Li₂CO₃ induced stable SEI formation: An efficient strategy to boost reversibility and cyclability of Li storage in SnO₂ anodes

Gang Wen, Liang Tan, Xuexia Lan, Hanyin Zhang, Renzong Hu^{*}, Bin Yuan, Jun Liu and Min Zhu^{*}

ABSTRACT The unstable interfaces between a SnO₂ anode and an electrolyte in a Li-ion battery dramatically impair the reversibility and cycling stability of lithiation and delithiation, resulting in low roundtrip Coulombic efficiency (CE) and fast capacity decay of SnO₂-based anode materials. Herein, a simple strategy of modifying the solid electrolyte interphase (SEI) is developed to enhance the interfacial stability and lithium storage reversibility of SnO₂ by compositing it with graphite (G) and an inorganic component of the SEI, such as Li₂CO₃ or LiF, which results in the SnO₂-Li₂CO₃/G and SnO₂-LiF/G composite anodes with high CEs, large capacities and long cycle lives. Specifically, the SnO₂-Li₂CO₃/G composite anode exhibits an average initial CE of 79.6%, a stable reversible capacity of 927.5 mA h g⁻¹ at a current rate of 0.2 A g⁻¹, and a charge capacity over 1200 mA h g⁻¹ with a CE >99% after 900 cycles at a higher current rate of 1 A g⁻¹. It is revealed that Li₂CO₃ induces the formation of a dense and stable SEI on SnO₂ grains and inhibits the coarsening of nanosized Sn particles generated from the dealloying reaction in the SnO₂-Li₂CO₃/G electrode. Moreover, the CE and cycling stability of other alloying-type (Si) and conversion reaction (MnO₂ and Fe₃O₄) anodes can also be greatly promoted by simply milling with Li₂CO₃. Thus, a universal and simple strategy is developed to achieve highly reversible and stable electrodes for large-capacity lithium storage.

Keywords: tin oxide, lithium carbonate, solid electrolyte interphase, lithium-ion battery, Coulombic efficiency

INTRODUCTION

Continuous efforts in promoting the cycle life, safety, energy and power density of lithium-ion batteries are essential in meeting the increasing demand for their applications in portable electric devices, electric vehicles and

energy storage stations [1,2]. There is currently a significant focus on replacing commercially used graphite (G) anodes because of their low theoretical specific capacity of only 372 mA g⁻¹ and safety concerns arising from facile Li dendrite growth, in particular, under fast charging or charging at low temperatures, due to the low lithiation potential of G at ~0.1 V vs. Li/Li⁺ [3–5].

Among the many candidate anode materials, tin dioxide (SnO₂) has attracted significant attention due to its abundance, environmental benignity and high theoretical capacity of 1494 mA g⁻¹ [6–8]. The lithium storage capacity of SnO₂ is based on a conversion reaction (SnO₂ + 4Li⁺ + 4e⁻ ↔ Sn + 2Li₂O), contributing a capacity of 711 mA h g⁻¹ at ~1 V vs. Li/Li⁺, and an alloying reaction (Sn + xLi⁺ + xe⁻ ↔ Li_xSn, 0 ≤ x ≤ 4.4), contributing a capacity of 783 mA h g⁻¹ at ~0.5 V vs. Li/Li⁺ [9,10]. However, three major obstacles hamper the commercialization of SnO₂-based anode materials. First, the huge volume change during lithiation/delithiation induces severe internal stress and splitting between the active material and the current collectors [11,12]. Second, aggregation and coarsening of nanosized Sn grains occurring in the dealloying reaction leads to partial inactivation of Sn and Li₂O and poor reversibility of the deconversion reaction and rapid capacity decay as a result [13–15]. Third, continual formation of a very thick and unstable solid electrolyte interface (SEI) during the initial cycles due to the large volume change of the electrode decreases the initial Coulombic efficiency (ICE) [16–19].

Research efforts have been devoted to solving those problems [20,21]. Compositing with carbonaceous materials can significantly improve the cycling stability of SnO₂. However, these SnO₂-carbon nanocomposites still suffer from a low ICE of <60% in general [22,23]. Fur-

School of Materials Science and Engineering, Guangdong Provincial Key Laboratory of Advanced Energy Storage Materials, South China University of Technology, Guangzhou 510640, China

^{*} Corresponding authors (emails: msrenzonghu@scut.edu.cn (Hu R); memzhu@scut.edu.cn (Zhu M))

thermore, the capacity is limited to the contribution from the alloying reaction in the potential range of 1–2 V while the contribution from the conversion reaction ($\text{Sn} + \text{Li}_2\text{O} \rightarrow \text{SnO}_2$) gradually degrades with Sn coarsening during cycling [24]. Indeed, the coarsening of Sn has a significant impact on the reversible capacity, CE, energy efficiency and Li-ion diffusion kinetics of SnO_2 electrodes [25].

Recently, we demonstrated that adding transition metals (TMs) such as Mn, Fe and Co, to SnO_2 can efficiently inhibit Sn coarsening to thus maintain the abundant interfaces and high reactivity between Sn and Li_2O during the lithiation of SnO_2 . This strategy can be used to achieve a high ICE of ~76% and a long lifetime with a stable reversible capacity of 700 mA h g^{-1} at a current rate of 2 A g^{-1} after 1000 cycles in a ternary SnO_2 -Mn-G composite [26]. However, owing to the addition of 20 wt% of the inactive TM component, the available capacity is only half of the theoretical capacity of SnO_2 . Furthermore, the TM nanoparticles tend to continuously catalyze the decomposition of electrolyte and SEI, resulting in unstable electrode/electrolyte interfaces and thus decreased CEs with cycling [27–29], which constantly consume electrolyte at the anode/electrolyte interface and eventually seriously shorten the cycle life of cells [30].

Based on the above considerations, it is necessary to explore novel strategies to effectively prevent Sn coarsening and stabilize the interfaces between SnO_2 and the electrolyte during long-term discharge and charge cycling whilst fully utilizing the high capacity of SnO_2 . Considering the strong interaction between alloy anodes and electrolytes, constructing a high-quality SEI, which is uniform and adheres well to the active materials in the anode, should be an effective strategy for maintaining high performance. Generally, the SEI formed on anodes within organic electrolytes is constructed by a more compact inner inorganic (e.g., Li_2O , LiF or Li_2CO_3) layer, an intermixed layer and an porous and less compact outer organic (e.g., LiOCH_3) layer [31]. The electrochemical and mechanical stability of the SEI along with cycling depends closely on the quality of the inner inorganic layer. Therefore, a facile strategy to form a high-quality inorganic layer and SEI film on the surface of active SnO_2 should be explored, by which the SEI is controllably induced and formed with the assistance of additives in the electrode or the electrolyte.

Herein, we report the combination of a small amount of Li_2CO_3 with nanoscale SnO_2 by simple ball milling, which can achieve significant enhancements in lithium storage performance. SnO_2 - Li_2CO_3 /G and SnO_2 -LiF/G

composites, with 5 wt% of Li_2CO_3 or LiF , respectively, exhibit high average ICEs of 79.6% and 78.9%, respectively, far superior to that (~67%) of SnO_2 and SnO_2 -G anodes. Furthermore, an extremely high capacity over 1200 mA h g^{-1} after 900 cycles at a current rate of 1 A g^{-1} , with a CE of >99%, is delivered in SnO_2 - Li_2CO_3 /G, superior to those of the previous designed ternary SnO_2 -Mn-G composite anode [29]. It is revealed that the pre-addition of Li_2CO_3 can induce the formation of a dense and stable SEI on the surface of SnO_2 grains during the initial lithiation process and inhibit the coarsening of Sn particles generated after the conversion reaction and dealloying of Li_xSn . It is also found that the ICE and cycling stability of other electrode materials, both alloying-type (Si) and conversion (MnO_2 and Fe_3O_4) anodes, can be promoted by simply milling with Li_2CO_3 , demonstrating that the strategy of constructing a surface SEI is universal in enhancing the structural integrity and interfacial stability of electrodes.

EXPERIMENTAL SECTION

Material preparation

The initial SnO_2 (1–3 μm , 99.9% purity) and Li_2CO_3 powders (2–5 μm , 99.9% purity) were purchased from Aladdin Industrial Inc., China. The G powder (~30 μm , 99.9% purity) was purchased from Shanghai Colloid Chemical Plant, China. A two-step ball-milling process was carried out to synthesize the SnO_2 - Li_2CO_3 /G composite using a planetary mill (QM-3SP4, China). First, a SnO_2 - Li_2CO_3 mixture with a mass ratio of 70:5 was milled for 20 h. The as-prepared SnO_2 - Li_2CO_3 precursor and natural G powder (~30 μm , 99.9% purity) with a mass ratio of 3:1 were then further milled for 10 h. All milling processes were carried out under an argon atmosphere with a stainless steel ball-to-sample weight ratio of 25:1 and a rotary speed of 400 r min^{-1} . For comparison, SnO_2 , SnO_2 /G and SnO_2 - Li_2CO_3 were milled under the same parameters for 30 h. For the preparation of other anode materials, the synthesis processes are almost the same. Si, MnO_2 , Fe_3O_4 , LiF (Aladdin Industrial Inc., China) and commercial LiFePO_4 (LFP, Shenzhen Kejing Star Technology Co., Ltd.) were used as raw materials without further purification.

Material characterization

The phase information of the samples was characterized by X-ray diffraction (XRD, Panalytical Empyrean) employing Cu-K α radiation. The morphologies of the samples were analyzed by a field emission scanning electron

microscope (SEM, Carl Zeiss Supra 40) and a transmission electron microscope (TEM, JEOL TEM 2100) operating at 200 kV. The elemental mapping was performed with an energy dispersive spectrometer (EDS) assembled with TEM. The Raman spectra were measured by a laser Raman spectrometer (Raman, Horiba) with a 632.81-nm laser. The surface chemistry of the cycled electrodes was conducted on a Nicolet iS50 Fourier transform infrared (FTIR) spectrometer equipped with an attenuated total reflectance technique. X-ray photoelectron spectroscopy (XPS) was carried out with an AXIS Ultra DLD spectrometer. For the *ex-situ* analyses, the corresponding materials were discharged/charged to the set conditions and then the coin cells were disassembled inside an Ar filled glove box to obtain the electrode sheets, which were washed with dimethyl carbonate and then dried for measurements.

Electrochemical measurements

The anode active materials, conductive agent (super-P) and binder (carboxymethyl cellulose) were stirred with distilled water in a weight ratio of 8:1:1 to make the electrode slurry, which was then coated onto copper foils and dried at 80°C for 12 h in a vacuum drying oven to form the electrodes. For the full cells, commercial LFP was used for the cathode, with 80 wt% LFP, 10 wt% super-P and 10 wt% polyvinylidene difluoride blended with *N*-methyl-2-pyrrolidene and then coated onto an aluminum foil and dried at 60°C for 12 h in a vacuum drying oven. The prepared electrodes were assembled into CR2016 coin-type cells in a glove box filled with high-purity argon (O_2 and H_2O <0.01 ppm) for electrochemical performance measurements. The electrolyte was 1 mol L⁻¹ LiPF₆ dissolved in a mixture of ethylene carbonate (EC) and diethyl carbonate (1:2, v/v) with a 10% fluoroethylene carbonate additive. A Celgard 2400 porous polypropylene membrane was used as the separator. Galvanostatic charge-discharge tests were conducted at a constant temperature of 30°C at different current rates on a LAND battery test system. The capacities of full cells were normalized by the weight of the SnO₂-Li₂CO₃/G anodes.

RESULTS AND DISCUSSION

The SnO₂-Li₂CO₃ composite was first prepared by milling. As shown in Fig. S1a, the diffraction peaks corresponding to SnO₂ are obviously broadened in the as-milled sample, which means that the grain size of SnO₂ is greatly refined after milling. However, the diffraction peaks of Li₂CO₃ become indistinguishable in the SnO₂-

Li₂CO₃ sample, indicating that the Li₂CO₃ is amorphized during milling. This is further revealed by the Raman analysis shown in Fig. S1b, indicating that both the pristine Li₂CO₃ and milled SnO₂-Li₂CO₃ samples present similar peaks at ~1090 and ~1470 cm⁻¹.

Fig. 1a shows the typical SEM images of the milled SnO₂ (left) and SnO₂-Li₂CO₃ (right) powders. It can be seen that the particle size distribution of the milled SnO₂ is not uniform and is between 50 and 300 nm. After adding Li₂CO₃, the particles of the SnO₂-Li₂CO₃ sample are obviously further refined and more uniform after milling, which suggests that Li₂CO₃ also plays the role of a milling agent. Fig. 1b shows a typical TEM image for a particle of the SnO₂-Li₂CO₃ composite. The particle consists of multiscale SnO₂ crystals and amorphous Li₂CO₃, as confirmed by its corresponding selected area electron diffraction pattern (inset), which presents only the diffraction patterns of SnO₂. The EDS elemental mapping of C is displayed together with Sn and O elements in Fig. 1c, obviously showing the uniform distribution of SnO₂ and Li₂CO₃ in the SnO₂-Li₂CO₃ composite. The high-resolution TEM (HRTEM) image, given in Fig. 1d, shows the presence of minute amorphous zones, which should be Li₂CO₃, among the SnO₂ nanocrystals.

Fig. 2 compares the electrochemical performances of the SnO₂, SnO₂/G and SnO₂-Li₂CO₃ electrodes. As shown in Fig. 2a, the SnO₂-Li₂CO₃ electrode possesses the highest average ICE of 77.2%, which is much higher than those of the SnO₂ and SnO₂/G electrodes. Obviously, the addition of Li₂CO₃ is the major reason for promoting the ICE of SnO₂. Both G and Li₂CO₃ promote the cycling performance. As shown in Fig. 2b, at a current rate of 0.2 A g⁻¹ between 0.01 and 3 V, the cyclic stabilities of SnO₂/G and SnO₂-Li₂CO₃ are both improved compared with pure SnO₂. Fig. 2c shows the galvanostatic charge-discharge curves of the SnO₂, SnO₂/G and SnO₂-Li₂CO₃ electrodes for the 2nd and 50th cycles at 0.2 A g⁻¹. The large differences between the 2nd and 50th charge curves at >1 V indicate the poor reversibility of the electrochemical reactions of pure SnO₂. In contrast, for the SnO₂-Li₂CO₃ electrode, the highly consistent 2nd and 50th curves demonstrate the good reversibility for the lithiation/delithiation process during cycling. It is worth noting that the capacities of the SnO₂/G and SnO₂-Li₂CO₃ electrodes yielded within the potential range of 2–3 V could be related to the decomposition of SEI layers and the electrochemical reduction of Li₂CO₃ [30].

In addition, the corresponding differential capacity *versus* potential (DCP) plots of the SnO₂, SnO₂/G and

Figure 1 (a) Typical SEM images of the as-milled SnO_2 (left) and $\text{SnO}_2\text{-Li}_2\text{CO}_3$ (right) powders. (b) TEM image and selected area electron diffraction pattern (inset) of the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ composite. (c) High angle annular dark field-scanning TEM (HAADF-STEM) image and corresponding EDS elemental mapping of C, Sn and O, and (d) HRTEM image of the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ composite.

$\text{SnO}_2\text{-Li}_2\text{CO}_3$ electrodes for the 2nd and 50th cycles are shown in Fig. 2d. Three groups of delithiation peaks appeared at 0.01–0.25, 0.25–1.0 and 1.0–2.4 V, corresponding to the dealloying ($\text{LiC}_6 \rightarrow \text{C}$ and $\text{Li}_x\text{Sn} \rightarrow \text{Sn}$) and deconversion ($\text{Li}_2\text{O} + \text{Sn} \rightarrow \text{SnO}_x$) reactions, respectively. With increasing cycle number for the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ composite, the intensity of the reaction peaks remains stable, while it decreases rapidly after 50 cycles for pure SnO_2 .

For the SnO_2/G electrode, although the peak intensity of the conversion reaction remains stable, the peak intensity of the alloying reaction decreases from the 2nd to the 50th cycle, which may be caused by the agglomeration and coarsening of the Sn particles. This indicates that the addition of Li_2CO_3 can efficiently inhibit the coarsening of Sn particles and improve reversibility for the lithiation/delithiation reaction of SnO_2 . However, as shown in Fig. S2, benefiting from the good conductivity of G, the

SnO_2/G electrode shows good rate performance, while the rate performance of the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ electrode is even poorer than the pure SnO_2 electrode because of the electronic insulation of Li_2CO_3 . Thus, G was further milled with $\text{SnO}_2\text{-Li}_2\text{CO}_3$ to synthesize a $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite with the aim of achieving improved cycling and rate performance.

Fig. 3a shows the XRD pattern of the as-milled $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite. The diffraction peaks corresponding to SnO_2 are obviously broadened compared with the unmilled $\text{SnO}_2\text{-Li}_2\text{CO}_3\text{-G}$ mixture, indicating that the grain size is refined. Fig. 3b shows the Raman spectra of carbon in the unmilled mixed powders and the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite, with both presenting D and G bands of carbon at 1350 and 1575 cm^{-1} , respectively, which are related to the disordered and G structures of carbon, respectively. The ratio of the D band to G band (I_D/I_G) represents the disorder degree of carbon materials

Figure 2 (a) Average ICEs, (b) cycling performances and (c) the 2nd and 50th charge-discharge curves with corresponding (d) differential DCP plots of the SnO_2 , SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3$ electrodes.

[32]. On this basis, the I_D/I_G value of $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ (~ 0.7) is greater than that of the unmilled $\text{SnO}_2\text{-Li}_2\text{CO}_3\text{-G}$ (~ 0.3), suggesting that the mechanical peeling effect of ball milling introduces more disordered structures of carbon, such as few-layer G and other defects in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite.

Fig. 3c shows the secondary electron SEM image of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ powders. There are many G nanosheets of several micrometers in size, which should be peeled off from G by the strain effect of ball milling, with many $\text{SnO}_2\text{-Li}_2\text{CO}_3$ nanoparticles loaded on them. High-magnification SEM images along different views of the G layer, shown in Fig. 3d, clearly demonstrate that the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ particles with a size of $\sim 50 \text{ nm}$ were either loaded on the surface or inserted among the G sheets, revealing the good contact state between $\text{SnO}_2\text{-Li}_2\text{CO}_3$ particles and G in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite. It is expected that this unique structure not only accelerates the charge conduction among the active particles, but also inhibits the volume expansion of the active material during lithiation/delithiation, thus, improving the cycling stability effectively.

Fig. 3e shows a typical TEM image of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite, clearly showing that the nanosized $\text{SnO}_2\text{-Li}_2\text{CO}_3$ particles (dark zone) are embedded in the G

matrix (bright zone). Fig. 3f presents the HRTEM image of the marked area in Fig. 3e, in which SnO_2 particles, dotted amorphous Li_2CO_3 and G sheets are identified. These results clearly demonstrate the unique microstructure of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite, which consists of composite particles of nanosized SnO_2 and amorphous Li_2CO_3 loaded on the G sheets.

Fig. 4a shows the initial charge-discharge curves for six $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes. The completely overlapping curves of these six half cells demonstrate the high repeatability of their electrochemical performance, as well as high uniformity of the composition and microstructure for the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite. The inset in Fig. 4a shows that these six $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ half cells exhibit a very high average ICE of 79.6%, which is further increased compared with the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ composite (77.2%). Fig. 4b shows the cycling performances of three $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ cells tested at a current rate of 0.2 A g^{-1} between 0.01 and 3 V. All three cells exhibit good cycle ability with a reversible specific charge capacity of $\sim 900 \text{ mA h g}^{-1}$ and achieve a high capacity retention of $>99\%$ after 100 cycles. Obviously, the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite possesses a cycling performance superior to $\text{SnO}_2\text{-Li}_2\text{CO}_3$ and SnO_2/G , which further proves that both Li_2CO_3 and G play an important role in improving the

Figure 3 (a) XRD patterns of the as-milled $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite and unmilled $\text{SnO}_2\text{-Li}_2\text{CO}_3\text{-G}$ mixed powders. (b) Raman spectra of carbon in $\text{SnO}_2\text{-Li}_2\text{CO}_3\text{-G}$ -unmilled mixed powders and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composites. (c, d) SEM images for different areas of the as-milled $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite powder. (e) TEM and (f) HRTEM images of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite.

cycling performance.

Fig. S3 presents the galvanostatic charge-discharge curves of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode for several typical cycles at 0.2 A g^{-1} . The highly consistent curves for different cycles from the 1st to the 100th demonstrate the good reversibility for the lithiation/delithiation process of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode during cycling. In addition, the corresponding DCPs of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite for the selected cycles are shown in Fig. 4c and the intensities

of the reaction peaks remain stable with an increasing number of cycles, which further proves the good reversibility for both the conversion and alloying reactions in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode [23,24]. And in the 1st cycle, there are two peaks for the dealloying reactions within 0.2–1.0 V, which should be the existence of polarization due to the coarsening of Sn and the aggregation of Li_xSn phases in the initial cycle. However, in the subsequent cycle, Li_2CO_3 induced the formation of dense SEI on

Figure 4 (a) Summary of the initial charge-discharge curves for six $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anodes and average ICE of $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode (inset). (b) Discharge capacity versus cycle number of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes tested at a current rate of 0.2 A g^{-1} between 0.01 and 3 V . (c) DCPs of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode for selected cycles at 0.2 A g^{-1} . (d) CE of SnO_2 , SnO_2/G , $\text{SnO}_2\text{-Li}_2\text{CO}_3$ and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes. (e) Charge curves for selected cycles of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode. (f) Sectional reversible capacities at $0.01\text{--}1.0$, $1.0\text{--}2.4$ and $2.4\text{--}3.0\text{ V}$ of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode.

SnO_2 grains and inhibited the coarsening of nano-Sn and Li_xSn particles, and thus enhancing the reaction kinetics during delithiation.

Fig. 4d displays the roundtrip CEs of the SnO_2 , SnO_2/G , $\text{SnO}_2\text{-Li}_2\text{CO}_3$ and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes. As can be seen, the CE of the pure SnO_2 electrode is the lowest and decays rapidly with cycling. This suggests that the SEI on the surface of the pure SnO_2 electrode is unstable, while there is continuous growth and dissolution of the SEI with the cycling process. With respect to the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ composite, the CE increased significantly, indicating that Li_2CO_3 promotes the formation of a stable SEI and avoids

Li^+ consumption due to continuous SEI growth. In addition, the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode shows an even higher roundtrip CE due to its high structural integrity with the G support and thus a more stable electrode/electrolyte interface.

The potential range for the dealloying of Li_xSn and reverse conversion of Li_2O to SnO_x can be clearly identified for the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode from the DCPs and charge curves shown in Fig. 4c, e. The charge process of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite can be divided into several voltage ranges, i.e., $0.01\text{--}1.0$, $1.0\text{--}2.4$ and $2.4\text{--}3.0\text{ V}$. All three potential ranges exhibit minimal

change during cycling. Fig. 4f shows the sectional reversible capacity of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode, in which the capacity in each cycle is divided into three parts for $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ at 0.2 A g^{-1} according to the voltage ranges shown in Fig. 4e. Stable capacity concentrations of ~ 370 and $\sim 430\text{ mA h g}^{-1}$ are delivered in the potential ranges of $0.01\text{--}1.0$ and $1.0\text{--}2.4\text{ V}$, respectively. This suggests that all of the Sn formed during dealloying within $0.01\text{--}1.0\text{ V}$ can be transferred to SnO_2 between 1.0 and 2.4 V , demonstrating the highly reversible conversion reaction of SnO_2 in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode. For the potential range of $2.4\text{--}3.0\text{ V}$, a capacity of $\sim 75\text{ mA h g}^{-1}$,

supposedly from the side reaction of the electrolyte, remains stable throughout cycling, which is different from the fact that the capacity gradually increases in $\text{SnO}_2\text{-Mn-G}$ [29]. These factors consolidate the higher stability of the electrode/electrolyte interfaces in $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$, which should contribute to the superb structural stability of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite.

Fig. 5a presents the long-term cycling performance of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite anode, in which almost the same reversible capacities, 967.3 and 938.7 mA h g^{-1} , are obtained at 0.2 and 1 A g^{-1} , respectively, demonstrating its excellent rate performance. Furthermore, a reversible

Figure 5 (a) Long-term cycling performance of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite at 1 and 0.2 A g^{-1} . (b) Voltage versus specific capacity profiles of the 1st charge-discharge cycles for LFP|| $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ full cell with different capacity ratios and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode half cell. (c) Cycling performances of $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode half cells tested at $0.01\text{--}1.0$, $0.01\text{--}2.4$ and $0.01\text{--}3.0\text{ V}$ with corresponding CE versus cycle number. (d) Cycling performances and (e) selected charge-discharge curves of LFP|| $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ full cell tested between 2.5 and 3.45 V at 0.2 A g^{-1} .

specific charge capacity of over 1200 mA h g^{-1} after 900 cycles is delivered at 1 A g^{-1} , demonstrating superior long-term cycling stability. The slight drop of the specific capacity during the initial cycles could be related to the volume change of the composite and the slight decline of the reversibility of de-conversion reactions. During afterward cycles, the rise of capacity mainly yielded within the high potential zone of $2.0\text{--}3.0 \text{ V}$ vs. Li/Li^+ , which could be related to the decomposition of electrolyte and/or SEI layers, as well as the reversible electrochemical reduction of Li_2CO_3 . And high current rate could be more helpful for the decomposition of SEI and electrochemical reduction of Li_2CO_3 . And thus, the rise of capacity in electrode cycled at 1 A g^{-1} is more remarkable than that at 0.2 A g^{-1} [30]. Furthermore, the tested batteries exhibit a high ICE of $\sim 80\%$ and the round-trip CE increased to over 99% after 400 cycles. Both the ICE and CE of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite are higher than those previously reported for a ternary $\text{SnO}_2\text{-Mn-G}$ anode [29], suggesting more stable SEI formation on SnO_2 by the pre-addition of Li_2CO_3 . Moreover, to exclude the possibility that the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite may exhibit better performance in the half cell because of the limitless Li source provided by Li foil as the counter electrode, full cells were also investigated using an LFP commercial cathode to match with the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode. The cut-off charging voltage of the full cell is determined to be 3.45 V by comparing the initial charge-discharge curve of the LFP cathode and the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode (Fig. S4).

In order to fully release the capacity of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode, the cut-off discharging voltage of the full cell is set at 0.01 V . As shown in Fig. 5b, the LFP|| $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ full cells with different capacity ratios of 1.5:1 and 2:1 between the cathode and anode show high ICEs of 77.8% and 80.0% , respectively, close to that of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ half cell. The charge-discharge curves of the two full cells are highly consistent with that of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ half cell, indicating that the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite could perform with the same electrochemical performance in full and half cells.

In order to improve the output voltage of the full cells, the cut-off voltage of discharging needs to be adjusted. Fig. 5c shows the cycling performance of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode of half cells tested at $0.01\text{--}1.0$, $0.01\text{--}2.4$ and $0.01\text{--}3.0 \text{ V}$ together with the corresponding CE *versus* cycle number. The battery tested in the potential range of $0.01\text{--}1.0 \text{ V}$, i.e., with only the alloying/dealloying reaction of SnO_2 , exhibits the best cycling performance and highest roundtrip CE, suggesting a stable reversible lithiation/delithiation process and minimum lithium

source consumption in this voltage region. Thus, the cut-off voltage range of the LFP|| $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ full cell is adjusted to $2.5\text{--}3.45 \text{ V}$ to meet the anode potential range of $0.01\text{--}1.0 \text{ V}$ at a current rate of 0.2 A g^{-1} .

As shown in Fig. 5d, a very stable reversible discharge capacity of $\sim 400 \text{ mA h g}^{-1}$ with a capacity retention of 95.5% is obtained after 100 cycles, which is the same as for the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ anode half cell tested between 0.01 and 1.0 V . This excellent reversibility of the lithiation/delithiation process is further demonstrated by their overlapped charge-discharge curves in different cycles from the 2nd to the 100th, as shown in Fig. 5e. The high output voltage ($\sim 2.9 \text{ V}$) of this LFP|| $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ full cell is comparable to commercial LFP||G full-cell systems ($\sim 3.0 \text{ V}$). The above results demonstrate that this $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite is a promising alternative anode for practical applications in Li-ion batteries.

Considering that the added Li_2CO_3 can induce the formation of the SEI film, which is mainly formed during the 1st lithiation process of the electrode, the initial charge-discharge curves of the SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes are compared. As shown in Fig. 6a, the 1st charge-discharge processes of the two composites are basically consistent with each other, but the electrochemical reaction platform at $\sim 1.2 \text{ V}$ for the lithiated curve is slightly different, which can be attributed to the reaction for the SEI formation. It is also clear in the corresponding initial charge-discharge DCPs of the SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composites shown in Fig. 6b that a reduction peak appears for the lithiated curve at $\sim 1.2 \text{ V}$ for the SnO_2/G electrode. This corresponds to the decomposition reaction of alkyl carbonate solvents (ethylene carbonate, diethyl carbonate and fluoroethylene carbonate) in the electrolyte [33], while for the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode, no such reduction peak appears. This suggests that Li_2CO_3 can induce the formation of a homogeneous and dense SEI on the surface of the electrode, which effectively protects the active material, and thus inhibits the continuous decomposition of electrolyte components and reduces the total amount of SEI formed.

To further examine the components of the SEI, FTIR spectroscopy was carried out on the SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes at different states. Fig. 6c shows the FTIR spectra for the electrodes discharged to 0.60 and 0.01 V at the initial cycle. The absorption peaks of $\nu_{\text{as}}\text{C=O}$, δCH_2 , $\nu_{\text{s}}\text{C=O}$ and $\nu_{\text{s}}\text{C-O}$ demonstrate the presence of ROCO_2Li ($(\text{CH}_2\text{OCOOLi})_2$) [34], which is the main organic component of the SEI produced by EC solvent decomposition. The absorption peaks of νCO_3^{2-} and CO_3^{2-} on the sides reveal the existence of Li_2CO_3 ,

Figure 6 (a) Initial charge-discharge curves and (b) corresponding DCPs of SnO₂/G and SnO₂-Li₂CO₃/G composites. (c) FTIR spectra of the SnO₂/G and SnO₂-Li₂CO₃/G electrodes discharged to 0.60 and 0.01 V at the 1st cycle, respectively. (d) FTIR spectra of the SnO₂/G and SnO₂-Li₂CO₃/G electrodes discharged to 0.01 V at different cycles. (e) TEM image of the SnO₂-Li₂CO₃/G electrode discharged to 0.01 V. (f) Schematic illustration showing SEI formation and structural evolution of the SnO₂ and SnO₂-Li₂CO₃/G electrodes during the initial cycles.

which is one of the main inorganic components in the SEI [35]. When discharged from 0.60 to 0.01 V, the absorption peak intensity of the SnO₂/G electrode increases obviously, while that of the SnO₂-Li₂CO₃/G electrode remains basically stable. According to the Beer-Lambert law [36,37], this means that the SEI of the SnO₂/G elec-

trode is unstable after formation, meaning that it cannot adequately protect the electrode material and continues to grow.

In contrast, the SnO₂-Li₂CO₃/G electrode possesses a firm SEI, which can prevent direct contact between the active material and the electrolyte. The XPS survey of LiF

(Fig. S5), which is another main inorganic component of the SEI, also reveals that less electrolyte is decomposed in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode. Furthermore, Fig. 6d presents the FTIR spectra for the SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes discharged to 0.01 V at different cycles. It can be seen that the absorption spectra of the SnO_2/G electrode do not remain consistent until the 5th cycle. Moreover, the CE of the SnO_2/G electrode (Fig. 4d) during the first 10 cycles is less than 98%, and the CE gradually decreases along cycle. In contrast, the FTIR absorption spectra of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode are already stable from the 1st to the 3rd cycle, and the CEs of the $\text{SnO}_2\text{-Li}_2\text{CO}_3$ and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ fast increase to 99% after the initial cycle, suggesting that the SEI of the SnO_2/G electrode forms/dissolves repeatedly during cycling, while that of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode remains stable after formation.

TEM observations reveal that an amorphous layer forms on the surfaces of both the SnO_2/G and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrodes (Fig. S6a, b). The amorphous layer observed under the electron beam irradiation is unstable and then decomposes, which also indicates that the amorphous layer is the SEI. It can be observed that the amorphous film on the surface of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode is uniform, thin (~ 10 nm) and dense, while that on the SnO_2/G electrode is much thicker (> 30 nm) and irregular. As carefully checked by HRTEM, as shown in Fig. 6e, the SEI film on $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ can be confirmed as a dense inorganic inner layer and an organic outer layer by their contrast. These results further confirm that Li_2CO_3 acts as the nucleating agent to induce fast growth of the dense inner inorganic layer during the initial SEI formation [38]. This can avoid the continual decomposition of the electrolyte and thus continuous growth of the SEI, leading to less Li^+ consumption and enhanced ICE.

Furthermore, as schematically shown in Fig. 6f, the dense inorganic layer can isolate the SnO_2 nanograins and block the long-range diffusion of Sn in the Li_2O matrix, therefore, inhibiting the coarsening of Sn grains and the pulverization of the electrode particles. The SEM and XRD analyses show no obvious variation in the surface morphology or the thickness of the cross section in the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ electrode during lithiation (Figs S7 and S8). In addition, the coarsening of Sn grains is completely prevented in the initial ten cycles in $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$. In contrast, the SnO_2/G electrode suffers from a severe volume expansion and the Sn grains agglomerate and coarsen significantly. These results demonstrate that the addition of Li_2CO_3 stabilizes the Sn nanograins in the

lithiation/delithiation process; hence, the reversibility of the conversion reaction and the ICE of the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite are significantly enhanced.

To further verify the universality of the strategy developed in this study, another alloying-type anode, Si, conversion-type anodes, MnO_2 and Fe_3O_4 , and another Li-based compound, LiF, were also investigated. As for the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composite, the Si- $\text{Li}_2\text{CO}_3/\text{G}$, $\text{MnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ and $\text{Fe}_3\text{O}_4\text{-Li}_2\text{CO}_3/\text{G}$ composites were synthesized by ball milling. As presented in Fig. 7 and Fig. S9, the ICEs of the Si- $\text{Li}_2\text{CO}_3/\text{G}$, $\text{MnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ and $\text{Fe}_3\text{O}_4\text{-Li}_2\text{CO}_3/\text{G}$ composites significantly increase from 17.6% to 81.2%, 21% to 74% and 7.7% to 74.8% compared with the milled pristine counterparts, respectively. Furthermore, the cycling performance of these samples dramatically improved compared with the rapid capacity decay of the pristine samples, as illustrated by the significantly smaller capacity loss at the same cycle times. This demonstrates that the method of adding Li_2CO_3 , which improves the quality of the SEI and stabilizes the structure of the electrode, is applicable to promote the ICE and cyclic stability for all types of anodes with different lithiation potentials.

In addition, as shown in Fig. 7e, the $\text{SnO}_2\text{-LiF}/\text{G}$ composite, with another inorganic component of the SEI, i.e., 5 wt% LiF, illustrates very similar lithiation/delithiation behavior in the initial cycle to the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ and also delivers a high ICE of 78.9%. However, the $\text{SnO}_2\text{-LiF}/\text{G}$ has a marginally higher stable reversible capacity than the $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ (Fig. 7f), which could be due to the higher volume fraction of LiF in the composite, thus inducing more intact SEI for boosting the reversible electrochemical reactions in SnO_2 . Besides, a composite containing both LiF and Li_2CO_3 together with SnO_2 and G ($\text{SnO}_2\text{-(Li}_2\text{CO}_3\text{-LiF)}/\text{G}$) was also prepared. As shown in Fig. S10, the $\text{SnO}_2\text{-(Li}_2\text{CO}_3\text{-LiF)}/\text{G}$ composite also exhibits enhanced ICE and cycling stability, similar to the $\text{SnO}_2\text{-LiF}/\text{G}$ and $\text{SnO}_2\text{-Li}_2\text{CO}_3/\text{G}$ composites. Nevertheless, these results further demonstrate the universality of the strategy presented in this work, which facilely enhances the quality of the SEI to promote electrode performance by simply designing the inorganic components of the SEI within electrode materials.

CONCLUSIONS

We have demonstrated a simple strategy to enhance the electrode/electrolyte interfacial stability and lithium storage reversibility of SnO_2 by adding SEI containing inorganic components, such as Li_2CO_3 and LiF, to the electrode. It has been revealed that the addition of Li_2CO_3

Figure 7 (a) Initial charge-discharge curves and (b) cycling performance of the milled Si and Si-Li₂CO₃/G composite. (c) Initial charge-discharge curves and (d) cycling performances of the milled MnO₂ and MnO₂-Li₂CO₃/G composite. (e) Initial charge-discharge curves and (f) cycling performances of the milled SnO₂ and SnO₂-LiF/G and SnO₂-(LiF/Li₂CO₃)/G composites.

leads to the formation of a thin and stable SEI on SnO₂ grains and inhibits the aggregation and coarsening of nanosized Sn particles generated from the dealloying reaction for the SnO₂-Li₂CO₃/G electrode. This results in high ICEs, large capacities and long cycle lives for the SnO₂-Li₂CO₃/G and SnO₂-LiF/G composite anodes. The SnO₂-Li₂CO₃/G composite anode exhibits an average ICE of 79.6%, with a stable reversible charge capacity of 927.5 mA h g⁻¹ at 0.2 A g⁻¹. A charge capacity over 1200 mA h g⁻¹ and a CE of no less than 99% is maintained after 900 cycles at a higher current rate of 1 A g⁻¹. Moreover, this strategy is also applicable to other alloy-

ing-type (Si) and conversion reaction (MnO₂ and Fe₃O₄) anodes. Their ICEs and cycling stabilities can also be significantly promoted by simply milling with Li₂CO₃. This work develops a universal strategy for modifying the SEI and provides a simple new route towards highly reversible and stable electrodes for large capacity lithium storage.

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Author contributions Hu R and Zhu M conceived the idea and designed the experiments. Wen G, Tan L and Lan X conducted the material preparation, electrochemical measurements and material characterization. Wen G and Zhang H performed the *ex-situ* measurements and the data analysis. Yuan B and Liu J checked the paper and corrected errors in the text. Wen G and Tan L wrote the paper with assistance from coauthors.

Conflict of interest The authors declare that they have no conflict of interest.

Supplementary information Supporting data are available in the online version of the paper.

Gang Wen received his Master degree in materials science in 2020 from the School of Materials Science and Engineering, South China University of Technology (SCUT). He has great research interests in the design and fabrication of Sn-based anode materials for lithium-ion batteries.

Renzong Hu is currently a professor at the School of Materials Science and Engineering, SCUT. He received his BS degree from Dalian University of Technology in 2005, and PhD degree in materials processing engineering from SCUT in 2011. His research interests include rational design, fabrication and *in situ/ex situ* characterization of alloy-based electrode materials and their applications in lithium-ion batteries and other energy conversion and storage systems.

Min Zhu is currently a professor at the School of Materials Science and Engineering, SCUT. He is the leader of Guangdong Key Laboratory of Advanced Energy Storage Materials. His research interests include hydrogen storage materials, lithium- and sodium-ion batteries, shape memory alloys, mechanical alloying and plasma milling.

Li₂CO₃诱导生长稳定SEI膜: 提升SnO₂储锂可逆性和稳定性的有效策略

文刚, 谭亮, 兰雪侠, 张涵茵, 胡仁宗*, 袁斌, 刘军, 朱敏*

摘要 电极与电解液之间的界面不稳定极大地损害了高比容量的储锂SnO₂负极锂化和脱锂过程的可逆性和循环稳定性. 本文提出了一种简单的改善固态电解质膜(SEI)不稳定问题的策略. 通过将SnO₂与石墨和SEI的无机成分(Li₂CO₃或LiF)复合来增强SnO₂的界面稳定性和储锂可逆性, 获得了具有高库仑效率、高容量和长寿命的复合电极. 其中, SnO₂-Li₂CO₃/G电极在0.2 A g⁻¹的电流密度下具有高达79.6%的首次库仑效率和927.5 mA h g⁻¹的可逆充电比容量, 在1 A g⁻¹的电流密度下, 经过900次循环仍能得到超过1200 mA h g⁻¹的稳定充电比容量, 表现出优异的长循环稳定性能. 此外, 通过与Li₂CO₃球磨复合, 合金化Si基负极、转化类MnO₂、Fe₃O₄负极的首次库仑效率和循环稳定性也可显著提升. 因此, 本文中提出的利用SEI膜中稳定成分与负极材料进行复合的策略对于提升大容量储锂电极材料的电化学性能具有普适性.