Journal of Power Sources 356 (2017) 115–123

Contents lists available at ScienceDirect

Journal of Power Sources

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

Synergistic effect of 3D electrode architecture and fluorine doping of $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ for high energy density lithium-ion batteries

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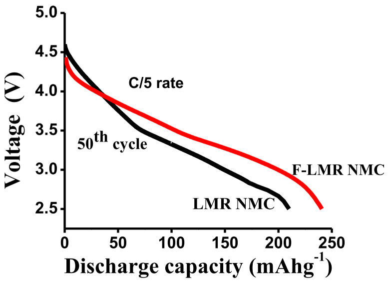
HIGHLIGHTS

- LMR NMC is synthesized by solution combustion method followed by LiF coating.
- LiF coating on to LMR NMC, partially replaces M—O bonds by M—F bonds.
- The fluorine doped cathodes deliver high capacity of ~300 mAh g^{-1} at C/10 rate.
- Voltage fade & capacity loss are reduced for F-doped compared to pristine LMR NMC.
- 3D carbon fiber electrode architectures help to retain high capacity at high C rates.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 January 2017
Received in revised form
15 April 2017
Accepted 22 April 2017

Keywords:
LMR NMC
F-substitution
3D electrode architecture
Lithium battery
Cycling
Voltage decay

ABSTRACT

$Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (LMR NMC) is synthesized by solution combustion method followed by LiF coating onto LMR NMC by solid state synthesis. The electrochemical performance of the pristine LMR NMC and corresponding F-doped samples as cathodes for Lithium ion Batteries (LIBs) are investigated by galvanostatic charge-discharge cycling and impedance spectroscopy. The fluorine doped cathodes deliver high capacity of ~300 mAh g^{-1} at C/10 rate (10–20% greater than the pristine LMR NMC cathodes), have high discharge voltage plateau (>0.25 V) and low charge voltage plateau (0.2–0.4 V) compared to pristine LMR NMC cathodes. Beside, irreversible capacity, voltage fade, capacity loss are significantly reduced in-relation to the pristine LMR NMC electrodes. LiF coating onto LMR NMC, partially replaces M—O bonds of the material by M—F bonds, thus increasing the interfacial and structural stability. Besides, the manuscript describes possible replacement of aluminium current collector with 3D carbon fiber current collector which delivers high capacity of >200 mAh g^{-1} at 1C rate, good capacity retentions for over 200 cycles. The study opens a possibility for LMR NMC cathode material which has almost double the capacity of currently used cathodes, can be a possible substitute cathode for LIBs used in electric vehicles.

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1. Introduction

Current research in lithium based batteries are focused to achieve high energy density batteries with reduced cost and improved safety [1,2]. State-of-art lithium ion batteries use transition metal

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http://dx.doi.org/10.1016/j.jpowsour.2017.04.077
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(TM, such as Ni, Mn, Co) oxide ($LiCoO_2$, $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ or $LiNi_{0.8}Co_{0.15}Al_{0.15}O_2$) or olivines ($LiFePO_4$, $LiMnPO_4$), spinels ($LiMn_2O_4$, $LiNi_{0.5}Mn_{1.5}O_4$ (NMS) based cathodes and graphitic carbon as anode [1–3]. The nominal capacity of most of these cathodes are in the range of 120–180 mAhg^{-1} when cycled up to 4.2 V, is only half the specific capacity of graphite anode (Theoretical capacity = 372 mAhg^{-1}) [1,4]. The issues of low energy density cathode materials, high energy density but highly unstable batteries (Li–S, Li-Air systems), limits the application of Li-ion batteries in electric vehicles [5,6]. Thus, there has been an intense research activity during the last decade to develop high capacity-high voltage or high energy cathodes for lithium-ion batteries. Lithium and manganese rich based transition metal oxide such as $Li_{1.2}Ni_{0.15}Mn_{0.55}Co_{0.1}O_2$ (LMR NMC) has almost double the capacity of layered TM oxides, is one of the stable, sustainable high energy cathode material which have suitable properties to use in the electric vehicles (Specific capacity – 372 mAh g^{-1} corresponding to 1.2 Li insertion/deinsertion and energy density ~1000 Wh kg^{-1}) [7,8]. To get high capacity from LMR NMC, the material need to be electrochemically cycled above 4.4 V. During high voltage cycling (>4.4 V), oxygen release takes place from Li_2MnO_3 component in the form of Li_2O and MnO_2 which causes interfacial instability of LMR NMC electrode [9]. The major issue of LMR NMC is voltage decay mostly due to structural transformation of layered to the spinel structure [10–13]. The structural change is associated with migration of transition metal ions to lithium layer during high voltage cycling (>4.4 V). The migration takes place because of vacancies created by oxygen release as Li_2O from Li_2MnO_3 component during high voltage cycling [9,12]. Because of migration, the layered structure slowly transforms to spinel during the course of cycling due to which there is decay in the voltage plateau from 3.7 V region to 2.8 V region which decreases the energy density [8,10–13]. The interfacial instability can be minimized by surface coatings such as metal oxides such as Al_2O_3, ZrO_2, TiO_2 etc., metal phosphate coatings such as $AlPO_4$, $LiFePO_4$ etc. blending with another cathode material [14–16]. And solid electrolyte coating like LiPON improved the capacity retention and rate performance of LMR NMC [13]. But voltage fade is not properly addressed by these surface coatings or blending.

Besides, F-substitution or coating helps in the improvement of electrochemical performance at high cutoff voltages, improves thermal stability and reduces charge transfer resistance [17,18]. Many researchers have postulated that substituting oxygen by fluorine is highly advantageous method to improve electrochemical performance [19,20]. In the literature it has been demonstrated that both F-substituted layered cathode materials such as $LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$ and $LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$ delivered stable cycling performance and improved high rate capacity [20,21]. F-doping in $LiNi_{0.5}Mn_{1.5}O_4$ (NMS) resulted in improvement of electrochemical performance like increase in initial capacity and high rate capability ~10% and also shows better thermal stability [22]. Manganese dissolution is also reduced (~30%), as electrode surface is less prone to HF attack. Generally 2–5% of fluorine is recommended for best electrochemical performance. In overall, the effect of fluorine on enhanced electrochemical performance of Lithium TM oxide compounds was proposed to originate from a combination of following features [23]. These include (1) the physical properties like high tap density (high volumetric energy density) [16], (2) enhanced cation ordering, (3) improved structural stability associated to the smaller c-axis variation during charge, and (4) in fluorine doped spinels, the presence of fluorine near the surface provides protection from HF attack at high voltages (~5 V) [22].

Here, we present a method of LiF coating which stabilizes interface and decreases the voltage fade. LiF coating prevents the electrode surface from direct contact of electrolyte thus reducing the electrolyte decomposed deposits on the surface, hence stabilizing the interface. Moreover, on coating and doping with LiF some of the M–O bonds are replaced by M–F bonds on the surface [17,18,23]. The M–F bond is stronger and thus stabilizes the structure during cycling. Partially O^{2-} is replaced by F^- on the surface of LMR NMC and due to which the average oxidation state of the surface metal ions is slightly decreased which lead to decrease in charge potential thus minimizing the electrolyte decomposition and delivering better electrochemical performance. There are also similar reports that LaF_3 coatings also enhances electrochemical performance of $LiMn_2O_4$ [24]. Besides, it is also reported that Al foil coated with porous layered cathodes of $LiNi_{0.8}Co_{0.15}Al_{0.5}O_2$ (NCA) is susceptible to under deposit corrosion in 3:7 ratio of ethylene carbonate (EC) and ethyl methyl carbonate (EMC) with 1.2 M $LiPF_6$ which is significantly contributing to the capacity fade of the battery [25]. So to avoid capacity and power fade due to corrosion of Al-foil, we made an attempt to replace Al-foil by highly conductive, corrosion resistant non-graphitic carbon fibers of ~10 μm in diameter. The cathode material disperses throughout the carbon fiber and thus making a good electronic contact with carbon fiber current collector.

2. Experimental

LMR NMC materials were synthesized by solution combustion method by taking stoichiometric amount of Li (NO_3), $Ni(NO_3)_2$ $6H_2O$, $Mn(NO_3)_2$ $4H_2O$, $Co(NO_3)_2$ $6H_2O$ (all chemicals are from Alfa Aesar, Chennai, India) as oxidants and glycine as fuel. The metal nitrates and glycine were dissolved in appropriate amount of water in a beaker, subsequently heated at 100 °C till viscous slurry was formed and placed it in a preheated furnace at 400 °C. Few minutes after keeping the material in the furnace at 400 °C auto ignition takes place forming amorphous LMR NMC. The as prepared sample was kept at 400 °C for about 30 min for complete removal of organics. Various weight ratios (100:1, 75:1, 50:1, 25:1) of LMR NMC and LiF were made by grinding in an agate mortar for about 30 min followed by annealing at 800 °C in an alumina crucible for 20 h in air (Hereafter this product is termed as F-LMR NMC). Similarly for comparison, pristine LMR NMC (No LiF coatings) was prepared from amorphous LMR NMC by annealing at 800 °C in an alumina crucible for 20 h in air. The Powder XRD measurements were performed by using an X'Pert Pro diffractometer (The Netherlands) (reflection $\theta-\theta$ geometry, Cu Kα radiation, receiving slit of 0.2 mm, scintillation counter, 30 mA, 40 KV). The diffraction data were collected at 0.02 step widths over a 2θ range from 10 to 70°. The structural parameters were refined by Rietveld refinement analysis that was performed using Full Prof Suite program. The surface morphology of the composite powders were further measured by scanning electron microscope (JEOL-JEM-2011(200 KV) and transmission electron microscopy (JEOL-JSM-700F) and compositions by energy dispersive X-ray microanalysis (EDAX) systems from Oxford instruments. It was further characterized by Raman spectroscopy using a micro Raman spectrometer HR800 (Jobin Yovn Horiba, France), with He-Ne laser (excitation line 632.8 nm) and a microscope objective (50×, Olympus Mplan, 0.4 mm working, numerical aperture 0.75 in back scattering configuration). X-ray photoelectron spectroscopy (XPS) measurements were carried out ESCA+, (Omicron nanotechnology, Oxford Instruments plc, Germany) equipped with monochromic AlKα (1486.6 eV) X-ray beam radiation operated at 15 kV and 20 mA, binding energy was calibrated vs. carbon (C1s = 284.6 eV). For these measurements, the powder samples were transferred to the XPS device using a hermetically sealed unit, which contains a sample holder attached to a magnetic manipulator, and a gate valve. The spectra were deconvoluted using Gaussian functions based on Origin 8.0 software. The

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