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Article

Amorphous CoSnO_3 @rGO nanocomposite as an efficient cathode catalyst for long-life Li- O_2 batteries

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ABSTRACT

An amorphous CoSnO_3 @rGO nanocomposite fabricated using a surfactant-assisted assembly method combined with thermal treatment served as a catalyst for non-aqueous lithium-oxygen ($\text{Li}-\text{O}_2$) batteries. In contrast to the specific surface area of the bare CoSnO_3 nanoboxes ($104.3 \text{ m}^2 \text{ g}^{-1}$), the specific surface area of the CoSnO_3 @rGO nanocomposite increased to approximately $195.8 \text{ m}^2 \text{ g}^{-1}$ and the electronic conductivity also improved. The increased specific surface area provided more space for the deposition of Li_2O_2 , while the improved electronic conductivity accelerated the decomposition of Li_2O_2 . Compared to bare CoSnO_3 , the overpotential reduced by approximately 20 and 60 mV at current densities of 100 and 500 mA g^{-1} when CoSnO_3 @rGO was used as the catalyst. A Li- O_2 battery using a CoSnO_3 @rGO nanocomposite as the cathode catalyst cycled indicated a superior cyclic stability of approximately 130 cycles at a current density of 200 mA g^{-1} with a limited capacity of 1000 mAh g^{-1} , which is 25 cycles more than that of the bare amorphous CoSnO_3 nanoboxes.

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1. Introduction

Owing to the ultrahigh theoretical energy density that is several times of the current state-of-the-art Li-ion batteries [1,2], non-aqueous Li- O_2 batteries are regarded as the next-generation energy storage systems [3–6]. However, before they can be used for practical application in industry, numerous challenges need to be solved, including the high overpotential, instability of the electrolyte, poor cyclic ability, and low roundtrip efficiency [7]. As is known, typical non-aqueous Li- O_2 batteries consist of a porous cathode, an electrolyte, and a Li metal anode. During the discharge process, Li^+ released

from the Li metal anode transports to the cathode zone and reacts with O_2 diffused from the external environment as follows: $2\text{Li}^+ + 2\text{e}^- + \text{O}_2 \rightarrow \text{Li}_2\text{O}_2$ [8]. The discharge products of Li_2O_2 possess the inherent character of insolubility in the common type of electrolyte and poor electrical conductivity [9]. Thus, during the charge process, discharge products of Li_2O_2 are hardly decomposed, leading to a high charge plateau. Because of the high charge voltage, the electrolyte becomes unstable under the attack of active O_2^{2-} as well as low roundtrip efficiency. Moreover, the undecomposed discharge products of Li_2O_2 accumulate on the porous cathode and can block the pathway for the diffusion of O_2 , resulting in a sudden death

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during the cycle.

Significant research efforts have been undertaken to find the key to solve these problems. Among the critical solutions is to find an effective and low-cost catalyst to reduce the overpotential while simultaneously improving the electrochemical performance. The most effective catalysts are noble metals and related alloys such as Pt, Pd, Ru, PtAu, Pd/Ir, and Pd₃Fe [10–15]. However, the high cost and rarity of these noble metals translate to no future use in practical applications. Other types of catalysts have also been explored, including transitional metals, transitional metal oxides, and carbon-related materials [5,16–21]. Transitional metal oxides have drawn significant attention as promising catalysts for Li-O₂ batteries owing to their low cost, environment friendliness, and abundance on earth. Lu et al. [22] prepared dandelion-like NiCo₂O₄ hollow microspheres as enhanced cathode catalysts for Li-O₂ batteries that can deliver a reversible capacity of 8019 mAh g⁻¹ at a current density of 300 mA g⁻¹ with a stable cycle performance of at least 40 times in ambient air. Spinel MnCo₂O₄ nanospheres have been synthesized by Lu et al. and used as an effective cathode electrocatalyst for rechargeable Li-O₂ batteries. These batteries exhibit a high discharge capacity of 8518 mAh g_{cathode}⁻¹ with a narrow overpotential of 0.85 V at a current density of 100 mA g_{cathode}⁻¹; their cycling stability is greater than 20 cycles [23]. Sn-based transitional metal oxides have been extensively investigated as candidates for LIB anodes because of their high theoretical capacity and excellent catalytic activity [24–32]. However, Sn-based transitional metal oxides as cathode catalysts for Li-O₂ batteries have been rarely reported. Yuan et al. [33] successfully synthesized SnO₂ and SnO₂@C as cathode catalysts for lithium-air batteries showing good oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs).

Although transitional metal oxides have numerous advantages, their inherent poor electrical conductivity restricts their further application. This deficiency can be reduced by combining them with materials of excellent electrical conductivity. Because of its excellent properties, including large specific surface area, ultrahigh electrical conductivity, high mechanical strength, and excellent chemical stability [34–36], graphene has been considered a promising supporting material for energy storage batteries that can improve charge transfer and mass transport when combined with a metal catalyst. Thus, transitional metal oxides combined with graphene are a good means to improve the electrochemical performance of Li-O₂ batteries. Our group synthesized novel flower-like porous structure NiO and CuCr₂O₄@rGO nanocomposites as cathodic catalysts for Li-O₂ batteries and showed outstanding cycling performance and superior OER/ORR catalytic activity [5,37].

To our knowledge, there are no studies on CoSnO₃ and CoSnO₃@rGO nanocomposites serving as cathode catalysts for Li-O₂ batteries. Herein, a facile route was reported for fabricating CoSnO₃ and a CoSnO₃@rGO nanocomposite by combining a surfactant-assisted assembly method with thermal treatment. When the CoSnO₃@rGO nanocomposite served as a cathode catalyst, the Li-O₂ batteries presented an overpotential reduction and improved cyclic stability compared to that of the bare

CoSnO₃ catalyst.

2. Experimental

2.1. Synthesis of CoSnO₃ nanoboxes

All the chemical reagents were analytically pure and used without further purification. First, CoCl₂·2H₂O (1 mmol) and sodium citrate (1 mmol) were dissolved into 31 mL of deionized water under magnetic stirring. Then, 4 mL of SnCl₄·5H₂O (1 mmol) ethanol solution was added to the mixed solution to form a homogeneous solution. Subsequently, 5 mL of NaOH (2 mol L⁻¹) aqueous solution was dropwise added to the homogeneous solution. After reacting for 1 h, another 20 mL of NaOH (8 mol L⁻¹) aqueous solution was added into the pink suspension and then reacted for 15 min. Then, the precursors were obtained via centrifugation separation and washed by ethanol and deionized water three times, respectively. Finally, the collections were annealed in argon at 400 °C for 3 h and the hollow structure CoSnO₃ nanoboxes were obtained. For comparison, the solid structure CoSnO₃ nanocubes were also synthesized using the same process except for the addition of 20 mL of NaOH (8 mol L⁻¹) aqueous solution. In addition, references to CoSnO₃ in the text hereafter are hollow structure CoSnO₃ nanoboxes unless otherwise noted. The formation mechanism of the CoSnO₃ hollow box is provided in Fig. S2(e).

2.2. Synthesis of the CoSnO₃@rGO nanocomposite

During a typical process, 0.1 g of the presynthesized hollow structure CoSnO₃ nanobox sample was dispersed in 10 mL of deionized water under magnetic stirring. Then, 30 mL of GO (2 mg mL⁻¹) was synthesized using the modified Hummers' method and added into the suspension. Subsequently, 10 mL of CTAB (2 mg/mL) aqueous solution was slowly added dropwise into the aforementioned mixed solution and constantly stirred to form a coagulum. The obtained coagulum was collected via centrifugation separation and washed by ethanol and deionized water three times. Finally, the collections were annealed in argon at 400 °C for 180 min obtaining the CoSnO₃@rGO nanocomposite.

2.3. Characterizations

The crystal structure of the synthesized samples was characterized using X-ray diffraction (XRD; Bruker D8, Cu K_α radiation, 40 kV, 40 mA). The morphology of the products was characterized using scanning electron microscopy (SEM; LEO-1530) and transmission electron microscopy (TEM; JEM-2100, 200 kV). A thermogravimetric analysis (TGA) survey was conducted using an SDT-Q600 thermal analyzer at 10 °C min⁻¹ under air. Raman spectroscopy was implemented to explore the graphene sheets using a LabRAM HR UV/vis/NIR PL by Horiba Jobin Yvon of France. The Brunauer-Emmett-Teller (BET) surface area was measured via nitrogen sorption at -196 °C on the surface area and the pore size distribution was calculated using the Barrett-Joyner-Halenda (BJH) method (using a TriStar 3020

system).

2.4. Electrochemical measurements

The slurry was mixed comprising the $\text{CoSnO}_3\text{@rGO}$ nanocomposite (as the active material), Ketjen carbon, and polyvinylidene difluoride (PVDF) in a weight ratio of 60:30:10. Then, it was spread on a customized carbon paper and desiccated at 70 °C for 12 h in a vacuum-drying chamber. The mass loading of the $\text{CoSnO}_3\text{@rGO}$ nanocomposite/KB/PVDF was approximately 1.0–1.3 mg cm^{-2} . The Li-O_2 batteries (CR2032) were combined in an Ar-filled glove box (<0.1 ppm of H_2O and 0.1 ppm of O_2). A lithium foil was used as the counter electrode and a Whitman glass microfiber separator filled with electrolyte as the separator. The electrolyte was 150 μL of 1 mol L^{-1} LiTFSI (lithium bis(trifluoromethanesulfonyl)imide) in tetraethylene glycol dimethyl ether (TEGDME). The Li-O_2 batteries were assembled in a chamber filled with pure O_2 (99.999%) for segregating the air when tested. The NEWARE Battery Testing System was employed to detect the galvanostatic electrochemical performance at different current densities. The potential territory during the cycles was from 2.0 to 4.5 V. For comparison, the ability of solid CoSnO_3 nanoboxes was also tested. All of the galvanostatic discharge/charge specific capacity values were calculated based on the mass of KB.

3. Results and discussion

The mechanism of the synthesis of hollow CoSnO_3 nanoboxes has already been reported [32,38]. Briefly, under an alkaline condition, Sn^{4+} , Co^{2+} , and OH^- stoichiometric rapidly coprecipitated and formed a solid CoSn(OH)_6 nanobox precursor. When the concentration of OH^- was exceeded, the CoSn(OH)_6 nanoboxes could be gradually dissolved forming a passivation layer composed of Co(III) species on the surface of the CoSn(OH)_6 crystals. Because of the existing inactivation layer, the outer surface of the CoSn(OH)_6 cubes were less reactive than the recently exposed interiors in the alkaline etching course. With sustaining evacuation of the core materials through the shell, hollow CoSn(OH)_6 nanoboxes finally formed

without the loss of high crystallinity.

Surfactant-assisted bottom-up assembly means were chosen to combine the hollow CoSnO_3 nanoboxes and graphene [39]. The graphene oxide (GO) synthesized via chemical routes has large amounts of oxygen-bearing groups on its framework, leading to a negative charge on its surface when dissolved in water [40]. Therefore, when the cationic surfactant CTAB (cetyltrimethylammonium bromide) was dissolved into the mixture solution, CTAB ions attracted to GO, which makes the GO surface transform from hydrophilic to hydrophobic. The hydrophobic interaction between the GO sheets forced the assembly of the hollow CoSn(OH)_6 nanoboxes and GO. After the thermal treatment, a $\text{CoSnO}_3\text{@rGO}$ nanocomposite was finally obtained.

XRD was used to detect the phase structure and fineness of the achieved samples. As shown in Fig. 1(a), XRD analysis of the synthesized precursor demonstrated that all the diffraction peaks could be properly indexed to crystal planes of CoSn(OH)_6 (JCPD card no. 13-356) and without any impurity. No significant change was observed in the XRD pattern in which CoSn(OH)_6 was wrapped with the GO (Fig. 1(a)). The characteristic of a broadened diffraction peak between 30° and 40° meant that the samples were of amorphous crystallization, which was consistent with the literature (Fig. 1(b)) [38]. The microstructure of the $\text{CoSnO}_3\text{@rGO}$ nanocomposite was also investigated using XRD. As shown in Fig. 1(b), the diffraction pattern of $\text{CoSnO}_3\text{@rGO}$ was similar to that of the CoSnO_3 nanoboxes, indicating that the crystal structure remained unchanged during the combining between the CoSnO_3 and graphene. In addition, the XRD results of the solid structure CoSnO_3 nanocubes were similar to those of the hollow CoSnO_3 nanoboxes (Supporting Information, Fig. S1).

TGA measurement has been used to ensure the transitional temperature of the CoSn(OH)_6 precursor into the CoSnO_3 product. Observing the TGA result of the red line shown in Fig. 2, it is obvious that the weight loss of the precursor nearly ceased when the temperature reached approximately 200 °C, indicating that the precursor of CoSn(OH)_6 was dehydrated and completely transformed into CoSnO_3 after thermal treatment. This value was not in good agreement with the theoretical

Fig. 1. (a) XRD patterns of CoSn(OH)_6 and $\text{CoSn(OH)}_6\text{@GO}$; (b) CoSnO_3 and $\text{CoSnO}_3\text{@rGO}$.

Fig. 2. TGA curves of the $\text{CoSn}(\text{OH})_6$ precursor (red line) and $\text{CoSnO}_3\text{@rGO}$ (black line) with a heating rate of $10^\circ\text{C min}^{-1}$.

weight loss of 19.3%, which was calculated using the reaction $\text{CoSn}(\text{OH})_6 \rightarrow \text{CoSnO}_3 + 3\text{H}_2\text{O}$ [38]; the possible reasons may be ascribed to the physically adsorbed water. The black line shown in Fig. 2 indicates the thermal behavior of the CoSnO_3 nanoboxes/rGO ($\text{CoSnO}_3\text{@rGO}$ nanocomposites) in the air. A mass loss of approximately 5.1% below 200°C is typically ascribed to the loss of physically adsorbed water [41–43]. The main loss at a temperature of approximately 400°C is the result of the combustion of the reduced graphene oxide (rGO) covered with the CoSnO_3 nanocube [42,43]. Based on the results of the TGA test, it can be confirmed that the contents of rGO in the $\text{CoSnO}_3\text{@rGO}$ nanocomposites is approximately 25.5%.

The Raman spectra of bare rGO and $\text{CoSnO}_3\text{/rGO}$ are shown in Fig. 3. It is obvious from the spectrum of bare rGO (black line) that only two typical carbon peaks occurred at approximately 1350 cm^{-1} and 1595 cm^{-1} , which are in good agreement with the disordered band and graphitic band of the carbon-based materials, respectively [37,44–46]. Two bands at 1355 cm^{-1} (D band) and 1590 cm^{-1} (G band) can be detected with the Raman spectrum for the $\text{CoSnO}_3\text{@rGO}$ nanocomposites (red line). It is well known that the D band belongs to the disorder and defects in the graphene layer, while the G band is ascribed to the sp^2 hybridized for crystalline graphitic carbon [29,44,45]. Here, in

Fig. 3. Raman spectra of GO, rGO, and $\text{CoSnO}_3\text{@rGO}$.

contrast to the D/G intensity, the ratio is approximately 0.72 for the GO; the rGO and $\text{CoSnO}_3\text{@rGO}$ nanocomposites exhibited an increased D/G intensity ratio of approximately 0.93 and 1.03, respectively, indicating more structural defect sites and a higher disordered degree and low graphitic crystallinity in the carbon layer. Here, the reduction of the mean size of the sp^2 domains leads to an increase in the intensity ratio with the GO, rGO, and $\text{CoSnO}_3\text{@rGO}$ nanocomposites, which can forecast that the GO had changed into graphene via a reduction reaction along the solvothermal route. This conclusion shows that more defects were imported into the nanocomposites by reason of the CoSnO_3 nanoboxes entwined into the rGO three-dimensional network forming the $\text{CoSnO}_3\text{@rGO}$ nanocomposites via this solvothermal route.

Fig. 4 (a) and (b) shows the SEM images of the $\text{CoSn}(\text{OH})_6$ precursor and CoSnO_3 nanoboxes. It can be seen that the $\text{CoSn}(\text{OH})_6$ precursor was composed of uniform nanoboxes and the average length of the cubes was approximately 250 nm. Compared to the solid structure $\text{CoSn}(\text{OH})_6$ precursor (Fig. S2), the surface of the cubes was rough, which should be ascribed to the sustaining evacuation of the core materials across the shell. As shown in Fig. 4(b), the size and morphology were maintained. In addition, the cracked cube demonstrated that the sample had a hollow structure. Fig. 4 (c) and (d) shows the $\text{CoSn}(\text{OH})_6\text{/GO}$ precursor and the obtained $\text{CoSnO}_3\text{@rGO}$ nanocomposite after calcination. It is obvious that the CoSnO_3 nanoboxes were entirely encapsulated by the rGO.

The TEM images of the CoSnO_3 nanoboxes and $\text{CoSnO}_3\text{@rGO}$ nanocomposites are shown in Fig. 5. In agreement with the SEM findings shown in Fig. 4(b), the nanocubes had a hollow structure and were uniformly distributed. The TEM images shown in Fig. 5(b) could obviously confirm that the nanoboxes were entirely encapsulated by the rGO. The nitrogen adsorption/desorption isotherm of the CoSnO_3 nanoboxes and $\text{CoSnO}_3\text{@rGO}$ nanocomposites was tested as shown in Fig. S3. CoSnO_3 nanoboxes presented a specific surface area of $104.3\text{ m}^2\text{ g}^{-1}$ and a total pore volume of $0.25\text{ cm}^3\text{ g}^{-1}$, which are much

Fig. 4. SEM images of (a, b) CoSnO_3 nanoboxes and (c, d) $\text{CoSnO}_3\text{@rGO}$ nanocomposites at different magnifications.

Fig. 5. TEM images of (a) CoSnO_3 nanoboxes and (b) CoSnO_3 @rGO nanocomposites.

lower than those of CoSnO_3 @rGO ($195.8 \text{ m}^2 \text{ g}^{-1}$ and $0.31 \text{ cm}^3 \text{ g}^{-1}$). Thus, the combination of rGO greatly increased the specific surface area, which significantly improved the electrochemical performance.

The CoSnO_3 nanoboxes and CoSnO_3 @rGO nanocomposites were used as cathode catalysts in rechargeable Li-O_2 batteries. The rGO as the cathode catalyst performer is shown in Fig. S8. Fig. 6 ((a) and (b)) shows the discharge/charge curves of the Li-O_2 batteries tested by CoSnO_3 and CoSnO_3 @rGO cathodes at a current density of 100, 200, and 500 mA g^{-1} during the first cycle. As shown in Fig. 6 (a and b), the potential plateaus of the discharge course are nearly similar and achieved a stabilized level at 2.75 V even under an extremely different current den-

sity, which implied fascinating ORR catalytic activity of the CoSnO_3 nanoboxes as well as the CoSnO_3 @rGO nanocomposites. In the discharge/charge course shown in Fig. 6(a), the overpotential of CoSnO_3 was 1.18 and 1.26 V at a current density of 100 and 500 mA g^{-1} , respectively. The increased overpotential could be ascribed to the non-decomposable discharge product Li_2O_2 deposition during the cycling process. The greater the current density, the more quickly discharge products accumulate. Compared to CoSnO_3 , CoSnO_3 @rGO reduced the overpotential by 20 and 60 mV at a current density of 100 and 500 mA g^{-1} , respectively. This enhancement could be ascribed to the vast surface area and superior electronic transmission capacity of the rGO. The vast specific surface area provided more space for the deposition of Li_2O_2 , while the improved electronic conductivity accelerated the decomposition of Li_2O_2 .

Fig. 6 ((c) and (d)) shows the discharge/charge curves of Li-O_2 batteries tested by CoSnO_3 and CoSnO_3 @rGO cathodes at a current density of 200 mA g^{-1} during different cycles. Before cycling for 80 cycles, the discharge/charge terminal voltages of CoSnO_3 slightly enlarged while the CoSnO_3 @rGO showed a negligible change. After 80 cycles, the overpotentials gradually increased and at 105 cycles, the charge terminal voltage of the Li-O_2 batteries assembled by the CoSnO_3 cathode near the cut-off voltage 4.5 V initially set, and the discharge curve also obtained the cut-off voltage of 2 V . During the following two cycles, the results obviously showed that the discharge curves

Fig. 6. (a, b) Galvanostatic discharge and charge curves of the CoSnO_3 and CoSnO_3 @rGO cathodes at different current densities (100, 200, and 500 mA g^{-1}); (c, d) Discharge/charge curves of the CoSnO_3 and CoSnO_3 @rGO cathodes with a current density of 200 mA g^{-1} . All the discharge and charge processes were measured via a limited capacity of 1000 mAh g^{-1} .

Fig. 7. Cyclic stability for the Li-O₂ battery with CoSnO₃ and CoSnO₃@rGO cathodes tested at a current density of 200 mA g⁻¹ and at a limited capacity of 1000 mAh g⁻¹.

could not obtain the limited capacity of 1000 mAh g⁻¹. However, the Li-O₂ batteries assembled by the CoSnO₃@rGO cathode could cycle another 25 cycles, and the discharge/charge curves show the same trend as that of the bare CoSnO₃ cathode catalyst material. Fig. 7 shows the cycle lifetime of the two types of cathodes at a current density of 200 mA g⁻¹ with a limited capacity of 1000 mAh g⁻¹. An arresting cycling life is obtained at approximately 105 cycles and 130 cycles in the Li-O₂ batteries based on CoSnO₃ and CoSnO₃@rGO, respectively. The dis-

charge/charge curves of the Li-O₂ batteries tested by the CoSnO₃@rGO cathodes at a current density of 100 and 500 mA g⁻¹ during the different cycles can be seen in Fig. S4. The electrochemical performance of the synthesized solid structure CoSnO₃ nanocubes were also measured (Fig. S4). Compared to the solid structure CoSnO₃ nanocubes, the hollow CoSnO₃ nanoboxes and the CoSnO₃@rGO nanocomposites have more active sites that can participate in electrocatalytic reactions because of the enhanced electrocatalytic performance. Another factor that must be considered for the improved electrochemical properties is the rGO twined-structure composites; the rGO with remarkable electrical properties can only act as a current collector to promote the charge migration efficiency. With the feature of a hollow structure and the rGO cladding, the CoSnO₃@rGO nanocomposites showed superior ORR/OER catalytic activity and good catalytic stability for the Li-O₂ batteries. From the full discharge/charge curve of the CoSnO₃@rGO cathodes with a current density of 100 mA g⁻¹, it was found that the Li-O₂ battery will be destroyed after 13 cycles (Fig. S6). For all of the discharge/charge process, the average round-trip efficiency is approximately 63%. Compared to the materials shown in Table S1, the CoSnO₃@rGO nanocomposite showed good performance.

To further understand the discharge/charge processes of the Li-O₂ batteries using the CoSnO₃@rGO as cathode catalysts, a number of batteries were disassembled and characterized

Fig. 8. (a) Discharge/charge curves of the 20th cycle of the Li-O₂ batteries at a current density of 100 mA g⁻¹ and a limited capacity of 1000 mAh g⁻¹; SEM images of CoSnO₃@rGO electrodes during the (b) after-discharge and (c) after-recharge stages; (d) XRD patterns of the cathodes after the discharge and after the recharge stages.

using SEM images in different statuses (Fig. 8(b) and (c)) at a current density of 200 mA g⁻¹ with a limited capacity of 1000 mAh g⁻¹. The black circles shown in Fig. 8(a) correspond to the after-discharge status (Fig. 8(b)) and after-charge status (Fig. 8(c)). As shown in Fig. 8(b), it is obvious that the surface of the cubes and sheets of the CoSnO₃@rGO nanocomposite fully covered via the Li₂O₂ film, while the nanoparticles of KB could be clearly observed. This phenomenon can be ascribed to the more effective ORR catalytic activity of CoSnO₃@rGO than that of KB. Behind the charge course, the discharge outcomes could be decomposed and nearly recover the morphology of the original. The cubes and rGO sheets can be clearly seen in Fig. 8(c). Fig. 8(d) shows the XRD patterns of the cathodes at the behind discharge and charge stages. Within the inserted XRD spectrum, a lower-speed and high-precision XRD spectrum, the existence of Li₂O₂ peaks after discharge was evident, which partly disappeared or were reduced after the charge process, which meant that Li₂O₂ was the main product during the charge/discharge course. Notably, some Li₂CO₃ occurred, which is a byproduct and belongs to the undecomposed and hazardous substances portion of the cyclic process. Li₂O₂ can be totally or partly decomposed during the charging course; some Li₂O₂ did not decompose at all and accumulated and covered the active sites finally leading to a poisoning of the catalyst. The ultimate ineffectiveness of Li-O₂ was caused by the continued accumulation of Li₂CO₃ and Li₂O₂. Moreover, the obvious Li₂O₂ and Li₂CO₃ chemical yield can be readily detected by the Raman spectrum (Fig. S7).

A feasible mechanism and a specific course can be speculated as follows. In the highly purified oxygen atmosphere, the oxygen could be easily attracted by the ultrahigh specific surface area of the CoSnO₃@rGO nanocomposites [37]. The adsorbed oxygen can react with the Li ions that reach the catalyst to form LiO₂. The formed LiO₂ further respond to the oxygen-containing species that had been adsorbed by the CoSnO₃ nanoboxes and forming lithium peroxide films (Li₂O₂). In the following charge course, the CoSnO₃ nanoboxes show superior catalytic properties, leading to easy decomposition of Li₂O₂. Meanwhile, the rGO, which was curled on the CoSnO₃ nanoboxes, offer superior electrical conductivity to accelerate rapid transmission [37,45]. Accompanied by the excellent catalytic performance of the CoSnO₃ nanoboxes and good electronic transmission capacity of the rGO nanosheets, the lithium peroxide films can be decomposed at a lower charge potential.

4. Conclusions

An effective cathode catalyst, a CoSnO₃@rGO nanocomposite, was synthesized using a surfactant-assisted assembly method combined with thermal treatment. The combination between the perovskite structure transitional metal oxide CoSnO₃ and rGO nanosheet led to an enhanced electric conductivity and enlarged surface area. The improved conductivity accelerated the Li ion and electron path speed, while the larger specific surface area increased the effective contact of the gas-liquid-solid three-phase systems among the electrolyte, catalyst, and oxygen. When used as a cathode catalyst for Li-O₂

batteries, the CoSnO₃@rGO nanocomposite exhibited excellent catalytic activity, leading to a reduced discharge/charge overpotential and a long-term cycling performance of more than 130 cycles. The enhanced electrochemical capability of the CoSnO₃@rGO nanocomposite catalyst demonstrated it to be a promising candidate as a cathode catalyst for high-capability Li-O₂ batteries.

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Graphical Abstract

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Amorphous CoSnO_3 @rGO nanocomposite as an efficient cathode catalyst for long-life Li-O_2 batteries

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Amorphous CoSnO_3 nanoboxes intertwined with the rGO as the highly efficient cathode catalyst for the Li-O_2 batteries to reduce the overpotential and improve the cycling performance.

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石墨烯包覆无定形 CoSnO_3 纳米复合材料用作锂空气电池阴极催化剂的性能

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摘要: 随着科技不断进步和人口快速增长, 化石能源日渐枯竭, 同时环境问题日趋严重, 开发新型绿色、环保、高效的能源迫在眉睫。锂-空气电池以其质量轻、成本低、环境友好和能量密度高的优点引起人们广泛研究。但对于锂-空气电池仍然需要解决诸如较差的材料和电解液的稳定性、较低的循环寿命以及过高的充放电过电势等难题。而开发高效正极催化剂

材料是解决这些问题的关键技术之一。其中,过渡金属氧化物以其地壳丰度高、成本低和性能优异等优点成为正极催化剂材料的研究热点。

本文采用化学法成功合成了 CoSnO_3 纳米盒子,对其进行复合后制得 $\text{CoSnO}_3@\text{rGO}$ 纳米复合材料,并系统研究了 CoSnO_3 及其纳米复合材料作为锂-空气电池正极催化剂的电化学性能。结果表明,通过石墨烯与 CoSnO_3 进行复合得到的 $\text{CoSnO}_3@\text{rGO}$ 纳米复合材料的比表面积从原来的 $104.3 \text{ m}^2 \text{ g}^{-1}$ 增加到 $195.8 \text{ m}^2 \text{ g}^{-1}$ 。作为阴极催化剂材料, $\text{CoSnO}_3@\text{rGO}$ 纳米复合材料的充放电过电位比 CoSnO_3 在100和500 mA g^{-1} 充放电电流密度下分别降低了20和60 mV。在限制容量为1000 mAh g^{-1} 、充放电电流密度为200 mA g^{-1} 时, $\text{CoSnO}_3@\text{rGO}$ 纳米复合材料作为阴极催化剂材料可以使该锂-空气电池稳定循环130圈,比单纯的 CoSnO_3 纳米盒子作为阴极催化剂材料多循环了25圈。

$\text{CoSnO}_3@\text{rGO}$ 纳米复合材料的优异性能归功于石墨烯良好的导电性能以及快速的电子和离子传输能力,同时由于其巨大的比表面积增大了电解液和催化剂材料活性位点的接触面积,为放电产物 Li_2O_2 的形成和分解提供了场所。 $\text{CoSnO}_3@\text{rGO}$ 的OER催化活性和循环稳定性在 CoSnO_3 基础上均得到提升。

关键词: 无定形 CoSnO_3 纳米盒子; 纳米复合物; 锂-空气电池; 阴极催化剂

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