Electronic supplementary information (ESI)

Elasticity-related periodical Li storage behavior delivered by porous graphene

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Table S1. The gradually increased Li capacity for nanomaterials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Typical pore size (nm)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Typical cycling performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>graphene and porous polyaryltriazine derived frameworks</td>
<td>3.7</td>
<td>1683</td>
<td>Figure 3b in [1]</td>
<td></td>
</tr>
<tr>
<td>Nitrogen-doped carbon nanotubes</td>
<td>Not mentioned</td>
<td>Not mentioned</td>
<td>Figure 2c in [2]</td>
<td></td>
</tr>
<tr>
<td>Porous graphene</td>
<td>~4</td>
<td>1654</td>
<td>Figure 3c in [3]</td>
<td></td>
</tr>
</tbody>
</table>
Table S2. The fluctuations in the cycling performance for porous carbon materials.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Typical pore size (nm)</th>
<th>Specific surface area (m² g⁻¹)</th>
<th>Typical cycling performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>A conductive microporous carbon matrix, containing S in the micropores</td>
<td>0.5 nm</td>
<td>936</td>
<td>Figure 4b in [4]</td>
<td></td>
</tr>
<tr>
<td>Carbon shells, encapsulating Si nanoparticles</td>
<td>~100 nm</td>
<td>Not mentioned</td>
<td>Figure 4E in [5]</td>
<td></td>
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<tr>
<td>Hollow carbon nanosphere</td>
<td>~60 nm</td>
<td>412</td>
<td>Figure 3a in [6]</td>
<td></td>
</tr>
<tr>
<td>RGO, graphene prepared via reduction of graphene oxide</td>
<td></td>
<td></td>
<td>Figure 3b in [7]</td>
<td></td>
</tr>
</tbody>
</table>
Figure S1. TG curve of the magnesium oxysulfate whiskers in an oxygen flow. The weight loss at ~ 314 °C corresponds to the release of crystal water in 5Mg(OH)$_2$·MgSO$_4$·3H$_2$O, and the weight loss at ~ 409 °C corresponds to the decomposition of Mg(OH)$_2$.

Figure S2. XPS survey (a) and S 2p peak (b) of PG-1.
Figure S3. Galvanostatic charge/discharge curves of the PG-1 electrode without pre-lithiation at the current density of 50 mA g$^{-1}$.

Figure S4. Cycling performance of a parallel sample of PG-1.
Figure S5. Illustration showing the variation of physical parameters during lithiation for a closed single nanopore (a), a semi-closed single nanopore (b) and interconnected nanopores (c, d). In a, $d$ and $d'$ are the interlayer spacings before and after lithiation. In b, $\Phi$ and $\Phi'$ are the opening degrees of the entrance before and after lithiation, $c_l$ and $p_i$ are the Li$^+$ concentration and the pressure in the nanopore, and $c_0$ and $p_0$ are the Li$^+$ concentration and the pressure in the bulk electrolyte (out of the nanopore). In c and d, $V$ and $L$ represent volume and length, respectively.

Discussion: The closed ball shown in Figure S5a is the simplest situation for a nanopore. In that case, the interlayer placing between graphene layers will increased from $d$ to $d'$ due to the intercalation of Li$^+$. Because the covalent bonds between C atoms are not destroyed during the lithiation, the diameter increase of the outer walls will lead to an increase of the contractility and inner pressure. The variations of Li$^+$ concentration and inner pressure are shown in Figure S5b. The openning degree of the entrance ($\Phi$) probably decreases after the lithiation because of the formation of SEI films and the expansion of the nanopore. The pressure in the lithiated nanopore ($p_i'$) should be higher than that before lithiation ($p_i$), because of the increased tensile force of the pore wall and the decreased opening degree. Because of the
good adsorbability of the nanopore, the \( \text{Li}^{+} \) concentration in the nanopore \( (c_i) \) should be larger than that in the bulk electrolyte \( (c_0) \). After lithiation, \( c_i \) is larger than \( c_0 \), because of the \( \text{Li}^{+} \) insertion. In the PG, almost all nanopores are interconnected with each other. Therefore, the cases shown in Figure S5c and d are closer to the actual situation. Obviously, the pore volumes of the interconnected pores will increase after lithiation, aroused by the stretching of outer walls. Therefore, it is concluded that the volume and surface area of the nanopore, the \( \text{Li}^{+} \) concentration in the pore, and the internal pressure will increase after the lithiation.

**Figure S6.** Rate capability of the PG-1 electrode at the current from 1 to 10 A g\(^{-1}\).
Figure S7. Low (a), middle (b & c) and high magnification (d) TEM images of PG-2 after cycling tests.

Discussion: As shown in Figure S7a, the 3D fibrous structure of PG-2 has been well kept after cycling. Blocking and reducing of the openings of nanopores due to the deposition of SEI films and the attachment of binder, thus forming semi-closed nanopores, are observed in the material, as indicated by the arrows in Figure S7b & c. Thick SEI films are observed on the surface of the porous graphene (Figure S7d).
Figure S8. Cycling performances of PG-1 at different pressure: 2 (a), 4 (b), 6 (c), 8 (d) and 10 (e) MPa at the current density of 1 A/g. (f) The standard deviation of the coulombic efficiency (CE) at different pressures.
Figure S9. (a) AC impedance curves and (b) charge-transfer resistances ($R_{ct}$) of the PG-1 electrode pressed at different pressures. The inset of b is the equivalent circuit for fitting of the impedance curves. In the equivalent circuit, $R_e$ represents the total resistance of electrolyte, electrode, and separator. $R_f$ and CPE$_1$ are the resistance and capacitance (expressed by a constant phase element) of the SEI films formed on the electrode. $R_{ct}$ and CPE$_2$ represent the charge-transfer resistance and the double layer capacitance, respectively, and $Z_w$ is the Warburg impedance related to the diffusion of lithium ions into the bulk electrode.

Discussion: The charge-transfer resistance ($R_{ct}$) significantly increases at the pressure of 10 MPa, indicating that the porous structure of PG-1 might be damaged.
Figure S10. Cycling performance of the PG-1 electrode with different PVDF contents: lithiation-delithiation capacities (a), CE (b) and the standard deviations of CEs (c).

Reference


