SUPPLEMENTARY INFORMATION

Amorphous iron oxide-selenite composite microspheres
with yolk-shell structure as highly efficient anode material
for lithium-ion batteries

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Experimental Section

1. Materials characterization

The morphologies of the prepared microspheres were investigated using scanning electron microscopy (SEM, VEGA3) and transmission electron microscopy (TEM, JEM-2100F). The crystal structures and chemical properties of the prepared microspheres were analyzed using X-ray diffraction spectroscopy (XRD, X'pert PRO with Cu Kα radiation, λ = 1.5418 Å) at the Korea Basic Science Institute, Daegu, and X-ray photoelectron spectroscopy (XPS, Thermo Scientific™, K-Alpha™). Ex-situ XPS analyses at the first fully discharged and charged states after argon-ion gun etching were also performed with the above measuring equipment. The properties and the amount of pitch derived carbon was characterized via thermogravimetric analysis (TGA, Pyris 1 Thermogravimetric Analyzer, PerkinElmer) in the range of 25–700 ºC at 10 ºC min⁻¹ in an air-based atmosphere, respectively. The surface area and porosities of samples were analyzed using the Brunauer–Emmett–Teller (BET) method with high-purity N₂.

2. Electrochemical measurements

The electrochemical properties of the prepared microspheres were analyzed using a 2032-type coin cell. The anode was prepared by mixing the active material, carbon black, and sodium carboxymethyl cellulose in a weight ratio of 7:2:1. Lithium metal and microporous polypropylene films were used as counter electrode and separator, respectively. The electrolyte was 1.0 M LiPF₆ dissolved in a mixture of fluoroethylene carbonate–dimethyl carbonate (FEC/DMC; 1:1 v/v). The discharge and charge characteristics of the samples were investigated by cycling in the potential range of 0.001–3.0 V at various current densities. Cyclic voltammograms (CVs) were measured at a scan rate of 0.1 mV s⁻¹. Electrochemical impedance spectroscopy (EIS) was performed on the electrode over a frequency range of 0.01–100 kHz. In-situ EIS analysis was performed at preselected potentials during the discharge and charge processes at a current density of 0.1 A g⁻¹.
Fig. S1. Morphologies of yolk-shell structured c-Fe$_2$O$_3$ microspheres.
Fig. S2. XRD patterns of c-Fe$_2$O$_3$, FeSe$_2$-C, and a-Fe$_2$O$_3$-FeSe$_{Ox}$ microspheres.
Fig. S3. TGA curves of FeSe$_2$-C and a-Fe$_2$O$_3$-FeSeO$_x$ microspheres.
Fig. S4. EDX spectrum of α-Fe₂O₃-FeSeOₓ microspheres.
Fig. S5. XPS survey scans of FeSe$_2$-C and a-Fe$_2$O$_3$-FeSeO$_x$ microspheres.
Fig. S6. (a) N$_2$ gas adsorption-desorption isotherm curves and (b) BJH pore size distributions of c-Fe$_2$O$_3$ and a-Fe$_2$O$_3$-FeSeO$_x$ microspheres.
\( R_e \): the electrolyte resistance, corresponding to the intercept of high frequency semicircle at \( Z_{re} \) axis

\( R_f \): the SEI layer resistance corresponding to the high-frequency semicircle

\( Q_1 \): the dielectric relaxation capacitance corresponding to the high-frequency semicircle

\( R_{ct} \): the denote the charger transfer resistance related to the middle-frequency semicircle

\( Q_2 \): the associated double-layer capacitance related to the middle-frequency semicircle

\( Z_w \): the Li-ion diffusion resistance

Fig. S7. Equivalent circuit model used for AC impedance fitting.
Fig. S8. Electrochemical properties of FeSe$_2$-C electrodes: (a) first galvanostatic discharge-charge profile, (b) rate performance, (c) cycling performance at a current density of 10 A g$^{-1}$. 
Fig. S9. SEM images of a-Fe$_2$O$_3$-FeSeO$_x$ microspheres obtained after 100 cycles.
Table S1. Compositions of the a-Fe$_2$O$_3$-FeSeO$_x$ microspheres determined from ICP-OES analysis.

<table>
<thead>
<tr>
<th>Materials</th>
<th>Fe [wt%]</th>
<th>O [wt%]</th>
<th>Se [wt%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-Fe$_2$O$_3$-FeSeO$_x$</td>
<td>65.40</td>
<td>29.12</td>
<td>5.48</td>
</tr>
</tbody>
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