

Electronic Supplementary information

High-Performance Si Anodes with Highly Conductive and Thermally Stable Titanium Silicide Coating Layer

Okji Park, Jung-In Lee, Myung-Jin Chun, Jin-Tak Yeon, Seungmin Yoo, Sinho Choi, Nam-

Soon Choi,* and Soojin Park*

Interdisciplinary School of Green Energy, Ulsan National Institute of Science and
Technology (UNIST), Ulsan 689-798, Korea

E-mail: spark@unist.ac.kr, nschoi@unist.ac.kr

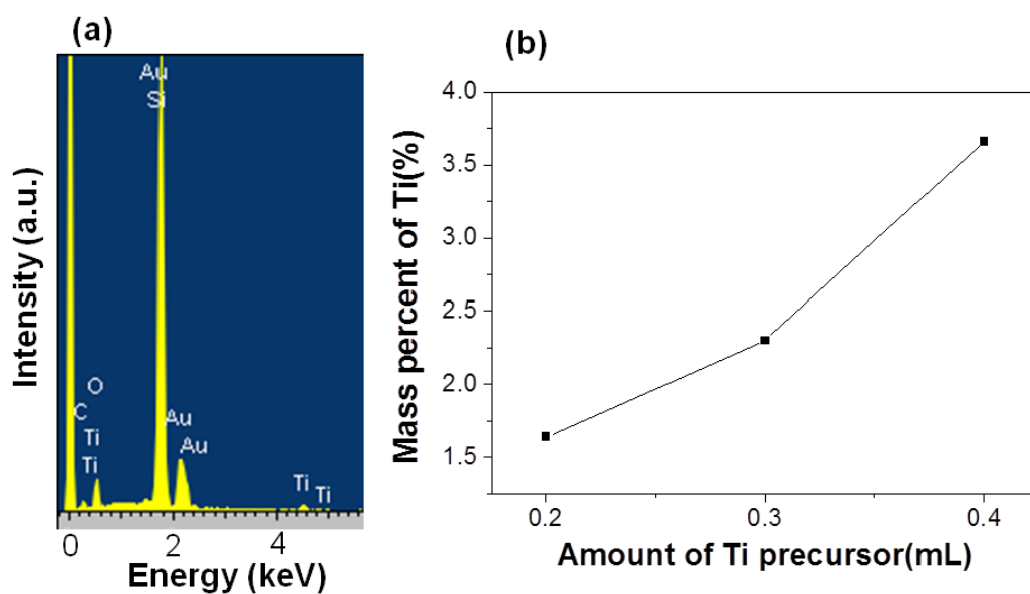


Figure S1. (a) EDAX profile showing 2.3 wt% Ti contents, and (b) Ti amounts in the final products (Ti_xSi_y -coated Si) prepared from various Ti precursor amounts.

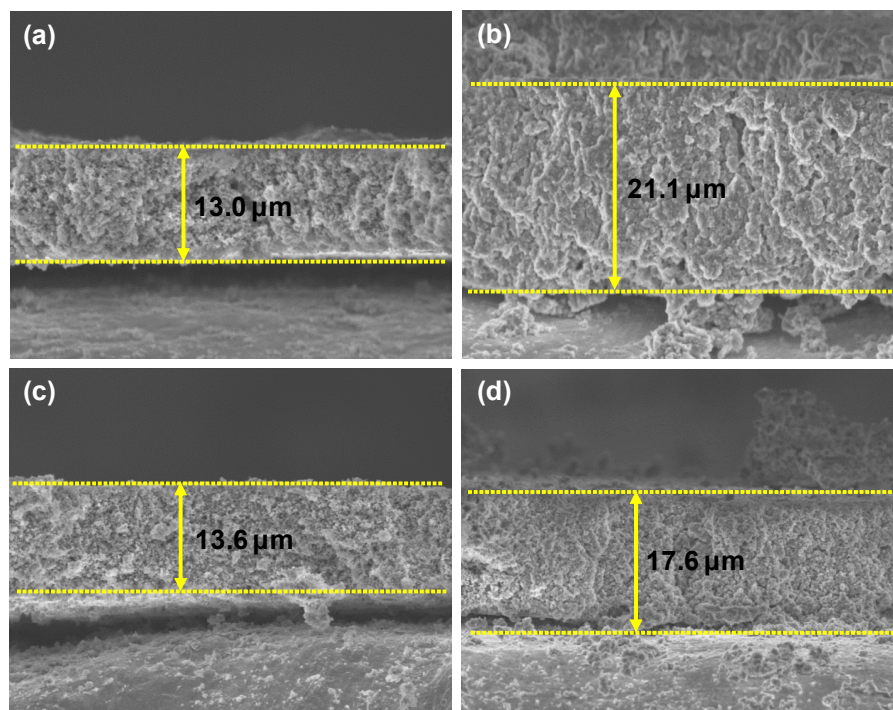


Figure S2. SEM images of Si nanoparticles of bare Si ((a) before and (b) after 30 cycles) and Ti_xSi_y -coated Si electrode ((c) before and (d) after 30 cycles).

XPS analyses for SEI layers

The XPS spectra (seen in Figure S3) of the pristine Ti_xSi_y -coated Si electrodes clearly shows a small peak belonging to the Si neutral atom (Si^0) at 99 eV and the pronounced peak corresponding to Si^{4+} at 104 eV. As expected, the binder species (COONa and COOR), evidenced by the C 1s peak at 289 eV, are observed for the pristine anode. In addition, three distinguishable peaks (284 eV, 286.5 eV, and 288.8 eV) in the C 1s spectrum correspond to the chemical environment of carbon atoms bonded to carbon, oxygen, and oxygen in a polymeric binder.^[S1] It is clear that there is a decrease in the peak intensity corresponding to Si^{4+} at 104 eV and Si^0 at 99 eV after cycling. It indicates that the SEI formed by the electrolyte decomposition covers the Ti_xSi_y -coated Si particles and causes changes in the relative intensity. It should be noted that FEC as a reducible additive, carbonate solvents (EC and DEC), and LiPF_6 salt are responsible for the formation of the SEI layer on the Ti_xSi_y -coated Si surface. Interestingly, the peaks attributed to Li_2CO_3 and ROCO_2Li at 291 eV, the peak at 136 eV arising from Li_xPOF_y and Li_xPF_y , and the LiF peak at 687.2 eV did not discernibly change between the 1st and 40th cycles, supporting good capacity retention of the Si anodes with the Ti_xSi_y coating layer.

Moreover, to investigate the difference of SEI layer between bare Si and Ti_xSi_y -coated Si, the XPS spectra obtained from bare Si and the Ti_xSi_y -coated Si electrodes after 40 cycles are shown in Figure S4. A noticeable feature in the XPS spectra of the Ti_xSi_y -coated Si is the appearance of the peak ascribed to LiPF_6 salt along with Li_xPF_y and/or Li_xPOF_y . In contrast, the SEI formed on bare Si electrode does not contain LiPF_6 salt unlike the coated Si. Interestingly, more intense peaks related to lithium alkylcarbonate, lithium carbonate, and ether carbon were observed in the SEI on bare Si electrode compared to the coated Si. The XPS analysis reveals that the SEI composition is closely linked to the surface chemistry of Si electrodes.

This is in good agreement with a high coulombic efficiency of over 99.5%, indicating no lithium consumption by the electrolyte decomposition.^[S2] The XPS results confirmed that Ti_xSi_y coating materials played a key role in maintaining the stable SEI layers on the surface of Si electrodes during cycling.

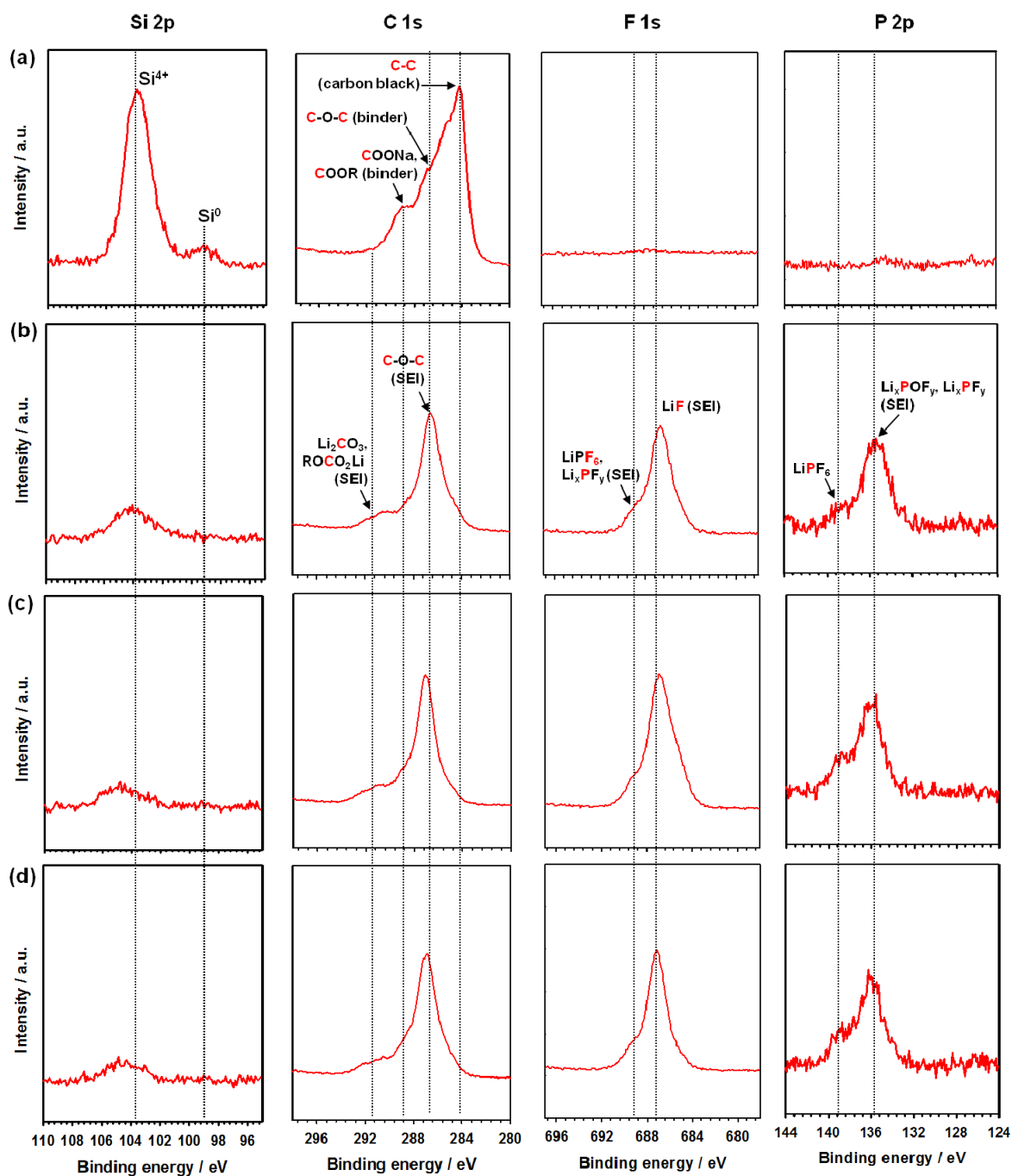


Figure S3. XPS spectra of Si 2p, C 1s, F 1s, and P 2p core level obtained from the Ti_xSi_y -coated Si electrodes; (a) before cycle, and after (b) 1 cycle, (c) 10 cycles, (d) 40 cycles.

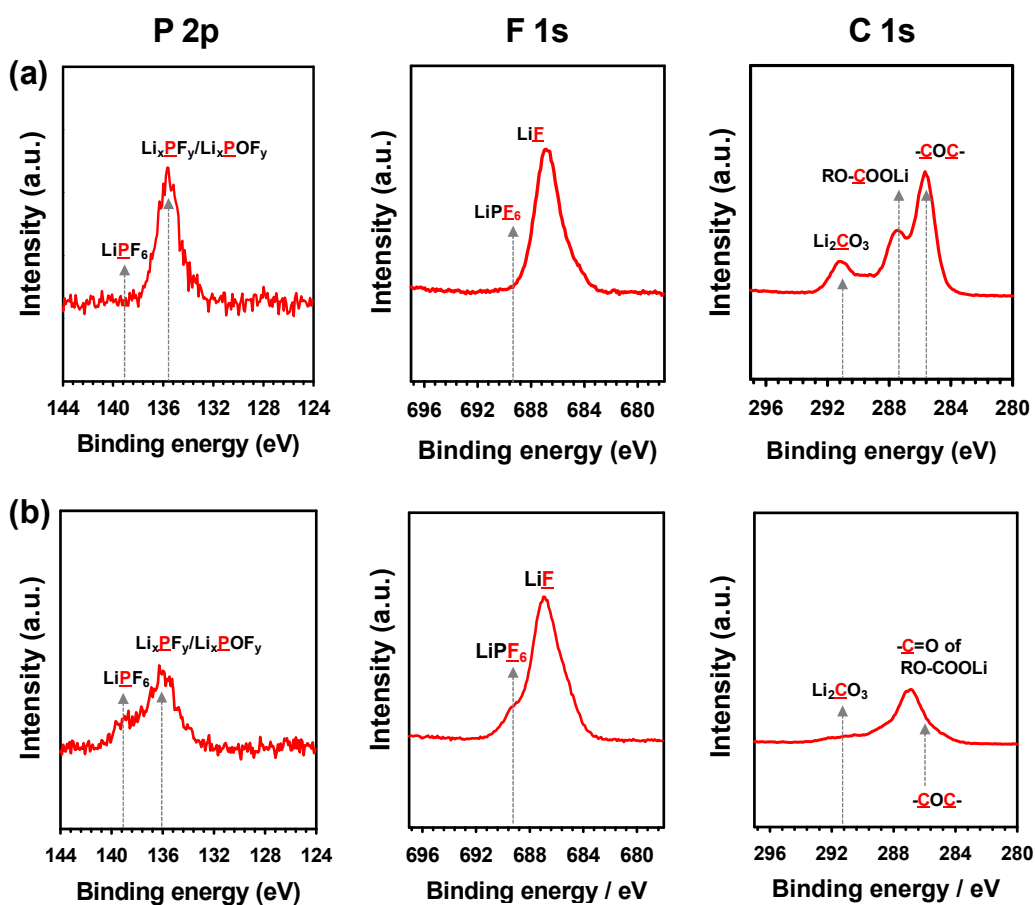


Figure S4. XPS spectra of P 2p, F 1s, and C 1s core level obtained from (a) bare Si and (b) the Ti_xSi_y -coated Si electrodes after 40 cycles.

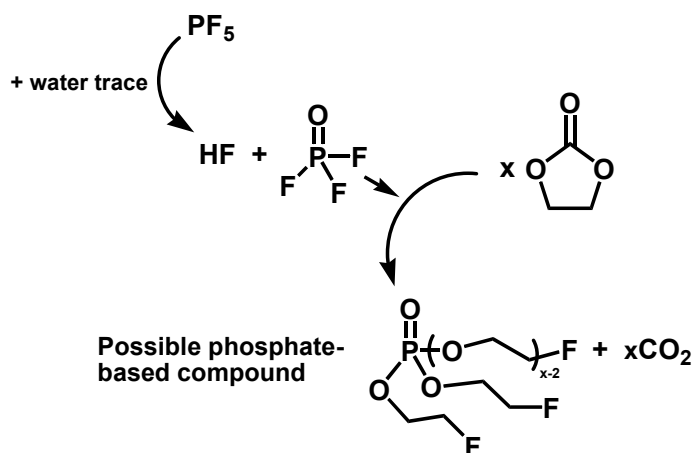


Figure S5. Schematic of thermal reaction between POF_3 and ethylene carbonate solvent at elevated temperatures.^[S3]

References

- [S1] B. Koo, H. Kim, Y. Cho, K. T. Lee, N.-S. Choi and J. Cho, *Angew. Chem. Int. Ed.* **2012**, *51*, 8762.
- [S2] N.-S. Choi, K. H. Yew, K. Y. Lee, M. Sung, H. Kim and S.-S. Kim, *J. Power Sources* **2006**, *161*, 1254.
- [S3] C. L. Campion, W. Li and B. L. Lucht, *J. Electrochem. Soc.* **2005**, *152*, A2327.