



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



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ABSTRACT

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.

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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 [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, LiPF₆, 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 [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.

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) [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 [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. [5]). Another limitation of Si is the so-called “capacity penalty” [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, MnO₂ and Mn₃O₄) are very interesting due to their natural abundance, low cost, high theoretical capacity and environmental friendliness [7].

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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 Li_2O . 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 ($<0.7\text{ V}$) and high density (5.43 g/cm^3), 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 mA/g ($\sim C/10$). 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 $\text{Mn}_{0.9}\text{Co}_{0.1}\text{O/CNT}$ 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 (KMnO_4), multiwall carbon nanotubes (MWCNTs, catalogue number 724769), hydrogen peroxide (H_2O_2 , 30%), sodium nitrate (NaNO_3), sulfuric acid (H_2SO_4), ethyl

alcohol, ($\text{CH}_3\text{CH}_2\text{OH}$), and ammonium hydroxide (NH_4OH), manganese(II) acetate tetrahydrate $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and cobalt(II) acetate tetrahydrate $\text{Co}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ 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 NaNO_3 was added to the mixture. Then, 1 mg KMnO_4 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% H_2O_2 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 $\text{Mn}_{0.9}\text{Co}_{0.1}\text{O/CNT}$

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 $\text{Mn}_{0.9}\text{Co}_{0.1}\text{O/CNT}$ 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 $\text{Cu K}\alpha$ radiation ($\lambda = 1.54184\text{ \AA}$) 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 multipoles (Φ Physical Electronics Industries Inc.), using $\text{Al K}\alpha$ radiation ($\lambda = 1486.6\text{ eV}$). 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/Co CNT supported), 20 wt% conductivity-booster carbon black (CNERGY 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

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