Oxygen vacancies boosted the electrochemical kinetics of Nb$_2$O$_{5-x}$ for superior lithium storage

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1. Experimental section

1.1. Preparation of Nb$_2$O$_{5-x}$ microflowers

All chemicals were analytical reagents and can be used directly without purification. Firstly, 7.5 mmol of niobium oxalate (C$_{10}$H$_5$NbO$_{20}$) and 1.5 mmol of ammonium carbonate ((NH$_4$)$_2$·CO$_3$) were added to 30 mL of deionized water under sonicating for 30 minutes. Then, the mixed suspension was transferred to a 50 mL of Teflon-lined stainless steel autoclave and kept at 200 °C for 12 hours. After the reaction, the product was collected, washed with deionized water and ethanol, and dried in an oven at 60 °C for 12 hours. Finally, the product was calcined at 450 °C for 30 minutes with a heating rate of 2 °C min$^{-1}$ in Ar/H$_2$ (95%/5%) to acquire the Nb$_2$O$_{5-x}$ microflowers.

1.2. Characterization

The composition and phase information of the samples were measured by a powder X-ray diffractometer (XRD, German Bruker D8 diffractometer with Cu radiation). The morphology and microstructure of the samples were tested by the scanning electron microscope (FE-SEM, JEOL, JSM-7800F) and the high-resolution transmission electron microscope (HRTEM, JEOL, JEM-2100F). The surface elemental composition and chemical states of the samples were performed by X-ray photoelectron spectroscopy (XPS, Thermo Scientific ESCALAB 250Xi system with a monochromated Al K$\alpha$ X-ray source 1486.6 eV). The Raman spectra were obtained on a DXR Raman spectrometer (Thermo Scientific) with a 532 nm laser for illumination. The electron spin resonance (EPR) was performed by using a BRUKER A300-10/12 instrument. The
thermogravimetric analysis (TGA) was characterized on a (Netzsch STA 449 F3, USA) instrument. Nitrogen adsorption–desorption isotherms were measured on a Beishide 3H-2000PS2 type specific surface area and pore size analyzer at 77 K. The Brunauer–Emmett–Teller (BET) specific surface areas ($S_{\text{BET}}$) were calculated using the BET equation, and the pore size distributions were determined using the Barret–Joyner–Halender (BJH) method.

1.3. Electrochemical measurements

The Nb$_2$O$_{5-x}$ microflowers (80 wt.%), super conductive carbon black (SCCB, Ketjenblack EC-600JD, Lion Corporation) (10 wt.%), and polyvinylidene fluoride (PVDF) (10 wt.%) were mixed in N-methyl-2-pyrrolidone (NMP) and then coated the slurry onto the copper foil. The loading mass was in the range of 0.9 to 1.2 mg cm$^{-2}$. Using CR2032-type coin cells assembled in an Ar-filled glove box (oxygen/moisture concentrations < 0.01 ppm) carried out the electrochemical test. The celgard 2400 porous polypropylene membrane was used as the separator. The lithium foil was used as the counter electrode. The lithium-ion electrolyte was 1 M LiPF$_6$ EC/DMC/DC solution. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a Gamry (Interface 1000E Potentiostat) electrochemical workstation. The galvanostatic discharge and charge and galvanostatic intermittent titration technique (GITT) tests were tested with the NEWARE-CT-4008 battery tester between 0.01 V and 3.0 V.
Fig. S1 Illustration of the preparation process of the Nb$_2$O$_{5-x}$ microflowers.
Fig. S2 (a, b) SEM, (c) TEM, and (d) HRTEM images of the Nb$_2$O$_5$ microflowers.
Fig. S3 XPS survey spectra of the Nb$_2$O$_5$ and Nb$_2$O$_{5-x}$.
Fig. S4 TGA curves of the Nb$_2$O$_5$ sample tested in air and argon, respectively.
Fig. S5 N₂ adsorption-desorption isotherms and pore size distribution plots (inset) of the Nb₂O₅ and Nb₂O₅–ₓ samples.

Table S1 BET specific surface area, BJH pore size, and pore volume of the Nb₂O₅ and Nb₂O₅–ₓ.

<table>
<thead>
<tr>
<th>Samples</th>
<th>BET surface area (m² g⁻¹)</th>
<th>BJH pore size (nm)</th>
<th>Pore volume (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb₂O₅</td>
<td>48.61</td>
<td>3.81</td>
<td>0.23</td>
</tr>
<tr>
<td>Nb₂O₅–ₓ</td>
<td>53.74</td>
<td>3.62</td>
<td>0.35</td>
</tr>
</tbody>
</table>
Fig. S6 CV curves of the Nb$_2$O$_5$ electrode at different scan rates.
Fig. S7 GCD curves of the (a) pristine Nb$_2$O$_5$ and (b) Nb$_2$O$_{5-x}$ at various current densities, respectively.
Fig. S8 (a) CV response of the Nb$_2$O$_5$ electrode with separation of the capacitive (green region) and diffusion current (blank region) at 1.0 mV s$^{-1}$. (b) Capacitive contribution ratio of the Nb$_2$O$_5$ electrode.
Fig. S9 GITT curves of the Nb$_2$O$_5$ and Nb$_2$O$_{5-x}$. 