Influence of Conductivity on the Capacity Retention of NiO Anodes in Li-ion Batteries

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Abstract

The roles of conductivity and structure in the reversibility, rate capability, capacity and capacity retention of nickel oxide anodes for lithium-ion batteries were investigated. Conductivity was controlled by the systematic addition of non-intercalating carbon. The NiO nanostructure was controlled through four different preparation procedures. Overall, the top-performing electrodes were made from tetrahedral-shaped particles with a broad particle size distribution that were derived from a simple direct calcination of nickel nitrate salt. Capacity values >700 mAh/g after 100 cycles at 1C were observed, and a rate capability >400 mAh/g at 5C was achieved for electrodes with 40% carbon added. The addition of carbon universally improved anode performance by influencing the charge transferability, as evidenced by SEI peak shifts and reduced resistances seen via EIS. Reversibility was greatly enhanced by the impartation of conductivity which enabled otherwise inactive anode particles to maintain activity after many cycles. This work suggests that improved conductivity, as opposed to the conventional opinion regarding nanostructure, is the key to creating high performance anodes for next generation lithium-ion batteries.

1. Introduction

Since its discovery as a reversible intercalation material over 30 years ago [1], graphite has remained the anode of choice for commercial lithium-ion batteries well into the 21st century [2-4]. However, as consumer demand continues to rise for enhanced capabilities of portable electronics such as laptops, tablets and smartphones, the need for higher capacity and higher energy density materials has emerged. The transition to lithium-ion batteries in fully-electric and hybrid-electric vehicles has also contributed to this accelerating demand [5,6], and it is clear that future generations of lithium-ion batteries will need to be dramatically improved in order to satisfy weight and power requirements. Therefore, materials with a higher capacity than graphite must be examined.

Numerous choices have been proposed in recent years for lithium-ion battery anode replacements, such as silicon [7-9], metal hydrides [10,11] and metal oxides [12-16]. Silicon has been widely investigated due to its extremely high theoretical capacity of over 4000 mAh/g; however, it suffers from massive volumetric expansion (more than 350%) during charge-discharge cycling, resulting in electrode pulverization and poor reversibility. Metal hydrides also offer high theoretical capacities above 2000 mAh/g and have shown reasonable cycling performance; however, there is still a lack of evidence for long-term reversibility and safety concerns remain an issue with regards to the possible release and buildup of combustible H₂ inside a battery [17].

Metal oxides, on the other hand, remain a promising candidate for next generation lithium-ion battery anodes, and one of the most commonly-studied metal oxides is nickel oxide (NiO) [18-27]. NiO undergoes a conversion reaction during charge-discharge which, similarly to silicon, can lead to electrode pulverization and reduced capacity retention. However, there are

several reports in the literature where a high degree of reversibility was demonstrated for particular NiO anodes, and almost without exception it appears that this is the result of one of three phenomena: i) only the first few charge-discharge cycles are shown, and the degree of capacity fade in subsequent longer-term cycling is unreported or unknown; ii) the active material loading was so low that during cycling it is likely that the current collector carried the bulk of the charge, even after NiO experienced phase segregation that would otherwise lead to loss of conductivity and capacity; or iii) a high percentage of graphite was added to the electrode layer. Therefore, whether via low anode loading or the addition of conductivity-boosting graphite, there appears to be a strong link between electrode conductivity and capacity retention that has yet to be thoroughly investigated in the literature.

In this study we use the systematic addition of carbon black into NiO anodes to investigate the effect of electrode conductivity on capacity retention. We also synthesize NiO with four distinct nanostructures in order to probe its contribution to capacity retention.

2. Experimental

2.1 NiO Synthesis Techniques

Four distinct nanostructures of NiO were prepared via different synthesis procedures: reflux-induced precipitation (denoted R-NiO), NaOH-induced precipitation (N-NiO), direct calcination of nickel salt (D-NiO), and ordered mesoporous NiO (O-NiO). For all synthesis methods, 18.2 M Ω deionized water from a Millipore Direct-Q 3UV purification system was used, and all reagents were used as received.

R-NiO was synthesized by preparing a 0.5M Ni(NO₃)₂ (Acros, 99%) solution in 10M NH₄OH (Fisher, certified ACS Plus) and boiling under reflux for 24 hours, followed by a rest

period at room temperature for an additional 24 hours. The precipitate was then rinsed and filtered with copious amounts of deionized water, dried overnight at 90°C, and calcined in air at 500°C for 3.5 hours.

N-NiO was synthesized by preparing an aqueous 0.5M $\text{Ni}(\text{NO}_3)_2$ solution and quickly adding 10M NaOH (Fisher, NF/EP/BP/FCC) while stirring until the pH rose to around 10. pH was actively monitored using an Accumet Excel XL60 Dual Channel pH/Ion/Conductivity/DO Meter. The solution was then set to rest and covered for 24 hours at room temperature. The precipitate was then rinsed and filtered with excess deionized water, dried overnight in air at 90°C, and calcined in air at 500°C for 3.5 hours.

D-NiO was synthesized by placing $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ salt directly onto a 160mm diameter ceramic evaporating dish and inserting it into a muffle furnace. The salt was then calcined in air at 400°C for 3.5 hours, causing dehydration and decomposition to pure NiO. The NiO powder was then finely ground using a dry mortar and pestle for 30 minutes.

O-NiO was fabricated via a template-based synthesis method using an ordered mesoporous silica template (SBA-15). Fabrication of SBA-15 can be found in our group's previous publications [28,29]. Wet impregnation of the SBA-15 template was performed dropwise with aqueous 0.5M $\text{Ni}(\text{NO}_3)_2$ until a ratio of approximately 6.3mL per g SBA-15 was reached. The resulting gel was manually stirred until homogeneous, followed by calcination in air at 400°C for 3.5 hours. Template was then etched away via two sequential 12-hour soaks in hot (100°C) 5M KOH with a deionized water rinse and centrifugation (2000 rpm for 30 minutes) using a Thermo Scientific Sorvall Stratos Centrifuge in between. The final product was then rinsed, centrifuged and dried overnight.

2.2 Physical Characterization

Scanning Electron Microscopy (SEM) was performed using an FEI Quanta FEG250 Scanning Electron Microscope. Transmission Electron Microscopy (TEM) was conducted using a JEOL 2010 FasTEM Microscope. Brunauer-Emmett-Teller (BET) analysis was completed via N₂ adsorption isotherms at 77K collected using a Micromeritics ASAP 2020 system. Samples for BET analysis were degased under vacuum at 150°C for 16 hours prior to N₂ adsorption.

SEM images for all four NiO materials are shown in Figure 1, where four distinct nanostructures were observed. R-NiO (Fig. 1A) displayed blade-like, porous features that resembled stacked plates. The N-NiO (Fig. 1B) showed a homogeneous distribution of nanosized spheres with an approximate diameter of 20-40 nm. The D-NiO (Fig. 1C) synthesis produced a wide particle size distribution of tetrahedral-shaped particles ranging from 50 nm to 500 nm. Finally, O-NiO (Fig. 1D) displayed a clear ordered mesoporous structure on the nanoscale with larger agglomerates. Since the O-NiO features were so small, TEM was also used to obtain a higher resolution image of its nanostructure (Supporting Information, Figure S1). BET analysis (Supporting Information, Figure S2) revealed a primary intraparticle porosity of ca. 3.3 nm, which was expected for materials cast from SBA-15 template, along with an interparticle mesoporosity of ca. 25-35 nm, which was on par with the observed cluster sizes.

2.3 Anode Fabrication and Coin Cell Assembly

Anodes were fabricated by preparing inks containing varying amounts of active material (NiO), conductivity-boosting carbon black (Vulcan XC-72R, Cabot), and a binder, polyvinylidene fluoride (PVDF, Kynar blend). The components were dispersed in the solvent N-methylpyrrolidone (NMP, Acros, 99.5% Extra Dry) and the ink was homogenized through

repeated and successive sonication and mechanical stirring. A copper foil (Alfa Aesar, 99.999%) was mechanically roughened and cleaned with isopropanol (Fisher, Optima) before being used as the current collector. The active material ink was sprayed onto the Cu foil to a uniform thickness, heated under vacuum at 100°C for 24 hours, then pressed at 1500 lbs and massed to obtain the loading. For all electrode fabricated in this study, the active loading was held between 0.3-1.5 mg NiO/cm².

Coin cells were constructed to test NiO anodes in a half-cell configuration. The materials used were 2.0 cm diameter coin cells (Hohsen Corp.), lithium metal (Alfa Aesar, 99.9%) as the cathode, and Celgard 2320 tri-layer PP/PE/PP as the separator. A 1M lithium hexafluorophosphate (LiPF₆, Acros 98%) solution in (1:1:1) ethylene carbonate (EC, Acros 99+%):dimethyl carbonate (DMC, Acros 98+%):diethyl carbonate (DEC, Acros 99%) was prepared and used as the electrolyte. In an argon-purged glove box (Labconco), 15 µL of electrolyte was pipetted onto each side of the separator, which was punched to a diameter of 1.9 cm, while the anode and cathode were cut to 1.5 cm diameter circles. The components were then pressed and sealed into the coin cell hardware before being safely removed from the glove box for electrochemical testing.

2.4 Electrochemical Testing

All charge-discharge C-rate calculations were based on the theoretical capacity for NiO of 718 mAh/g. All electrochemical experiments, with the exception of impedance tests, were conducted using an Arbin MSTAT battery test system. Electrochemical Impedance Spectroscopy (EIS) was performed using an Autolab PGSTAT302N Potentiostat (Eco Chemie) between 100 kHz – 50 mHz with a 5 mV amplitude at open circuit voltage. Cyclic Voltammetry (CV) was collected between 0.001 – 3.0 V at a scan rate of 0.1 mV/s.

3. Results and Discussion

CVs were collected for all four NiO nanostructures at 0%, 10%, 20%, 30% and 40% added carbon. The CVs for R-NiO are shown in Figure 2 while the remaining CVs for the other three NiO materials are provided in the Supporting Information (Figures S3-S5). Five CVs were run for each carbon loading over the entire voltage range (0.001 to 3.0V vs Li/Li⁺) at a scan rate of 0.1 mV/s. For all cases, the first negative-going scan (solid black line) saw a very large reduction peak from the formation of the solid-electrolyte interphase (SEI), and the potentials for this SEI reduction peak for all NiO materials as a function of the added carbon content are shown in Figure 2F. Interestingly, the reduction potential for SEI formation always shifted to more positive values as the carbon loading was increased, suggesting that the presence of carbon influences the SEI formation. At the same time, adding carbon did not substantively increase the area under the SEI region of the negative-going CV until the carbon loading was > 20 wt% (Supporting information, Figure S6). In combination, these observations suggest that the dominant mechanism for improving the reaction reversibility is a reduction in IR resistance of the electrode layer as carbon was added. This observation was further supported by EIS data, which will be discussed in detail later.

Though conductivity enhancement via carbon addition influences the SEI formation (and anode reversibility, which will be shown in detail later), the initial structure of NiO determines the overall electrode morphology and how carbon is distributed within the electrode. Therefore, the SEI reduction potential, and its response to carbon incorporation, was impacted by the NiO nanostructure. D-NiO, N-NiO and O-NiO showed similar responses to carbon inclusion, though the reduction of D-NiO was the highest over the entire range. N-NiO was initially slightly higher than O-NiO, but the trend was reversed with 40% added carbon. R-NiO showed the most

interesting behavior of any of the NiO materials. The initial SEI reduction potential was significantly higher than any of the other samples, but it finished the lowest of all samples. The observed trend is very interesting. D-NiO was comprised of the largest particles and largest particle size distribution. R-NiO has a large particle size, but is a very high aspect ratio structure. O-NiO also has a high aspect ratio, but its overall size is approximately the same as the spherical N-NiO. Clearly the interaction between the carbon and NiO plays a key role in the SEI formation, and is something that we will investigate more thoroughly moving forward.

In addition to the SEI formation, the conductivity enhancement, and hence reaction reversibility, enabled by the carbon nanoparticles and the differing structures also play key roles in the charge-discharge behavior. With a few exceptions [21,24,27,30], NiO is well known to have very poor capacity retention [16,25,26,31-34]. The poor cyclability is caused by the active material becoming trapped in the charged state (right side of Equation 1), and has been linked by some to phase separation of the reaction products and poor electronic conductivity of Li₂O as its domain size increases, rendering it electrochemically inactive [15,16,24,25,31].

Parsing the literature referenced above more finely, a very clear trend can be observed that points directly to the conductivity as a controlling parameter in terms of capacity retention. In nearly every study where the NiO capacity retention is noted as excellent, the electronic conductivity has been artificially enhanced, either through the addition of excess carbon or by the substrate due to low loading. The common link is that the active material was not utilized to carry the charge. An additional consideration is that many literature studies on NiO report capacity retention data at low C-rates such as C/5 or C/10, which are not representative for how they

would be used in real mobile devices where charge-discharge cycles are carried out at higher rates like C/2 or 1C.

To investigate the influence of enhanced conductivity on capacity retention under representative device operating conditions, NiO half cells for all four materials were assembled and tested. At least three cells were assembled for each material, and representative data are presented and discussed below. The cells were cycled 100 times between 0.001 and 3.0 V vs. Li/Li⁺ at 1C. Raw experimental data and plots of selected charge-discharge cycles are provided in the Supporting Information (Figures S7-S16). The resulting capacity retention data is presented in Figure 3.

Without exception, introducing carbon into the electrode improved the capacity retention. The top-performing material was D-NiO, which showed the highest sustainable capacity values and the slowest capacity fade. The D-NiO performance was followed by R-NiO, then N-NiO and O-NiO. Interestingly, this followed the trend in the SEI reduction potential, which points to the importance of using primary particle size and the distribution of carbon to improve capacity retention. Additionally, introducing carbon increased not just capacity retention, but also the overall achievable capacity, although some of this was due to secondary Li⁺ storage sites in the SEI on the Vulcan XC-72R [20,35]. Evidence for this was seen in differential capacity vs. voltage curves shown in Figure S17 (Supporting Information) which showed corresponding activity around 0.0V vs. Li/Li⁺, similarly to the CVs shown in Fig. 2. Particularly for the 40% carbon electrode, the cathodic and anodic activity indicated additional Li⁺ intercalation and storage in carbon which artificially boosted the capacity beyond the theoretical value for NiO. Combined with the CVs in Fig. 2, these plots illustrate the individual roles NiO and carbon

played in the electrodes during charge-discharge, and highlight how carbon both improves conductivity and provides secondary Li^+ storage sites.

To elucidate the contributions from both NiO (primary storage) and carbon (secondary storage), capacity values from Fig. 3 were normalized based on the combined mass of NiO and carbon rather than just the NiO alone (see Supporting Information, Figure S18). If adding carbon simply improved capacity via secondary Li^+ storage sites in the SEI and had no effect on the primary storage through NiO, one would expect to see similar capacity values when normalizing for increasing carbon percentages. However, this is not what was observed in Fig. S18. Similarly to Fig. 3, increasing carbon content still resulted in improved capacity retention and overall achievable capacity. This result indicates that carbon had a synergistic effect on the NiO anode performance likely by imparting conductivity to phase-separated, and/or minimally-conductive, species (Li_2O), which facilitated phase transformation between NiO and $\text{Ni}+\text{Li}_2\text{O}$ longer. Charge-discharge curves shown in Figures S7-S16 in the Supporting Information further support this point, as the plateau corresponding to the NiO/ $\text{Ni}+\text{Li}_2\text{O}$ reaction (Eq. 1) between 1.0 – 1.5V vs. Li/Li^+ was still observed even after 100 cycles at 1C for anodes with added carbon.

It should be noted that other methods for coating carbon onto lithium-ion battery electrodes, such as calcination or deposition of various precursors [36,37,38], can be used to efficiently minimize carbon loading for conductivity enhancement. In this study, however, emphasis was not placed on reducing carbon loading or determining an optimum percentage, but rather on systematically increasing the overall electronic conductivity by physically adding greater quantities of carbon black to the electrode layer.

Conventional thinking would suggest that the improved NiO capacity retention is a result of improved structural reversibility. However, this was not the case. In our previous work [39],

we developed a new identical location TEM (IL-TEM) technique for Li-ion battery materials. This technique allows for the same particle to be imaged as a function of cycle number, a critical tool for NiO materials that undergo significant changes in chemistry and structure during cycling. We used O-NiO in this work because it has a predictable, well-characterized nanostructure that can be conveniently imaged by TEM. The IL-TEM results are shown in Figure 4 for O-NiO before and after two charge-discharge cycles with 0% carbon and 40% carbon. After two cycles, the 0% carbon O-NiO looks as one would expect with the overall structure being reproduced during charge-discharge; however, the 40% carbon O-NiO shows very different results. Though the microstructure (overall shape) of the particles is not changed between charge and discharge, the nanostructure is completely transformed when carbon is added. The TEM images suggest that the domain size for the Ni+Li₂O phase is kept very small with the addition of the high conductivity carbon, allowing for more of the capacity to be retained. This is a very surprising result that provides new insight into future approaches for improving the capacity retention of metal oxide anodes in general.

The impact of structure was further investigated through initial capacity losses between the first and second cycles for all four NiO structures and all carbon loadings. O-NiO exhibited an average capacity loss of 23.6%, which was the highest among all NiO structures and was consistent both with poor overall performance issues seen in Fig. 3, and with the previously-mentioned structural degradation seen with IL-TEM. Interestingly, the next-to-worst material for initial capacity loss was D-NiO which had an average loss of 23.2%. This result was surprising since D-NiO was the best overall performing material studied in this work. The lowest average capacity loss was for R-NiO (14.9%), while N-NiO showed an average initial capacity fade of 20.6%. Clearly, structure played a role in the performance of the various NiO

electrodes studied in this work; however, the lack of a definitive correlation between capacity retention and initial capacity fade, in conjunction with the effects of carbon addition, seems to indicate that conductivity is a much more crucial property to overall performance than structure.

The addition of carbon to the NiO electrodes, and the NiO structure, also impacted the rate capability. This is shown in Figure 5. In fact, it is only the addition of carbon to the electrodes that allowed the rate capability to be tested for these materials at all. It should be noted that it is not practical for real lithium-ion battery anodes to contain as much as 40% carbon; however, for the sake of this study it was relevant to investigate high carbon loadings in order to probe the effects of conductivity more thoroughly. Future work will focus on imparting high conductivity into the NiO electrodes at low loadings of novel materials. All of the 0% C samples experienced such high capacity fading that the experiment could not be run in its entirety. In all cases, the 40% carbon samples yielded the best rate capability and capacity retention. Of these samples, D-NiO and R-NiO again substantially outperformed N-NiO and O-NiO in terms of the capacity values and recovered capacity at C/10. Though it should be noted that even O-NiO (with 40% C) was able to achieve a reversible capacity > 300 mAh/g at 5C. The best performing material, D-NiO, achieved > 400 mAh/g and saw a negligible amount of capacity fade during the experiment, which can be seen from the C/10 data taken at the beginning and end of the test. The data in Figure 5 also suggests that the small domain size observed by IL-TEM that is enabled by the high conductivity carbon allows the NiO to rapidly form and destroy chemical bonds, alleviating a key concern with reacting storage where bond breakage and formation steps can be rate limiting. The results also show that the mass transport of Li^+ is not impacted negatively by the presence of the carbon.

The influence of carbon on the charge-discharge kinetics, SEI and mass transport was also studied by EIS. To keep the presented dataset small, representative data from 0% C – 40% carbon N-NiO is shown in Figure 6. The general shape of all of the Nyquist plots is the same. The high frequency intercept ($Z_i = 0$) corresponded to the Ohmic resistance of the electrolyte. Two semicircles were observed; the first was born in the charge transfer (both electronic and ionic) resistance of the SEI, and the second was the kinetics for the NiO/Ni conversion reaction (Eq. 1). For all anodes, there was a clear trend in decreasing resistance with the inclusion of carbon. This is particularly true for the charge transfer resistance, which was reduced enough at high carbon contents to resolve the SEI semicircle. The improved kinetics with increased carbon content exactly correlates with the experimental results of improved capacity retention and rate capability observed with increased carbon content in the half cells, as well as the improved reversibility observed by CV. Between 20% and 40% carbon, the SEI resistivity was also substantially decreased, which also corroborates the CV results discussed above.

The second distinct trend observed in Figure 6 was in the low frequency Warburg impedance region. The angle of the straight line in the Nyquist plot was approximately 43° for 0% carbon NiO; however the angle increased to approximately 74° for 40% carbon NiO. The increase in angle of the Warburg impedance region can be attributed to a diffusion process in porous media that is approaching pure capacitive behavior (which would be a vertical line) [40,41]. This suggests increasing the carbon loading also improves Li^+ diffusion in the electrode via the pore structure of the carbon black additive [42], explaining the excellent rate capability in Figure 5. Finally, the similarity in plots for the higher carbon content anodes (particularly 40 wt% C) for the 3x- and 100x-cycled samples further corroborates the capacity retention and rate

capability data shown in this work. With the 0% carbon anode, on the other hand, there is a large difference in both shape and magnitude of charge transfer resistances before and after cycling.

4. Conclusions

The importance of conductivity on the cyclability of NiO anodes for lithium-ion batteries is paramount. In this study, varying amounts of carbon were added to NiO anodes to probe its effects on rate capability and reversibility, and in all cases the addition of carbon greatly enhanced the performance. Structural effects were also investigated using four distinct NiO nanostructures, and the best performing material studied was D-NiO which exhibited a capacity of >700 mAh/g at 1C with 40% added carbon after 100 cycles, and also maintained >400 mAh/g rate capability at 5C. SEI peak shifting, areas under the curve, and charge-transfer resistance decreases indicated that the addition of carbon in the NiO structure played a vital role in the SEI formation and, by extension, the electrode cyclability, which was confirmed by charge-discharge data. Total mass-averaged capacities also indicated that carbon not only improved performance via secondary Li^+ storage sites, but also by imparting conductivity to otherwise inactive $\text{Li}_2\text{O}+\text{Ni}$ particles, enhancing NiO reaction reversibility after many cycles. This point was also evidenced by the presence of the NiO/ $\text{Li}_2\text{O}+\text{Ni}$ reaction plateau even after 100 cycles at 1C. While the majority of researchers continue to focus efforts on producing anode materials with new and innovative morphologies, this work suggests that while structure is relevant, the key property associated with anode reversibility and capacity is conductivity. Improving the conductivity,

either via carbon additives or another means, may be the most crucial step in developing the next generation of high performance lithium-ion batteries.

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Figure Captions

Figure 1. SEM images for four different NiO microstructures prepared via different synthesis methods. (A) R-NiO; (B) N-NiO; (C) D-NiO; (D) O-NiO.

Figure 2. Cyclic Voltammograms for the first five (5) cycles for R-NiO samples with several additions of Vulcan XC-72R carbon: (A) 0%; (B) 10%; (C) 20%; (D) 30%; (E) 40%. (F) shows measured potentials for SEI reduction peak for each NiO microstructure and added carbon %.

Figure 3. Capacity retention plots over 100 cycles at 1C for R-NiO, N-NiO, D-NiO and O-NiO microstructures with increasing carbon content from 0% to 40%.

Figure 4. Identical location TEM images for O-NiO deposited onto a Cu TEM finder grid with 0% and 40% added carbon before and after two charge-discharge cycles.

Figure 5. Rate capability and capacity retention plots for R-NiO, N-NiO, D-NiO and O-NiO with added carbon content from 0% to 40%. Ten charge-discharge cycles were conducted at increasing C-rates: C/10, C/5, C/2, 1C, 2C, 5C, and finally C/10 again.

Figure 6. EIS Nyquist plots for N-NiO anodes with added carbon contents from 0% to 40% after 3 and 100 charge-discharge cycles.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6