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Rice husk-derived carbon@SnO$_2$@graphene anode with stable electrochemical performance used in lithium-ion batteries

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Abstract

In this study, we adopted a novel method to synthesize a rice husk- derived carbon@SnO$_2$@reduced graphene oxide (rGO) composite with a multi-level structure as an anode electrode for lithium-ion batteries. The carbon source of composite was cellulose extracted from RH. The material exhibits excellent performance of LIBs with large reversible capacity and outstanding cycle performance. It shows a reversible capacity of 1206.9 mAh g$^{-1}$ at a current density of 0.2C after 100 cycles. Excellent cycle performance is due to unique multi-level structure, which increases active site of lithium ion. Furthermore, SnO$_2$ nanoparticles (SnO$_2$ NPs) and carbon skeleton have strong chemical bonds to prevent SnO$_2$ NPs from falling out of the three-dimensional network during cycling, thereby making material a promising anode material for LIBs.

1. Introduction

Lithium-ion battery (LIB) has been widely used because of its advantages, such as large capacity, small volume, light weight, high working voltage, long cycle life, small memory effect and small self-discharge [1, 2]. But the current performance of LIB has been unable to keep up with the rapid development of integrated circuits trend, which cannot meet the growing energy demand. In order to enhance the performance of lithium-ion batteries, it is necessary to develop new materials with better performance or to improve the original lithium-ion battery materials [3, 4]. Because of transition metal oxides not only have a high theoretical capacity, but also has a new conversion mechanism, therefore it is expected to be high-performance material for LIB [5, 6].

Among many of the anode materials, the theoretical specific capacity of SnO$_2$ is 782 mA h g$^{-1}$, which is much higher than the conventional graphite material (372 mA h g$^{-1}$) [7, 8]. As an excellent anode material, SnO$_2$ has a voltage platform of about 0.5 V, which reduces the safety hazard caused by metal lithium deposition during high current charging and discharging. However, In the process of lithium ion insert and exit material, Large volume expansion occurs in SnO$_2$ material (∼300%) [9], which will result in pulverization of the material. As a result, battery capacity decays rapidly during cycling, limiting practical applications. Various methods have been proposed for solving this problem. One of the effective strategies is to minimize the material to reduce the size of the particles and to prepare the special morphology of the SnO$_2$ materials, such as nanowires [10], nanorods [11] and spherical [12] materials. Another effective method is to load SnO$_2$ particles on the substrate to form a composite. The substrate can slow down the volume change of SnO$_2$, thereby improving the storage capacity performance of lithium. Carbon material is considered to be the candidate material for the most promising buffer matrix [13] due to its good cushioning effect and high conductivity. However, the synthesis of SnO$_2$/C composites is currently limited by raw materials and costs. Therefore, it is necessary to develop a low-cost SnO$_2$/C composite anode material. Among all carbon sources, RH [14, 15] is a good biomass raw materials. In addition, RH is the product of extensive rice grown around the world, which is easy to collect, store and transport [16]. Therefore, using activated carbon is a good choice, which is prepared by the RH as the base of SnO$_2$. However, because of the carbon matrix is prepared by the RH, it does not improve the electrochemical
performance of tin oxide very well. For example, Li Yao et al prepared the RHC-SnO₂ for lithium ion batteries, which showed about 55% retention (420 mA h g⁻¹) of the initial capacity after 30 cycles [17], so the SnO₂/RHC composites need to be further improved.

Graphene has a unique two-dimensional structure, which can effectively improve the conductivity and reduce the agglomeration of nanoparticles [18]. In addition, graphene can also help reduce mechanical strain during charge and discharge and improve material cycle stability. Reduced graphene oxide (rGO) has similar physical and chemical properties compared to graphene, and rGO has strong conductivity. Therefore, rGO may be very useful for lithium-ion battery composites [19]. For instance, Rajesh Kumar et al embedded Fe₂O₃ into rGO by microwave method. The material has high capacity and outstanding cycle stability. The material has a capacity of 540 mA h g⁻¹ after 120 cycles at a current density of 100 mA g⁻¹ [20]. Agnese Birrozi et al prepared a reduced graphene oxide - tin dioxide (rGO-SnO₂) composite. After 140 cycles, the material have a discharge capacity of 430 mA h g⁻¹ at a current density of 500 mA g⁻¹ [21]. As can be seen, rGO-SnO₂ is still subject to rapid capacity fading problems. Since the volume change of lithium ions in the movement of rGO and SnO₂ is different, it is easy to cause separation of materials and poor contact of active materials [22].

Therefore, for the above reasons, we can use RHC and rGO as the matrix of SnO₂, rGO as the matrix of SiO₂ generally alleviates structural changes caused by volume changes of SnO₂ in the electrochemical cycle while avoiding agglomeration of materials. In addition, the introduction of RHC significantly improves the conductivity of SnO₂. The distribution of carbon-coated SnO₂ on the surface of rGO makes the formation of conductive network more favorable for the movement of electrons. At the same time, the carbon material acts as the intermediate matrix to reduce the problem of material shedding or poor contact due to volume changes.

In this paper, we used a novel preparation process to synthesize RHC@SnO₂@rGO nanometer composites. The final products display superior electrochemical performance with high reversible capacity and good cycle performance due to their unique structural characteristics which makes the SnO₂ particles avoid agglomeration and shedding.

2. Experimental

2.1. Preparation of RH-cellulose

In a typical process, the RH should be washed with deionized water for several times. After that, the as-prepared products were collected and dried in a 60 °C oven. Then, 2 g of as obtained RH was immersed in 30 ml NaOH with the concentration of 2 mol 1⁻¹ under room temperature. And then the mixture was transferred to a teflon-lined stainless steel autoclave for 12 h at 180 °C. The obtained product was filtered when cooling to room temperature and washed with deionized water until the pH of the filtrate was 7. After being refluxed with 2 mol/L HCl solution at 80 °C in a water bath for 2 h, the pea green precipitate was collected and washed with deionized water until the pH was 7. The obtained sample was named as RH-Cellulose.

2.2. Preparation of GO

Graphene oxide was synthesized using a modified Hummer’s method. 1.0 g NaNO₃ was added into 32 ml concentrated sulfuric acid, then the mixture was stirred in an ice bath. 1.0 g natural graphite was added into the solution when it was stirred evenly. After that, keep stirring for an hour at a slow pace. Subsequently, KMnO₄ (4.5 g) was slowly added into the above mixture under continual stirring at 46 °C for 1 h. 50 ml distilled water was added slowly into the mixture and it was heated for 30 min at 98 °C. The remaining unreacted KMnO₄ in above mixture was removed by the reaction with 40 ml of 30% hydrogen peroxide. The dark brown precipitate was obtained by centrifugation and repeatedly washed with 5% dilute hydrochloric acid and deionized water until pH was 7. At last the GO was obtained using freeze-drying technology.

2.3. Preparation of RHC@SnO₂@rGO composites

The cellulose obtained in 1.2 g of RH was dispersed in 120 ml deionized water. SnCl₂ · 2H₂O (0.42 g) was dissolved in a small amount of ethanol, and the dissolved solution was poured into the cellulose suspension. Then 0.06 g GO was added to the mixture solution. After that the above solution was sonicated for 2 h, and then it was carried out in a reaction vessel at 200 °C for 36 h. The cooled solution was washed with deionized water and ethanol until the pH was 7. Then the product was dried in a 60 °C oven overnight. Finally, the dried sample was carbonized in a tube furnace at 500 °C for 2 h under the protection of argon, and the final sample was denoted as RHC@SnO₂@rGO. For comparison, the RHC@SnO₂ and rGO@SnO₂ composites were synthesized in the same method.
2.4. Characterization
The measurement of powder x-ray diffraction (XRD) was carried out by a Siemens D5000 x-ray diffractometer based on Cu K radiation. The raman spectroscopy was tested by a Renishaw in Via instrument. X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Escalab250Xi, Al-Kα as x-ray source) were performed to evaluate the valence state of the C, O and Sn elements on the surface of sample. The morphologies of these materials were observed by a Cold Field Scanning electron microscope (JEOL JSM-7500F) and a transmission electron microscope (JEOL JEM-2100F). The specific surface area and pore size distribution of the materials were measured using nitrogen adsorption–desorption measurements (Micromeritics, ASAP 2020). Thermogravimetric analysis (TGA) was performed by using an STA 449 Jupiter (NETZSCH) thermogravimetry analyser.

2.5. Electrode fabrication and electrochemical measurements
The active material with a mass fraction of 80% is mixed with a carbon black having a mass fraction of 10% and a polyvinylidene difluoride (PVDF) binder having a mass fraction of 10% in n-methyl-2-pyrrolidone (NMP). A uniform slurry is formed and uniformly adhered to the copper foil to form a working electrode. The prepared working electrode was dried in a vacuum oven at 120 °C for 12 h, and then the copper foil was manually pressed into small pieces having a diameter of about 12 mm. Lithium foil is used as the counter electrode and the reference electrode. In a mixture of ethyl carbonate and diethyl carbonate at 50:50 w/w, 1 M LiPF₆ was used as the electrolyte. Cyclic voltammetry was performed on a CHI660C electrochemical workstation with a scan rate of 0.1 mV s⁻¹ at a voltage window of 0–3.0 V. On the terrestrial (CT2001A) battery test system, a constant current charge and discharge test was performed at a rate of 0.2 C between 0.01 V and 3.0 V. Electrochemical impedance spectroscopy was performed at the CHI660C electrochemical workstation with a frequency range from 10 kHz to 10 MHz.

3. Result and discussion

3.1. Preparation procedures
The synthesis process of the RHC@SnO₂@rGO nanocomposite is shown in figure 1: Graphite oxide has many oxygen–containing functional groups on their surface. Sn²⁺ will combine with hydroxyl during the ultrasound stage. In the hydrothermal process, Sn²⁺ which deposited on the surface of GO will be oxidized to SnO₂ and GO will be reduced to rGO at the same time. In the meantime, through a series of hydrolysis reactions, rice husk cellulose will transform into RHC during that process. The surface of RHC also contains many oxygen–containing functional groups which will deposit a lot of tin oxide particles. The RHC and rGO may be combined with each other in two ways: 1. The functional groups of rGO and RHC could experience the esterification reaction between hydroxyl and carboxyl, which makes them combine together; 2. The RHC will combine with SnO₂ on the surface of rGO. Therefore, the three substances will react with each other in the hydrothermal phase to form a multi-level structure of RHC@SnO₂@rGO composite.

3.2. Morphological and structural characterizations
The C and rGO in the sample can be clearly seen through Raman spectroscopy. Figure 2(a) shows the Raman spectra of the RHC@SnO₂@rGO, rGO@SnO₂ and RHC@SnO₂ composites, in which we can observe the typical carbon material spectra. The characteristic peaks around 1595 cm⁻¹, 1594 cm⁻¹, and 1590 cm⁻¹ correspond to the G bands of RHC@SnO₂@rGO, rGO@SnO₂, and RHC@SnO₂, respectively, which is produced by stretching the sp² atom in a carbon ring or a long chain. And the characteristic peaks around 1367 cm⁻¹, 1355 cm⁻¹, and 1361 cm⁻¹ correspond to the D bands of the materials, respectively, which is mainly affected by boundaries, defects and disordered carbon. Usually I_D/I_G is an important indicator for evaluating the crystallinity of carbon materials. In addition, the characteristic peak near the 617 cm⁻¹ (B band) effectively indicates the presence of SnO₂. The I_D/I_G ratio of the RHC@SnO₂@rGO and RHC@SnO₂ are 1.02, and 0.85, respectively. The I_D/I_G ratio of RHC@SnO₂@rGO is higher than RHC@SnO₂, which may be attributed to the fact that the graphene sheet after chemically peeling usually contains a smaller sp² domain, whereas the small sp² domain usually results in a higher I_D/I_G ratio [23, 24]. Compared with RHC@SnO₂, the clearer D band indicates that there are more boundaries and defects in the structure of RHC@SnO₂@rGO, which will provide more reactive sites and increase the reaction rate on the surface of the material to increase storage capacity for LIBs.

XRD is commonly used to explore the crystallinity of materials. The characteristic peak of GO is about 12°, which represents the weak Van der Waals force between GO layers. As shown in figure 2(b), the typical diffraction peaks of GO were not observed in the RHC@SnO₂@rGO, rGO@SnO₂, and RHC@SnO₂ samples, which indicate GO was reduced to rGO during hydrothermal process. The strong diffraction peak of the samples at around 22° can respond to the reflections from (002) crystal planes of parallel-stacked graphene sheets.
The four main broad peaks of (110), (101), (200) and (211) crystal planes are attributed to the SnO$_2$ phase (JCPDS 41-1445), indicating the formation of tetragonal SnO$_2$ nanocrystals. The XRD patterns of RHC@SnO$_2$@rGO, rGO@SnO$_2$ and RHC@SnO$_2$ are very similar, and all the characteristic peaks are similar to the rutile phase SnO$_2$ (JCPDS 41-1445) [20], which indicates the crystal structure of SnO$_2$ still unchanged even in the presence of carbon. All three patterns showed broad diffraction peaks indicating fine grain size of the SnO$_2$ nanocrystals.

The chemical and oxidation states of the surface of RHC@SnO$_2$@rGO were identified by x-ray photoelectron spectroscopy (XPS). According to the scanning spectrum (figure 2(c)), it can be seen that there are only C, Sn, and O elements in the sample. This is consistent with the XRD results. And the atomic percentage (at%) of C, O and Sn were 56.57, 29.87 and 13.56, respectively. The high-resolution XPS spectrum of Sn 3d is shown in figure 2(d). The Sn spectrum has two peaks corresponding to Sn 3d$_{3/2}$ and 3d$_{5/2}$, respectively, and their binding energies are 495.48 eV and 487.03 eV, respectively, which further demonstrating the presence of SnO$_2$ in RHC@SnO$_2$@rGO.

In order to obtain the surface morphology of the material, we used a field emission scanning electron microscope (FESEM) to characterize RHC@SnO$_2$@rGO, rGO@SnO$_2$ and RHC@SnO$_2$. The multi-stage structure of RHC, SnO$_2$ and rGO is clearly seen from figure 3(a) due to the interaction between the three phases in the hydrothermal phase. Figures 3(b) and (c) correspond to the morphology of rGO@SnO$_2$ and RHC@SnO$_2$, respectively. It can be seen from the figure 3(c) that the agglomeration of SnO$_2$ which are deposited on the corresponding carbon matrix are more serious than it in figure 3(a). The main reason is that the addition of graphene reduces the pressure of SnO$_2$ loaded on RHC, which is conducive to improving the electrochemical properties of materials. Figure (a$_1$) is an enlarged view of the red box in figure (a), we can see that the spherical SnO$_2$ is evenly distributed on the carbon material substrate. We use element mapping to further explore the distribution of elements in the RHC@SnO$_2$@rGO composite. As shown in figures 3(a$_2$)−(a$_4$), C, Sn and O appear almost in the entire selected region, which indicates that the connection between the SnO$_2$ nanocrystal and the carbon skeleton is tight, thereby ensuring high electrical conductivity and structural stability of the composite. Figure 3(d) is the EDS corresponding to figure (a$_1$). It can be seen from the figure that the presence of the Si element is due to the presence of the silicon wafer, and thus may be disregarded. In addition, the mass percentages of Sn, O, and C elements are 43.6%, 39.6%, and 16.9%, respectively.

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To further understand the topographical features of RHC@SnO$_2$@rGO, we characterized the samples by transmission electron microscopy (TEM) and high resolution TEM (HRTEM). Figure 4(e) shows that a large number of SnO$_2$ NPs are randomly deposited on a carbon substrate. As shown in figure 4(f), we can clearly see the lattice fringes of SnO$_2$ NP by HRTEM, in which the 0.26 nm wide lattice fringes correspond to the (101) plane of SnO$_2$. As shown in figure 4(c), compared with RHC@SnO$_2$, the SnO$_2$ NPs were grown within the rGO network, which can efficiently prevent the aggregation and restacking of nanoparticles. And the interfacial distance of 0.33 nm can be observed by HRTEM of rGO@SnO$_2$ in figure 4(d), which can be indexed as the (110) plane of rutile SnO$_2$. The TEM and HRTEM images as shown in figures 4(a), 4(b) give the details of the distribution of RHC@SnO$_2$@rGO. In addition to observing corrugated graphene sheets and SnO$_2$ NPs, we also found RHC on the surface of SnO$_2$ NPs. This indicates that the RHC is not only in contact with the graphene sheet, but also the surface is covered by the SnO$_2$ NPs. The three formed a multi-level structure. Therefore, SnO$_2$ NP is entangled on the three-dimensional carbon skeleton, which provides a conductive carbon network that promotes electron transfer and reduces volume changes, thereby improving the electrochemical performance of the anode material as a lithium ion battery.

We characterized specific surface area and pore size RHC@SnO$_2$@rGO using nitrogen adsorption - desorption isotherms. As shown in figures 5(a), (b), the isotherm is a typical nitrogen adsorption branch type IV, with obvious hysteresis loop, described the presence of mesoporous structure. Adsorption - desorption isotherm hysteresis loop closure can be divided into type H3, indicating the presence of a large number of slit apertures in the material structure. Formation of cracks due to superimposition of the material is flaky, massive, spherical structure. The BET model shows that the specific surface area of RHC@SnO$_2$@rGO is 128.02 m$^2$ g$^{-1}$. Shown in figure 5(b), RHC@SnO$_2$@rGO wide distribution of pore size distribution in the range of 1-20 nm, an average pore diameter of 5.26 nm. The larger the specific surface area, the more electrochemical active sites of lithium ion insertion/extraction, which is beneficial to increase the capacity. A large number of pores in the RHC@SnO$_2$@rGO provide more diffusion path of lithium ions, promote electron transport.

We investigated the thermal properties, composition and carbon content of RHC@SnO$_2$@rGO, RHC@SnO$_2$ and rGO@SnO$_2$ by thermogravimetric analysis (TGA) under air. The TGA curves for RHC@SnO$_2$@rGO, RHC@SnO$_2$, rGO@SnO$_2$ and rGO are given in the figure 6. We saw that all samples reacted rapidly at temperatures ranging from 320 to 530 °C. Among them, the reaction of RHC@SnO$_2$ and
RHC@SnO₂@rGO samples is divided into two temperature ranges of 320 °C~380 °C and 380 °C~530 °C. The most likely cause is that RHC is mainly decomposed in the weight loss of 320 °C~380 °C, and then the weight loss in the range of 380 °C~530 °C is mainly due to rGO combustion. After calculation, we obtained that the carbon content in the RHC@SnO₂@rGO, RHC@SnO₂ and rGO@SnO₂ composites is about 28%, 22% and 13%, respectively. In addition, we could see that rGO still has a certain weight after high temperature calcination, which may be due to the weight of ash remaining after calcination.

Figures 7(a)–(c) shows the charge and discharge curve of RHC@SnO₂, rGO@SnO₂ and RHC@SnO₂@rGO with a voltage range of 0.01 to 3 V and a current density of 0.2 C, 1 C=(C w% * 372 + SnO₂ w% * 782) mA g⁻¹. The discharge and charge specific capacities of RHC@SnO₂@rGO are 2440.6 mA h g⁻¹ and 1525.9 mA h g⁻¹, respectively, and the initial coulombic efficiency is 62.5%, 37.5% irreversible capacity loss due to decomposition of solid electrolyte interface (SEI) layer and electrolyte and formation of Li₂O [26]. The initial coulomb efficiency of the RHC@SnO₂@rGO composite is much higher than that of the rGO@SnO₂. It is caused by the prevention of direct contact between electrolyte and some SnO₂ NPs by amorphous carbon, thus decreasing the formation of irreversible SEI layers. In addition, Amorphous carbon can form a stable SEI layer in the charge and discharge cycle, which can effectively reduce the transport resistance of lithium ions and prevent the formation of a new SEI layer during the cycle to improve the coulombic efficiency of RHC@SnO₂@rGO.

Figure 7(d) shows the cycling performance of RHC@SnO₂@rGO electrode. After 100 cycles, the specific capacity of the RHC@SnO₂@rGO electrode was as high as 1206.9 mA h g⁻¹, which is much higher than the theoretical capacity of SnO₂ (782 mA h g⁻¹). In contrast, the discharge capacity of the RHC@SnO₂ and rGO@SnO₂ electrodes have been reduced to 403 mA h g⁻¹ and 165 mA h g⁻¹ after 100 cycles. It is clear that the cycling performance of the RHC@SnO₂@rGO electrode is superior to that of the RHC@SnO₂ and rGO@SnO₂. The reason for the excellent cycle performance is that the SnO₂ NPs have a multi-level structure and there is a
strong internal chemical bond between the SnO₂ NPs and the carbon skeleton, which prevents the SnO₂ NPs from leaving the three-dimensional network during the cycle. The Incorporation of graphene can effectively improve the stability of the RHC@SnO₂@rGO composites and increase the active sites, thereby increasing the charge-discharge specific capacity of the RHC@SnO₂@rGO composites. The capacity of the RHC@SnO₂@rGO during the cycle is slightly fluctuated. This may be due to the large volume change of the material during charging and discharging, which causes the material to break slightly. The newly exposed surface reacts with the electrolyte to form a new SEI film and consumes a part of lithium ions. When the cycle is repeated for several cycles, the SEI film tends to stabilize and the capacity is increased by a small amount.

Figure 4. TEM images (a), (c) and (e) and HRTEM images (b), (d) and (f) of RHC@SnO₂@rGO, rGO@SnO₂ and RHC@SnO₂ samples.

Figure 5. Nitrogen adsorption-desorption isotherms (a) and pore sizes distribution (b) of RHC@SnO₂@rGO.
Figure 8 shows the rate capability of RHC@SnO\textsubscript{2}@rGO, RHC@SnO\textsubscript{2} and rGO@SnO\textsubscript{2} at different current rates (0.2C–5C). It can be seen that the capacities of the RHC@SnO\textsubscript{2}@rGO electrodes at 0.2C, 0.5C, 1C, 2C, and 5C are 1322, 935.3, 718.7, 504.9, and 259 mA h g\(^{-1}\), respectively. In contrast, the RHC@SnO\textsubscript{2} and rGO@SnO\textsubscript{2} electrodes have much lower capacity. Moreover, when the current density is recovered to 0.2C, the capacity of RHC@SnO\textsubscript{2}@rGO can be recovered to 941 mA h g\(^{-1}\). The RHC@SnO\textsubscript{2}@rGO electrode has good capacity retention and excellent rate performance.

RHC@SnO\textsubscript{2}@rGO, RHC@SnO\textsubscript{2} and rGO@SnO\textsubscript{2} were assembled as electrode materials into a half-cell with a voltage range of 0–3 V and a scan rate of 0.1 mV s\(^{-1}\). The first three cyclic voltammetry curves (CV) were
shown in figures 9(a)–(c). The curves of the three sets of samples are very similar, therefore, a sample of RHC@SnO2@rGO is used. In the first cycle of the RHC@SnO2@rGO, three clearly defined cathodic peaks were observed. At the vicinity of 0.8 V is obvious and in the 0.02 V and 1.6 V nearby are tiny. The peak near 0.8 V is most likely to form SEI layers on the surface of the active material, and SnO2 is reduced to Sn, while Li2O is formed, as described in SnO2 + 4Li + 4e− → Sn + 2Li2O. From the second lap, the peak value is significantly reduced, and similar phenomena appear in rGO@SnO2 and RHC@SnO2, but the peak intensity of RHC@SnO2@rGO is much smaller than the peak intensity of rGO@SnO2 because of the introduction of carbon reduces the irreversible reaction. The alloy of Sn corresponding to the peak at 0.02 V forms a Li1.5Sn alloy, as shown by (Sn + xLi + xe− ↔ Li1.5Sn, 0 ≤ x ≤ 4.4). The peak near 1.60 V may be due to the reaction of Li with carbon materials [27]. Li reacts with the C skeleton to form LixC, as given in (C + xLi + xe− ↔ LixC). In the

Figure 8. Rate performance of RHC@SnO2@rGO, RHC@SnO2 and rGO@SnO2 at 0.2–5 C.

Figure 9. Cyclic voltammogram (CV) profiles of (a) RHC@SnO2@rGO, (b) rGO@SnO2 and (c) RHC@SnO2. (d) Nyquist plots of RHC@SnO2@rGO, rGO@SnO2 and RHC@SnO2.
anode scan, the electrode shows three peaks, and the peak near 0.23 V corresponds to the delithiation reaction of Li,C. A peak near 0.70 V corresponds to Li detaching from Li,Sn, and a broad peak at 1.25–2.5 V belongs to Sn oxidation to SnO2. After the second cycle, the continuous CV curve is basically the same, indicating that the material can be used as a very stable anode material for LIB.

In addition, the electrochemical impedance spectroscopy (EIS) was measured to further study the mechanism of electrochemical performance of RHC@SnO2@rGO, RHC@SnO2, and rGO@SnO2 as shown in figure 9(d). The Nyquist diagram of RHC@SnO2@rGO, RHC@SnO2, and rGO@SnO2 consists of a semicircle in the high frequency region and a straight line in the low frequency region. And in the equivalent circuit (inset), $R_{el}$ is the sum of the resistance of the electrolyte, diaphragm and electrical contacts in the high frequency region. $R_{ct}$ represents a charge transfer resistor. The slope of the low frequency region represents the Warburg impedance, and the CPE represents a constant phase angle element containing a double layer capacitor. Compared to the other two samples, the semicircular diameter of the RHC@SnO2@rGO is much smaller, indicating that enhance electron and lithium ion transport. The smaller resistance of RHC@SnO2@rGO can be attributed to the uniform electron and lithium ion transport. The smaller resistance of RHC@SnO2@rGO can be attributed to the uniform distribution of SnO2 NPs and the formation of special multi-level structures. Moreover, the rapid charges transfer help improve the electrochemical performance of RHC@SnO2@rGO.

4. Conclusions

In summary, in this study, we successfully fabricated the multi-level structure of RHC@SnO2@rGO composites by a novel synthetic process. Compared to RHC@SnO2 and rGO@SnO2, the composite exhibits excellent electrochemical performance with a high capacity of 1206.9 mA h g$^{-1}$ after 100 cycles at a current density of 0.2 C. The excellent electrochemical performance is mainly due to the synergistic effect of carbon framework and SnO2 NPs. The unique multi-level structure effectively buffers the volumetric expansion of SnO2 NPs and avoids SnO2 NPs shedding. The solution is not only applicable to SnO2, but also providing a new idea for other electrode materials which are used in LIB.

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