar morphology to the GeO₂/C sample, where granulation was observed and the individual particle size remaines relatively small. This is consistent with the BET analysis results described previously. In addition, the morphology of the GeO₂-bulk sample is presented in Figure S3a and b, consisting of large particles with diameters up to 30 micrometers. At higher magnification, it can be seen that each particle is made up of rod-like agglomerates.



Figure S4. (a) Coulombic efficiency of the cells (corresponding to Figure 4a) tested at 1 C; (b) cycling performance of the GeO2/Ge/C and GeO₂/C sample at 1C (2.1 A/g) with higher loading of 1.4 mg/cm²; (c) cycling performance of the GeO2/Ge/C and GeO₂/C sample at 10 C (21 A/g) with loading of 0.5 mg/cm².

The GeO₂/Ge/C and GeO₂/C was tested at 1C with a higher loading of active materials (1.4 mg/cm²) and the results are shown in Figure S4b. Both samples shows lower capacity compared to those tested with a lower loading amount (Figure 4a). This is due to the poorer kinetics of a thicker electrode. Nevertheless, the GeO₂/Ge/C sample still shows stable cycling performance over 50 cycles with capacity retention of 1100 mAh/g.

In order to study the cycling stability at higher rates, GeO₂/Ge/C and GeO₂/C were tested at 10C over 50 cycles and the results are shown in Figure S4c. The capacity of GeO₂/Ge/C recorded was 1650 mAh/g which is comparable to the capacity from the rate capability tests (1680 mAh/g; Figure 4c). Slight capacity fading was observed after the 40th cycle similar to the cycling tests at 1C rate. The GeO₂/C sample showed very poor cycleability at 10C rate, where a sharp drop in capacity was observed from the initial cycling. The results from the cycling test at 10C rates, shows that additional Ge in the GeO₂/Ge/C, plays a crucial role as a catalyst to ensure the reversibility of the conversion reaction at high rates.



Figure S5. Differential plots of (a) GeO_2 -bulk, (b) GeO_2 -nano, (c) GeO_2/C and (d) $GeO_2/Ge/C$ at the 15th cycle. The insets are the corresponding voltage profiles.



Figure S6. (a)Raman spectra of GeO₂-nano, GeO₂/C, and GeO₂/Ge/C. The spectrum of GeO₂nano shows peaks corresponding to GeO₂. The spectrum of GeO₂/Ge/C shows a peak at 300 cm⁻¹ corresponding to germanium. The D and G bands of amorphous carbon are indicated by the peaks at 1338 cm⁻¹ and 1594 cm⁻¹ for GeO₂/Ge/C, and 1347 cm⁻¹ and 1606 cm⁻¹ for GeO₂/C, respectively; (b) Fourier transform infrared spectra of all the samples. All three samples show peaks corresponding to GeO₂. The peaks at 753 cm⁻¹ and 728 cm⁻¹ correspond to GeO₂ synthesized at low temperature.

The samples were characterised using Raman spectroscopy (WITec Alpha300R; 532.6 nm laser), and the spectra are presented in Figure S6a. The spectrum of GeO2-nano shows peaks that match well with previous reports in the literature, where all the peaks can be related to the vibrations of GeO2. [8] The bands at 883 and 964 cm⁻¹ correspond to the Ge-O stretching within

tetrahedral GeO₄ units, while Ge-Ge stretching is represented by the bands at 518 and 592 cm⁻¹. The band at 448 cm⁻¹ is the symmetric Ge-O-Ge stretching, while the bands at 167 and 260 cm⁻¹ correspond to the complex translation and rotation of the GeO₄ tetrahedra. The 773 cm⁻¹ band, which is not present in crystalline GeO₂, is most likely caused by the low temperature synthesis of GeO₂, as reported by Autchin et al..¹ The spectrum of GeO₂/Ge/C shows a band at 300 cm⁻¹ which corresponds to crystalline germanium and a band at 448 cm⁻¹ which corresponds to the Ge-O-Ge symmetric stretching of GeO₂. These two peaks confirm the results of XRD, where both germanium and GeO₂ are present in the sample. Two maxima at 1338 and 1594 cm⁻¹ correspond to the D and G bands of carbon, with an I_D/I_G ratio of 1, which indicates the disordered nature of the carbon.² In the spectrum of GeO₂/C, only the D and G bands of carbon can be detected at 1347 and 1606 cm⁻¹. The reason for the absence of bands representing GeO_2 could not be determined, although characterisation over several sample batches has been carried out. To further investigate, we performed Fourier transform infrared spectroscopy (FTIR; JASCO FT/IR-4100) on the GeO₂/C sample to detect the presence of GeO₂. The spectrum of GeO_2/C shows a triplet at 516, 552, and 585 cm⁻¹, indicating the hexagonal structure of the GeO₂ crystal, and the band at 882 cm⁻¹ corresponds to the vibration mode of GeO₄ tetrahedra. The spectrum of GeO₂/Ge/C shows identical peaks to the spectrum of GeO₂/C, indicating the presence of hexagonal GeO₂ in the sample. The spectrum of GeO₂-nano, however, includes two more absorption bands at 728 and 753 cm⁻¹, which correspond to the P3221 symmetry of GeO₂ nanocrystals synthesised at low temperature.¹

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