



Letter

Enhanced elevated temperature performance of LiFePO_4 modified spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodeWon Hee Jang^a, Min Chul Kim^a, Sol Nip Lee^a, Jae Youn Ahn^a, Vanchiappan Aravindan^{a,b}, Yun Sung Lee^{a,*}^a Faculty of Applied Chemical Engineering, Chonnam National University, Gwang-ju 500-757, Republic of Korea^b Energy Research Institute @ NTU (ERI@N), Nanyang Technological University, Singapore 637553, Singapore

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ABSTRACT

A dramatic improvement in the elevated temperature performance of spinel phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode is achieved by surface modification with LiFePO_4 . Presence of strong covalent P–O bond in the olivine phase translates necessary thermal stability to $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode and renders ~89% of initial reversible capacity after 50 cycles at 55 °C. Though the LiFePO_4 modified phase exhibits marginal reduction in the initial reversibility than bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, displayed exceptional capacity retention characteristics irrespective of either ambient or elevated temperature.

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1. Introduction

Development of high energy density Li-ion power packs for hybrid electric vehicles (HEV) and electric vehicles (EV) completely depends on the utilization of high voltage cathodes, since in practical cells carbonaceous anodes essentially serve as buffer medium during charge–discharge process [1–5]. In order to fulfill the requirements, few high voltage cathodes such as olivine phosphates (LiCoPO_4 – 4.8 V vs. Li and LiNiPO_4 – 5.1 V vs. Li) [6–8], pyrophosphates ($\text{Li}_2\text{CoP}_2\text{O}_7$ – 4.9 V vs. Li) [9] fluorophosphates ($\text{Li}_2\text{CoPO}_4\text{F}$ – 4.9 V vs. Li and $\text{Li}_2\text{NiPO}_4\text{F}$ – 5.1 V vs. Li) [10], fluorosulphates (LiCoSO_4F – 4.7–4.9 V vs. Li, LiNiSO_4F – 5.2–5.4 V vs. Li and LiCuSO_4F – 5.1 V vs. Li) [11], oxysulphates (LiCoOSO_4 – 5.1 V vs. Li and LiNiOSO_4 – 5.1 V vs. Li) [11], silicates ($\text{Li}_2\text{NiSiO}_4$ – 4.8 V vs. Li) [12], spinel ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ – 4.7 V vs. Li) [3] and vanadates (LiNiVO_4 – 4.8 V vs. Li) [4,13] are proposed. Amongst, Ni-doped spinel phase compound $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is appealing in terms of performance, high energy density, ease in synthesis, eco-friendliness and low cost. The theoretical capacity is calculated to 147 mA h g^{-1} for one mole of reversible Li-insertion which exists in ordered and disordered polymorphs [3,5]. The ordered phase exhibits very flat operating potential at ~4.7 V vs. Li, whereas disordered phase shows the discrete charge–discharge profiles up to ~4 V vs. Li. This clearly shows the important role of synthesis technique to yield highly ordered spinel phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ to enable very flat

operating potential at high voltages. On the other hand, high operating potential of such spinel phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exceeds the thermodynamic stability window of conventional carbonate based electrolytes [14]. As a result, capacity fading is noted during cycling. The main issue of such a high voltage, promising $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode is the poor elevated temperature performance, which forbids the possibility of using them in high power Li-ion power packs for aforesaid HEV and EV applications [15–21]. Therefore, many research works are focused to improve the high temperature performance of the high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. In general, at elevated temperature conditions the side reactions are prone to accelerate which results in very severe fading. Therefore, improved electrochemical profiles at elevated temperature conditions are anticipated, which is one of the pre-requisite for the construction of high energy density Li-ion power packs to drive HEV and EV [1]. In order to overcome the above issue two main attempts have been explored to improve the electrochemical properties of such high voltage cathodes likely co-doping in Mn sites with metals (Al, Fe, Cu, Co, Ti, Cr, Mg, Zn and Ru) [22] and secondly surface modification with metals (Au, Ag and Zn), oxides (Bi_2O_3 , Al_2O_3 , SiO_2 and ZnO), phosphates (AlPO_4 , Li_3PO_4 and ZrP_2O_7) and fluorides (AlF_3 and BiOF) [23]. Metal doping certainly provides the improvement in electrochemical profiles at ambient conditions, but still the elevated temperature performance issue remains unsolved. Conversely, surface modification with mentioned compounds shows significant improvement in the electrochemical performance at elevated temperature conditions, but still the performance is not in the expected level [22]. This is mainly due

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to the inherent electronic/ionic conductivity of mentioned coating substances leads to the drop in the reversible capacity at elevated temperature conditions and metal modification certainly provides heterogeneous coating which also leads to significant fade [22]. Surface modification with well-known electro-active olivine phase LiFePO_4 certainly provides remarkable improvement in electrochemical performance which has been convincingly proven by us for olivine phase LiCoPO_4 [24] and layered type $\text{LiNi}_{0.5}\text{Co}_{0.2}\text{Mn}_{0.3}\text{O}_2$ [25] and Wang *et al.* [26] for layered type LiCoO_2 . To date, there is no report available on the surface modification with olivine LiFePO_4 for either native spinel compound (LiMn_2O_4) or Ni-doped phase ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$) to improve the electrochemical performance at ambient/elevated temperature conditions. However, Liu *et al.* [27] attempted to adopt LiFePO_4 modification over spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles by mechano-fusion dry process, unfortunately the procedure requires large amount of coating substance (20 wt.% LiFePO_4). As a result, composite formation is noted ($\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ - LiFePO_4) instead of thin layer of coating. Although the significant improvements in the electrochemical profiles are noted, but resultant cathode exhibits discrete discharge profiles at ~ 4.7 and ~ 3.4 V vs. Li which is not useful for the practical applications. In this line, we made an attempt to employ carbon coated LiFePO_4 modification over $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particulates without much affecting electronic/ionic conductivity of the spinel phase compound by adipic acid mediated sol-gel process. Extensive electrochemical studies are carried out for bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases and described in detail.

2. Experimental section

Spinel phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders were synthesized through scalable sol-gel technique described by us [28]. Briefly, starting materials such as $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$ (Junsei Chem, Japan), $\text{Ni}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (Aldrich, USA), and $\text{Mn}(\text{CH}_3\text{COO})_2\cdot 4\text{H}_2\text{O}$ (Aldrich, USA) were separately dissolved according to the stoichiometric ratio and mixed together with appropriate amount (0.7 mol with respect to total metal ions present) of adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$, Sigma-Aldrich, USA). The mixture was stirred continuously at 90°C to yield precursor powder. Then it was pre-calcined at $\sim 450^\circ\text{C}$ for 10 h to decompose the acetate moieties. The intermediate product was collected, pelletized, and sintered at 700°C for 12 h in air to yield single-phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. For LiFePO_4 coating, the starting materials $\text{Li}(\text{CH}_3\text{COO})\cdot\text{H}_2\text{O}$, $\text{Fe}(\text{CH}_3\text{COO})_2$ and H_3PO_4 were dissolved in ethanol and $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ particles were dispersed into above solution. An appropriate amount of (0.2 M) adipic acid containing solution was also added. Then, it was dried at 80°C to evaporate the ethanol and calcined at 650°C for 6 h in Ar to produce LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases [29–31].

Structural properties were analyzed through Rint 1000, Rigaku, Japan X-ray diffractometer equipped with a Cu K α radiation. Morphological features of the powders were analyzed by field emission scanning electron microscopy (FE-SEM, S4700, Hitachi, Japan) CR2032 coin-cell assembly was used for the electrochemical characterization. The test electrodes were fabricated with accurately weighed 20 mg of active material, 3 mg conductive additive (super P), and 3 mg of teflonized acetylene black (TAB-2). The resulting composite film was pressed over a 200 mm 2 stainless steel mesh current collector and it served as current collector. The half-cells were assembled with a composite cathode and a 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 (1:1 by vol., Soulbrain Co., Ltd., Korea) solution. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) studies were conducted in a coin-cell assembly using a Bio-Logic electrochemical work station (SP-150, Biologic, France), in which metallic lithium served as both working and counter electrode. Galvanostatic cycling 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} .

3. Results and discussion

Powder X-ray diffraction (XRD) pattern of bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases were given in Fig. 1a. There is no obvious difference between the XRD reflections of bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases and it clearly showed that the LiFePO_4 did not influence the structural properties of spinel phase. Further, lesser the amount of LiFePO_4 used for coating

(1 wt.%); hence it is very hard to detect through XRD. The thickness of LiFePO_4 is found ~ 2 – 4 nm over spinel particulates which measured by TEM measurements (TEM not given here). Therefore, elemental mapping has been carried out to ensure the presence of LiFePO_4 (Fig. 2). The observed reflections are indexed according to the spinel structure with P4 $_3$ 32 space group. Similar to XRD pattern, it is too complicated to distinguish the difference between the particulate morphology which is mainly because of the too low content used for coating. Therefore, electrochemical performance is the only way to provide the noticeable difference between such bare and LiFePO_4 modified spinel phase compounds.

Galvanostatic charge–discharge studies were performed in half-cell configuration between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in ambient temperature conditions and illustrated in Fig. 3a. Bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibited very flat discharge curves at ~ 4.7 V vs. Li, whereas discrete capacity profiles are observed for LiFePO_4 modified phase. This very flat operating potential corresponds to the well-ordered structure of spinel phase with $\text{Ni}^{2+/4+}$ redox couple and consists of Mn^{4+} ions [22]. Appearance of distorted curve *i.e.* flat potential at ~ 4.7 and ~ 4 V vs. Li is associated with the presence of mixed valance states of manganese (Mn^{3+} and Mn^{4+}). The small reduction of Mn^{4+} to Mn^{3+} is mainly due to the usage of chelating agent adipic acid, which generally hinders the particle growth during the synthesis of LiFePO_4 and also converted into pyrolyzed carbon to provide the sufficient electronic conductivity for olivine phase [30]. The presence of trace amount of carbon (0.133 wt.%) during the LiFePO_4 modification under Ar atmosphere results in carbo-thermal reduction of Mn^{4+} into Mn^{3+} . Moreover, carbo-thermally reduced Mn^{3+} also involved in the electrochemical reaction and contributes some capacity [3]. As expected slightly lower reversible capacity of $\sim 126\text{ mA h g}^{-1}$ is observed for LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compared to bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ($\sim 141\text{ mA h g}^{-1}$). Moreover, the operating potential

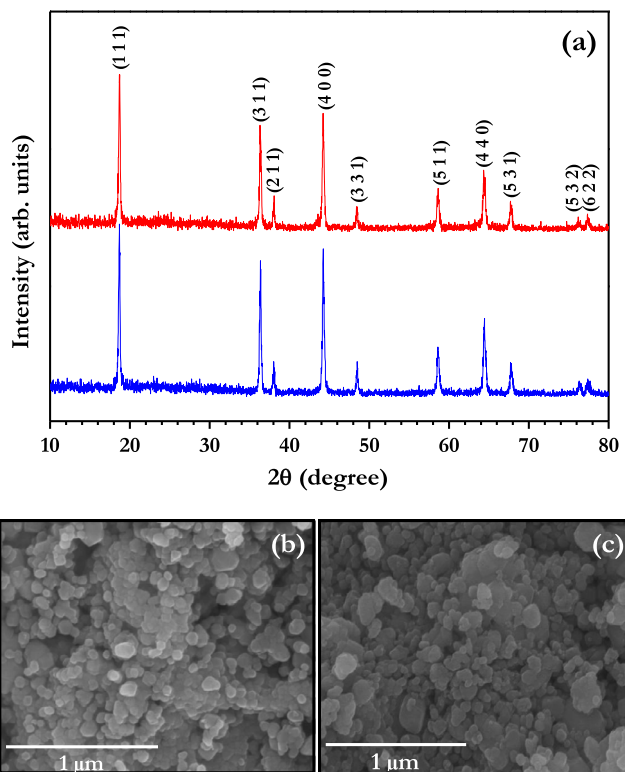


Fig. 1. (a) XRD pattern of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and LiFePO_4 (1 wt.%) coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes (55°C), (b) SEM picture of bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and (c) SEM picture of LiFePO_4 coated $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

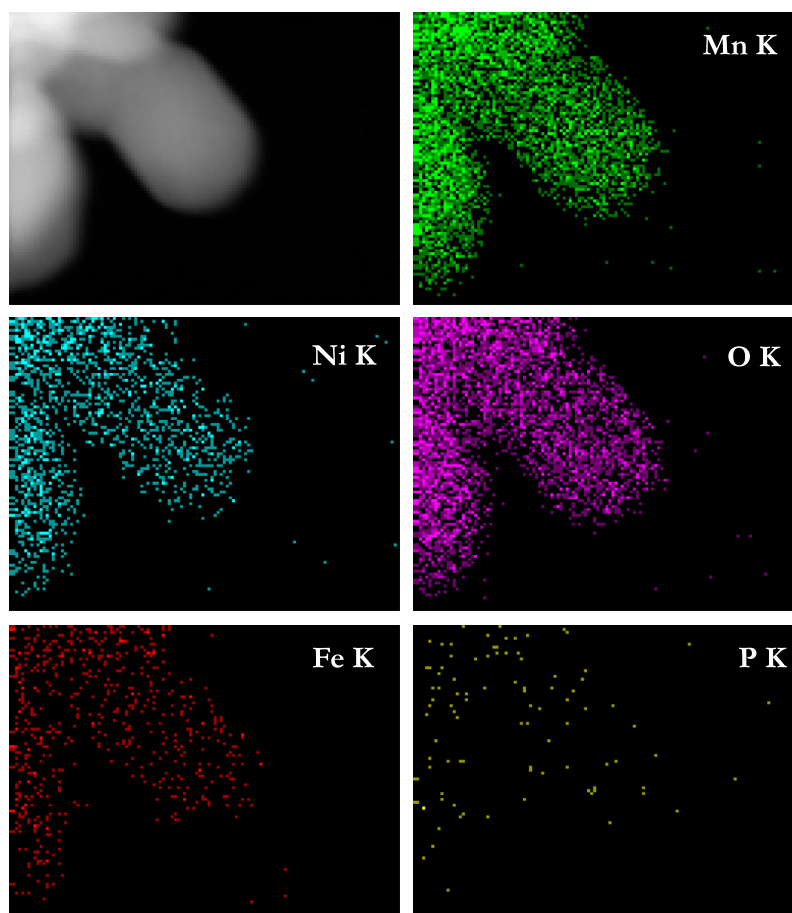


Fig. 2. Elemental mapping of LiFePO₄ modified LiNi_{0.5}Mn_{1.5}O₄ cathodes.

window is higher for LiFePO₄, therefore sol–gel coated olivine phase material necessarily to act as an electrochemically inactive material in the tested potential window and translate electrochemical stability [30]. Plot of discharge capacity vs. cycle number at ambient temperature is given in Fig. 3b. It is interesting to note that both bare and LiFePO₄ modified LiNi_{0.5}Mn_{1.5}O₄ phases delivered good cycleability up to 80 galvanostatic cycles. The test cells retained ~88% and ~95% of initial reversible capacity (calculated from 2nd cycle) for bare and LiFePO₄ modified LiNi_{0.5}Mn_{1.5}O₄ phases, respectively. This clearly showed the important role of LiFePO₄ on the electrochemical performance high voltage spinel phase cathode LiNi_{0.5}Mn_{1.5}O₄.

One of the major issues of spinel phase LiNi_{0.5}Mn_{1.5}O₄ cathode is its elevated temperature performance [3,5]. Though LiFePO₄ modification results slight reduction in the initial reversibility, but offers excellent capacity retention characteristics than bare LiNi_{0.5}Mn_{1.5}O₄ in ambient conditions. In this line, to study the influence of such LiFePO₄ coating on the electrochemical performance of LiNi_{0.5}Mn_{1.5}O₄ at elevated temperature conditions, a duplicate cell have been fabricated and tested between 3.5–4.8 V vs. Li at current density of 0.8 mA cm⁻² in 55 °C and shown in Fig. 3c. At elevated temperature conditions, the upper cut-off potential has been reduced to 4.8 V vs. Li to suppress the severe reactivity with electrolyte solutions. From Fig. 3c, there is a clear splitting of flat potential region is noted for both cases, which is mainly due to obvious oxidation states of Ni^{2+/3+} (~4.7 V vs. Li) and subsequent Ni^{3+/4+} (~4.6 V vs. Li). In ambient temperature conditions splitting of intermediate oxidation states (2+ to 3+ and 3+ to 4+) of Ni has been merged together and appeared as single redox

couple (Ni^{2+/4+}) [3,5]. The discharge capacity of ~138 and ~130 mA h g⁻¹ is observed for bare and LiFePO₄ modified LiNi_{0.5}Mn_{1.5}O₄ phases, respectively. At high temperature operation test-cells will deliver higher reversible capacity than room temperature conditions in general. As expected, LiFePO₄ modified phase displayed slightly higher capacity than ambient conditions, whereas bare LiNi_{0.5}Mn_{1.5}O₄ delivered lower capacity which is mainly due the severe reactivity of the electrolyte counterpart, particularly HF attack [3,5,14,22]. As a result, oxidation of electrolytes takes place and subsequently leads to the deposition of inorganic by-products as insoluble mass over the surface of the active particles, which drastically increases the cell impedance [14,32]. In addition, the self-discharge of cathode cannot be ruled out for such lower capacity profiles especially at high temperature operation. Plot of discharge capacity vs. cycle number in elevated temperature conditions is presented in Fig. 3d. As mentioned earlier, severe reactivity results in increase of cell impedance which upon cycling leads to the drastic capacity fade and retains only ~26% after 50 cycles (calculated from 2nd cycle onwards). On the other hand, LiFePO₄ modified delivers excellent cycleability and rendered ~89% of initial capacity. This drastic improvement is mainly due to the protective coating of LiFePO₄ over spinel particles which prevents severe attack of HF from the electrolyte solution, since at high temperature the reaction is prone to accelerated than ambient conditions [14]. More clearly, the LiFePO₄ consists of strong P–O covalent bond, which translates the necessary thermal stability for such olivine phase material [8,24–26]. This result certainly provides the boost for development of such high voltage spinel's with simple and scalable sol–gel mediated LiFePO₄ coating process with

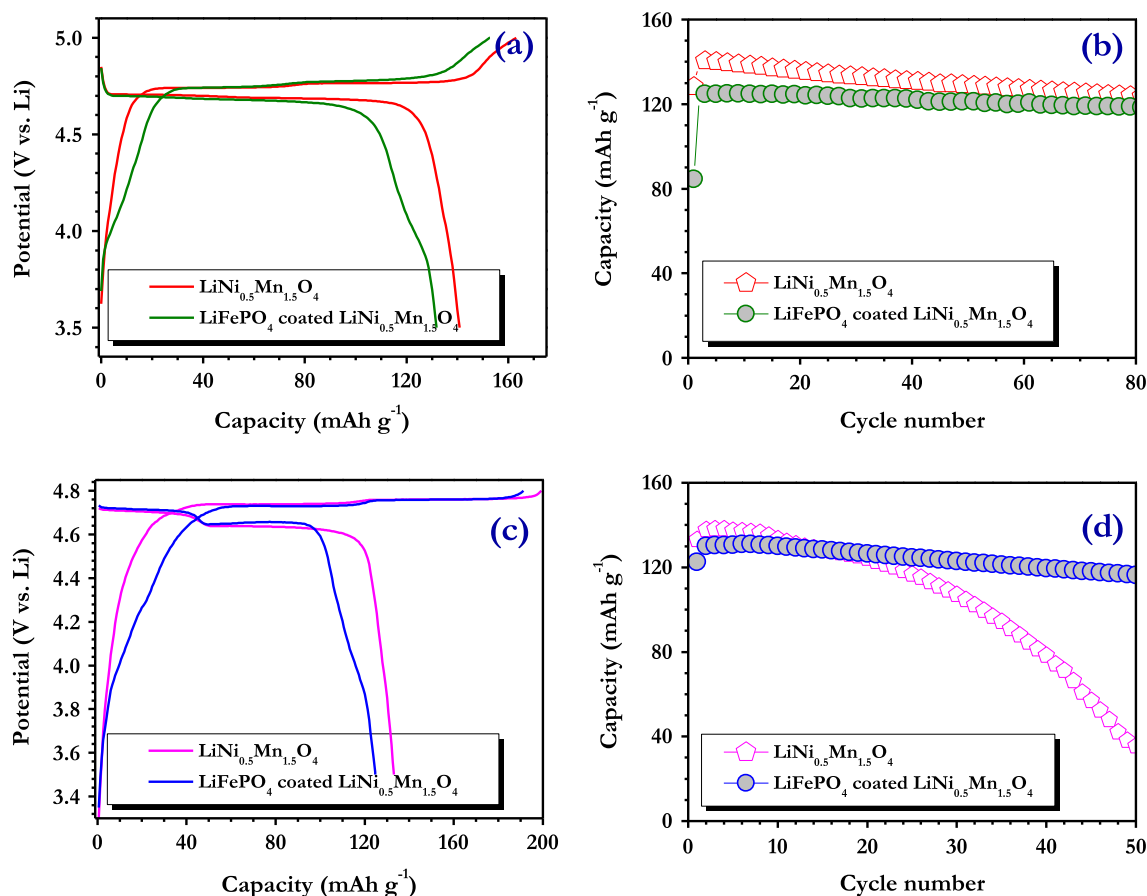


Fig. 3. (a) Typical galvanostatic charge–discharge curves of Ni-doped spinel cathodes in half-cell assembly between 3.5–5 V vs. Li at current density of 0.8 mA cm^{-2} in ambient temperature conditions, (b) plot of discharge capacity vs. cycle number, (c) typical charge–discharge curves of Ni-doped spinel cathodes in half-cell assembly between 3.5–4.8 V vs. Li at current density of 0.8 mA cm^{-2} in elevated temperature conditions (55°C) and (d) plot of discharge capacity vs. cycle number.

excellent elevated temperature performance. Further studies, particularly to suppress the carbo-thermal reduction of Mn^{4+} ions are in progress to improve the net energy density of Li-ion cell.

In order to support the reactivity of the electrode and electrolyte, EIS spectra of the bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cells were recorded and given in Fig. 4. It can be seen that the EIS composed of three main regions namely, high frequency (associated with solution resistance), medium frequency (related to charge-transfer, CT resistance) and low frequency or vertical tail inclined at 45° (Warburg tail associated with Li-diffusion) regions [15,33]. Before cycling, no obvious difference between the solution ($\sim 5 \Omega$) and CT resistances ($\sim 30 \Omega$) are noted for bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases. However, after 50 cycles at elevated temperature conditions, a drastic increase in both solution ($\sim 10 \Omega$) and CT resistance ($\sim 448 \Omega$) for bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compared to LiFePO_4 modified one (solution resistance: $\sim 14 \Omega$ and CT resistance: $\sim 47 \Omega$). Such an enormous increase in the CT resistance parallels the severe reactivity of the electrode toward the electrolyte solution [24,34]. The EIS study clearly reveals the presence of LiFePO_4 layer is beneficial for the betterment of high temperature electrochemical activity of the Ni-doped spinel.

Cyclic voltammetry is another convenient tool to investigate the electrochemical redox couple of the transition metal elements. In this regard, a duplicate cells comprising bare and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phases in two-electrode configurations were subjected to CV analysis at slow scan rate of 0.1 mV s^{-1} in ambient conditions between 3.5–5 V vs. Li and presented in Fig. 5. As observed in galvanostatic charge–discharge profile of bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase, a pair of broad peak associated with $\text{Ni}^{2+/4+}$ redox couple is observed

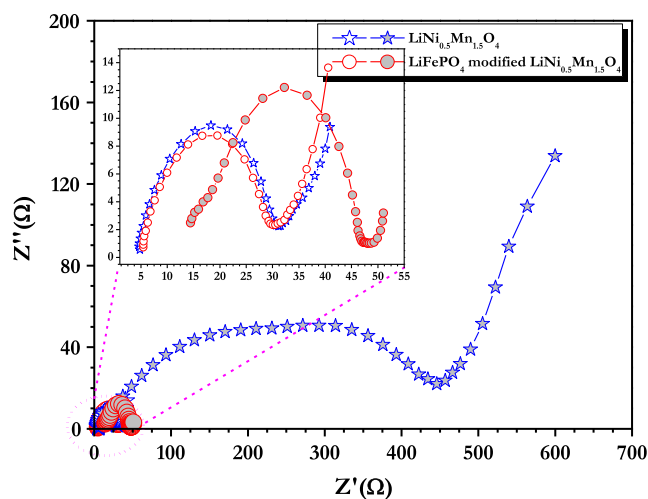


Fig. 4. Electrochemical impedance spectroscopy (EIS) traces of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ and LiFePO_4 modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes recorded in two electrode coin-cell configurations before and after cycling (50 cycles) at elevated temperature conditions. Open and filled symbols correspond to the EIS traces of before and after cycling, respectively.

at $\sim 4.9 \text{ V}$ and $\sim 4.55 \text{ V}$ vs. Li for anodic and cathodic scans, respectively. In addition to above redox pair, shoulder like peak at $\sim 4 \text{ V}$ vs. Li is noted, which corresponds to the $\text{Mn}^{3+/4+}$ redox couple and it is formed during the LiFePO_4 coating process i.e. carbo-thermal. Presence of $\text{Mn}^{3+/4+}$ redox couple leads to the slight

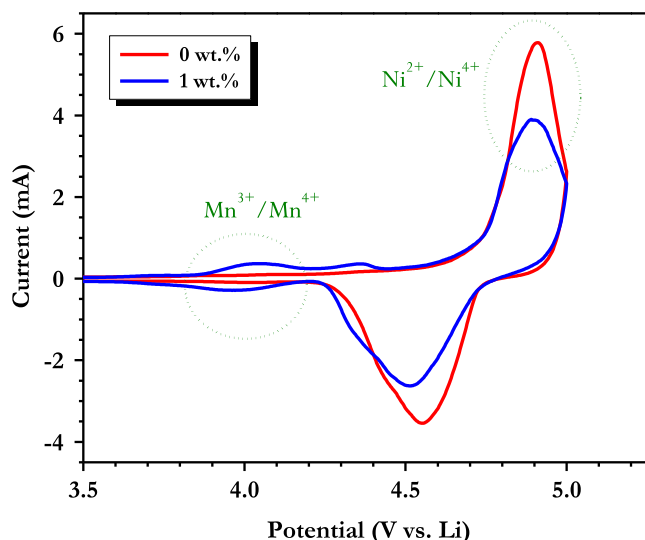


Fig. 5. Cyclic voltammetry traces of Ni-doped spinel cathodes in assembly between 3.5–5 V vs. Li at slow scan rate of 0.1 mV s^{-1} in ambient temperature conditions.

shift in the insertion potential toward lower voltages ($\sim 4.51 \text{ V}$ vs. Li) than bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase ($\sim 4.55 \text{ V}$ vs. Li). The observed redox couples clearly validates the insertion/extraction mechanism described above and consistent with literature as well [3].

4. Conclusions

To conclude, highly enhanced electrochemical performance at elevated temperature conditions (55°C) was noted for LiFePO_4 modified spinel phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode. Though such LiFePO_4 modified cathodes offered slight reduction in initial reversible capacity than bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ but rendered excellent cycling profiles of ~ 97 and $\sim 89\%$ of initial capacity for ambient and elevated temperature conditions (after 50 cycles), respectively. This study certainly provides the new direction for the development of such high voltage spinel cathode for high energy density Li-ion power packs for possible application toward HEV and EV with much more safety features.

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