



Article Intercalating Sn/Fe Nanoparticles in Compact Carbon Monolith for Enhanced Lithium Ion Storage

Jie Deng ^{1,*}, Yu Dai ², Hui Dai ^{2,3} and Luming Li ^{1,4,*}

- ¹ College of Pharmacy and Biological Engineering, Chengdu University, Chengdu 610106, China
- ² Department of Chemical Engineering, Sichuan University, Chengdu 610065, China;
- daiyuscu@gmail.com (Y.D.); daihui18@cdut.edu.cn (H.D.)
- ³ College of Materials and Chemistry & Chemical Engineering, Chengdu University of Technology, Chengdu 610065, China
- ⁴ Institute of Advanced Study, Chengdu University, Chengdu 610106, China
- * Correspondence: dengjie@cdu.edu.cn (J.D.); liluming@cdu.edu.cn (L.L.)

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Abstract: Given its high-capacity of multielectron (de-)lithiation, SnO₂ is deemed as a competitive anode substance to tackle energy density restrictions of low-theoretical-capacity traditional graphite. However, its pragmatic adhibition seriously encounters poor initial coulombic efficiency from irreversible Li₂O formation and drastic volume change during repeated charge/discharge. Here, an applicable gel pyrolysis methodology establishes a SnO₂/Fe₂O₃ intercalated carbon monolith as superior anode materials for Li ion batteries to effectively surmount problems of SnO₂. Its bulk-like, micron-sized, compact, and non-porous structures with low area surfaces $(14.2 \text{ m}^2 \text{ g}^{-1})$ obviously increase the tap density without compromising the transport kinetics, distinct from myriad hierarchically holey metal/carbon materials recorded till date. During the long-term Li⁺ insertion/extraction, the carbon matrix not only functions as a stress management framework to alleviate the stress intensification on surface layers, enabling the electrode to retain its morphological/mechanic integrity and yielding a steady solid electrolyte interphase film, but also imparts very robust connection to stop SnO₂ from coarsening/losing electric contact, facilitating fast electrolyte infiltration and ion/electron transfer. Besides, the closely contacted and evenly distributed Fe₂O₃/SnO₂ nanoparticles supply additional charge-transfer driving force, thanks to a built-in electric field. Benefiting from such virtues, the embedment of binary metal oxides in the dense carbons enhances initial Coulombic efficiency up to 67.3%, with an elevated reversible capacity of 726 mAh/g at 0.2 A/g, a high capacity retention of 84% after 100 cycles, a boosted rate capability between 0.2 and 3.2 A g^{-1} , and a stable cycle life of 466 mAh/g over 200 cycles at 1 A g^{-1} . Our scenario based upon this unique binary metal-in-carbon sandwich compact construction to achieve the stress regulation and the so-called synergistic effect between metals or metal oxides and carbons is economically effective and tractable enough to scale up the preparation and can be rifely employed to other oxide anodes for ameliorating their electrochemical properties.

Keywords: anode; lithium ion battery; tin oxide; carbon materials

1. Introduction

Lithium ion batteries (LIBs) presently prevail among the power source markets for the portable electronics and constitute the most fascinating clean-energy technology for the flourishing large-scale stationary energy storage, smart grids, and vehicular electrics. However, traditional LIBs (depending upon the insertion composite substances, including the graphite-positive electrode and lithium transition metal oxide or phosphate negative electrodes) have reached their inherent ceiling regarding

specific energy (roughly 210 Wh kg⁻¹), which falls short of satiating the ever-increasing requirement of ever-larger energy and power. To pursue the novel higher-capacity electrode substances owning the stable lifetime to supplant the traditional graphite anodes (low capacity of 372 mA h g⁻¹) is in high demand for LIBs [1–5]. Both the alloy-type and conversion-type substances feature the rather great theoretical capacities as anodes because of the multiple electron reactions and transportations [6–9]. Among them, the tin dioxides (SnO₂) emerge as one most potential anode alternative, given its very low discharge potential versus Li/Li⁺ and great capacity contributed by two electrochemical events of (de-)alloying and (de-)conversion, as expressed [10–12]:

$$SnO_2 + 4Li^+ + 4e^- \rightarrow Sn + 2Li_2O \tag{1}$$

$$Sn + 4.4Li^+ + 4.4 e^- \leftrightarrow SnLi_{4.4}$$
⁽²⁾

Production of an electrochemically passive and resistive Li₂O component during the first conversion stage described by Equation (1) can deprive an irreversible capacity up to 731 mA h g⁻¹ during initial lithiation events, inducing a limited initial Coulombic efficiency (< 50%) [13,14]. Though, the second alloying process (Equation (2)) can deliver a high theoretical reversible capacity of 783 mA h g⁻¹, an extremely serious volume swelling beyond 300% ensues, hence thwarting its practical usage [15–17]. Electrochemical lithiation triggers generation of boundary areas between Li-rich Li_xSn and Sn crystals and resultantly yields the stress reinforcement. The gain in the strain energy engenders an anisotropic expansion and exotic volume fluctuation, giving rise to some parasitic aftereffects, including the grim surface fracture, even electrode pulverization, and electrical disconnection with the current collector. The phenomena supra re-expose the fresh Sn surfaces to electrolyte, calling forth a continuous rise in the solid electrolyte interface (SEI) tier thickness over the prolonged battery cycling and eventually an acute battery performance deterioration [18–21].

Pursuant to the rationale that structural strains can come under assuagement via the particulate downscaling toward the nanometer, a threshold dimension for the fracture reproduction and spread has turned out to be 150 nm [18–21]. Thus, multitudinous elaborate structural modification strategies (via delicate nanotechnology) involving generating the sophisticated nanostructures and hybridizing with a powerful surface coating (carbon, SiO_x, TiO₂, SiOC, and so forth) have been universally adopted to fulfil the buffering of structural strains of SnO_2 and improve the ICE in the course of (de-)lithiation [22–28]. Typically, signally cushioning the volume expansion and enhancing the cyclic stabilities have come true by constructing the well-designed fine structures ranging from 1D to 3D, for example, SnO₂ nanotubes, SnO₂ hollow nanospheres, Sn/SnO₂ yolk-shell configurations, hierarchically porous organizations, and so on. However, aside from the synthetic expensiveness, cumbersomeness, low throughout, and eco-malignance, realistic implementation of preceding avenues still confronts grand challenges about both a small tap density in the range of < 0.4 g cm⁻³ of foregoing architectures caused by abundant empty volumes and other morphostructural caveats [29,30]. Worse still, protecting the pre-engineered void spaces militates against their virtues during tight calendaring procedures in that an overwhelming majority of the pores and shells will get totally impaired [31]. Till now, assembling the compact secondary layouts of inactive/active buffers by nanocomposites can largely augment tap density. Out of such dense configurations, a conductive and elastic carbon-based matrix has aroused tremendous interests to effectively relax the mechanic strains to mitigate the volume evolutions and curb the structural cracking of Sn [32].

Even if integration of the nanometer SnO_2 with carbon coating can elongate cyclic longevity via inhibiting the capacity decay, the substantial initial irreversible capacity degeneration still takes place, appreciably whittling down the coulombic efficiency. Because Li₂O hardly participates in the reverse process of Equation (1), it makes a great difference to foil the Sn coarsening during lithiation, restrain the interparticle migration between Sn and Li₂O, and manipulate the reversibility of the conversion reaction [33–36]. In this context, building the multicomponent hybrids or intermetallic alloys to ease structural strains of Sn has been postulated, where nanoscale alien metals can impose

multiple effects on the Li ion chemistry of SnO₂ [14,32,37–40]. Particularly, in addition to serving as spacers/barriers against the diffusion/agglomeration of Sn in the hybrids, Fe can function like an efficient catalyst to accelerate the Li₂O decomposition, leading SnO₂ to reversibly form through the backward process of Equation (1). Studies further evidence that Fe in intimate contact with Sn can form heterostructures with the crystal-mode-controlled charge transport as a result of the superior interface effects and of generation of built-in potentials (internal electric field) around hetero-interfaces [32,41–48]. This multicomponent synergy can notably aid in mitigating the structural strains to stabilize the morphological integrity of active materials, expediting the reaction dynamics and ion/electron transfer, and thus consolidating the electrochemical behavior (particularly the rate capability).

Based upon the viewpoints above, coupling the advantages of the compact structures and the multicomponent collaboration (for energy storage on Sn-based materials) to construct a compatible Sn-Fe/carbon-based matrix composite with more stable structure and faster conductivity is one of most promising strategies toward coping with the microstructural defect issues of SnO₂ anodes, especially given that the carbon substrate is able to extra heighten electronic connection/conduction of the overall electrode. Herein, we show the fabrication and improved (de-)lithiation behavior of a novel anode material based upon the ultrasmall (sub-10 nm) SnO₂/Fe₂O₃ binary nanoparticles uniformly/densely implanted inside a micro-sized compact carbon skeleton. When we used a scalable and straightforward gel pyrolysis approach, the xerogels comprising the binary metal ion-homogeneously coordinated adducts produced via polymerizing a clear gel of citrate and metal salts experienced a thermal crystallization in N₂, at a fixed temperature, to result in the dense metal nanoparticles-intercalated carbon monolith, which excels in delivering the electrons/ions and modulating the structural stress during Li ion storages. Unlike the priorly chronicled protocols which need both sophisticated nano-techniques and exquisite apparatus to assemble the SnO₂/carbon nano-compounds, our currently demonstrated study merely deals with the maturely industrial procedures. By virtues of multicomponent synergy and compact secondary architecture, the as-synthesized samples feature several unique merits as follows: (1) the amorphous carbon works as a protective matrix to not only ensure the swift electron/ion mobility through the overall electrode but also accommodate the mechanic strain to hurdle the diffusion/aggregation of the active materials and disintegration of electrode. (2) Small-sized metal nanoparticles guarantee the boosted electrochemical reaction kinetics based on both the maximized interface boundary with the closely contacted carbon and short pathways for movement of Li⁺ and electrons. (3) The non-porous and micro-sized compact structure gives the high tap density and avoids the morphological issues to enhance the structural stability and volumetric battery performance. (4) A combination of Fe_2O_3 with SnO_2 can not only produce the closely spaced nanostructures with an internal potential for offering extra charge transfer driving force, quickening the reaction dynamics and the electron/ion migration across their boundary areas, but also promote the input/output of external charges outside SnO₂ due to the great electronic conductivity of Fe₂O₃. (4) Ultra-small metal nanoparticles are firmly inlayed between carbon layers instead of simple physical stacking, which largely boosts overall structural durability of the electrode materials. As a novel configuration of the compact materials, the microstructure without the highly hierarchical porosity possesses the conductive protecting carbon sheath and no free void spaces, thus owing the greater flexibility in the tight calendaring processing of electrode, full usage of electroactive materials, relief of volume expansion, and mass fabrication. With such encouraging superiorities, this dense composite monolith can withstand a stress-induced volume variation of the SnO₂-based nanoparticles to maintain the structural framework and thus endows the outstanding anodic performances for LIBs in terms of the stable cycle stability, good rate performance, and big specific capacity. This study develops a facile way to prepare the promising anode material for LIBs, and, at the same time, it will motivate the chemists to further explore other advanced SnO₂-based LIB anodes.

2. Materials and Methods

2.1. Material Preparation

The schematic synthesis of our anode materials is described in Scheme 1. Preparation of the Sn/Fe oxides-intercalated carbons (SFO@C) includes several simple steps. Briefly, SnCl₄ salt (Kelon, Chengdu, China) and citric acid (Kelon, Chengdu, China) were first dissolved in deionized water, by ultrasonication, under constant magnetic stirring (Minhang Hongpu Instrument, Shanghai, China), to generate the 0.2 M SnCl₄ aqueous solution, and the citric acid concentration in the 0.2 M SnCl₄ aqueous solution was fixed at 0.15 g/ml. K₄[Fe(CN)₆] salts (Kelon, Chengdu, China) and citric acid (Kelon, Chengdu, China) were dissolved in deionized water by sonication under vigorous mechanical agitation, to produce the 0.2 M K_4 [Fe(CN)₆] aqueous solution, and the citric concentration in the formed K_4 [Fe(CN)₆] aqueous solution was determined at 0.15g/mL. Then, the above 0.2 M SnCl₄ aqueous solution and 0.2 M K_4 [Fe(CN)₆] aqueous solution were simply mingled with a volume ratio of 2:1, at room temperature, under the magnetic stirring, and a clear gel was derived after a few minutes. Afterward, the as-prepared gel was placed in a refrigerator (Haier, Shandong, China), at 4 °C, for 12 h, and then transferred to -20 °C for an additional 12 h. Then, the frozen jell was placed in liquid nitrogen for about 30 s, followed by a freeze-drying in a lyophilizer (Boke Scientific Instrument, Shandong, China), at -80 °C, under 1 Pa, for 24h to acquire a xerogel. The resultant xerogels were placed in an alumina crucible and kept in a quartz tube furnace (Nanda Instrument, Nanjing, China), to experience the pyrolysis and carbonization. The tube was heated to 400 °C, at a heating rate of 5 °C/min and kept firstly at 400 °C, in air for pyrolysis for 2 h, and then at 400 °C for 2 h, under the atmosphere of a flowing N_2 for carbonization. After cooling down to ambient temperature in N_2 atmospheres, the derived product was washed with the distilled water and ethanol, to eliminate the impurities and dried at 100 °C in the electric oven (PuDong Rong-Feng Scientific Instrument Company, Shanghai, China) in air. The final sample was denoted as SFO@C-400. SFO@C-350 and SFO@C-450 were synthesized by a similar method, but with different calcination temperatures (350 and 450 °C). SFO was prepared by thermal annealing of the xerogels at 600 °C, in air, for 2 h.



Scheme 1. Synthetic diagram of our binary metal oxides/composite materials.

2.2. Structure and Morphology Characterization

Crystal phase structures of SFO@C were determined via X-ray powder diffraction (XRD, DX-2700, Cu K_{α} radiation, $\lambda = 1.542$ Å, Haoyuan Instrument, Liaoning, China). The carbon amount in a series of SFO@C was monitored through thermogravimetric analysis (TGA, Bulid 193, Henven Instrument, Beijing, China). The carbon structure in SFO@C was checked by Raman spectra on a LabRAM HR Raman spectrometer (Tokyo, Japan), using laser excitation at 632.8 nm. Scanning electron microscopy (SEM, JEOL, JSM-7500F, Tokyo Japan) and transmission electron microscopy (TEM, Tecnai G2 F20 S-Twin, FEI, Hillsboro, OR, USA) were carried out to detect the microstructure of samples. The surface chemistry of SFO@C was inspected, using an X-ray photoelectron spectroscope (XPS, AXIS Ultra DLD, Kratos, Manchester, UK). Nitrogen volumetry was executed on a NOVA1000e analyzer (Quantachrome Instruments, Boynton Beach, FL, USA) to study the textural properties.

2.3. Performance Evaluation

The working electrode was prepared by mixing the active materials (SFO@C or SFO), conducting carbon and polyvinylidene fluoride binder in N-methyl-2-pyrrolidinone, to form a homogeneous slurry with a weight ratio of 8:1:1. The slurry was doctor bladed on copper foil current collector and then dried in a vacuum oven (Kunshan Rongshida Electronic Equipment Company, Jiangsu, China) for 12 h. The copper foil coated with active materials was then stamped into rounds with a diameter of 14 mm. The areal active material loading in each electrode reaches about 2 mg/cm². Electrochemical measurements were performed by using the CR-2032-type coin cells, which were assembled in a glove box (O_2 and H_2O contents < 1 ppm) filled with highly pure argon. A pure lithium foil was utilized as the counter electrode, the Celgard 2400 microporous polypropylene membrane (Celgard, 2400, 25μ m in thickness, NC, USA) acted as the separator, and a mixture of 1 M LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (Kelon, Chengdu, China) with a volume ratio of 1:1 was applied as the electrolyte. The galvanostatic charge/discharge measurements were done on a Neware battery measurement system (CT-3008, Neware technology, Shenzhen, China). Both the cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) tests were implemented on a CHI 660E electrochemical workstation (CHI 660E, Shanghai, China). The charge or discharge capacity (Q) was computed according to the formula: $Q = I\Delta t/m$, wherein I denotes the current density, Δt represents the discharge or charge duration, and *m* means the mass of active materials.

3. Results and Discussion

The powder XRD measurements of final samples were utilized to investigate the component and crystal structure. Figure 1a describes XRD patterns of the as-formed composites pyrolyzed at various temperatures and the carbon-free SFO specimen. All products share the similar reflections peaks that correspond to the tetragonal rutile SnO₂ (JCPDS card No. 41-1445) and the rhombohedral Fe_2O_3 (JCPDS card No. 33-0664), confirming the successful conversion of metal ions into coexistence of SnO₂ and Fe₂O₃ phases and their nanocrystalline nature. Moreover, no visible reflection signals linked with graphite emerge, possibly revealing that the carbon in all samples may be amorphous in crystallinity or inappreciable in quantity. The sharp diffraction peaks with the small full width at half-maximum (FWHM) values unravel the excellent crystallinity of the Sn and Fe nanograins. No other impurities but both the Fe_2O_3 and SnO_2 phases are found. On account of the simplicity, scalability, and most significantly the circumvention of harnessing expensive/eco-unfriendly raw materials, our current way considerably gains an advantage over the prior studies regarding preparing the carbon/Sn/Fe hybrids, and thus is more amenable to practical adhibitions [16,22,25–28]. The average size of the SnO₂ nano-crystallites within hybrids is computed as roughly 9 nm according to the Scherrer formula (d = $0.9\lambda/\beta\cos\theta$, wherein θ represents the Bragg angle, β means FWHM in radian, λ refers to the X-ray wavelength, and d stands for average crystalline particle size), employing Sn (100) peak. The textural properties were clarified via N2 porosimetry, and the corresponding results were depicted in Figure 1c. The type III isotherms without the distinguishable hysteresis loop are obtained for all products, uncovering the distinctive signatures of non-porous materials. BET specific surface areas of SFO@C-350, SFO@C-400, SFO@C-450, and SFO are estimated to be 9.1, 14.2, 56.4, and 141.2 m² g⁻¹, respectively. The large value of SFO can be attributed to internal void structures. It is worth noting that the surface areas rise dramatically with the increase of oxidation temperature, which may be related to the gas derived from the decomposition of carbon source in gel precursor. The BET surface area of B-SFO@C-400 approaches only 14.2 m² g⁻¹, one order of magnitude below a host of the nanometer SnO_2 -based structures (>100 m² g⁻¹) reported previously [29,30]. This textural characteristic unveils the compact and non-porous nature of B-SFO@C-400, finally resulting in a large tap density of about 0.70 g cm^{-3} , 2–3 times outnumbering a great deal of the hitherto-reported elaborated SnO₂-based materials with the highly hierarchical porosity and morphology [29,30].



Figure 1. (a) XRD patterns; (b) N₂ adsorption/desorption isotherm curves, and TGA curves (c) of all samples; (d) Raman spectra of SFO@C-400 sample.

The carbon contents in all samples are identified via the thermogravimetry analysis (TGA) at the wide temperature range of 25–800 °C in air, as illustrated in Figure 1b. In TGA curves, a slight weight loss below 1% observed up to 110 °C ought to originate from removal of physically absorbed and free water from atmosphere. The total weight loss at high temperature is assigned to the combustion of carbon into CO_2 in air upon heating. Thus, the weight percentage of carbon in these composites can be calculated to be roughly 54.7 wt.% (SFO@C-350), 39 wt.% (SFO@C-400), and 32.7 wt.% (SFO@C-450). That is to say, the total metal or/and metal oxide fraction sequentially equals 45.3%, 61%, and 67.3%, revealing that an appropriate carbonization temperature can result in a rather high metal loading concentration. Combined with absence of XRD diffraction peaks assignable to graphite, the relatively high content proportion also suggests that the carbons in composites are in a non-crystalline state. The carbon crystal structure can be further substantiated through Raman spectroscopy. No Raman scattering characteristic bands indexed to SnO₂ and Fe₂O₃ are detected. The two sharp bumps located at around 1344 and 1588 cm⁻¹ well matching with the D and G peaks of the carbon materials are discerned [49]. It has been reported that the D band typifies a defect-induced breathing mode of sp^2 rings, which stems from the strongly dispersed LO phonons around the K point activated in double resonance processes, namely, k-point phonons of A1g symmetry. The G band is responsible for the characteristic doubly degenerate E_{2g} mode (iTO and LO) of the sp² domains or atoms, i.e., the first-order phonon scattering vibrations in the in-plane of the ideal graphite. To be more precise, a Kohn anomaly at K has been indicated as the real source of the D band due to the greatest optical branch starting from the K-A'₁ mode, which features the largest electron–phonon coupling among K phonons. Thus, the D band can elucidate the degree of disorder and structural defects in the graphite layer of carbon materials, whose quantitative level can be appraised by the intensity ratio of D to G band (I_D/I_G) [50–53]. Commonly, an improved I_D/I_G value implies the smaller sp² domains within the carbon materials and restoration of sp^2 carbon. This value on the typical SFO@C-400 sample is as high as 1.14, disclosing that the carbon in SFO@C-400 is the amorphous nanocarbon with the disorder structure or small sp^2

microdomain [54]. This partial graphitization of carbon matrix can simultaneously support the decent electrical conductivity and mechanic elasticity or flexibility, which can be beneficial for accelerating the charge transfer rate, stabilizing the metal oxide/metal heterointerfaces, and boosting the electrode mechanic stability.

The microstructures and morphology of the samples were further observed via SEM and TEM. As shown in Figure 2a-c, all SFO@C-350, SFO@C-400, and SFO@C-450 samples exhibit a similar bulk-like structure with a size of $10-15 \ \mu m$ and no bulk metal aggregations. This monolithic morphology evolves with the pyrolysis temperature. Under a lower temperature of 350 and 400 °C (Figure 2a,b), no observable macropores exist on surfaces of monoliths, whereas at a higher temperature of 450 °C many irregular macropores/cavities of $1-2 \mu m$ in diameter abound (Figure 2c). This could be caused by the gas generated during decomposition of carbon precursors and accounts for the huge difference in the BET specific surface area between SFO@C-350, SFO@C-400, and SFO@C-450. The magnified SEM image of SFO@C-400 in the inset of Figure 3b demonstrates that the surface of SFO@C-400 is made up of the closely packed ultrafine particles and no discernable interparticle small openings/voids are monitored, symptomatic of a dense configuration of SFO@C-400. However, the micron-sized bulk structure can no longer be well maintained in the case of SFO, which manifests a loosely stacked organization comprising lots of agglomerates with an average size of 200 nm. This clearly evidences that the carbon matrix is indispensable to result in unique structural motifs of micro-dimensionality and compactness. TEM measurements were carried out to acquire more detailed information of the microstructure of the typical SFO@C-400 sample. Commonly speaking, Figure 2e presents a typical panorama possessing no detectable porosity (involving the mesopores and macropores), confirming the non-porous and dense nature from the BET data. It is clearly found that numerous metal oxide nanoparticles are uniformly distributed in a continuous carbon matrix. Instead of being completely coated, these nanoparticles closely connect with the carbon matrix or get partially embedded inside the carbon layers, inducing a unique metal particles-in-carbon sandwich-like geometry. This distinct metal-intercalated configuration can be further evidenced by HRTEM image of Figure 2f, where the metal nanoparticles are evenly intercalated between carbon layers. The average particle size is about 5–10 nm, in excellent consistency with XRD results. Two sets of well-defined crystalline facet fringes with the marked lattice inter-spacings of 0.33 and 0.27 nm are clearly observed, which belong to the (110) facet of SnO₂ and (104) plane of Fe₂O₃, respectively. More importantly, SnO₂ and Fe₂O₃ are in intimate contact. These closely distributed/embedded metal oxide nanoparticles and the typical carbon layers must result in ample robust heterointerfaces or heterojunctions between two metal oxide nanoparticles (as highlighted by yellow dash lines across these joint particle boundary in Figure 2f), which can bridge these two nanocrystals and unleash huge possibility to create the synergic effect (particularly the internal potentials) during (de-)lithiation for the much enhanced electrochemical performance [41–48]. Furthermore, the worm-like entities intimately surrounding the nanoparticles with both the high transparency and indistinct crystallographic diffraction stripes represent non-crystallized carbon tiers, accordant to the phase structures verified by XRD and Raman tools. Such a finding, indeed, signifies that the nanocrystals constructing the $SnO_2/Fe_2O_3@C$ micro-particulates are together conjoined via the strong chemical bonds in place of the physical stacking so that this metal-in-carbon geometry can be reinforced to much great extent. In this case, after lithiation, every SnO₂ particle would change to a single/separate district constituted by Sn and Li₂O. Even if the dimension of the initially generated Sn phases within such 5–10 nm SnO_2 crystals is considerably smaller than 5–10 nm, they will endlessly grow and become bigger than the initial size of SnO_2 in that the Sn is unable to diffuse from other adjacent Sn-Li₂O zones. As a result, the lithiation-triggered coarsening of the Sn crystals can be avoidable within this SFO@C electrode. Moreover, no pronounced microporous characteristics can be found in these amorphous carbon regions, further corroborating the extremely small BET specific surface area. Such morphological uniqueness and structural uniformity may tolerate the large mechanic strains of the Sn nanoparticles, to alleviate the volume variation of SnO₂, inhibit their pulverization and



agglomeration during (de-)lithiation, and facilitate the electron transfer between the active materials, thereby giving rise to the improved rate capability and prolonged cycle stabilities.

Figure 2. (a) SEM images of (a) SFO@C-350, (b) SFO@C-400, (c) SFO@C-450, and (d) SFO samples; (e) TEM images of SFO@C-400 sample and (f) corresponding HRTEM image.





Figure 3. XPS spectra of SFO@C-400 sample: (a) survey spectrum, (b) C 1s, (c) Sn 3d, and (d) Fe 2p.

The surface electronic structure and chemical element valance state of the typical SFO@C-400 material was explored by utilizing the X-ray photoelectron spectroscopy (XPS), as delineated in Figure 3. In the survey-scan spectrum (Figure 3a), the noticeable peaks related with C, Sn, Fe, and O elements are detected, explicitly validating the co-presence of the C, Sn, Fe, and O elements in the composite. The fine spectrum of C1s core emission (Figure 3b) can be compartmentalized into three evident components, sourced from the sp²-hybridized graphitic C atoms of C-C/C=C (284.6 eV), sp³-hybridized C atoms of epoxy groups (C-O, 286 eV), and functional groups on the carbon surfaces such as carbonyl groups (C=O, 288.6 eV) [55]. The high-resolution Sn 3d spectrum (Figure 3c) clarifies the chemical bonding state of Sn, with a pair of strong envelops positioned at 487.6 and 495.8 eV being indexed to Sn $3d_{5/2}$ and Sn $3d_{3/2}$ for Sn⁴⁺ of SnO₂, respectively [56]. The peak separation or distance between these two bands is about 8.2 eV, which is very consistent with the splitting binding energy of Sn(IV) ion (indexed Standard ESCA Spectra of the Elements and Line Energy Information, Φ Co., USA). It is noteworthy that these binding energy values are somewhat smaller than the counterparts reported before, and this most possibly results from fewer oxygen neighbors around Sn on average because of a certain reduction of SnO₂ over surfaces by the closely contacted amorphous carbon [57]. This shrunken binding energy for Sn^{4+} also mirrors the strong interaction between SnO_2 and carbon, further supporting that the Sn metal nanoparticles are strongly bonded to carbon layers instead of the simple physical stacking, as analyzed from TEM images. The narrow-scan Fe2p core-level spectrum (Figure 3d) consists of two prominent spin-orbit doublets emerging at around 712.1 and 716.8 eV, which are relevant to the characteristic $Fe^{3+} 2p_{3/2}$ and $Fe^{3+} 2p_{1/2}$, respectively [43]. Overall, the data imply the coexistence of Sn⁴⁺ and Fe³⁺ in SFO@C-400, and further manifest that the Sn and Fe atoms are in the form of SnO₂ and Fe₂O₃, respectively.

The galvanostatic charge/discharge measurement in the range of 0.005–3.0 V (vs. Li/Li⁺) was carried out in coin-type cells with Li counter electrodes to evaluate the electrochemical performance of all samples. Figure 4a presents the initial discharge/charge curves of the SFO@C-350, SFO@C-400, SFO@C-450, and SFO electrodes, which state representative characteristics of the Sn-carbon composite

anodes. In the discharge profile, the voltage declines rapidly below 1.2 V and expresses a discharge plateaus at 0.8-1.2 V, linked with reduction of SnO_2 to Sn. The discharge plateaus spanning from 0.3 to 0.5 V deal with the Li-Sn alloying toward creation of Li_xSn alloy, which accords with the CV plots analyzed later [33,34]. Correspondingly, the charge profile also shows two sloping charge plateaus located at about 0.5 and 1.25 V, which are attributed to dealloying of Li_xSn and the reversible reaction of Sn and Li₂O to SnO₂, which can be more clearly confirmed by differential capacity (dQ/dV) curves, as seen in Figure 5. Note that, as a result of relatively sluggish Li⁺ diffusion kinetics within SnO₂, the potential plateaus of conversion reaction shifts to below 1.0 V, triggering off a lower capacity produced between open current voltage and 1.0 V during the discharging. Under such a circumstance, the portion of the conversion process and alloying event superposes at a potential smaller than 1.0 V, inducing a considerably greater capacity than the value beyond 1.0 V. Nevertheless, the overpotential will enable the re-conversion event occurring at potential above 1.0 V in the course of charging, bringing about a bigger capacity at 1.0–3.0 V in the course of discharging. Thus, the SFO@C-350, SFO@C-400, SFO@C-450, and SFO electrodes deliver an initial discharge/charge capacity of 1100/723, 1301/876, 1468/955, and 1353/842 mAh g^{-1} , yielding an initial coulombic efficiency (ICE) of roughly 65.7%, 67.3%, 65%, and 62.2% for SFO@C-350, SFO@C-400, SFO@C-450, and SFO, respectively. Albeit still smaller than the pre-lithiation transition metal oxides like Li₃V(MoO₄)₃ or pre-lithiation SnO₂ foil [58,59], the ICE values here surpass these of multitudes of tailor-made SnO₂-based hybrid materials (< 50%) reported so far. The comparatively low ICE is mainly ascribed to the formation of the solid electrolyte interface (SEI) film and the irreversible part of the conversion reactions of SnO_2 and Li because the increasing surface areas of electrodes supply the sufficient contact areas between electrode and electrolyte and consume the increasing quantity of Li ions [60]. This much-improved ICE of our system expresses that the binary metal-in-carbon compact monolith bears stronger capability to confine and stabilize the Sn/Li₂O nanocrystals against coarsening and hence shun the adverse side reactions (e.g., the irreversible conversion events between Sn/SnO₂ and Li⁺ ions and the electrolyte dissociation reaction) to promote the conversion reaction reversibility, in good line with the CV data. Interestingly, ICE of SFO@C-350, SFO@C-400, and SFO@C-450 are all higher than that of the SFO electrode, which could be attributed to the fact that the very low surface area of SFO@C-350, SFO@C-400, and SFO@C-450 reduces the irreversible capacity loss caused by formation of a thick SEI film. Moreover, coulombic efficiency of SFO@C-400 rapidly increases to 92.8% and maintains over 98% in subsequent cycles, suggesting a high reversible capacity.

To probe cyclability and Li⁺ insertion/extraction processes, Figure 4b describes CV characteristics for the initial three consecutive cycles of the SFO@C-400 electrode at a sweep rate of 0.1 mV s⁻¹ from 0.005 to 3.0 V, to scrutinize the electrochemical reaction pathways. All CV curves basically reproduce the analogous electrochemical behaviors. In the first sweep, several irreversible peaks are detected. According to the prior reports, during the first discharging stage, the predominant cathodic peak observed at 1.41 V can pertain to the reduction of SnO_2 and Fe_2O_3 to metallic Sn and/or Fe (conversion reaction), accompanied by formation of Li₂O phases that act as buffer matrix to mitigate the volume fluctuation for the subsequent alloying reaction [32,41-44]. Upon further discharging, the subsequent peak at 0.77 V is ascribed to production of a solid electrolyte interface (SEI) film (related to electrolyte decomposition). With a continuous cathodic sweeping, the following broad cathodic peak at <0.7 V originates from the ensuing alloying process of Li⁺ inserting into Sn to form the Li-Sn compound due to the multistep lithiation mechanism, in which case the Sn comes from the previously formed Sn via the reduction of SnO₂. Some rather weak redox peaks at high voltages such as ~2.4 V plausibly derive from the Li insertion/extraction from oxygen-containing functional groups on carbon [61]. After the initial cycle, it can be clearly found that almost no apparent changes take place in the reduction peaks, indicating that the irreversible reaction primarily exists during the first cycle, and creation of the solid electrolyte interphase (SEI) film on the electrode surfaces merely arises in the first cycle. It needs to be stressed that, because of the electrochemical inertness between Fe and lithium, Fe works as inactive buffer toward regulating the thickness of the SEI layer and securing the nanoparticles' structural

alteration [43]. Notwithstanding, from a second scan onward, all (de-)lithiation events progressively turn reversible. During the following anodic scan process (the charging step), these first cathodic peaks are replaced by two strong anodic/oxidation peaks at 0.6 and 1.3 V, which are sequentially caused due to the phase transition process of dealloying of various Li_xSn alloys to Sn phases and the partially reversible conversion reaction of Sn and Li_2O to yield the SnO₂ nanocrystals [62]. The weak peak at 1.8 V is typical of insertion of Li^+ into Fe_2O_3 . The reduction peaks are less sharp than oxidation peaks, showing the slower reaction kinetics of alloying than dealloying. Furthermore, the correlative plateau zones of the electrode can be also determined by charge/discharge patterns (Figure 4a). After the initial cycle, the cathodic peaks at < 0.7 V sees a conspicuous displacement, whereas other peaks encounter the slight shift, documenting the influence of SEI layers. Contrarily, the oxidation peaks do not witness the notable variation, revealing the superior reversibility of Fe₂O₃ and SnO₂. After the first cycle, the following second and third cathodic and anodic cycles practically overlap each other (namely the reduction/oxidation peaks remain unaltered in terms of the current densities and voltage positions), shedding light upon the outstanding cyclability and reversibility of these electrochemical reactions (namely the (de-)lithiation processes have no changes). This superior reversibility surely manifests that our sample can well manage structural stress of SnO₂ to arrest the volume variations and clustering of the Sn nanoparticles. Through making a comparison between the second/third cycle and the first cycle, one can clearly discover that the reduction peak at 0.77 V disappears and tends to be stable subsequent to the first cycle, stating the irreversible generation of SEI film because of the electrolyte decomposition. The diminished intensity regarding wide cathodic peaks within the scope between 0.005 and 1.0 V verifies the successful oppression of the gain in the SEI layer thickness. In addition, the recognizable negatively shifted anodic peaks (concomitant with discernable positively moved cathodic peaks) in the SFO@C-400 electrode expounds its improved dynamic performance, viz., easier mobility of Li ion across SEI layers and quicker charge transport. Relevant electrochemical events on lithiation/de-lithiation can be expressed as follows:

Conversion reactions: $SnO_2 + 4Li^+ + 4e^- \leftrightarrow Sn + 2Li_2O$

 $Fe_2O_3 + 6Li^+ + 6e^- \leftrightarrow 2Fe + 3Li_2O$

Alloying/de-alloying process: $Sn + xLi^+ + xe^- \leftrightarrow Li_xSn \ (0 \le x \le 4.4)$

Figure 4c plots the electrochemical kinetics and rate capability of these hybrids at a series of progressively increased current densities ranging from 0.2 to 3.2 A g⁻¹. The electrochemical performance is unstable, and the electrode capacity gradually decreases with the current density increment. Fortunately, when the current rate rises successively from 0.2, 0.4, 0.8, and 1.6 to 3.2 A g^{-1} , an average capacity of SFO@C-400 is calculated to be about 829, 732, 597, 451, and 331 mAh g^{-1} , respectively, showing the best rate capability. The steady capacity at 3.2 A g^{-1} is as high as 40 % of the one at 0.2 A g⁻¹, significantly outperforming those of other three electrodes. Even at a high current density of 3.2 A g^{-1} , the average capacity of 331 mAh g^{-1} is very close to the theoretical capacity of the graphite anode (374 mAh g^{-1}). Markedly, when abruptly switching the current density from 3.2 Ag^{-1} back to 0.2 Ag^{-1} after 10 cycles under various current densities, the average capacity can instantly revert to 681 mAh g⁻¹ after 10 cycles, reinstating 83% of the original level, indicating a good structural stability. This reveals that the binary metal-in-carbon structure conduces to electron/ion migration, augmenting the rate capability. These values are undeniably superior to the counterparts of SFO@C-350 and SFO@C-450, which is due to the less sluggish Li⁺ diffusion resistance and charge transfer impedance of SFO@C-400, as verified by EIS test (Figure 6a). Among all electrodes, SFO presents the worst rate capability with an average capacity of 552, 282, and 138 mAh g^{-1} at 0.2, 0.4, and 0.8 A g^{-1} , respectively, and hardly delivers the capacity at 1.6 and 3.2 A g⁻¹, proving that the carbon matrix is indispensable for improving the rating performance, especially under high current rates. It is worth emphasizing that, even after a light cycling at a large current density of 3.2 A g^{-1} for several cycles, the reversible capacity of SFO cannot immediately be recovered when the current is reset at

 0.2 A g^{-1} , which exclusively proves a poor rate capability. Generally, the rate capability of the electrode material is closely related to the kinetics of electrochemical reactions, including the charge transfer and the Li⁺ ion diffusion. The outstanding rate capability of SFO@C-400 most possibly results from its unique protection nanostructure and the refined crystals. The uniform carbon layer is able to function as a greatly conducting matrix. The ultrasmall SnO₂ nanoparticles can shorten the transport distance for both electrons and lithium ions. As a result, the faster charge transfer and Li⁺ ions diffusion enable Li ions to be intercalated into more particles particularly at high current densities [63,64]. The data show that the SFO@C-400 composite could endure the altered discharge current densities and possess a superior application prospect in high power LIBs.



Figure 4. Electrochemical properties: (**a**) initial discharge/charge curves scanned at 0.2 A g^{-1} ; (**b**) CV curves of SFO@C-400 at 0.1 mV s⁻¹; (**c**) rate capability at various current densities from 0.2 to 3.2 A g^{-1} ; (**d**) cycling stability of 100 cycles at 0.2 A g^{-1} ; (**e**) long-term cyclic life up to 200 cycles at 1 A g^{-1} .



Figure 5. Differential charge capacity curves at 0.2 A/g of (**a**) the SFO@C-400 electrode and (**b**) the SFO electrode at the 1st, 2nd, 10th, and 50th cycle; reversible capacities versus cycle number of (**c**) the SFO electrode and (**d**) the SFO@C-400 electrode separated into potential ranges of 0.005–1.0 V and 1.0–2.5 V; SEM images of the SFO@C-400 electrode (**e**) before and (**f**) after 100 cycles at 0.2 A/g.

Figure 4d compares cyclabilities of all samples to gain the in-depth insights into the momentous role of structural design in influencing the Li ion storage properties of electrode substances. The electrochemical stability was examined under galvanostatic cycling, in a voltage range of 0.005-3.0 V at 0.2 A g⁻¹. Because of creation of SEI layers and unavoidable electrolyte decomposition, the delivered discharge-specific capacity falls notably during the early several cycles and tends to be stable in subsequent cycles. Despite being subjected to a capacity fading, SFO@C-400 delivers the considerably better Li ion storage capacity throughout entire cycles than other three samples, indicating the best cyclic stability. The SFO electrode suffers from most severe reversible capacity loss, maintaining only 132 mAh g⁻¹ (about 15.6% retention of the second discharge capacity) after 50 cycles, indicating the important role of carbon matrix in improving the cyclic performance. In sharp contrast, the cyclic performance of SFO@C-350, SFO@C-400, and SFO@C-450 exhibits a great improvement. After 100 cycles, the discharge capacity is stabilized at 411 mAh g⁻¹ for SFO@C-350, 519 mAh g⁻¹ for SFO@C-450,

but 726 mAh g^{-1} for SFO@C-400, corresponding to a 55%, 54%, and 84% capacity retention of from the second discharge capacity to the 100th cycle, respectively. This value of SFO@C-400 after 100 values is about two times more than the theoretical capacity of graphite and very close to theoretical value of SnO₂ (781 mAhg⁻¹). In comparison with the 20th cycles (one randomly chosen steady cycle), a reversible capacity retention of up to 97% can still be estimated for the 100 consecutive cycles, clearly unveiling that practically no capacity degradation occurs upon cycling and our designed electrode structure can well tackle the stress-induced huge volume expansion upon (de-)lithiation and inhibit the aggregation over cycling Li⁺ insertion/extraction processes. This kind of electrochemical behavior, namely the charge/discharge capacity identical with the theoretical value, has also been reported in the literature, the reason for which can result from the unvaried SEI layer thickness on the electrode surfaces over cycling. To emphasize the robust nature of our designed structure of binary metal-in-carbon compact monolith, the long-term cyclic performance of SFO@C-350, SFO@C-400, SFO@C-450, and SFO electrodes was further assessed at a large current density of 1 A g^{-1} for 200 cycles, in which the hybrids will be subjected to the fiercer Li⁺ insertion and extraction events. It is worth mentioning that the first cycle was carried out at 0.2 A g^{-1} to complete the formation of SEI film. Again, a good cycling performance without the obvious capacity decay is monitored on the SFO@C-400, giving a highest discharge capacity of 466 mAh/g (about 73% retention since the second capacity) after 200 cycles, which is still much higher than theoretical specific capacity of commercial graphite anodes. This further confirms the advance of our designed architecture in terms of the applications to LIBs. Strikingly, for SFO@C-400, all coulombic efficiencies at different current densities during cycling are well sustained almost above 98%, which is the symbol of a stable SEI films and a good (de-)lithiation [65]. In contrast, the quick specific capacity decays during the overall cycling at the different current densities for SFO must be due to huge volume changes of SnO₂ in the charge/discharge processes, which causes it to not be in close contact with each other, leading to the much increased resistance, difficult electron transfer, and electrochemical reactions. All in all, the improved electrochemical performance can be ascribed to advantages of nanomaterials and intercalation structure.

To further grasp the origins of difference in cyclic stability between the SFO@C-400 and SFO electrodes, their differential charge capacity (dQ/dV) plots (DCCs) for the different cycles at a current density of 0.2 A/g are evaluated to characterize the de-lithiations of the SnO_2 material implicating dealloying and de-conversion reactions in diverse potential ranges. Thus, its charge capacity is reasonably divided into two portions on the basis of two potential ranges, that is, 0.005–1.0 V and 1.0–3 V. In the first cycle, the foregoing plots of both electrodes (Figure 5a,b) have the distinguished sharp peaks at 0.5 V and several wide bands nearby 1.25, 2.0, and 2.8 V, with ones below 1V belonging to the Li_xSn dealloying into Sn and the rest above 1V referring to the de-conversion reactions of Sn to SnO₂, as analyzed in CV curves. The great integral intensity of the peaks in 1–3 V unveils the elevated electroactivity of the reversed conversion of Sn into SnO_2 in the initial cycles. It elaborates that most of Sn have reacted with Li to generate Li_xSn phases. Although the DCC peaks of SFO@C-400 (Figure 5a) in the range of 1.0–2.5 V, become weakened to some extent after 50 cycles, they are still clearly visible with substantial intensities, suggesting that the majority of Sn metals can reversibly react with Li₂O to form the SnO₂ nanocrystals during the long-term cycling. Besides, the DCC peaks at about 0.5 keep strong and split into two ones and progressively move toward larger potentials, meaning the growing polarization for the Li_xSn dealloying. These may mainly result from reconstruction of Sn and Li_xSn crystals within the lithiated SnO₂ layer, because Sn coarsening and Li_xSn agglomeration can dwindle the reaction dynamics during (de-)lithiation. By sharp contrast, as the cycle number increases, all DCC peaks of SFO ascribed to the de-conversion reactions quickly decay and utterly vanish in the 10th cycle, indicating that the electroactivity of the de-conversion reaction drops fiercely; meanwhile the DCC peaks indexed to the dealloying reactions experience an appreciable attenuation in the fiftieth cycle (Figure 5b), further interpreting the poor cyclability. Considering that the dealloying reaction of Li_x Sn to Sn occurs in the range of 0.005-1.0 V and the reversion of Sn to SnO₂ takes place at between 1.0 and 2.5 V, the segmentalized charge capacities (Figure 5c,d) in the regions of 0.005–1.0 V and 1.0–2.5 V in

each cycle are further calculated based upon the charge curves to quantify the individual contribution and evolution of dealloying and de-conversion reactions between Sn and Li phases. In the case of SFO (Figure 5c), the segmentalized reversible capacity delivered at potential ranges of 0.005–1.0 V and 1.0–2.5 V is only 3.119 and 32 mAh/g with capacity retention of 0.6% and 11% after 100 consecutive cycles, respectively, indicating a drastic and complete degradation of the reversible capacity. What is worse, the segmentalized reversible capacity in the range of 1.0–2.5 V slumps by 40% in the second cycle. This evolution hints that the generation of the Li_xSn and SnO₂ components has been seriously impeded by the increased impedance, which may ensue from the SEI thickening or formation of the isolated/separated granules. Apparently, both the structural stability of electrode and reversibility of conversion reaction for the SFO electrode are very unsatisfactory. Conversely, the segmentalized reversible capacity in the range of 1.0–2.5 V on the SFO@C-400 does not suffer from a dramatical decrement upon cycling. In spite of a gradual fading of the segmentalized reversible capacity during the subsequent cycles, a segmentalized reversible capacity up to 358 mAh/g in the potential range of 1.0–2.5 V is still preserved after 100 cycles (about 76% retention of the first cycle segmentalized charge capacity), which sets forth the persistent reversibility of de-conversion reactions during cycling. Besides, an exceedingly stable segmentalized charge capacity in the range of 0.005–1.0 V of 310 mAh/g (which is about 95.6% of the initial segmentalized charge capacity at 0.005–1.0 V) can be well maintained, even over 100 cycles. The variations in the segmentalized charge capacity at these two potential regions reveal that the capacity deterioration of the SFO@C-400 electrode takes place primarily in the potential range of 1–3 V because of the reversible decay of de-conversion of Li₂O/Sn to SnO₂. These can pertain to the stepwise coarsening of the Sn particles amidst the Li₂O matrix. The Sn nanoparticle coarsening can notably decline proportions of the Sn-Li₂O interphases, abating the interphase diffusion between Sn and LiO_2 and eventually a segmentalized reversible capacity produced from the re-conversion reactions (1–3 V vs. Li/Li⁺). This slight decay of SFO@C-400 in contrast to SFO demonstrates that the Sn coarsening is inhibited to great extent by the metal-in-carbon structure. Nevertheless, as to (de-)alloying events, the electroactive Li_xSn/Sn districts get well encircled by the Li₂O matrix. While the particle size of Sn nanocrystals may grow from several nanometers up to several ten nanometers, such Li₂O phases in combination with the carbon matrix function as the cushion substrate for the volume fluctuation of Li_xSn/Sn, imparting the superior structural stability and integrity of the electroactive substances in the potential region of 0.005–1 V vs. Li/Li⁺. Besides, the better transfer kinetics of the Li⁺ ions into Sn in the course of de-alloying could likewise contribute to the more excellent capacity retention in the de-alloying segment. In nature, as for SFO, the rapidly decaying segmentalized capacity unearths that a big deal of electric energy undergoes an irreversible dissipation within electrodes in the course of (de-)conversion events. The substantial rise of the surface/interphase boundaries and structural stresses experienced within SnO_2 in the course of the lithium insertion and extraction reactions can elucidate the huge electricity depletion [66,67]. The change in the surface areas caused by both the new component (Sn and Li₂O) generation and the occurrence of micro-/nano-fractures triggers off the great surface and interface energy at the cost of electricity conserved through the conversion actions. Such phenomena bring about the poor energy efficacy of the SFO specimen cycled in 0.005–3 V and 1–3 V. The very elevated Gibbs free energy status of the nanotextured Sn/L₂O hybrids renders them unsteady, thereby leading Sn to synchronically coarsen and diffuse onto the surfaces of the Li₂O substrate or the carbon matrix within the lithiated electrode to maximally lower the surface and interface energy [35,68]. The well-acknowledged battery degradation mechanism has evidenced that the giant structural stress intensification on the electrode surface underlies the drastic volume change during the dealloying–alloying process, finally sparking off a serious pulverization and crushing of SnO_2 electrodes and so the notorious capacity fading. The extremely stable segmentalized charge capacity at 0.005–1.0 V for SFO@C-400 unambiguously pinpoints the effective stress management and superb structural stability, as further affirmed by SEM image of the SFO@C-400 electrode before and after 100 cycles (Figure 5e,f). It can be spotted that a continuous layer of the SEI film tightly covers the electrode surfaces and no palpable cracking transpires to SEI films after 100 cycles, unveiling a

stable SEI layer and no disintegration/exfoliation of the electrode materials during cycling. More significantly, the whole electrode remains intact after repeated volume changes, further certifying the eminent morphological robustness of the SFO@C-400 electrode and explaining reasons for its good cyclic function.



Figure 6. (a) Electrochemical impedance spectra of the SFO@C electrodes and SFO electrode after the first cycle in a fully charged state; (b) the equivalent circuit and (c) the corresponding fitted results of the resistance of SEI layer (R_{SEI}) and the charge transfer impedance (R_{ct}) of SFO@C electrodes and SFO electrode; (d) Warburg impedance spectra.

The disparity in the kinetics of electrochemical reactions between the SFO@C electrodes and SFO electrode after the first cycle is further revealed via performing electrochemical impedance spectra (EIS) measurement (Figure 6). The spectra of all samples are made up of the arc in the high-frequency regions, the semicircle at high-medium frequencies, and the linear line at lower frequencies, which correspond to resistance of SEI layer (R_{SEI}), charge transfer resistance (R_{ct}) on the electrode–electrolyte interphase and the Warburg impedance related to the Li⁺ diffusion process, respectively [69,70]. The depressed half-loop at high frequency of SFO@C (particularly SFO@C-400) is substantially smaller than that of SFO, substantiating the enhanced electronic conductivity and rate capability. Markedly, EIS curves of SFO features two obvious semicircles, highlighting the gradual SEI layer generation on the electrode surfaces at the elevated frequency regions. Although the SEI layer formation can terminate the further electrolyte decomposition, provide the expedient passages for the Li⁺ migration, and hence favor the rating behavior, its giant accumulation and progressive thickening will militate against the initial coulombic efficiency and lengthen the Li⁺ transfer distance [71]. The R_{SEI} value can likewise be diminished via a carbon coating because of circumvention of the direct contact between SnO₂ and electrolyte, thereby oppressing the occurrence of side reactions around interface boundaries. Two depressed semicircles on a series of SFO@C electrodes tend to merge into one at high-medium frequency particularly for SFO@C-400, showing the fast assembly of the thin and stable SEI layers, further indicating that the metal-in-carbon monolith structure cannot only mitigate the

volume effect but also improve the electron conductivity and Li⁺ diffusion. The EIS plots are well fitted, using the equivalent circuit as shown in Figure 6b, and the corresponding fitted results are provided in Figure 6c, which includes resistance of SEI layer (R_{SEI}) and charge transfer impedance (R_{ct}) . For the equivalent electrical circuit, R_e means the electrolyte impedance derived from the intercept of high-frequency half-loop on the Z' axis, CPE1 is the constant phase element (CPE) in the high-frequency regions, and CPE2 represents the related double layer capacitors corresponding to the semicircle in the medium-frequency regions [55,72]. In the case of R_e , all four electrodes do not present appreciable discrepancy, showing that the corresponding cells get suitably constructed and measured under the identical circumstances. Apparently, the R_{SEI} and R_{ct} of the SFO@C-400 electrode are 4.37 and 11.27 Ω , respectively, which are slightly lower than those of the SFO@C-350 and SFO@C-450 electrodes, manifesting the superiority of SFO@C-400 in augmenting the activation and dynamics of electrochemical events. This could be due to a stable formation of the thin SEI layers, likewise in good line with the irreversible capacity decay in the initial several cycles. The SEI film as a Li⁺ reservoir is able to achieve a supererogatory Li⁺ storage over surfaces of SFO@C, which telescopes the Li⁺ migration pathways. In reality, such "stored or trapped" Li⁺ in SEI layer is highly itinerant relative to their counterparts in the electrolyte and electrode interiors, bringing about the expedited surface charge transfer [73]. The unvaried SEI film can likewise be envisaged to be a Li⁺ swapping and electron transport film, guaranteeing the boosted coulombic efficiency and outstanding rate capability [65]. However, the R_{SEI} and R_{ct} of the SFO electrode are 71.63 and 229.7 Ω , respectively, which are almost 20 times larger than those of SFO@C-400 electrode. The significant differences in values of R_{SEI} and R_{ct} between SFO@C electrodes and SFO electrode can be attributed to the following two reasons: (i) The carbon matrix in the SFO@C electrodes effectively enhances the conductivity of electrodes; and (ii) the Li₂O generated during the discharge process, which has been proven to be not only electrochemically inactive, but also a bad electric conductor [74], has been completely converted back to Li by the reversible conversion reactions in the SFO@C electrodes. Furthermore, the Warburg impedance spectra of the electrodes (Figure 6d) demonstrate that the slope of linear plots for SFO@C electrodes is very close. However, the slope of linear plot for the SFO electrode is 232.8, considerably larger than that (122.7) of the SFO@C-400 electrode, clearly disclosing a faster Li⁺ ion diffusion in the latter electrode than the former electrodes. The outcomes of impedances can extraordinarily coincide with the cycling performance, which evidences that the intact structure ensures the electronic channels in electrodes for fast kinetics of electrochemical reactions, thereby contributing to the highly reversible conversion reactions and accounting for the good rate capability.

4. Discussion

In general, the electrochemical performance of our optimal SFO@C composite outperforms both carbon-free SFO counterpart and multifarious SnO₂-based anode substances recorded in the literature so far, signifying the preponderant structural design and multicomponent synergy in ameliorating the energy storage. The distinguished Li⁺ storage properties supra between a series of SFO@C and SFO composites can be associated with its distinct nanoscale complex configurations, as demonstrated by a unique scheme in Figure 7. Firstly, the ultrasmall-sized sub-10 nm SnO₂/Fe₂O₃-based nanoclusters furnish a myriad of electroactive centers for Li to access without incurring any serious degeneration of electrodes due to the nanoscale size effects, namely the low structural strains/stresses in the course of (de-)lithiation events and substantially dwindled solid-state migration/transport distance for Li⁺. At the same time, such nanometer granules firmly implanted in the carbon substrates do conduce to thwarting the Sn' locomotion/interdiffusion and accordingly frustrating their coarsening into bulk Sn crystals in the process of (de-)alloying reactions, if any, they still get "trapped or sequestrated" within continuous protecting carbon matrix and keep the active materials in close contact with carbon matrix during cycling, thus preserving its outstanding electrical contact/connection to facilitate the charge transfer to active materials. Secondly, the robust and conducting carbon skeleton not only guarantees the rapid/efficient electron mobility, but also contributes to sustaining the mechanical integrity of the

hybrid electrode throughout a long-term cyclic ion insertion/extraction. Besides, the compact nature of the hybrids can prevent the morphological issues of highly hierarchical porous architectures and provide a continuous pathway for Li⁺/e⁻ transfer across the whole electrode and, more significantly, is able to powerfully buffer the volume change of the SnO₂-based nanocrystals to restrict the electrode fractures. Thirdly, both decomposition of Li₂O triggered by Fe reduced from Fe₂O₃ and enhancement of electric conductivity and Li⁺ ions diffusion synergistically cause the conversion reaction of SnO₂ to occur and maintain the high reversibility during the repeated cycling. Fourthly, the carbon coating or encapsulation around the SnO₂ or Fe₂O₃ nanoparticles can also avert the direct touch between electrolyte and active materials, which greatly benefits the production of stable and thin SEI films over cycling. Lastly, the in situ generated SnO_2/Fe_2O_3 heterostructures offer the additional charge transfer driving force as a result of the built-in internal electric (potential) field, and stabilize the intercalation compact structure over cycling due to the collaborative interaction within this binary system [32,41–48]. In short, due to the striking integration of the elastic carbon matrix, metal-in-carbon construction, and multicomponent effect, the inevitable stress-induced volume variation is robustly accommodated, accompanied by the much-facilitated reaction kinetics. As a consequence, a good electrochemical performance with the improved rate capacity, initial coulombic efficiency, and long-term cyclic lifetime is achieved, which can significantly vie against the counterparts of most of cutting-edge SnO₂ anode materials hitherto chronicled in the literature and even some other transition metal-oxide-based materials, such as the MnO₂, TiO₂, Fe₂O₃/TiO₂, TiO₂/SnO₂, ZnCo₂O₄/ZnO, MnSnO₃, TiO₂/C@Fe₃O₄, NiCo₂S₄, Na₂SnO₃, Sn₄P₃/SnO₂@C, and Cu₆Sn₅ @SnO₂@carbon, as comprehensively compiled and compared in Table 1. Although our results are not the best in comparison with the elaborated composite nanostructures with high hierarchy and porosity (derived via the sophisticated synthesis nanotechnology), Table 1 clearly evidences that our optimal anode can still escalate into the impressive echelon of the same type of materials. In particular, given the overarching superiorities in terms of synthetic tractability, inexpensiveness, sustainability, high tap density, large mass loading, and non-porous nature, the as-prepared SnO₂/Fe₂O₃ oxide nanoparticles-intercalated carbon compact monolith holds the promising pragmatic prospect for the lithium ion batteries.



Figure 7. Schematic diagram of SFO@C as anode materials during cycling.

Table 1. The thorough recapitulative comparison of electrochemical performance of the optimal SFO@C with some cutting-edge SnO_2 -based materials and other metal-based anodes recorded till date. The loading of coating mostly varied from 1 to 2 mg/cm².

Electrode Materials	Current Density (Ag ⁻¹)	Initial Coulombic Efficiency	Retained Capacity (mAh g ⁻¹)	Cycle Numbers	Refs.
B-SFO@C-400	0.2	67.3%	726	100	This work
Carbon-encapsulated Porous SnO ₂	1 0.05	41.6%	466 870.9	200 120	[75]
SnO ₂ @CNT	0.2	62.5%	546	100	[76]
- *CO/Eq. Q. / SpQ	1	62%	398	150	[77]
$(30)/Fe_2O_3/(30O_2)$	0.4	03 /0	700	100	[//]
nanorods/RGO	0.2	46%	795	220	[78]
SnO ₂ .Fe ₂ O ₃ /SWCNTs	0.2	64.9%	692	50	[79]
Sandwich-like C@SnO2/Sn/void@C hollow spheres	0.5	65.9%	786.7	60	[26]
SnO ₂ /Fe ₂ O ₃ hybrid nanofibers	0.4	Non	672	100	[80]
Carbon shelled porous $\text{SnO}_{2\text{-}\delta}$ nanosheet array	1	74.3% (at 0.1 Ag ⁻¹)	543	1000	[81]
Nanoflaky MnO ₂ /carbon nanotube nanocomposites	0.2	57%	620	50	[82]
Hierarchical TiO ₂ nanowire@α-Fe ₂ O ₃ nanothorn core–branch arrays	0.1	Non	709	50	[83]
Hierarchically branched TiO2@SnO2 nanofibers	0.5	Non	453.3	100	[84]
Mesoporous ZnCo ₂ O ₄ -ZnO hybrid nanotube arrays	0.2	82.8%	1064	100	[85]
TiO2@Fe2O3 core-shell nanotube arrays with double-wall coating	0.1	Non	450	600	[86]
Hollow amorphous MnSnO3 nanohybrid with N-doped graphene	0.2	54.8%	707	110	[87]
TiO2@C@Fe3O4 core-shell branch hybrid nanoarrays	0.5	Non	433	200	[88]
Highly porous Mn ₃ O ₄ micro/nanocuboids@C	0.5	58.4%	1014	500	[89]
Nanowire interwoven NiCo2S4 nanowall arrays	0.2	56%	713	100	[90]
Fe ₃ O ₄ /carbon core-shell nanotubes	0.5	73%	560	100	[91]
SnO ₂ nanocrystals in amorphous carbon	0.62	43.5%	400	100	[92]
Boron doped graphene SnO2	0.2	49.2%	558	75	[56]
boton doped graphene onog	0.1	17.270	744	100	[00]
SnO ₂ quantum dots@3D S-doped RGO	0.5	Non	606	500	[93]
Na_2SnO_3	0.2	Non	480	100	[94]
SnO_2 quantum dots on reduced graphene	0.5	INON	635.9	100	[95]
Hierarchical hano-branched c-Si/ShO ₂ hanowires	0.36	50%	1200	100	[96]
embedded in carbon film with honey-like structure	0.1	45.7%	928.9	100	[97]
Dual carbon shells coated SnO_2 hollow nanospheres	0.2	58%	712.6	300	[98]
Porous hollow SnO ₂ -graphene aerogel hybrid	0.05	65.84%	620	200	[25]
Cu ₆ Sn ₅ intermetal@SnO ₂ -carbon core-shell	0.2	Non	619	500	[99]
Branched α-Fe ₂ O ₃ /SnO ₂ nano-heterostructures	1	Non	230	30	[41]
Sn@SnO _x /C nanocomposites	0.25	57.1%	500	70	[100]
Mesoporous Sn ₄ P ₃ /SnO ₂ @C nanosphere	0.4	77%	733	200	[101]
Double-shell micro-cube assembled by nanosized Co ₃ Sn ₂ /SnO ₂					
heterostructures with amorphous carbon layers wrapped in 3D graphene	0.1	69.6%	605	300	[102]
Centrifugally spun α -Fe ₂ O ₃ /TiO ₂ /carbon composite fibers	0.1	Non	340	100	[103]
Nanometric sulfur TiO ₂ core-shell powder	0.1C	Non	450	100	[104]
Intermetallic Ni-Sn-based composite	0.1	68%	615	100	[105]
Pomegranate-like porous carbon coated Cu _x Sn _y /Sn/SnO ₂ submicrospheres	0.1	Non	605	150	[106]
SnO ₂ /Sn hybrid hollow spheres	0.1	82.3%	401	50	[107]
1D SnO ₂ nanorod array	0.1	58.8%	580	100	[108]
8 nm SnO ₂ coated on Ni	0.5	Non	500	100	[100]
nanofoam	0.5	INOIT	300	100	[109]
1D V ₂ O ₅ @SnO ₂ core-shell nanowire array	0.2	Non	140	100	[110]
Branched α -Fe ₂ O ₃ /SnO ₂ nano-heterostructures	1	69.4%	230	90	[41]
SnO ₂ @C/MWCNTs/LiF	0.1	64.7%	483	100	[111]
Multilayered hollow TiO ₂ @SnO ₂ @C sphere	0.2	69.4%	484	300	[112]
Ultrathin SnU ₂ on carbon nanotubes	0.1	Non	516	100	[113]
SnO_2 flower-like structures	0.1	65%	457	50	[114]
Hierarchical york-shell L_{14} $L_{15}O_{12}$ -ShO ₂ composite	1	INON	253.2	200	[115]
WU3-5nU2 nollow nanospheres	1	INON	351	500	[116]
Hierorchical SpC /SpC papacehore	0.1	1NON 74 749/	334 599 15	50 50	[11/]
ruerarciucai 5052/5002 nanospheres	0.1	/4./470	500.15	50	[110]

5. Conclusions

In summary, a high-performance LIB anode comprising the sub-10 nm SnO_2 and Fe_2O_3 oxide nanocrystals intercalated inside a compact carbon monolith is successfully excogitated through an expeditious gel pyrolysis protocol to integrate the advanced nature of the embedding structure and multicomponent synergy. As a result of spatial confinement effect for effectively relaxing mechanical stress originating from the volume expansion of the SnO_2 nanoparticles, the improved electronic conductivity by the continuous carbon matrix and the enhanced Li^+/e^- transfer by the driving of the built-in electric field generated at around heterointerfaces between SnO_2 and Fe_2O_3 , the SnO_2 grain

coarsening/aggregation is endured to ensure mechanical integrity, and reversibility of conversion reactions between SnO_2 and Li_xSn is boosted to induce a fast kinetics during Li^+ uptake/release. Thus, the optimal hybrid affords good Li^+ ion storage properties in terms of the elevated reversible capacity of 726 mAh/g at 0.2 A g⁻¹, good rate capability of 40% from 0.2 to 3.2 A g⁻¹, stable capacity retention of 84% after 100 cycles at 0.2 A g⁻¹, stable cycle life of 466 mAh g⁻¹ over 200 cycles at 1 A g⁻¹ (without no discernable capacity decay), and high initial coulombic efficiency of 67.3%. This bulk-like structure composed of the carbon-protected nanocrystals describes a fresh approach to assemble efficient anode materials with the anti-pulverization properties and quickened reaction kinetics. Our recipe to prepare the SnO_2 /carbon composites is scalable and compatible with the industrial manufacturing standards, which prospectively enables a massive generation toward the pragmatic deployments, not only in LIBs but also other nascent energy areas. Significantly, the techniques may be universally adaptive to many other alloy/conversion-type anode materials (like Sb and Ge) for the next generation high-performance rechargeable batteries, which likewise undergo a giant-volume-variation-triggered capacity decay during discharging/charging.

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