The origin of cycling enhanced capacity of Ni/NiO species confined on nitrogen doped carbon nanotubes for lithium-ion battery anodes

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A B S T R A C T

We demonstrate that the confinement effect of the NiO compound can directly enhance the electrochemical performance upon cycling. Fabricating the core-shell C-coated Ni/NiO nanofibers (e.g., Ni and NiO, nitrogen doped carbon respectively) composite electrode largely increases the capacity (1332 mAh g⁻¹ vs 718 mA h g⁻¹) and improve the long-term cycling stability. The High Angle Annular Dark Field results reveal that the doped pyridine-like nitrogen shell will divide the NiO into smaller nanoparticle during the charging and discharging process. In addition, the density functional theory calculation suggests the confined nanoscale NiO(Ni) will absorb and react with Li ions more easily. With cycling, smaller NiO/Ni nanoparticle will bring more active sites, leading additional interfacial lithiation capacity. At the same time, the confinement effect of the NiO compound further increases the capacity of the nanocomposites.

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1. Introduction

Li ion battery has been intensively utilized in portable electronics and show significant promise for applications [1–3]. The energy density and cycling performance of lithium ion batteries depend on the physical and chemical properties of both cathode and anode materials. Transitional metal oxides, such as NiO based nanomaterials have attracted considerable attention as potential substitutes for graphite because of their numerous appealing features, including abundance, low cost, environmental benignity, and high theoretical capacity [4–7]. Nanostructured coating can restrain the volumetric change in the electrode and prevent the aggregation of the active materials which can enhance the cycling stability of batteries [8–12]. For lithium ion anode materials, an effective implementation of this concept is to use a multilayer thin film structure comprised of Si (or other high capacity materials) and inert metal layers (e.g., Ti, Al, and Zn) [10,13–15]. Studies of Si-based multilayer electrodes show strong differences in reversible capacity and cycling stability as a function of the thicknesses of the buffer and active layers. The technical challenges of Li-alloying reactions (e.g., with Si) are similar to those found in the conversion reactions of metal oxides electrodes [10,15]. As for the NiO, study results [16] show that the lithiation of NiO involve the formation and decomposition of Li₂O, with the reduction and oxidation of metal nano-particles in the range of 5–10 nm in diameter. In particular, nanoscale confinement of nanosized metal oxide particles is believed to improve the lithiation and delithiation electrochemical performance.

In order to explore the critical role of nanoscale confinement effect in electrochemical process of the formation/decomposition of Li₂O, we design a core-shell C-coated Ni/NiO nanofibers composite electrode. In particular, NiO is a promising anode material for LiBs due to its high theoretical specific capacity (718 mA h g⁻¹), abundant material supply and low cost. As NiO has low electronic conductivity, it is always composites with conductive materials. These composite anodes exhibited high reversible capacity and excellent electrochemical performance. However, the capacity of NiO based anode usually shows a decrease during lithiation and...
delithiation process due to the formation of the SEI layer [16–22]. Interestingly, the increase in cycling induced capacity has been found in the NiO and other metal oxide electrodes upon long cycles. These phenomena may partly attribute to the activation of the conductive materials. Its origin arouses much attention and much effort has been devoted to the search. Nevertheless, the reason for the increased capacity with the cycling still remains unclear. One of the possible reasons is the lack of an effective model which can explain the activation mechanism based on experiment and calculation results. On the other hand, NiO based anodes are usually composited with other additives, increasing the difficulty to identify the confinement effect in electrochemical process.

Here, we design a core-shell C-coated Ni/NiO nanofibers composite electrode by employing the electrospinning and Chemical Vapor Deposition (CVD) methods. With the N-doped carbon coating, the core–shell C-coated Ni/NiO nanofibers exhibits remarkable reversible capacity and capacity retention. The formed nano reactor between the inner cavity of C-coated layer and NiO excludes other factor caused by the outside additives, and give an isolated space to explore the activation mechanism. The results find the nano reactor can facilitate effective lithiation and delithiation processes as well as NiO/Ni redox by confinement effect. In addition, the density functional theory calculation suggests that the confined NiO/Ni can absorb and react with Li ions more easily.

2. Experimental

2.1. Synthesis of C-coated Ni/NiO nanofibers

Firstly, C-coated Ni/NiO nanofibers electrocatalysts were fabricated by electrospinning–chemical vapor deposition method. In detail, 0.8 g PVP and 0.45 g Ni(AC)₂·4H₂O were dissolved in 10 mL ethanol and then magnetically stirred at room temperature for 12 h. Afterwards, the resulting homogeneous mixture was loaded into a spinneret which was linked to a high-voltage equipment with 15 kV working voltage. Aluminum foil was used as collector to gain the spinning sample at the rate of 2 ml h⁻¹ by syringe pump in the relative humidity of 30%, and the primary spinning sample was heated at 660 °C for 2 h at rate of 2 °C/min in a furnace. After the heating treatment, sample was grinded and then placed on horizontal quartz tube of furnace. The furnace reaction chamber was evacuated and flushed with N₂ for several times to remove oxygen and moisture, then the reactor was heated to 800 °C and evacuated and then heated at 660 °C for 2 h at rate of 2 °C/min in a furnace. After the CVD process, samples at around 300 °C were loaded in the reactor between the inner cavity of C-coated layer and NiO isothermally reduced over C-coated Ni/NiO nano reactor by the CVD treatment. The XRD diffraction peaks for carbon nanofibers electrocatalysts were assigned well to (111), (200), (220), (311) and (222) diffraction of NiO (JCPDS 65-0380), corresponding to (111), (200), and (220) of Ni (JCPDS 65-0380), respectively. Moreover, the intensity of NiO diffraction peaks was reduced over C-coated Ni/NiO nanofibers due to the existence of Ni, indicating partial NiO was reduced into Ni in the process of carbon coating by the CVD treatment. The XRD diffraction peaks for carbon layers can be probed at 21.2°, 30.3°, 31.6°, 76.1°, which may be attributed to the produced C-coated layer. Raman spectroscopy is often used to investigate the production and its graphitization structure of carbon nanomaterials. As seen in Fig. 1b C-coated Ni/NiO nanofibers sample presents two primary peaks at 1342 and 1576 cm⁻¹ corresponding to the vibrations of carbon atoms in the disordered graphite structure (i.e., defects, named D band) and the E₂g mode of graphite (i.e., graphite structure, named G band), and thus the intensity ratio of G band to D band (I_D/I_G) presents the graphitization degree. In Fig. 1b, we can see that I_D/I_G is about 0.6, indicating the existence of poor graphite structure for C-coated Ni/NiO nanofibers.

To further investigate the surface composition of NiO nanofibers and C-coated Ni/NiO nanofibers, the XPS spectra (Fig. 1c) of Ni 2p for the two samples distributions the regions of 850–857.5 eV and 875.5–866 eV, corresponding to Ni 2p3/2 and satellite peak. The Ni 2p3/2 peak of two samples can be deconvoluted into two components centered at 871.8 and 874.89 eV, ascribable to the characteristic of Ni²⁺ and Ni species, respectively. A quantitative analysis based on the integrated area of two decomposed peaks could give rise to the relative proportion of Ni to Ni²⁺ species. The molar ratio of Ni/Ni²⁺ is 1.6:1 and 1:2.4 for NiO nanofiber and C-coated Ni/NiO nanofibers, suggesting the existence of Ni after coating.

Fig. 2a presents the morphologies and structures of the samples examined by TEM. We can see that NiO nanofiber was coated with carbon. Moreover, NiO nanofiber with length of 600–800 nm were continuous dispersed in the C-coated layer, thus the formed nano reactor between the inner cavity of C-coated layer and NiO is...
beneficial to lithiation and delithiation processes as well as NiO/Ni redox by confinement effect. In Fig. 2b, the lattice fringes with a spacing of 0.24 nm were observed in the C-coated Ni/NiO nanofibers, corresponding to the (111) plane of NiO. The ring-like mode in the selected-area electron diffraction (SAED) pattern can confirm the NiO species in the C-coated Ni/NiO nanofibers.

3.2. Electrochemical performance

The electrochemical activity of the prepared anode electrodes was firstly tested at a 200 mA g\(^{-1}\) in Fig. 3a. NiO nanofiber electrode can only achieve an initial charge capacity of 743 mAh g\(^{-1}\), and the charge capacity continuously decreases with cycling, and drop to 383 mAh g\(^{-1}\) after 40\(^{th}\) cycle because of the growth of SEI film, with
the charge capacity efficiency reduced by 52%. Nevertheless, initial charge capacity of C-coated Ni/NiO nanoﬁbers electrode can reach at 545 mAh g\(^{-1}\), moreover, the charge capacity efﬁciency continuously increases by 22.4%, and reached 667 mAh g\(^{-1}\) after 40th cycle. Combined with Figs. 1 and 2, we can see the electrocatalytic activity of C-coated Ni/NiO nanoﬁbers was enhanced by the improved composites, morphology, and electronic characteristics by coating with carbon layer. In Fig. 3b, the reversible capacities of C-coated Ni/NiO nanoﬁbers can reach to 1662 mAh g\(^{-1}\) at a current density of 0.1 A g\(^{-1}\), which C-coated Ni/NiO nanoﬁbers presents good charge-discharge capability.

Fig. 3c shows the potential versus capacity proﬁles of C-coated Ni/NiO nanoﬁbers during the 1st, 2nd, and 3rd cycles at 100 mA g\(^{-1}\). The charging/discharging proﬁles of C-coated Ni/NiO nanoﬁbers are similar in the cycles process. The ﬁrst discharging capacity of C-coated Ni/NiO nanoﬁbers is 1600 mAh g\(^{-1}\), which is much higher than the previous reported electrocatalysts. Moreover, the potentials of C-coated Ni/NiO nanoﬁbers at approximately 1.0 V in these cycles, indicate the highly efﬁcient conversion between NiO and Ni (\(\text{NiO} + 2\text{Li}^+ = \text{Li}_2\text{O} + \text{Ni}\)) due to the conﬁnement effect of C-coated layer.

To verify the assumption, Ni/NiO was fabricated according to pulsed laser deposition and used as the cathode in the charge and discharge test of lithium battery. The recycle electrocatalytic performances of Ni/NiO and C-coated Ni/NiO nanoﬁbers were shown in Fig. 3d at 200 mA rate. The ﬁrst discharge capacity over Ni/NiO reached to 1092 mAh g\(^{-1}\), however, the capacity for Ni/NiO decreased to 907 mAh g\(^{-1}\) in the second recycle. More positively, compared with Ni/NiO electrocatalyst, C-coated Ni/NiO nanoﬁbers shows a higher reversible electrocapacity and retention. In Fig. 3d, it can be seen that the electrocatalytic capacity over C-coated Ni/NiO nanoﬁbers increased to 1046 mAh g\(^{-1}\) after 100 cycles. Therefore, C-coated Ni/NiO nanoﬁbers presents high electrocatalytic activity and stability due to the conﬁnement effect of C-coated layer on the redox of NiO/Ni as well as the adsorption and insertion of lithium ion in the charge and discharge process of lithium battery.

In order to conﬁrm effective redox capability between NiO to Ni with the aid of C-coated layer conﬁnement effect, the morphology and composition of C-coated Ni/NiO nanoﬁbers were investigated after charge-discharge recycle. The HAADF result shows that, compared with the size before lithiation, Ni/NiO NPs were smaller with the size of 5–180 nm, as illustrated in Fig. 4a, and the corresponding TEM and HRTEM show that Ni/NiO species diffused into nano layer of C-coated layer, as conﬁrmed by EDS characterization [27]. Moreover, we investigated the adsorption behavior of Li\(^+\) on Ni (111) crystal surface by calculating binding energy between Li atoms and nickel clusters. In Fig. 5, it is seen that the binding energy is \(-1.37\text{eV}\) when the ratio of Li\(^+\)/Ni is 0.25, indicating Li ions were preferentially adsorbed on the surface of Ni. Furthermore, the binding energy remain negative when increasing the ratio of Li\(^+\)/Ni.
from 0.25 to 2.5. When the ratio of $\text{Li}^+/\text{Ni}$ increased to 2.75, the binding energy shows the positive value, suggesting the accumulated Li ions enhance the adsorption energy barrier. The calculation results show that the nano scale Ni/NiO can store 25 percent Li more than theoretical value. On the other hand, the result indicates the reaction of $\text{Li}_2\text{O}$ to $\text{Li}_2\text{O}_2$. Usually, the reaction of $\text{Li}_2\text{O}$ to $\text{Li}_2\text{O}_2$ does not happen because the highly insulating $\text{Li}_2\text{O}_2$ can automatically shut down the reaction [28]. However, the smaller NiO particle upon the cycling may acts as catalyst in such a reaction. Therefore, the smaller NiO particles provide more active surface area and may act as catalyst in the reaction of $\text{Li}_2\text{O}$ to $\text{Li}_2\text{O}_2$.

4. Conclusions

In summary, the C-coated Ni/NiO nanofibers were prepared by a simple electropinning approach followed by CVD reaction. The specific combination of composition shows superior features with a specific discharge capacity of 1662 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. Experimental evidence confirm the N-doping brings multifold revolutionary effects on the Li storage of Ni/NiO hybrid composite electrodes. The increasing active sites of NiO serves as a major contributor to the enhanced capacity upon long cycling. The confinement effect of the nano scale NiO effectively enhancing the electrochemical performance and showed a better characteristic in storing lithium. Our finding will shed new light on understanding of oxide conversion reactions in lithium ion batteries, guiding new nanostructure design of N-coating metal-oxide-based electrodes. The possibility of nanoscale NiO promoting the reversible formation and decomposition of $\text{Li}_2\text{O}_2$ may inspire the study of the Li-O$_2$ cells.

Conflict of interest

The authors declare that they have no conflict of interest.

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