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Short communication

$Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–Polyaniline hybrids as cathode active material with ultra-fast charge–discharge capability for lithium batteries

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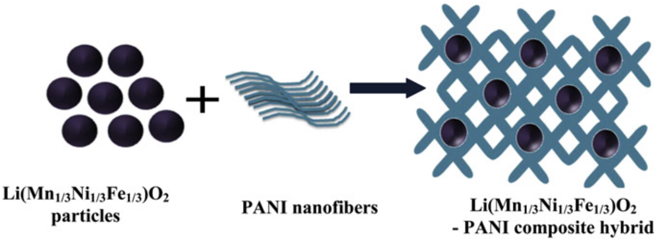
HIGHLIGHTS

- ► Ultra-fast charge–discharge capability is achieved for Fe based layered composites with polyaniline.
- ► $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–polyaniline composite delivered reversible capacity of ~110 mAh g^{-1} at 40 C rate.
- ► Extraordinary performance is mainly due to drastic improvement of electronic conductivity.

GRAPHICAL ABSTRACT



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ABSTRACT

We first report the ultra-fast charge–discharge capability of organic–inorganic ($Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–Polyaniline (PANI)) nanocomposites prepared by mixed hydroxide route and followed by polymerization of aniline monomers with different concentrations (0.1 and 0.2 mol concentration of PANI). Li-insertion properties are evaluated in half-cell configuration, test cell ($Li/Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–PANI) comprising 0.2 mol. PANI delivered the reversible capacity of ~127, ~114 and ~110 mAh g^{-1} at ultra-high current rate of 5, 30 and 40 C, respectively with exceptional cycleability between 2 and 4.5 V *vs.* Li. Such an exceptional performance is mainly due to the conducting pathways promoted by PANI network and it is revealed by impedance measurements. This result certainly provides the possibility of using such layered type Fe based cathode materials in high power Li-ion batteries to drive zero emission vehicles such as hybrid electric vehicles or electric vehicles applications in near future.

1. Introduction

Of late immense research focus is directed toward the development of high capacity, high voltage, low cost and eco-friendly cathode for Li-ion batteries (LIB) typically containing layered structure [1–6]. Since the commercialization of LIBs by Sony Inc. in 1991, layered type $LiCoO_2$ and graphite were dominated as cathode and anode materials, respectively [7]. In such combination, graphitic anode essentially serves as buffer medium during Li-insertion/extraction; hence any advancement in LIB technology relies on the development of high performance cathodes [8–10]. Although the theoretical capacity of Li_xCoO_2 is 274 mAh g^{-1}, complete removal of 1 mol lithium is found difficult due to the structural transformation from hexagonal to cubic which results in severe fade during cycling. Hence, the practical capacity is restricted to ~140 mAh g^{-1}. Apart from the capacity, $LiCoO_2$ displayed

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poor high current performance, toxicity of cobalt and its expensiveness is another important concern, therefore search for alternate high performance cathodes is warranted. In this line, other layered type cathodes such as $LiMnO_2$, $LiNiO_2$, $LiFeO_2$ and Li_2MnO_3 were proposed, however practical application of such candidates are too limited due to their own setbacks [10–12]. Eco-friendly, spinel $LiMn_2O_4$ and olivine $LiFePO_4$ were also proposed as potential alternatives, nevertheless former one suffers Mn^{3+} dissolution issue and later compound lacks of conductivity and limited operating potential problems, respectively [13]. Latter, Yabuuchi and Ohzuku [14] reported the performance of layered $LiCo_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathode with reversible capacity over 200 mAh g^{-1} which is higher capacity than reported elsewhere on layered compounds. On the other hand, aforementioned cathode still contains Co and also suffers high rate operations, which is one of the pre-requisite to power zero emission vehicles such as hybrid electric vehicles (HEV) and electric vehicles (EV). Recently, a series of “cobalt-free” Fe based layered type cathodes were reported by Tabuchi et al. [15,16] and delivered the reversible capacity over 200 mAh g^{-1} in the initial cycles. However, severe capacity fading is encountered for said layered type compounds and also complex synthetic process was employed to yield single phase material and inherent electronic conductivity issues as well. Very recently, we reported Fe based layered type $Li_{1.2}(Mn_{0.32}Ni_{0.32}Fe_{0.16})O_2$ cathodes by a simple sol–gel technique in the presence of adipic acid with good electrochemical properties [17]. As expected, in general Fe based materials are generally experiencing poor electrochemical behavior at high current operations due to the intrinsic nature such compounds [18]. In this line, we made an attempt to synthesize $LiFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$ cathodes by simple co-precipitation technique and followed by annealing. To alleviate the inherent properties of said compound, the concept of making composite cathode was developed by using a conducting polymer, polyaniline (PANI) to form composite inorganic-organic hybrids [19,20]. Among the conducting polymers reported, PANI has certain advantageous likely, higher chemical stability, high electrical conductivity in its oxidized/protonated form, better acid–base properties and stable electrochemical behavior [19]. In addition, few reports based on PANI based composites cathodes were already reported to promote the conducting nature of cathodes, for example $LiFePO_4$–PANI [20–22] and $LiNi_{0.8}Co_{0.2}O_2$–PANI [23]. In the present work, a novel organic–inorganic hybrid $LiFe_{1/3}Ni_{1/3}Mn_{1/3}O_2$–PANI cathode was prepared first time by co-precipitation and followed by sonication with two different concentration of polymer (0.1 and 0.2 mol). Li-insertion properties were evaluated in half-cell configuration with ultra-high rate of 40 C (mass loading of active material 10 mg cm^{-2}) and described in detail.

2. Experimental

The $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$ was prepared using a mixed hydroxide method. Analytical grade LiOH (95%), $Fe(NO_3)_3 \cdot 9H_2O$ (98%), and $Ni(NO_3)_3 \cdot 6H_2O$ (97%) were procured from Junsei chemicals, Japan and $MnCl_2 \cdot 4H_2O$ (99.9%) was obtained from Wako Japan and used as such. In the typical synthesis procedure, stoichiometric amounts of transition metal salts were dissolved in distilled water separately and mixed together to enable solution phase reaction. Later, aqueous solution containing LiOH was added by drop wise into the solution and stirred for 6 h to produce mixed hydroxide precipitates. Then the precipitate was aged overnight, filtered and washed to remove residual Li salts and dried at 60 °C for 10 h. The resultant product was obtained by firing the precipitate with slightly excess amount of LiOH at 800 °C for 10 h under oxygen flow.

PANI was synthesized by chemical polymerization method, for instance 0.1 and 0.2 mol of aniline and ammonium persulfate (APS) were separately dissolved in 5 ml of 1 M HCl. Chemical polymerization was initiated by the slower addition of APS into aniline solution. The polymerization was completed within 10 min with formation of highly viscous black precipitate containing PANI. Then hybrid nanocomposites were prepared by the inclusion of 0.1 g of $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$ particles into the above solution and sonicated. After 10 min, the black precipitate was filtered, washed several times with deionized water and dried overnight in a vacuum at 60 °C before conducting characterization studies. From the TGA curves (Figure S1), concentration of PANI was ~9.5% (0.1 mol) and ~18.25% (0.2 mol) for $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–P1 and $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–P2 hybrids, respectively.

X-ray diffraction patterns (XRD) were recorded by Rint 1000, Rigaku, Japan using Cu K_α radiation. Surface morphology of the powders was analyzed by transmission electron microscopy (TEM, JEM-2000 FX-II, JEOL, Japan). FT-IR spectroscopic measurements were carried out on IR Prestige-21, Japan spectrometer. The Brunauer–Emmett–Teller (BET) surface area analysis was performed through a Micromeritics ASAP 2010 surface analyzer (Micromeritics, USA). Thermogravimetric analysis (TGA) was performed at 5 °C min^{-1} under oxygen flow using thermal analyzer system (STA 1640, Stanton Redcroft Inc., UK) to estimate the wt.% of PANI. All the electrochemical studies were conducted in two electrode CR 2032 coin-cell configurations. The composite cathodes were prepared by pressing the mixture of 75% active material (10 mg), 15% Ketjen black (2 mg) and 10% Teflonized acetylene black (1.25 mg), TAB-2 in to a 200 mm^2 area stainless steel mesh, which serves as current collector. Before conducting the cell assembly under Ar filled glove box, composite electrode was dried at 160 °C for 4 h in a vacuum oven. The test cells were fabricated with composite cathode and lithium metal as anode which was separated by a porous polypropylene separator (Celgard 3401). 1 M $LiPF_6$-ethylene carbonate/dimethyl carbonate (1:1 vol.) was used as electrolyte solution obtained from Techno Semichem Co., Ltd., Korea. Galvanostatic cycling studies were conducted between 2 and 4.5 V *vs.* Li at different current densities in ambient temperature conditions.

3. Results and discussion

Fig. 1a represents the powder-XRD patterns of pristine $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$, $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–PANI-0.1 mol (hereafter abbreviated as $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–P1) and $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–PANI-0.2 mol (hereafter abbreviated as $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$–P2). The observed XRD reflections are indexed according to the α-$NaFeO_2$ structure with $R\bar{3}m$ space group. Apparent to notice the formation of phase pure layered structure without any impurity traces, more importantly the absence secondary peaks associated with PANI, which indicates the amount of PANI used to make hybrids are very less and it is too lower for the detectable limitation of XRD instrument. Lattice parameter values are calculated and found to be $a = 2.898$ and $b = 14.311$ Å ($c/a = 4.94$) which is good agreement with similar layered type compound $Li(Mn_{1/3}Ni_{1/3}Co_{1/3})O_2$ by Yabuuchi and Ohzuku [14]. The $I_{(0\,0\,3)}/I_{(1\,0\,4)}$ ratio is found to 1.09 which clearly demonstrate the positive-electrode material contains a good layered structure with very small amount of cation mixing [24,25]. In general, oxygen sub-lattice in the α-$NaFeO_2$ type structure is distorted from the *fcc* array in the direction of hexagonal *c*-axis. This distortion gives rise to splitting of the XRD reflections corresponding Miller indices (0 0 6)/(1 0 2) and (1 0 8)/(1 1 0) which is the characteristic of typical layered structure. Further, there is no deviation from the crystalline peaks noted during sonication with different concentrations of PANI and this suggests the presence of PANI does not affect the structural properties of layered $Li(Mn_{1/3}Ni_{1/3}Fe_{1/3})O_2$. FT-IR spectra were recorded to ensure the