



Stable cyclic performance of nickel oxide–carbon composite anode for lithium-ion batteries



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ABSTRACT

Nickel oxide (NiO) directly grown on nickel foam is regarded as a promising lithium ion battery anode material which shows good cyclic and rate performances with a theoretical specific capacity of 718 mA h g^{-1} . In this study, we demonstrated a carbon-incorporated NiO anode (NiO–C) with a capacity per unit area of $2.11 \text{ mA h cm}^{-2}$ and $1.76 \text{ mA h cm}^{-2}$ at 0.2 C and 0.5 C rates, respectively, fabricated by thermal oxidation of carbon coated nickel foam. The specific capacity of our NiO–C composite samples at 0.5 C rate is found to be typically $389.16 \text{ mA h g}^{-1}$, with a stable cyclic performance up to more than 100 cycles. This remarkable performance is apparently superior to the control samples of pure NiO samples. The improved performance is contributed to carbon incorporation which serves as a fluent channel for electrons and a flexible network preventing NiO nanostructures from structural deformation during charge and discharge processes. The advantage of using our approach is the easy preparation of the NiO–C composite using a simple two-step process: chemical vapor deposition of ethanol and annealing in air.

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1. Introduction

Tarascon's group [1] has found that transition metal oxide can be promising anode materials for lithium ion batteries where the conversion reaction of the transition metal oxide and formation/decomposition of Li_2O are reversible. One of the transition metal oxide candidates is NiO anode, having a theoretical capacity of 718 mA h g^{-1} . Thereafter, it has been noted that the anode performance of NiO nanostructures [2–10] is much better than that of bulk NiO anode due to decreased diffusion lengths of Li ion. Even though NiO nanostructures have many advantages for the anode application over bulk NiO, they do have several weaknesses, for example, 1) they must be mixed with binders and carbon conductors to form slurry which is then casted on a metal current collector. The attachment of the slurry to the current collector is typically weak, resulting in a short cycle life. 2) Due to aggregation and expansion/contraction of active nano-NiO structures during lithiation/delithiation, their structures might not be preserved during cycling. Thus the anodes based on nanostructure NiO suffer from poor cycling performance. In order to improve the performance of nanostructure NiO, the incorporation of carbon

composite [11–18] is reported as an effective method to achieve a good cycle life. Another approach is to substitute the casting process with thin film approach whereby NiO nanostructures are directly grown on metal current collector [19–25]. No report combines both approaches to achieve the carbon coating on directly grown NiO nanostructures on 3D interconnected metal current collectors because NiO could be reduced at high temperature when coating the carbon in the hydrogen environment.

Nickel foam, an interconnected 3D mesoporous nickel open network, is of a large surface area, good electrical conductivity, strong mechanical characteristic and high flexibility. So far, reported 3D nickel foam includes porous NiO/polyaniline film on nickel foam [26], porous NiO films on nickel foam [27–31], sandwich-like NiO film on nickel foam [32], NiO nanocone on nickel foam [33], and mesoporous NiO nanosheet networks on nickel foam [34]. However, most of these reports involved a series of complex step, which is less suitable for industrial application.

In this paper, we present a simple technical approach to achieve carbon coating on directly grown NiO nanostructures on 3D interconnected metal current collectors, which could maintain the better cycle life by incorporating nanostructure, 3D interconnected metal current collectors and carbon coating. Furthermore, a large mass loading up to around 4.5 mg cm^{-2} could be achieved, compared with other reported anodes ($<1.0 \text{ mg cm}^{-2}$) [27,31,32]. Finally, compared to several

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reported techniques of incorporating carbon [11–18], our approach is very simple that it involves only chemical vapor deposition (CVD) of ethanol & thermal annealing in air.

2. Experimental

2.1. NiO–C fabrication

Fig. 1a shows the schematic of the fabrication steps of NiO–C sample. Nickel foam (Latech Scientific Supply Pte. Ltd., $0.03\text{--}0.04\text{ m}^2\text{ g}^{-1}$ specific surface area, >96% porosity, 100–110 pores per inch, $600\text{--}700\text{ g m}^{-2}$ area density, 2 mm thickness) was cut into 1.2 cm diameter disks and cleaned using ultrasound for 30 min in propan-2-ol (isopropyl alcohol) and then dried inside a vacuum oven at $80\text{ }^\circ\text{C}$ for 4 h. First, carbon was deposited by heating the nickel foam disks at $650\text{ }^\circ\text{C}$ for 20 min inside a tube furnace where ethanol was bubbled using a mixture of 200 sccm argon and 50 sccm hydrogen gas. The ramp up (down) time was 20 (70) min. During the ramp up and down processes, a mixture of 200 sccm argon and 50 sccm hydrogen gas flowed directly without going through the ethanol bubbler. We found that the gas flow rate and the temperature distribution inside the furnace affected the reproducibility of the samples. In the experiments, the sample locations and experimental conditions were carefully controlled. Second, the obtained carbon coated nickel foam (Ni–C) was heated inside a Thermolyne Type 47900 furnace at $500\text{ }^\circ\text{C}$ for 6 h in air, to oxidize the nickel to nickel oxide, i.e., NiO–C. The mass of the samples was measured using Mettler Toledo XP26 DeltaRange balance with readability of 0.002 mg.

2.2. NiO fabrication

Fig. 1b shows the schematic of NiO fabrication step. The NiO fabrication was done by heating the nickel foam disks inside a Thermolyne Type 47900 furnace at $500\text{ }^\circ\text{C}$ for 6 h in air. The NiO is used as the control sample.

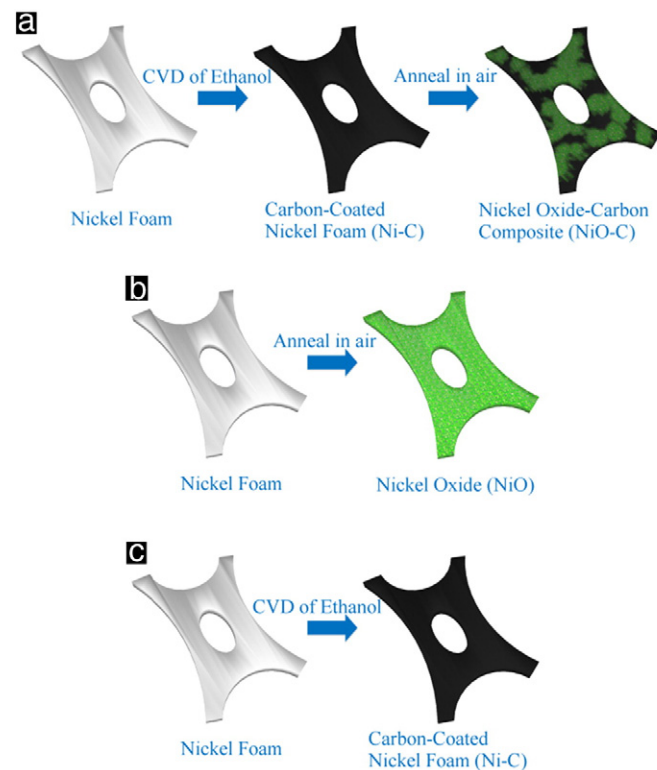


Fig. 1. Schematic of the fabrication steps of (a) NiO–C sample, (b) NiO sample and (c) Ni–C sample.

2.3. Ni–C fabrication

For comparison, Ni–C samples were fabricated. The Ni–C fabrication has followed the same procedure as that of NiO–C electrode, except without oxidizing the nickel using a Thermolyne Type 47900 furnace. Fig. 1c shows the schematic of Ni–C fabrication process.

2.4. Physical characterization

Scanning Electron Microscopy (SEM) of LEO 1550 Gemini was used to characterize the morphology of the samples. The SEM accelerating voltage was set to 5 kV. Raman spectroscopy of WITec with excitation wavelength of 532 nm and X-ray diffraction (XRD) of Siemens D5005 with Cu K α of 0.154 nm were used to characterize nickel oxide and carbon structures of the samples. Transmission Electron Microscopy (TEM) of JEOL 2010 was used to characterize the presence of NiO and carbon in NiO–C. The TEM accelerating voltage was set to 200 kV. Thermogravimetric analysis (TGA) was performed using a Shimadzu DTG-60H from 30 to $750\text{ }^\circ\text{C}$ at a heating rate of $5\text{ }^\circ\text{C}/\text{min}$ under dry air.

2.5. Half-cell fabrication

The samples, Celgard 2300 separator and pure Li metal, were assembled in coin cells (2032) inside an argon glove box (Innovative Technology, USA) with oxygen and moisture level less than 5 ppm. The liquid electrolyte used was 1 M LiPF $_6$ dissolved in ethylene carbonate and diethyl carbonate (EC/DEC, 1:1 by volume). Since the NiO, Ni–C and NiO–C were tested in a half-cell configuration where the lithium metal serves as an anode, we refer to them as NiO, Ni–C and NiO–C samples, respectively.

2.6. Electrochemical characterization

Battery cycle life testing was carried out using Neware battery testers. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were performed using Autolab machine.

3. Results and discussion

From Fig. 2a, one can see that all samples have Ni peaks at 44.49° , 51.86° , and 76.41° which correspond to Ni(111), Ni(200), and Ni(220), respectively (JCPDS 4-850, Face-centered cubic, Fm3m). The NiO and NiO–C samples show the peaks at 37.25° , 43.29° , and 62.90° , corresponding to NiO(101), NiO(012) and NiO(104), respectively (JCPDS 44-1159, Rhombohedral, R-3m). A weak and broad carbon peak at about 26.4° can be observed in Ni–C and NiO–C samples. This confirms the existence of amorphous carbon in the two samples. No Raman peak is found from Ni foam, see Fig. 2b. The NiO–C and Ni–C samples have carbon peaks at about 1352 cm^{-1} (D band) and 1590 cm^{-1} (G band) and shoulder at about 1625 cm^{-1} (D' band), suggesting the existence of graphitic carbon.

The ratio of the D to G bands of NiO–C and Ni–C samples was 1.20 and 1.94, respectively, suggesting that some carbon structural defects (the origin of the D peak) in the NiO–C sample might be annealed out during the high temperature oxidation process [35]. The shoulder peak at 1625 cm^{-1} corresponds to another disorder-induced band from carbon. In addition, second-order bands of carbon [35] at about 2700 cm^{-1} and 2950 cm^{-1} were observed for both NiO–C and Ni–C samples. The Raman spectra of NiO–C and NiO show a broad peak at about 520 cm^{-1} , which can be attributed to Ni–O stretching mode [28,36], and other peaks at about 1100 cm^{-1} and 1500 cm^{-1} due to 2LO (two-longitudinal-optical) and 2M (two-magnon) phonon modes of NiO, respectively [37]. The peaks at 1100 cm^{-1} and 1500 cm^{-1} on NiO–C sample were not clearly shown due to high intensity of the D, G, and D' carbon peaks.

Fig. 3 shows the SEM images of Ni foam, Ni–C, NiO, and NiO–C samples before battery assembly. Initially, nickel foam (Fig. 3a and b)

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