Graphene Assisted NMC Based Cathode Electrodes with Enhanced Charge Rate and Energy Storage

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Abstract

LiNi₁/₃Mn₁/₃Co₁/₃O₂ (NMC) cathode electrode was synthesized by using facile sol-gel method. Graphene reinforced NMC freestanding electrodes were then synthesized through a vacuum filtration process. The crystal structure and surface morphology and electrochemical properties were characterized via X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), energy dispersive spectrometry (EDS), The results shows that the layered NMC and NMC decorated graphene were successfully produced. Electrochemical performance was investigated with galvanostatic charge–discharge tests, cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements. The results present that NMC decorated graphene shows improved electrochemical performance.

1. Introduction

Today, the importance of energy storage in telecommunication, automotive, energy and satellite technologies gradually increase [1]. Lithium ion technology are lately extensively employed energy storage device for electric vehicles and all portable electronics [2]. The reason for the use of Li ion batteries in these applications is their relatively high energy density (>150 Wh kg⁻¹), low cost, safety and improved performance [3]. Due to the need for high energy density, high power of batteries, the development of new materials for Li-ion batteries has become attractive for researchers [4].

Layered LiMO₂ (M = Ni, Fe, Co, Mn or mixture), olivines LiMPO₄ olivines or spinel LiMn₂O₄ based cathodes are commonly used for Li ion batteries [5]. Among these cathode materials, NMC is most promising cathode for Li-ion batteries because of its lower cost, lesser toxicity and better stability during cycling at high temperature [6]. NMC provides high specific capacity in the range of 140-160 mAh/g with fast lithiation/delithiation owing to its layered structure [7]. NMC which has R₃m rhombohedral space group is consisted of edge sharing TM₆ octahedral [TM= Ni, Mn, Co] separated by lithium ions occupying octahedral sites. In this structure, Ni is the electrochemically active, Mn supplies structural stability while Co promotes ordering of lithium and nickel ions onto their respective lattice sites [8,9].

Unfortunately, NMC has three serious drawbacks hindering its further applications. The first one is the undesired interfacial reactions between NMC and electrolytes that causes to the catalytic effects of the redox couple of Co³⁺/⁴⁺ that is inserted during NMC is being charged up to a high cut-off voltage of 4.55V [10]. The second one is the structure corruption is cation disorder between Li⁺ and Ni²⁺ in the NMC crystal lattice that can cause low specific capacity. The third one is low lithium ion mobility and electronic conductivity that lead to the inferior rate capability and serious electrode polarization [11,12]. To overcome these issues, different stoichiometrically cation and anion additives have been studied for improving performance of NMC in previous studies [13]. Also, surface coating such as CeO₂, Al₂O₃, and FePO₄ has been tried to provide good electronic, ionic conductivity and stability with electrolyte [14]. In particular, carbon coating has been an effective modification method due to protecting the particles from chemical attack from the electrolyte and enhancing the conductivity of the metal oxide [15].

Owing to the high electronic conductivity, large specific surface area and excellent structural stability, multi walled carbon nanotube (MWCNT) have been used as conductive nanostructured carbon matrices to improve the electronic conductivity, specific capacity, rate capability and cycling stability of the LiNi₁/₃Co₁/₃Mn₁/₃O₂. improve the particle-to-particle electronic transfer of the active material. It is necessary to avoid the self-aggregation while constructing a three-dimensional carbon network by sufficiently utilizing the advantages of one-dimensional (1D) MWCNT [16,17].

In this study, we aimed to produce of NMC and NMC decorated MWCNT cathode materials for Li ion batteries. For producing NMC powder, fast and facile sol-gel method was used. Obtained NMC powder was decorated between graphene layers by chemical reduction method to improve
conductivity and rate performance. The effect of the MWCNT on the electrochemical properties was investigated.

2. Experimental Procedure

2.1. Synthesis of NMC powders:

NMC powders were synthesized via sol-gel method that providing high purity, homogeneity and uniform crystal morphology. In this process, 1M Li-nitrate (CH₃COO)₂.H₂O, Ni-acetate (Ni(CH₃COO)₂.4H₂O), Mn-acetate (C₃H₆MnO₄. 4H₂O.C₄), Co-acetate (C₃H₆CoO₄.4H₂O) (1/3: 1/3: 1/3 molar ratios) were used as starting materials and citric acid was also used as a binding agent. Li-nitrate (CH₃COO)₂.H₂O, Ni-acetate (Ni(CH₃COO)₂.4H₂O), Co-acetate (C₃H₆CoO₄.4H₂O), Mn-acetate (C₃H₆MnO₄. 4H₂O.C₄) were dissolved in 60 ml distilled water and stirring was continued by adding citric acid. The solution was stirred at 90 °C for 4 hours until a clear viscous gel was formed. The gel-like solution is dried for 12 hours at 70 °C and then calcined at 350 °C for 4 hours and 900 °C for 9 hours in air at a rate of 5 °C / min to get the NMC powders.

2.2. NMC/MWCNT Freestanding Electrode Preparation:

MWCNTs used in this study are provided by Arry International Co., Ltd., Germany. No further purification or doping has been applied to MWCNTs by the supplier. The length and the diameter of the MWCNTs were 50 nm and 1μm, respectively. The purity of the MWCNTs were more than 95%, while impurity contents such as metal catalyst, amorphous carbon and ash were less than 5 wt.% according than 95%, while impurity contents such as metal catalyst, amorphous carbon and ash were less than 5 wt.% according to the supplier specifications. Before producing the bucky papers, MWCNTs are purified and functionalized as a specified recipe. Amorphous carbon content is removed by heating the MWCNTs at 350 °C for 8 h. Heat-treated product was then magnetically stirred at 140 °C for 4 h in a nitric acid solution in order to remove the metal catalysts. Finally, modified MWCNTs are chemically oxidized in a solution, containing H₂SO₄ and HNO₃ acids at a ratio of 3:1 for 3 h. The chemically oxidized MWCNTs were used to prepare freestanding buckypapers. In a typical process, 25 mg functionalized MWCNTs and 25 mg NMC particles are dispersed in bidistilled water containing 60 mg sodium dodecyl sulphate (SDS, Sigma Aldrich) and ultrasonicated for 2 h. The suspended product was then vacuum filtrated by a metal mask covering on a sheet of filter paper. The bucky papers were then peeled-off from paper and dried in a vacuum oven at 60 °C for 12 h.

2.3. Characterization Techniques

The morphology and chemical composition of NMC powders and NMC/MWCNT freestanding electrode were investigated with FEI field emission scanning electron microscopy (FESEM) coupled with energy dispersive X-ray spectroscopy (EDS) analysis. The crystal structures of the NMC powders and NMC/ MWCNT freestanding electrode were determined by using X-ray diffraction (XRD) system with Cu Kα radiation from 10° to 90°.

A coin type cell (CR2016) was assembled in argon filled glove box. NMC and NMC/ MWCNT cathode electrode materials were used as working electrode and lithium metal foil was used as a counter electrode. 1 M LiPF₆ dissolved in mixture of ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 by volume) was used as an electrolyte while a polypropylene (Celgard 2400) was used as a separator to prevent short circuit. The galvanostatic charge- discharge tests of electrodes were performed with a constant current density 0.02 μAh and cut off voltages between 2.5 V and 4.6 V vs. Li/Li⁺.

3. Result and Discussion

Fig. 1 displays the XRD patterns of NMC powders and NMC decorated MWCNT freestanding cathode materials. As seen from the XRD results, NMC peaks are quite sharp, clear and, well-defined. All NMC peaks are consistent with the hexagonal a-NaFeO₂ structure with a space group of R-3m without any impurity phases (JCPDS 44-0145) [18]. The lattice constants for LiNi1/3Mn1/3Co1/3O₂ are a = 2.851 Å and c = 14.219 Å and for LiNi1/3Co1/3Mn1/3O₂/MWCNT are a=2.857 Å and c=14.227 Å [19]. The transition metal atoms (M=Ni, Co, Mn) are assumed to distribute on the 3b sites, while Li atoms are situated in the 3a sites and O atoms are situated in the 6c sites. The clear splitting of hexagonal doublets (006)/(012) and (108)/(110) near 38° and 65° observed for both of these samples indicates the highly ordered layer structure of NMC. The integrated intensity ratio of the (006)/(102) lines in the XRD patterns is determined to be 1.33 and 1.37 for NMC and the NMC/MWCNT composite, respectively [19,20]. The result exhibits that the NMWCNT layers has no influence on the crystalline structure of NMC submicron particles.

The surface morphology of the as-synthesized NMC cathode electrodes were examined by FESEM and shown in Fig 2. The as-synthesized particles are polyhedral in shape and having a particle size of 270-750 nm. It can also be concluded from the Fig. 2 that the particles are fused together and forming a macro porous structure. It is also reported that uniform distribution of particles can provide good the electrode–electrolyte contact area and facilitating the transportation of Li⁺ and electrons.
The morphological examination of cross-sectional images NMC/CNT freestanding electrodes were also investigated and shown in Fig. 3. Higher magnification images clearly indicate that MWCNT have shown an irregular curly and wavy 1D shape. NMC particles are also surrounded by MWCNT. NMC particles are homogenously distributed all over the cross-sectional area after the vacuum filtration process. Fig. 3 also confirms that the NMC particles act as a spacer in order to prevent the agglomeration or re-stacking of MWCNT.

Fig 4 presents galvanostatic charge/discharge tests of NMC and NMC/MWCNT freestanding electrodes. The electrochemical tests was carried out between a potential window of 2.2-4.6V at 1C rate (1C=280 mAh g⁻¹). It should be noted that pristine NMC electrode presents a specific discharge capacity of 210.2 mAh g⁻¹, while NMC/MWCNT cathode electrode exhibits a specific discharge capacity of 209.2 mAh g⁻¹ during the initial discharging. Moreover, as shown in Fig. 4(a) and 4(b), a specific discharge capacities of 157.7 mAh g⁻¹ and 199.2 mAh g⁻¹ after 250 cycles at a high rate of 280 mAh g⁻¹ is obtained for NMC and NMC/MWCNT samples, respectively. In addition, NMC/MWCNT cathode electrode still deliver a specific discharge capacity with a capacity retention of 95.22% after 250 cycles (vs. to the first discharge capacity), whereas only a 75% capacity retention is obtained from the pristine NMC sample.
Figure 5. Cycle number vs. Specific discharge capacities of the NMC and NMC/MWCNT half-cells.

Long term charging and discharging tests of NMC and NMC/CNT half cells are also studied by an extended cyclic study and shown in Fig. 5. NMC/MWCNT sample has clearly shown higher capacities than pristine sample. Electrochemical tests also confirmed that freestanding electrodes based on CNT could be an efficient way from enhanced battery performance. The improved battery performance is mostly due to the unique one dimensional architecture provided by the MWCNT. This structure reduces the ohmic resistance arising between electrolyte and cathode electrode.

4. Conclusion
In summary, sub-micron NMC particles were produced by a facile sol-gel method. Submicron NMC particles were then decorated between the layers of MWCNT. The novel architecture with the embedment of NMC particles within MWCNT nano layers, more space in the interior of freestanding structure and an extraordinary electron conductivity, relieved the volume change and stress during the alloying/dealloying processes, providing superior cycling stability that remained above 199.2 mAh g⁻¹ after 250 cycles.

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