**Influencing factors of low- and high-temperature behavior of Co-doped
Zn₂SnO₄–graphene–carbon nanocomposite as anode material for lithium-ion batteries**

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Abstract

Zn_2SnO_4 -based anode materials have recently attracted considerable attention due to their high capacity and low price for lithium-ion batteries. However, their performance is affected by temperature and temperature-dependent characters have not been investigated sufficiently. In this regard, we tested the electrochemistry performance of Co-doped Zn_2SnO_4 -graphene-carbon (Co-ZTO-G-C) nanocomposite anode at various temperatures (-25 , 25 and 60 °C) and analyzed the main limitations and improvements of its low- and high-temperature behavior. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) results demonstrated that severe concentration polarization, the absence of $\text{Zn}_2\text{SnO}_4/\text{Zn}(\text{Sn})$ redox couple and large charge-transfer resistance R_{ct} limited its low-temperature performance. Further electrochemical performance analysis indicated that the doped Co could effectively decrease R_{ct} of the nanocomposite and improve its capacity at low temperature. It also suggested that graphene and carbon layer contributed to maintaining its capacity during high-temperature cycles. Field emission scanning electron microscopy (FESEM) and X-ray diffraction (XRD) results revealed that the performance degeneration of the nanocomposite at elevated temperature was mainly attributed to severe volume expansion/contraction of Zn_2SnO_4 nanoparticles and destruction of Zn_2SnO_4 cubic structure. The XRD results also showed that the cubic structures of Zn_2SnO_4 at all temperatures were destroyed after cycling, which led to cyclic performance degeneration of the Co-ZTO-G-C nanocomposite.

Keywords: Anode; Zn_2SnO_4 ; Low-temperature performance; High-temperature performance

1. Introduction

Owing to its high energy and power density, long life cycle and environmental friendliness [1, 2], rechargeable lithium-ion battery (LIB) has been widely employed as energy source for portable supplies. Literatures show that the performance of LIB is sensitive to its operating temperature [3–5]. When working at low ($<0\text{ }^{\circ}\text{C}$) or elevated temperatures ($40\text{--}80\text{ }^{\circ}\text{C}$), LIB may not perform very well. Temperature has been long considered as a popular research interest, because it is related to the performance, lifespan and safety of LIB [6]. At low temperature, especially under $-20\text{ }^{\circ}\text{C}$, the energy and power densities of LIB decrease significantly, which is mainly caused by the large charge-transfer resistance at electrode-electrolyte interface, and the limited lithium ion diffusion in the electrode, electrolyte and the solid-electrolyte-interphase (SEI) film [7, 8]. In addition, the lithiation process is typically more difficult than the delithiation process in the anode at low temperature, which results in the formation of lithium dendrites on the anode electrode surface. The formed lithium dendrites will lead to the subsequent growth of the SEI film and even cause safety issues [9]. At elevated temperature, electrode materials degenerate increasingly, and the electrolyte decomposition and undesirable electrolyte-electrode interfacial reaction are accelerated greatly [6]. These factors would decrease the capacity, shorten battery life and even provoke the onset of thermal runaway [10]. In short, the low- and high-temperature performance of LIBs greatly depends on anode materials [9, 11, 12]. Therefore, anode electrode materials should be the focus of the research on widening the operating temperature range of LIBs.

As the conventional anode material, graphite suffers from low capacity, limited rate performance and poor safety at temperatures below $-20\text{ }^{\circ}\text{C}$ and above $50\text{ }^{\circ}\text{C}$ [10, 13, 14]. On one hand, various methods have been used to improve the electrochemistry performance of graphite at low and elevated temperatures, such as mild oxidation [15], metal doping [16], design and assembly of electrode [7] and coating [17]. On the other hand, plenty of studies attempted to look for alternative anode materials with high cyclic capacity and rate capability for Li-ion batteries [18–23]. Among them, the temperature-dependent characters of carbon [6], $\text{Li}_4\text{Ti}_5\text{O}_{12}$ [24, 25], Li_3VO_4 [26] and the oxides (TiO_2 , SiO) [10, 13, 27] have been reported. However, the reports about the performance of zinc tin oxide anodes at low and elevated temperatures are few. Zinc stannate (Zn_2SnO_4) is a promising candidate anode, owing to its excellent high theoretical capacity (1231 mAh g^{-1}), high electrical conductivity and

low price [28, 29]. But it is well known that the large volume changes restrict its application. To improve its performance, Zn_2SnO_4 is combined with carbonaceous to increase its conductivity and reduce its volume expansion during alloying/dealloying process [30, 31]. Doping is another strategy to enhance its electrochemical performance by improving the conductivity of electron and ion in the Zn_2SnO_4 nanoparticles [32, 33]. Recently, our group has prepared the Co-doped Zn_2SnO_4 -graphene-carbon (Co-ZTO-G-C) nanocomposite through a facile one-step hydrothermal method. The reversible capacity of the hybrid was up to 699 mAh g^{-1} at 0.1 C after 50 cycles. The formed carbon layer and graphene substrate acted as the carbonaceous media. Co was a dopant. Although the electrochemical performance of the Co-ZTO-G-C nanocomposite at normal temperature has been investigated [33], its performance analyses at low and elevated temperatures are still valuable.

In this study, we analyzed the factors affecting the electrochemistry performance of Co-ZTO-G-C nanocomposite anode for LIBs at -25 , 25 and 60 °C. The L^+ intercalation/deintercalation mechanism of Co-ZTO-G-C nanocomposite at all temperatures was firstly obtained by cyclic voltammetry (CV). Furthermore, the effects of each component of Co-ZTO-G-C nanocomposite, such as the doped Co, graphene and carbon layer, on its cyclic durability and electrochemical impedance were investigated to understand the contribution of each component to its electrochemistry performance at various temperatures. Finally, X-ray photoelectron spectroscopy (XPS), field emission scanning electron microscopy (FESEM) and X-ray diffractometer (XRD) were employed to analyze the surface composition, morphology and crystal structure of the Co-ZTO-G-C nanocomposite electrodes after cycles, respectively. This was for further understanding the degradation mechanism of its electrochemistry performance at various temperatures.

2. Experimental

2.1. Sample synthesis

The synthesis of sample was according to a previous report [33]. All of the reagents used in our experiments were analytically pure. In a typical fabrication, 5 ml of ethylene glycol mixed with 15 ml of 1.8 mg ml^{-1} graphene oxide aqueous suspension was used as a solvent. 1.5 mmol $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$ with 0.3 mmol $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and 1.5 mmol $\text{Na}_2\text{SnO}_3 \cdot 3\text{H}_2\text{O}$ were separately dissolved into the above mixed solvents. Subsequently, the two solutions were mixed

uniformly by vigorous stirring. Afterward, ammonia solution was added into the hybrid to adjust its pH to around 9, which was followed by adding 1 mmol L-ascorbic acid. After stirring, the mixed liquor was transferred into a Teflon-lined autoclave and heated at 180 °C for 12 h. After cooling down to the room temperature, the precipitate was collected by centrifugation, washed with deionized water and ethanol for three times, and dried at 60 °C. The final products were obtained by heat treatment at 450 °C for 3 h in N₂ atmosphere and denoted as Co-ZTO-G-C. With the same synthesis procedure of the Co-ZTO-G-C, the composites prepared without adding Co(CH₃COO)₂·4H₂O were named ZTO-G-C; those prepared without adding ammonia solution and L-ascorbic acid were named Co-ZTO-G; and those prepared without graphene oxide were named Co-ZTO-C. In addition, commercial graphite (99.8%, Alfa Aesar Chemical Co. Ltd., China) was used as a reference.

2.2. Electrochemical Measurements

CR2025 half-coin cells were used. For the preparation of the working electrode, active materials, acetylene black (AB) and polyvinylidene fluoride (PVDF) binder in a weight ratio of 70:20:10 were homogeneously dispersed in N-methyl-2-pyrrolidone. The mixture was loaded onto a Cu foil uniformly. After drying in vacuum at 60 °C, Cu foil was cut into wafer (6 mm in diameter) as working electrode. The cells were assembled in an argon-filled glove box with 1 M LiPF₆ in ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC) (1:1:1 vol.) as electrolyte, Celgard 2300 as separator, and Li foil as counter and reference electrodes. In this electrochemical test, the weight of active material on the electrode was about 1.0 mg.

The galvanostatic charge/discharge and rate performances were recorded on Land battery measurement instrument (LAND CT2001A, Wuhan Jinno Electronics Ltd., China) in a potential range of 0.01–3 V (vs. Li⁺/Li) at –25, 25 and 60 °C. The cyclic voltammetry (CV) and Electrochemical impedance spectra (EIS) were performed on a CHI650D electrochemical workstation (Shanghai Chenhua Instruments Ltd., China) at –25, 25 and 60 °C. The measured cells in CV and EIS were fresh without cycling.

2.3. Material characterizations

The surface composition and oxidation state of the electrodes were characterized by X-ray photo-electron spectrometry (XPS) recorded on an ESCALAB 250 spectrometer. The morphologies of

electrode surface were observed by a field emission scanning electron microscope (FESEM, JSM-6700F, Japan). The crystalline phases of the anode after cycles were tested by X-ray diffractometer (XRD, DMax /2500P, Rigaku, Japan) utilizing Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$). Samples of XPS, SEM and XRD for investigations were prepared by dismounting the cell in the glove box, subsequently cleaning the anode electrode with dimethyl carbonate, and drying it in air. The measured cells were in charged (delithiated) state.

The synthesis and structure characterization of Co-ZTO-G-C nanocomposite have been reported by our group [33]. The ultrafine (3–5 nm) Co-doped Zn_2SnO_4 nanoparticles showed cubic structure with a space group Fd3m. The carbon layer was formed from the carbonization of L-ascorbic acid during the hydrothermal process. The graphene nanosheets were crumpled and embedded in the composite. In Co-ZTO-G-C nanocomposite, the total weight percentage of carbon, including carbon layer and graphene nanosheets, was about 12.5%. The integral morphologies of Co-ZTO-G-C nanocomposite pristine electrode, which was composed of Co-ZTO-G-C nanocomposite, AB and PVDF, are shown in Fig. 1.

Fig. 1. Field emission scanning electron microscope (FESEM) images of Co-doped Zn_2SnO_4 -graphene-carbon (Co-ZTO-G-C) nanocomposite pristine electrode.

3. Results and discussion

Fig. 2. Charge/discharge curves of Co-ZTO-G-C nanocomposite at 0.1 C at (a) -25, (b) 25 and (c) 60 °C. (d) Coulombic efficiency of Co-ZTO-G-C nanocomposite at 0.1 C at -25, 25 and 60 °C.

Fig. 3. Cyclic voltammograms of Co-ZTO-G-C nanocomposite at (a) -25, (b) 25 and (c) 60 °C.

Figs. 2a, 2b and 2c show the charge/discharge curves of Co-ZTO-G-C nanocomposite obtained at 0.1 C in the potential range of 0.01–3.0 V at -25, 25 and 60 °C respectively. The nanocomposite delivered initial discharge and charge specific capacities of 625 and 196 mAh g⁻¹ at -25 °C, 1395 and 870 mAh g⁻¹ at 25 °C, and 1552 and 965 mAh g⁻¹ at 60 °C, respectively. After the first cycle, its capacity at -25 °C retained 23% of that operating at the room temperature. At the same current density, the capacity of commercial graphite after the first cycle at -20 °C was only 12 % of that at 20 °C [34]. At 25 and 60 °C, the first discharge specific capacities of the nanocomposite exceeded the theoretical

capacity of Zn_2SnO_4 (1231 mAh g^{-1}), which might be caused by the formation of SEI layer, the insertion of lithium ions into graphene, carbon layer and acetylene black, and interfacial storage [35]. Apparently, its initial discharge and charge specific capacities increased with the increasing temperature. Fig. 2d displays the coulombic efficiency of Co-ZTO-G-C nanocomposite at various temperatures. The initial coulomb efficiencies of the nanocomposite were 31%, 62% and 61% at -25 , 25 and 60 $^{\circ}\text{C}$, respectively. Its initial coulomb efficiency at -25 $^{\circ}\text{C}$ was only half of that at 25 $^{\circ}\text{C}$. Its initial coulombic efficiency at 60 $^{\circ}\text{C}$ was equivalent to that at 25 $^{\circ}\text{C}$, indicating that elevated temperature did not greatly increase the irreversible reaction between the Co-ZTO-G-C nanocomposite electrode and electrolyte. From the second cycle, its coulomb efficiencies increased to 79%, 93% and 91% at -25 , 25 and 60 $^{\circ}\text{C}$, respectively. To investigate the Li^+ intercalation and deintercalation mechanism of Co-ZTO-G-C nanocomposite at various temperatures, the cyclic voltammetry test was carried out in the voltage window of 0.01 – 3.0 V at a scan rate of 0.1 mV s^{-1} (Fig. 3). From Fig. 3a, the broad peak centered at 0.35 V in the first cathodic scan at -25 $^{\circ}\text{C}$ was assigned to the reduction of Zn_2SnO_4 and the formation of Li-Sn alloy. The peak centered at 0.09 V corresponded to the formation of Li-Zn alloy. In the first anodic scan, the peaks at 2.31 V and 2.75 V were respectively consistent to the dealloying process of Li_xSn (Li_yZn) and the oxidation of Sn (Zn). However, only one redox couple, originating from the alloying/dealloying process of Li_xSn and Li_yZn , appeared in the second cycle. As shown in Fig. 3b and c, the reduction of Zn_2SnO_4 and the oxidation of Sn (Zn) occurred at 0.80 and 1.45 V at 25 $^{\circ}\text{C}$, and 0.80 and 1.34 V at 60 $^{\circ}\text{C}$, respectively. The alloying of Sn and Zn with Li appeared at 0.36 and 0.11 V at 25 $^{\circ}\text{C}$, and 0.34 and 0.12 V at 60 $^{\circ}\text{C}$, respectively. Correspondingly, the dealloying of Li_xSn and Li_yZn appeared at 0.67 V at 25 $^{\circ}\text{C}$, and 0.58 V at 60 $^{\circ}\text{C}$, respectively. Comparing the peaks in CVs measured at the three temperatures, it could be found that higher temperatures caused the increase of the peak numbers and strengths, and the decrease of anodic peak locations. It suggested that elevated temperatures accelerated the rate of reduction/oxidation reactions and Li^+ irreversible intercalation, and decreased the onset voltage of oxidation reaction. This was because the enhanced temperature could effectively improve the ion/electron transmission rate, reaction rate of lithium and electrolyte, and reduce the concentration polarization during charge process. It also could be used to explain why the coulomb efficiency and discharge/charge specific capacities of the nanocomposite were higher at higher temperatures. In the first cathodic scan, some irreversible peaks were located at 0.98 V at 25 $^{\circ}\text{C}$, and 1.10 , 0.67 , 0.49 and 0.23 V at 60 $^{\circ}\text{C}$, respectively. These

cathodic peaks, which disappeared in the second cycle, were related to the irreversible intercalation of Li^+ . This was why the initial coulomb efficiencies of the nanocomposite at 25 and 60 °C just reached to 62% and 61%. At -25 °C, in the first cathodic scan, there were no obvious irreversible peaks and the locations of anodic peaks were high to 2.31 V and 2.75 V. Therefore, the low initial coulomb efficiency of the nanocomposite was primarily because that it suffered from the severe concentration polarization during charge process at low temperature [11, 12]. Notably, only at -25 °C, the redox couple comprised of Zn_2SnO_4 and Sn (Zn) vanished after the first cycle. This was an important reason for the low capacity of the nanocomposite after the first cycle.

Fig. 4. Cyclic performance of Co-ZTO-G-C, ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites at 0.1 C at (a) -25, (b) 25 and (c) 60 °C. (d) Rate performance of Co-ZTO-G-C nanocomposite at 0.1–2 C at various temperatures.

The durabilities of Co-ZTO-G-C nanocomposite during 50 cycles at -25, 25 and 60 °C are shown in Figs. 4a, 4b and 4c. To analyze the effect of each component on low- and high-temperature performance of Co-ZTO-G-C nanocomposite anode, the cyclic performance of ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites are also presented. When cycling less than 20 times at -25 °C, Co-ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites all displayed higher capacities than ZTO-G-C nanocomposite, among which Co-ZTO-G nanocomposite performed more remarkably. The observation showed that in the previous cycles the influence of dopant on the

low-temperature performance of Co-ZTO-G-C nanocomposite was dominating while graphene nanosheets only played a minor role. However, after the 30th cycle, the capacities of all the nanocomposites almost became identical. At 25 °C, the capacity differences of ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites during cycling were not significant, but it still could be found that the nanocomposites containing Co presented higher capacity than ZTO-G-C nanocomposite in the middle stage of cycling. At 60 °C, the cycle capacities of all the nanocomposites could be ranked as Co-ZTO-G-C > ZTO-G-C > Co-ZTO-G > Co-ZTO-C. According to the ranking, graphene had a prominent effect on its improved high-temperature performance and carbon layer acted as an assistant role. On one hand, graphene could offer a 3D ionic transit net to increase the conductivity of the whole nanocomposite and the formed carbon layer contributed to the improvement of longitudinal conductivity between the graphene nanosheets. On the other hand, as the substrate of Zn₂SnO₄ nanoparticles graphene nanosheets could decrease the volume change of anode materials and carbon layer also could protect Zn₂SnO₄ nanoparticles from dropping off from graphene substrate [31, 33]. Hence, graphene and carbon layer had a greater influence on the improved high-temperature performance of Co-ZTO-G-C nanocomposite. It was noted that the contribution of graphene and carbon layer to the low-temperature cyclic performance of the nanocomposite was small and consistently increased with the test temperature. This suggested that the poor cyclic performance of Co-ZTO-G-C nanocomposite at -25 °C was mainly limited by the ion/electron transmission rate in the Zn₂SnO₄ nanoparticles. This was also the reason why the doped Co played a dominating role on its low-temperature cyclic performance. The capacities of Co-ZTO-G-C nanocomposite after 50 cycles reached about 50, 695 and 636 mAh g⁻¹ at -25, 25 and 60 °C, respectively. In fact, its capacity at 60 °C only showed a slightly faster degradation than that at 25 °C. Furthermore, the rate capabilities of Co-ZTO-G-C nanocomposite were investigated at 0.1–2 C (Fig. 4d). At -25 °C, when the current density was over 0.5 C, the capacity of Co-ZTO-G-C nanocomposite fell below 20 mAh g⁻¹. But the recovery of capacity could be observed, when the current density was reversed to 0.2 C. The Co-ZTO-G-C nanocomposite exhibited excellent rate performance at 60 °C, in which the capacities were higher than those at 25 °C at each current density. At the current density of 2 C, a high capacity of 350 mAh g⁻¹ was still retained. The improved rate capacity arose from high electron/ion conductivity and low concentration polarization at high temperature, which agreed with the results of CV test.

Fig. 5. Electrochemical impedance spectra of Co-ZTO-G-C, ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites in the frequency range of 0.01–100 kHz with 5 mV potential amplitude at (a) –25, (b) 25 and (c) 60 °C. The insert in Fig. 5a shows the equivalent circuit.

The EISs were measured to further investigate the electrochemistry performance of Co-ZTO-G-C nanocomposite at various temperatures. The EISs of ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites were also recorded for comparison and analysis. These impedance responses were collected at open circuit voltage. As shown in Fig. 5, each of EIS consists of a semicircular pattern at high frequency region and an inclined line at low frequency region [33, 36]. The intercept of the plot and abscissa reflects the bulk resistance of the cell (R_e), which is a combined resistance of electrode, electrolyte and separator. The diameter of the semicircle is attributed to the charge-transfer resistance (R_{ct}). The inclined line is assigned to the Warburg impedance (Z_w) caused by lithium ion diffusion in anode electrode. Comparing the EISs of Co-ZTO-G-C nanocomposite at –25, 25 and 60 °C, the diameters of the semicircles largely decreased with the increasing temperature. It indicated that when the temperature was lower than ambient temperature, the R_{ct} values became quite large, which was a main reason for its poor low-temperature performance. Specifically, from Fig. 5a, at –25 °C the R_{ct} value of ZTO-G-C nanocomposite was larger than those of the other nanocomposites, suggesting that the doped Co could effectively decrease the R_{ct} of Co-ZTO-G-C nanocomposite. The same conclusions could be reached from Fig. 5b and c, but the effect of doping Co on the decrease of its R_{ct} values at 25 and 60 °C was not significant. As we can see from Fig. 4, the contribution of doping Co to the cyclic performance of Co-ZTO-G-C nanocomposite distinctly decreased with the increasing temperature. Based on this observation, it could be concluded that at low temperature doping Co in nanocomposite could greatly decrease its R_{ct} and improve cyclic performance by accelerating the ion/electron transmission in the Zn_2SnO_4 nanoparticles. At elevated temperature, its limited cyclic performance was no longer due to R_{ct} value. Notably, Co-ZTO-G-C nanocomposite exhibited much

larger R_e value at 60 °C than those at -25 and 25 °C, and so did the other nanocomposites ZTO-G-C, Co-ZTO-G and Co-ZTO-C nanocomposites. Therefore, the large bulk resistance R_e was an important factor to influence the high-temperature performance of Co-ZTO-G-C nanocomposite.

Fig. 6. X-ray photoelectron spectroscopy (XPS) spectra of Co-ZTO-G-C nanocomposite electrodes after the first and 50th cycles at -25, 25 and 60 °C: (a, b and c) C 1s spectra, and (d, e and f) F 1s spectra.

Fig. 6 exhibits XPS spectra of Co-ZTO-G-C nanocomposite electrodes after the first and 50th cycles to investigate the effect of SEI composition on the cell performance. Figs. 6a, 6b and 6c depict the C1s spectra of Co-ZTO-G-C nanocomposite electrodes after cycles at -25, 25 and 60 °C, respectively. At -25 and 25 °C, C1s peak could be fitted into three components primarily at about 284.6 eV, 285.8 eV and 288.6 eV corresponding to C-C, polymer and COOR, respectively [37]. The strong C-C type bonds originated from acetylene black, graphene and carbon layer. The polymer was commonly believed to consist of $-\text{CH}_2-\text{CH}_2-$ bonds. The COOR existed in alkyl lithium carbonate. The $-\text{CH}_2-\text{CH}_2-$ and alkyl lithium carbonate were the main reduction products of EC, which covered on the Co-ZTO-G-C nanocomposite electrode to form the common SEI layer [38]. At -25 °C, it could be found that the binding energy of the polymer slightly increased with the cyclic numbers, indicating that the oxidation state of the polymer was enhanced by cycling. The peak shapes of C spectra at -25 and 25 °C were very similar and the effect of cyclic number on the carbon composition was non-significant. However, when the test temperature increased to 60 °C, the polymer peak shifted

to higher binding energy and the COOR peak was replaced by the peaks of semicarbonate and polycarbonate. The semicarbonate, as metastable alkyl lithium carbonate, was located at about 289 eV [37]. After 50 cycles, its relative peak intensity decreased greatly, because semicarbonate could be decomposed into stable Li_2CO_3 . However, no Li_2CO_3 peaks could be detected in Fig. 6c. This was because Li_2CO_3 could react with tracing HF to form stable LiF. The polycarbonate was formed from the polymerization of EC, which was initialized by PF_5 . This suggested that the decomposition of electrolyte LiPF_6 had already occurred after the first high-temperature cycle. After 50 high-temperature cycles, the improved relative peak intensity and peak shape of polycarbonate indicated the increased electrolyte decomposition. The decomposition of semicarbonate and electrolyte both could cause the increase of LiF. This result could be verified by the corresponding F1s spectra in Fig. 6f. It should be pointed that the decomposition reactions could produce lots of gas, which would be absorbed on the electrode surface and broaden the distance between positive and negative electrode in the cell [17]. This was the reason why the bulk resistance R_e at 60 °C was much larger than those at -25 and 25 °C. Figs. 6d, 6e and 6f show the F1s spectra of Co-ZTO-G-C nanocomposite electrodes after cycles at -25, 25 and 60 °C, respectively. The obtained F1s spectra were mainly made up of two peaks located at 685.8 eV and 688.8 eV, which could be attributed to LiF and PVDF, respectively. By the contrast analysis of measured F 1s spectra, it could be found that the relative intensity of LiF increased with the temperature and cyclic number and that of PVDF turned to be the opposite. It was in accord with the conclusion of C spectra. Because LiF was both ionic and electrical insulator, its rapid increase during cycling certainly decreased the cyclic performance of Co-ZTO-G-C nanocomposite at elevated temperature. In addition, the Li 1s spectra of Co-ZTO-G-C nanocomposite electrodes after 50 cycles at -25, 25 and 60 °C are shown in Fig. S1. The Li 1s spectra measured at all temperatures were similar, and the only peak at about 55 eV was attributed to alkyl lithium carbonate [39]. This result suggested that Co-ZTO-G-C nanocomposite did not suffer from the formation of lithium dendrites even at low temperature, which made it safer than the commercial graphite [9].

Fig. 7. FESEM images of Co-ZTO-G-C nanocomposite electrodes after 50 cycles at (a and b) -25 , (c and d) 25 and (e and f) 60 $^{\circ}\text{C}$.

Fig. 8. X-ray diffractometer (XRD) patterns of Co-ZTO-G-C nanocomposite pristine electrode and electrodes after 50 cycles at -25 , 25 and 60 $^{\circ}\text{C}$.

The surface morphologies of the electrodes after 50 cycles are displayed in Fig. 7. In the pristine electrode (Fig. 1), the crumpled Co-ZTO-G-C nanocomposite sheets and acetylene black particles

were clearly visible. By contrast, in the electrodes after cycles, Co-ZTO-G-C nanocomposite sheets were covered with films, which were the SEI layers. At $-25\text{ }^{\circ}\text{C}$, Co-ZTO-G-C nanocomposite sheets were still coarse after cycles (Figs. 7a and 7b). While when the test temperature increased to $25\text{ }^{\circ}\text{C}$ (Figs. 7c and 7d), Co-ZTO-G-C nanocomposite sheets became considerably lustrous, and some acetylene black particles still could be detected. When the test temperature further increased to $60\text{ }^{\circ}\text{C}$, Co-ZTO-G-C nanocomposite sheets became smooth, and acetylene black nanoparticles could not be distinguished. In short, the densification of Co-ZTO-G-C nanocomposite surfaces after 50 cycles increased with the increasing temperature. In other words, higher temperatures resulted in the formation of thick SEI layer on electrode surfaces. This result was due to the fact that higher temperatures accelerated the decomposition of electrolyte, which was consistent with the result of XPS. According to the report of Andersson, the surface of graphite electrode stored at $60\text{ }^{\circ}\text{C}$ for a week in the LiPF_6 case would be covered by large size LiF crystallites, which could be clearly observed by SEM [37]. However, there were no detectable LiF crystallites on the surface of Co-ZTO-G-C nanocomposite under continued cycling at $60\text{ }^{\circ}\text{C}$ for more than a week (Figs. 7e and f). This might be because graphene nanosheet and carbon layer were covered on the surface of Zn_2SnO_4 nanoparticles in Co-ZTO-G-C nanocomposite and protected the nanoparticles from the erosion of the electrolyte. Hence, the limited amount of LiF on the Co-ZTO-G-C nanocomposite surface might be not the main reason for its high-temperature performance degeneration. Remarkably, there were evident cracks on the electrodes cycled at 25 and $60\text{ }^{\circ}\text{C}$, and the cracks increased with the temperature. It could be attributed to the severe volume expansion and contraction of Zn_2SnO_4 nanoparticles, which were caused by the rapid alloying/dealloying process of Li_xSn and Li_yZn . From Figs. 7d and 7f, we could distinctly find that the coating near the cracks was particular dense, indicating that the appearance of cracks on the electrode surface would make more active materials expose to electrolyte, increase the irreversible lithium loss and decrease cyclic performance of Co-ZTO-G-C nanocomposite at higher temperature. To further understand the mechanism of cyclic performance degeneration at various temperatures, X-ray diffraction patterns of Co-ZTO-G-C nanocomposite after 50 cycles were recorded (Fig. 8). The sample in the XRD test was the whole anode electrode, which was made up of electrode materials and Cu current collector. To observe the character of electrode materials clearly, the strong diffraction peaks from Cu were removed in Fig. 8. XRD spectra of commercial graphite (99.8%, Alfa Aesar Chemical Co. Ltd., China) electrodes under the same cell preparation technology and cyclic

condition were also investigated, as shown in Fig. S2. The distinct and strong graphite peaks indicated that the crystal structure of graphite could remain stable after continuous cycling at various temperatures. However, from Fig. 8, it could be found that the cubic structure of Zn_2SnO_4 (JCPDS no. 24-1470) vanished in all the cycled electrodes at -25 , 25 and 60 °C. The destruction of Zn_2SnO_4 cubic structure during cycles might lead to the disappearance of the redox couple arising from Zn_2SnO_4 and Sn (Zn) at higher temperatures and would greatly decrease the cyclic capacities at all temperatures. This was also the reason why the effect of doping Co on the low-temperature performance of Co-ZTO-G-C nanocomposite was only remarkable in the first 20 cycles.

Fig. S1. Li 1s spectra of Co-ZTO-G-C nanocomposite electrodes after 50 cycles at -25 , 25 and 60 °C.

Fig. S2. XRD patterns of commercial graphite electrodes after 50 cycles at -25 , 25 and 60 °C.

4. Conclusions

In summary, we analyzed the factors affecting the electrochemistry performance of Co-ZTO-G-C nanocomposite anode for LIBs at -25, 25 and 60 °C. At -25 °C, severe concentration polarization, the absence of $\text{Zn}_2\text{SnO}_4/\text{Zn}(\text{Sn})$ redox couple and large charge-transfer resistance R_{ct} limited its cyclic performance. Doping Co in nanocomposite could effectively decrease its R_{ct} and significantly improve its capacity by accelerating the ion/electron transmission in the Zn_2SnO_4 nanoparticles. However, due to the destruction of Zn_2SnO_4 cubic structure during cycling, the effect of doping Co on cyclic performance disappeared after 20 low-temperature cycles. Nevertheless, some improvements on low-temperature performance and safety over commercial graphite were observed. At 60 °C, the large bulk resistance R_{e} , thick SEI layer and increasing LiF caused by electrolyte decomposition decreased the high-temperature cyclic performance of Co-ZTO-G-C nanocomposite to some extent. However, the main reasons for the degeneration of its high-temperature performance were severe volume expansion/contraction of Zn_2SnO_4 nanoparticles and the destruction of Zn_2SnO_4 cubic structure. Graphene and carbon layer contributed to maintaining capacity during high-temperature cycles by improving conductivity, buffering the volume change and decreasing electrolyte decomposition. Hence, the Co-ZTO-G-C nanocomposite still exhibited excellent cyclic and rate performance at 60 °C. Above all, the cubic structures of Zn_2SnO_4 were destroyed after cycling at all temperatures, therefore the improvement of Zn_2SnO_4 structural stability should be given priority to in the further study of Zn_2SnO_4 -based anode material. Our results provided a certain reference for the study of performance of anode materials in a large range of operating temperatures.

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