



Enhancing the elevated temperature performance of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by V doping with *in-situ* carbon and polyimide encapsulation



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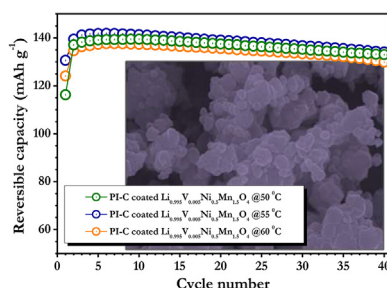
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HIGHLIGHTS

- V-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is prepared by scalable sol–gel technique.
- $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ has been modified with dual layer *i.e.* polyimide-carbon.
- Excellent elevated temperature performances are noted at 50, 55 and 60 °C.

GRAPHICAL ABSTRACT



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ABSTRACT

We report the enhanced electrochemical performance of high voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode by small amount of aliovalent doping in Li-site ($\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$) and polyimide-carbon (PI-C) coating as well. Such small amount of V-doping in Li-sites leads to the crystallization of ordered spinel. The performances of the cathodes are studied in half-cell assembly at elevated temperature conditions (50, 55 and 60 °C). Although, the notable improvement in elevated temperature conditions are noted for $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase at 50 °C, but not sustained while increasing to 55 and 60 °C. Nevertheless, the combined advantages of mixed conducting (ionic and electronic) features of PI-C, an excellent performance are noted for the $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase after introducing the PI-C layer, irrespective of the testing temperature. Cyclic voltammetry and impedance studies are also performed to corroborate the Li-ion kinetics.

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1. Introduction

Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is considered as a promising cathode for the construction of high energy density lithium-ion power packs owing to its high working potential (~4.7 V vs. Li), higher theoretical capacity (~147 mAh g⁻¹), 3D Li-ion conducting channels, good

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electrical conductivity ($\sim 10^{-5} \text{ S cm}^{-1}$) and appreciable high current performance [1]. Unfortunately, the poor elevated temperature is a serious issue than the higher working potential of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, since the operating potential is higher than decomposition potential of conventional organic solvents [2–8]. Generally, the spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ crystallizes in to two polymorphs like well ordered structure (space group: $\text{P4}_3\text{32}$) and disordered one (space group: $\text{Fd}\bar{3}\text{m}$). In the ordered spinel, Li on 8c, Ni on 4b, Mn on 12d, and O(1) and O(2) oxygen ions will occupy the 24e and 8c Wyckoff positions, respectively. Further, there is an absence of Mn^{3+} ions. As a consequence, theoretically, Jahn-Teller distortion issue will be no longer present in the Ni-doped spinel compared to the native compound, LiMn_2O_4 . Hence, Ni^{2+} only involved in the electrochemical reaction and such $\text{Ni}^{2+/4+}$ redox reactions occurred at $\sim 4.7 \text{ V}$ vs. Li region with flat plateau. On the other hand, discrete electrochemical profiles are observed for the case of disordered phase *i.e.* exhibits the additional plateau at $\sim 4 \text{ V}$ vs. Li region [9,10]. Irrespective of the synthesis procedure employed, good electrochemical profiles are noted at ambient conditions for both ordered and disordered phases. However, the disordered phase exhibits slightly better high current performance than ordered one. At elevated conditions, the poor thermal stability of PF_6^- anions are highly accelerated and reacts with available moisture content which in turn produces a dangerous HF and strong PF_5 Lewis acid. Eventually, presence of HF in the electrolyte is certainly destroying the transition metal and cation (Li^+) as well [11,12]. In addition, the higher working potential also leads to the formation of thick by-products (formation of thick solid electrolyte interface, SEI) from oxidation of electrolyte solution which results the increase in cell impedance and eventually ruin the cycleability. So far, various approaches like surface modification with carbonaceous materials, metal oxides, metal fluorides, metal phosphates and polymers, and co-doping with isovalent and aliovalent materials have been exploited to overcome the aforesaid issue [1]. Although, significant improvement in the high temperature profiles are noted for all the cases, but still the results are not sufficient for the real time applications. In this line we made an attempt to improve the elevated temperature performance of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ by two ways, (i) V-doping in to the Li-sites and (ii) dual polyimide and carbon (PI-C) coating over V-doped $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase. The choice of dopant, V will certainly promotes the conducting profiles of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase. The PI is a well known ionic conductor with high thermal stability [13]. The blending of *in-situ* generated carbon aids the electronic conducting properties of the layer which in turn promotes the electrochemical activity of the active material. Extensive electrochemical and structural studies were performed and described in detail.

2. Experimental section

Sol-gel procedure was used to synthesize the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ powders with and without V-doping as described in our previous work [14]. In a typical synthesis procedure, stoichiometric amounts of starting materials such as $\text{Li}(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}$ (Junsei Chem, Japan), $\text{Ni}(\text{CH}_3\text{COO}) \cdot 4 \text{ H}_2\text{O}$ (Aldrich, USA), and $\text{Mn}(\text{CH}_3\text{COO}) \cdot 4 \text{ H}_2\text{O}$ (Aldrich, USA) were dissolved separately in distilled water and mixed together with the appropriate amount of chelating agent, adipic acid ($\text{C}_6\text{H}_{10}\text{O}_4$, Sigma-Aldrich, USA). The mixture was continuously stirred at 90°C to obtain a precursor powder and subsequently pre-calcined at $\sim 450^\circ\text{C}$ for 10 h. The intermediate product was calcined at 700°C for 12 h to yield a single-phase $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The same procedure was repeated for the vanadium doped spinel phase and V_2O_5 (Sigma-Aldrich, USA) was used as the source.

For the PI-C modification process, we completely followed our

previous work on LiCoO_2 cathode [15]. In a typical process, First, polyamic acid solution was synthesized by using the pyromellitic dianhydride (PMDA)/oxydianiline (ODA) (= 1.00/1.01, molar ratio)-with di-methyl acetamide (DMAc) as a solvent under nitrogen atmosphere. The above solution was mixed with sucrose ($\text{Mw} = 342 \text{ g/mol}$, Aldrich) by keeping equal weight ratio. Then, the $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was added and sonicated to ensure the uniform distribution. After filtering and subsequent vacuum-drying, the cathode, $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ composed of thin layer of polyamic acid/sucrose mixture over the surface. Finally, the resultant compound was subjected for thermal treatment to carbonize the sucrose and imidization process. To ensure both processes, the thermal treatment condition was set as 60°C for 30 min $\rightarrow 120^\circ\text{C}$ for 30 min $\rightarrow 200^\circ\text{C}$ for 60 min $\rightarrow 300^\circ\text{C}$ for 60 min $\rightarrow 400^\circ\text{C}$ for 10 min under nitrogen atmosphere [5]. In the final product, the carbon content was found to be $\sim 3.7 \text{ wt\%}$.

X-ray diffractometer (Rint 1000, Rigaku, Japan) equipped with a Cu K_α radiation source was used to study the structural properties. The surface morphology of the powder was analysed by field emission scanning electron microscopy (FE-SEM, S4700, Hitachi, Japan) and transmission electron microscopy (TEM, TECNAI, Philips, The Netherlands). Electrochemical studies were performed in CR2032 coin-cell assembly. The composite electrodes were formulated with 20 mg of active material, 3 mg super P, and 3 mg of teflonized acetelene black (TAB-2) using ethanol. The resulting film was pressed over a 200 mm^2 stainless steel mesh current collector. The test cells were assembled in a Ar environment with a

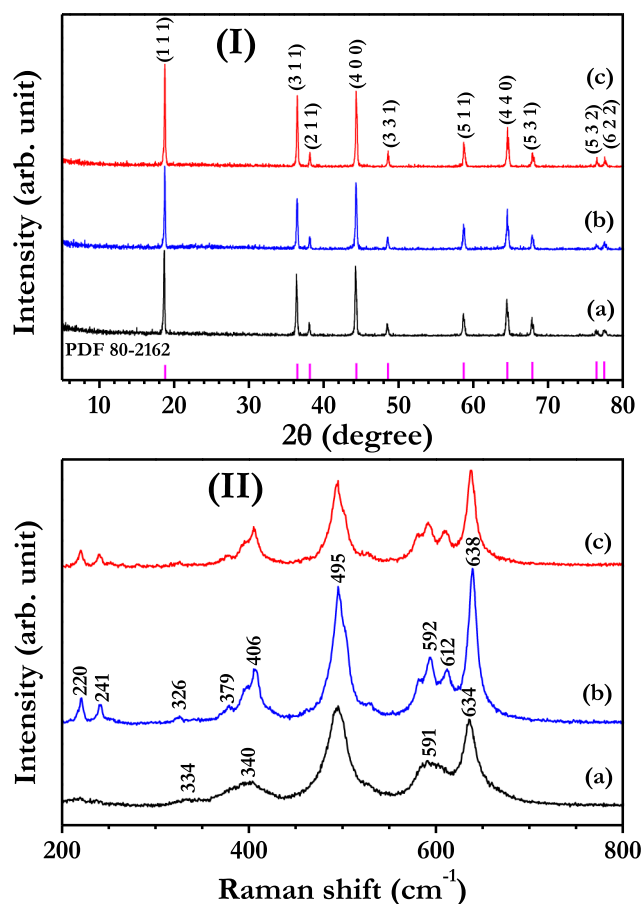


Fig. 1. (I) XRD pattern of (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and (c) PI-C coated $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and (II) Raman spectra of (a) $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, (b) $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and (c) PI-C coated $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

composite cathode and a metallic lithium anode separated by porous polypropylene film (Celgard 3401, USA) filled with 1 M LiPF₆ in ethylene carbonate (EC):di-methyl carbonate (DMC) (1:2 by vol., Soulbrain Co., Ltd., Korea) solution. Cyclic voltammetry (CV) and Electrochemical impedance spectroscopy (EIS) were performed in a half-cell assembly using a Bio-Logic electrochemical work station (SP-150, Biologic, France), in which metallic lithium served as both a working and a counter electrode. Galvanostatic cycling studies were conducted between 3.5 and 5 V vs. Li at a constant current density of 0.8 mA cm⁻² in 50, 55 and 60 °C.

3. Results and discussion

Fig. 1a represents the powder XRD pattern of LiNi_{0.5}Mn_{1.5}O₄, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ and PI-C modified Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄. High intense sharp reflections clearly indicate the presence of highly crystalline nature of the spinel phase. There is no deviation from the diffraction patterns are noted and it is very difficult to distinguish the space group. Hence, Raman spectra has been recorded to ensure the phase formation and depicted in Fig. 1b. Since, Raman study is one of the simplest approaches to distinguish both ordered and disordered phases [16,17]. Interestingly, V-doping in to Li-sites certainly leads to the ordering of the spinel phase *i.e.* ordered phase with P4₃32 space group. This has been clearly evidenced from the appearance of doublet bands at ~220 and ~240 cm⁻¹ for, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ phase. Similarly, the appearance of doublets at ~592 and ~612 cm⁻¹ confirms the formation of ordered phase. On the other hand, absence of the mentioned peaks is associated with the disordered nature of the phase. The observed Raman bands are consistent with the previous reports on the phase formation [16,17].

The ordered phase is retained after the dual PI-C coating over such Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ phase and supported from the Raman spectra. Also, the PI-C dual layer is too thin for the detectable limitations of the X-ray diffractometer.

Morphological features of the three spinel phases were investigated by means of SEM and given in Fig. 2. The SEM pictures of LiNi_{0.5}Mn_{1.5}O₄ clearly revealed the formation of irregular shaped sub-micron sized (<200 nm) particulates. Increase in the particulate size is evidenced after the incorporation of aliovalent V in to the Li-sites which is clearly observed from the SEM pictures (Fig. 2b). Since the dual PI-C coating has been conducted over the Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ particulates, so, there is no much deviation from the particulate sizes are observed. The TEM picture cleared showed the presence of dual layer *i.e.* carbon and polyimide.

Electrochemical profiles of the three spinel cathodes have been evaluated by means of in half-cell assembly with metallic Li at elevated temperature conditions only (50, 55 and 60 °C). The cells were tested between 3.5 and 5 V vs. Li at current density of 0.8 mA cm⁻² and corresponding profiles at 50 °C are depicted in Fig. 3. Apparent to note that, the presence of flat discharge profile at ~4.7 V vs. Li clearly revealed the characteristic of such high voltage spinel. As expected, less reversibility is noted for initial few cycles. Increase in capacity is noted at second cycle compared to first cycle irrespective of the spinel cathodes tested. At second cycle, the cell delivered reversible capacities of ~138, 142 and ~137 mAh g⁻¹ for LiNi_{0.5}Mn_{1.5}O₄, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ and PI-C modified Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, respectively. However, the observed charge capacity for all the three spinel cathodes is higher than the theoretical capacity. This is mainly because of the oxidation of electrolyte solution, since the conventional carbonate based solutions are stable

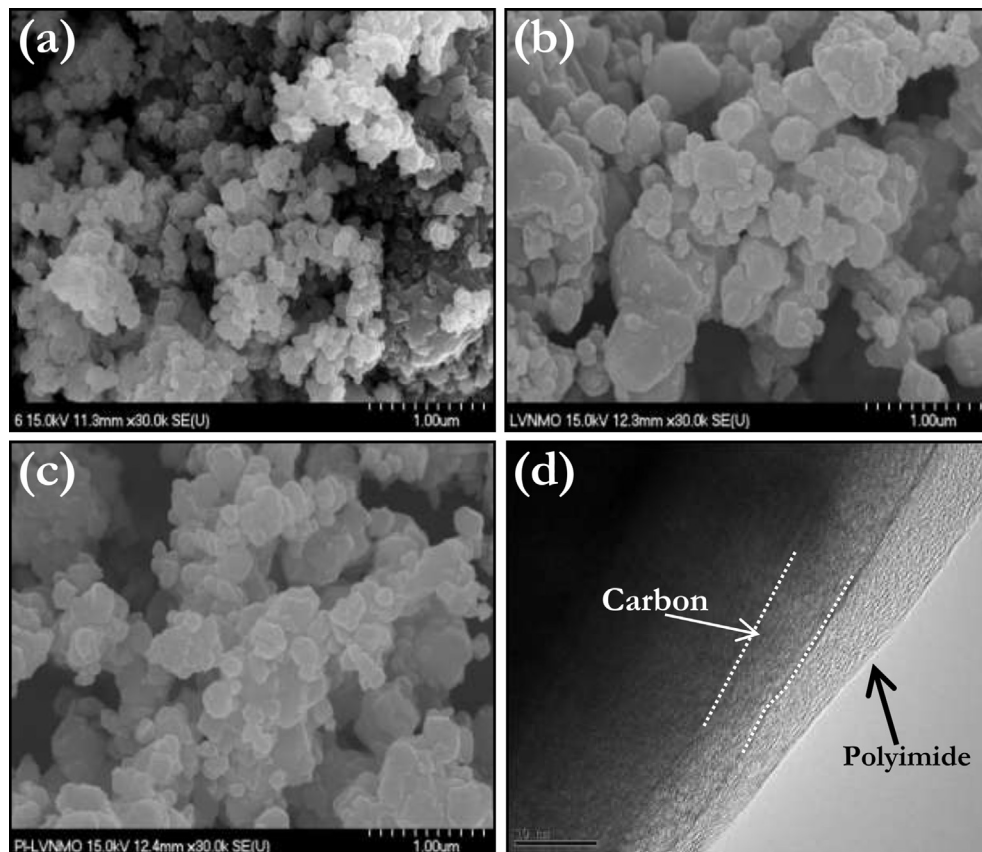


Fig. 2. SEM pictures of (a) LiNi_{0.5}Mn_{1.5}O₄, (b) Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, and (c) PI-C coated Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, and (d) high resolution TEM image of PI-C coated Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄.

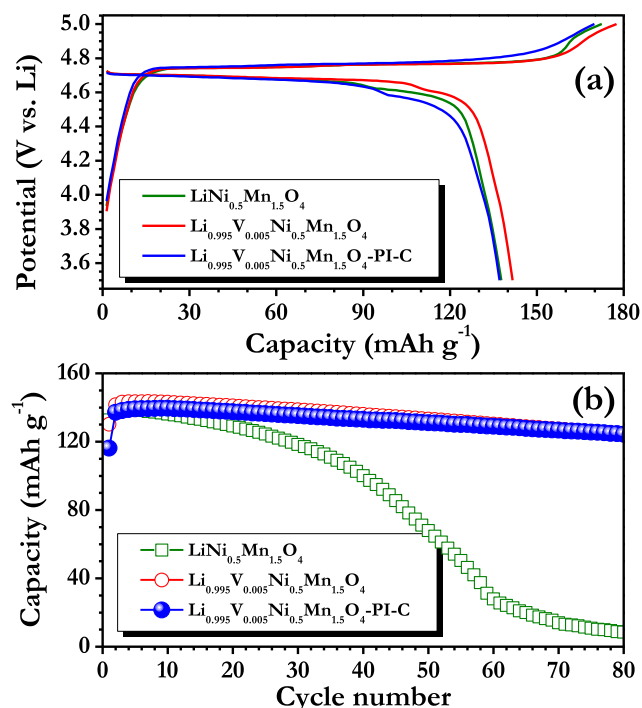


Fig. 3. (a) Typical galvanostatic charge–discharge curves (second cycle) of LiNi_{0.5}Mn_{1.5}O₄, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, and PI-C coated Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ in half-cell configuration with metallic Li between 3.5 and 5 V vs. Li at current density of 0.8 mA cm^{−2}. The galvanostatic studies were conducted at 50 °C, (b) Plot of discharge capacity vs. cycle number.

up to ~4.6 V vs. Li only. The observed electrochemical activity is mainly due to the utilization of Ni^{2+/4+} redox couple, and a very small contribution from the Mn^{3+/4+} at ~4 V vs. Li region cannot be ruled out. After 45 cycles, the test cells retained ~49, ~94 and ~96% of initial reversible capacity (calculated from second cycle) for LiNi_{0.5}Mn_{1.5}O₄, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ and PI-C modified Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, respectively. It is known fact that, at elevated temperature conditions the reactions are highly accelerated and PF₆[−] is thermally unstable which decomposes in to PF₅ and LiF. However, the PF₅ is strong Lewis acid and can easily react with the trace amount of moisture absorbed by the electrolyte and eventually produces the dangerous HF. The HF can easily destroy the cation and transition metal present in the cathode as well. In addition, the transition metal dissolution is also another problem for such spinel candidates which certainly deteriorate the cell performance upon cycling. The observed results are consistent with our previous work Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ cathode with 1:1 concentration of EC and DMC at 55 °C [18]. Here, we doubled the DMC concentration with respect to EC (2:1) for suppressing the gas evolution behaviour (preferably CO₂), especially operating at elevated temperature conditions [19], apart from the formation of polycarbonates and compounds with carboxylic acid groups upon oxidation [11,20–23]. Nevertheless, only marginal increase in capacity retention is noted for the case of PI-C modified Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄. Of course the marginal increase in capacity retention characteristics is mainly attributed to the presence of mixed conducting protective layer of PI-C.

The temperature condition is increased to 55 and 60 °C to evaluate the performance of three materials in half-cell assembly under the same testing conditions (Current density: 0.8 mA cm^{−2} and Potential window: 3.5–5 V vs. Li) and corresponding electrochemical profiles are illustrated in Fig. 4. Irrespective of the

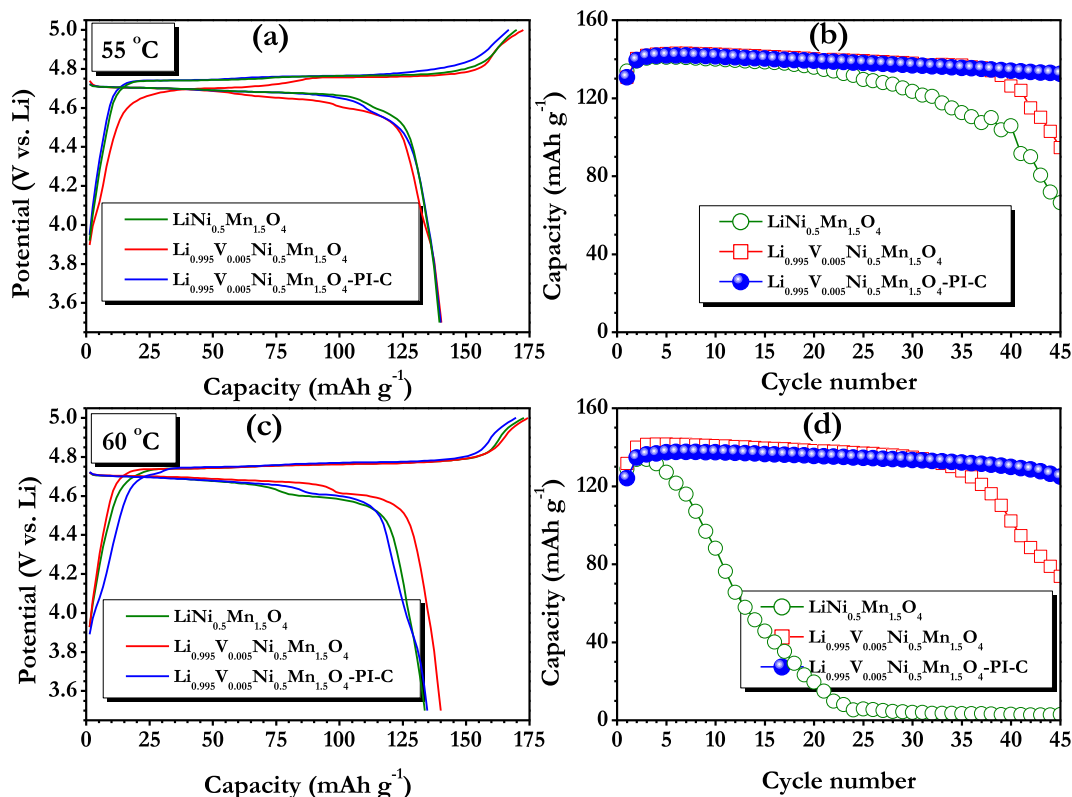


Fig. 4. (a) Typical galvanostatic charge–discharge curves (second cycle) of LiNi_{0.5}Mn_{1.5}O₄, Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄, and PI-C coated Li_{0.995}V_{0.005}Ni_{0.5}Mn_{1.5}O₄ in half-cell configuration with metallic Li between 3.5 and 5 V vs. Li at current density of 0.8 mA cm^{−2}. The galvanostatic studies were conducted at 55 °C, (b) Plot of discharge capacity vs. cycle number, (c) Typical galvanostatic charge–discharge curves (second cycle) recorded at 60 °C, and (d) Plot of discharge capacity vs. cycle number.

temperature, there is no much variation from the initial capacities noted for all the three materials. Presences of prominent plateaus are also observed in both temperature conditions at ~ 4.7 V vs. Li. Obvious difference is noted for the three materials upon cycling. Very poor cycling profiles are observed for bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. More clearly, increasing the temperature from 50 to 60 °C severely affects the cycleability *i.e.* stability is decreased with temperature. On the other hand, $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ exhibits better cycleability compared to bare $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. However, the stability phase is in decreasing trend with temperature. Further, it is worth to mention that, the performance of $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is contradicting with our previous work at 55 °C operation, in which cathode is found superior in terms of cycleability compared to bare one. Here also the case, but there is no long term stability is observed. This is mainly because of the DMC concentration in the electrolyte solution. This clearly showed that, the linear carbonate concentration also plays a vital role to determine the electrochemical properties of high voltage cathodes in elevated conditions (Figure S1). Nevertheless, good electrochemical properties are noted for PI-C modified $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ phase, irrespective of the temperature conditions (50, 55 and 60 °C). Apart from the mixed conductivity of PI-C layer which certainly prevents the direct contact with the electrolyte solution and thereby prevents the nucleophilic attack of HF. As a consequence, improved electrochemical profiles are noted for such PI-C modified $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

In order to understand the PI-C layer towards the Li-ion kinetics, CV and electrochemical impedance spectroscopy (EIS) measurements were performed and given in Fig. 5. CV studies

were conducted at a slow scan rate of 0.05 mV s^{-1} . Sharp anodic and cathodic peaks are observed at ~ 4.86 and ~ 4.6 V vs. Li, respectively. This is mainly because of the utilization of $\text{Ni}^{2+/4+}$ redox couple. Further, small peaks at ~ 4.05 and ~ 3.95 V vs. Li upon cathodic and anodic sweeps are associated with the electrochemical activity of $\text{Mn}^{3+/4+}$ redox couple. This clearly indicates the disordered nature of the spinel phase and consistent with the structural properties. The area underneath the CV curves is directly related to the capacity of the material and consistent with the galvanostatic cycling at initial cycling. EIS spectra clearly showed the presence of three main regions (i) high frequency region corresponds to the contact resistance or electrode/electrolyte interface, (ii) medium frequency region is associated with the charge transfer (CT) resistance of the said interface, and (iii) 45° inclined vertical tail corresponds to the Li-ion diffusion kinetics and co called Warburg impedance [24]. The resistance of $\sim 5 \Omega$ is noted for all the three cases, which is correlated to the solution resistance. Nevertheless, a notable difference is noted in the CT resistance of the materials, for example, increase in the value from ~ 41 to $\sim 55 \Omega$ is noted for the case of $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ compared to pure $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$. The dual, PI-C coating certainly decreases the CT resistance to $\sim 47 \Omega$ because of the conducting nature of the layer. This layer not only improves the conducting profiles of the spinel compound, also provides necessary stability at elevated temperature operation. Although the necessary improvement is observed after V-doping, but the electrolyte concentration strongly influenced the elevated temperature operation. The concept of introducing the mixed ion conducting layer approach not only improves the elevated temperature operation and also delivers negligible lose in capacity perspective compared to the rest. Therefore, we strongly believe, this is one of the efficient approaches to enhance the elevated temperature conditions of the cathodes for the fabrication of high energy density cathodes. Further, the fundamental aspects like interaction of such dual layer with electrolyte solution and related studies are underway and it will be communicated later.

4. Conclusion

We demonstrate the significance of PI-C modification over high voltage spinel cathode with mixed conducting properties. The PI-C layer not only provides the improvement in the capacity retention characteristics and also maintains the high reversibility irrespective of the testing temperature. Also the dual PI-C layer certainly prevents the nucleophilic attack of HF and eventually translates the better electrochemical activity at high temperature operation which is one of the fundamental issues of this cathode. This simple and inexpensive process certainly opens the new avenues for the possible commercialization and also, extended for other electro-active materials to improve the high temperature performance.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jpowsour.2015.08.053>.

References

- [1] A. Manthiram, K. Chemelewski, E.-S. Lee, *Energy & Environ. Sci.* 7 (2014)

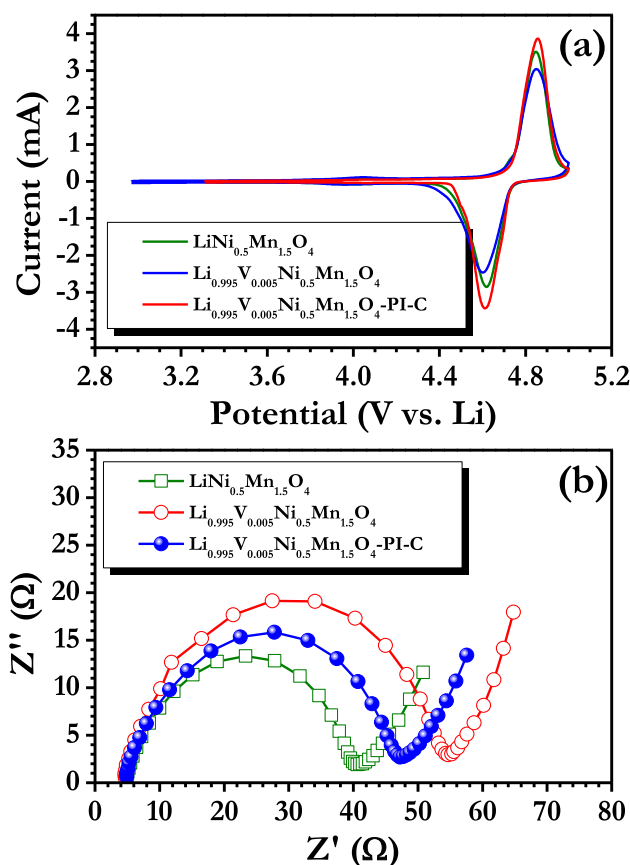


Fig. 5. (a) Cyclic voltammogram of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$, PI-C coated $\text{Li}_{0.995}\text{V}_{0.005}\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes recorded in half-cell configuration between 3.5 and 5 V vs. Li at slow scan rate of 0.05 mV s^{-1} in ambient temperature, and (b) Nyquist plot of aforesaid materials in half-cell configuration.

- 1339–1350.
- [2] J. Liu, A. Manthiram, *Chem. Mater.* 21 (2009) 1695–1707.
- [3] J. Song, D.W. Shin, Y. Lu, C.D. Amos, A. Manthiram, J.B. Goodenough, *Chem. Mater.* 24 (2012) 3101–3109.
- [4] N. Arun, V. Aravindan, S. Jayaraman, N. Shubha, W.C. Ling, S. Ramakrishna, S. Madhavi, *Nanoscale* 6 (2014) 8926–8934.
- [5] M.C. Kim, S.H. Kim, V. Aravindan, W.S. Kim, S.Y. Lee, Y.S. Lee, *J. Electrochem. Soc.* 160 (2013) A1003–A1008.
- [6] W.H. Jang, M.C. Kim, S.H. Kim, V. Aravindan, W.S. Kim, W.-S. Yoon, Y.-S. Lee, *Electrochim. Acta* 137 (2014) 404–410.
- [7] W.H. Jang, M.C. Kim, S.N. Lee, J.Y. Ahn, V. Aravindan, Y.S. Lee, *J. Alloys Compd.* 612 (2014) 51–55.
- [8] N. Arun, A. Jain, V. Aravindan, S. Jayaraman, W. Chui Ling, M.P. Srinivasan, S. Madhavi, *Nano Energy* 12 (2015) 69–75.
- [9] R. Santhanam, B. Rambabu, *J. Power Sources* 195 (2010) 5442–5451.
- [10] V. Aravindan, Y.S. Lee, S. Madhavi, *Adv. Energy Mater.* 5 (2015) 1402225.
- [11] V. Aravindan, J. Gnanaraj, S. Madhavi, H.-K. Liu, *Chem. – A Eur. J.* 17 (2011) 14326–14346.
- [12] V. Aravindan, J. Gnanaraj, Y.-S. Lee, S. Madhavi, *J. Mater. Chem. A* 1 (2013) 3518–3539.
- [13] J.-H. Park, J.-S. Kim, E.-G. Shim, K.-W. Park, Y.T. Hong, Y.-S. Lee, S.-Y. Lee, *Electrochem. Commun.* 12 (2010) 1099–1102.
- [14] Y.S. Lee, Y.K. Sun, S. Ota, T. Miyashita, M. Yoshio, *Electrochem. Commun.* 4 (2002) 989–994.
- [15] J.-H. Park, J.-M. Kim, C.K. Lee, S.-Y. Lee, *J. Power Sources* 263 (2014) 209–216.
- [16] N. Amdouni, K. Zaghib, F. Gendron, A. Mauger, C.M. Julien, *Ionics* 12 (2006) 117–126.
- [17] L. Wang, H. Li, X. Huang, E. Baudrin, *Solid State Ionics* 193 (2011) 32–38.
- [18] M.C. Kim, K.-W. Nam, E. Hu, X.-Q. Yang, H. Kim, K. Kang, V. Aravindan, W.-S. Kim, Y.-S. Lee, *ChemSusChem* 7 (2014) 829–834.
- [19] F. Joho, P. Novák, *Electrochim. Acta* 45 (2000) 3589–3599.
- [20] L. Xing, O. Borodin, *Phys. Chem. Chem. Phys.* 14 (2012) 12838–12843.
- [21] M. Moshkovich, M. Cojocaru, H.E. Gottlieb, D. Aurbach, *J. Electroanal. Chem.* 497 (2001) 84–96.
- [22] T. Matsushita, K. Dokko, K. Kanamura, *J. Power Sources* 146 (2005) 360–364.
- [23] L. Yang, B. Ravdel, B.L. Lucht, *Electrochem. Solid-State Lett.* 13 (2010) A95–A97.
- [24] V. Aravindan, K. Karthikeyan, K.S. Kang, W.S. Yoon, W.S. Kim, Y.S. Lee, *J. Mater. Chem.* 21 (2011) 2470–2475.