One step preparation of high performance Ge/C nanocomposites anode for lithium ion batteries by tandem plasma reactions

Preparation
The Ge/C composite samples are deposited in a home-designed tandem plasma reactor which consists of a magnetron sputtering source and an inductively coil (Figure 1). The distance between the target and the substrate is 15 cm. The inductively coupled plasma (ICP) coil is located 2 cm above the substrate. The chamber is first evacuated to $8 \times 10^{-4}$ Pa by a diffusion pump. Ar (99.995%) and CH$_4$ (99.95%) are inlet separately for Ge sputtering and carbon coating, respectively. The working pressure of the chamber is maintained at 2.0 Pa. Ge particles are generated by magnetron sputtering of a high purity Ge target (99.995%), and are coated with carbon in the ICP zone by decomposition of CH$_4$. The products are directly deposited on copper foils and silicon substrates at room temperature. And the obtained products are uniform films with sufficient adhesion to the substrates, which can be directly used as the electrodes without further treatment.

Characterization
The products deposited on substrates can be directly characterized by scanning electron microscopy (SEM, Hitachi S4800, 10 kV) with an energy dispersive X-ray spectroscopy (EDS) analyzer. For transmission electron microscopy (TEM, JEOL JEM-2100, 200 kV) measurement, the samples are scratched from the SiO$_2$/Si substrate to copper grids.

The X-ray photoelectron spectroscopy (XPS) analysis was performed on an AXIS-Ultra instrument from Kratos Analytical using monochromatic Al Kα radiation (225 W, 15 mA, 15 kV) and low energy electron flooding for charge compensation. To compensate the surface charge effects, binding energies were calibrated using the C 1s hydrocarbon peak at a binding energy (BE) of 284.8 eV. As there is usually carbon contamination on the surface, the sample surface is etched by Ar ion bombardment.

The electrodes used in electrochemical performance measurements are fabricated by direct deposition of Ge/C composite on copper foils. Coin type half-cells were assembled in an argon-filled glove-box. A lithium foil was utilized as the counter electrode. 1 M LiPF$_6$ in ethylene carbonate/dimethyl carbonate = 1/1 in volume was used as the electrolyte. Polypropylene films (Celgard 2400) were used as the separators. All the cells were tested at a current density of 2000 mA g$^{-1}$ for both charge and discharge at room temperature in the voltage range of 0.005 - 1.5 V (versus Li/Li$^+$). Cyclic voltammetric measurements were performed in the voltage range of 2.5 - 0 V (versus Li/Li$^+$) at a scan rate of 0.1 mV s$^{-1}$.

![Fig. S1 EDS spectrum of the Ge/C composite on the SiO$_2$/Si substrate.](image-url)
Fig. S2 XPS spectrum of the Ge/C composite on the SiO₂/Si substrate, (a) etching 5 nm; (b) etching 10 nm. The percentage of C is 52 At% and 54 At%, which is equivalent to 15 wt% and 16 wt%, respectively.