Capacity Contribution Mechanism of rGO for SnO₂/rGO Composite as Anode of Lithium-ion Batteries

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Abstract
Compared with ordinary graphite anode, SnO₂ possesses higher theoretical specific capacity, rich raw materials and low price. While the severe volume expansion of SnO₂ during lithium-ion extraction/intercalation limits its further application. To solve this problem, in this work the reduced graphene oxide (rGO) was introduced as volume buffer matrix of SnO₂. Herein, SnO₂/rGO composite is obtained through one-step hydrothermal method. Three-dimensional structure of rGO could effectively hinder the polymerization of SnO₂ nanoparticles and provide more lithium storage sites attributed to high specific surface area and density defects. The initial discharge capacity of the composite cathode is 959 mA·h·g⁻¹ and the capacity remained at 300 mA·h·g⁻¹ after 1000 cycles at 1 C. It proved that the rGO added in the anode has a capacity contribution to the lithium-ion battery. It changes the capacity contribution mechanism from diffusion process dominance to surface driven capacitive contribution. Due to the addition of rGO, the anode material gains stable structure and great conductivity.

Keywords: SnO₂/rGO composite, Lithium-ion battery, Capacity contribution, Diffusion coefficients

1 Introduction
Lithium-ion batteries have realized large-scale application in electric and hybrid vehicles. In the past few decades, SnO₂ has attracted extensive attention as electrode material. Compared with ordinary graphite anode materials, SnO₂ possesses higher theoretical specific capacity (790 mA·h·g⁻¹), rich raw materials and low price. While the volume expansion of SnO₂ during lithium-ion extraction/intercalation reaches more than 50%, the high stress caused by volume expansion may lead to the fracture failure of electrode material which makes the specific capacity of the material decrease rapidly, while the rate performance and cycle stability decreasing [1–3]. Therefore, the key to realize the application of SnO₂ cathode materials in lithium-ion batteries is to find ways to effectively slow down the volume dilatation effect of SnO₂ during the lithium-ion extraction/intercalation process and upgrade the electrochemical performance of electrode materials [4–7]. Graphene is a 2D material with good conductivity and high specific capacity. Graphene nanosheets can not only effectually prevent the volumetric change and particle aggregation of SnO₂, but also improve the conductivity. As an active material for lithium storage, graphene nanosheets keep the structural integrity of electrode [8–10]. Chen et al. synthesize a reduced graphene and SnO₂ nanospheres composite and obtain good performance in the application of lithium-ion batteries or sodium-ion batteries [11]. Zhou et al. built a SnO₂/GO structure by hydrothermal method [12]. It’s worth noting that they researched the influence of GO dosage in SnO₂/GO anode and found that the lithium ions storage capability increases with the raise of GO dosage. Lu et al. focused on the drying process after hydrothermal process [13]. By comparing
anodes treated by spray-drying and freeze-drying, novel composition of SnO\textsubscript{2} and GO achieved after spray-drying process obtained favorable lithium-ion transmission during charging/discharging process. The combination of rGO and anode materials of lithium-ion batteries or sodium-ion batteries can increase the capacitance contribution, which has been confirmed by much research [14–17]. While, for SnO\textsubscript{2}, the influence of rGO on capacitance contribution rate has not been studied. In this work, we report to synthesize SnO\textsubscript{2}/rGO composite by the sample single step method. We analyze the lithiation/delithiation process and find that the addition of rGO will significantly improve the mobility of lithium ions. When the scan rate comes to 1 mV·s\textsuperscript{-1}, the capacitive contribution rate raises from 56% to 71% after the addition of rGO. It confirms that the addition of rGO changes the capacity contribution mechanism from diffusion process dominance to surface driven capacitive contribution dominance attributed to high specific surface area, abundant defects and high conductivity of rGO.

2 Materials and Methods

2.1 Preparation of SnO\textsubscript{2}/rGO Composite

The GO dispersion was prepared by the oxidation of graphite powder in acidic environment according to a modified Hummers method [18–20]. The as-obtained aqueous suspension of GO was dispersed under ultrasonication for 6 h and purified with deionized water. In a typical synthesis, 0.904 g (4 mmol) SnCl\textsubscript{2} 2H\textsubscript{2}O, 2.3528 g (8 mmol) sodium citrate, 10 ml ethanol and 15 ml GO dispersion (2 mg·mL\textsuperscript{-1}) were mixed together to form a uniform solution on a magnetic stirrer. During magnetic stirring, the mixture will be ultrasonically treated for a period of time in order to make the solute fully dispersed. Then the mixture was transferred to a 30 ml reaction kettle for hydrothermal treatment at 180 °C for 6 h. Thereafter, the cooled down product was washed by continuous centrifugation method. Finally, the as-obtained product was dried at 60 °C for the whole day, the ratio of rGO to SnO\textsubscript{2} is about 4:1. The synthesizing procedure of SnO\textsubscript{2} nanoparticles is just in common with that of SnO\textsubscript{2}/rGO in which GO dispersion was replaced by equal amount of deionized water.

2.2 Electrochemical Measurement

CR2025 coin cells were assembled for the following electrochemical investigation. In order to prepare the anode, active materials, conductive carbon black and polyvinylidene difluoride were mixed together to form slurry by 8:1:1. The active material loaded on the Cu foil electrode was about 1.6 mg cm\textsuperscript{-2}. 1 M LiPF\textsubscript{6} in ethylene carbonate was added to dimethyl carbonate (1:1, V/V) as the electrolyte during the battery assembly process. Constant current charge and discharge test at various rates were performed by LAND CT2001A battery testing system within a voltage range of 0.001–3 V and the electrochemical characterizations were performed by electrochemical workstation (CHI660C, Shanghai).

2.3 Materials Characterization

The microstructure and composition were analyzed by X-ray diffraction (XRD, Rigaku D/max 2500 pc X-ray diffractometer), Fourier transform infrared spectroscopy (FTIR, Nicolet-6700 Thermofisher), Raman spectra (HORIBA Jobin Yvon LabRAM HR800) and X-ray photoelectron spectroscopy (XPS, Thermo Scientific, Waltham, MA, USA). The microstructure was explored by scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, FEI, Talos F200). The specific surface area was tested by N\textsubscript{2} adsorption/desorption (NOVA 2000, Quanta chrome).

3 Results and Discussion

For the sake of analyzing the morphology and nanostructure of hydrothermal product, SEM test was carried out on SnO\textsubscript{2} and SnO\textsubscript{2}/rGO powders. Figure 1a shows the pure SnO\textsubscript{2} obtained by hydrothermal treatment presents spherical morphology with a diameter of around 1 to 3 microns. Figure 1b illustrates that SnO\textsubscript{2} spheres (with a diameter of approximately 3 μm) are composed of several spherical nanoflowers with a diameter of about 200 nm.
As for SnO$_2$/rGO (Figure 1c and d), spherical SnO$_2$ are equally absorbed on the surface of rGO nanosheets, meanwhile the SnO$_2$ spherical structure remains unchanged. It’s obviously that SnO$_2$ nanoflowers grown on rGO nanosheets, while the size is obviously smaller than that of SnO$_2$ powders which is about 100 nm. The reduction of the diameter of the nanosphere means the increase of the specific surface area.

TEM spectra (Figure 1e, f) further illustrate the morphology and nanostructure of as prepared materials. It is highly consisted with the results obtained in previous SEM test. SnO$_2$ nanoparticles are absorbed onto the rGO nanosheets with favorable connection. As for high-resolution TEM spectra (Figure 1f), SnO$_2$ crystal grains are relatively visible and the rGO nanosheets could be obviously observed and the lattice spacing of 0.33 nm, corresponding to the (110) planes of tetragonal SnO$_2$. X-ray diffraction (XRD) is tested for the component analysis of SnO$_2$/rGO and SnO$_2$ powder (Figure 2a). As for the XRD spectroscopy of SnO$_2$/rGO, diffraction peaks in the curve could correspond to that of tetragonal tin dioxide with cassiterite structure (JCPDS Card No.41-1445). While, it’s of particular interest that, the XRD spectroscopy of SnO$_2$ failed to correspond the standard peak one-to-one. This is because the crystallinity of SnO$_2$ obtained after 6 h of hydrothermal reaction is not high enough, which shifts the peak of 33.8° to the left [22]. Since SnO$_2$/rGO failed to detect the diffraction peak of rGO, the XRD spectrum results could not prove the existence of rGO.

For the common homonuclear diatomic pairs in carbon-based materials, their Raman activity will be strong, so their Raman peaks can be easily detected in Raman spectra, thus the Raman spectroscopy was used for further composition analysis (Figure 2b). There are two obvious peaks appearing in ~ 1350 cm$^{-1}$ and ~ 1580 cm$^{-1}$ corresponding to the D and G bands of graphene respectively. The $I_D/I_G$ significantly increases from 0.98 of GO to 1.76 of SnO$_2$/rGO, which indicates that the sp2 domain of SnO$_2$/rGO composites is smaller. Meanwhile it illustrates that oxygen content of GO reduced during hydrothermal process [21].

In order to further analyze the components and verify the partial reduction of GO during the hydrothermal process. FT-IR spectra of as-prepared nanocomposites are plotted (Figure 2c). Both spectra show the peak of 3440 cm$^{-1}$ and 1629 cm$^{-1}$ which correspond to O-H stretching vibrations of absorbed water molecules and O-H bending vibrations, the absorption band of around 1220 cm$^{-1}$ corresponding to C-O. After compounding with SnO$_2$, similar oxygen-containing groups are found in the SnO$_2$/rGO spectra, which illustrates that GO is partially reduced in hydrothermal treatment, and a strong peak at 669 cm$^{-1}$ is attributed to O-Sn-O stretching mode [22, 23]. N$_2$ adsorption/desorption test is carried out to analyze the specific surface area of SnO$_2$ particles (purchase from enterprise), SnO$_2$ nanoflower and SnO$_2$/rGO composite in Figure 2d. The BET specific surface area of SnO$_2$ particles is only 23.16 cm$^2$·g$^{-1}$, while it comes to 63.17 cm$^2$·g$^{-1}$ when the morphology of SnO$_2$ turns into spherical nanoflower. As for SnO$_2$/rGO composite, it reaches 126.74 cm$^2$·g$^{-1}$, which is much higher than that of SnO$_2$. It illustrates that the assistance of rGO could significantly increase the specific surface area [13]. The larger specific surface area means that SnO$_2$/rGO can have better contact with electrolyte and absorb more lithium ions at the same time.

To obtain the exact composition of SnO$_2$/rGO powders, we tested it with X-ray photoelectron spectroscopy (XPS), since XPS could display the chemical environment of Sn, O and C elements. Figure 3a displays the XPS survey spectra of SnO$_2$/rGO powders. In C1s fitting patterns (Figure 3b), there are C-C bond at 284.7 eV, C-O bond at 285.6 eV and C=O bond at 286.8 eV, in which C-C bond takes an absolute dominant position. It corresponds to a common rGO chemical bond composition as mentioned in previous study [24]. In O1s spectroscopy (Figure 3c), Sn-O bond at 531.6 eV and C-O-Sn bond at 532.8 eV make different contribution in fitting patterns. The obvious C-O-Sn bond fitting peak indicates that there exists surpassing chemical bonding among SnO$_2$ and rGO [25]. In Sn3d spectrum (Figure 3d), there are two obvious peaks located at 495.9 eV and 487.6 eV, which correspond to Sn3d 3/2 and Sn3d 5/2 respectively [26]. The peaks generally consist with that reported in pure SnO$_2$ powder; it illustrates that major constituent of SnO$_2$/rGO powders is SnO$_2$. For the sake of researching the influence on lithium-ion battery performance after compounding with rGO,
Sn + xLi^+ + xe^- → Li_xSn(0 ≤ x ≤ 4.4).

When the specific current reaches 0.1 C, the galvanostatic discharge-charge curves of 1st, 2nd, 5th and 10th for the SnO_2/rGO are shown in Figure 4b. In the first cycle, the discharge and charge capacity of the composite are 1114.3 mA·h·g^{-1} and 731.9 mA·h·g^{-1}, respectively. Compare our study with other SnO_2/rGO materials as the anode for Li ion batteries, the capacitance performance of SnO_2/rGO at 0.1C (1114.3 mA·h·g^{-1}) is superior to SnO_2 NPs/rGO (1100 mA·h·g^{-1}) [11], CGN/ SnO_2 composites (1048.7 mA·h·g^{-1}) [32] and SnO_2-RGO (665 mA·h·g^{-1}) [33]. A voltage plateau appears at approximately 1 V in the first cycle, while it can’t be observed in the subsequent cycles. It mainly due to irreversible reduction of SnO_2 and electrolyte decomposition. In the following profiles, the voltage plateaus can be observed in the ranges of 0.01–0.5 V and 0.5–1 V corresponding to combination reaction of Li-Sn alloy. These results are highly consistent with the verdicts obtained in previous CV tests.

The cyclic performance and coulombic efficiency of two materials under current density of 0.1 C is displayed in Figure 4c. The initial cycle of SnO_2/rGO galvanostatic discharge-charge give out 959.2 mA·h·g^{-1} for discharge capacity. In contrast, SnO_2 delivers a discharge capacity of 754.6 mA·h·g^{-1} with coulombic efficiency of 59.04%. It’s obviously that, SnO_2/rGO composite possess much higher discharge capacity and coulombic efficiency than that of SnO_2 nanoparticles. Besides, the decline of discharge capacity with the increase of cycle number for SnO_2/rGO composite is significantly faster than that of SnO_2 nanoparticles. When the cycle number comes to 100, SnO_2/rGO remains discharge capacity of 469.6 mA·h·g^{-1}, and SnO_2 nanoparticles reach to 121.1 mA·h·g^{-1}. The above phenomenon is mainly caused by the following two reasons. Firstly, the SnO_2/rGO composite possess much smaller grain size, which will lead to more active materials participating in the reaction during charge and discharge. Secondly, rGO provides an attached framework for SnO_2. This structure puts out an effective buffer for the volume change in the reaction process. Meanwhile it facilitates the insertion and detachment of lithium ions. The rate performance of two materials at gradient current densities are displayed in Figure 4d. After 10 cycles charge-discharge process, SnO_2/rGO composite remains capacity of 773.7 mA·h·g^{-1} at 0.1 C, while SnO_2 nanoparticles come up to 500.9 mA·h·g^{-1} at the same condition. With rate raising up from 0.1 C to 2 C, rate capability diminishes gradually, moreover, the lithium ions storage capability difference of two materials becomes much
larger. The reversible capacity of SnO$_2$/rGO composite come up with 210 mA·h·g$^{-1}$, demonstrating admirable reversible capacity and structure stability under large steady current density [12]. When the rate turns back to 0.1 C, the rate capability of SnO$_2$/rGO composite is basically restored indicating the great reversible capacity. As for Figure 4e, SnO$_2$/rGO displays great long-cycle stability even at current charge and discharge rate of 1 C. When the cycle number comes to 1000, the discharge capacity still remains about 300 mA·h·g$^{-1}$. Obviously, the excellent rate performance and cycle stability are attributed to the addition of rGO. It remarkably improves the electrode material stability and provides more lithium ions storage sites [34].

EIS spectra were performed to determine the electrical conductivity and electrochemical kinetics of two electrodes (Figure 5a). The composition of the equivalent circuit was shown above the fitting plot, which can be used for quantitative analysis. A lower charge transfer resistance ($R_{ct}$) value of SnO$_2$/rGO composite (65.7 ohms) indicates that the electrode gains better kinetics after introducing rGO into SnO$_2$ nanoparticles. The reason is that rGO can amend the connections among SnO$_2$ nanoparticles and present sufficient electronic transmission channels which is favorable for electron transfer [12]. For the sake of further exploring the lithium-ion transfer mechanism, linear fitting of $Z'$ and $\omega^{-1/2}$ at low frequency were carried out in Figure 5b. Lithium-ion diffusion coefficient is a momentous parameter for
evaluating the performance of electrode materials. The following equation is applied to calculate the diffusion coefficients ($D_{Li}$) of lithium ions (Eq. (3)).

$$D_{Li} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2},$$  \hspace{1cm} (3)$$

where, $R$ represents gas constant, $T$ stands for Kelvin temperature, $A$ represents the area of electrode, $n$ is the number of electrons transferred during the reaction. $F$ is Faraday constant, $\sigma$ is the slope of $Z'$ vs $\omega^{-1/2}$ and $C$ is lithium-ion phase concentration [35]. From the date in Table 1, we can find that the $D_{Li}$ of SnO$_2$/rGO electrode is much larger than that of SnO$_2$. It illustrates that the structure of SnO$_2$/rGO composite is conducive to the electrolyte diffusion and facilitates Li$^+$ migration during lithiation/delithiation process.

The lithium storage kinetics of SnO$_2$/rGO anode were researched by contrasting CV profiles at different scan rates. By estimating the pseudocapacitive contribution, the high rates performance of SnO$_2$/rGO anode can be investigated. Meanwhile the influence in complexing rGO in SnO$_2$ would be further discussed. Figure 6a is the CV profiles of SnO$_2$/rGO composite under the larger current range as scanning rate raises from 0.1 mV·s$^{-1}$ to 2 mV·s$^{-1}$, the capacity contribution mechanism can be expressed by Eq. (4).

$$i = \alpha v^b,$$  \hspace{1cm} (4)$$

$$\log(i) = b \log(v) + \log(\alpha),$$  \hspace{1cm} (5)$$

where, $b$ value could be acquired by drawing $\log(i)$–$\log(v)$ curves and fitting the line to obtain the slope (Eq. 5). Generally, when $b = 0.5$, the capacity contribution is mainly determined by diffusion process, if $b = 1$, it represents to the typical capacitive charge storage for the surface faradaic redox reaction [36]. The $b$ value obtained from the fitting line of cathodic and anodic peaks are 0.85 and 0.80 for SnO$_2$/rGO composite in Figure 6b. It indicates that the capacitance contribution of capacitor driving in electrochemical behavior is larger than that of diffusion process for SnO$_2$/rGO anode. The $b$ value of SnO$_2$ anode is much closer to 0.5, suggesting that the capacitive contribution is mainly acquired by diffusion process for SnO$_2$ anode. The significantly higher $b$ value of SnO$_2$/rGO anode indicates that much larger specific surface area obtained by adding three-dimensional rGO is the main reason for the obvious increase of capacitive contribution. For the sake of investigating the capacity contribution mechanism, total current ($I$) is separated into two parts by Eqs. (6) and (7).

$$I = k_1 v + k_2 v^{1/2},$$  \hspace{1cm} (6)$$

$$I/v^{1/2} = k_1 v^{1/2} + k,$$  \hspace{1cm} (7)$$

where, $k_1 v$ and $k_2 v^{1/2}$ represents the current attributed to conversion behavior and diffusion-controlled reaction respectively [37]. As shown in Figure 6c and d, when the scan rate comes to 1 mV·s$^{-1}$, the capacitive contribution of SnO$_2$/rGO anode is 71%, which is significantly larger than that of SnO$_2$ anode (56%). This result shows that among two lithium storage mechanisms in SnO$_2$/rGO anode, the capacitive drive process takes an absolute dominant position owing to large specific surface area [38]. The capacitive contribution gets bigger and bigger in

| Materials   | $R_i$ (Ω) | $R_r$ (Ω) | $\sigma$ (Ω·s$^{-1/2}$) | $D_{Li}$ (cm$^2$·s$^{-1}$) |
|-------------|-----------|-----------|------------------------|--------------------------|
| SnO$_2$/rGO | 58.72     | 65.7      | 210                    | $1.7 \times 10^{-10}$  |
| SnO$_2$     | 85.15     | 97.4      | 313                    | $8.5 \times 10^{-11}$  |
SnO$_2$ nanoparticles, which is consistent with the result of that the structure of rGO could inhibit the aggregation of stability and rate performance [21]. Besides, it certifies capacitive behaviors. Meanwhile it is beneficial to cycling of storing lithium ions.

Conclusions

(1) In this paper, via a one-step hydrothermal synthesis, graphene was added to SnO$_2$ to alleviate the volume expansion of SnO$_2$ in the charging-discharging process of Li ion batteries.

(2) Taking the advantage of specific surface area, high conductivity and density defects of graphene, the aggregation of SnO$_2$ can alleviate structurally.

(3) The capacity contribution mechanism changed from diffusion dominated to surface driven capacitive contribution, which provided more sites for storing lithium ions.

(4) Even at high current density of 1C and long cycle of 1000 times, the specific capacity of SnO$_2$/rGO can maintain at 300 mA·h·g$^{-1}$ which has a better practical perspective.

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Author contributions

LD was in charge of the whole trial; QL wrote the manuscript; GZ, YQ, ZZ, JW and MZ assisted with sampling and laboratory analyses. All the authors read and approved the final manuscript.

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Competing interests

The authors declare no competing financial interests.

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