RSC Advances

PAPER

Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C (M=Fe, Co) composite cathodes with extended solubility limit and improved electrochemical behavior

Kalidas Nathiya, Dharmarajan Bhuvaneswari, Gangulibabu, Duraisamy Nirmala and Nallathamby Kalaiselvi*

A first attempt has been made to prepare Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C (M=Fe, Co) composite solutions by adopting a novel oxalic dihyrazide assisted combustion (ODHAC) method. The pillaring effect of Fe in Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C and the possible electrochemical activity of the Co$^{3+/4+}$ redox couple of Li$_3$Co$_x$V$_{2-x}$(PO$_4$)$_3$/C at a 4.8 V limit increases the structural and cycling stability of the native Li$_3$V$_2$(PO$_4$)$_3$/C cathode respectively, thereby ultimately improving the electrochemical behaviour of Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C solid solutions. An extended solubility limit of x = 0.10 for Fe dopant has been achieved for the first time through the present study against the reported value of x = 0.05 in Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C compounds. The study demonstrates the suitability of the ODHAC synthesis approach in preparing a wide variety of phase pure Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C cathodes. Further, the superiority of Li$_3$Co$_{0.10}$V$_{1.90}$(PO$_4$)$_3$/C in exhibiting the highest capacity (178 mAh g^{-1}) and negligible fade (4%) and the demonstrated cyclability under the influence of 10 C rate has been understood as a function of the synergistic effect of the ODHAC synthesis method and the optimum concentration of Co dopant chosen for the study.
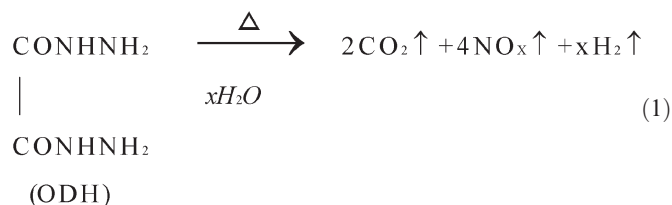
1. Introduction

Among the recently celebrated phosphate cathode materials,[1–3] monoclinic Li$_3$V$_2$(PO$_4$)$_3$ with larger interstitial lithium sites has been considered predominantly for reasons such as facile lithium ion mobility, high specific capacity and good thermal stability.[4–6] In native Li$_3$V$_2$(PO$_4$)$_3$ with a theoretical capacity of 197 mAh g^{-1}, all the three lithium ions can be completely extracted and inserted, especially when the same is synthesized in the monoclinic form and cycled between 3.0–4.8 V. However, partial substitution of V with suitable metals to form Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C solid solutions attracted the attention of researchers due to added advantages such as improved electronic conductivity and enhanced lithium transport kinetics. Hence, the present study is aimed on the synthesis and characterization of carefully chosen Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C (M=Fe, Co) solid solutions, wherein the possibility of improving the electrochemical behaviour, especially when the same are exploited as lithium intercalating cathode materials, has been explored.
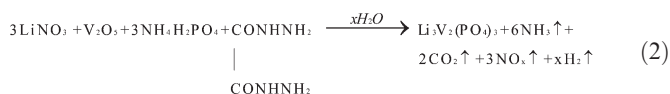
Based on our earlier investigation, 5 wt.% of super P carbon has been chosen as the carbon source.[7] Among the reported dopants such as divalent Co^{2+} and Mg^{2+},[8–10] trivalent Fe^{3+}, Al^{3+}, Cr^{3+}, Co^{3+}, tetravalent Zr^{4+}, Ti^{4+}, pentavalent Nb^{5+} and a rare earth metal ion (Y^{3+}) for the vanadium in the Li$_3$V$_2$(PO$_4$)$_3$ cathode incorporated to improve properties such as electronic conductivity,[11] specific capacity,[12] rate capability[13] and cycling stability at

Central Electrochemical Research Institute, Karaikudi-630006, India.
E-mail: kalaiselvicecri@gmail.com (N. KALAISELVI);
Fax: +91-4565-227779; Tel: +91-4565-241427

extended voltage limits,[14] only a few metals are reported to enhance the electrochemical performance.[15–18] Because, certain metal dopants improve the cycling stability at the expense of reduced discharge capacity values.[11,13,15,16] Further, in most of the cases, only lower concentration of (x < 0.5) dopant has been reported to improve the electrochemical behaviour, due to solubility limit related issues. However, Fe^{3+} (0.64 Å) and Co^{3+} (0.63 Å), possessing similar ionic radii value closer to that of V^{3+} (0.64 Å) ions have been chosen for the current study with a view to increase the structural and cycling stability of Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C along with the possibility of improving the solubility limits.

Quite different from the reported synthesis approaches,[11,14] a combustion method with a novel fuel, *viz.*, oxalic dihydrazide (ODH) has been chosen to prepare Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C cathodes, which is the highlight of the study. ODH, a fuel with a fuel calorific value (FCV = 10) greater than those of conventionally used fuels, such as urea (FCV = 6) and glycine (FCV = 9),[19,20] decomposes at a temperature as low as 250 °C and aids the process of combustion of the selected precursor. Subsequently, an instantaneous and exorbitant evolution of NO$_x$ and CO$_x$ gases takes place (according to eqn(1) and (2)) to impart the desired porosity to the final product.

$$\begin{array}{c} CONHNH_2 \\ | \\ CONHNH_2 \\ (ODH) \end{array} \xrightarrow[xH_2O]{\triangle} 2CO_2\uparrow + 4NO_x\uparrow + xH_2\uparrow \qquad (1)$$

$$3LiNO_3 + V_2O_5 + 3NH_4H_2PO_4 + CONHNH_2 \xrightarrow{xH_2O} Li_3V_2(PO_4)_3 + 6NH_3\uparrow +$$
$$2CO_2\uparrow + 3NO_x\uparrow + xH_2\uparrow \quad (2)$$
$$| $$
$$CONHNH_2$$

The liberated hydrogen plays a vital role in reducing the oxidation state of vanadium from +5 to +3, thus leading to the formation of a stoichiometric $Li_3V_2(PO_4)_3$ compound. Similarly, the use of a Ar/H_2 atmosphere for furnace heating is helpful in preventing further oxidation of V^{3+} during the course of the reaction. Herein, ODH acts as a combustible fuel and as carbon source to offer rapid formation of the final product in the form of a composite and the added super P carbon imparts a continuous carbon wiring on the $Li_3V_2(PO_4)_3$ matrix, which is the significance of the study.

Based on this mechanism, a series of $Li_3M_xV_{2-x}(PO_4)_3/C$ solid solutions have been prepared using the ODHAC method and the effect of the synthesis method and concentration of dopants on improving the solubility limit and electrochemical properties of the synthesized solid solutions are discussed in this communication.

2. Results & discussion

2.1 Phase characterization—XRD analysis

The XRD pattern of the $Li_3M_xV_{2-x}(PO_4)_3/C$ (M=Fe, Co) compounds (Fig. 1 and 2) can be indexed to a monoclinic structure with P21/n space group, an indication that the Fe and Co dopants are incorporated in the V site of the $Li_3V_2(PO_4)_3/C$ compound. Formation of single phase $Li_3Fe_xV_{2-x}(PO_4)_3/C$ without any undesirable impurities has been noticed upto $x = 0.10$ (Fig. 1b), especially when synthesized at 950 °C. In other
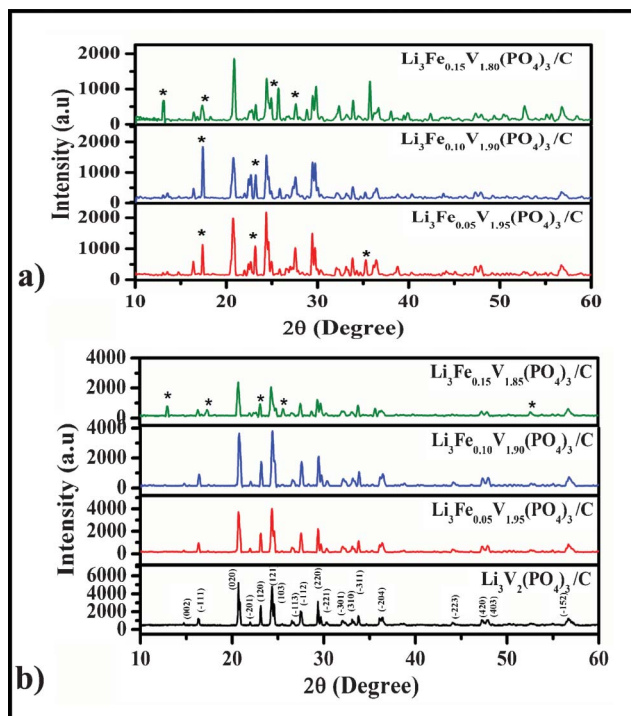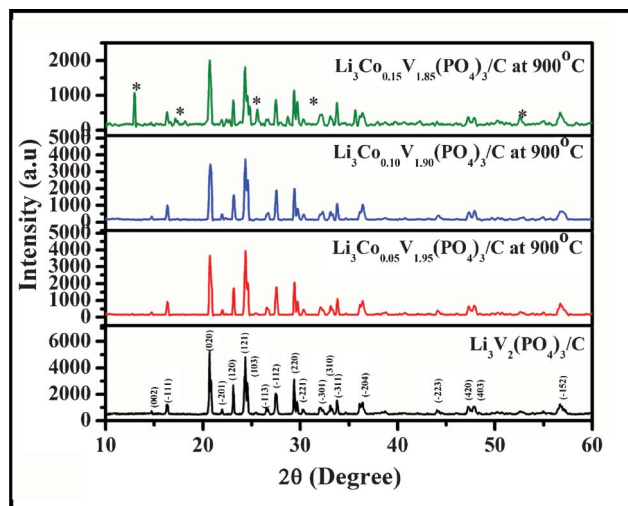
Fig. 2 XRD pattern of $Li_3Co_xV_{2-x}(PO_4)_3/C$ ($x = 0.00, 0.05, 0.10, 0.15$) synthesized at 900 °C.

words, impurities that are found to co-exist with $Li_3Fe_xV_{2-x}(PO_4)_3/C$ ($x = 0.05, 0.10$) compounds at a temperature of 900 °C (Fig. 1a) are eliminated completely, when the same are synthesized at 950 °C (Fig. 1b). More interestingly, the solubility limit of $Li_3Fe_xV_{2-x}(PO_4)_3/C$ has been extended from $x = 0.05$ to $x = 0.10$, which is noteworthy. Because, the maximum solubility limit of $Li_3Fe_xV_{2-x}(PO_4)_3/C$ series is reported as $x = 0.05$[11] only. Therefore, the extended solubility limit observed in the present study could be attributed to the advantageous effect of the currently explored ODHAC synthesis in forming phase pure $Li_3Fe_xV_{2-x}(PO_4)_3/C$ solid solutions with optimized reaction parameters.

Phase pure $Li_3Co_xV_{2-x}(PO_4)_3/C$ ($x = 0.05, 0.10$) have been synthesized at 900 °C (Fig. 2), wherein the observed solubility limit of $x = 0.10$ is in agreement with the reported results.[14] Quite similar to $Li_3Fe_xV_{2-x}(PO_4)_3/C$ compounds, attempts made to synthesize $Li_3Co_xV_{2-x}(PO_4)_3/C$ with $x = 0.15$ resulted in the formation of desired $Li_3Co_xV_{2-x}(PO_4)_3/C$ compound with co-existing impurity phases. Hence, a maximum solubility limit of $x = 0.10$ has been achieved with respect to Fe and Co dopants in a $Li_3M_xV_{2-x}(PO_4)_3/C$ (M=Fe, Co) series of solid solutions when the ODHAC method is followed. No significant change in lattice parameter values has been noticed either with the incorporation or with the increasing concentration of the Co/Fe dopant, which may be corroborated with the similarity in the ionic radii of Co^{3+} and Fe^{3+} ions with that of V^{3+} ions.[21] Though the synthesis approach involves the addition of a calculated amount of 5 wt.% super P carbon, the total carbon content of the synthesized compounds is found to be 11%, thus substantiating the fact that ODH also acts as a carbon source, as well as a combustible fuel.

2.2 TEM analysis

The presence of spherically distributed nanocrystalline particle (SEM) of $Li_3M_xV_{2-x}(PO_4)_3/C$ (M=Fe, Co) solid solutions interconnected with each other effectively through carbon wiring (TEM) is evident from the recorded microscopic images (Fig. 3 and 4). Such formation of a carbonaceous network will effectively impede the growth of particles at high calcination
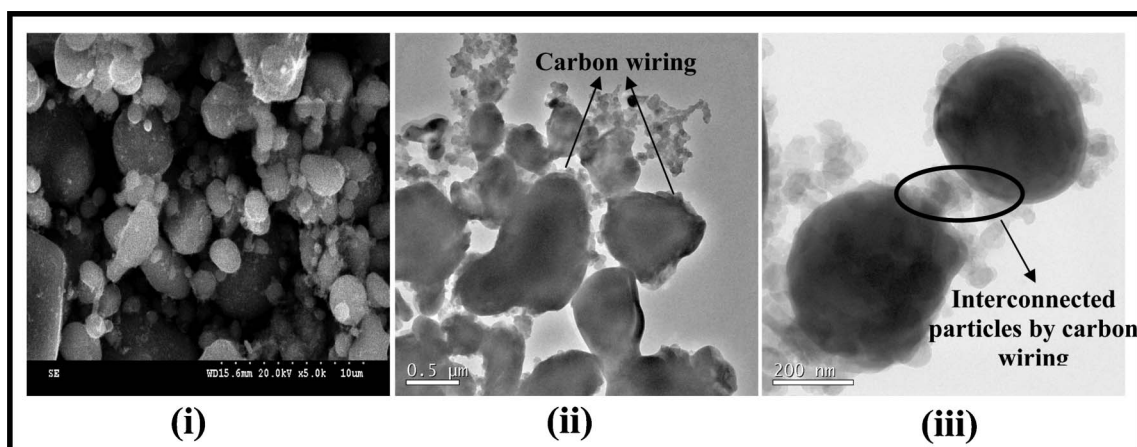

Fig. 1 XRD pattern of a) $Li_3Fe_xV_{2-x}(PO_4)_3/C$ ($x = 0.05, 0.10, 0.15$) synthesized at 900 °C (b) $Li_3Fe_xV_{2-x}(PO_4)_3/C$ ($x = 0.00, 0.05, 0.10, 0.15$) synthesized at 950 °C.

Fig. 3 (i) SEM and (ii), (iii) TEM images of $Li_3Fe_{0.05}V_{1.95}(PO_4)_3$/C synthesized at 950 °C.
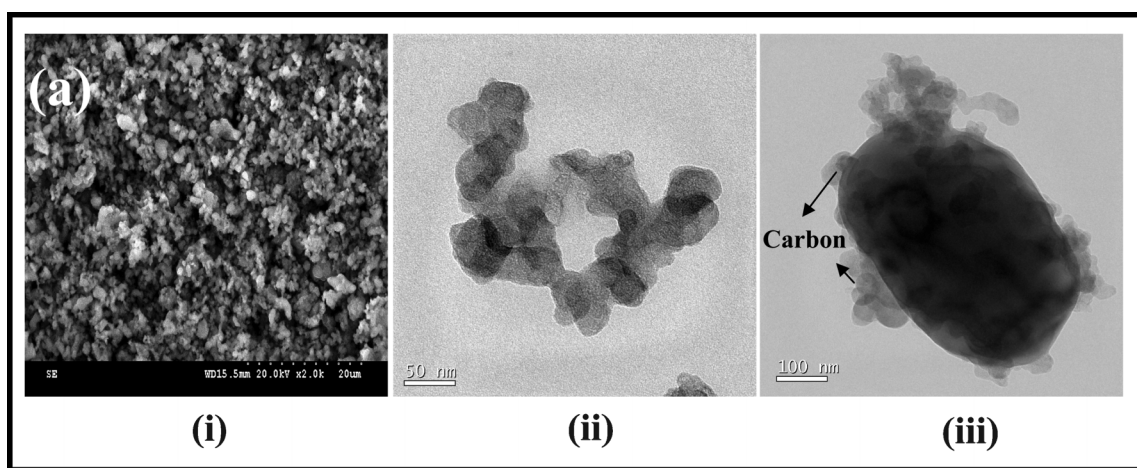
Fig. 4 (i) SEM and (ii), (iii) TEM images of $Li_3Co_{0.10}V_{1.90}(PO_4)_3$/C synthesized at 900 °C.

temperature and hence the formation of nanocrystalline particles of the order of 100–200 nm has been obtained from ODHAC synthesis (Fig. 3(ii), (iii) and 4 (ii), (iii)). Herein, the synergistic effect of ODH fuel and super P carbon is believed to be responsible for the formation of ultrafine powders of $Li_3M_xV_{2-x}(PO_4)_3$/C (M=Fe, Co) with growth controlled particles.

2.3 Charge–discharge studies

The cycleability of ODHAC synthesized $Li_3M_xV_{2-x}(PO_4)_3$/C (M=Fe, Co) cathodes has been appended in Fig. 5 and 6. The corresponding voltage *vs.* capacity behaviour of the $Li_3M_xV_{2-x}(PO_4)_3$/C (M=Fe, Co) cathodes is furnished as insets of Fig. 5a and 6a respectively. It is evident from Fig. 5a that the $Li_3Fe_{0.05}V_{1.95}(PO_4)_3$/C cathode exhibited appreciable capacity values of 174 and 167 mAh g^{-1} against the initial (174 mAh g^{-1}) and the 50th cycle (150 mAh g^{-1}) capacity values of the native $Li_3V_2(PO_4)_3$/C cathode, which is quite interesting. Such an improved electrochemical behaviour demonstrated by the $Li_3Fe_xV_{2-x}(PO_4)_3$/C cathode with $x = 0.05$ is superior to the electrochemical behaviour reported by Ren *et al.*[11] for $Li_3Fe_xV_{2-x}(PO_4)_3$/C with an inferior solubility limit of $x = 0.02$–0.04. Herein, the electrochemical inactivity of the $Fe^{3+/4+}$

and $Fe^{4+/5+}$ redox couples[22] originated a pillaring effect of the Fe dopant and has improved the electrochemical performance by way of increasing the structural stability.

On the other hand, $Li_3Fe_xV_{2-x}(PO_4)_3$/C cathodes with $x = 0.10$ and $x = 0.15$ are found to suffer from unacceptable capacity fade problems, compared to that of a pristine $Li_3V_2(PO_4)_3$/C cathode. From this, the role of concentration of dopant and the need to choose an optimized concentration of dopant in improving the electrochemical behavior of $Li_3Fe_xV_{2-x}(PO_4)_3$/C cathodes are understood. In other words, despite the extended solubility limit ($x = 0.10$) realized with the currently adopted ODHAC method, the electrochemical studies recommend only the $Li_3Fe_{0.05}V_{1.95}(PO_4)_3$/C cathode for practical applications. Based on the same, the effect of ODHAC synthesis in extending the solubility limit of $Li_3Fe_xV_{2-x}(PO_4)_3$/C solid solutions and the requirement of a synergistic effect of synthesis method and optimised dopant concentration to improve the electrochemical behaviour of solid solution cathodes are substantiated.

The rate capability behaviour of native $Li_3V_2(PO_4)_3$/C, $Li_3Fe_{0.05}V_{1.95}(PO_4)_3$/C and $Li_3Fe_{0.10}V_{1.90}(PO_4)_3$/C cathodes has been studied as a function of different discharge rates *viz.*, C/10, C/5, C/2, C, 2C, 3C, 5C, and 10C upon continuously progressing cycles and the performance of each cathode is displayed in
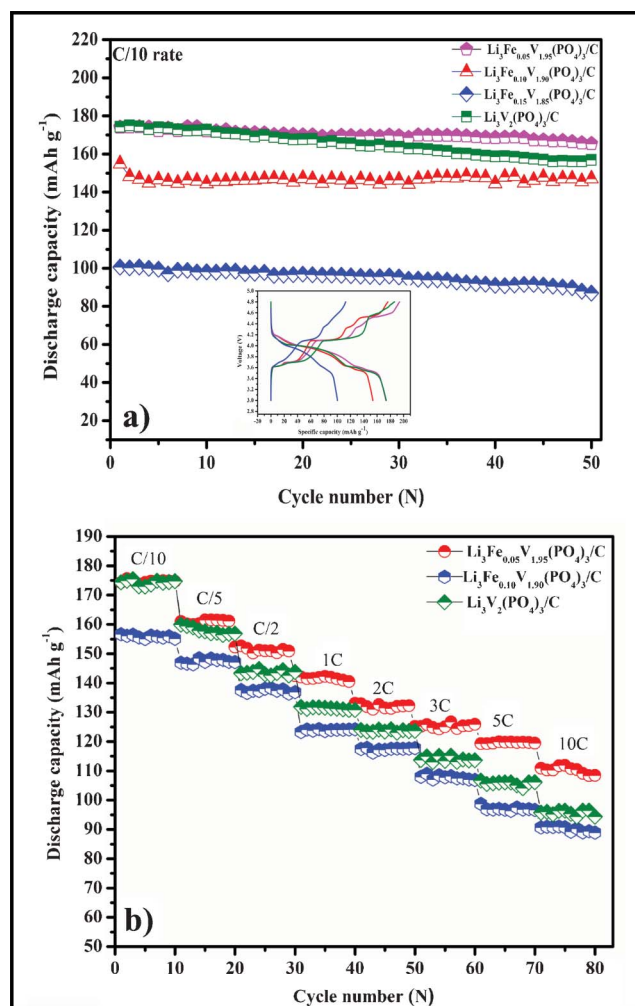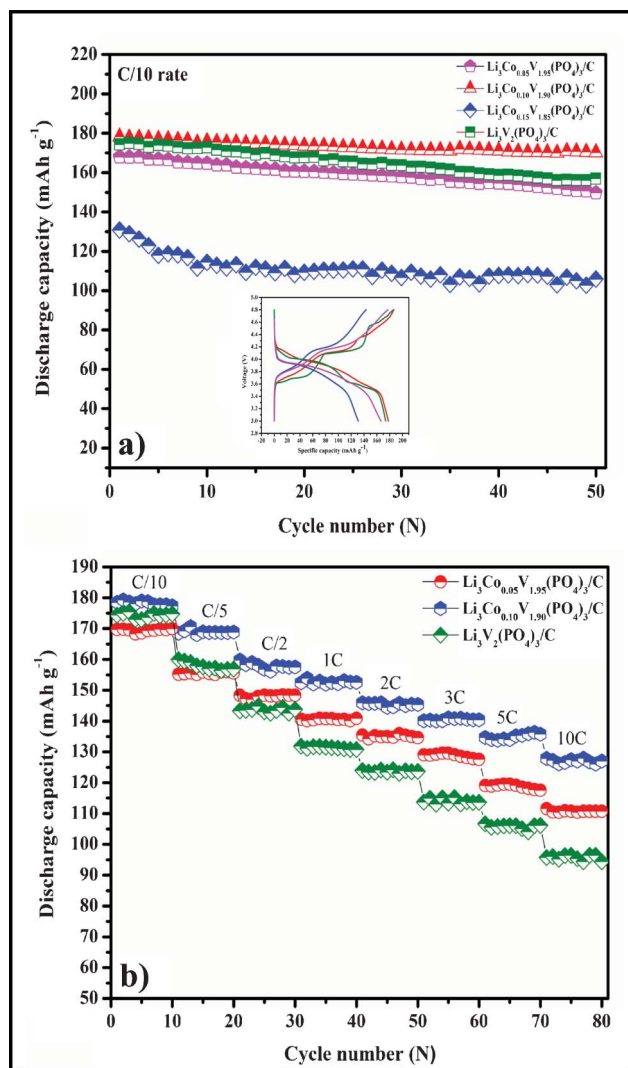
Fig. 5 a) Cycling behavior of Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C and Li$_3$V$_2$(PO$_4$)$_3$/C cathodes at C/10 rates. Inset: voltage *vs.* capacity behavior of Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C cathodes b) comparison of rate capability behavior of Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C and Li$_3$V$_2$(PO$_4$)$_3$/C cathodes.

Fig. 5b. Appreciable specific capacity values of 141 mAh g^{-1} (1C), 119 mAh g^{-1} (5C) and 110 mAh g^{-1} (10C) have been exhibited by Li$_3$Fe$_{0.05}$V$_{1.95}$(PO$_4$)$_3$/C against 131, 105, and 95 mAh g^{-1} exhibited by the Li$_3$V$_2$(PO$_4$)$_3$/C cathode under similar conditions of 1C, 5C and 10C rates respectively. On the other hand, reduced capacity values of 125 (1C), 95 (5C) and 88 mAh g^{-1} (10C) have been observed for the Li$_3$Fe$_{0.10}$V$_{1.90}$(PO$_4$)$_3$/C cathode, thus substantiating the inevitable role of dopant concentration in improving the electrochemical behaviour of solid solution cathodes. Hence, a dopant concentration of $x = 0.05$ has been marked as the optimum concentration of Fe dopant in Li$_3$Fe$_x$V$_{2-x}$(PO$_4$)$_3$/C solid solutions and the synergistic effect of ODHAC synthesis and the optimized concentration of Fe dopant in the Li$_3$Fe$_{0.05}$V$_{1.95}$(PO$_4$)$_3$/C cathode is thought to be responsible for the improved electrochemical properties of the same in comparison with Li$_3$V$_2$(PO$_4$)$_3$/C and Li$_3$Fe$_{0.05}$V$_{1.95}$(PO$_4$)$_3$/C cathodes.

On the other hand, an enhanced initial capacity of 178 mAh g^{-1} has been exhibited by the Li$_3$Co$_{0.10}$V$_{1.90}$(PO$_4$)$_3$/C cathode against the reported capacity of 160 mAh g^{-1},[14] which upon progressive cycling has produced 168 mAh g^{-1} of capacity with the lowest (4%) capacity fade behaviour (Fig. 6a). Such an initial capacity of

178 mAh g^{-1} is superior than 156 mAh g^{-1} of capacity exhibited by the corresponding Li$_3$Co$_{0.05}$V$_{1.95}$(PO$_4$)$_3$/C solid solution cathode. Hence, the optimum concentration of Co dopant in Li$_3$Co$_x$V$_{1-x}$(PO$_4$)$_3$/C is found to be $x = 0.10$, wherein the synergistic effect of ODHAC synthesis approaches and the optimized concentration of Co dopant has played a vital role in improving the capacity to the extent of 178 mAh g^{-1} and reducing the capacity fade from 11% (Li$_3$V$_2$(PO$_4$)$_3$/C) to 4%. It is quite interesting to note that the Li$_3$Co$_{0.10}$V$_{1.90}$(PO$_4$)$_3$/C cathode of the present study has exhibited not only the highest initial and progressive capacity values (169 mAh g^{-1} after 50 cycles), but also has significant reduced the capacity fading to the extent of 4% (Fig. 6a) against 11 and 6% observed for Li$_3$V$_2$(PO$_4$)$_3$/C and Li$_3$Fe$_{0.05}$V$_{1.95}$(PO$_4$)$_3$/C cathodes (Fig. 5a) respectively. Based on the same, the Li$_3$Co$_{0.10}$V$_{1.90}$(PO$_4$)$_3$/C cathode is recommended as the better performing solid solution cathode compared to Li$_3$M$_x$V$_{2-x}$(PO$_4$)$_3$/C (M=Fe, Co and $x = 0.00, 0.05, 0.10$) series of cathodes. From the study, it is derived that the electrochemi-

Fig. 6 a) Cycling behavior of Li$_3$Co$_x$V$_{2-x}$(PO$_4$)$_3$/C and Li$_3$V$_2$(PO$_4$)$_3$/C cathodes at C/10 rates. Inset: voltage *vs.* capacity behavior of Li$_3$Co$_x$V$_{2-x}$(PO$_4$)$_3$/C cathodes b) comparison of rate capability behavior of Li$_3$Co$_x$V$_{2-x}$(PO$_4$)$_3$/C and Li$_3$V$_2$(PO$_4$)$_3$/C cathodes.

cally active $Co^{3+/4+}$ redox pair, by virtue of appearing at the 4.8 V region enhances the structural and cycling stability of the native $Li_3V_2(PO_4)_3$/C cathode.[14]

The rate capability behaviour of $Li_3Co_xV_{2-x}(PO_4)_3$/C (x = 0.00, 0.05, 0.10) cathodes has been depicted in Fig. 6b. Among the two solid solutions chosen for the study, $Li_3Co_{0.10}V_{1.90}$ $(PO_4)_3$/C cathode exhibits higher capacity values such as 159 mAh g^{-1} (1C), 135 mAh g^{-1} (5C) and 128 mAh g^{-1} (10C rate) compared to145 mAh g^{-1}(1C), 120 mAh g^{-1}(5C) and 115 mAh g^{-1} (10C rate) of $Li_3Co_{0.05}V_{1.95}(PO_4)_3$/C cathode. As discussed earlier, due to the synergistic effect of ODHAC synthesized method and the optimum concentration of Co dopant (x = 0.10), $Li_3Co_{0.10}V_{1.90}(PO_4)_3$/C has exhibited better rate capability behaviour also. An overall comparison of electrochemical behaviour favours the $Li_3Co_{0.10}V_{1.90}(PO_4)_3$/C cathode over the $Li_3Co_{0.05}V_{1.95}(PO_4)_3$/C and other Fe/Co based solid solution cathodes within the solubility limit.

3. Conclusion

ODHAC, a new synthesis approach has been adopted to prepare $Li_3M_xV_{2-x}(PO_4)_3$/C (M=Fe, Co) category solid solutions, wherein ODH acts as a combustible fuel and a carbon source. The combined effect of residual carbon resulting from ODH and the added super P carbon has resulted in the formation of carbon wiring, desirable to reduce the particle size and to improve the electrochemical behaviour. The optimum concentration of dopant required to improve the electrochemical performance is found to vary as a function of the type of metal, such as x = 0.05 for Fe and x = 0.10 for Co, irrespective of the extended solubility limit realized with the synthesis approach. An enhanced specific capacity of 174 and 178 mAh g^{-1} has been exhibited by $Li_3Fe_{0.05}V_{1.95}(PO_4)_3$/C and $Li_3Co_{0.10}V_{1.90}(PO_4)_3$/C cathodes (C/10 rate) along with better rate capability behaviour up to 10C rate compared to the native $Li_3V_2(PO_4)_3$/C cathode. An extended solubility limit of x = 0.10 for Fe dopant has been achieved by adopting the ODHAC method and superior electrochemical properties of the $Li_3Co_{0.10}V_{1.90}(PO_4)_3$/C cathode along with a negligible capacity fade (4%) has been observed due to the synergistic effect of the ODHAC method and the deployment of the optimum concentration of metal (Co) substituent.

4. Experimental

4.1 Synthesis of $Li_3M_xV_{2-x}(PO_4)_3$/C

$Li_3M_xV_{2-x}(PO_4)_3$/C (M=Fe, Co) (x = 0.05, 0.10, 0.15) samples were prepared by combustion method using oxalic dihyrazide (ODH) as fuel with the combination of precursors, $viz.$, $LiNO_3$ (Alfa Aesar), V_2O_5 (Alfa Aesar), $NH_4H_2PO_4$ (Merck) and Co_3O_4 (Alfa Aesar) or $Fe(NO_3)_3$ (Alfa Aesar). Primarily, the select reactants were added one by one to distilled water with magnetic stirring and heated at 80 °C to get a homogeneous solution. ODH was added to the hot solution and to the clear solution, 5wt.% super P carbon has been added. The process of stirring and heating was continued to get a thick mass. The mass was initially dried in hot air oven at 120 °C for one night and heated to 350 °C for 4 h in a furnace at a heating rate of 5 °C min^{-1} using Ar : H_2 (90 : 10) gas mixture. Further, the powder was heated to 900 °C for 8 h with an intermittent grinding to obtain $Li_3Co_xV_{2-x}(PO_4)_3$/C compound. The procedure was repeated to synthesize $Li_3Fe_xV_{2-x}(PO_4)_3$/C at 950 °C.

4.2 Physical and electrochemical characterization

Phase characterization was done by powder X-ray diffraction technique on a PANalytical X′pert PRO X-ray diffractometer using Ni-filtered Cu–Kα radiation (λ = 1.5406 Å). The total carbon content of the as prepared $Li_3M_xV_{2-x}(PO_4)_3$/C compounds has been calculated based on the reported procedure.[23] SEM images were captured with Jeol S-3000 H scanning electron microscope and TEM was recorded with JEOL 2010F TEM operating at 200 keV. Charge–discharge studies were carried out using ARBIN charge–discharge cycle life tester. Details pertinent to electrode preparation and coin cell fabrication are reported elsewhere.[24]

References

1 A. K. Padhi, K. S. Najundaswamy and J. B. Goodenough, *J. Electrochem. Soc.*, 1997, **144**, 188.
2 F. Zhou, K. Kang, T. Maxisch, G. Ceder and D. Morgan, *Solid State Commun.*, 2004, **132**, 181.
3 J. Xu, G. Chen, Y. J. Teng and B. Zhang, *Solid State Commun.*, 2008, **147**, 414.
4 Y. Z. Li, X. Liu and J. Yan, *Electrochim. Acta*, 2007, **53**, 473.
5 J. Barker, M. Y. Saidi, R. K. B. Gover, P. Burns and A. Bryan, *J. Power Sources*, 2007, **174**, 927.
6 X. C. Zhou, Y. M. Liu and Y. L. Guo, *Solid State Commun.*, 2008, **146**, 261.
7 Gangulibabu, N. Kalaiselvi, D. Bhuvaneswari and C. H. Doh, *Int. J. Electrochem. Sci.*, 2010, **5**, 1597.
8 Q. Kuang, Y. M. Zhao, X. N. An, J. M. Liu, Y. Z. Dong and L. Chen, *Electrochim. Acta*, 2010, **55**, 1575.
9 C. S. Dai, Z. Y. Chen, H. Z. Jin and X. G. Hu, *J. Power Sources*, 2010, **195**, 5775.
10 J. S. Huang, L. Yang, K. Y. Liu and Y. F. Tang, *J. Power Sources*, 2010, **195**, 5013.
11 M. M. Ren, Z. Zhou, Y. Z. Li, X. P. Gao and J. Yan, *J. Power Sources*, 2006, **162**, 1357.
12 J. Barker, R. K. B. Gover, P. Burns and A. Bryan, *J. Electrochem. Soc.*, 2007, **154**, A307.
13 Y. H. Chen, Y. M. Zhao, X. N. An, J. M. Liu, Y. Z. Dong and L. Chen, *Electrochim. Acta*, 2009, **54**, 5844.
14 Q. Kuang, Y. M. Zhao, X. N. An, J. M. Liu, Y. Z. Dong and L. Chen, *Electrochim. Acta*, 2010, **55**, 1575.
15 M. Sato, H. Ohkawa, K. Yoshida, M. Saito, K. Uematsu and K. Toda, *Solid State Ionics*, 2000, **135**, 137.
16 S. Q. Liu, S. C. Li, K. L. Huang and Z. H. Chen, *Acta Phys.-Chim. Sin.*, 2007, **23**, 537.
17 Y. Xia, W. Zhang, H. Huang, Y. Gan, C. Li and X. Tao, *Mater. Sci. Eng., B*, 2011, **176**, 633.
18 S. K Zhong, L. Liu, J. Jiang, Y. Li, J. Wang, J. Liu and Y. Li, *J. Rare Earths*, 2009, **27**, 134.
19 N. Kalaiselvi and A. Manthiram, *J. Power Sources*, 2010, **195**, 2894.
20 N. Jayaprakash, N. Kalaiselvi and Y. K. Sun, *Electrochem. Commun.*, 2008, **10**, 455.
21 Y. Chen, Y. Zhao, X. An, J. Liu, Y. Dong and L. Chen, *Electrochim. Acta*, 2009, **54**, 5844.
22 D. Morgan, G. Ceder, M. Y. Saidi, J. Barker, J. Swoyer, H. Huang and G. Adamson, *Chem. Mater.*, 2002, **14**, 4684.
23 P. Fu, Y. Zhao, Y. Dong, X. An and G. Shen, *J. Power Sources*, 2006, **162**, 651.
24 D. Bhuvaneswari, Gangulibabu, N. Kalaiselvi, N. Jayaprakash and P. Periasamy, *J. Sol-Gel Sci. Technol.*, 2009, **49**, 137.