Support information

One-Pot spray-dried graphene sheets-encapsulated nano-Li₄Ti₅O₁₂ microspheres for a hybrid BatCap system

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Figure S1. (a)-(d) FE-SEM images of SP-A, SP-B, SP-C, and SP-D, respectively.

Figure S2. XRD patterns of products (A, B, C, D) obtained from SP-A, SP-B, SP-C, and SP-D, respectively, calcined at 700 °C for 3 h in Ar/H₂ (5 %). (*) anatase TiO₂

Figure S3. High-resolution XPS spectra of Ti 2p in (a) LTO@GS-A, (b) LTO@GS-B, (c) LTO@GS-C and (d) LTO@GS-D composites, respectively.

As shown in Figure S3(a), two peaks corresponding to $Ti2p_{3/2}$ and $Ti2p_{1/2}$ for LTO@GS-A sample appeared at 458.4 and 464.1 eV respectively, which demonstrate the existence and occupying of Ti^{4+} in an octahedral environment. That is in good consensus with the 4+ oxidation of titanium in LTO. Another pair of peaks at 457.8 and 463.0 eV is attributed to $Ti2p_{3/2}$ and $Ti2p_{1/2}$, indicating the existence of Ti^{3+} .^{1,2} The chemical state of $Ti^{4+}2p_{3/2}$, $Ti^{4+}2p_{1/2}$, $Ti^{3+}2p_{3/2}$ and $Ti^{3+}2p_{1/2}$ can also be determined in LTO@GS-B, C and D samples (Figure S3(b)-(d)). The ratios of the Ti^{4+}/Ti^{3+} for LTO@GS-A, B, C and D samples are calculated to be 4.56, 4.29, 4.07 and 3.95 respectively. A decrease in ratios of the Ti^{4+}/Ti^{3+} may due to the increased GO contents in the composites.

Figure S4. TGA curves of LTO@GS composites calcined in the air.

LTO@GS samples are heated to 800 °C in the air at a heating rate of 10 °C min⁻¹ to monitor the mass changes. Based on the TGA results in Figure S4, the mass reduction below 350 °C is considered as the volatilization of residue water in the samples, and above 350 °C, there is a clear decline in the mass of LTO@GS-B, C, and D samples, which correspond to a combustion reaction of carbon. From TGA results, the contents of GS in the samples are 1.93 %, 4.46 % and 6.63 %, respectively. However, TGA of LTO@GS-A indicated no mass change with temperature in the air.

Figure S5. (a) Raman spectra and (b) highlighted range view of LTO@GS composites.

As can be seen from Figure S5a, the Raman spectrum of LTO@GS-A displays peaks at around 235 cm^{-1} (the bending vibrations of O–Ti–O), 335 and 430 cm^{-1} (the stretching–bending vibrations of the Li–O bonds in LiO_6 and LiO_4 polyhedra) and 740 cm^{-1} (vibrations of Ti–O bonds in TiO_6 octahedra), which confirms the specific characteristics of the LTO particles.^{3,4} While the intensity of LTO characteristic peaks of LTO@GS-B, C, D decreases significantly with the cover level of the GS. Besides, the Raman spectra of LTO@GS-B, C, D also exhibit another two peaks at around 1355 cm^{-1} and 1597 cm^{-1} , which are identified respectively as the D band and G band of GS. As highlighted in Figure S5b, a stronger G band is observed than D band, indicating a good electronic conductivity of the obtained GS.

Figure S6. BJH pore size distribution plots and nitrogen adsorption-desorption isotherm (insets) of (a) LTO@GS-A (b) LTO@GS-B (c) LTO@GS-C and (d) LTO@GS-D

Figure S6 show the pore size distribution curves calculated by the BJH method and nitrogen adsorption-desorption curves (insert images) of LTO@GS with various GS contents. As shown in Figure S6a, almost negligible nanopores with the pore volume of only $0.0138 \text{ cm}^3 \text{g}^{-1}$ is observed for LTO@GS-A, which may be caused by grown-up particle size of LTO during high-temperature sintering process. The insert images of Figure S6b-d exhibit a distinct large hysteresis loop from 0.45 to 1 of relative partial pressure (P/P_0), which is assigned to a porous structure. The pore volume obtained from nitrogen adsorption-desorption are 0.0827 , 0.0754 and $0.0536 \text{ cm}^3 \text{g}^{-1}$ for LTO@GS-B, C, D respectively, which are 4-6 times of LTO@GS-A. BJH analysis indicates that the three samples have rather narrow pore size distribution about 2-4 nm. The narrow pore size distribution illustrates that the samples have very regular pore channels in the nanoporous region.

Figure S7. Charge-discharge profiles from 1 to 3 V at different rates for (a) LTO@GS-A; (b) LTO@GS-B; (c) LTO@GS-C and (d) LTO@GS-D

The charge/discharge curves of LTO@GS||Li half cells at various rates from 1C to 40 C in the potential range of 1.0-3.0 V vs. Li/Li⁺ are shown in Figure S7. At a rate of 1 C, the discharge specific capacities of LTO@GS-A, B, C, D are 166.6, 174.4, 173.2, and 171.0 mAh g⁻¹, respectively. And with an increase in the charge/discharge rate, the specific capacities of the four samples decline accordingly. The capacities of LTO@GS-A and LTO@GS-D decrease steeply whereas those of LTO@GS-B and LTO@GS-C decrease much slower at the same rate. It is noteworthy that at the rate of 40 C, LTO@GS-A and LTO@GS-D have no clear discharge voltage plateau, and the capacity is only 69.9 and 76.5 mAh g⁻¹, respectively. While for LTO@GS-B and LTO@GS-C, although the cell voltage also decreases with increasing current density, flatter potential plateaus are shown even at 40 C, and the capacities retain 90.6 and 84.5 mAh g⁻¹, respectively. From Figure 6S, a different process of

polarization of the four samples also can be seen clearly. the values of the plateau potentials margin for LTO@GS-B and LTO@GS-C (with 21.5 and 22.3 mV at 1 C rate, and 492.9 and 378.0 mV at 40 C rate, respectively) are much smaller than those of LTO@GS-A and LTO@GS-D (with 55.5 and 84.1 mV at 1 C rate, and 208.4 and 199.8 mV at 40 C rate, respectively).

Figure S8. (a) Electrochemical impedance spectra of LTO@GS composites at the discharged voltage of 1.6 V. A magnified view of the high frequency region of LTO@GS-B, C, D is provided in the inset; (b) Equivalent circuit evaluated based on the AC impedance spectra.

The impedance analysis of the samples was carried out to understand the charge transfer kinetics. EIS data for the LTO@GS | electrolyte | Li

cells were compared over the frequency range from 100 kHz to 0.01 Hz under an open circuit out at 1.6 V after preliminary equilibration. The Nyquist plots and equivalent circuit of the samples are shown in Figure S8a and b. The resistance values are normalized by multiplying the mass of the active material of each sample to attain a reference comparison.

Table S1 Impedance parameters and Values of A , dE/dx and Li^+ diffusion coefficient D of LTO@GS electrodes

sample	R_s (Ω g)	R_{ct} (Ω g)	R_f (Ω g)	A	dE/dx	D (cm^2s^{-1})
LTO@GS-A	1.80×10^{-2}	1.17×10^{-1}	8.31×10^{-3}	26.78	7.33	6.53×10^{-9}
LTO@GS-B	2.17×10^{-3}	1.11×10^{-2}	7.65×10^{-4}	11.65	12.20	9.68×10^{-8}
LTO@GS-C	1.49×10^{-3}	2.59×10^{-2}	1.02×10^{-3}	12.19	8.79	4.58×10^{-8}
LTO@GS-D	6.36×10^{-3}	2.67×10^{-2}	5.98×10^{-3}	23.95	7.41	8.40×10^{-9}

The impedance analysis results given in Table S1 clearly demonstrate that the ohmic resistance of electrolyte and electrode (R_s), charge transfer resistance at the active material interface (R_{ct}) and polarization resistance related with surface charge/discharge process and contacting resistance between electrode particles (R_f) of the LTO@GS-B, C, D were much smaller than those of LTO@GS-A.

Figure S9. Real and imaginary parts of the complex impedance vs. $\omega^{-1/2}$ of LTO@GS-A, B, C, D at potentials about 1.6 V

The chemical diffusion coefficient of Li^+ inside LTO@GS samples can be estimated from the impedance results. The following expression for Z_w is derived by solving Fick's law:^{5, 6}

$$Z_w = A\omega^{-1/2} - jA\omega^{-1/2} \quad (1)$$

$$A = \frac{V_M(dE/dx)}{\sqrt{2}zFD^{1/2}a} \quad (2)$$

Where, ω is the frequency, $j = \sqrt{-1}$, and the pre-exponential factor A is a constant which contains a concentration independent chemical diffusion coefficient, as shown in Eq.(1). As demonstrated in Eq. (2), the pre-exponential factor A is inversely proportional to the chemical diffusion coefficient, D , therefore, the larger A , the slower diffusion rate

of Li^+ ions in the solid matrix of the electrode should be, which can be obtained from Figure S8. V_M is the molar volume of LTO ($45.73 \text{ cm}^3 \text{ mol}^{-1}$). dE/dx is the slope of the electrode potential curve vs. x insertion of Li^+ . z is the charge transfer number ($z=1$ in the lithium intercalation reaction). a is the electroactive surface area of the electrode, which is 1.13 cm^2 in our testing electrode. F is the Faraday constant. The specific calculation referred to the author's previous publication.⁷ The values of dE/dx , A and D of LTO@GS-A, B, C, D samples are listed in Table S1. The D of the LTO@GS-B ($9.68 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) and LTO@GS-C ($4.58 \times 10^{-8} \text{ cm}^2 \text{ s}^{-1}$) are one order of magnitude higher than the value for the LTO@GS-A ($6.53 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$) and LTO@GS-D ($8.40 \times 10^{-9} \text{ cm}^2 \text{ s}^{-1}$), suggesting that the Li^+ ion diffusion kinetics of LTO@GS-B and LTO@GS-C are significantly better than LTO@GS-A and LTO@GS-D.

Figure S10. Rate discharge behaviors of the LTO@GS||AC hybrid BatCap between 1.5 and 3.0 V at C-rate values ranging from 1 C (20 mA g⁻¹) to 80 C (1600 mA g⁻¹). Inset shows the photo of soft packed BatCap and the discharge profiles at current density of 1 C and 2 C for clarification

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