Electronic Supporting information

A double-layered Ge/carbon cloth integrated anode for high performance lithium ion battery

Xiaohong Zhang, [a, b] Shimou Chen, [a]* Jia Yu, [a, b] Daliang Fang, [a, b] Suojiang Zhang [a] *

[a.] Beijing Key Laboratory of Ionic Liquids Clean Process, Key Laboratory of Green Process and Engineering, State Key Laboratory of Multiphase Complex Systems, Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, PR China. E-mail: chenshimou@ipe.ac.cn; sjzhang@ipe.ac.cn

[b.] University of Chinese Academy of Sciences, No. 19A Yuquan Road, Beijing 100049, PR China.

Experimental

1. Materials

The ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) amide , ([Emim]Tf_2N], 99%) was purchased from Linzhou Keneng Materials Technology Co., Ltd. (China) and used after drying under vacuum at 60 °C for 48 h. $GeCl_4$ (99.9999%) was purchased from Alfa Aesar. Commercial carbon cloth (from Hubei Rocktek Instrument Limited Co., Ltd., China) was cleaned by sonicating in a mixture of acetone, deionized water, and ethanol (1:1:1, vol%) for 30 min. Ge powder (99.999%) was purchased from Aladdin Industrial Co., Ltd.

2. Synthesis of the double layered porous Ge film on flexible carbon cloth

The Ge/carbon cloth electrode was synthesized by electrodeposition in an argon-filled glove box (Vigor Glove Box, Suzhou, China) with water and oxygen contents below 2 ppm on a CHI660D electrochemical workstation (Shanghai Chen Hua). A three-electrode system was assembled with a carbon cloth as the working electrode, a Pt film as the counter electrode, and an Ag wire as the quasi-reference electrode. The electrolyte was a

0.1 mol L^{-1} $GeCl_4$/[Emim]Tf_2N solution. For this experiment, the deposition potential was maintained at -1.64V for 60 min. After the electrochemical deposition, the deposit was rinsed with isopropanol for five times to remove the residual ionic liquid.

3. Characterization

Morphological characterization was performed with a Hitachi SU8020 scanning electron microscope (SEM) operating at 5 kV. Raman spectra was measured on a Confocal Lab RAM HR800 spectrometer with the 514 nm laser. X-ray photoelectron spectroscopy (XPS) was carried out on a Thermo Scientific ESCALAB 250Xi system with an Al Ka source.

4. Electrochemical Measurement

The electrochemical performance was measured in a LIR2025 coin-type cells. The flexible Ge/carbon cloth composite electrode was directly used as the working electrode. Li metal was used as the counter and reference electrodes, Celgard 2400 as the separator, and a mixture of 1M $LiPF_6$ in ethylene carbonate, dimethyl carbonate, diethyl carbonate (1:1:1 vol%) as electrolyte. Commercial Ge powder electrode was prepared by the common method in which the commercial Ge powder, carbon black, and poly(vinylidene fluoride) (PVDF) at a weight ratio of 8 : 1 : 1 were dissolved uniformly in N-methyl-2-pyrrolidone (NMP) and then the slurry was pasted on pure Cu foil. The cells were assembled in a glove box as mentioned above. The cells were aged for 10 h before electrochemical measurement to ensure the fully contact of electrode materials with electrolyte. Cyclic voltammogram (CV) was conducted on a CHI660D electrochemical workstation (Shanghai Chen Hua).The CV experiment was carried out in the range of 0.01 to 2.0 V (Li/Li^+) at a scan rate of 0.1 mV s^{-1}. Galvanostatic charge/discharge cycles were performed from 0.01V to 2.0V at room temperature on a Land battery measurement system (LAND CT-2001A, Wuhan, China). The EIS performance was measured in the frequency range of 0.01 to 100 kHz with an AC amplitude of 5 mV (Gill AC Serial no 1572, ACM).

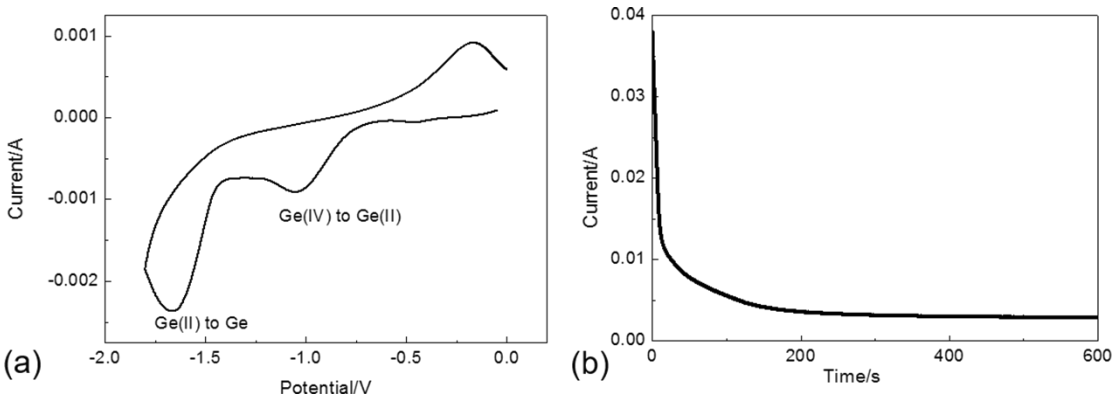

Fig. S1 (a)Cyclic voltammogram of 0.1 mol L^{-1} $GeCl_4$ in [Emim]Tf_2N at room temperature with a piece of commercial carbon cloth as the working electrode, a Pt film as the counter electrode and an Ag wire as the quasi-reference electrode, respectively. The scan rate was 10 mV s^{-1}. (b) Current-time(I-t) curve of Ge electrodeposition at -1.64 V

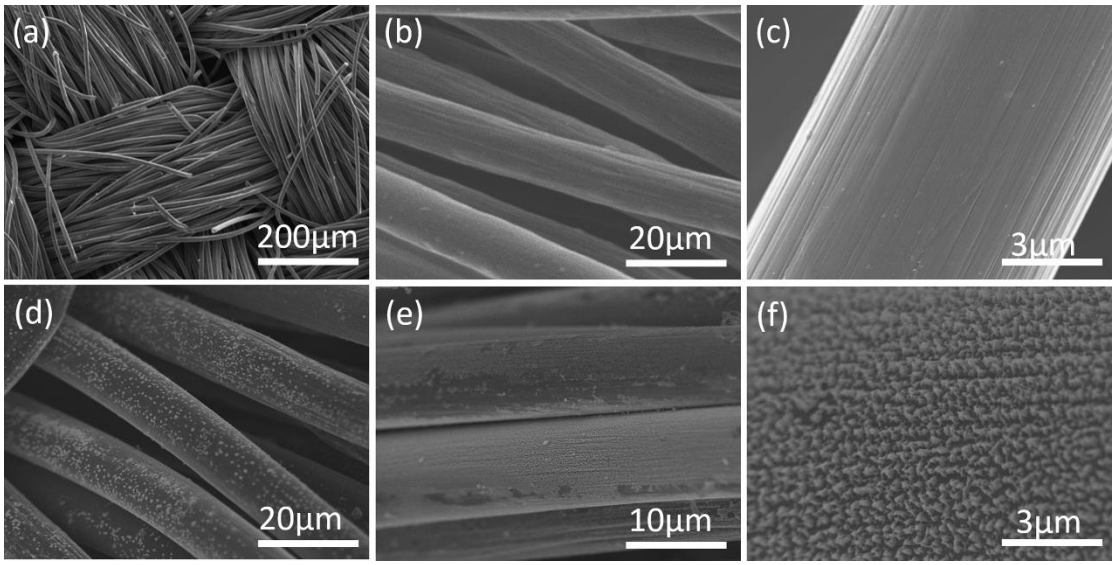

Fig. S2 SEM image of pure carbon cloth. (a) The low magnification SEM image of carbon cloth with 3D architectures. (b, c) The high magnification SEM image of carbon cloth fibers. (d) Ge island nanoparticles on carbon cloth fibers after electrodeposition for 30s. (e, f) Ge island arrays after electrodeposition for 120s at different magnifications.

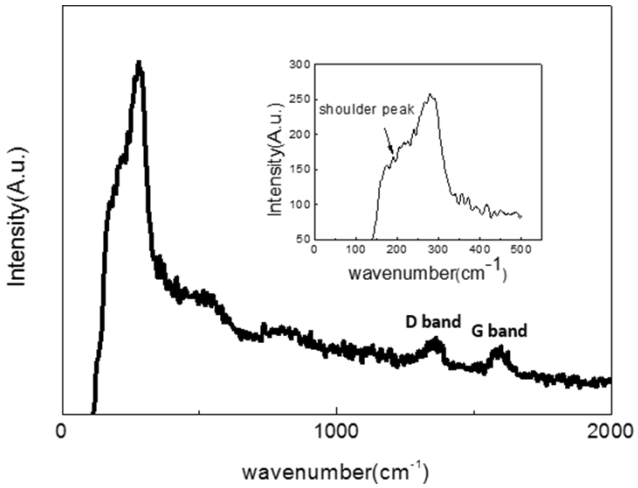

Fig. S3 Raman spectrum of the double-layered Ge film coating on carbon cloth.

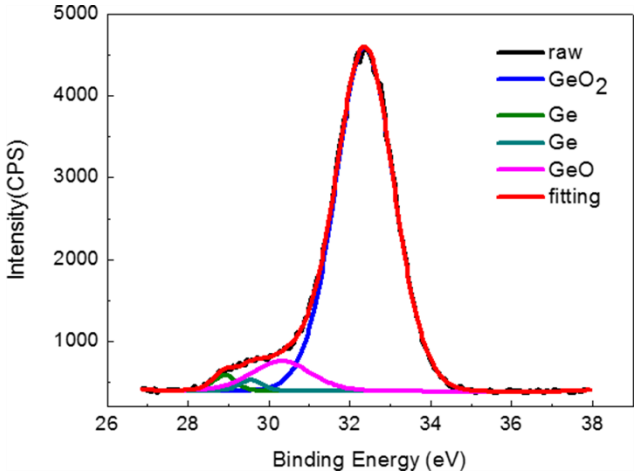

Fig. S4 Ge 3d XPS spectra of the porous double-layered Ge film electrodeposited from [Emim]Tf_2N.

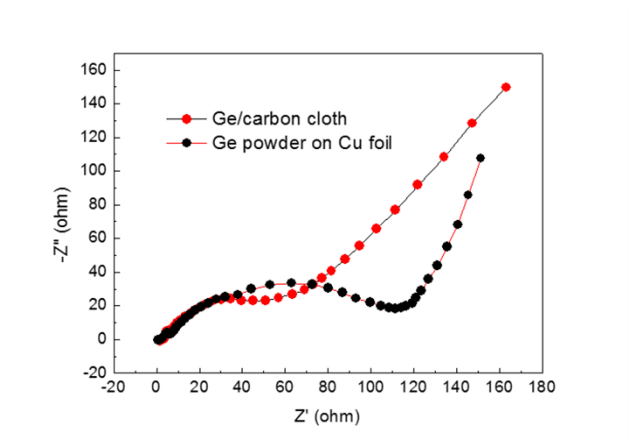

Fig. S5 Nyquist plots of the Ge/carbon cloth integrated electrode and Ge powder coating on Cu foil electrode.