Li-rich Li-Si alloy as a lithium-containing negative electrode material towards high energy lithium-ion batteries

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S1. Energy density of a LIB cell versus capacity of a negative-electrode material

The relation between energy density of a LIB cell (W_{cell} [Wh kg^{-1}]) and gravimetric capacity of negative electrode material (C_n [mAh g^{-1}]) was calculated by the following method. A common cylindrical 18650 cell contains ca. 50 wt% of active materials. This is expressed as follows:

$$\frac{m_p + m_n}{m_{cell}} = 0.5 \tag{1}$$

where m_p [g], m_n [g], and m_{cell} [g] are the mass of positive electrode material, the mass of negative electrode materials, and the weight of a LIB cell, respectively. To maximize the capacity of a LIB cell (C_{cell} [mAh g^{-1}]), the capacities of positive and negative electrodes should be the same. Therefore, the following relation should be established.

$$C_p m_p = C_n m_c \tag{2}$$

where C_p [mAh g^{-1}] is a gravimetric capacity of positive electrode material. The capacity of a LIB cell (C_{cell}) can be calculated by the following equation.

$$C_{cell} = \frac{C_p m_p}{m_{cell}} = \frac{C_n m_n}{m_{cell}} \tag{3}$$

By adopting (1) and (2) into (3), the following equation can be obtained.

$$C_{cell} = \frac{0.5 C_p C_n}{C_a + C_c} \tag{4}$$

The unit of C_{cell} (mAh g^{-1}) is equivalent to Ah kg^{-1}. Therefore, W_{cell} can be expressed as a function of C_n as follows, when C_p and operating voltage (E [V]) are given.

$$W_{cell} = C_{cell} E = \frac{0.5 C_p C_n E}{C_a + C_c} \tag{5}$$

S2. Spontaneous potential of Li-Si alloy before and after ball-milling

Each of Li-Si powders before and after ball-milling was packed with a nickel-mesh bag, which is a current collector. The bag thus prepared was immersed into the electrolyte solution (1 M $LiPF_6$ in a mixture of ethylene carbonate and diethyl carbonate (1:1 by volume)) together with a reference electrode (Li foil). After a stabilization period (60 min), a potential of the Li-Si alloy against Li foil was measured with a voltmeter. The potentials of Li-Si alloy before and after ball-milling were 0.05 and 0.28 V (vs. Li/Li^+), respectively. This result indicates that some amount of lithium was released from the Li-Si alloy during the ball-milling process, due to oxidation or unexpected degradation.

S3. Differential capacity plots of $Li_{21}Si_5$(0.2–2 µm)

Figure S1 shows differential capacity plots of $Li_{21}Si_5$(0.2–2 µm). In the pre-delithiation step, this sample shows a sharp peak at 0.45 V, corresponding to delithiation reaction. Then, in the 1st~3rd cycles, two peaks appear around 0.25 and 0.1 V during lithiation process, and delithiation peaks are located around 0.3 and 0.5 V. Such lithiation/delithiation behavior after the pre-delithiation is almost the same as that of amorphous Si.[1]
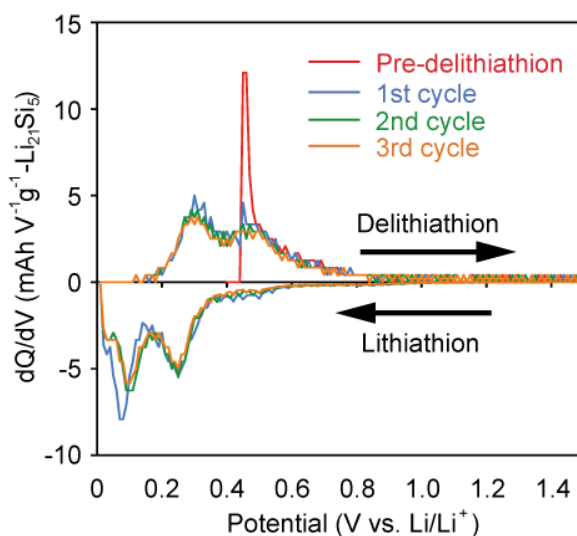

Figure S1. Differential capacity plots of $Li_{21}Si_5$(0.2– 2 µm), corresponding to the charge/discharge curves shown in Figure 4a.

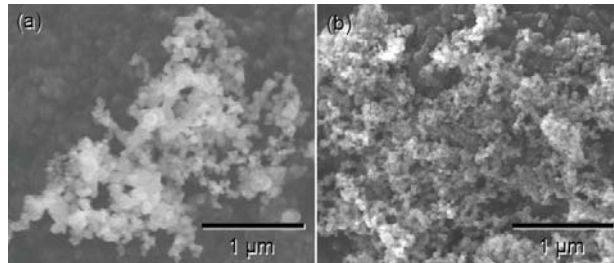**S4. SEM images of carbon blacks and Li$_{21}$Si$_5$(0.2–2 μm) coated with the carbon blacks**

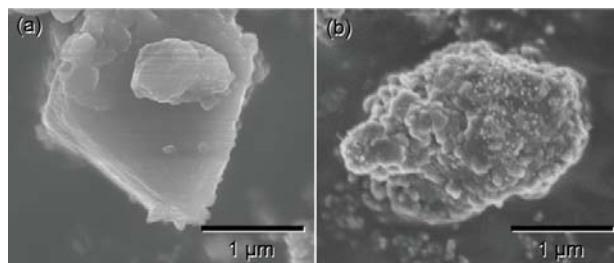**Figure S2.** SEM images of (a) acetylene black and (b) ketjen black.

Figure S3. SEM images of Li$_{21}$Si$_5$(0.2–2 µm) particles (a) before and (b) after coating with CBs.

Reference

[1]   S. Iwamura, H. Nishihara, T. Kyotani, J. Power Sources 2013, 222, 400.