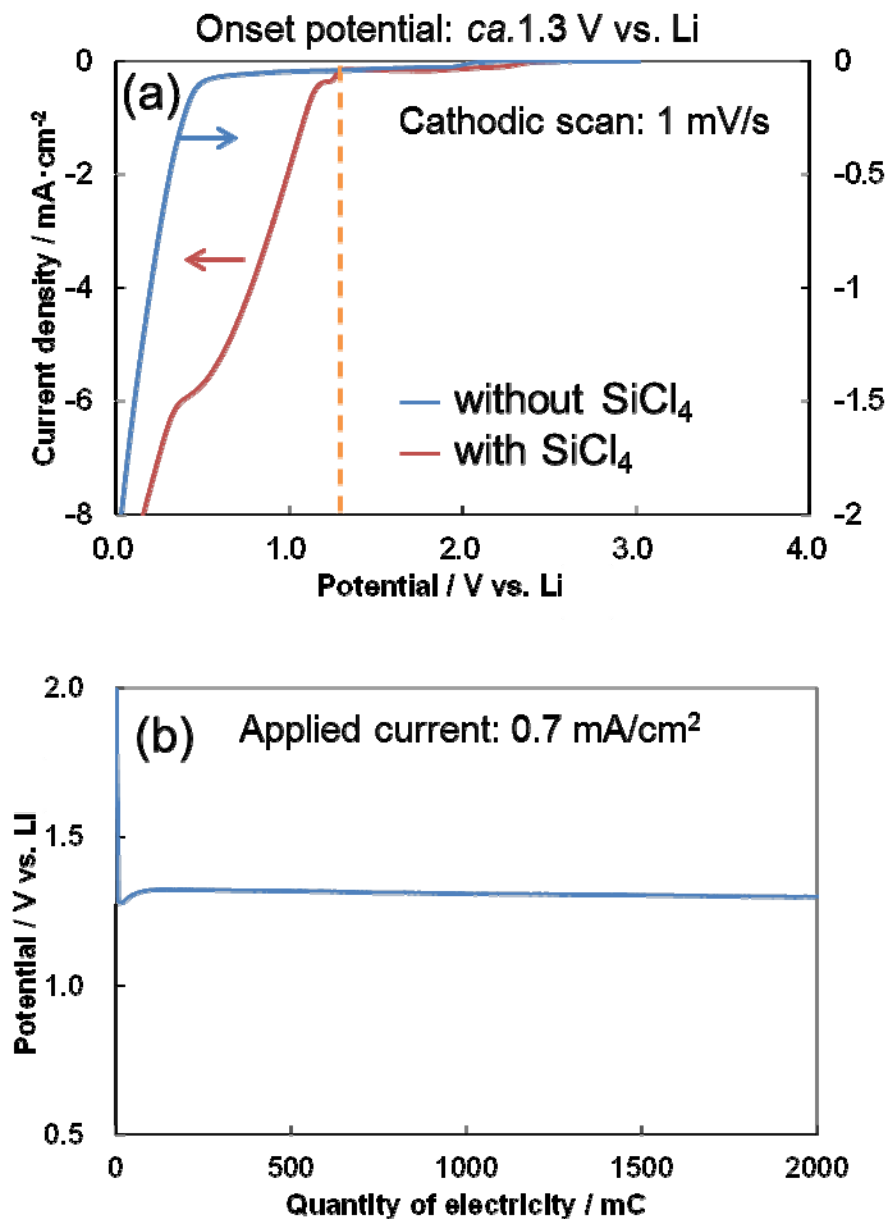
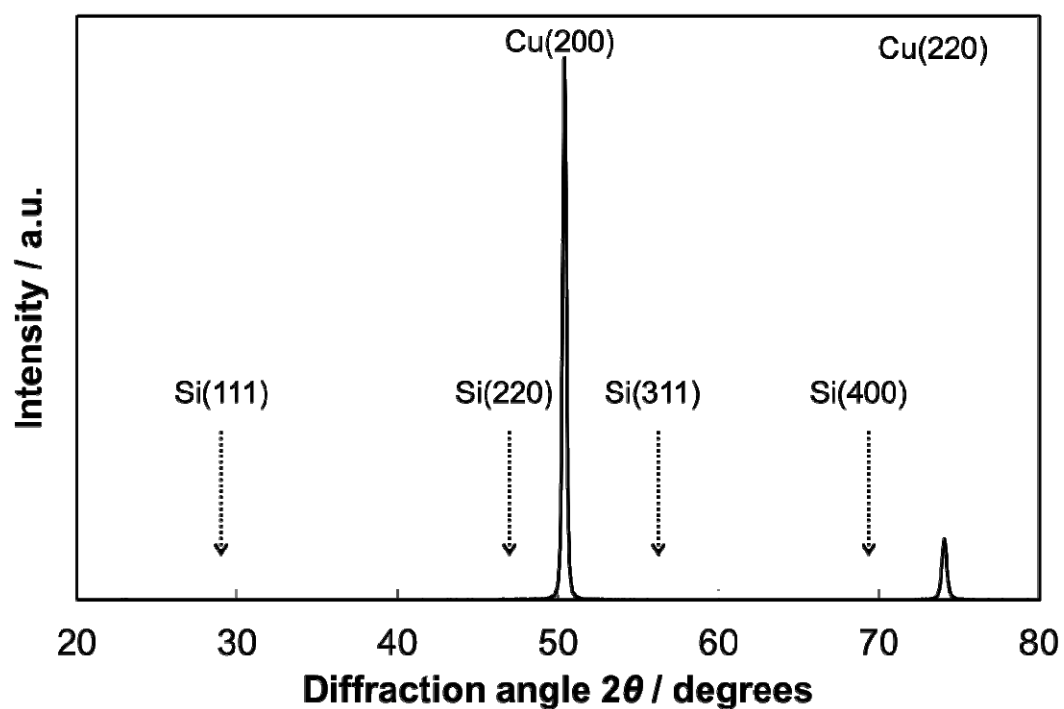


Supporting information, Figure S1



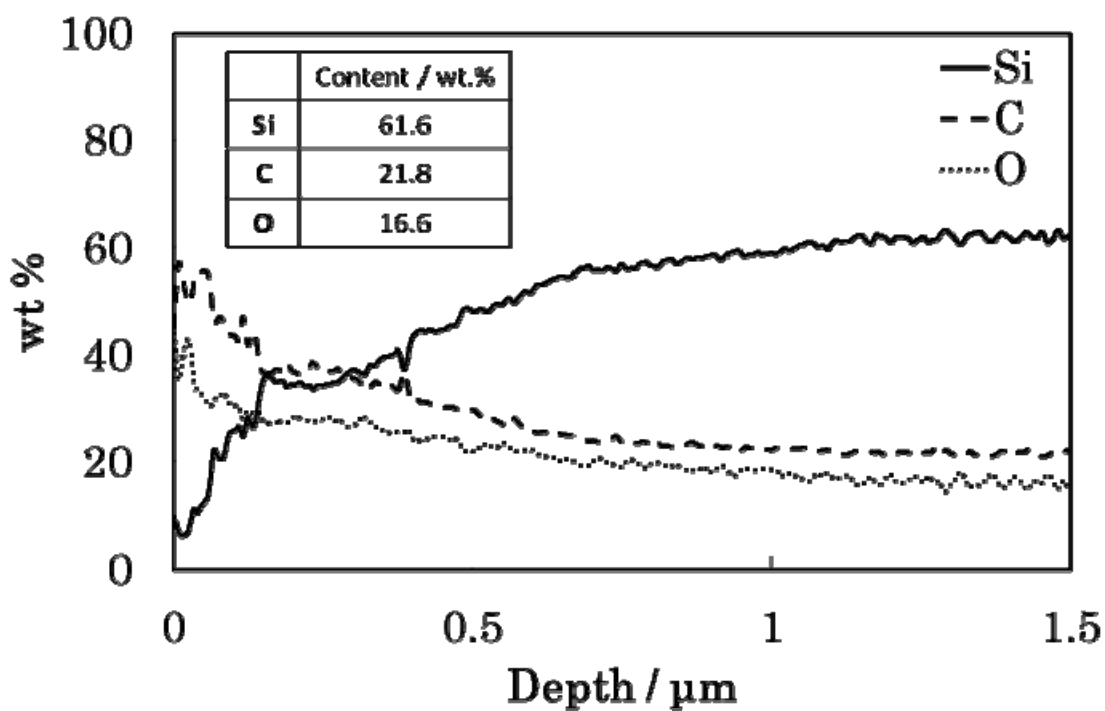
**Fig. S1** (a) Linear sweep voltammogram measured with the electrochemical cell equipped with a Li reference electrode, a 1.00 cm<sup>2</sup> Cu foil as a working electrode and a Pt counter electrode in the electrolyte solution of 0.5 mol dm<sup>-3</sup> SiCl<sub>4</sub> and 0.5 mol dm<sup>-3</sup> TBAP in PC. (b) Chronopotentiogram during the electrodeposition of silicon measured with the above cell containing SiCl<sub>4</sub>.

Supporting information, Figure S2



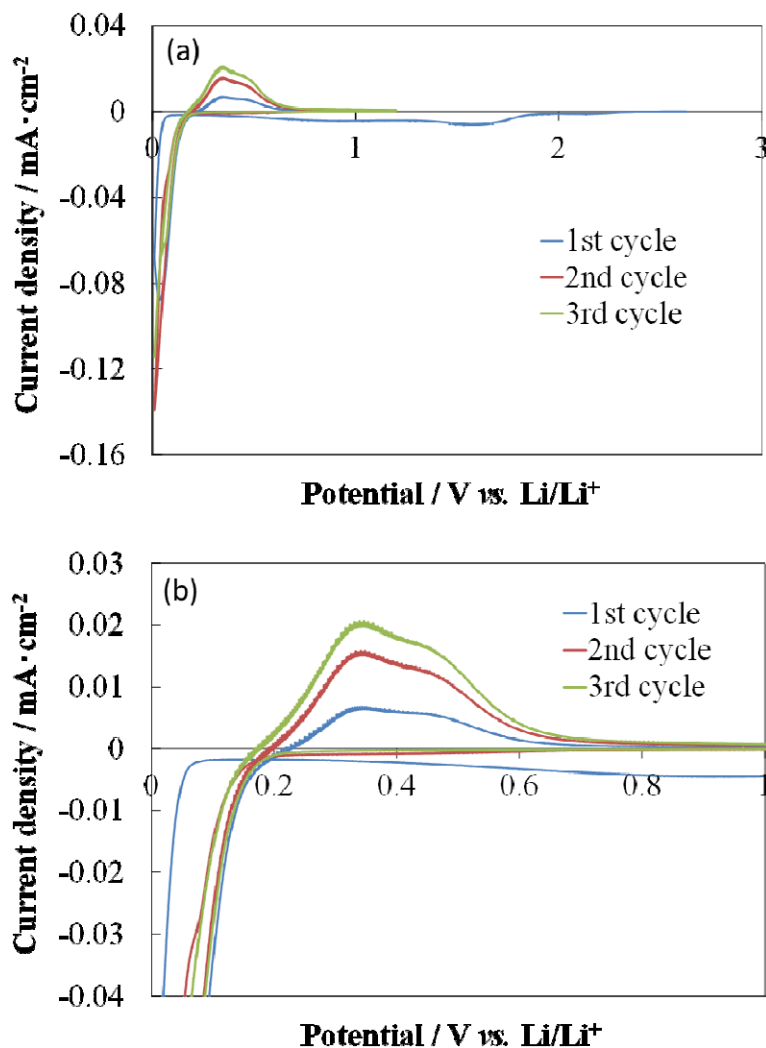
**Fig. S2** XRD pattern of the deposit prepared by the electrodeposition of silicon. The dotted arrows indicate the positions of the peaks for silicon.

Supporting information, Figure S3



**Fig. S3** GDOES depth profiles for the elements of Si, C, and O in the deposit, represented by solid line, dashed line, and dotted line, respectively. The inset indicates the composition by average weight at the depth of 1.0 to 1.5  $\mu\text{m}$ .

Supporting information, Figure S4



**Fig. S4** Cyclic voltammogram of overall (a) and enlarged (b) measured with the electrochemical cell equipped with a Li/Li<sup>+</sup> reference electrode, the SiOC composite electrode as a working electrode and a Li counter electrode in the electrolyte solution of 1 mol dm<sup>-3</sup> LiClO<sub>4</sub> in EC-PC. The CV was measured between 0.01 and 1.2 V vs. Li/Li<sup>+</sup> with the scan rate of 0.1 mV/sec.

The reductive current above *ca.* 0.4 V vs. Li/Li<sup>+</sup> and below *ca.* 0.1 V vs. Li/Li<sup>+</sup> which are attributable to side reactions like electrolyte decomposition and lithiation of SiOC electrode, respectively, were observed at the first cathodic scan. The oxidative current peaks at 0.32 and 0.46 V vs. Li/Li<sup>+</sup> which correspond to delithiation of SiOC electrode were observed at anodic scan. The reductive current below *ca.* 0.2 V vs. Li/Li<sup>+</sup> which is also attributable to lithiation of SiOC electrode.