A series of rutile-type (Ti,Sn)O$_2$ solid solutions with nanorod architecture were successfully synthesized in this study by varying their calcination temperatures of tin-modified titanium dioxide (Sn/TiO$_2$) nanocomposites under a nitrogen atmosphere. During the delithiation process, the (Ti,Sn)O$_2$ nanorods obtained at 500 °C delivered a specific capacity of about 300 mA h g$^{-1}$ and showed minimal capacity fading even at a high current density of 3 A g$^{-1}$. Owing to the increasing demand for portable high-efficiency energy storage devices, the development of lithium ion batteries (LIBs) with superior lithium storage capabilities is one of the imperative issues. Instead of extensively used carbon-based materials, metal oxides (M$_x$O$_y$, M = Fe,$^{12}$ Co,$^{13}$ Sn,$^{14-18}$ etc.) were considered as promising anode materials for LIBs because of their highly specific capacities for lithium storage. However, undesirable volume expansions were generated during the insertion of lithium ions into the metal oxide structures, resulting in severe capacity fading. To mitigate this drawback, two-dimensional graphene nanosheets functioning as buffer layers were progressively reported,$^{11-15}$ but the resulting hybrids still remained challenging.

Titanium dioxide (TiO$_2$) with various polymorphs, e.g., anatase, brookite and rutile, had been demonstrated as another attractive anode material for LIBs due to its low cost, environmental benignity and easy availability.$^{16}$ Depending on its polymorph, the voltage of lithium insertion/extraction is in the range of 1.4 V to 1.8 V vs. Li/Li$^+,$ which is in the stable window of common liquid electrolytes.$^{17}$ Compared to the bulk system, the nano-sized one exhibited excellent cycling retention and high rate performance at room temperature.$^{18-20}$ For instance, a reversible accommodation of lithium into the structure was up to $\sim$Li$_{0.5}$TiO$_2$ (168 mA h g$^{-1}$) at 1–3 V vs. Li/Li$^+.$ It could be attributed to the fast lithium diffusion ($\sim$10$^{-6}$ cm$^2$ s$^{-1}$) along the c-axis channels according to the theoretical calculation.$^{21}$ Nevertheless, its capacity was still not able to meet the standard of practical application.

Nanocrystalline rutile-type (Ti,Sn)O$_2$ solid solutions with tuneable compositions and spherical morphologies have been recently examined as the alternative anodes for LIBs.$^{22,23}$ As a result, not only good electrochemical performances in terms of specific discharge capacity and cyclability but also no structural change during lithium insertion/extraction were observed. The improved characteristics ascribed to such binary solid solutions could synergistically overcome the limitations of their parent oxides, such as low capacity of TiO$_2$ and high fading of SnO$_2$.

So far, versatile technologies involving solid-state reactions,$^{24}$ high-energy mechanochemical processes,$^{25}$ sol–gel routes,$^{26-28}$ co-precipitation methods,$^{29-31}$ microwave-assisted hydrothermal syntheses$^{32}$ have been developed to synthesize the nanocrystalline rutile-type (Ti,Sn)O$_2$ solid solutions. Unlike the methods developed previously, the calcination of the tin-modified TiO$_2$ (Sn/TiO$_2$) nanocomposite in a nitrogen atmosphere was developed to synthesize a (Ti,Sn)O$_2$ solid solution. Temperature dependence of their crystallinities, local structures, chemical environments, morphologies and electrochemical performances of as-prepared (Ti,Sn)O$_2$ solid solutions was scrutinized. Furthermore, the thermal stability of the lithiated (Ti,Sn)O$_2$ electrode was determined by using the differential scanning calorimetry (DSC) analysis.

Prior to the synthesis of (Ti,Sn)O$_2$ solid solutions, a Sn-modified TiO$_2$ (Sn/TiO$_2$) nanocomposite was first prepared by chemical reduction. For the typical procedure, a desired amount of needle-like rutile TiO$_2$ ($S_{BET} = 170$ m$^2$ g$^{-1}$, Ming Yuh Co.) nanopowders were dispersed into a Sn precursor solution
of 49.3 mL of Sn(BF₄)₂ (50% aqueous solution, Acros Organics), 41.5 mL of HBF₄ (55% aqueous solution, Panreac) and 186 mL of deionized water. The reducing agent comprising 18 g of Na₂S₂O₃·5H₂O (99.5%, Hsing Chia Chemical Industrial Co.) and 23 mL of HBF₄ was sequentially added to the aforesaid mixture. The resulting suspension was heated at 60 °C for 0.5 h with vigorous stirring. Following filtration, repeated rinsing with excess deionized water and C₂H₅OH (ACS reagent, Sigma–Aldrich), and complete drying in a vacuum oven at 100 °C for 12 h, the as-prepared Sn/TiO₂ was obtained. To yield a series of (Ti,Sn)O₂ solid solutions, the Sn/TiO₂ powders were individually calcined in a nitrogen atmosphere for 2 h at 450 °C, 500 °C and 600 °C. The synthesized (Ti,Sn)O₂ solid solutions were denoted as ST-450, ST-500 and ST-600, respectively.

To identify the crystalline and local structures of the as-synthesized (Ti,Sn)O₂ solid solutions, X-ray diffraction (XRD) patterns and X-ray absorption fine structure (EXAFS) spectra were collected on BL01C2 and BL17C1, respectively, at National Synchrotron Radiation Research Center (NSRRC), Taiwan. The corresponding XRD patterns were further refined by GSAS with the Rietveld method to evaluate the lattice constants. The EXAFS spectra were analyzed by IFEFFIT-based program packages with calibrated energies to Sn and Ti metal K-edge. The pseudo radial structure function (RSF) for the central absorbing atom was obtained from Fourier transformation of the k³-weighted EXAFS oscillations over the k range of 2.7–12.2 Å⁻¹. The chemical environments were elucidated by X-ray photoelectron spectroscopy (ESCA 210, V. G. Scientific Ltd.) under Al Kα radiation (λ = 8.3406 Å), in which the binding energy was calibrated to the C 1s peak of graphite at 284.1 eV. The morphologies and corresponding selected area electron diffraction (SAED) patterns were observed using a high-resolution transmission electron microscope (HRTEM, Tecnai F20 microscope) at 200 kV. Atomic ratios for Ti and Sn were determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES, Optima 2000DV, PerkinElmer Inc.). The thermal stability of each lithiated electrode that was fully charged to 0.1 V at a current density of 0.03 A g⁻¹ was examined by differential scanning calorimetry (DSC, Model 2010, TA Instruments Inc.).

To evaluate its electrochemical properties, each (Ti,Sn)O₂ solid solution was mixed with the conductive additive, Super S (Timcal Ltd.) and a binder, poly(vinylidenedifluoride) (PVDF, M_w ≈ 304 000, Solef® 6020, Solvay Chemicals), in a weight ratio of 60 : 20 : 20 in N-methylpyrolidinone (NMP, ultra, ISP Technologies Inc., USA). The homogenous slurry was coated onto a copper foil (10 μm, Nippon Foil Co., Japan) and then dried at 90 °C to ensure that the solvent was completely removed. Cyclic voltammograms were recorded between 0.1 V and 3.0 V at a scan rate of 1.0 mV s⁻¹ using an electrochemical analyzer (Autolab PGSTAT30, Eco Chemie), which was connected to a three-electrode cell. The electrolyte was a 1 M LiPF₆ EC–DEC (1 : 1 w/w) solution (battery grade, Ferro Corp.), whereas lithium foil served as the counter and reference electrodes. During the measurement, the entire apparatus was placed in a glove box to avoid any impurities present in the system. For the capacity tests, the coin-type cells fabricated in an argon-filled glove box were cycled in a potential range from 0.1 V to 3.0 V using a computer-controlled charger workstation that was manufactured by AculTech systems Co., Ltd., Taiwan. The current density was varied from 0.03 A g⁻¹ to 3.0 A g⁻¹, and the testing environment was controlled at 25 °C.

The thermal stability of a lithiated (Ti,Sn)O₂ electrode that was fully charged to 0.1 V at a current density of 0.03 A g⁻¹ was determined by differential scanning calorimetry (DSC) analysis and compared with that of a lithiated graphite electrode. The lithiated electrode with ~4 mg was hermetically sealed in a copper DSC pan in the glove box. The DSC thermograms were obtained in a N₂ atmosphere with a heating rate of 10 °C min⁻¹. The graphite used for reference was obtained from China Steel Chemical Co., Taiwan with an average particle size of ~20 μm and a Brunauer–Emmett–Teller (BET) surface area of 5 m² g⁻¹.

In Fig. 1 the XRD patterns of Sn/TiO₂ and (Ti,Sn)O₂ solid solutions calcined at different temperatures are plotted. The diffraction peaks of the as-prepared Sn/TiO₂ in Fig. 1a were mainly assigned to the (1 1 0), (1 0 1), (1 1 1) and (2 1 1) planes of the rutile TiO₂ phase (JCPDS 21-1276), implying that the modified Sn was amorphous. After the Sn/TiO₂ was calcined at 450 °C, however, the peaks in Fig. 1b slightly shifted to the location between those of SnO₂ and TiO₂, suggesting that a single-phase (Ti,Sn)O₂ solid solution was successfully formed.²²,²³,²⁴ Importantly, their crystalline structures were not significantly affected even at elevated temperature, as revealed by the fact that patterns in Fig. 1c and d were similar to those of Fig. 1b. Table S1 (ESI†) listed the lattice constants of a unit cell (denoted as a, b, c, where a = b ≠ c in the rutile form) for Sn/TiO₂ and (Ti,Sn)O₂ solid solutions. Compared with the Sn/TiO₂, it was found that the ST-450 exhibited an obvious decrease in a and b axes but an increase in the c axis as well as the cell volume expansions, which were attributed to the formation of a (Ti,Sn)O₂ solid solution. The enhancement of the c axis would be beneficial for the diffusion of Li ions within the (Ti,Sn)O₂ solid solution.²⁴ Additionally, no significant structural change was

![Fig. 1 XRD patterns of (a) Sn/TiO₂ and (b) (Ti,Sn)O₂ solid solutions calcined at (b) 450 °C, (c) 500 °C and (d) 600 °C.](image-url)
noticed as the calcination temperature was further increased, showing an excellent thermal stability of the (Ti,Sn)O2 solid solution.32

To understand the influence of calcination temperature on the chemical environment and local structure of (Ti,Sn)O2 solid solutions, measurements on X-ray photoelectron spectroscopy (XPS), X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS) were conducted. From the XPS core level spectra in Fig. S1 (ESI†), the peaks for both Ti and Sn were slightly shifted to higher binding energy as increasing the calcination temperature, which might be due to the incorporation of Sn into TiO2. Furthermore, the peak positions were still in the range assigned for the Ti4+ and Sn4+.33,34 Fig. S2 (ESI†) shows the Ti and Sn K-edge XANES spectra to further identify the chemical state of each (Ti,Sn)O2. As can be seen, all (Ti,Sn)O2 solid solutions exhibited the same spectra as those of TiO2 and SnO2, indicating that both Ti and Sn elements present in each (Ti,Sn)O2 solid solution were in the chemical state of Ti4+ and Sn4+. Those results confirmed the formation of (Ti,Sn)O2 solid solution, which were in good agreement with the XRD results. The normalized Ti and Sn K-edge Fourier-transformed (FT)-EXAFS spectra are depicted in Fig. 2a and b, respectively. No differences among the EXAFS Ti K-edge spectra of each sample at different calcination temperatures are observed from Fig. 2a, indicating that the added Sn did not affect the primary crystalline structure of TiO2 even after calcination. Since that, the next step is to explore how the added SnO2 interacted with TiO2. From Fig. 2b, it is evident that there was a little expansion in the bond length of Sn–O and the peak intensity of the first shell was increased as the calcination temperature increased but peaked at 500 °C. This implied that the locally ordered structures of Sn compounds were induced. From the peak concentrated by the second shell, the position was slightly shifted with increasing the calcination temperature, which may be caused by the stronger bonding of Ti–O–Sn. However, Ti in the rutile crystal structure was not replaced by Sn. The most possible situation was to form the solid solution, which was also consistent with the XRD results.

To confirm the morphology and uniformity of (Ti,Sn)O2 solid solutions calcined at various temperatures, the low-magnification TEM images are provided in Fig. S3 (ESI†). Instead of the needle-like pristine TiO2 in Fig. 3a, the nanorod architecture of (Ti,Sn)O2 solid solution is displayed. In addition, the aspect ratio of each (Ti,Sn)O2 nanorod evaluated from Fig. S3d–f† was about 3–5, indicating that high uniformities of (Ti,Sn)O2 nanorods were achieved even for the synthesis at elevated temperature. Fig. 3 shows the HRTEM images and their corresponding selected area electron diffraction (SAED) patterns of pristine TiO2 and (Ti,Sn)O2 solid solutions calcined at various temperatures. The chemical compositions in the different regions of the (Ti,Sn)O2 solid solutions were further analyzed using energy-dispersive X-ray (EDX) spectroscopy, whereas the results are listed in Table S2 (ESI†). For the ST-450 in Fig. 3b, it was found that the atomic ratio of Sn in region II was about 117% higher than that in region I. In contrast to the above results, the values obtained for ST-500 and ST-600 in region I were similar to those in region II. The Sn/Ti ratio did not show a similar trend with temperatures, which may be attributed to the fact that Sn was not easy to diffuse into the inner when the Sn/TiO2 was calcined at 450 °C, resulting in the different concentration gradient. Consequently, the atomic ratio of Ti to Sn was 9/1, consistent with the ICP-AES results presented in Table S3 (ESI†). Moreover, (Ti,Sn)O2 solid solutions maintained their polycrystalline nature as revealed by the inset SAED patterns.

To evaluate the electrochemical properties of (Ti,Sn)O2 solid solutions, cyclic voltammograms plotted in Fig. S4 (ESI†) were recorded using a traditional three-electrode cell in 1 M LiPF6 EC–DEC (1 : 1 w/w) solution at a scan rate of 1.0 mV s⁻¹ between 0.1 V and 3.0 V. During the first cycle, an irreversible cathodic peak at around 1.0 V was detected from each (Ti,Sn)O2 solid solution, which was ascribed to the formation of Li2O and/or a solid electrolyte interface (SEI) layer during the lithiation process. The higher current density generated from the ST-600 was probably due to the distance of the c-axis was longer than the others, facilitating Li⁺ insertion. Following the second cycle, the contributions in the range from 1.5 V to 1.8 V indicated that Ti3+/4+ was active. Fig. 4a compares the specific charge and discharge capacities of pristine TiO2 and each (Ti,Sn)O2 solid
solution in the first cycle. Among them, the ST-600 delivered the highest discharge capacity, 336 mA h g$^{-1}$, which was approximately 76% higher than that of pristine TiO$_2$, owing to the additional contribution from the SnO$_2$ and the increase of the c-axis as well. Nevertheless, it was noticed that the ST-500 maintained a specific discharge capacity of 217 mA h g$^{-1}$ after fifty cycles (Fig. 4b). This value shows around 12% increase as compared with the ST-600, in other words, the ST-500 exhibited superior cycling performance. It is worth mentioning that the ST-500 exhibited the least capacity fading (superior cycling performance. It is worth mentioning that the compared with the ST-600, in other words, the ST-500 exhibited current density of 3 A g$^{-1}$) was 9/1, which was in good agreement with the ICP-AES results. The ST-500 was probably attributed to the less cell volume expansion during the delithiation process. (Fig. 4c). The higher cycling performance and rate capability of the ST-500 was probably attributed to the less cell volume expansion (Fig. 4c). The higher cycling performance and rate capability of graphite electrode in Fig. S4 (ESI†). The evidences collected from their XPS, XANES and EXAFS spectra also confirmed the formation of (Ti,Sn)O$_2$ solid solution. The atomic ratio of Ti to Sn determined by HRTEM-EDX was 9/1, which was in good agreement with the ICP-AES results. The ST-500 delivered the highest specific capacity after fifty cycles and exhibited the least capacity fading even at a high current density of 3 A g$^{-1}$ during the delithiation process. Importantly, the thermal stability of lithiated ST-500 was superior to that of lithiated graphite as evidenced by DSC analysis. Accordingly, the ST-500 can be potentially employed as an efficient anode with favorable lithium storage in LIBs.

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