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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 mA h cm⁻² and 1.76 mA h cm⁻² at 0.2 C and 0.5 C rate, 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 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.

Keywords:

anodes; carbon; composites; lithium-ion batteries; nickel oxides

1. Introduction

Tarascon 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 is reversible. One of 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 is directly grown on metal current collector [19-25]. No report combine 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 reported techniques of incorporating carbon [11-18], our approach is very simple that involves only chemical vapor deposition (CVD) of ethanol & thermal annealing in air.

2. Experimental

2.1. NiO-C Fabrication

Figure 1a shows the schematic of the fabrication steps of NiO-C sample. Nickel foam (Latech Scientific Supply Pte. Ltd., $0.03 - 0.04 \text{ m}^2 \text{ g}^{-1}$ specific surface area, $>96 \%$ porosity, 100-110 pores per inch, $600-700 \text{ g m}^{-2}$ area density, 2 mm thickness) was cut into 1.2 cm diameter disks and cleaned using ultrasound for 30 minutes in propan-2-ol (isopropyl alcohol) and then dried inside vacuum oven at 80°C for 4 hours. First, carbon was deposited by heating the nickel foam disks at 650°C for 20 minutes 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) minutes. During the ramp up and down processes, a mixture of 200 sccm argon and 50 sccm hydrogen gas was 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°C for 6 hours 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

Figure 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°C for 6 hours in air. The NiO is used as the control sample.

2.3. Ni-C Fabrication

For comparison, Ni-C samples were fabricated. The Ni-C fabrication was followed the same procedure as NiO-C electrode, except without oxidizing the nickel using Thermolyne Type 47900 furnace. Figure 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 Shimadzu DTG-60H from 30 to 750 °C at heating rate of 5 °C/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 1M LiPF₆ 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 them as NiO, Ni-C and NiO-C sample, 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 figure 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 figure 2b. The NiO-C and Ni-C samples have carbon peaks at about 1352 cm⁻¹ (D band), 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 sample were 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 sample. 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.

Figure 3 shows the SEM images of Ni foam, Ni-C, NiO, and NiO-C samples before battery assembly. Initially, nickel foam (figure 3a and 3b) had a smooth surface with obvious grain boundaries. Ni-C (figure 3c) has multiwall carbon nanotubes (figure 3k) and other carbon allotropes (figure 3d). NiO, which is the control sample, shows a uniform surface of nanostructure (figure 3e and figure 3f). On NiO-C samples, as nickel was previously roughened due to carbon deposition, the nickel oxide in NiO-C samples was found to grow non-uniformly, see figure 3g. The NiO-C sample consists of mainly two regions: the carbon-rich and the NiO-rich region, shown as dark and bright area, respectively, in figure 3g and 4a. The NiO-rich region is located at location 1, while the carbon-rich region is located at location 2, in figure 4a. The energy dispersive x-ray spectroscopy (EDS) shows that in all locations, NiO and carbon were present, as shown in figure 4b. The nanostructure of nickel oxide in the NiO-C sample (figure 3h) looks similar to that in the NiO sample (figure 3f). However, the former (figure 3j) looks slightly finer than the latter (figure 3i). From the TEM image in Figure 5, the thickness of carbon in NiO-rich region of NiO-C sample was found to be about a few nm. We cut the NiO and NiO-C samples and performed cross-section SEM. We found that the thickness of carbon in carbon-rich region of NiO-C sample was about 1130 nm, while the thickness of carbon in Ni-C sample was about 1153 nm. The thickness of nickel oxide in NiO-C sample and NiO sample were about 221 nm and 206.9 nm, respectively. Note that the thickness value presented serves only as a rough guide, as it might not be uniform across the sample.

During thermal oxidation of Ni-C sample at $500\text{ }^{\circ}\text{C}$ for 6 hours, although the multiwall carbon nanotubes were significantly removed (figure 3l), the amorphous carbon and graphitic carbon, as well as NiO, were present in the NiO-C sample. Significant amount of carbon still survives and eventually incorporates into the NiO, as evidenced by XRD (figure 2a), Raman (figure 2b), EDS (figure 4b) and TEM (figure 5). The presence of carbon and NiO after annealing at $500\text{ }^{\circ}\text{C}$ for 6 hours in air was revealed by

high-resolution TEM, presented in figure 5. NiO-C sample was ultrasonically dispersed in isopropyl alcohol and then dropped onto a holey-carbon-coated copper grid. The fringe spacing of 0.245 and 0.210 nm are observed in figure 5, corresponding to the (101) and (012) planes of NiO, respectively. Another fringe spacing of 0.332 nm corresponds to the graphitic carbon. Figure 5 shows that most of the carbon was amorphous carbon. The NiO particle was surrounded and covered by amorphous carbon.

The resulting carbon percentage of NiO-C sample was found to be 7.39 % in overall. In comparison, by definition, the carbon percentage of Ni-C and NiO samples were 100 % and 0 %, respectively. The carbon percentage of NiO-C sample was determined by heating NiO-C sample at 400 °C for 10 hours under a mixture of 100 sccm Ar and 100 sccm H₂ gas, to reduce nickel oxide to nickel. During this process, the nickel oxide in NiO-C was reduced become nickel, while the carbon was stable. Based on the thermodynamics, the reduction of NiO by hydrogen gas is spontaneous ($\Delta G < 0$) at 400 °C.

Also, the C was not able to reduce NiO ($\Delta G > 0$) at 400 °C.

The TGA of excess carbon grown on another sample confirmed the stability of the carbon coating at 400 °C in air, see figure 6. Since during reduction, there was no oxygen introduced, the stability of carbon should be more pronounced than in air. Hydrogen adsorption on carbon was also negligible as high temperature (400 °C) was used. The hydrogen adsorption is less than 1 wt% at room temperature, and increases only if the temperature is lowered, due to the physical adsorption nature of hydrogen on carbon [38]. Thus, it is safe to assume that C did not change mass during reduction.

Figure 7 shows the XRD and Raman spectra of NiO-C sample after reduction treatment at 400 °C for 10 hours under Ar (100sccm) and H₂ (100sccm). The nickel and carbon peaks were found in figure 7a.

The carbon peaks were also found in figure 7b. NiO peaks were not found in both XRD and Raman spectra of figure 7a and 7b, respectively.

To calculate the percentage of C and the mass of NiO in the NiO-C sample, Equation (1) to (4) were used:

$$\text{The mass of O} = \text{the mass after oxidation} - \text{the mass after reduction} \quad \text{Equation (1)}$$

$$\text{The mass of C} = \text{the mass after reduction} - \text{the mass of nickel foam} \quad \text{Equation (2)}$$

The mass of NiO in NiO-C sample was determined as follow:

The mass of NiO

$$\begin{aligned} &= \left(\frac{\text{MW of Ni} + \text{MW of O}}{\text{MW of O}} \right) \times \text{the mass of O} \\ &= \frac{74.69}{16} \times \text{the mass of O} = 4.67 \times \text{the mass of O} \end{aligned} \quad \text{Equation (3)}$$

The percentage of carbon in the NiO-C sample was determined using equation:

$$\text{Percentage of Carbon} = \frac{\text{the mass of C}}{\text{the mass of C} + \text{the mass of NiO}} \times 100\% \quad \text{Equation (4)}$$

The calculated mass of NiO and the carbon content percentage of NiO-C sample are shown in table 1.

The mass of O in the NiO sample is determined as follow:

$$\text{The mass of O} = \text{the mass after oxidation} - \text{the mass of nickel foam} \quad \text{Equation (5)}$$

The active mass loading of NiO-C and NiO samples were 4.54 mg cm^{-2} and 4.76 mg cm^{-2} , respectively. The active mass loading (nickel oxide mass loading) of NiO-C sample was calculated using Equation (1) and (3) and then normalized with the NiO-C area. The nickel oxide mass loading of NiO sample was calculated using Equation (3) and (5) and then normalized with the NiO area. The active mass loading of NiO-C sample was slightly lower than NiO sample, indicating thin carbon coating was slightly resistive to oxygen access to Ni for nickel oxidation. The reason could be that on carbon-coated nickel foam, the oxygen needs to diffuse through the carbon layer to reach the nickel foam-carbon interface. The carbon coating acts as a barrier layer. While on pure nickel foam, there was no barrier layer. The nickel oxide mass loading used was quite large (around 4.5 mg cm^{-2}) to increase the areal capacity (mA h cm^{-2}) of the electrode. Figure 8 shows that by increasing the mass loading of nickel oxide on the NiO sample, the cycle life degrades. The larger the mass loading (the thicker the NiO layer), the higher the electrical resistance and the worse the NiO pulverization during lithiation/delithiation. To solve this problem, carbon

incorporation was used in the NiO-C sample to maintain the cycle life at relatively large active mass loading.

The battery testing performance of the NiO-C and NiO samples is shown in figure 9a and 9b. The discharge-charge cycling performance was performed at 0.5 C rate ($1\text{ C} = 718\text{ mA g}^{-1}$) for 102 cycles in a potential window of 0.02-3.0 V vs. Li. Figure 9a shows that the specific capacity of the NiO-C sample was found to be $389.16\text{ mA h g}^{-1}$ after 102 cycles, much higher than $197.59\text{ mA h g}^{-1}$ for the NiO sample. Figure 9a show that after 102 cycles, NiO-C sample could keep about 100 % of the 2nd cycle capacity, but the capacity loss of NiO sample after 102 cycles was 49.7 % of the 2nd cycle capacity, which indicate that the NiO-C cycling performance was found to be significantly better than the NiO sample due to carbon incorporation which serves as a buffering matrix of nickel oxide and as a conductor of electron. Figure 9b shows that the NiO-C sample has a stable and good capacity per unit area of 1.76 mA h cm^{-2} after 102 cycles, compared with 0.94 mA h cm^{-2} for the NiO sample. Figure 9c and 9d show that during the first discharge, the NiO-C and NiO samples exhibit a wide cell potential plateau at 0.49~0.50 V, respectively, followed by a sloping curve. This plateau is originated from initial reduction of NiO to Ni and formation of amorphous Li_2O and solid electrolyte interface (SEI) happened during the first discharge [24, 27, 39]. In the subsequent charge and discharge processes, the plateau was positioned at about 2.2 V and 1.2 V, respectively, for the NiO-C sample. The initial discharge and charge capacity of the NiO-C sample were $710.90\text{ mA h g}^{-1}$ and $374.94\text{ mA h g}^{-1}$, respectively. In contrast, the initial discharge and charge capacity of the NiO sample were $695.79\text{ mA h g}^{-1}$ and $392.88\text{ mA h g}^{-1}$, respectively. The initial irreversible capacity loss for the NiO-C and NiO samples were 47.26 % and 43.53 %, respectively (corresponding to first cycle's Coulombic capacity of 52.74% and 56.47% for NiO-C and NiO samples, respectively, in Figure 9a and 9b), probably due to the possible irreversible changes, say electrolyte decomposition or/and SEI layer formation [1, 25, 40], etc. The initial irreversible capacity loss of the NiO-C sample was larger than the NiO sample, probably because of additional electrolyte decomposition on graphitic carbon structure [41]. The reversible discharge and charge capacity of the NiO-C sample at the 102nd cycle was $389.16\text{ mA h g}^{-1}$ and $384.92\text{ mA h g}^{-1}$, respectively, corresponding to the Coulombic efficiency of 98.91 %. In comparison, the reversible discharge and charge capacity of the NiO sample at the 102nd cycle was only $197.59\text{ mA h g}^{-1}$ and $193.36\text{ mA h g}^{-1}$, respectively, corresponding to a Coulombic efficiency of 97.86 %. Although the initial irreversible capacity loss of the NiO-C sample was slightly larger than that of the NiO sample, after

102 cycles, the Coulombic efficiency and cycle performance of the NiO-C were found to be apparently better than the control sample of NiO sample. Moreover, the initial irreversible capacity loss of NiO-C sample could be minimized to 37.59 % by using lower rate of 0.11 C.

Figure 9e shows the specific capacities of the NiO-C and NiO sample for 10 cycles at different charge and discharge rates of 0.2 C, 0.5 C, 1 C, 2 C, 4 C (1 C= 718 mA g⁻¹), respectively. The NiO-C sample showed slightly lower polarization at the rates of 2 C and 4 C, indicating that the NiO-C sample structure was well preserved at the high discharge rates. To confirm this, the rate was tuned to 0.2 C for 20 cycles after the 4 C charge and discharge processes. The NiO-C sample exhibited a significant recovery of its specific capacities. In a sharp contrast, the specific capacities of the NiO sample at the 0.2 C (after the 4 C) decreased significantly with the cycle number, further suggesting that the NiO-C sample was of a better rate capability than the NiO sample. The capacity of the NiO-C in the final few cycles at 0.2 C was slightly higher than the initial cycles at the same rate may be contributed from the reversible growth of polymer/gel-like film from the electrolyte degradation [42-44].

The CV of the NiO, Ni-C, and NiO-C samples was performed at the 0.1 mV s⁻¹ scan rate from 0.02 to 3.0 V, respectively. From the first and second cycle voltammetry (figure 9f and 9g, respectively), one can find that the NiO-C and NiO sample showed a similar response. In the first cycle (figure 9f), the two samples showed a peak at around 0.27 V which can be attributed to initial reduction of NiO to Ni and formation of amorphous Li₂O and SEI [24, 27, 39]. While during the first anodic scan, a peak at around 2.2 V could be an indication of NiO formation and Li₂O decomposition [39, 45]. Differently, the Ni-C sample had a peak at around 0.51 V during the first cathodic scan, which could result from the formation of SEI layer [41] and a peak at around 0.32 V during the first anodic scan, probably due to the de-intercalation of the Li-ions from the graphitic carbon [46]. On the second cycle of the cathodic and anodic scan, see figure 9g, the NiO-C and NiO samples had the peaks at 1.18 V and 2.25 V, respectively. The shift of peaks of 1st and 2nd cycle of NiO-C and NiO samples was due to the drastic lithium driven, structural or textural modifications [25, 47]. A peak at 0.30 V was observed in the second cycle of the Ni-C anodic scan, suggesting the de-intercalation of Li-ions from the graphitic carbon [46]. This peak was not found in both NiO-C and NiO sample, indicating that the active material of NiO-C sample was mainly dominated by

nickel oxide, not by graphitic or/and amorphous carbon. This is also the reason why the NiO sample is used as a control sample instead of Ni-C sample.

Figure 9h shows the equivalent circuit used to fit the Nyquist plots of the NiO-C and NiO sample (figure 9i and figure 9j). The curves were fitted using Nova 1.9 software and the values were presented in table 2. The charge transfer resistances of the NiO-C and NiO sample after 102 cycles were 13.19 Ω and 11.08 Ω , respectively, which comparable within the uncertainty in the fitting. This suggests that the nickel foam was of high conductance and it had a good electrical contact with NiO, the active material, during the charge/discharge cycles. The fitting to EIS was based on two semicircles and diffusion component. The semicircle at higher frequencies is related to the formation of SEI film and/or contact resistance, while the semicircle at medium frequency is related to Li absorption/desorption or the charge-transfer impedance on electrode/electrolyte interface [48, 49]. The equivalent circuit was using the components as follow [49]. R_e is the resistance of electrolyte, while R_f and C_f are the resistance and capacitance of the SEI film, respectively. The R_{ct} and C_{dl} are the charge-transfer resistance and double-layer capacitance, respectively. The diffusion component consists of Z_w and Z_t corresponding to Warburg impedance and Tangent hyperbolic, respectively.

The comparison of the performance of our NiO-C sample with the reported results by several other groups is listed in table 3. The porous NiO [27], nanoporous NiO [31], and sandwich-like NiO [32] had only small mass loading of $\leq 1 \text{ mg cm}^{-2}$. They achieved a cycle life of ≥ 50 cycles at rate of $\geq 359 \text{ mA g}^{-1}$. The NiO films [24] had a higher mass loading of 3 mg cm^{-2} . It showed a stable performance at low rate, with a cycle life of 50 cycles. Compared to NiO films [24], our NiO-C composite sample has better cycle life of 102 cycles. Through this comparison, the key points of our NiO-C samples can be drawn: (1) our NiO-C sample has the highest mass loading of 4.54 mg cm^{-2} ; (2) our NiO-C sample has the highest mass loading with a stable cycle life more than 100 cycles at rate of 359 mA g^{-1} and (3) our NiO-C sample has a practical capacity per unit area of $2.11 \text{ mA h cm}^{-2}$ and $1.76 \text{ mA h cm}^{-2}$ at rate of 143.6 mA g^{-1} and 359 mA g^{-1} , respectively.

One might argue that the mass loading is related to the thickness of nickel foam and the level of oxidation. Ideally, the same kind of nickel foams should be used by all works in Table 3 for a fair comparison. However, it is impossible here because References [27, 31, 32] did not provide nickel foam

parameters, while Reference [24] only provided few nickel foam parameters. We believe that two parameters of specific surface area and thickness of nickel foam are sufficient to represent the nickel foam. Other parameters such as the porosity, pore size, pore density and area density are all reflected in specific surface area of nickel foam. The specific surface area and thickness of nickel foam used in Reference [24] were $3.9 \text{ cm}^2 \text{ mg}^{-1}$ and 0.16 cm , respectively. We used nickel foam with specific surface area and thickness of $0.3 - 0.4 \text{ cm}^2 \text{ mg}^{-1}$ and 0.2 cm , respectively. We showed that our mass loading is higher than that in Reference [24] by normalizing the mass loading with the specific surface area and thickness of the nickel foam, shown in Equation (6). Our normalized NiO mass loading of 56.75 to $75.67 \text{ mg}_{\text{NiO}} \text{ cm}^{-5} \text{ mg}_{\text{Ni}}$ was higher than $4.81 \text{ mg}_{\text{NiO}} \text{ cm}^{-5} \text{ mg}_{\text{Ni}}$ of Reference [24].

Normalized NiO mass loading

$$= \frac{\text{NiO mass loading } (\text{mg}_{\text{NiO}} \text{ cm}^{-2})}{\text{nickel foam specific surface area } (\text{cm}^2 \text{ mg}_{\text{Ni}}^{-1}) \times \text{nickel foam thickness } (\text{cm})} \quad \text{Equation (6)}$$

The excellent performance of the NiO-C/nickel foam sample probably results from high electrical conductance and mechanical flexibility of graphitic or/and amorphous carbon coating, which not only provide an efficient channel for electrons, but also function as a network preventing NiO nanostructures from structural deformation during charge and discharge processes. SEM images of the NiO-C and NiO samples after 102 cycles (figure 10) show that the nanostructure of NiO-C looks more uniform and preserved (figure 10b) than NiO (figure 10d). In addition, we use ultrasonication to qualitatively measure the mechanical stability of NiO-C and NiO sample after cycling. The NiO-C sample is more resistant to be peeled off after ultrasonication in IPA for 30 minutes, as shown in figure 11. In figure 11b, more remaining films were found attached to substrate, compared to figure 11d. It indicates that the NiO-C sample has a better mechanical ability. The mechanical ability is important during charge/discharge because the nickel oxide expands and contracts during battery cycling.

4. Conclusions

We have fabricated NiO-C sample, using a simple two-step process of CVD using ethanol and annealing in air, in which a large amount of NiO active material directly forms on carbon coated nickel foam current collector. The high mass loading of active NiO of around 4.5 mg cm^{-2} enables the NiO-C sample to have the capacity of $2.11 \text{ mA h cm}^{-2}$ and $1.76 \text{ mA h cm}^{-2}$ at 0.2 C and 0.5 C rate, respectively. At

0.5 C rate, the capacity is stable at 382.13~389.16 mA h g⁻¹ from the second up to 102nd cycle. The cycling and rate performances of the high NiO mass loaded NiO-C sample are found to be much better than those of a counterpart NiO sample where no carbon is introduced. The role of the incorporated carbon could be twofold, i.e., a fluent channel for electrons and a flexible network preventing NiO nanostructures from structural deformation during charge and discharge processes.

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Figure 1. Schematic of the fabrication steps of (a) NiO-C sample (b) NiO sample and (c) Ni-C sample.

Figure 2. (a) The XRD spectra and (b) The Raman spectra of NiO-C, NiO, and Ni-C samples as well as Ni foam substrate, respectively.

Figure 3. SEM images of (a, b) Ni foam, (c, d) Ni-C sample, (e, f) NiO sample, (g, h) NiO-C sample.

Comparison of (i) NiO and (j) NiO-C at higher magnification. Comparison of (k) Ni-C and (l) NiO-C at carbon nanotubes area.

Figure 4. (a) SEM image of NiO-C sample. (b) The EDS shows NiO-rich and carbon-rich region.

Figure 5. TEM image of NiO-C sample.

Figure 6. TGA of carbon coating at $5\text{ }^{\circ}\text{C min}^{-1}$ heating rate and 20 ml min^{-1} flow rate of dry air.

Figure 7. (a) The XRD spectra and (b) The Raman spectra of NiO-C sample that has been reduced at 400 °C for 10 hours under a mixture of 100 sccm Ar and 100 sccm H_2 gas

Figure 8. The effect of mass loading to the cyclic performance of NiO samples.

Figure 9. (a) The specific capacity vs. cycle number and (b) the capacity per unit area vs. cycle number of NiO-C and NiO sample. The cell potential vs. specific capacity for different cycles of (c) NiO-C and (d) NiO sample. (e) The rate capabilities for NiO-C and NiO sample. The CV of NiO, Ni-C, and NiO-C sample at (f) 1st cycle and (g) 2nd cycle. (h) The equivalent circuit for the NiO-C and NiO sample. (i, j) EIS of NiO-C and NiO sample, after 102 cycles, at 2 V.

Figure 10. SEM images of (a, b) NiO-C sample after 102 cycles and (c, d) the NiO sample after 102 cycles.

Figure 11. SEM images of NiO-C sample after 102 cycles, (a) before and (b) after ultrasonication for 30 minutes in Isopropyl Alcohol. SEM images of NiO sample after 102 cycles, (a) before and (b) after ultrasonication. The arrow shows the remaining film after ultrasonication.

Table 1. Percentage of carbon content in NiO-C sample.

Mass of nickel foam (mg)	Mass after carbon deposition (mg)	Mass after oxidation (mg)	Mass after reduction (mg)	Mass of O (mg)	Mass of C (mg)	Mass of NiO (mg)	Percentage of Carbon (%)
69.217	72.649	70.729	69.627	1.102	0.411	5.14	7.39

Table 2. Equivalent circuit fitting parameters of the NiO-C and NiO sample.

Element	Parameter	NiO-C		NiO	
		Value	Estimated Error (%)	Value	Estimated Error (%)
Re	R	5.0075	1.772	6.5068	4.193
Rf	R	3.2463	15.381	3.8895	25.623
Cf	Y0	6.22E-05	60.423	7.53E-05	91.731
	N	0.77902	7.33	0.66345	13.26
Rct	R	13.19	16.759	11.082	14.641
Cdl	Y0	0.000205	31.807	0.001066	25.932
	N	0.8388	6.601	0.59565	8.248
Zw	Y0	0.018605	1.323	0.012792	0.884
Zt	Y0	0.4461	772.423	0.26556	141.254
	B	0.14956	773.383	0.18812	142.213
	χ^2	0.009837		0.003025	

Table 3. The comparison of NiO sample on nickel foam works.

Works	Mass loading of active material (mg cm ⁻²)	Capacity per unit area (mA h cm ⁻²)	Rate (mA g ⁻¹)	Cycle number (cycles)	Ref.
Porous NiO on nickel foam	1	0.56	718	100	[27]
Nanoporous NiO on nickel foam	0.39	0.21	359	100	[31]
Sandwich-like NiO on nickel foam	0.92	0.37	1436	50	[32]
NiO films on nickel foam	3	1.95	78.98	50	[24]
NiO-C composite on nickel foam	4.54	2.11	143.6	10 ^{a)}	This work
	4.54	1.76	359	102	

^{a)} Stopped after 10 cycles to facilitate rate capability testing (figure 9e)

Highlights

- We demonstrated a directly grown NiO-C anode on nickel foam substrate
- NiO-C anode was made using simple processes: CVD of ethanol and annealing in air
- The NiO-C anode has a stable cycle life up to 102 cycles
- It has an acceptable areal capacity ($1.76 \text{ mA h cm}^{-2}$ at 0.5 C rate) for practical use
- Carbon provides electrons path and buffering matrix preventing NiO pulverization