Rational design of oxide/carbon composite to achieve superior rate-capability via enhanced lithium-ion transport across carbon to oxide

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Table S1. Brunauer–Emmett–Teller (BET) specific surface areas and pore volumes of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites

<table>
<thead>
<tr>
<th></th>
<th>BET surface area (m² g⁻¹)</th>
<th>Pore Volume (cm³ g⁻¹)</th>
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</thead>
<tbody>
<tr>
<td>LTO/rGO</td>
<td>25.4</td>
<td>0.208</td>
</tr>
<tr>
<td>LTO/L-NPG</td>
<td>43.7</td>
<td>0.311</td>
</tr>
<tr>
<td>LTO/M-NPG</td>
<td>44.1</td>
<td>0.327</td>
</tr>
<tr>
<td>LTO/H-NPG</td>
<td>41.9</td>
<td>0.364</td>
</tr>
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Fig. S1. TGA profiles of SnO$_2$/rGO composites with different loading amounts of SnO$_2$. 
As illustrated in Fig. S2, we assumed the hemispherical SnO$_2$ nanoparticles deposited on the basal plane of graphene in calculating the number of nano-perforations in the NPG. Since nano-perforations were created only at the contact points with the hemispherical SnO$_2$ nanoparticles, number of nano-perforations in the NPG was determined by the number of hemispherical SnO$_2$ nanoparticles in the composite. The number of SnO$_2$ nanoparticles ($N$), which is equivalent to the number of nano-perforations, in the composites was calculated by dividing the weight of SnO$_2$ in SnO$_2$/rGO composites by the weight of a single hemispherical SnO$_2$ nanoparticle.

\[
N = \frac{(Wx/100)}{(4\pi r^3 \rho/3)/2} \tag{Eq. S1}
\]

where $W$ is the weight of SnO$_2$/rGO composite (g) used for TGA, $x$ is the weight percent of SnO$_2$ nanoparticles in SnO$_2$/rGO composite (wt%) from TGA, $r$ is the radius of a SnO$_2$ nanoparticle (3 nm), $\rho$ is the density of SnO$_2$ (6.95 g cm$^{-3}$).
As the weight percent of SnO$_2$ nanoparticles in SnO$_2$/rGO composite increases, the weight percent of rGO in SnO$_2$/rGO composite decreases. Therefore, the area of rGO available for SnO$_2$ nanoparticle deposition decreases. Finally, number density of nano-perforations, which is the number of nano-perforations per unit area, in the NPG was calculated as follows: (1) the area of rGO ($S$, m$^2$) available for SnO$_2$ nanoparticle deposition in SnO$_2$/rGO composite was calculated by multiplying the weight of rGO in the composite and the specific surface area of rGO; and (2) the number density of nano-perforations in the NPG ($\mu$m$^{-2}$) was calculated by dividing the number of nano-perforations in the NPG by the area of rGO in SnO$_2$/rGO composite:

\[ S = W(1-(x/100))A \]  
\[ \text{Number Density} = N/S \]

where $A$ is the specific surface area of rGO (300 m$^2$ g$^{-1}$) measured in BET analysis.
Fig. S3. Raman spectra of (a) NPG, (b) acid-treated NPG (a-NPG), and (c) heat-treated a-NPG.
Fig. S4. TEM images of (a) a-NPG and (b) heat-treated a-NPG.
Fig. S5. TGA profiles of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.
Fig. S6. XRD patterns of (a) JCPDS card No. 490207, (b) bare LTO, (c) LTO/rGO composite, (d) LTO/L-NPG composite, (e) LTO/M-NPG composite, and (f) LTO/H-NPG composite.
Fig. S7. XPS C1s spectra of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.
Fig. S8. XPS Ti 2$p$ spectra of bare LTO and LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.

The Ti2$p$ XPS spectra of bare LTO and LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites were analyzed to investigate the oxidation state of Ti in the composites (Fig. S8†). All the LTO composites and bare LTO could be deconvoluted into two different peaks centered at 458.3 and 464.0 eV, corresponding to Ti2$p_{2/3}$ and Ti2$p_{1/2}$, respectively, which was the characteristic peaks of Ti$^{4+}$. In addition, the binding energy difference of 5.7 eV between the two peaks was observed for all the LTO composites and bare LTO, indicating that the oxidation state of Ti was Ti$^{4+}$. 
Fig. S9. N$_2$ gas adsorption/desorption isotherms of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.
Fig. S10. SEM image (inset) and N\textsubscript{2} adsorption/desorption isotherms of pure LTO microspheres without NPG.
Fig. S11. N\textsubscript{2} adsorption/desorption isotherms of (a) rGO and (b) NPG.
Fig. S12. Raman spectra of rGO, L-NPG, M-NPG, and H-NPG.
Fig. S13. Linear plot of the resistance as a function of the pellet thickness for calculating the electronic conductivity of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.
Fig. S14. GCD profiles of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites normalized with respect to the specific discharge capacities at 1 C.
Fig. S15. Overvoltage plots of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites at normalized capacities of (a) 0.5 and (b) 0.85.
Fig. S16. Cycle performance of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites.

Fig. S16† compares the cyclabilities of LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites over 300 cycles at 10 C. The LTO/NPG composites showed better cycling stabilities than LTO/rGO composite. After 300 cycles, LTO/rGO, LTO/L-NPG, LTO/M-NPG, and LTO/H-NPG composites could retain 83.7, 89.7, 95.4, and 98.6% of their initial discharge capacities, respectively.
Fig. S17. CV profiles of (a) LTO/L-NPG and (b) LTO/M-NPG composites at increasing scan rates from 0.05 to 10 mV s$^{-1}$. 
Fig. S18. Plot of real part of impedance vs. $\omega^{-1/2}$ (angular frequency$^{-1/2}$) for LTO/rGO, LTO/L-NPG, LTO/M-NPG and LTO/H-NPG composites.

To further analyze the EIS data of the LTO composites, the real part of the impedance in the low-frequency region ($Z'$) was plotted against the reciprocal square root of the angular frequency ($\omega^{-1/2}$) at low frequencies in Fig. S18†. The linearity in Fig. S18† is associated with solid state diffusion of lithium ions in the bulk LTO. Equations S4 and S5 show the relationship between $D_{\text{app}}$ and the Warburg factor ($\sigma$).

\[
Z' = R_s + R_I + R_{ct} + \sigma\omega^{-1/2} \quad \text{(Eq. S4)}
\]

\[
D_{\text{app}} = \frac{(R^2T^2)/(2A^2n^4F^4C_{Li}^2\sigma^2)} {\quad \text{(Eq. S5)}}
\]
where $D_{app}$ is the apparent diffusion coefficient, $R$ is the gas constant, $T$ is the absolute temperature, $A$ is the specific surface area of the electrochemically active sites (m$^2$·g$^{-1}$), $n$ is the number of electrons per molecule during the reaction, $F$ is the Faraday constant, $C_{Li}$ is the concentration of the reactant, and $\sigma$ is the Warburg factor calculated from the slope of the linear part of the EIS profiles between the real axis $Z'$ and $\sigma^{-1/2}$ using Equation S4.

In this EIS analysis, we again set $D_{app}$ a constant ($10^{-12}$ cm$^2$·s$^{-1}$) for LTO in the LTO composites according to the assumptions used for the CV data analysis using Randles–Sevcik equation Fig. 6(c). Finally, Equations S4 and S5 were used to calculate $A$ for LTO/H-NPG, LTO/M-NPG, LTO/L-NPG, and LTO/rGO composites. $A$ was calculated to be 4.327, 2.202, 1.092, and 0.847 m$^2$·g$^{-1}$ for LTO/H-NPG, LTO/M-NPG, LTO/L-NPG and LTO/rGO composites, respectively.
As shown in Fig. S19†, the XRD patterns of the LFP composites exhibited all the standard peaks observed for olivine LFP with the $P_{nma}$ space group (JCPDS card No. 83-2092). No impurity peaks were observed in the XRD patterns of the LFP composites, indicating that the spray-drying process and heat treatment did not cause any structural changes of the olivine LFP.

Fig. S19. XRD patterns of bare LFP, LFP/rGO composite, and LFP/H-NPG composite.
Fig. S20. TEM images of (a) LFP/rGO and (b) LFP/H-NPG composites.

Fig. S20† shows TEM images of LFP/rGO and LFP/H-NPG composites. A typical low-magnification TEM image reveals that the primary LFP nanoparticles were densely packed, consisting of secondary spherical micro-particles with diameters of ~3 µm. In addition, the appearance of the edge of an individual composite particle at higher magnification reveals that the LFP particles were wrapped by a thin layer of NPG (or rGO).
Fig. S21. Electrochemical properties of bare LFP, LFP/rGO composite and LFP/H-NPG composite in 1 M LiPF$_6$ 1:1 EC/DMC electrolyte in the 2.0–4.3 V potential window. The GCD profiles of (a) bare LFP, (b) LFP/rGO composite and (c) LFP/H-NPG composite at increasing C-rates from 0.1 to 100 C. (d) Plots of the rate capability of bare LFP, LFP/rGO composite, and LFP/H-NPG composite.