Multilayer-Coating on Silicon Nanoparticles Assisted by Supercritical CO_2 for Better Li-ion Batteries

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ABSTRACT

Silicon (Si) anode architectural design is an important factor to develop better Li-ion batteries (LIBs)[1]. In this work, a systematic study to make optimal multilayer-coating on silicon nanoparticles (C/SiO_x/Si) nanoparticles to withstand volume expansion and stabilize solid electrolyte interphase[2] has been conducted. A green and facile method for multilayer-coating has been developed by a supercritical carbon-dioxide ($SCCO_2$) process[3]. It beneficially uses liquid-like CO_2 as a primary solvent and is supported by ethanol as a co-solvent. C/SiO_x/Si produced from $SCCO_2$ uses several kinds of saccharide precursors, such as glucose (SC-G) and sucrose (SC-S), also citric acid (SC-CA). Furthermore, glucose is also applied with a traditional wet-chemical mixing process (T-G) for comparison. The experimental results show that SC-G has a better coating layer than T-G, SC-S, and SC-CA. For example, the SC-G has a high tap density due to a more compact and homogeneous coating layer. In addition, the SC-G electrode exhibits high reversible capacities of >2150 and ~920 mAh g^{-1} at 0.2 and 5 A g^{-1}, respectively. The same electrode can retain ≈65 % of its initial capacity after 300 charge-discharge cycles at 1 A g^{-1}. The obtained energy density of a SC-G||$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ full cell (based on the total mass of anode and cathode active materials) is ≈555 Wh kg^{-1}, which indicates the excellence of the proposed anode. This study demonstrates the great potential of using $SCCO_2$ for Si surface multilayer-coating. The process is facile and easily scaled-up for producing better Si-based anode materials for LIBs application.

Keywords: Carbon precursors, green process, lithium-ion battery, silicon-based anodes.

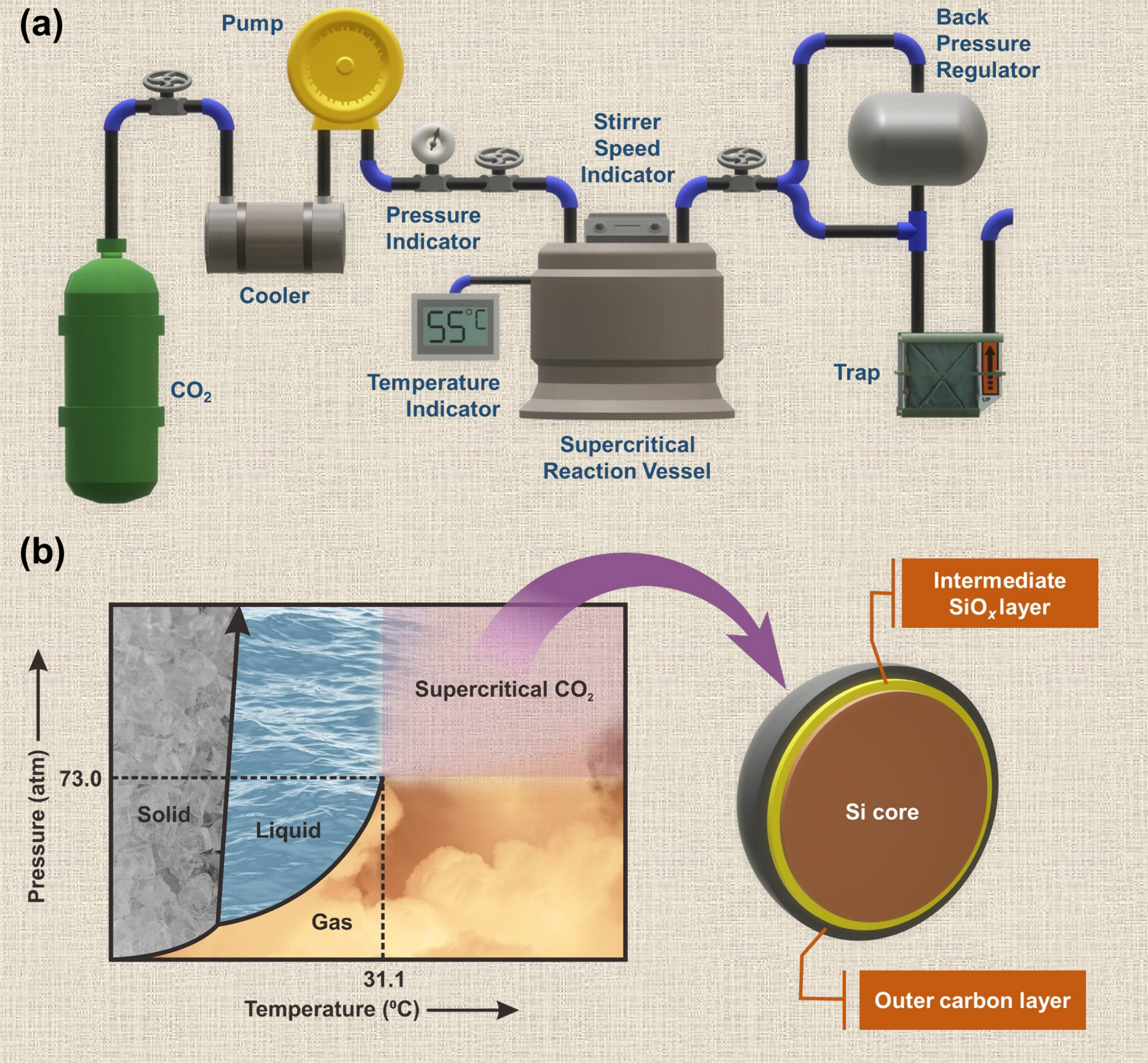

Figure 1. Schematic illustration of (a) $SCCO_2$ apparatus. (b) Phase diagram of CO_2 and scheme of $SCCO_2$-fabricated C/SiO_x/Si particle.

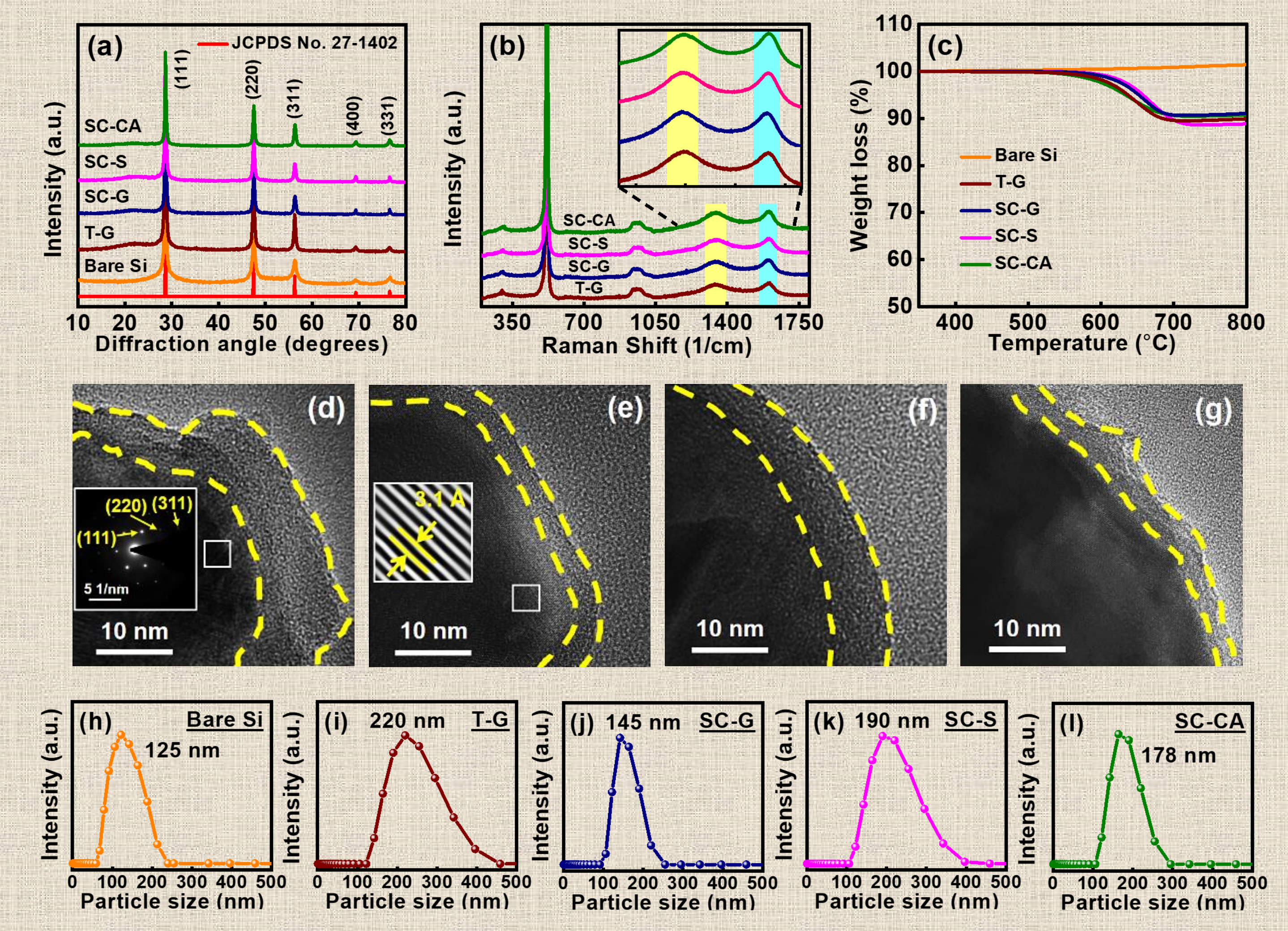

Figure 2. (a) XRD patterns, (b) Raman spectra, and (c) TGA curves of bare Si and various coated Si samples. High-resolution TEM images of (d) T-G, (e) SC-G, (f) SC-S, and (g) SC-CA. Particle size distribution data of (h) bare Si, (i) T-G, (j) SC-G, (k) SC-S, and (l) SC-CA measured using DLS.

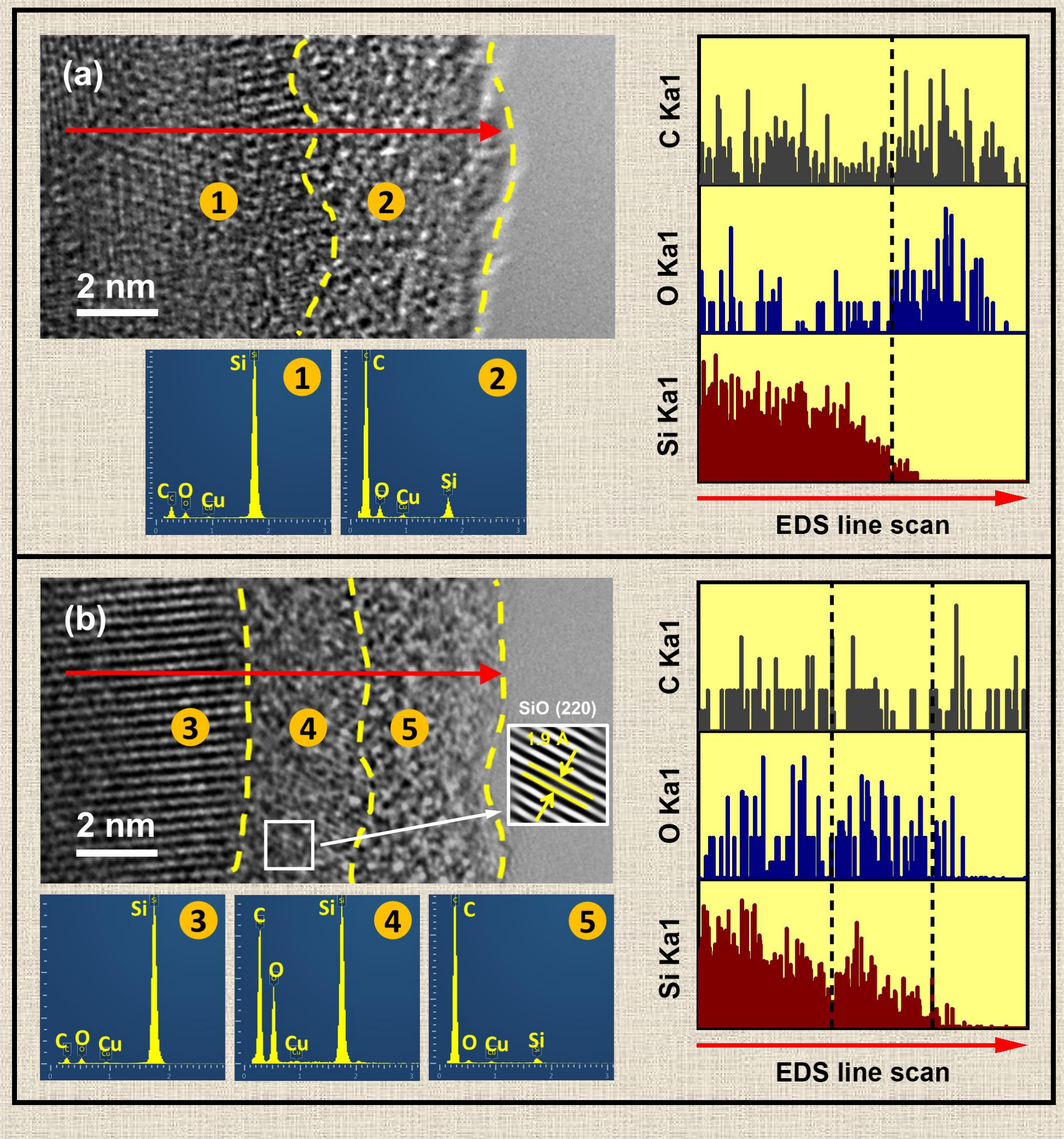

Figure 3. High-resolution TEM images, EDS spectra, and EDS line-scan data of (a) T-G and (b) SC-G samples. The EDS spectra are taken at the positions labeled in the TEM images.

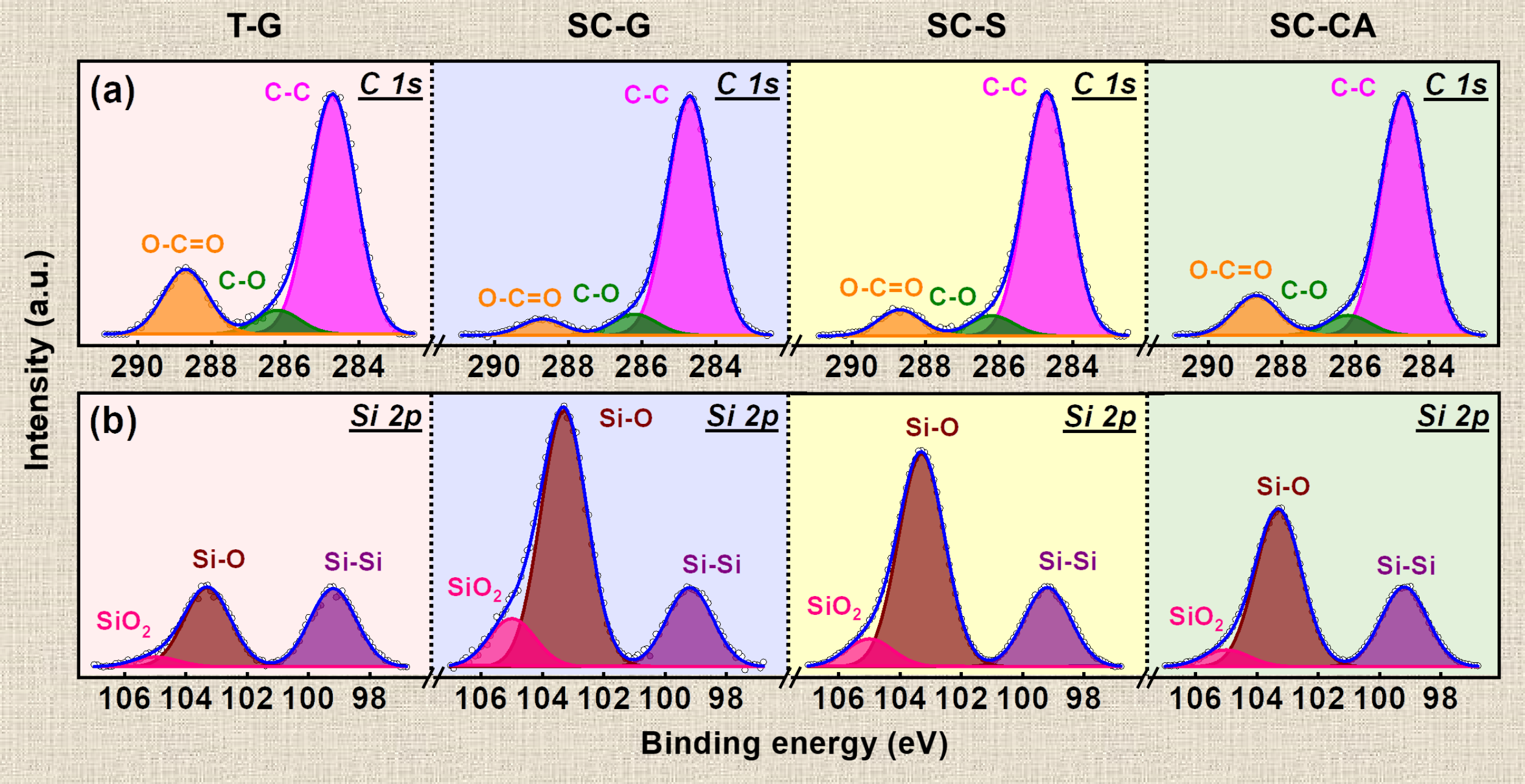

Figure 4. XPS (a) C 1s and (b) Si 2p spectra of various samples.

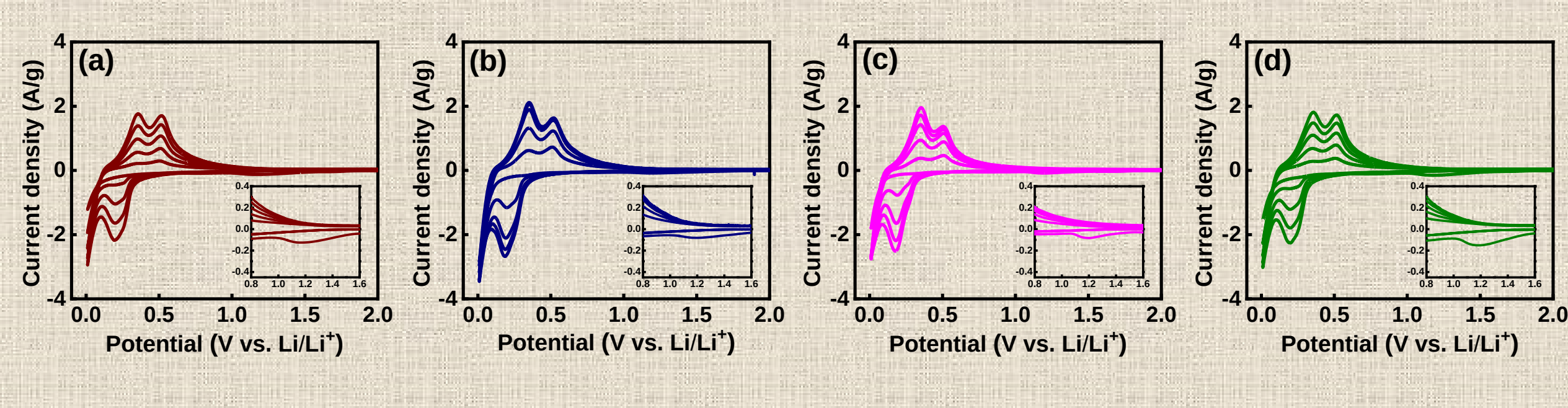

Figure 5. CV curves of (a) T-G, (b) SC-G, (c) SC-S, and (d) SC-CA electrodes measured at a potential sweep rate of 0.1 mV s^{-1}.

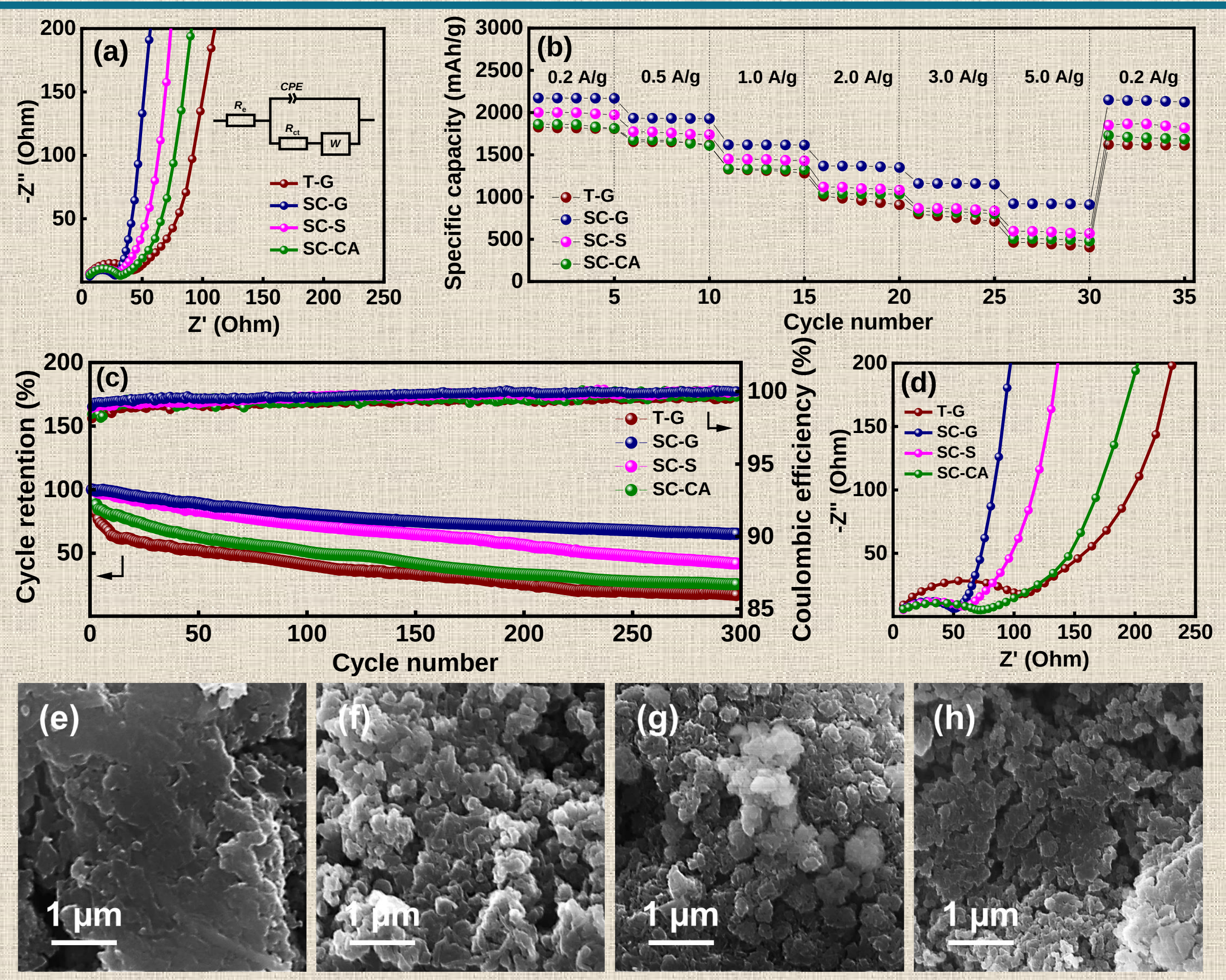

Figure 6. (a) EIS spectra of various electrodes and equivalent circuit used for data fitting. (b) Comparative rate performance of various electrodes. (c) Cycling stability of various electrodes measured at 1 A g^{-1}. (d) EIS spectra of various electrodes after 300 charge–discharge cycles. SEM images of (e) T-G, (f) SC-G, (g) SC-S, and (h) SC-CA electrodes after cycling.

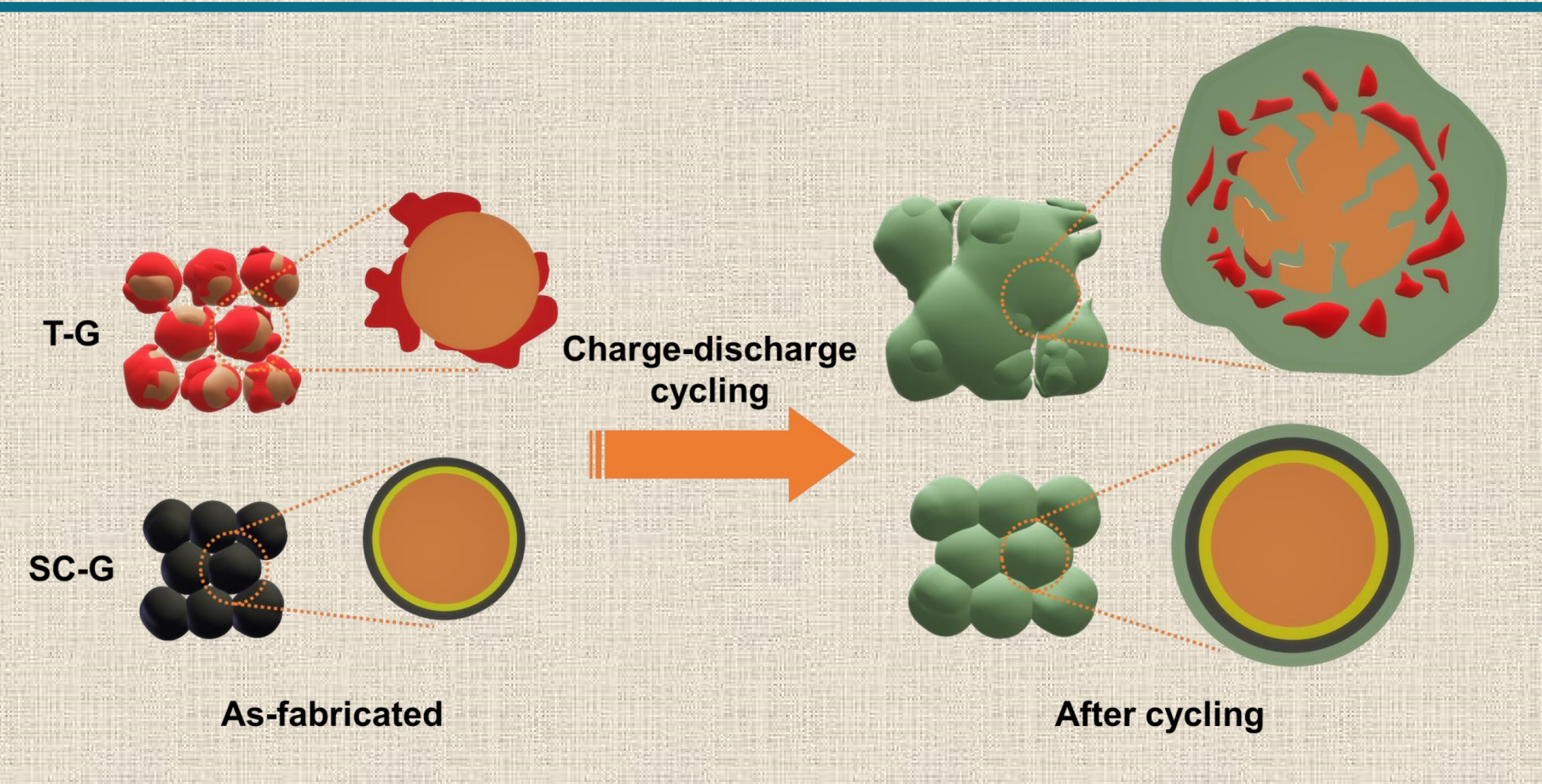

Figure 7. Schematic illustration of T-G and SC-G electrode morphologies before and after charge–discharge cycling.

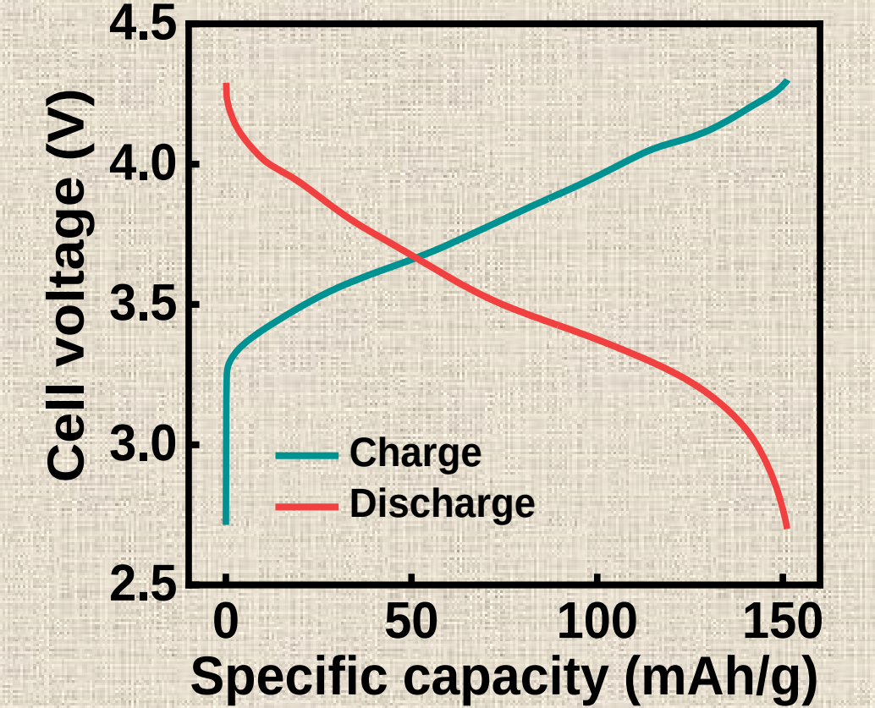

Figure 8. Charge-discharge curves of SC-G||$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ full cell measured at 0.1 C.

CONCLUSION

A $SCCO_2$ coating method for producing SiO_x/carbon multilayers on Si nanoparticles was developed. The low oxygen-containing functional groups of the carbon layer, leading to higher electronic conductivity. Its first-cycle CE was 84%. After 300 cycles, the electrode retains ≈65% of its initial capacity. Thus, the proposed anode and material design/synthesis strategy have great potential for high-energy-density and high-power-density LIB applications.

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