ARTICLE IN PRESS
SOSI-13900; No of Pages 9
Solid State Ionics xxx (2016) xxx–xxx

Contents lists available at ScienceDirect

Solid State Ionics

journal homepage: www.elsevier.com/locate/ssi

Correlation between transport properties and lithium extraction/insertion mechanism in Fe-site substituted phosphoolivine

Andrzej Kulka [a], Konrad Świerczek [a], Katarzyna Walczak [a], Artur Braun [b], Janina Molenda [a,*]

[a] AGH University of Science and Technology, Faculty of Energy and Fuels, Department of Hydrogen Energy, al. A. Mickiewicza 30, 30-059 Krakow, Poland
[b] Laboratory for High Performance Ceramics, Empa — Swiss Federal Laboratories for Materials Science and Technology, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland

ARTICLE INFO

Article history:
Received 17 July 2015
Received in revised form 15 January 2016
Accepted 21 January 2016
Available online xxxx

Keywords:
Li-ion batteries
Cathode materials
Fe-site substituted $LiFePO_4$
In-situ XRD
Li extraction/insertion mechanism

ABSTRACT

$LiFePO_4$, $LiCo_{0.25}Fe_{0.75}PO_4$ and $LiCo_{0.1}Mn_{0.1}Fe_{0.8}PO_4$ phosphoolivines were characterized in terms of their structural and electrochemical properties. Detailed analysis of transport and electrochemical properties was conducted using electrical conductivity, Seebeck coefficient and $Li/Li^+/Li_xFe_{1-y-z}Mn_yCo_zPO_4$ cell open circuit voltage (OCV) measurements. In-situ XRD studies were employed in order to elucidate Li extraction/insertion mechanism in the studied systems. Correlation between the observed structural modification ongoing during the electrochemical reaction and physicochemical properties of the studied phosphoolivines has been proposed.

1. Introduction

Since the demonstration of reversible lithium extraction/insertion in $LiFePO_4$ by Goodenough and coworkers [1], olivine-type phosphates with a general formula of $LiMPO_4$ (M = Mn, Fe, Co and Ni) have attracted considerable attention as cathode materials for Li-ion batteries [2–4]. Numerous research papers provided evidence that electrochemical reaction of phosphoolivine with lithium ions for materials with moderate size grains (i.e. >50 nm) leads in equilibrium conditions to a phase separation in a broad lithium concentration, with only a slight lithium solubility in the end-member phases [5–8]. The observed two phase-type lithium extraction/insertion mechanism was initially considered as one of the limiting factors for $LiFePO_4$ to become a high-rate cathode material, due to the sluggish kinetics of propagation of the two-phase interface within particles of the material [1]. However, further research showed that $LiFePO_4$ particles of platelet-like nanomorphology [2,9] or the ones coated with conductive carbon [10] or glassy phases [11] may deliver high capacities upon charging and discharging, even with very high current rates. These findings were unexpected in the light of the first assumption about sluggish kinetics of lithium extraction, and resulted in extensive theoretical [12,13] and experimental work [14–16] on the nature of lithium extraction/insertion mechanism in the phosphoolivine.

Among several models explaining electrochemical reaction of $LiFePO_4$ in Li-ion batteries Delmas et al. [17] proposed a domino-cascade model, describing the presence of either a fully lithiated or delithiated phosphoolivine particle. This was observed for particles possessing size below 50 nm. Wagemerker et al. [18] also showed that the existence of fully delithiated/lithiated phosphoolivine particles or a two phase region within one particle depends on the particle size of the material. Ab initio simulations done by Ceder et al. [12] revealed that extraction/insertion of lithium ions from/into the Li_xFePO_4 particles, even at very low overpotentials, may proceed via a non-equilibrium, one phase-type mechanism. This phenomenon bypasses nucleation of a secondary (delithiated $FePO_4$-type) phase, and is believed to be responsible for enhanced kinetics of electrochemical reaction of the phosphoolivine via non-equilibrium, single phase Li_xFePO_4 ($0 < x < 1$). This would be consistent with the general opinion that high-rate lithium-ion battery electrode materials form solid solutions over a large lithium composition range. It also shows that change of the lithium extraction/insertion mechanism from two phase to diffusional one may improve the electrochemical properties of phosphoolivine material. As described previously by Molenda et al. [19], such change of the mechanism in phosphoolivines may be induced not only by means of reduction of a grain size of the material or applying higher overpotential to the cell, but also through chemical modification of the active material. Researchers of work [19] showed that substitution of iron by manganese in $LiFe_{0.55}Mn_{0.45}PO_4$ increases electronic conductivity, as well as enables a one phase-type lithium intercalation mechanism in this compound. This finding suggests that electrical conductivity has a great influence on the nature of the electrochemical reaction mechanism of phosphoolivine compounds, and is an important factor from the electrode engineering perspective. In the case of $LiFePO_4$ the electronic

---

* Corresponding author. Tel./fax: +48 12 617 2522.
E-mail address: molenda@agh.edu.pl (J. Molenda).

http://dx.doi.org/10.1016/j.ssi.2016.01.034
0167-2738/© 2016 Elsevier B.V. All rights reserved.

Please cite this article as: A. Kulka, et al., Correlation between transport properties and lithium extraction/insertion mechanism in Fe-site substituted phosphoolivine, Solid State Ionics (2016), http://dx.doi.org/10.1016/j.ssi.2016.01.034

Table 1
Unit cell parameters for studied $LiFe_{1-y-z}Mn_yCo_zPO_4$ phosphoolivines.

	a [Å]	*b* [Å]	*c* [Å]	*V* [$Å^3$]
$LiFePO_4$	10.3281	6.0074	4.6925	291.15
$LiCo_{0.25}Fe_{0.75}PO_4$	10.2982	5.9883	4.6953	289.56
$LiCo_{0.1}Mn_{0.1}Fe_{0.8}PO_4$	10.3256	6.0067	4.6967	291.30

component of electrical conductivity is related to a hopping of a hole-type small magnetic polaron [20]. Spin of a hole, which in $LiFePO_4$ is related to Fe^{3+} $(t_g\uparrow)^3(e_g\uparrow)^2$ ion, is ferromagnetically coupled with a surrounding Fe^{2+} $(t_g\uparrow)^3(e_g\uparrow)^2t_g\downarrow$ via double exchange mechanism, and therefore, along with a distortion, the moving electrons carry also a spin-polarization cloud [20]. Fe^{3+} cations originate from a presence of lithium vacancies in the material. On the other hand, the ionic component of conductivity is due to Li^+ hopping, which, owing to the structural constrains, is favored along the [010] direction [21,22]. The observed total conductivity of $LiFePO_4$ at room temperature has a dominant electronic component, and is of the order of 10^{-9} S cm^{-1} with the activation energy equal to 0.65 eV [19,20,23]. There were

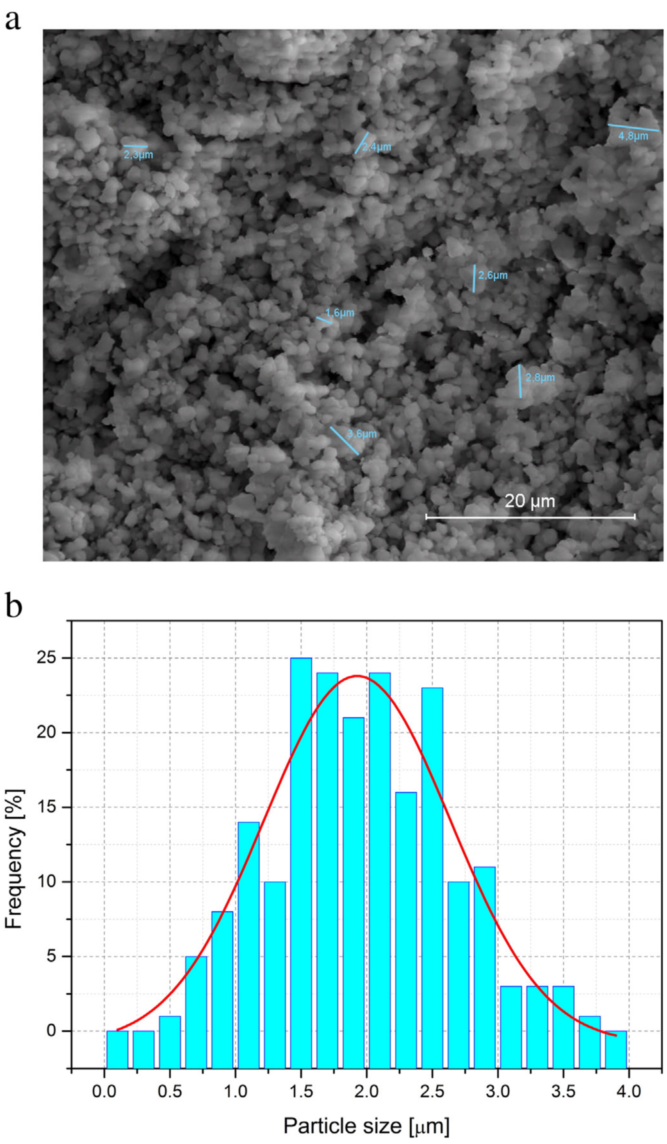

Fig. 1. Scanning electron micrograph of $LiCo_{0.25}Fe_{0.75}PO_4$ powder (a) along with grain size distribution (b).

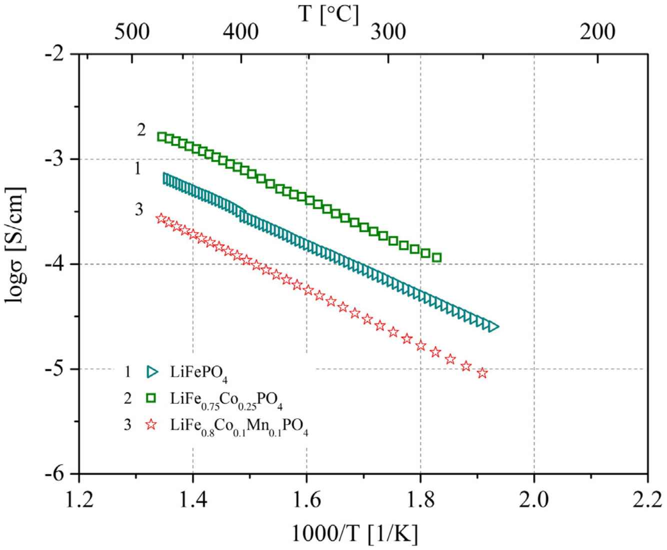

Fig. 2. Temperature dependence of electrical conductivity (σ) for studied $LiFe_{1-y-z}Mn_yCo_zPO_4$ phosphoolivines.

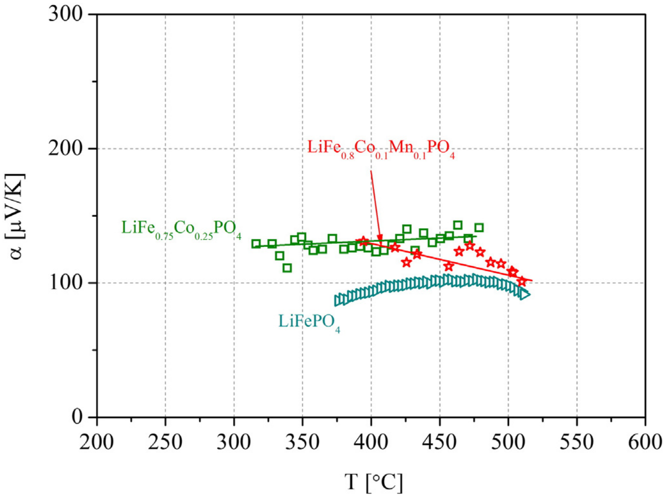

Fig. 3. Temperature dependence of Seebeck coefficient (α) for studied $LiFe_{1-y-z}Mn_yCo_zPO_4$ phosphoolivines.

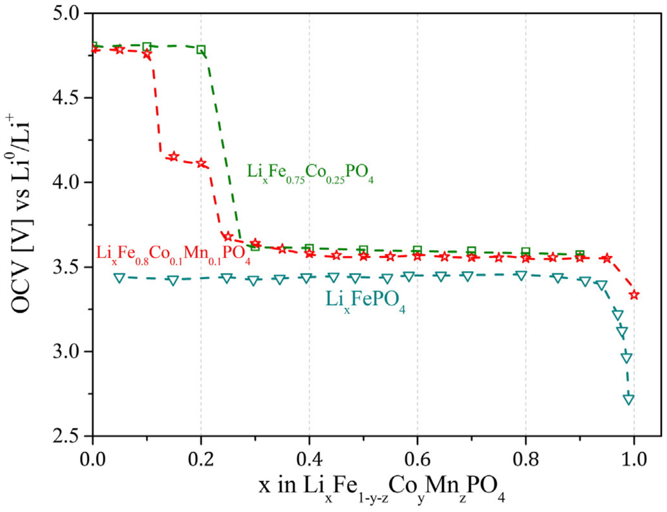

Fig. 4. Open circuit voltage (OCV) as a function of lithium concentration in cathode material for studied $Li/Li^+/Li_xFe_{1-y-z}Mn_yCo_zPO_4$ cells. The lines are only a guide for the eye.

Please cite this article as: A. Kulka, et al., Correlation between transport properties and lithium extraction/insertion mechanism in Fe-site substituted phosphoolivine, Solid State Ionics (2016), http://dx.doi.org/10.1016/j.ssi.2016.01.034