

Available online at www.sciencedirect.com



C electrochemistry communications

Electrochemistry Communications 9 (2007) 620-628

www.elsevier.com/locate/elecom

On the electrochemical behavior of $\text{LiM}_X\text{Fe}_{1-X}\text{PO}_4$ [M = Cu, Sn; X = 0.02] anodes – An approach to enhance the anode performance of LiFePO₄ material

N. Jayaprakash, N. Kalaiselvi *

Central Electrochemical Research Institute, Karaikudi, India

Received 10 October 2006; received in revised form 19 October 2006; accepted 19 October 2006 Available online 27 November 2006

Abstract

An attempt, for the first time, has been made to explore the possible electrochemical activity of partially substituted LiFePO₄ as negative electrode for lithium battery applications. In this regard, cationic substitution of Cu and Sn to the native LiFePO₄/C electroactive material has been made individually via. ball milling treatment. This simple procedure has resulted in the formation of metal substituted LiFePO₄ powders of phase pure nature and finer crystallite size ($<1 \mu$ m) with better distribution of particles. Herein, 2% of metals such as Cu (transition) and Sn (non-transition) were chosen as dopants with a view to understand the effect of transition and non-transition metals upon LiFePO₄ individually. It is interesting to note that irrespective of the nature of the dopant metal, the simple route of cationic substitution via. ball milling endowed with improved conductivity of LiFePO₄, as evidenced by the augmented reversible specific capacity values of substituted LiFePO₄ anodes. In other words, the LiCu_{0.02}Fe_{0.98}PO₄/C anode delivered a reversible capacity of ~380 mAh/g with an enhancement in the capacity retention behavior and excellent coulumbic efficiency value compared to that of LiFePO₄. In contrast, LiSn_{0.02}Fe_{0.98}PO₄/C anode displayed an appreciable reversible capacity of ~400 mAh/g with a significant steady discharge profile. Results of Fourier Transform Infra Red (FTIR) spectroscopy and Cyclic Voltammetric studies of LiM_xFe_{1-x}PO₄ (M = Cu, Sn)/C composites are also appended and correlated suitably.

© 2006 Elsevier B.V. All rights reserved.

Keywords: LiFePO4 anodes; Cationic substitution; Synthesis; Coulumbic Efficiency

1. Introduction

Over the past few years, phosphate based olivine compounds have created substantial interest as battery active material for rechargeable Li-ion batteries. Among the phospho-olivines of composition LiMPO₄ (M = Fe, Mn, Co and Ni) [1–3] that belong to the general class of polyanionic compounds, LiFePO₄ has gained paramount importance due to the easy availability of iron resources, eco benign nature and economically viable preparation methods. LiFePO₄, with a theoretical capacity of 170 mAh/g, possesses very good electrochemical stability (even when it is used with common organic electrolyte systems) [2–7], structural stability due to the strong covalent bonding of oxygen with P^{5+} to form the $(PO_4)^{3-}$ tetrahedral polyanion [1], and better thermal stability [8]. It is quite unfortunate that despite the mentioned advantages, certain critical and hampering issues such as poor rate capability and electrical conductivity [8] associated with the material makes it difficult to exploit the entire capacity made available for rechargeable Li-ion battery applications.

Basically, investigations to improve the local cation structure and environment of the material for conductivity enhancement and to have better understanding of the electro active LiFePO₄ material [6,9,10] are well documented

^{*} Corresponding author. Tel.: +91 4565 227550 559 [10 lines]; fax: +91 4565 227779.

E-mail addresses: prakash_rdy@yahoo.co.in (N. Jayaprakash), kala-kanth2@yahoo.com (N. Kalaiselvi).

^{1388-2481/\$ -} see front matter @ 2006 Elsevier B.V. All rights reserved. doi:10.1016/j.elecom.2006.10.040

in terms of Mossbauer spectroscopy [6,9], XAFS [10], magic angle spinning nuclear magnetic resonance techniques [11]. FTIR and Raman studies [12] of native LiFePO₄. On the other hand, efforts to improve the conductivity of LiFePO₄ by surface modification [13,14] or by acting on the phase composition through cationic substitution [15] are also reported. Among the two methods of improving conductivity, the former has led to the formation of composite electrodes by the addition of conducting carbon [6], sucrose [13] etc., that has exhibited capacity values closer to 170 mAh/g and with high rate capability [16]. However, addition of more amount of conductive carbon would result in the decreased volumetric energy density and tap density to an unacceptable level that may disqualify LiFePO₄ for battery applications [17]. Therefore, it is necessary indeed to gain a complete understanding of effect of various parameters upon the performance of LiFePO₄. Literature is replete with the finding that factors such as phase purity of the active material [6], particle size [6], amount of added carbon [17], form/type of carbon added [18] and also the structure of the surface carbon [19], play significant roles independently in determining the electrochemical performance of the battery, wherein the said factors are mainly synthetic route dependent.

The alternate method to enhance the electrochemical behavior of LiFePO₄ cathodes [20] via. cationic substitution has been reported whereas no such doped derivative of LiFePO₄/C composite has been investigated for possible anode characteristics till date. Hence, exploring the possibility of enhancing the electrochemical behavior of LiFePO₄ anodes via. introduction of suitable dopants is an entirely newer approach and the same is the highlight of the present study.

It is quite interesting that Yamada et al., have recently demonstrated the possibility of realizing >95% of the theoretical capacity of LiFePO₄ by sintering the precursor materials at an optimum temperature, say 550 °C, for the production of smaller particles with larger surface area available for the intercalation of Li-ions [6]. This in turn has directed a newer pathway of deployment of suitable synthesis method with optimized synthesis conditions to modify both the physical as well as electrochemical characteristics of LiFePO₄ material. Therefore, it is quite obvious that not only the approach being adopted to improve the overall performance of LiFePO₄ electrode material gains importance, but also the selection and deployment of suitable synthesis methodology. Because, variety of synthesis methods that include mixing of precursor salt with a carbon gel, addition of sugar as carbon source [17], deployment of sol-gel [21], co-precipitation [22], emulsion drying [23], and microwave assisted synthesis methods [24] and the dispersal of carbon powders via. aqueous gelatin [18] are reported to have favorable impact over LiFePO₄ material.

Recently, our group has reported on the possible anode characteristics of native LiFePO₄ with a reversible capacity of ~300 mAh/g for lithium battery applications [25]. As a sequel to that work, the present study has been designed mainly to examine the anode characteristics of partially substituted LiFePO₄/C composite electrode material and towards this attempt, a transition (Cu) and a non-transition (Sn) metal have been chosen as dopant to be incorporated into the native LiFePO₄ matrix individually. Hence, a set of two compounds viz., LiCu_{0.02}Fe_{0.98}PO₄/C and LiSn_{0.02}Fe_{0.98}PO₄/C composite anodes have been synthesized and characterized for the present study. Correlation of enhanced specific capacity values as a function of both cation substitution and the chosen category synthesis methodology is also reported.

2. Experimental

2.1. Synthesis procedure

Stochiometric amount of Li₂CO₃, Fe₂(C₂O₄)₃ · 6H₂O, (NH₄)₂HPO₄ and Cu(CH₃COO)₃ or SnCl₂(for substituted LiFePO₄) were mixed thoroughly along with 10 wt% carbon and the mixture was ball milled for about 12 h. to ensure intimate and homogeneous mixing. The added carbon is expected to form an uniform surface coating over the reactant mixture which may prevent the formation of unacceptable impurities, developed along with the required LiFePO₄ product at the final step. The ball milled fine powders of the precursor mixture was subjected initially to a lower calcination temperature of 450 °C for 6 h and subsequently to 750 °C for 3 h (rate of heating: 5 °C per min) with the deployment of periodical and intermittent grinding after every 3 h duration. The ultra fine powders obtained after the high temperature calcination of 750 °C was collected from furnace and subjected further to systematic characterization studies.

2.2. Structural and morphological characterization

Phase characterization was done by powder X-ray diffraction technique on a Philips 1830 X-ray diffractometer using Ni filtered Cu K α radiation ($\lambda = 1.5406$ Å) in the 2θ range of 15–60 at a scan rate of 0.04°/s. Surface morphology of the particles was examined through SEM images obtained from Jeol S-3000 H scanning electron microscope. Fourier Transform Infra Red spectroscopic study was performed on a Perkin–Elmer paragon-500 FTIR spectrophotometer using KBr pellets in the region of 400–1600 cm⁻¹. Electrochemical studies such as cyclic voltammetry and charge–discharge studies were carried out using Auto lab electrochemical analyzer and MAC-COR charge–discharge cycle life tester.

2.3. Electrochemical characterization

The anode electrode was prepared and used as described elsewhere [25].

3. Results and discussion

3.1. Structural results – PXRD studies

The XRD pattern of $LiM_XFe_{1-X}PO_4/C$ [M = Cu, Sn]/ C composites synthesized via. mechanical ball milling method is shown in Fig. 1a-b. The Bragg peak pattern of native LiFePO₄ is given as an inset for comparison. The existence of sharp and well-defined Bragg peaks ensures the presence of phase pure crystalline products. Despite the fact that carbon has been added to improve the conductivity, no peak due to carbon is visible in the PXRD pattern of resultant $LiM_{x}Fe_{1-x}PO_{4}/C$ composite material (Fig. 1a-b), which is an indication for the presence of carbon in a disordered or amorphous state [26]. Similarly, irrespective of the nature of the metal dopant (Cu/Sn), there exists a striking similarity in the PXRD pattern of the partially substituted LiFePO₄/C composites synthesized through the present study. In other words, both the Cu and Sn doped LiFePO₄/C composites have exhibited standard orthorhombic olivine type LiFePO4structure with *Pnma* space group (a = 10.35, b = 6.028 and c = 4.703). The miller indices (hkl) of the peaks of doped LiM_X- $Fe_{1-x}PO_4$ powders are also indexed in the XRD pattern of the samples (Fig. 1a-b). The deployment of optimum synthesis temperature (750 °C) with an intermittent grinding has resulted in the formation of phase pure product without any undesirable peaks due to lithium ortho phosphate (Li₃PO₄). Similarly, the peak due to Fe (II, III) pyrophosphate that co-exist normally when the sintering

temperature is raised above 700 °C has been eliminated in the present study, as reported elsewhere [25]. Besides, the presence of sharp peaks with definite boundary authenticates the positive impact of sintering temperature over enhanced crystallinity of the synthesized material in the preferred range. Similarly, all the peaks of doped LiFePO₄/C composite powders were indexed against standard JCPDS pattern (No: 83 2092) and the existence of 101 (Fig. 2a) plane ($2\theta = 27.7^{\circ}$) and 202 & 133 (Fig. 2b) planes ($2\theta = 44.7^{\circ}$ and 45.2°) may be attributed respectively to the presence of Cu and Sn, irrespective of the individual concentration (2%) of the dopants.

The average grain size (*D*) calculated using Scherrer's formula (1) was found to remain around 800 nm and 1 μ m, which was further confirmed by the scanning electron micrograph images, obtained for the LiM_xFe_{1-x}PO₄ samples.

$$D = 0.9\lambda/\beta\cos\theta \tag{1}$$

where $\lambda = X$ -ray wavelength (Å); $\theta = B$ ragg angle (in radians); $\beta = FWHM$ (in radians, values corrected for instrumental line broadening) and the calculated *D* values are furnished in Table 1.

As it is well known that Scherrer's calculation does not take into consideration of lattice strain, it has been decided to calculate the Stoke's strain independently, with a view to understand the effect of crystallite size and lattice strain on the synthesized powders individually. Because, it is also reported that apart from the finite crystallite size, peak broadening may be correlated to instrumental effects and



Fig. 1. XRD pattern of (a) LiCu_{0.02}Fe_{0.98}PO₄ and (b) LiSn_{0.02}Fe_{0.98}PO₄ (shown inset is the XRD pattern of native LiFePO₄ [25]).



Fig. 2. Scanning electron micrographs of (a) $LiCu_{0.02}Fe_{0.98}PO_4$ and (b) $LiSn_{0.02}Fe_{0.98}PO_4$ (shown inset is the SEM image of native $LiFePO_4$ [25]).

atomic deformation from ideal position in a non uniform manner which is usually called as the strain that becomes extended defects [27] in certain cases. However, in the present study, it is understood that the peak broadening is due to the finite crystallite size only (Table 1) and not due to the instrumental effect or strain, based on the smaller Stoke's strain values calculated using the following formula:

$\varepsilon_{\text{Strain}} = \beta/4 \tan \theta$

where $\varepsilon_{\text{Strain}}$ = weighted average strain and β = the integral breadth of a reflection (in radians 2 θ) located at 2 θ . The calculated strain values are found to be very small (1.02 for LiCu_{0.02}Fe_{0.98}PO₄ and 0.96 in case of LiSn_{0.02}. Fe_{0.98}PO₄) and based on the same, it is further substantiated that the Cu and Sn substituted LiFePO₄/C composites have been synthesized with preferred physical properties such as strain free crystal lattice, purity and crystallinity.

| hysical and electro | chemical _f | oarameter | s of LiSı | 1 _{0.02} Fe _{0.98} PO ₄ and I | $ICu_{0.02}Fe_{0.98}PO_4$ | | | | | | | | | |
|--|-----------------------|-----------|-----------|--|---------------------------|----------------------------------|--------------|------------------------------|----------|---------------|----------------|-----------|------------------------------|----------------|
| Compound | Lattice | cons | | Cell vol ($Å^3$) | Crystal size (µm) | Stokes strain (ϵ_{Str}) | Electro | ochemical | perforr | nance | | | | |
| | a Å | b Å | cÅ | | | | $Q_{ m d} l$ | \mathcal{Q}_{c} 1 | η^1 | $Q_{ m d} 15$ | $Q_{\rm c}$ 15 | $\eta 15$ | $\mathcal{Q}_{\mathrm{d}}30$ | $Q_{\rm c} 30$ |
| iCu _{0.02} Fe _{0.98} PO ₄ | 10.35 | 6.02 | 4.70 | 293.4 | 1.10 | 1.02 | 527 | 402 | 92 | 389 | 387 | 66 | 380 | 379 |
| iSnon-Fenar PO4 | 10.35 | 6.02 | 4.70 | 293.4 | 0.93 | 1.23 | 795 | 529 | 99 | 422 | 415 | 92 | 396 | 380 |

Table 1

– discharge capacity in mAh/g, Q_d – charge capacity in mAh/g and η – % efficiance sas per cycle number

å

 $\frac{\eta 30}{99}$

3.2. Morphological results – SEM analysis

Surface morphology of $\text{LiM}_{x}\text{Fe}_{1-x}\text{PO}_{4}/\text{C}$ [M = Cu, Sn] composites and the nature of the carbon coating have been investigated by scanning electron microscopy. Fig. 2a and b shows the scanning electron micrographs (SEM) of LiCu_{0.02}Fe_{0.98}PO₄/C and LiSn_{0.02}Fe_{0.98}PO₄/C composite powders synthesized from the solid-state technique. Unlike the literature evidence that supports the formation of irregularly shaped larger particles via. solid-state technique [28], the present study has demonstrated the presence of well-defined spherical particles with finer particle size (Fig. 2a-b). Also, it is oblivious that the synthesized doped derivatives of LiFePO₄/C composites have encountered the absence of particle agglomeration, which is a preferred property of any electrode material to exhibit better electrochemical property [29]. In general, sintering the precursor above 700 °C makes the particles to fuse together partially to form large porous agglomerates [28] regardless of the method of grinding/grinding time after the decomposition step. However, neither an increased particle size nor particle agglomeration was found to be present with the set of chosen category $\text{LiM}_X\text{Fe}_{1-X}\text{PO}_4/\text{C}$ materials. Further, micrographs obtained for both the metal substituted LiFePO₄/C powders show similarity in grain structure with an average grain size of $\sim 1 \mu m$, which agrees with the average crystallite size calculation deduced from XRD, using Scherer's formula.

3.3. Local cation environment – FTIR study

Generally, vibrational modes that are attributed to the motion of cations with respect to their oxygen neighbors are sensitive to the point group symmetry of the cations in the oxygen host matrix [30], and hence, the local environment of the cations in a lattice of close-packed oxygens can be studied by FTIR spectroscopy [31]. Consequent to the first major study on the spectra-structure calculations of phosphorus based compounds undertaken by Daasch et al. [32], the spectral correlation of the study was extended by Bellamy et al. [33], apart from the additional correlations that have been made from solid state studies of certain phosphate salts, whose absorption is highly characteristic of the type of anion present [34]. It has already been demonstrated that the resonant frequencies of alkali metal cations in their octahedral interstices (LiO_6) that are present in inorganic oxides are located in the frequency range of 200–400 cm⁻¹ [31,35]. However, it is generally not possible to assign specific IR frequencies to vibrations, which involve a single cation and its oxide neighbors [36] as the resultant vibrations of any transition metal oxide involve contributions from all possible atoms [37]. Because, it is only the differences in mass, charge and covalency of lithium and the transition metal cation that lead to the motion of lithium ions and the respective vibrational spectrum [38]. Besides, it is customary that the middle frequency region of FTIR is mainly considered for the analysis, and hence the present study is restricted to the assignment of various vibrational modes of metal oxide compounds within the frequency range $400-2000 \text{ cm}^{-1}$.

The FTIR signatures for both the native and doped LiFePO₄ materials are displayed in Fig. 3. The tetrahedral PO_4^{3-} ion has its fundamental vibrational frequencies at 1082, 515, and 980 and 363 cm⁻¹ [39], wherein the later pair being normally infrared inactive [40]. Since the orthophosphates show main bands at 1060–1000 cm⁻¹ [41] and



Fig. 3. Room temperature FTIR spectrum of (a) LiFePO₄, (b) LiCu_{0.02}Fe_{0.98}PO₄ and (c) LiSn_{0.02}Fe_{0.98}PO₄.



Fig. 4. Cyclic voltammogram of (a) $LiFePO_4$, (b) $LiCu_{0.02}Fe_{0.98}PO_4$ and (c) $LiSn_{0.02}Fe_{0.98}PO_4$.

at 580–520 cm⁻¹ [42], the FTIR spectra obtained in the present study (Fig. 3) can be correlated with those of the results obtained in the earlier studies on the phosphate based compounds. In addition, the FTIR spectrum of the native LiFePO₄ compound matches well with that of the standard pattern [43], which is the significance of the study.

3.4. Electrochemical characterization results

3.4.1. Cyclic voltammetric studies

Generally, kinetics of lithium intercalation in any composite electrode material can be studied using cyclic voltammograms (CVs) [44] and so CV analysis was performed for the $\text{LiM}_X\text{Fe}_{1-X}\text{PO}_4/\text{C}$ composite anodes at a slow scan rate of 1 mA/s. Fig. 4a–c shows the cyclic voltammograms of the Cu/Sn substituted and native LiFePO₄/C composite electrodes, in the potential range of 3.5–0 V versus Li/Li⁺ in the cathodic direction and back to 3.5 V in the anodic direction. This potential range covers all the irreversible interactions between the host, lithium and the electrolytes and also the lithium interaction reaction into the composite [44]. In addition, this potential range is representative of the process at the anode under the normal battery operating conditions.

It is noteworthy that all the LiFePO₄ electrodes (native and doped) exhibited almost similar voltammograms, with one oxidation and reduction peak. This is an indication that only one redox reaction is proceeding during the insertion and extraction of Li-ions, which is the reported behavior of LiFePO₄ electrode [26]. Basically, the reduction peak for the native LiFePO₄ occurs at a potential of 0.8 V as obvious from Fig. 4a also. In contrast, the reduction peak of LiCu_{0.02}Fe_{0.98}PO₄ occurs at a potential of 0.7 V and that of LiSn_{0.02}Fe_{0.98}PO₄/C at a much more lower potential (0.5 V). However, kinetics of Li intercalation for all the LiFePO₄ samples remains low up to1.5 V, beyond which, a sharp increase in the current is observed. According to Gnanaraj et al. [45], electrolyte decomposition starts at a potential of 1.1 V versus Li/Li⁺ and continuous reduction of the solvent molecules and the formation of the ionically conducting and electronically insulating SEI (solid electrolyte interface) layer occurs around a potential of 0.56 V. Similar shift towards a lower potential region, for the $LiM_{0.02}Fe_{0.98}PO_4/C$ composite is observed in the present study, as for the oxidation peak is concerned. The reason for such a shift may be attributed to the difference in the mechanism of the intercalation-deintercalation reaction and the electrochemical property of such oxide materials essentially depends upon other factors viz. crystallinity, morphology and microstructure [46]. Since the present set of chosen category LiM_{0.02}Fe_{0.98}PO₄/C materials possess good crystallinity (XRD), preferred morphology and microstructure (SEM) and excellent reversibility (CV), it is thus believed that the approach of partial substitution of Cu and Sn individually to LiFePO₄/C matrix via. ball milling has a remarkable role in improving both the physical as well as electrochemical characteristics of native LiFePO₄ compound. The same is further demonstrated through charge-discharge studies.

3.4.2. Charge-discharge studies

The capacity and cycleability behavior of metal substituted LiFePO₄/C composite anodes examined at room temperature under a constant current drain of 0.5 mA and at a potential window of 0–3 V is shown in Fig. 5. The capacity versus cycleability behavior of native LiFePO₄/C composite [25] is given as an inset for comparison of results. A maximum capacity of 527 and 790 mAh/g



Fig. 5. Capacity versus cycle number of LiCu_{0.02}Fe_{0.98}PO₄.



Fig. 6. Capacity versus cycle number of LiSn_{0.02}Fe_{0.98}PO₄ (shown inset is the cycle life behavior of native LiFePO₄ [25]).

has been exhibited by the $\text{LiCu}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ and $\text{LiSn}_{0.02}\text{Fe}_{0.98}\text{PO}_4/\text{C}$ composite anodes, which are almost twice the capacity of the existing LiFePO₄cathodes (170 mAh/g) or LiFePO₄anodes (~300 mAh/g) and carbonaceous anodes (~370 mAh/g) [47]. In addition to the enhanced initial capacity, the composite anodes have demonstrated a better reversible and steady state capacity of ~380 and 400 mAh/g corresponding to LiCu_{0.02}Fe_{0.98}-PO₄/C and LiSn_{0.02}Fe_{0.98}PO₄/C electrodes.

Also, it is noteworthy that the composite anodes illustrated an improved capacity retention behavior (>86%) with excellent coulumbic efficiency values (96-98%), which are greater than the native LiFePO₄/C composite anodes [25], especially upon progressive cycling. As a striking evidence for the possible exploitation of substituted LiFePO₄/ C composite materials as anodes in Li-ion battery, the synthesized doped category LiM_{0.02}Fe_{0.98}PO₄ anode materials showed a nominal first cycle irreversible capacity loss of (~20% and 25%) with respect to $LiCu_{0.02}Fe_{0.98}PO_4/C$ and $LiSn_{0.02}Fe_{0.98}PO_4/C$ composite materials. However, this unavoidable initial and minimal fade in capacity may be attributed to the meager structural variations or loss of contact between the conductive binder [48] and the active material particles resulting from volume variation during lithium extraction [25]. Despite the slight initial capacity fade behavior, both the Cu and Sn doped LiFePO₄/C anodes exhibited high initial discharge capacity (527 and 795 mAh/g) values and progressive steady state reversible capacity values (380 and 400 mAh/g), thus qualify themselves as probable anode candidates for rechargeable Li-ion batteries.

Generally, tin based anodes with larger particle size pulverize rapidly during charge–discharge cycles due to volume mismatch, resulting in a rapid drop in reversible capacity, upon cycling. However, this pulverization would be less extensive with respect to smaller [micron/submicron sized] particles, because the micron-sized cavities within the powder can absorb the expansion of materials during the formation of lithium compounds [49]. On the other hand , it is understood from the present study that size reduced particles of the $LiSn_{0.02}Fe_{0.98}PO_4$ material synthesized through the present study has reduced the extent of pulverization and thereby enhanced the electrochemical behavior of $LiFePO_4$ anodes upon cycling, as a function of incorporation of suitable dopant (Sn) and the methodology adopted Fig. 6.

4. Conclusion

Cationic substitution of native LiFePO₄by a transition (Cu) and a non-transition (Sn) metal was carried out via. ball milling process. Phase pure sub-micron sized particles with strain free crystal lattice obtained were investigated further for possibly enhanced anode performance characteristics against lithium metal. As expected, the effect of cation substitution was found to enhance the electrochemical performance of the native LiFePO₄anode either in terms of increased specific capacity or maintenance of steady-state capacity upon progressive cycling, respectively as a function of Cu and Sn as dopant. In particular, the $LiM_{0.02}Fe_{0.98}PO_4$ anodes when discharged at a constant current drain of 0.5 mA exhibited a specific capacity of 795 mAh/g with Sn and 527 mAh/g with Cu as dopant. In addition to the enhanced initial capacity, the composite anodes have demonstrated a better reversible and steady state capacity of \sim 380 and 400 mAh/g corresponding to $LiCu_{0.02}Fe_{0.98}PO_4/C$ and $LiSn_{0.02}Fe_{0.98}PO_4/C$ electrodes. Hence the reasonably improved electrochemical performance of $LiM_{0.02}Fe_{0.98}PO_4$ (M = Cu, Sn) makes it feasible for consideration in high-power lithium-ion batteries applications.

References

- A.K. Padhi, K.S. Nanjundaswamy, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1188.
- [2] A.K. Padhi, K.S. Nanjundaswamy, C. Masquelier, S. Okada, J.B. Goodenough, J. Electrochem. Soc. 144 (1997) 1609.
- [3] K. Amine, H. Yasuda, M. Yamachi, Electrochem. Solid St. 3 (2000) 178.
- [4] J.J. Papike, M. Camaron, Rev. Geophys. Space Phys. 14 (1976) 37.
- [5] J.-M. Tarascon, M. Armand, Nature (London) 414 (2001) 359.
- [6] A. Yamada, S.C. Chung, K. Hinokuma, J. Electrochem. Soc. 148 (2001) A224.
- [7] A.S. Andersson, J.O. Thomas, B. Kalska, L. Haggstroem, Electrochem. Solid St. 3 (2000) 66.
- [8] Y. Iriyama, M. Yokoyama, C. Yada, S.K. Jeong, I. Yamada, T. Abe, M. Inaba, Z. Ogumi, Electrochem. Solid St. A7 (2004) 340.
- [9] A.S. Anderson, B. Kalska, L. Haggstrom, J.O. Thomas, Solid State Ionics 130 (2000) 41.
- [10] A. Yamada, Y. Kudo, K.Y. Liu, J. Electrochem. Soc. A148 (2001) 1153.
- [11] M.C. Tucker, M.M. Doeff, T.J. Richardson, R. Finones, J.A. Reimer, E.J. Cairnes, Electrochem. Solid St. A5 (2002) 95.
- [12] C.M. Burba, R. Frech, J. Electrochem. Soc. 151 (2004) A1032.
- [13] N. Ravet, J.B. Goodenough, S. Besner, M. Simoneau, P. Hovington, and M. Armand, in: Abstract 127, The Electrochemical Society Meeting Abstracts, vol. 99-2Honolulu, Hi, October 17–22, 1999.
- [14] P.P. Prosini, D. Zane, M. Pasquali, Electrochim. Acta 46 (2001) 3517.
- [15] S.Y. Chung, J.T. Bloking, Y.M. Chiang, Nat. Mater. 1 (2003) 123.
- [16] F. Sauvage, E. Baudrin, M. Morerette, J.M. Raeascon, Electrochem. Solid St. 7 (2004) A15.
- [17] Z. Chen, R. Dhan, J. Electrochem. Soc. 149 (2002) 1184.
- [18] R. Domniko, M. Geberscek, J. Drofenik, M. Bele, S. Pejovnik, J. Jamnik, J. Power Sources 119–121 (2003) 770.
- [19] M.M. Doeff, Y. Hu, F. Mclarnon, R. Kostecki, Electrochem. Solid St. 6 (2003) A207.
- [20] J. Barker, M.Y. Saidi, J.L. Swoyer, Electrochem. Solid St. 6 (2003) A53.
- [21] J. Yang, J.J. Xu, Electrochem. Solid St. 7 (2004) A515.
- [22] K.S. Park, J.T. Son, H.T. Chung, S.J. Kim, C.H. Lee, H.G. Kim, Electrochem. Commun. 5 (2003) 839.
- [23] S.T. Myung, S. Komaba, N. Hirosaki, H. Yoshiro, N. Kumogai, Electrochim. Acta 49 (2004) 4213.

- [24] M. Higuchi, K. Katayama, Y. Azuma, M. Yukawa, M. Suhara, J. Power Sources 119–121 (2003) 259–267.
- [25] N. Kalaiselvi, C.H. Doh, C.W. Park, S.I. Moon, M.S. Yun, Electrochem. Commun. 6 (2004) 1110.
- [26] X.Z. Liao, Z.F. Ma, L. Wang, X. Ming, Y. Jiang, Y.S. He, Electrochem. Solid St. 7 (2004) A522.
- [27] R. Jenkins, R.L. Snyder, Introduction to X-ray powder diffractometry, Wiley-Interscience, 1996.
- [28] Yaoqin Hu, Marca M. Doeff, Robert Kostecki, Rita Finones, J. Electrochem. Soc. 151 (2004) A1279.
- [29] P. Kalyani, N. Kalaiselvi, N. Muniyandi, Mater. Chem. Phys. 77 (2003) 662.
- [30] C.J. Rougier, G.A. Nazri, C. Julian, Mater. Res. Soc. Symp. Proc. 453 (1997) 647.
- [31] A. Rouier, G.A. Nazri, C. Julian, Ionics 3 (1997) 170.
- [32] L.W. Daasch, D.C. Smith, Analyt. Chem. 23 (1951) 853.
- [33] L.J. Bellamy, L. Beecher, J. Chem. Soc. (1952) 475.
- [34] D.E.C. Corbridge, E.J. Lowe, J. Chem. Soc. (1954) 493.
- [35] J. Preudhomme, P. Tarte, Spectrochim. Acta 26A (1970) 747.
- [36] J. Himmrich, H.D. Lutz, Solid State Commun. 79 (1991) 447.
- [37] P. Kalyani, N. Kalaiselvi, N. Muniyandi, J.Power Sources 111 (2002) 232.
- [38] P. Tarte, A. Rulmont, M. Leigeois-Duyclaerts, R. Cahay, J.M. Winand, Solid State Ionics 42 (1990) 177.
- [39] D.E.C. Corbridge, J. Appl. Chem. 6 (1956) 456.
- [40] G. Hersberg, Infra-Red and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York, 1945.
- [41] F.A. Miller, C.H. Wilkins, Analyt. Chem. 24 (1952) 1253.
- [42] C. Duval, J. Lacompte, C. R. Acad. Sci. Paris 239 (1954) 249.
- [43] Inorganic Library of FTIR Spectra Minerals, ©NICODOM, vol. 1, 1998, Pattern No-Q538.
- [44] B. Veeraraghavan, J. Paul, B. Haran, B. Popov, J. Power Sources 109 (2002) 377.
- [45] J.S. Gnanaraj, M.D. Levi, E. Levi, G. Salitra, D. Aurbech, J.E. Fischer, A. Claye, J. Electrochem. Soc. 148 (2001) 525.
- [46] G.X. Wang, Y. Chen, K. Konstantinov, M. Lindsey, H.K. Liu, S.X. Dou, J. Power Sources 109 (2002) 142.
- [47] Julian Morales, Luis Sanchez, Solid State Ionics 126 (1999) 219-226.
- [48] P.P. Prosini, M. Carewska, S. Scaccia, P. Wisniewski, M. Pasquali, Electrochim. Acta 48 (2003) 4205.
- [49] P. Patel, I.S. Kim, J. Maranchi, P. Kumta, J. Power Sources 135 (2004) 273.