Supporting Information

**Oxygen vacancies boosting lithium-ion diffusion kinetics of lithium germanate for high-performance lithium storage**

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1. Preparation of Li-Ge-PVP nanofiber precursor

All chemical reagents were of analytical grade and were used as received. First, GeO$_2$ (0.625 mmol) and LiCl (0.625 mmol) were dissolved in a mixed solution of water (7.5 mL) and ethanol (7.5 mL). Subsequently, polyvinylpyrrolidone (PVP, MW = 130 000) was dissolved in 15 g of dimethylformamide (DMF) to form a transparent solution. The resultant solution was loaded into a plastic syringe equipped with a 7-gauge stainless-steel nozzle. A piece of alumina foil as a fiber collector was placed at 15 cm from the tip of the needle. The feeding rate was set at 0.3 mL h$^{-1}$. A high voltage of 15 kV was exerted to collect the nanofibers. After the electrospinning process, the as-electrospun nanofibers were peeled off from the collector and then were transferred into a furnace for stabilization.

2. Characterizations

The phase composition was identified using powder X-ray diffraction (XRD, Bruker D8, Cu-Kα). The morphologies of the prepared materials were observed by scanning electron microscopy (SEM, HITACHI S-4800) and transmission electron microscopy (TEM, JEOL JEM-2010). N$_2$ sorption was performed to analyze the total specific surface areas (SBET) with the Brunauer-Emmett-Teller (BET) method and pore size distribution plots using the Barret-Joyner-Halenda (BJH) method. The X-ray photoelectron spectroscopy (XPS) spectra were measured on ESCALAB 250 spectrometer (Perkin-Elmer). Raman spectra were analyzed using in-Via Raman spectrometer. The photoluminescence (PL) spectra were obtained by using a Cary Eclipse florescence spectrometer (Varian, USA) with Xe lamp as the excitation source. The X-ray absorption spectroscopy (XAS) was conducted at Beamlines 1W1B at the Beijing Synchrotron Radiation Facility.

3. Electrochemical measurements

To prepare the working electrode for LIBs, the as-obtained material, acetylene black, and sodium carboxymethyl cellulose binder (CMC) with a mass ratio of 7:2:1
were firstly mixed together by trace water to form a homogeneous slurry, which then was coated onto Cu foil and dried at 120 °C for 36 h in vacuum oven. The mass loading of each as-prepared working electrode was around 1 mg. The cell [coin cell (CR2025)] assembly was operated in an Ar-filled glovebox. The Celgard 2400 microporous polypropylene membrane and Li foil were used as the separator and the counter electrode, respectively. The non-aqueous electrolyte used was 1 M LiPF₆ dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) mixture (1:1:1, in vol.%). The cyclic voltammetry (CV) tests were carried out at scan rates ranging from 0.1 to 3 mV s⁻¹ on a CHI-760E workstation. Galvanostatic cycling experiments of the cell were performed on a LAND CT2001A cell at different current densities in the voltage range of 0.01-3.00 V vs. Li⁺/Li at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were recorded in a frequency range of 100,000 to 0.01 Hz with AC oscillation of 5 mV at the open circuit voltage.

A complete Li-ion battery is assembled by coupling the Li₂GeO₃₋ₓ/C anode with commercially available LiFePO₄ cathode. Before the complete cell is assembled, the Li₂GeO₃₋ₓ/C anode is pre-lithiated by cycling for 30 cycles. Upon designing the battery, it is of paramount importance to reach an optimal balance of the cathode and anode electrodes both in term of weight and electrochemical properties. The Li₂GeO₃₋ₓ/C and LiFePO₄ show reversible discharge capacities of ca. 800 mA h g⁻¹ at 1000 mA g⁻¹ (Figure 4c) and ca. 125 mA h g⁻¹ at 170 mA g⁻¹ (Figure S10), respectively. Thus, the mass ratio of the Li₂GeO₃₋ₓ/C anode to the LiFePO₄ cathode is selected to be ca. 1:6.4 for the complete cell. According to the principle of capacity balance with a slight excess of the cathode to ensure the efficient utilization of the anode materials, the mass ratio of Li₂GeO₃₋ₓ/C to LiFePO₄ thus is determined to be about 1:7.7 and the loading values of Li₂GeO₃₋ₓ/C and LiFePO₄ in our experiment are 0.77–1.05 and 5.39–8.09 mg, respectively.
4. The calculation of apparent activation energy ($E_a$)

The apparent activation energy ($E_a$) was calculated using the Arrhenius equation:

$$i_0 = \frac{RT}{nFR_{CT}}$$  \hspace{1cm} (1)

$$i_0 = Ae^{-\frac{E_a}{RT}}$$  \hspace{1cm} (2)

Here $A$ is the temperature-independent coefficient, $R$ is the gas constant, $T$ is the absolute temperature, $n$ is the number of electrons transferred, and $F$ is the Faraday constant.
5. Supplementary Figures

**Figure S1** SEM image of Li-Ge-PVP nanofiber precursor.

**Figure S2** N$_2$ adsorption-desorption isotherms of (a) Li$_2$GeO$_{3-x}$/C, (b) Li$_2$GeO$_3$/C and (c) Li$_2$GeO$_3$. 
**Figure S3** Pore size distributions of (a) Li$_2$GeO$_{3-x}$/C, (b) Li$_2$GeO$_3$/C and (c) Li$_2$GeO$_3$ nanofibers derived from N$_2$ adsorption-desorption isotherms.

**Figure S4** High-resolution XPS Ge 3d spectra of Li$_2$GeO$_{3-x}$/C, Li$_2$GeO$_3$/C and Li$_2$GeO$_3$ nanofibers.
Figure S5 Raman spectra of Li$_2$GeO$_{3-x}$/C, Li$_2$GeO$_3$/C and Li$_2$GeO$_3$ nanofibers.

Figure S6 The first discharge/charge voltage profiles of (a) Li$_2$GeO$_3$/C and (b) Li$_2$GeO$_3$. 
**Figure S7** SEM image of Li$_2$GeO$_{3-x}$/C after 100 cycles at 0.1 A g$^{-1}$.

**Figure S8** CV curves of (a) Li$_2$GeO$_{3-x}$/C and (b) Li$_2$GeO$_3$/C at different scan rates from 0.1 to 1 mV s$^{-1}$. Log (i) vs. log (v) plots at each redox peak of (c) Li$_2$GeO$_{3-x}$/C and (d) Li$_2$GeO$_3$/C.
Figure S9 CV profiles of (a) Li$_2$GeO$_{3-x}$/C and (b) Li$_2$GeO$_3$/C at a sweeping rate of 1 mV s$^{-1}$. The estimated capacitive current contribution is shown in the shaded region. The capacity contributions of (c) Li$_2$GeO$_{3-x}$/C and (d) Li$_2$GeO$_3$/C at different scan rates (0.1, 0.2, 0.4, 0.6, 0.8, and 1 mV s$^{-1}$).

Figure S10 Cycling performance of the commercially available LiFePO$_4$ at a current density of 1 C.