Journal of Power Sources 276 (2015) 46–53

Contents lists available at ScienceDirect

Journal of Power Sources

journal homepage: www.elsevier.com/locate/jpowsour

Influence of conductivity on the capacity retention of NiO anodes in Li-ion batteries

Neil S. Spinner [a], Alessandro Palmieri [a], Nicole Beauregard [a], Lichun Zhang [b], James Campanella [a], William E. Mustain [a, b, *]

[a] Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States
[b] Institute of Materials Science, University of Connecticut, Storrs, CT 06269, United States

HIGHLIGHTS

- We investigate the importance of conductivity on NiO anodes.
- Four distinct NiO nanostructures were prepared via different synthesis methods.
- Capacity retention, reversibility, and rate capability studied.
- Addition of non-intercalating carbon vastly improved performance.
- Conductivity the key to future high capacity lithium-ion battery anodes.

ARTICLE INFO

Article history:
Received 1 September 2014
Received in revised form
27 October 2014
Accepted 18 November 2014
Available online 20 November 2014

Keywords:
Lithium-ion batteries
Conductivity
Nickel oxide
Anode

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 mA h/g after 100 cycles at 1C were observed, and a rate capability >400 mA h/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 as the conductivity was improved through carbon addition, 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 mA h/g; however, it suffers from massive volumetric expansion (more than 350%) during charge–discharge cycling,

---

* Corresponding author. Department of Chemical & Biomolecular Engineering, University of Connecticut, Storrs, CT 06269, United States.
E-mail address: mustain@engr.uconn.edu (W.E. Mustain).

http://dx.doi.org/10.1016/j.jpowsour.2014.11.089
0378-7753/

resulting in electrode pulverization and poor reversibility. Metal hydrides also offer high theoretical capacities above 2000 mA h/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 H_2 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 that, 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 MΩ 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 0.5 M $Ni(NO_3)_2$ (Acros, 99%) solution in 10 M NH_4OH (Fisher, certified ACS Plus) and boiling under reflux for 24 h, followed by a rest period at room temperature for an additional 24 h. 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 h.

N–NiO was synthesized by preparing an aqueous 0.5 M $Ni(NO_3)_2$ solution and quickly adding 10 M 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 h 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 h.

D-NiO was synthesized by placing $Ni(NO_3)_2 \cdot 6H_2O$ salt directly onto a 160 mm diameter ceramic evaporating dish and inserting it into a muffle furnace. The salt was then calcined in air at 400 °C for 3.5 h, causing dehydration and decomposition to pure NiO. The NiO powder was then finely ground using a dry mortar and pestle for 30 min.

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 0.5 M $Ni(NO_3)_2$ until a ratio of approximately 6.3 mL/g_{SBA-15} was reached. The resulting gel was manually stirred until homogeneous, followed by calcination in air at 400 °C for 3.5 h. Template was then etched away via two sequential 12-h soaks in hot (100 °C) 5 M KOH with a deionized water rinse and centrifugation (2000 rpm for 30 min) 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 N_2 adsorption isotherms at 77 K, collected using a Micromeritics ASAP 2020 system. Samples for BET analysis were degased under vacuum at 150 °C for 16 h prior to N_2 adsorption.

SEM images for all four NiO materials are shown in Fig. 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, Fig. S1). BET analysis (Supporting information, Fig. 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 h, 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 and 1.5 mg NiO/cm^2.

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 1 M lithium hexafluorophosphate ($LiPF_6$, 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.