High Performance Bi-Metallic Manganese Cobalt Oxide/Carbon Nanotube Li-ion Battery Anodes

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\textbf{A B S T R A C T}

Metal oxide compounds are a promising category of materials for the Li-ion battery anode due to their high theoretical capacity and natural abundance, although acceptable capacity retention and cycle life has not yet been achieved. In this work, we significantly improve the cycle life of manganese oxide through simultaneous cobalt doping and impregnation with a low 10% mass loading of carbon nanotubes (CNTs). The MnO/CNT anode was able to retain its capacity of ca. 550 mAh/g over 300 cycles at 400 mA/g. To the best of our knowledge, this is among the best cycle life data reported for any MnO/CNT-based anode. The composite also shows excellent rate capability, still supplying 400 mAh/g at a current rate of 1600 mA/g.

Conversely, there is a broad range of anodic materials presently under investigation that could not only yield a higher power density than graphite, but also lead to next-generation lithium ion batteries that exceed the USABC EV targets.

In recent years, the most widely investigated alternative to graphite at the anode has been silicon due to its very high theoretical capacity (up to 4000 mAh/g)\textsuperscript{[3]}. However, Si undergoes a very large volume expansion (more than 250% of the original volume) during cycling due to materials strain caused by radical structural changes, leading to electrode pulverization and short device life. Therefore, researchers have tried several approaches to improving the cycleability of Si-based anodes including voltage cutoffs, Si-C composites (even 50:50 wt%) or Si mixed with various advanced carbons\textsuperscript{[4]}. Unfortunately, these approaches practically limit the achievable energy density of Si anodes to around 1000 mAh/g. In this range, metal oxide (MO) anodes may be a better option than Si due to higher density and reduced volumetric expansion (only ~63% for MnO based on the lattice calculations outlined in Ref.\textsuperscript{[5]}). Another limitation of Si is the so-called “capacity penalty”\textsuperscript{[6]} that arises when the intrinsic anode capacity (mAh/g) is so much higher than the cathode material that the cathode electrode becomes impractically thick, leading to significant losses in the cathode.

Of the MOs, manganese oxides (MnO, MnO\textsubscript{2} and Mn\textsubscript{3}O\textsubscript{4}) are very interesting due to their natural abundance, low cost, high theoretical capacity and environmental friendliness\textsuperscript{[7]}.

1. Introduction

Li-ion batteries (LIBs) are the leading technology among all of the rechargeable options for portable power applications. The LIB industrial market was valued at over $12 billion in 2010, over $30 billion at the end of 2015 and it is estimated to grow up to $53.7 billion by 2020\textsuperscript{[1]}. Today, commercial LIBs are composed of a graphite anode and a Li-metal oxide cathode, principally lithium cobalt oxide; the typical electrolyte is composed of a lithium salt, LiPF\textsubscript{6}, dissolved in a mixture of organic carbonates. However, state-of-the-art commercial Li ion batteries are able to supply at most 150 Wh/kg, which is half of the value that is required to power electric vehicles with an acceptable driving range. Therefore, materials with higher energy density are required at both electrodes without sacrificing cycle life\textsuperscript{[2]}. Many cathode studies have been reported in the literature; however, the best performing materials still do not exceed 300 mAh/g due to the fact that only a few compounds meet all of the requirements for the cathodic side of the cell, namely: including lithium in the chemical structure, being resistant to corrosion and providing high electrochemical reversibility over a large number of cycles, especially during the more critical charge process where the cathode is de-lithiated.
Nevertheless, manganese oxides still suffer from volumetric expansion during cycling (though much less than Si), and only partial reversibility of the conversion electrochemical reaction due to its low electronic conductivity [8]. Among the electroactive Mn oxides, MnO possesses the lowest single oxidation state for these oxides. Thus during the charge reaction to metallic manganese, MnO undergoes a single conversion reaction, yielding a theoretical capacity of 755 mAh/g, where it is transformed by oxidation with Li⁺ to metallic manganese and Li₂O. This is entropically more favorable compared to the other forms of manganese oxide, which undergo more than one conversion reaction. Thus, a higher reversibility of the former with respect to the latter is reasonably expected. MnO is also characterized by relatively low voltage hysteresis (<=0.7V) and high density (5.43 g/cm³), and therefore high specific and volumetric energy [9].

MnO has been previously investigated by several research groups. The performance of raw MnO nanoparticles was reported by Ding and Wu [10], showing a very poor capacity retention, less than 100 mAh/g after only 16 cycles. To overcome this behavior, one of the most common approaches is to add carbon in order to simultaneously limit electrode volumetric expansion and increase electronic conductivity. Liu and Pan [11] reported a study on the effect of adding Vulcan carbon to MnO, demonstrating that a 10% addition enhances the performance up to 650 mAh/g although only 50 cycles were reported at a very low rate, 100 mAh/g (5C/10). Additionally, capacity retention data at practical rates was not reported and Vulcan carbon is not desirable because it is “dilutive”, meaning that it occupies a considerable volume within the electrode while not contributing to the overall capacity of the cell since it does not provide a matrix for Li⁺ intercalation. In recent years, new forms of non-dilutive carbon have been used as anodic materials for LIBs as well. Graphene [11] has been added to MnO because of its high electronic conductivity and good mechanical properties [12,13], although the most stable performance of a MnO/graphene anode that has been reported in the literature includes only 50 cycles at a rate of only 100 mA/g. MnO/carbon nanotubes (MnO/CNT) composites have also been investigated [10,14] showing 700 mAh/g at a C/10 rate, although only a limited number of cycles were shown. In fact, few MnO studies in the literature have demonstrated acceptable rate, capacity or stability under realistic cell conditions.

In this work, we report a high rate, high capacity, long cycle life MnO/CNT based anode for Li-ion batteries. This was accomplished through the facile synthesis of a Co-doped MnO/CNT composite. The CNTs act as a solid matrix to increase electronic conductivity and to provide a buffer for the volumetric expansion of MnO. Small amounts of Co were added because cobalt oxides have generally shown higher capacity and better capacity retention than manganese oxide [15], and recent supercapacitor studies have shown that Co-doping can stabilize the redox behavior of manganese oxide, inhibiting anodic dissolution and improving cyclic stability [16,17]. The capacity retention over 300 charge/discharge cycles and rate capability of a MnO₀.₅Co₁.₅O/CNT anode was investigated. Electrochemical impedance spectroscopy (EIS) was carried out before and after the 300 cycles in order to investigate the changes occurring at the electrode/separator interface during charge transfer including the solid electrolyte interphase (SEI).

2. Experimental

2.1. Reactants

Potassium permanganate (K₃MnO₄), multiwall carbon nanotubes (MWCNTs, catalogue number 724769), hydrogen peroxide (H₂O₂, 30%), sodium nitrate (NaNO₃), sulfuric acid (H₂SO₄), ethyl alcohol, (CH₃CH₂OH), and ammonium hydroxide (NH₄OH), manganese(II) acetate tetrahydrate Mn(CH₃COO)₂·4H₂O and cobalt(II) acetate tetrahydrate Co(CH₃COO)₂·4H₂O were purchased from Sigma-Aldrich. All chemicals were used as received without any further purification.

2.1.1. Controlled Oxidation of Multi-Wall Carbon Nanotubes (MWCNT)

Multiwall carbon nanotubes were oxidized similar to a modified Hummers’ method with a lower concentration of the oxidizing agent [18,19]. First, 60 mL of concentrated sulfuric acid was added to 1 g of multiwall carbon nanotubes (MWCNT) in a 250 mL round-bottom flask and stirred at room temperature for 24 h. The flask was then heated in an oil bath at 40 °C and 0.1 g of NaNO₃ was added to the mixture. Then, 1 mg KMnO₄ was slowly added to the solution while keeping the reaction temperature below 20 °C in an ice-water bath. The reaction was removed from the ice-water bath after 30 min and was transferred to an oil bath at 45 °C and allowed to stir for 30 min. Then, 3 mL of DI-water was added, followed by another 3 mL after 5 min and 40 mL after 10 min. After 15 min, the flask was removed from the oil bath and 140 mL of DI-water and 10 mL of 30% H₂O₂ was added to quench the reaction. The obtained product was centrifuged and washed with 5% HCl solution two times. The homogeneous supernatant was collected by centrifugation.

2.1.2. Synthesis of Mn₉O₄Co₉O/CNT

In a typical synthesis, 90 mg of the oxidized MWCNTs was well dispersed in a 122.5 mL ethanol/DI water solution with a ratio of 48:1 for 1 hr. In the next step, 3 mL of manganese(II) acetate tetrahydrate (0.6 M in DI-water) solution was added. To achieve a 10 mol% Co doping in Mn, stoichiometric moles of Mn precursor was replaced with cobalt(II) acetate tetrahydrate. The mixture was transferred to an oil bath and re-fluxed for 24 hours after adding 2.5 mL of ammonium hydroxide solution. The solids were collected by centrifugation and dried in vacuum at room temperature for 72 hrs. Finally, the Mn₉O₄Co₉O/CNT anode material was obtained by annealing the dried sample at 600 °C for 3 hours in an argon atmosphere.

2.2. Chemical and Structural Characterization

Powder X-ray diffraction (XRD) patterns were collected on a Bruker D2 Phaser with Cu Kα radiation (λ = 1.54184 Å) at room temperature with an operating voltage and current of 30 kV and 10 mA. X-ray photoelectron spectroscopy (XPS) was conducted on a PHI model 590 spectrometer with multiropes (Filips Physical Electronics Industries Inc.), using Al Kα radiation (λ = 1486.6 eV). Transmission electron microscopy (TEM) was performed using a FEI Talos F200X TEM/STEM at an accelerating voltage of 200 kV.

2.3. Anode Fabrication

LIB Anodes were fabricated by preparing inks containing 70 wt% of active material (Mn/C Co CNT supported), 20 wt% conductivity-enhancing black carbon (NERGY Super C65, Imerys) and 10 wt% binder, polyvinylidene fluoride (PVDF, Kynar blend). The components were dispersed in N-methylpyrrolidone (NMP, Acros, 99.5% Extra Dry) solvent and the final ink (typically 90 mg of active material dispersed in 800 μL of solvent) was homogenized through repeated and successive 15 minute sonications (4 times) and mechanical stirring overnight. 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 by hand with an Iwata model sprayer onto the Cu foil to a uniform thickness, heated under vacuum at 100 °C for 24 hours, then pressed at 1500 lbs, calendared
with a 0.3 mm gap and massed to obtain the loading. For all electrodes fabricated in this study, the active loading was held between 1.0 and 1.5 mg/cm² and the capacity was calculated based on the active material mass of the electrode (calculation shown in the Supporting Information). The average packing density of the electrodes was 610 mg/cm³.

2.4. Coin Cell Assembly

Coin cells were constructed to investigate the electrochemical behavior of the MnO-Co/CNT 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 (LiPF₆, Acros 98%) electrolyte was prepared from a 1:1:1 volumetric fraction ethylene carbonate (EC, Acros 99+%), dimethyl carbonate (DMC, Acros 98+%), and diethyl carbonate (DEC, Acros 99%). The separator was punched to a diameter of 1.9 cm while the anode was cut to a 1.5 cm diameter disk. In an argon-purged glove box (Labconco), the lithium foil cathode was also punched to a 1.5 diameter disk. Afterwards, 15 µL of electrolyte was pipetted onto each side of the separator and placed in between the anode and the cathode. Lastly, the gasket, spacer disc, spring and upper case were positioned on top of the cathode and all of the components were then crimped and sealed into the coin cell hardware before being safely removed from the Ar atmosphere-controlled glove box for electrochemical testing.

2.5. Electrochemical Testing

Charge-discharge measurements were carried out at various rates between 0.001 and 3 V using an Arbin MSTAT battery test system. The MSTAT system was also used to collect cyclic voltammograms (CVs) at a scan rate of 0.1 mV/s over the same voltage windows as the charge/discharge cycles. All potentials are reported vs. Li/Li⁺. Electrochemical Impedance Spectroscopy (EIS) was conducted between 100 kHz–50 mHz with a 5 mV amplitude at the coin cell open circuit voltage, using an Autolab PGSTAT302 N Potentiostat (Eco Chemie).

3. Results and Discussion

The XRD pattern for Mn₀.₉Co₀.₁O is shown in Fig. 1a. There were 5 well-defined peaks, all matching the face centered cubic (FCC) Miller planes for MnO [20]. Moreover, there was no evidence of the primary CoO peaks at 37 and 42° degrees [21], which is an indication of the fact that there was no phase separation between manganese and cobalt, and that the sample was instead doped with cobalt, which now replaced some Mn atoms in the 6-6 oxygen-manganese octahedral coordination matrix. The average crystallite size was calculated from the XRD pattern using the Sherrer equation, 17 nanometers. The composition of the Mn₀.₉Co₀.₁O was confirmed (Supporting Information), and the cobalt and manganese oxidation states were determined, by XPS, Fig. 1b. The high resolution spectra for Mn 2p₁/₂ and 2p₃/₂ are shown in Fig. 1c. Two peaks were identified at 652 and 640 eV, which is typical for Mn⁺⁺ [22]. The displacement among the two peaks is due to the difference in electronic spin and was found to be equal to 11.6 eV, which is in good agreement with archival data for MnO. Moreover, peak deconvolution showed that the fitting of only two peaks was possible, confirming that no metallic manganese or higher oxidation state Mn compounds were present on the surface. Fig. 1d shows a TEM image of the Mn₀.₉Co₀.₁O nanoparticles, which possessed an almost spherical shape and were well embedded into the carbon nanotubes matrix. The shown particle had a diameter of ca. 13 nm, which is in good agreement with the XRD analysis. Fig. 1e

![Fig. 1. (a) XRD pattern for Mn₀.₉Co₀.₁O. (b) XPS General Survey Spectrum. (c) XPS High Resolution Spectrum for Mn 2p. (d) TEM image of a Mn₀.₉Co₀.₁O nanoparticle. (e) Higher magnification image, detail of multiwall carbon nanotubes feature. (f) TEM diffraction pattern for the Mn₀.₉Co₀.₁O material.](image-url)
is a magnification of the previous image on the top right corner of the particle. The image clearly highlights the multi-wall feature of the carbon nanotubes, which had an average diameter of 3 nm. Lastly, Fig. 1f shows the corresponding selected area electron diffraction (SAED) pattern of the sample. The concentric rings confirm the growth of the MnO nanoparticles on the multiwall carbon nanotubes with polycrystalline character.

Cyclic voltammograms (CV) for Mn$_{0.9}$Co$_{0.1}$O/CNT in 1 M LiPF$_6$ dissolved into 1:1:1 EC:DMC:DEC is shown in Fig. 2a. Several cathodic and anodic features were observed in the CV, which can be attributed to the formation of the SEI layer as well as the storage of Li$^+$ both intercalated into the CNTs and conversion of the metal oxide. In the first cycle, the small single cathodic peak at 0.4 V can be mainly attributed to the conversion reaction of the Mn$_{0.9}$Co$_{0.1}$O material to its reduced metallic form. The second, and more distinct, peak at 0.05 V represents the formation of the SEI and possibly the intercalation of Li ions into the carbon nanotubes [23]. In the anodic sweep, only a single peak was observed at 1.3 V, which is most likely due to the reformation of the metal oxides from the reactions of Mn$_{0.9}$Co$_{0.1}$O with the Li$_2$O phase.

In the second cycle, there remained a single anodic peak that did not change position but increased in intensity as an increased amount of the metal oxide was able to participate in the conversion reaction. This peak retained a consistent size and shape from Cycle 2-Cycle 5. The behavior during the cathodic sweep was more complex. In Cycle 2, two clearly distinct peaks emerged at 0.45 and 0.35 V, which appear to arise from the splitting of the singular peak in Cycle 1. The peak at 0.45 V was previously ascribed to the MnO conversion reaction [23], according to the stoichiometry:

$$\text{MnO} + 2\text{Li}^+ + 2e^- \rightarrow \text{Mn} + \text{Li}_2\text{O}$$  \hspace{1cm} (1)

It is unlikely that the latter peak is due the conversion of CoO to Co + Li$_2$O. Indeed, in the literature, the CoO conversion peak is reported at higher potentials [21] and the raw MnO/CNT material CV showed a congruent behavior (see supporting information). Interestingly, this peak splitting suggests that during discharge, and reformulation of the metal oxide, there is formation of two distinct Mn oxides, MnO and most likely Mn$_2$O$_4$ according to [24]:

$$3\text{Mn} + 4\text{Li}_2\text{O} \rightarrow \text{Mn}_2\text{O}_4 + 8\text{Li}^+ + 8e^-$$  \hspace{1cm} (2)

Mn$_2$O$_4$ is the most likely secondary phase because of the mixed Mn(II)/Mn(III) states, which only partial oxidation of the MnO to a higher oxidation state, unlike the formation of MnO$_2$ which would require two additional electrons per Mn [25].

Although not visible in the cyclic voltammogram, the high intrinsic capacity of the material suggests that Co conversion is also happening, according to the following stoichiometry:

$$\text{CoO} + 2\text{Li}^+ + 2e^- \rightarrow \text{Co} + \text{Li}_2\text{O}$$  \hspace{1cm} (3)

During subsequent cycles, the peak at 0.45 V became much sharper than the peak at 0.35 V, suggesting that the quantity of the second Mn oxide phase comprised only a small amount of the active material. Lastly, the displacement between anodic and cathodic peaks was relatively small compared to most other metal oxides (i.e. nickel oxide which has a peak separation of around 1.5 V [26]), which points to improved reaction kinetics, and hence better stability and rate capability than other MOs. In full cells, this would directly result in higher round-trip thermodynamic efficiency. Finally, the peak at 0.05 V can be ascribed to Li$^+$ intercalation into the carbon nanotubes matrix as the SEI has been fully formed by Cycle 5 and a significant signal remains.

The reversibility and stability of Mn$_{0.9}$Co$_{0.1}$O/CNT at the Li-ion anode was further investigated through 300 charge/discharge cycles at a 400 mA/g rate. The results of the capacity retention tests are shown in Fig. 2b, and the capacity of the Mn$_{0.9}$Co$_{0.1}$O/CNT was nearly a flat line with an average value of 550 mAh/g, which corresponds to more than a 50% increase in the capacity that is available from commercial graphite electrodes at the same rate (Fig. S1 of the Supporting Information). Another important consideration is that the bulk density of MnO is nearly 2.5 times that of graphite, meaning that the volumetric energy density can be up to 3.5 times better for MnO vs. graphite. Additionally, its irreversible capacity loss from the formation of the SEI was small compared to other MnO based materials in the literature [27], only ~25%. The discharge cycles have been included in Fig. 1b as well, showing an almost identical pattern, and the coulombic efficiency was almost always greater than 99%. This represents a significant improvement when comparing it with the non-doped MnO/CNT material (Fig. S4 of the Supporting Information), which shows significant capacity fade after only 100 cycles, displaying a final capacity of ca. 310 mAh/g after 300 cycles.

Charge/discharge curves at several discharge rates are shown in Fig. 3a. The Mn$_{0.9}$Co$_{0.1}$O/CNT anodes showed very good rate performance. At 1600 mA/g, the material was able to supply almost 300 mA/g, which is not only excellent for MnO, but competitive with the best performance reported for higher oxidation state Mn oxides as well [28]. As expected, as the charge/discharge rate was increased voltage separation from the electrode polarization also increased. However, at all rates the shape of the charge/discharge
increasing performance is CNT
plateaus of charge/discharge
the of ions

Supporting curves
Fig. 3. (a) Galvanostatic charge/discharge profiles of the Mn0.9Co0.1O/CNT composite cycled at a current rate of 40, 400, 800 and 1600 mA/g between 0.01 and 3 V (vs. Li/LiI). (b) Rate capability of the Mn0.9Co0.1O/CNT electrode.

curves were almost identical. During the charge, two different plateaus were observed. The first plateau began at approximately 1.0 V, which is usually ascribed to the conversion reactions of the metal oxides. The second plateau started at ca. 0.55 V, signaling the end of the conversion reaction along with the intercalation of Li ions into the CNT matrix. Lastly, for all four charge/discharge rates, the coulombic efficiency was always greater than 98%.

The rate capability and stability of the Mn0.9Co0.1O/CNT anodes is shown in Fig. 3b. At a current rate of 40 mA/g, the Mn0.9Co0.1O/CNT supplied a capacity of ca. 600 mA/h, which is 84.15% of the theoretical value based on a mass normalized theoretical capacity of the active material (713 mA/h, calculation shown in the Supporting Information). At a current rate of 400 mA/g, the capacity was reduced by only 100 mA/h, and the recorded capacity was around 500 mA/h. After doubling the current rate to 800 mA/g, the active material showed a decrease of only 60 mA/h. Finally, after increasing the current to 1600 mA/h, the capacity was still very high, leveling just below 400 mA/h. Also, the cell performance seemed to improve with increasing cycle number.

Comparing the first and second analysis at 40 mA/g, including their charge/discharge curves, the most likely explanation for the performance increase is CNT partial exfoliation during cycling, increasing number of Li intercalation sites [29].

Fig. 4a shows the results of electrochemical impedance spectroscopy (EIS) tests carried out after 3 (black line) and 300 (green line) charge/discharge cycles. Both EIS spectra showed two semicircles. At very high frequency, the overall signal was dominated by the migration of lithium ions in the electrolyte. The higher frequency semicircle (low Z values), is rooted in the ionic and charge transfer resistance of the solid electrolyte interphase (SEI). The low frequency semicircle (intermediate Z values) indicates the charge transfer resistance occurring at the anode/electrolyte interface. The straight line on the right-hand side of the Nyquist plot (at low frequency) is caused by the solid-state diffusion of Li ions into the electrode. The equivalent circuit in Fig. 4b [30] was used to interpret and deconvolute the EIS data. Four sets of elements were used to account for the total resistance of the half cell. Starting from the left hand side, R1 is the inner resistance of the electrolyte solution. R3 and C3 are the resistance and capacitance for Li ion diffusion at the separator/electrode interface caused by SEI formation. R2 and C2 account for the conversion charge transfer resistance and double layer capacitance. Lastly, W corresponds to a Warburg element that accounts for the diffusion of Li ions into the electrode. Both R1 and R2 + R3 were greater for the battery after 300 cycles, showing that the cell impedance does increase during cycling. As expected, the electrolyte resistance, R1 was not significantly affected by cycling. However, the SEI and MnO conversion resistances were increased. Prior to cycling, two semicircles were not easily separated in the Nyquist plot. After 300 cycles, two semicircles are clearly observed, with a considerable amount of the impedance increase assigned to R2. When combined with the stable capacity performance observed in Fig. 2b, it is most likely that the growth of the SEI during cycling is the primary cause of the increased impedance [31] and that the Mn0.9Co0.1O/CNT is stable over 100 s of cycles under realistic lithium ion battery operating conditions. Because of the high performance of the Mn0.9Co0.1O/CNT, the increased SEI resistance at 400 mA/h was not enough to induce significant performance losses; however, some performance losses would likely be observed under high rate discharges, as inferred by the voltage polarization which is already detected at 400 mA/h between cycle 3 and cycle 300 (Fig. S5 in the Supporting Information).
4. Conclusions

Metal oxide materials are one of the most promising classes of materials to replace graphitic anodes in next generation high energy density Li ions batteries. A high performing bimetallic Mn$_{0.9}$Co$_{0.1}$O carbon nanotube composite material and its outstanding anodic performance in lithium ion batteries has been presented in this work. The Mn$_{0.9}$Co$_{0.1}$O anode showed excellent capacity retention over 300 cycles, with a coulombic efficiency constantly higher than 98.5% as well as high rate capability. The concomitant doping of Mn with Co and complexity with the 10% weight CNT allowed for the very high performance of the MnO-based anode under realistic Li-ion battery operation.

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Appendix A. Supplementary data

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References