

Understanding the exceptional elevated temperature performance of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes by LiFePO_4 modification



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ARTICLE INFO

Article history:

Received 3 February 2014

Received in revised form 21 May 2014

Accepted 9 June 2014

Available online 14 June 2014

Keywords:

Lithium-ion battery

High voltage spinel

Olivine phosphate coating

Sol-gel

ABSTRACT

Exceptional elevated temperature performance of high voltage spinel cathodes are realized by LiFePO_4 coating in a single-step process at 600°C under Ar flow. First, the single-phase spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is prepared via sol-gel route by optimizing the adipic acid concentration (0–1 mol.). Then, the high performing spinel phase (0.7 mol. adipic acid treated) is subjected to LiFePO_4 modification by conventional two-step coating procedure with various coating concentrations (1–3 wt.%). Single-step LiFePO_4 coating procedure also performed at 550°C under Ar atmosphere for the comparison. Although LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered appreciable performance in elevated temperature (55°C), but it is not sufficient for the practical applications. Therefore, fine tuning of the LiFePO_4 (1 wt.%) formation temperature (500 – 600°C) have been varied to achieve excellent electrochemical profiles at elevated temperature conditions. The presence of thin LiFePO_4 have been confirmed by high resolution TEM studies and supported well with EDAX measurements.

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1. Introduction

Ni-substituted spinel cathode ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) is attracted as promising high voltage candidate for the fabrication of high energy density Li-ion power packs to drive zero emission transportation applications especially electric vehicles (EV) [1–5]. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is considered as ~ 4.7 V vs. Li candidate for Li-ion battery applications by utilizing $\text{Ni}^{2+/4+}$ redox couple which is slightly higher than the thermodynamic stability window of carbonate based electrolyte [1,2,6–9]. Therefore, achieving good electrochemical performance is quite challenging for this kind of cathodes. In addition, the said phase exists in two polymorphs likely disordered $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_{4-\delta}$ (non-stoichiometry) structure with $Fd\bar{3}m$, space group, and ordered stoichiometric $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compound with $P4_332$ space group. In the disordered phase, Ni and Mn, Li and O atoms are occupied in the $16d$ octahedral sites, $8a$ tetrahedral sites and $32e$ sites, respectively. However, Ni, Mn, and Li atoms are occupied in the $4a$, $12d$, and $4c$ sites and O ions are occupied in the $8c$ and $24e$ sites for the ordered structure. Ni and Mn are distributed

randomly in the $16d$ octahedral sites for the disordered phase whereas very regular ordering is noted for stoichiometric phase [2,10]. In addition, disordered phase consists of trace amount of Mn^{3+} ions which translates increase in electrical conductivity profile. Very flat and discrete discharge profiles at ~ 4.7 V vs. Li are noted for ordered and disordered phases, respectively [1]. Irrespective of the polymorph, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ delivered good electrochemical profiles at ambient temperature conditions. Unfortunately, the elevated temperature performance is the main issue for the development of such high voltage cathodes and it is one of the important pre-requisite for EV applications [2]. In this regard, several approaches like metal doping in transition metals sites, Li-sites and creating O_2 deficiencies are also been carried out [2]. In addition, surface modification with carbonaceous materials, metals, metal oxides, metal fluorides, phosphates and so on. Although improvement in the elevated temperature performances have been achieved, but still significant improvements are anticipated for such high voltage spinel cathode. In this line, taking the advantages of olivine phase LiFePO_4 cathodes like high thermal stability due to the strong P–O co-valent bond, eco-friendliness and low cost, we made an attempt to employ LiFePO_4 modification over $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates by sol-gel process [4,11,12]. Unfortunately, the previous attempt by Liu *et al.* [13] over spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates by LiFePO_4 modification using

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mechano-fusion dry process results the heterogeneous coating which results discrete discharge capacity profiles at ~ 4.7 and ~ 3.4 V vs. Li. Further, such coating process requires relatively large amount of coating substance (20 wt.% LiFePO_4) which leads to the formation of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4\text{-LiFePO}_4$ composite instead of thin layer of LiFePO_4 coating. Optimization of the high performance LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes with extensive structural and electrochemical properties were carried out and described in detail.

2. Experimental

Scalable adipic acid assisted sol-gel technique was adopted to synthesize Ni-doped spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders described by us [14,15]. Very briefly, $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ (Junsei Chem, Japan), $\text{Ni}(\text{CH}_3\text{COO})\cdot 4\text{H}_2\text{O}$ (Aldrich, USA), and $\text{Mn}(\text{CH}_3\text{COO})\cdot 4\text{H}_2\text{O}$ (Aldrich, USA) were dissolved separately in double distilled water according to the stoichiometric ratio and mixed together with appropriate amount of adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$, Sigma-Aldrich, USA). Then the mixture was stirred continuously at 90°C to yield precursor powder. The precursor powder was pre-calcined at $\sim 450^\circ\text{C}$ for 10 h to decompose the organic moieties. Finally, the intermediate product was collected, pelletized, and fired at 700°C for 12 h in air to yield single-phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. For the LiFePO_4 modification, the stoichiometric amount of starting materials like $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$ and H_3PO_4 were dissolved in ethanol and an appropriate amount of adipic acid containing solution was also added together. Later, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were dispersed in to above solution and dried at 80°C to evaporate the ethanol to obtain the precursor powder. The precursor powder was fired directly in a single step to yield the LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases or the olivine coating was done in a two-step process like LiFePO_4 synthesis at 400°C for 3 h and 670°C for 5 h. Both single and two-step process calcination has been performed under Ar atmosphere.

X-ray diffraction (XRD) measurements were performed using Rint 1000, Rigaku, Japan X-ray diffractometer equipped with a $\text{Cu K}\alpha$ radiation. Surface morphological features of the powders were analyzed by field emission scanning electron microscopy (FE-SEM, S4700, Hitachi, Japan). Internal structural of the spinel particles were carried out using transmission electron microscopy (TEM, TECNAI, Philips, The Netherlands). Raman spectra were also recorded using a lab Raman dispersive spectrometer (Lab Ram HR 800, Horiba, Japan). All the electrochemical studies were performed using CR 2032 coin-cell configuration. The composite electrodes were formulated with accurately weighed 20 mg of active material, 3 mg conductive additive (super P), and 3 mg of teflonized acetelene black (TAB-2) using ethanol. The resulting composite slurry was pressed over a 200 mm^2 stainless steel mesh current collector. The half-cells assembly was constructed with composite cathode and

metallic lithium anode, which was separated by porous polypropylene film (Celgard 3401, USA) and gelled with 1 M LiPF_6 in ethylene carbonate:dimethyl carbonate (WC:DMC, 1:1 by vol., Soulbrain Co., Ltd., Korea). Galvanostatic charge-discharge studies were carried out between 3.5–5 V vs. Li under ambient and elevated temperature (55°C) conditions at constant current density of 0.8 mA cm^{-2} .

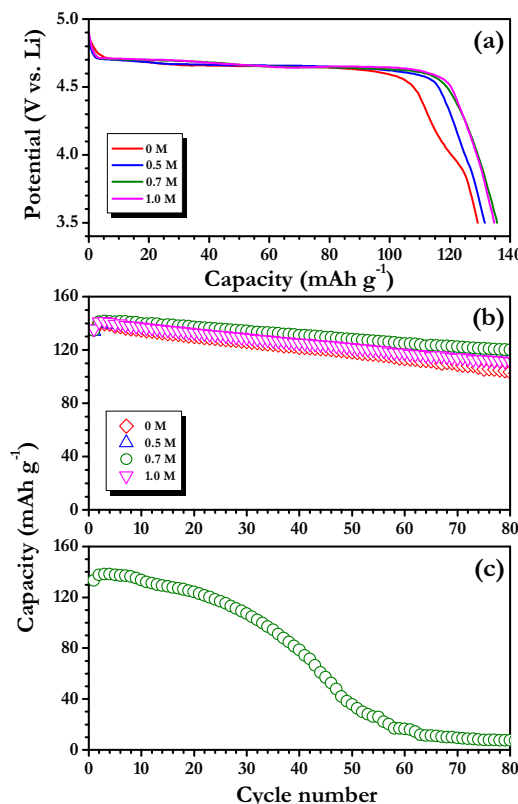


Fig. 2. (a) Initial discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} for various molar ratio of adipic acid to total metal ions, (b) Plot of discharge capacity vs. cycle number at ambient temperature conditions, and (c) Plot of discharge capacity vs. cycle number for adipic acid to total metal ion concentration is 0.7 molar at 55°C .

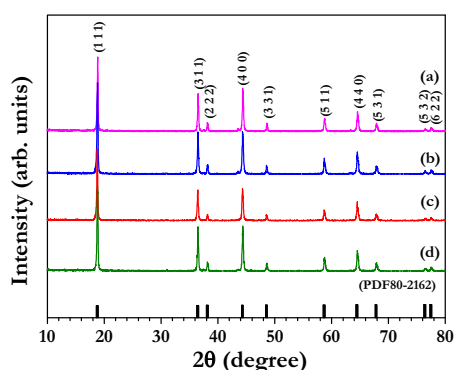


Fig. 1. XRD patterns of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ obtained with various molar ratio of adipic acid to total metal ions, (a) 0, (b) 0.5, (c) 0.7, and (d) 1.0.

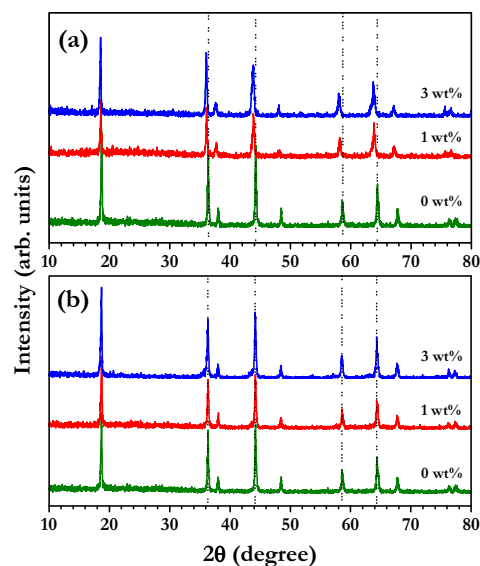


Fig. 3. XRD patterns of $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes with LiFePO_4 coating (a) two step calcination at 400°C for 3 h and 670°C for 5 h in Ar flow, and (b) one step calcination at various concentrations at 550°C for 6 h in Ar flow.

3. Results and discussion

3.1. Optimization of adipic acid concentration

Fig. 1 represents the XRD pattern of spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles prepared with various concentrations of adipic acid from 0 to 1 mol with respect to total metal ions present in the compound prepared at 700°C for 12 h. All the prepared phase materials exhibited single phase without any noticeable impurity except $\text{Li}_x\text{Ni}_{1-x}\text{O}$ which is inevitable during the synthesis of Ni-doped spinel irrespective of the synthesis technique [10]. The observed reflections are indexed according to the $\text{P4}_3\text{32}$ space group with well ordered structure [16]. The formation of $\text{P4}_3\text{32}$ space group was further confirmed by Raman analysis (Figure S1) which is consistent with previous report [16]. Galvanostatic cycling profiles were performed between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in ambient conditions and given Fig. 2. The discharge capacity curves shows

very flat operating potential at $\sim 4.7\text{ V}$ vs. Li, which clearly suggests the presence of well ordered structure irrespective of the adipic acid concentration. Further, there is no splitting occurred between the oxidation of $\text{Ni}^{2+}/\text{Ni}^{4+}$ ($\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$). All the test cells delivered a reversible capacity in the range of $130\text{--}135\text{ mAh g}^{-1}$ in ambient temperature conditions. In addition, the spinel phase prepared by adipic acid free (0 mol.) clearly showed the presence of trace amount Mn^{3+} , whereas rest of the phases showed well-ordered structure composed of Mn^{4+} ions. This clearly suggests the importance of the usage of surfactant for the complete oxidation of Mn^{3+} to Mn^{4+} during the synthesis. From one cycle it is very hard to identify best composition for the further studies. Therefore, cycling studies are continued up to 80 cycles under the same testing conditions (Fig. 2b). Apparent to note that, spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ prepared with 0.7 molar adipic acid concentration is found promising compared to rest of the concentrations. Hence, a duplicate cell was fabricated with 0.7 molar adipic acid assisted

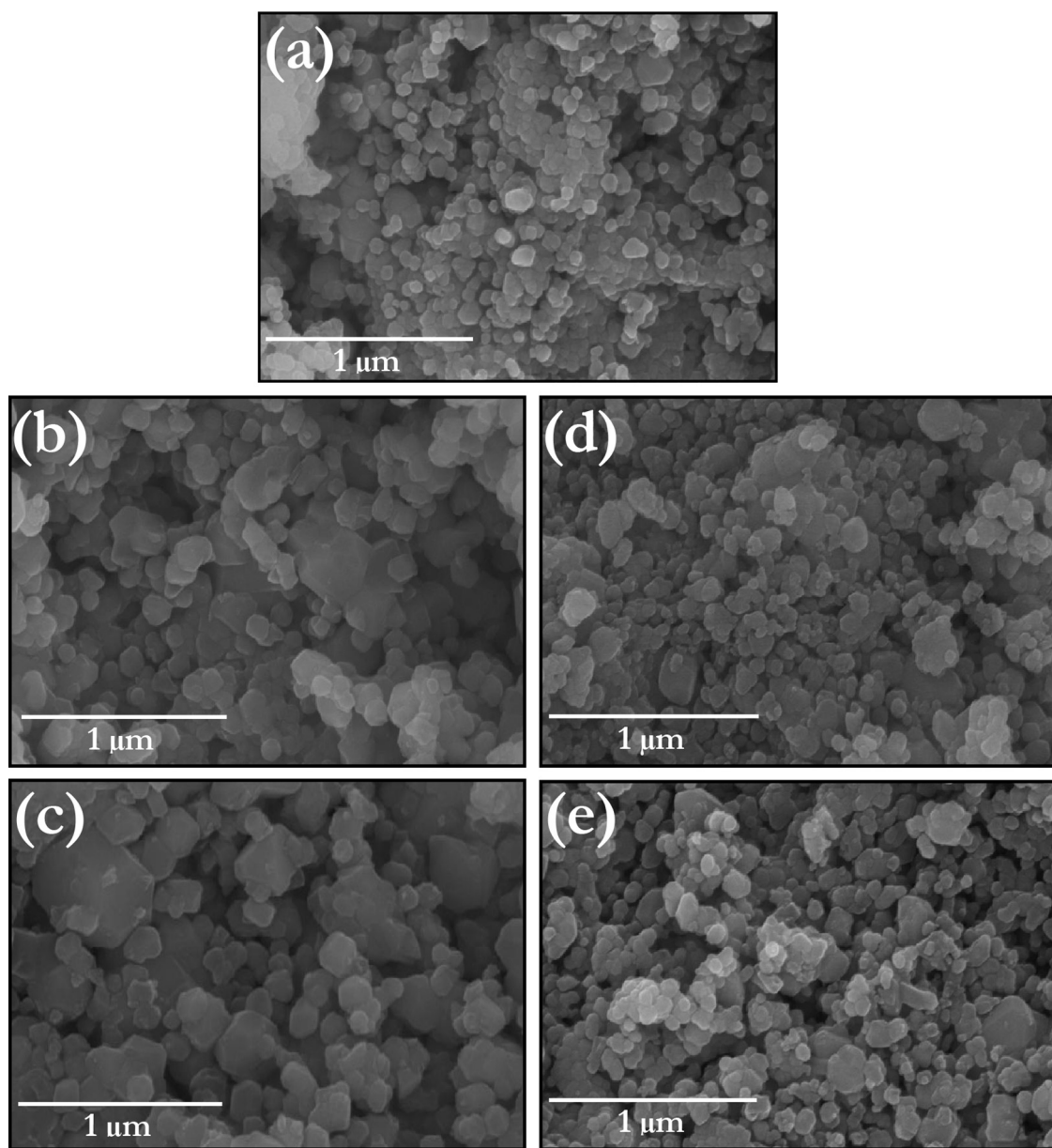


Fig. 4. FE-SEM pictures of (a) pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes, (b) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes modified with 1 wt.% LiFePO_4 and (c) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes modified with 3 wt.% LiFePO_4 by two step calcination at 400°C for 3 h and 670°C for 5 h in Ar flow, and (d) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes modified with 1 wt.% LiFePO_4 and (e) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes modified with 3 wt.% LiFePO_4 by one step calcination at 550°C for 6 h in Ar flow.

spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase compound and tested in elevated temperature conditions (55°C) and illustrated in Fig. 2c. Severe capacity fading in noted during the cycling and found that the test cell is dead within 50 cycles. This kind of poor performance at elevated temperature conditions is the main obstacle to employ them in high performance applications in EV and HEV applications [3]. This poor elevated temperature performance opens the research activities extensively to improve such high voltage cathode. As mentioned earlier, there are several works attempted to improve the high temperature performance likely surface modification and transition metal site doping. In the present case, based on our previous successful attempts to improve the high temperature performance of layered type $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ by LiFePO_4 modification [17], we attempted same strategy $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates. In general, the LiFePO_4 synthesis will be carried out in a two-step sol-gel process and described elsewhere [18–20]. In order to ensure the synthesis of LiFePO_4 , we repeated our previous procedures in the same synthetic strategy by adipic acid assisted sol-gel route (Figure S2) and satisfactory electrochemical profiles are noted (Figure S3).

3.2. Influence of LiFePO_4 coating protocol

The LiFePO_4 coating over spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates (0.7 molar adipic acid) were performed in two approaches with two different weight ratios of olivine phase (1 and 3 wt.%). First, the LiFePO_4 coating has been performed similar to the conventional sol-gel synthesis by two-step manner under Ar atmosphere (two-step calcination at 400°C for 3 h and 670°C for 5 h) and secondly, the LiFePO_4 coating has been done in a single step at 550°C under Ar flow. Fig. 3 represents the XRD pattern of LiFePO_4 modified spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders in single and two-step process under Ar atmosphere. Apparent to note that, there is no peak positions are observed related to LiFePO_4 phase, which is too low for the detectable limitations of the X-ray diffractometer. Further, there is no variation in the peak position of the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ noted for single-step LiFePO_4 coating. On the other hand, shifting of peak positions towards lower angles are observed for two-step process, except (1 1 1) peak. Fig. 4 shows the surface morphological features of the LiFePO_4 modified spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. Weakly aggregated particulate morphology is noted for the 0.7 mol. adipic acid assisted spinel phase. Highly dispersed particulate morphology is observed for single-step process, whereas highly aggregated morphology is apparent for two-step process. This clearly suggests that two-step LiFePO_4 coating strongly influence the structural and morphological properties of spinel cathode.

Electrochemical profiles of the LiFePO_4 modified spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders are carried out between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in ambient temperature conditions and shown in Fig. 5. The cell delivered the maximum reversible capacity of ~ 141 , ~ 125 and 120 mAh g^{-1} for pure (0.7 mol. adipic acid treated) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ modified with LiFePO_4 modified 1 wt.% and 3 wt.%, respectively by single step process. All the three phases presented the very flat operating potential of $\sim 4.7\text{ V}$ vs. Li, but LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders showed the presence of trace amount of Mn^{3+} which is clearly evident from the small flat region around $\sim 4\text{ V}$ vs. Li. The presence of $\sim 4\text{ V}$ vs. Li in the LiFePO_4 modified phases is mainly due to the carbo-thermal reduction reaction of residual carbon present in the olivine phase precursors which includes the surfactant adipic acid. On the other hand, unusual charge-discharge curves are observed for the LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders by conventional two-step process with less reversible capacity compared to the pure (0.7 mol. adipic acid treated) and single-step LiFePO_4 treatment in ambient temperature conditions. The test cells delivered the reversible capacity of ~ 65 and $\sim 67\text{ mAh g}^{-1}$ for LiFePO_4 modified phases treated with two-step process

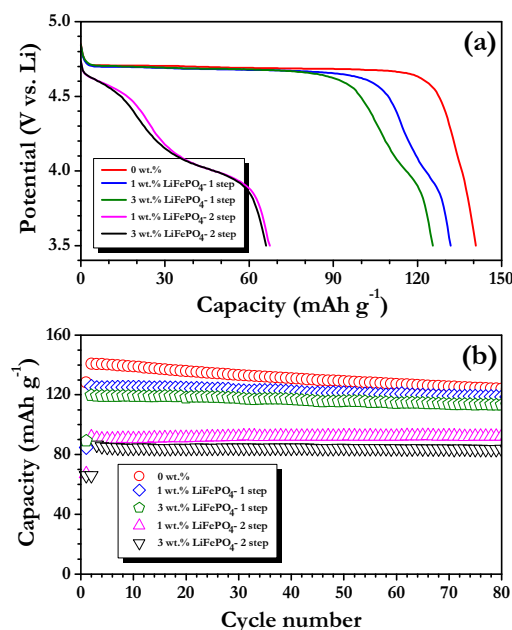


Fig. 5. (a) Typical discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} for various concentrations of LiFePO_4 concentration and calcination process, (b) Plot of discharge capacity vs. cycle number at ambient temperature conditions.

by 1 and 3 wt.%, respectively. Plot of reversible capacity vs. cycle number is given in Fig. 5b. Very stable cycling profiles are noted for the LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders prepared by single step process at 550°C under Ar flow. For example, the test cell retained ~ 88 , ~ 95 and $\sim 95\%$ of initial capacity after 80 cycles for pure (0.7 mol. adipic acid treated) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ modified with LiFePO_4 modified 1 wt.% and 3 wt.%, respectively by single step process. Although, 1 and 3 wt.% of LiFePO_4 modification showed more or less similar retention behavior, but the reversible capacity values of entirely different which is worth to mention here. However, the LiFePO_4 modification carried out in two-step process delivered less reversible capacity, but showed very stable cycling behavior for the tested 80 cycles. In both cases 1 wt.% LiFePO_4 is found promising in terms of reversibility and cycleability and hence, further studies are carried out with mentioned phases.

The elevated temperature profiles are carried out between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} and presented in Fig. 6. As expected, test cells delivered the discharge capacity of ~ 133 , ~ 125 and $\sim 75\text{ mAh g}^{-1}$ for pure (0.7 mol. adipic acid treated) and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ modified with LiFePO_4 modified 1 wt.% by single-step and two-step processes, respectively. Unlike that of ambient temperature performance, splitting of the discharge curves are noted which is mainly because of the oxidation of $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$. In the case of ambient temperature, the intermediate splitting of $\text{Ni}^{2+/3+}$ and $\text{Ni}^{3+/4+}$ has been merged ($\text{Ni}^{2+/4+}$) as a prominent single plateau at $\sim 4.7\text{ V}$ vs. Li [9]. The discharge capacity profiles at elevated temperature conditions are given in Fig. 6b. Apparent to note that, LiFePO_4 modification over (0.7 mol. adipic acid treated) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulate certainly provides the improved performance. Amongst, the LiFePO_4 modification by single-step process is found appealing in terms of reversible capacity and cycleability which delivered appreciable cycleability up to 60 cycles. Afterwards, a drastic capacity fading is noted, which clearly suggest further optimization of the LiFePO_4 coating over (0.7 mol. adipic acid treated) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates are required to sustain the improved performance.

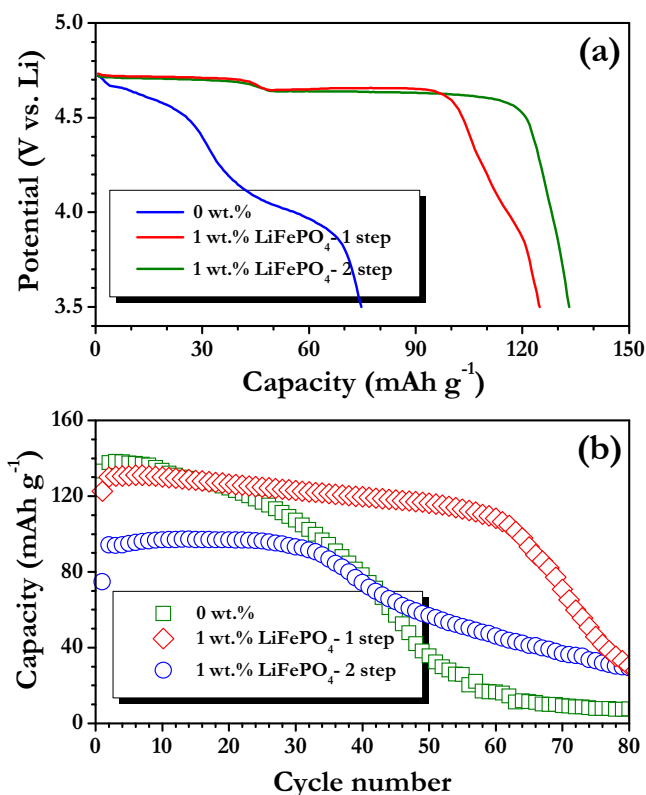


Fig. 6. (a) Typical discharge curves $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} with 1 wt.% of LiFePO_4 concentration modified by different calcination process at 550°C under Ar atmosphere in elevated temperature conditions, (b) Plot of discharge capacity vs. cycle number at 55°C .

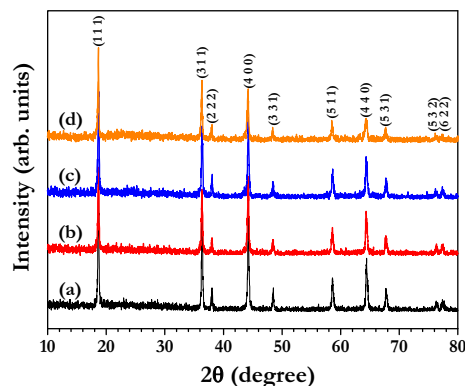


Fig. 7. (a) XRD patterns of pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$, and the $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes modified with 1 wt.% LiFePO_4 by one step calcination at various sintering temperatures for 6 h in Ar flow (b) 500°C , (c) 550°C and (d) 600°C .

3.3. Optimization of LiFePO_4 coating by single-step process

Except LiFePO_4 sintering temperature, rest of the parameters like adipic acid concentration and LiFePO_4 concentration have been well documented. Therefore, optimization of LiFePO_4 (1 wt.%) formation temperature is very crucial to achieve high performance cathode active material. Fig. 7 represents the XRD patterns of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates by single-step process at various temperature conditions along with pure spinel phase (0.7 mol. adipic acid treated). It can be seen that there is no shift in the peak positions are noted, which clearly suggests synthesis LiFePO_4 did not influence of structural properties. The morphological features of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates by single-step process at various temperatures under Ar atmosphere is given in Fig. 8. SEM pictures clearly revealed the

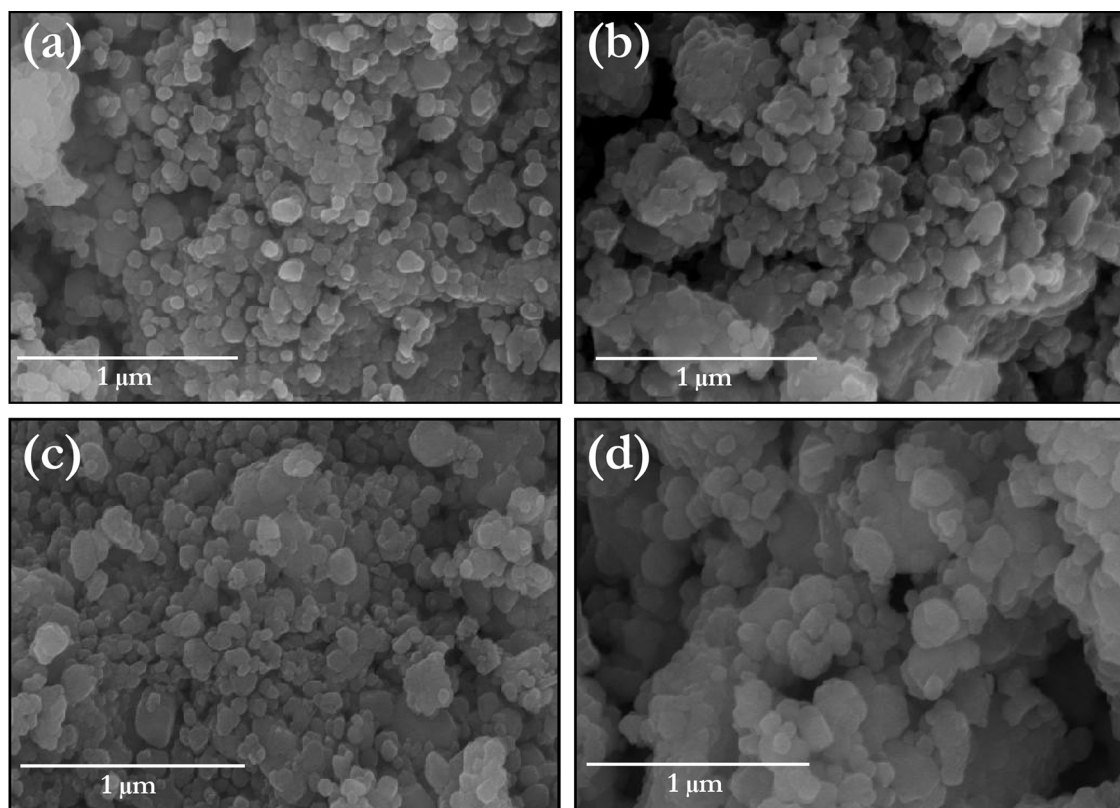


Fig. 8. FE-SEM pictures of (a) pure $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes, (b) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes with 1 wt.% LiFePO_4 sintered at 500°C for 6 h, (c) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes with 1 wt.% LiFePO_4 sintered at 550°C for 6 h, and (d) $\text{LiMn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ cathodes with 1 wt.% LiFePO_4 sintered at 600°C for 6 h.

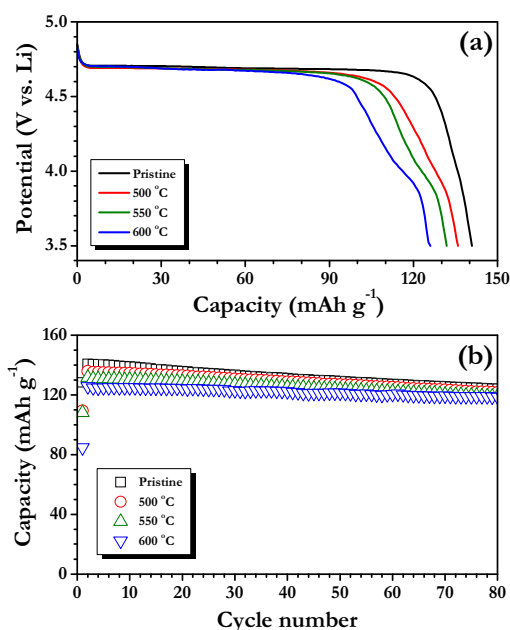


Fig. 9. (a) Typical discharge curves of the 1 wt.% of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} with various calcination temperatures for 6 h along with pure phase compound in ambient temperature conditions and (b) Plot of discharge capacity vs. cycle number.

presence of particulate morphology irrespective of the sintering temperature. At 600°C , slightly aggregated morphology is noted compared to the rest of the calcination temperatures and pure phase.

Electrochemical profiles of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders are carried out between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in ambient temperature and given in Fig. 9. The test cells delivered the reversible capacity of ~ 141 , ~ 136 , ~ 132 and ~ 125 for pure (0.7 mol. adipic acid treated), 500, 550 and 600°C , respectively. It is worth to mention that, a trace amount of Mn^{3+} is found in all the LiFePO_4 modified phases which has been clearly evident from the presence of a small region around $\sim 4 \text{ V}$ vs. Li. Obvious to notice that increase in carbo-thermal reduction activity of $\text{Mn}^{4+/3+}$ reduction with increase in sintering temperature. In addition to reduction of more Mn^{4+} ions, decrease in capacity trend is also noted with increase in temperature. Plot of reversible capacity vs. cycle number is given in Fig. 9b. In ambient temperature

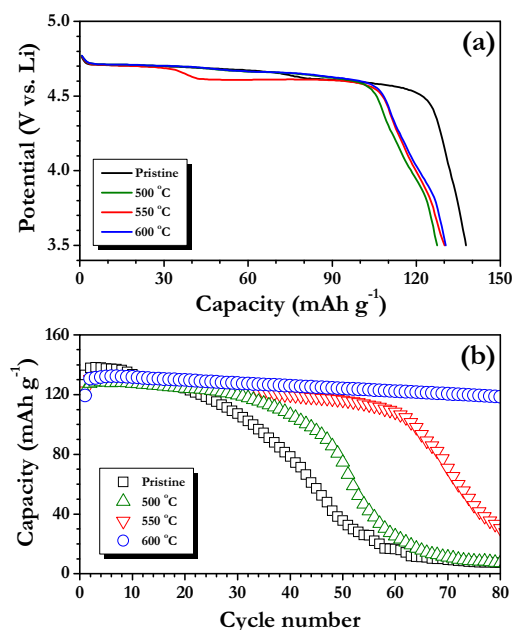


Fig. 10. (a) Typical discharge curves of the 1 wt.% of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} with various calcination temperatures for 6 h along with pure phase compound in 55°C , and (b) Plot of discharge capacity vs. cycle number.

Fig. 10 (a) Typical discharge curves of the 1 wt.% of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} with various calcination temperatures for 6 h along with pure phase compound in 55°C , and (b) Plot of discharge capacity vs. cycle number.

conditions, all the cells delivered very stable discharge capacity profiles. The test cells rendered ~ 88 , ~ 89 , ~ 90 and $\sim 95\%$ of reversible capacity after 80 cycles (calculated from 2nd cycle) for pure (0.7 mol. adipic acid treated), 500, 550 and 600°C , respectively. Although LiFePO_4 modification carried out at 600°C delivered lower capacity, but presented an appreciable capacity retention characteristics in ambient temperature conditions. Another important criterion is the high temperature performance, which is essential to employ them in high performance applications like HEV and EV [21].

Elevated temperature performance was carried out between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in elevated temperature conditions and illustrated in Fig. 10. As noted in the

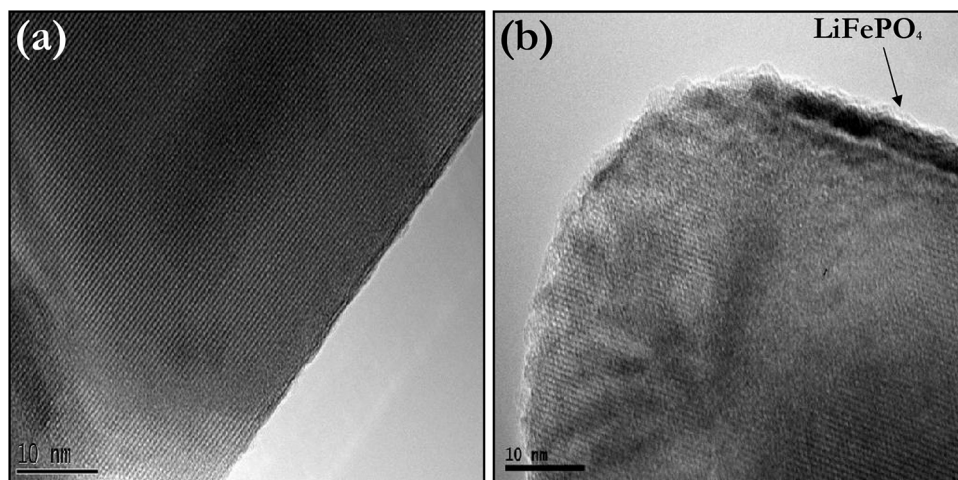


Fig. 11. High-resolution TEM pictures of (a) pure phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and (b) 1 wt.% LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes prepared by one step calcination at 600°C for 6 h under Ar flow.

ambient temperature conditions, decreasing capacity profiles are noted when increasing the LiFePO_4 sintering temperature. However, variation in the reversible capacity is negligible irrespective of the sintering temperature compared to ambient temperature, for example test cells delivered the maximum discharge capacity of ~ 138 , ~ 130 , ~ 127 and ~ 131 for pure (0.7 mol. adipic acid treated), 500, 550 and 600°C , respectively. Cycling profiles clearly showed the exceptional elevated temperature of LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders (600°C) compared to rest of the phases tested and retained $\sim 91\%$ of initial capacity. This clearly showed that the presence of LiFePO_4 layer certainly provides the necessary thermal stability for the high voltage spinel cathode in elevated conditions [22]. As a result, excellent elevated performance are noted, since it is well known that, the existence of strong covalent P–O bonding in olivine phase certainly translates improved high temperature performance [23]. Further, appropriate optimization of such LiFePO_4 layer formation and its shielding to prevent the undesired activity towards electrolyte solution to achieve such outstanding performance for high voltage spinel cannot be ruled out. Moreover, the presence of such coating not only enables the improvement in high temperature performance and also the safety of the Li-ion cell as well.

To validate the presence of LiFePO_4 coating, high resolution TEM studies have been performed and given in Fig. 11. Pure spinel phase (0.7 mol. adipic acid treated) also compared with the LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 600°C . Obvious to notice the presence of very smooth surface profiles, whereas LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ showed a very thin coating layer of $\sim 2\text{ nm}$ thick. The thin layer is none other than LiFePO_4 , which is further supported by energy dispersive X-ray analysis (Figure S4).

4. Conclusion

To conclude, an outstanding electrochemical performance at elevated temperature conditions was noted for LiFePO_4 modified high voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes. Adipic acid concentration, LiFePO_4 concentration, single or two-step coating process, LiFePO_4 formation temperature were optimized to achieve high performing cathode active material to construct high energy density Li-ion power packs. Presence of strong P–O covalent bonding in the olivine phase LiFePO_4 translates the necessary thermal stability to spinel cathode to realize the high temperature performance. This clearly provides that, the LiFePO_4 coating can be easily adopted to rest of the cathodes like LiMn_2O_4 , LiCoO_2 , $\text{Li}(\text{CoNiMn})_{1/3}\text{O}_2$ etc. to improve the cell safety and elevated temperature profiles as well.

Acknowledgment

This study was supported by the IT R&D program of MKE/KEIT (KI10039182, Development of 5 V cathode material which capacity is 125 mAh g^{-1} & high-voltage electrolyte which decomposition is over 5 V for lithium secondary battery).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.electacta.2014.06.054>.

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