Supporting Information

Graphene Encapsulated Metallic State Ce$_2$Sn$_2$O$_7$ as a Novel Anode Material for Superior Lithium-Ion Batteries and Capacitors

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Experimental Section

**Materials:** \( \text{K}_2\text{SnO}_3\cdot3\text{H}_2\text{O} \) (Aladdin Reagent, AR), \( \text{Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) (Beijing Chemical Works), NaOH (Beijing Chemical Works), Polyvinylidene Fluoride (PVDF, DuPont Company, 99.9%), Acetylene black (Hong-Xin Chemical Works), N-methyl-2-pyrrolidinone (NMP, Aladdin Reagent, AR), Separator (polypropylene film, Celgard 2400), Commercial activated carbon (AC, Aladdin Reagent), Deionized water (Laboratory preparation). Graphite oxide (GO) was produced from natural graphite flakes by a modified Hummers method.¹

**Characterizations:** The microstructures of the nanomaterials were observed by scanning electron microscopy (SEM Hitachi S-4800) and transmission electron microscope (TEM) recorded on a Tecnai. The crystal phases were evaluated by X-ray diffraction (XRD) patterns recorded on a Rigaku-Dmax 2500 diffractometer with Cu Ka radiation. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 simultaneous thermal analyzer between 25 and 1000 °C at a heating rate of 10 °C min⁻¹ in Air. The specific surface areas of the powders were calculated from a Brunauer Emmett Teller (BET) analysis of the nitrogen adsorption and desorption measurements (Tristar 3000). X-ray photoelectron spectroscopy (XPS) analysis was conducted with ESCALAB MK II X-ray instrument to analyze the composition of the nanomaterials.

**Computational details:** The density functional theory (DFT) calculations were employed the linear combination of the atomic orbital and spin-unrestricted methods and implemented in the Dmol₃ package. The generalized gradient approximation (GGA) in PBE functional form together with an all-electron double numerical basis set with polarization function (DNP) was adopted. In calculating the density of states (DOSs) and band structures, a denser k-point mesh \((4 \times 4 \times 4)\) was used. Electronic convergence was set to \(10^{-6}\) eV, while atomic positions were optimized until the final forces were below 0.01 eVÅ⁻¹.
Figure S1. (a) Low and (b) high-resolution SEM images of Ce$_2$Sn$_2$O$_7$ particles.
**Figure S2.** (a) Low and (b) high-resolution SEM images of Ce$_2$Sn$_2$O$_7$/RGO-4. (c) Low and (d) high-resolution SEM images of Ce$_2$Sn$_2$O$_7$/RGO-12.
Figure S3. (a) Low and (b) high-resolution TEM images of Ce$_2$Sn$_2$O$_7$/RGO-8.
Figure S4. Energy-dispersive spectrometer (EDS) of Ce$_2$Sn$_2$O$_7$/RGO-8.
Figure S5. XRD patterns of $\text{Ce}_2\text{Sn}_2\text{O}_7$, $\text{Ce}_2\text{Sn}_2\text{O}_7$/RGO-4, $\text{Ce}_2\text{Sn}_2\text{O}_7$/RGO-8 and $\text{Ce}_2\text{Sn}_2\text{O}_7$/RGO-12.
Figure S6. The crystal structural of Ce$_2$Sn$_2$O$_7$. 
Figure S7. (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore-size distributions of $\text{Ce}_2\text{Sn}_2\text{O}_7$/RGO-8.
Figure S8. High-resolution XPS spectra of (a) C 1s and (b) O 1s in Ce₂Sn₂O₇/RGO-8.

The C 3d spectrum can be deconvoluted into four peaks at 284, 285, 286 and 288 eV, corresponding to the conductive carbon, C–C (or C–H), C–O and C=O bonds.\textsuperscript{2-4} For the O 1s spectrum, three peaks at 529.2, 531.1 and 532.9 eV are pointing to the metal-oxygen bonds, OH⁻ groups and the physically/chemically adsorbed water or near the surface.\textsuperscript{5,6}
Figure S9. CV curves of $\text{Ce}_2\text{Sn}_2\text{O}_7$ at 0.1 mV s$^{-1}$. 
Figure S10. Cycling performance of Ce$_2$Sn$_2$O$_7$/RGO-8 at 2 A g$^{-1}$. 
Figure S11. Rate capability of various samples at varied current densities.
Figure S12. Nyquist plots of Ce$_2$Sn$_2$O$_7$, Ce$_2$Sn$_2$O$_7$/RGO-4, Ce$_2$Sn$_2$O$_7$/RGO-8 and Ce$_2$Sn$_2$O$_7$/RGO-12 in fresh LIBs.
Figure S13. (a, b) SEM images of Ce$_2$Sn$_2$O$_7$ at 0.1 A g$^{-1}$ after 50 cycles in LIBs.
Figure S14. (a, b) SEM images of Ce$_2$Sn$_2$O$_7$/RGO-8 at 0.1 A g$^{-1}$ after 50 cycles in LIBs.
Figure S15. (a) Relationship between the peak current and the scan rate. (b) Contribution ratio of surface-driven and diffusion-controlled behaviors at a scan rate of 0.8 mV s$^{-1}$. 
According to the CV curves at different scan rates, the contribution ratio of surfacedriven and diffusion-controlled behaviors can be calculated. The detailed calculation process is given as following:

From Figure 5a, the power-law relationship between the current (i) and the scan rate (v) can be described as the following Equations (S1) and (S2) (a and b are constants):

\[ i = av^b \]  \hspace{1cm} \text{(S1)}

\[ \log(i) = b\log(v) + \log(a) \]  \hspace{1cm} \text{(S2)}

Based on the values of slope \( b \), the electrochemical properties are determined. The electrochemical behavior can be dominated by the diffusion-controlled mechanism (\( b \) value approaches to 0.5) and the surface capacitance-dominated process (\( b \) value approaches to 1). According to the strongest reduction and oxidation peaks, the linear relationship between the log(i) and log(v) is obtained.

More specifically, the contribution proportion of the pseudocapacitive charge storage can be calculated by the following Equation (S3) and (S4):

\[ i = k_1v + k_2v^{0.5} \]  \hspace{1cm} \text{(S3)}

\[ i/v^{0.5} = k_1v^{0.5} + k_2 \]  \hspace{1cm} \text{(S4)}

The \( i \)-value is composed of two parts: the pseudocapacitive effective (\( k_1v \)) and diffusion-controlled insertion (\( k_2v^{0.5} \)). According to Equation (S3), by plotting \( i/v^{0.5} \) versus \( v^{0.5} \) at different potentials, \( k_1 \) and \( k_2 \) were calculated using the Equation (S4). The percentage of pseudocapacitance can be observed using the Equation (S3) (Pseudocapacitive = \( k_1v/(k_1v + k_2v^{0.5}) \)).
The detailed calculation processes of diffusion coefficient according to electrochemical impedance spectroscopy (EIS):

The straight line in the low frequency can evaluate the diffusion process of Li\(^{+}\). According to the straight line, we could calculate the ions diffusion coefficient (D) of the Ce\(_2\)Sn\(_2\)O\(_7\)/RGO-8 by the following Equation S5 and S6:\(^8\)

\[ Z_{re} = R_e + R_{ct} + \sigma \omega^{-1/2} \]  \hspace{1cm} (S5)

\[ D = (R^2T^2)/(2A^2n^4F^4C^2\sigma^2) \]  \hspace{1cm} (S6)

\( A \) is the surface area of the electrode, \( n \) is the number of electron transfer, \( F \) is the Faraday constant, \( C \) is the molar concentration of Li\(^{+}\), and \( \sigma \) is the Warburg factor calculated from the slope of the lines between \( Z_{re} \) and \( \omega^{-1/2} \).
Figure S16. (a) Nyquist plots after different cycles. (b) Dependence of $Z_{re}$ on the reciprocal square root of the frequency in the low-frequency region.
The diffusion coefficient can be calculated according to the galvanostatic intermittent titration technique (GITT). And the detailed calculation process is given as following:

According to Fick's second law of diffusion, the diffusivity coefficient of lithium/sodium ions ($D_{Li^+}$) can be calculated based on the following equation:

$$D_{Na^+} = \frac{4}{\pi \tau} \frac{m_B V_M}{M_B S} \frac{(\Delta E_s)^2}{(\Delta E_t)^2}$$  \hspace{1cm} (S7)

where $\tau$ is the pulse duration, $m_B$ is the mass of active material, $M_B$ is the molar mass of SnO$_2$, $V_M$ is the molar volume, and $S$ is the active surface area of the Ce$_2$Sn$_2$O$_7$ electrode and Ce$_2$Sn$_2$O$_7$/RGO-8 electrode. $\Delta E_s$ and $\Delta E_t$ can be gotten from the GITT curves. The corresponding Li$^+$ diffusion coefficient at different discharge/charge states of the Ce$_2$Sn$_2$O$_7$ and Ce$_2$Sn$_2$O$_7$/RGO-8 in Li$^+$ half cells can be observed using the Equation (S7).
Figure S17. Nyquist plots of CeO$_2$, SnO$_2$ and Ce$_2$Sn$_2$O$_7$ in fresh LIBs.
Figure S18. (a) XRD patterns and (b) SEM image of commercial LiCoO₂.
Figure S19. (a) Schematic illustration of LiCoO$_2$/Ce$_2$Sn$_2$O$_7$/RGO-8 full cell configuration. (b) Discharge/charge curves of LiCoO$_2$ and Ce$_2$Sn$_2$O$_7$/RGO-8 at 0.1 A g$^{-1}$. 
Figure S20. (a) Discharge/charge curves and (b) cycling performance of LiCoO$_2$/Ce$_2$Sn$_2$O$_7$/RGO-8 full cell at 0.1 A g$^{-1}$. 
Figure S21. Rate capability of LiCoO$_2$/Ce$_3$Sn$_2$O$_7$/RGO-8 full cell at different current densities (the inset shows that one coin full cell can lighten on the small car lamp).
Figure S22. Cycling performance of Ce₂Sn₂O₇/RGO-8//AC LICs at 0.1 A g⁻¹.
References


