



Defining role of the surface and bulk contributions in camphoric carbon grafted lithium nickel manganese oxide powders for lithium ion batteries

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Abstract

In the present study, lithium nickel manganese oxide powders grafted with camphoric nano-carbons have been exploited to fabricate high voltage, high capacity rechargeable electrodes for Li storage. The prepared lithium nickel manganese oxide particles were pyrolyzed using a camphoric solution to graft porous camphoric carbon layer on to the surface. A detailed study was performed to elucidate the effect of carbon content on the performance of the electrode. Relative contributions of capacitive and diffusion-controlled processes underlying these composite electrodes have been mathematically modeled. The lithium nickel manganese oxide composites showed two times higher conductivity as compared to the pristine samples. These electrodes exhibited a specific capacity value of $\sim 154 \text{ mAhg}^{-1}$ and showed good rate capability. The capacity fading was found to be $\sim 17\%$ at the end of 200 cycles for 100% depth of discharge. The specific capacity and capacity retention for these blends were found to be $\sim 10\%$ and $\sim 40\%$ higher respectively than pristine powders which are promising considering their low cost and facile fabrication process.

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1. Introduction

The market for lithium ion batteries has been rapidly growing with the increasing demand for energy storage systems since its inception in 1990s. Although lithium ion battery technology enjoyed great success for portable electronic device applications, its performance is still not at par in aspects of energy and power density, rate capability, cycle life, and cost as per the requirements raised by electric vehicles (EVs), hybrid electric vehicles (HEVs), and plug-in hybrid electric vehicles (PHEVs) applications [1–4]. In order to meet the requirements for the above applications, increasing the working voltage of lithium ion batteries has become one of the most important strategies whereby the energy density can be enhanced [5]. As the voltage of a lithium ion battery is

mainly governed by the type of cathode material that is utilized, the research for new lithium ion battery cathodes has gained a lot of attention in the research community. Lithium nickel manganese oxide (LNMO, $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$) is a high voltage cathode material with a theoretical capacity of $\sim 147 \text{ mA h}^{-1} \text{ g}^{-1}$ and a high working voltage plateau of 4.7 V [6]. LNMO has shown $\sim 20\%$ and $\sim 30\%$ higher energy density than LiCoO_2 and LiFePO_4 , respectively, making it a potential candidate to be used in EVs [7–12]. However, major limitation of LNMO is its relatively low conductivity [13]. Moreover, the electrochemical stability of LNMO at such a high working voltage in carbonate-based liquid electrolyte causes serious capacity fading during cycling due to the interfacial side reaction between the high-voltage charged LNMO and the liquid electrolyte [14,15]. There are trace presence of Mn^{3+} ions in the LNMO crystal which have a tendency to decompose into Mn^{2+} and Mn^{4+} . Mn^{2+} ions have a tendency to dissolve into the electrolyte and deposit on to the anode. This deposition increases the overall impedance of the battery and causes capacity

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fading [16]. One of the potential solutions to overcome this problem is to modify the surface of LNMO with a thin layer of coating material. Earlier literature of some coating materials on LNMO, such as Ag [17], Au [18], Bi₂O₃ [19], ZrO₂ [20], BiOF [14], ZrP₂O₇ [20], ZnO [15,21], conductive carbon [13], and polyimide [22] has shown improvement in the capacity performance to a certain degree. However, these coatings were subjected to single charge discharge conditions, which makes it difficult to judge the effect of coating for higher number of cycles. For the coating materials mentioned above, the metal oxide and metal fluoride coatings played the role of a protection shell, but could not enhance the electron conductivity of LNMO. One of the metal oxide systems i.e. Bi₂O₃ showed phase transformation to Bi metal during cycling. This transformation was advantageous considering the fact that it could help with fast electron transfer. But the cycling stability was not enhanced due to the microstructural changes of Bi₂O₃ during the cycling process [19]. Direct metallic coating of Au and Ag on LNMO showed limited improvement in the capacity and in some instances deteriorated its performance [17,18]. Conductive carbon coating has been sought as a good alternative, since it can work as a protective layer and also act as a current collector for LNMO enhancing its rate capability and energy density. Although this strategy has been effective on many other materials, it is difficult for LNMO since a reduction atmosphere is required for the carbon source to carbonize at high temperature at graft itself onto the surface. LNMO needs an oxygen atmosphere to avoid too many oxygen vacancies in the crystal which otherwise can affect its conductivity and stoichiometry. This effect was shown in one of the reports where conductive carbon coating on LNMO [13], showed slow charge rate and low coulombic efficiency was low. In this regard, it is important to find an alternative coating technique that can act as a protective layer and at the same time enhance the conductivity of LNMO. Recent studies on employing graphene and graphene oxide have shown improvement in cycling stability and rate performance in lithium ion batteries and lithium sulfur batteries [23–28]. Graphene and graphene oxide have shown to provide stable wrapping layer during the charge–discharge process where the conductivity and interaction with the active materials can be modulated by tuning the degree of oxidation of graphene. Even as these techniques have shown promising results, they also have limitations. For instance, graphene tend to agglomerate easily during the cathode fabrication because of the binder and intrinsic Van der Waals attractive forces [29,30]. Thus, use of surfactants is required which reduces the conductivity of the electrode when processed in bulk. Moreover, the high processing cost associated with such bulk production of these carbons is also an issue. Based on this account, the present study demonstrates a simple and cost effective exploitation of LNMO particles subjected to camphorization through pyrolysis such that nanocarbons are anchored onto its surface providing a conductive and protective layer. The results indicate that camphoric carbon coated LNMO showed good cycling stability and rate capability as a high voltage cathode material at low cost. This technique has a great potential for high energy density and long life lithium ion batteries.

2. Experimental

2.1. LNMO powder synthesis

Reagents used in the present study were obtained from Sigma Aldrich. Firstly, 6 M MnSO₄·H₂O and 3 M NiSO₄·6H₂O were separately dissolved in 20 mL distilled water and mixed together under stirring condition. To this solution 12 M NaOH was added. pH=8 was maintained by dropwise addition of 1 M NH₄OH. This solution was autoclaved in a teflon-lined container at 180 °C for 6 h and furnace cooled. The 8 M of the resultant powder was uniformly dispersed in 1 M LiOH solution. This dispersion was subjected to sintering (ramp rate 5 °C min⁻¹) in air at 350 °C for 30 min and 1000 °C for 20 h and furnace cooled.

2.2. Camphor carbon grafting

1.5 M of camphor was completely dissolved in 3 mL methanol. To this solution, optimal amount (80 wt. %) of LNMO was added and pyrolyzed. The powders were designated as LNMO and LNMO-C where L and C represent LNMO and carbon, respectively. The amount of carbon in the nano-blends was confirmed by CHN analysis.

2.3. Phase and morphological analysis

Morphology and phase analyses were performed using high resolution-transmission electron microscopy (HR-TEM, JEOL, JEM-2100F), Raman spectroscopy (WITEC ALPHA 300 RA) and X-ray diffraction analyses (XRD, X'Pert PRO Analytical). Surface area measurement was done using Brunauer–Emmett–Teller (BET) analysis (Micromeritics Instrumentation, USA).

2.4. Electrochemical characterization

Coin cells (CR2032, Bat-Sol, India) were used for the present study. LNMO-C powder blends (10 mg), lithium foil, polyethylene membrane (BAT-SOL, India) and 1 M LiPF₆ dissolved in a mixture (3:7 ratio) of ethylene carbonate (EC) and dimethylcarbonate (DMC) solvents was used as cathode, anode, separator and electrolyte, respectively. The electrochemical performance tests such as cyclic voltammetry, electrochemical impedance spectroscopy and charge discharge were done on the assembled coin cells in an electrochemical work station (AUTOLAB). Scanning electrochemical microscopy measurements (SECM, Nanotech, Munich) were done using a Pt probe (~25 μm²) and the above mentioned electrolyte as the conducting medium.

3. Results and discussion

Fig. 1(a&b) shows the typical SEM and TEM images of the camphor carbon grafted LNMO particles (LNMO-C samples) subjected to pyrolysis. SEM images did not reveal the presence of any carbon phase possibly due to the poor phase contrast and nano-metric size. The particles showed polyhedral morphology with diameter between 1–2 μm. TEM images (Fig. 1(b)) showed LNMO particles being surrounded by carbon phase. At higher

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