Supplementary Information

High energy density anodes using hybrid Li intercalation and plating mechanisms on natural graphite

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Materials and Methods

Preparation of SG and Gel electrolyte

For a homogeneous deposition of Si nanolayer on natural graphite, the chemical vapor deposition process using high-purity silane gas (99.9999%, KOSEM) was conducted to 50 g of graphite at 475 °C for 60 min (50 sccm). 1.3 M LiPF₆ in mixture of ethylene carbonate (EC), Ethyl methyl carbonate (EMC) and diethyl carbonate (DEC) (3:5:2) with 0.2wt% LiBF₄, 10 wt% fluoroethylene carbonate (FEC), and 0.5wt% Vinylene carbonate (VC) was used as liquid electrolyte. 2wt% of cyanoethyl polyvinyl alcohol (PVA-CN) polymer was dissolved in the liquid electrolyte for gel electrolyte. All electrolytes mixing was conducted in a glove box under controlled atmosphere with < 0.1 ppm oxygen and moisture. The assembled cells with gel electrolyte were stored at 60 °C for 12 hours to initiate gelation of electrolyte after formation cycles.

Electrochemical characterization

The electrodes were fabricated by the slurry casting method on a current collector. The slurry comprised of the active material (PG and SG), the binder materials (sodium carboxymethyl cellulose (CMC) and styrene butadiene rubber (SBR)), and conductive agent (Super P) was homogeneously mixed by revolution-rotation mixer in the mass ratio of 90:3:3:4. The loading levels of electrode were adjusted to achieve 3.3 mAh/cm². The electrodes were dried at 80 °C for 1 h, and then calendered to achieve electrode density over 1.2 g/cm³ by roll press machine. The electrode was vacuum dried at 120 °C for 6 hours. Coin type-cell were assembled in an argon-filled glove box under controlled atmosphere with < 0.1 ppm oxygen and moisture. Microporous polyethylene (Celgard) was used as a separator. In the case of half-cell test, lithium metal was adopted as a counter electrode. Electrochemical properties of half-cell were investigated under the lithiation capacity cut-off up to 600 mAh/g and delithiation up to 1.5 V with 0.05C for formation 2 cycles and 0.5C for extended cycling. In the case of full-cell evaluation, lithium cobalt oxide (LCO) was used as cathode electrode with 1.05 of N/P ratio. The cathode electrode was composed of the active material, carbon black (Super P), and polyvinylidene fluoriade binder (PVDF) in a mass ratio of 90:5:5. The mass loading of the electrode was around 23 mg/cm² and the electrode was calendered up to 3.0 g/cm³. Electrochemical properties of full-cell were estimated in the potential window between 4.45

and 2.00 V. Here, the weight and volume of the separator, current collector, electrolyte, and exterior package are excluded because the coin-type cell has a big disadvantage for calculating specific energy and energy density. The weight and volume of active, binder, and conducting carbon materials are exclusively utilized for calculating specific energy and energy density. A LAND cycler (Wuhan Land Electronic Co., Ltd.) was used for cycling and GITT test, and a VMP3 potentiostat (BioLogic) was used for LSV and EIS test. Details of electrochemical methods was described in the following separate note.

Materials characterization

The morphological characterization of the samples was conducted using scanning electron microscopy (SEM, Leo Variable pressure SEM with an acceleration voltage of 10 kV and VERIOS 460 (FEI) for the cross-sectional image with energy-dispersive spectroscopy (XFlash 6130, Bruker)). Dual-beam focused ion beam (FIB, NX2000, Hitachi) and ion milling system (IM40000, Hitachi) was carried out for observing the cross-sectional view of the particles. Also, high-resolution transmission electron microscopy (HR-TEM, JEM-2100F, JEOL) operating at 200 kV was performed for detailed analysis. Crystalline structure was examined by using a Bruker D8 Advance (Cu K α radiation, 6°/min scan). Porosity and macropore volume distribution were obtained using mercury-porosimetry (Autopore V9500, Micromeritics).





Figure S1. SEM images of (a) G and (b) Si/G. Scale bar = $10 \ \mu m$ for (a and b). (c) XRD patterns of G and Si/G. (d) Cross-sectional SEM image of Si/G. EDS atomic element mapping of (e) carbon and (f) silicon on SEM image (c).



Figure S2. Cross sectional SEM images of (a) Li/G@gel electrode after formation (b) Li/Si/G@liquid electrode after formation (c) Li/G@gel electrode after 20 cycles, and (d) Li/Si/G@liquid electrode after 20 cycles (inlet: Magnified image). Scale bar = 25 μ m for (a), (b), (c) and, (d), 5 μ m for inlet (d).



Figure S3. Formation voltage profiles of Li/G@liquid, Li/G@gel, and Li/Si/G@gel electrodes. (a) 1st formation cycle and (b) 2nd formation cycle. (c) delithiation capacity and ICE during formation cycles.



Figure S4. Formation voltage profiles with normal lithiation condition (constant currentconstant voltage (CC-CV) mode, CC: 0.1 C down to 0.005 V, CV: 0.005 V down to 0.02C) which is not inducing lithium plating. (a) voltage profiles of G and Si/G, (b) delithiation capacity and ICE during formation cycle.



Figure S5. Cross sectional SEM images of (a) Li/G@liquid electrode after formation (b) Li/Si/G@gel electrode after formation (inlet: Top SEM images of same electrodes). Scale bar = 5 μ m for (a) and (b) and 50 μ m for (a) and (b) inlets.



Figure S6. Linear sweep voltammetry of Li/G@liquid, Li/G@gel, Li/Si/G@gel, and G@liquid samples.



Figure S7. Raw results of GITT technique. (a) Li/G@liquid, (b) Li/G@gel, and (c) Li/Si/G@gel.



Figure S8. GITT derivatives of Li/G@liquid, Li/G@gel, Li/Si/G@gel, and G@liquid. (a) IR drops in potential range 0.0.08 V, (b) IR drops in potential range 0.1-0.4 V, (c) IR drops in potential range 0.4-0.8 V. (d) overpotentials in potential range 0.0.08 V, (e) overpotentials in potential range 0.1-0.4 V, (f) overpotentials in potential range 0.4-0.8 V.



Figure S9. Half-cell performance of Li/Si/G@liquid electrode (a) formation voltage profile of Li/Si/G@liquid, (b) Cycling performance of Li/Si/G@liquid half-cell in 0.5C rate charging/discharging.



Figure S10. Electrochemical performance comparison with reference samples. (a) formation profiles of reference samples: Li/LSi/G@gel, HSi/G@liquid, and HLi/Si/G@gel (b) delithiation capacity and ICE during the formation cycle.

1st Efficiency (%)

89.5

92.1

91.6



Figure S11. Half-cell performance of LCO cathode and full-cell result. (a) formation voltage profile of LCO half cell, (b) Cycling performance of LCO half cell in 0.5C rate charging/discharging. (c) voltage profiles of full cell. (d) cycling performance of full cell in 0.5 C-rate.

	Half Cell Specification			Full Cell Specification		
	Areal Capacity (mAh/cm²)	Volumetric Capacity (mAh/cm³)	ICE (%)	N/P ratio	Specific Energy (Wh/kg)	Energy Density (Wh/L)
This work	3.35	656	91.8	1.05	474	912
				Based on the weight and volume of electrode materials		
Ref. 9 in main text	1.25	-	83*	-	-	-
				Areal capacity: 2.4 mAh/cm ² , Cell size: 250 mAh		
Ref. 10 in main text	9.8	1960	-	2.6	300	-
				Cell size: 1.0 Ah pouch cell		
Ref. 22 in main text	6.31	-	-	1.5	381	-

 Table S1. Comparison of Electrochemical Performance with previous publications

Supplementary Note 1. Method to calculate the porosity of electrode with density and a theoretical capacity of the proposed concept

To calculate **electrode porosity**, electrode composition and density, and true density (which is the density of solid materials supposing zero pores and grain boundary) of electrode materials should be known.

$$Electrode\ Porosity, (\%) = \left(1 - \frac{Electrode\ Density}{1/\sum_{i=1}^{Materials\ Weight\ Ratio}}\right) \times 100$$

For example, when

The electrode density = 1.35 g/cm^3

The electrode composition ratio and true density of graphite: 90wt% and 2.25 g/cm³

The electrode composition ratio and true density of carbon black: 4wt% and 1.95 g/cm³

The electrode composition ratio and true density of CMC: 3wt% and 1.50 g/cm³

The electrode composition ratio and true density of SBR: 3wt% and 0.90 g/cm³

Then, the porosity of this graphite electrode: 36%

To calculate **theoretical capacity** when the voids in our graphite anode would be filled Li metal plating, we assumed the graphite anode with 1.35 g/cm³ of electrode density, 7.5 mg/cm² of mass loading (Electrode thickness is 55 μ m), 90wt% of active materials ratio in electrode composition and 14 pi electrode cutting (Electrode area: 1.54 cm²) for coin-type cell assembly.

Then,

The capacity gained by graphite: $360 \text{ mAh/g} \times 7.5 \text{ mg/cm}^2 \times 90 \text{wt\%} \times 1.54 \text{ cm}^2 = 3.74 \text{ mAh}$ The additional capacity by Li plating: $2061 \text{ mAh/cm}^3 \times (1.54 \text{ cm}^2 \times 55 \text{ }\mu\text{m} \times 36\%) = 6.28 \text{ mAh}$

Therefore, the total theoretical capacity of this concept is

 $(3.74 + 6.28 \text{ mAh})/(7.5 \text{ mg/cm}^2 \times 1.54 \text{ cm}^2 \times 90 \text{wt\%}) = 963 \text{ mAh/g}$

Supplementary Note 2. Method of LSV, GITT, and EIS

To investigate the electrochemical properties of each sample, we conducted LSV, GITT, and EIS. The LSV and GITT were examined from 600 mAh/g lithiated state after formation. The scan rate for LSV was 0.04 mV/s, and the cut-off condition was potential from OCV to 1.5 V. The C-rate of pulse current in GITT was 0.1 C for 20 minutes, and it took 2 hours as rest time. The pulse current process was repeated when it reached 1.5 V. The EIS analysis was conducted after formation, 20, and 50 cycles. The EIS measurement was carried out over the frequency range from 1000 kHz to 2 mHz with an amplitude of 10 mV.



Figure S11. One representation peak of GITT analysis

IR drops are measured by the voltage difference between current end/rest start point to vertically dropped point. Overpotentials are measured by the difference between current end/rest start point and the next rest end/current start point. As a result of GITT, we compared IR drops and overpotentials of Li/G@liquid, Li/G@gel, and Li/Si/G@gel electrodes during the delithiation process and separated delithition of (i) Li stripping (<0.1 V vs. Li⁺/Li), graphite deintercalation (0.1-0.3 V), and Si dealloying (>0.3 V). Overall, the IR drops and overpotentials in Li stripping of Li/G@liquid, Li/G@gel, and Li/Si/G@gel were a similar extent. However, those in graphite deintercalation of and Li/Si/G@gel were lower than those in Li/G@liquid and Li/G@gel.

Supplementary Note 3. Full cell design method (N/P ratio) and calculatation method for specific energy and energy density

To make full cell design, we used charge and discharge N/P ratio concept as below.

 $ChargeN/P \ ratio = \frac{Anode \ lithiation \ capacity \ (mAh/cm^2)}{Cathode \ delithiation \ capacity \ (mAh/cm^2)}$

DischargeN/P ratio

 $= \frac{Anode \ delithiation \ capacity \ (mAh/cm^2)}{Cathode \ delithiation \ capacity - Anode \ irreversible \ capacity}$

For example (Li/Si/G@gel full cell),

ChargeN/P ratio =
$$\frac{3.640 \text{ mAh/cm}^2}{3.473 \text{ mAh/cm}^2} = 1.048$$

 $DischargeN/P \ ratio = \frac{3.3526 \ mAh/cm^2}{3.473 - 0.288 \ mAh/cm^2} = 1.053$

To calculate the specific energy and energy density, we used the weight and volume of the anode and cathode materials.

For example (Li/Si/G@gel full cell),

The energy obtained from the cell: 9.85 mWh

The weight of electrode materials: 4.76 (anode) + 16.02 (cathode) = 20.78 mg

The volume of electrode materials: 0.785 cm^2 (area) $\times 0.0137 \text{ cm}$ (thickness) = 0.0108 cm^3

Therefore, specific energy of the cell: 9.85 mWh \div 20.78 mg = 474 Wh/kg

energy density of the cell: 9.85 mWh \div 0.0108 cm³ = 912 Wh/L