

Supplementary Information

High-Coulombic-Efficiency Si-Based Hybrid Microspheres Synthesized by Combination of Graphene and IL-Derived Carbon

Sang-Hoon Park, Dong-Jun Ahn, Young-Min Choi, Kwang Chul Roh,* and Kwang-Bum Kim*

Contents

- Figure S1. N₂ adsorption–desorption isotherms of the Si/rGO and Si/rGO/C microspheres.
- Figure S2. SEM images of the spray-dried samples from (a) GO alone and (b) from a GO/IL mixed suspension
- Figure S3. High magnification TEM image of Si/rGO/C
- Figure S4. SEM images of Si nanoparticles used in this study
- Figure S5. Rate capability of Si/rGO/C and Si/rGO microsphere based electrodes
- Figure S6. Long-term cycling stability of Si/rGO/C microsphere electrode
- Table S1. XPS C1s peak positions and relative atomic percentages of sp², sp³, and oxygen-containing functional groups for the Si/GO/IL and Si/rGO/C microspheres.
- Equation S1. Calculation of the cell capacity based on the anode and cathode capacities.
- Equation S2. Calculation of the expected specific capacity of the Si/rGO/C microsphere electrode.

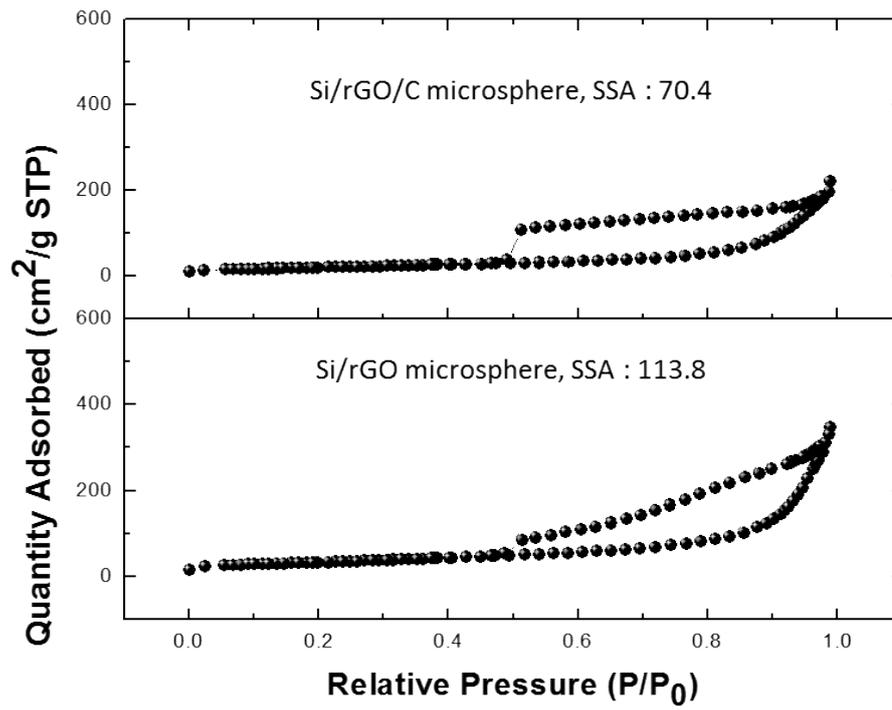


Figure S1. N₂ adsorption–desorption isotherms of the Si/rGO microspheres (BET specific surface area (SSA): 113.8 m²/g) and the Si/rGO/C microspheres (SSA: 70.4 m²/g).

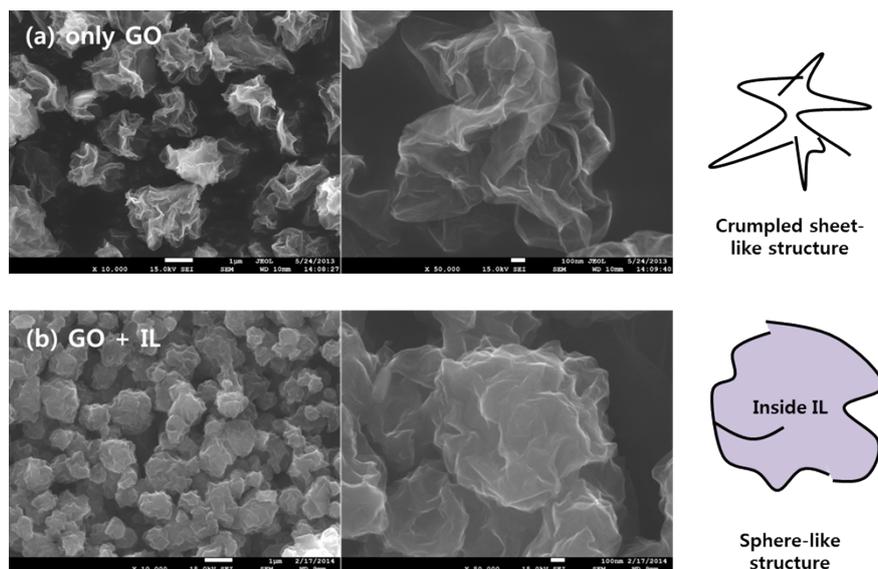


Figure S2. SEM images of the spray-dried samples from (a) GO alone and (b) from a GO/IL mixed suspension without silicon nanoparticles.

Figures S2 (a) and (b) show SEM images of the samples synthesized from GO alone and a GO/IL mixed suspension by the same spray drying process. While the GO sample (Figure S2 (a)) shows a crumpled sheet-like structure, the GO/IL sample (Figure S2 (b)) has a more sphere-like structure. These different morphologies could be due to the presence of IL as secondary component inside the resulting structure. During the spray drying process, the IL is trapped inside the droplets and encased by GO nanosheets, leading to the formation of sphere-like structures. This result clearly supports our hypothesis that the IL mostly exists inside the structures and is surrounded by nanosheets as shown in right scheme of Figure S2 (b). Thus, after the carbonization process, IL-derived carbon is formed mostly inside the microspheres.

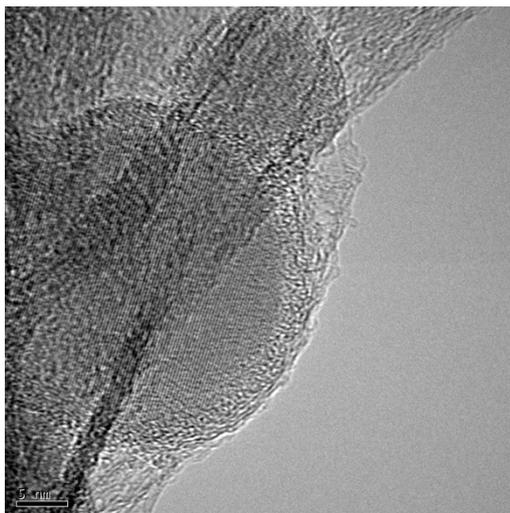


Figure S3. High magnification TEM image of Si/rGO/C microspheres. The crystalline silicon nanoparticle was coated by a 2–3 nm carbon layer and then wrapped in graphene nanosheets.

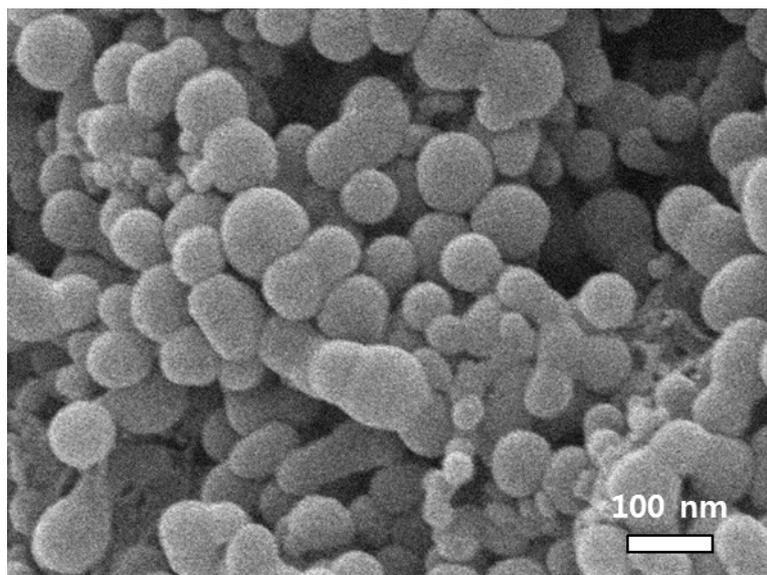


Figure S4. Representative SEM image of Si nanoparticles used in this study. The particle size is between 40–100 nm.

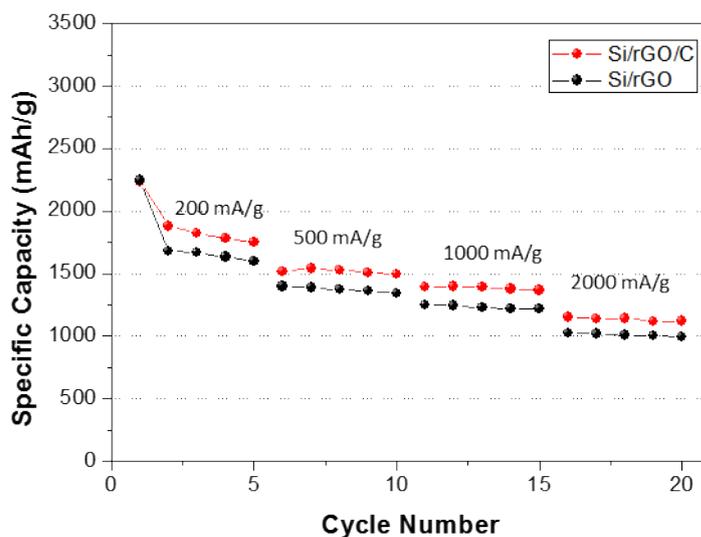


Figure S5. Rate capability of Si/rGO/C and Si/rGO microsphere based electrodes at different current densities. We applied current densities from 200 to 2000 mA/g under a normal CC mode instead of the CC-CV mode. The lithiation capacities of the Si/rGO/C microsphere electrodes were 1748, 1493, 1369, and 1121 mAh/g at 200 (after 5 cycles), 500 (after 10 cycles), 1000 (after 15 cycles) and 2000 A/g (after 20 cycles), respectively; these values are higher than those of the Si/rGO electrode (1597, 1344, 1216 and 992 mAh/g at 200, 500, 1000 and 2000 mA/g, respectively).

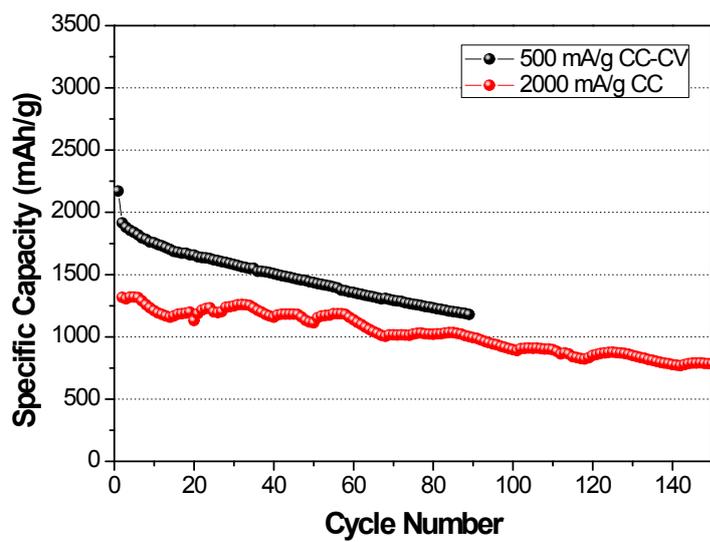


Figure S6. Long-term cycling stability of Si/rGO/C microspheres electrode in different conditions. (Black: cycling performance at 500 mA/g CC-CV mode, Red: cycling performance at 2000 mA/g CC mode)

Table S1. XPS C1s peak positions and relative atomic percentages of sp², sp³, and oxygen-containing functional groups for the Si/GO/IL and Si/rGO/C microspheres.

Sample	C=C	C-C	C-O	C=O	O-C=O
Si/GO/IL microsphere	42.8% (284.6 eV)	14.1% (284.6 eV)	29.0% (286.6 eV)	8.2% (287.4 eV)	5.9% (288.6 eV)
Si/rGO/C microsphere	69.1% (284.6 eV)	16.0% (285.6 eV)	9.2% (286.4 eV)	3.5% (287.5 eV)	2.2% (289.6 eV)

Equation S1. The irreversible reaction has the effect of balancing the cathode and anode and can be expressed as follows:

$$Q_{\text{cathode charge}} - Q_{\text{cathode discharge}} = Q_{\text{cathode irreversible}},$$

$$Q_{\text{anode charge}} - Q_{\text{anode discharge}} = Q_{\text{anode irreversible}},$$

$$Q_{\text{Latent}} = Q_{\text{cathode discharge}} - Q_{\text{anode discharge}},$$

where $Q_{\text{cathode (anode) charge}}$, $Q_{\text{cathode (anode) discharge}}$, and $Q_{\text{cathode (anode) irreversible}}$ represent the charge capacity, discharge capacity, and irreversible capacity in the cathode (anode), respectively.

[1-2] If $Q_{\text{anode irreversible}}$ is higher than $Q_{\text{cathode irreversible}}$, and $Q_{\text{cathode charge}}$ and $Q_{\text{anode charge}}$ are equal, $Q_{\text{cathode discharge}}$ is greater than $Q_{\text{anode discharge}}$. Therefore, the discharge capacity of the cell is simply $Q_{\text{anode discharge}}$. As regards the cathode, the difference in the discharge capacity between the cathode and anode, $Q_{\text{cathode discharge}} - Q_{\text{anode discharge}}$, cannot be discharged. This reduces the energy density of the cell. This can be defined as the latent capacity, Q_{Latent} .

Equation S2. Expected specific capacity of the Si/rGO/C microsphere electrode, determined on the basis of the total masses of Si and the carbons in it. The specific capacity was calculated using the following expression:

$$\text{Si/rGO/C}_{\text{specific capacity}} = \text{Si}_{\text{wt\%}} \times \text{Si}_{\text{specific capacity}} + \text{rGO}_{\text{wt\%}} \times \text{rGO}_{\text{specific capacity}} + \text{C}_{\text{wt\%}} \times \text{C}_{\text{specific capacity}}$$

Here, the wt% values of Si, rGO, and the IL-derived C were 72.9, 24.4, and 2.7, respectively. The measured specific capacity for the Si nanoparticles used in the Si/CB electrode ($\text{Si}_{\text{specific capacity}}$, based on only the Si mass) was the maximum (2511 mA h/g). If we consider the specific capacity of rGO ($\text{rGO}_{\text{specific capacity}}$) to be 372 mA h/g and exclude the specific capacity of the IL-derived C ($\text{C}_{\text{specific capacity}}$), owing to the low content of the IL-derived C and because this value is difficult to predict, then $\text{Si/rGO/C}_{\text{specific capacity}}$ was 1921 mA h/g. (Here, we considered $\text{rGO}_{\text{specific capacity}}$ to be 372 mA h/g, instead of using the theoretical value of ideal graphene (744 mA h/g), since the rGO in the resulting microspheres might not have had a perfectly exfoliated structure, given the assembly process.)

Reference

1. S.-I. M. Chil-Hoon Doh, Mun-Soo Yun, Chang-Soo Jin, Bong-Soo Jin, Seung-Wook Eom, *CARBONLETT*, 2000, **1**, 5.
2. H.-S. K. Chil-Hoon Doh, Seong-In Moon, *CARBONLETT*, 2001, **1**, 5.