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# Electronic Aspect of Intercalation in Layered, Spinel and Olivine Type Cathode Materials*

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The ability and efficiency of lithium intercalation into transition metal compounds has been found to depend strongly on their electronic structure. This work is a brief review of physicochemical properties of intercalated transition metal compounds with layered, spinel or olivine type structure in order to correlate their microscopic electronic properties *i.e.* the nature of electronic states with the efficiency of lithium intercalation process which is directed by the chemical diffusion coefficient of lithium. The data concerning cell voltages and character of discharge curves for various materials are correlated with the nature of chemical bonding and electronic structure. The nature of the metallic type conductivity of doped phospho-olivine is discussed and some fundamental arguments against the bulk nature of the observed high electronic conductivity are presented.

**Key words**: Li-ion batteries, intercalation, transition metal compounds, $LiFePO_4$

Transition metal compounds with a general formula $A_xM_aX_b$ (A = alkaline metal, M = transition metal, X = O, S, Se) constitute a group of potential electrode materials for a new generation of lithium ion batteries. This application is related to the fact that these compounds can reversibly intercalate high amounts of alkaline ions (1 or more moles per mole of $M_aX_b$) already at room temperature, without significant changes in their crystallographic structure. In the numerous group of $M_aX_b$ compounds capable of intercalating foreign ions, particularly interesting are those having a layered or frame structure. The ionic transport in these systems is related to significant mobility of alkaline ions in two-dimensional interlayer spaces or tunnels, whereas the electronic transport is related to *d* electrons. Investigations of the $A_xM_aX_b$ intercalated compounds carried out in numerous laboratories all over the world [1–3] are connected with their principal application, *i.e.* in alkali cells. The investigations are concentrated on search of an electrode material of high energy efficiency. Investigations of the properties are limited to studies of the crystallographic structure and its modification in the intercalation process and to measurements of the chemical diffusion coefficient of lithium. Practically there is lack of basic research on the transport and electronic phenomena in the intercalated electrode materials. The published funda-

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* Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

mental parameters of the cells frequently refer to undefined initial structure of the ionic and electronic defects of the cathodic material. The attempts made so far to explain the observed diverse in electrochemical properties of $A_xM_aX_b$ compound, based on their crystallographic structure, formation of a superstructure *etc.* are not satisfactory and do not lead to determination of criterion of electrochemical performance of the systems.

**Electronic aspect of intercalation process**. The author of this work basing on numerous investigations on $A_xM_aX_b$ has pointed out that the electronic structure of these materials plays an important role in the intercalation process [4–8]. The intercalation of alkaline metal into transition metal compounds showing metallic or semiconducting properties can be considered as a reversible topotactic redox reaction, in which the transition metal changes its valence. The insertion of alkaline metal A to a conducting $M_aX_b$ lattice proceeds *via* simultaneous introduction of alkaline ions $A^+$ and the equivalent number of electrons:

$$xA^+ + xe^- + M_aX_b \Leftrightarrow A_xM_aX_b \tag{1}$$

For a $Li/Li^+/Li_xM_aX_b$ type battery, where the concentration of charge carriers in cathode material is determined by the concentration of intercalated lithium ions, one can demonstrate the relation between the change of battery electromotive force and the position of the Fermi level in the cathode material [9,10]. The battery electromotive force E is the difference in lithium chemical potential between cathode and anode (Li) materials:

$$\mu_{Li}(\text{cathode}) - \mu_{Li}(\text{anode}) = -FE \tag{2}$$

If the potential of the anode is constant, the variations of electromotive force E can be ascribed solely to the variation of the $\mu_{Li}$(cathode), *i.e.* $-F\Delta E = \Delta\mu_{Li}$(cathode). Lithium chemical potential in the cathode material can be written as a sum of lithium ion and electron chemical potentials:

$$\mu_{Li}(\text{cathode}) = \mu_{Li}^{+} + \mu_e \tag{3}$$

Lithium ion chemical potential in the cathode material can be expressed as:

$$\mu_{Li}^{+} = \mu_{Li^+}^{0} + k_BT\ \ln a_{Li}^{+} \tag{4}$$

and, as in the considered concentration range $a_{Li}^{+} \sim [Li^+]$ then

$$\Delta\mu_{Li^+} = k_BT\ln\frac{[Li^+]_f}{[Li^+]_i} \tag{5}$$

where *f* and *i* denote the final and initial states, respectively.

Chemical potential of electrons in the cathode material can be identified as Fermi level energy, which changes are determined by the electronic structure (DOS function) in the vicinity of Fermi level and can vary of the order of 1 eV (roughly band width) upon electrons introduction during lithium intercalation. For the change in lithium ions concentration $[Li^+] \sim 1$, the change of lithium ions chemical potential in the cathode material $\mu^+_{Li}$ is of the order of $k_BT$, *i.e.* ~0.025 eV at room temperature (Eq. (5)), while the change of the chemical potential of electrons in the cathode material is two orders of magnitude higher ($\Delta\mu^+_{Li} << \Delta\mu_e$). Therefore variations of electromotive force of the $Li/Li^+/Li_xM_aX_b$ cell, which accompany the intercalation reaction, correspond mainly to those of chemical potential of electrons (Fermi level) of a cathode material brought about by alkaline metal doping.

Figs. 1–2 show the expected cathode potential variations in function of electronic structure of the cathode material $A_xM_aX_b$. The character of density of states function determines the shape of the discharge curve. The concept of the Mott localization makes possible to explain the two types (step-like and monotonous) of discharge curve (Fig. 2). For the metallic systems with rather featureless density of the states (Fig. 2a) the monotonous variations of the Fermi energy and consequently monotonous character of the discharge curves are observed. For Mott insulators (Fig. 2b) the majority of electrons are localized and the density of states curve is usually spiky with a rather complicated type of shape as a function of particle energy. This explains the step-like character of the discharge curve as due to a nonmonotonous variations of the Fermi energy. Localization of electronic states at the Fermi level makes a kinetic barrier for the intercalation process and leads to a narrow range of alkaline nonstoichiometry (capacity of a battery). Such an approach gives explanation for both monotonous and step-like shapes of discharge curves and permits to design useful properties of the intercalated electrode materials.

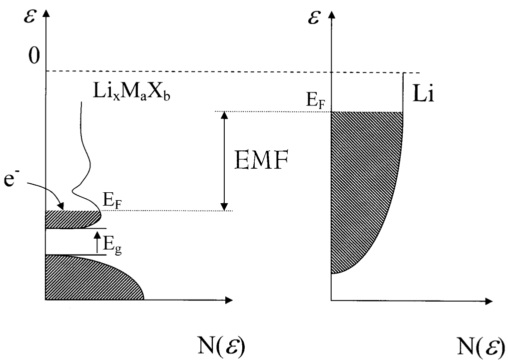

**Figure 1.** Density of states of $Li_xM_aX_b$ and lithium illustration electrochemical potential of electrons and related EMF of $Li/Li^+/Li_xM_aX_b$ cell.

It follows from the presented model that examination of the $A_xM_aX_b$ compounds potential by measuring the EMF of $A/A^+/A_xM_aX_b$ cells is an excellent tool of solid state physics which permits direct observation of the Fermi level changes during the

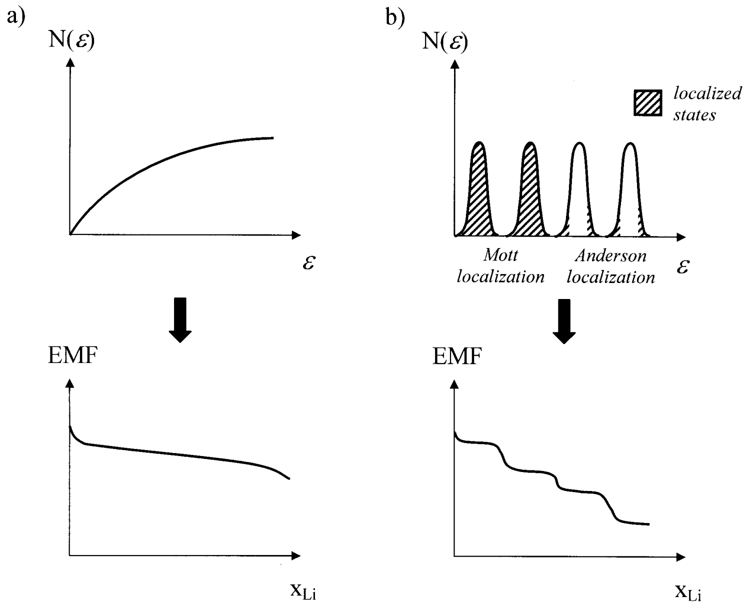

**Figure 2.** Electronic structure of the cathode material and related changes of the EMF of the $Li/Li^+/Li_xM_aX_b$ cell a) for metallic systems and b) for Mott insulators.

intercalation process. The investigations of physico-chemical properties of the intercalated systems in function of alkaline metal concentration have an important congnitive aspect. Modification of electronic structure of the intercalated material permits to follow the relations among crystallographic and electronic structure, composition, valence of transition metal, disorder and reactivity of solids which still remains an open question in materials science.

**Chemical diffusion coefficient of lithium in different cathode materials.** Fig. 3 shows the lithium chemical diffusion coefficient as a function of the mobility of lithium ions and electrons in various cathode materials. The lithium chemical diffusion coefficient determines the current density of a battery. In layered and skeleton structures, there exist paths of rapid diffusion and they ensure sufficiently high mobility of lithium ions, which does not limit the efficiency of the intercalation process. However, the localization of the electronic states, often observed in transition metal compounds, leads to a kinetic limitation of the intercalation process.

The best electronic transport conditions are found in the transition metal sulfides (*e.g.* $TiS_2$) and selenides because of high density of states close to the Fermi level and their delocalization. These materials, however, yield low voltages (2 V *vs.* Li).

In the $LiCoO_2$ oxide (battery voltage 3.6 V), due to the decreasing Co–Co distance upon the lithium deintercalation, on can observed a transition from the localized states with low electron mobility to the delocalized ones with higher mobility. Good performace of this commercially used material is related to a existence of the effective energy band with metallic properties in wide range of lithium non-stoichiometry ($x_{Li}$ = 0.9 mole/mole) [5].

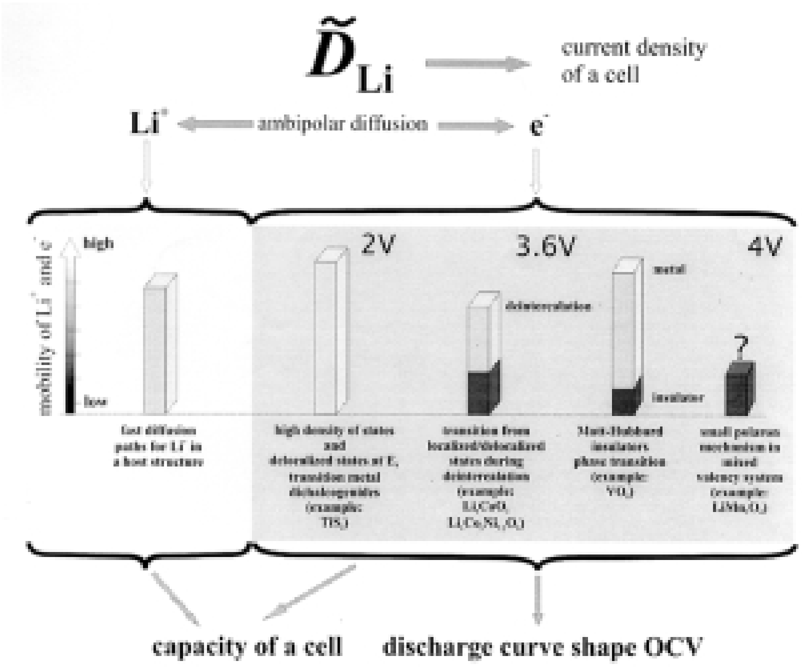

**Figure 3.** Lithium chemical diffusion coefficient as a function of the mobility of lithium ions and electrons in various cathode materials – schematic presentation.

Compounds for which the insulator-metal transition of the Mott-Hubbard type occurs (*e.g.* $VO_2$) show a close relation between the nature of electronic states and reactivity with lithium. The localization of electronic states and antiferromagnetic order in the non-metallic region of the transition leads there to a total absence of electrochemical activity in relation to lithium. The delocalization of electronic states at the metallic side of the transition yields high efficiency of the lithium intercalation process [7].

The manganese spinel is an interesting cathode material (4 V batteries). This material shows a high efficiency of intercalation process in spite of difficult conditions for electronic transport. Electrical conductivity at room temperature is $10^{-4}$ S/cm, with high activation energy (~0.3 eV) and proceeds *via* a small polaron mechanism. It has been found [11,12] that, compared to the $Li_xMn_2O_4$ material in the equilibrium states, the charge transport is much easier in the spinel cathode material operating in a battery.

The above analysis (Fig. 3) indicates that increase in the cathode potential, observed on passing from $TiS_2$ through $LiCoO_2$ to $LiMn_2O_4$ is obtained at the expense of the increase of ionic character of the M–O bond as compared to the M–S one. This occurrence however leads to a significant determination of electronic transport properties. Fig. 4 is the illustration of this conclusion and shows the values of the electrical conductivity for $Li_xM_aX_b$ transition metal compounds at room temperature compared

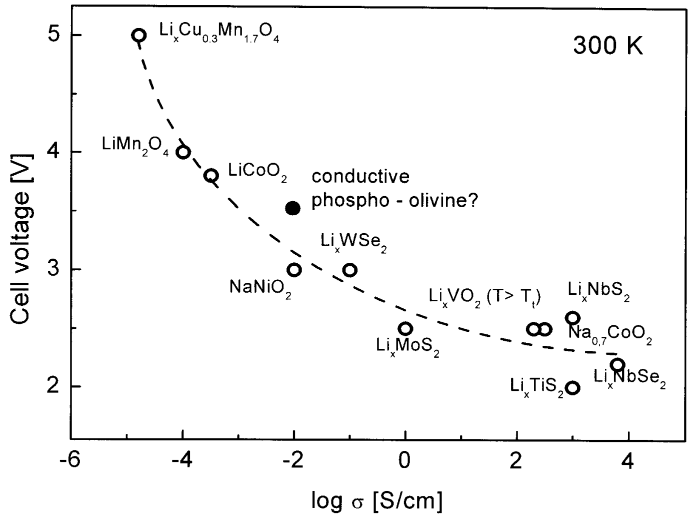

**Figure 4.** Electrical conductivity for different $A_xM_aX_b$ cathode material at room temperature compared to the voltage values of the corresponding $Li/Li^+/Li_xM_aX_b$ cells.

to the voltage values of the corresponding $Li/Li^+/Li_xM_aX_b$ cells. One can notice that poor electronic transport in a cathode material is related with higher voltage of corresponding cell.

**Toward enhanced electronic conductivity of doped $LiFePO_4$ phospho-olivines**. Novel group of cathode materials, olivine structured $LiFePO_4$ based, are stable, "green" and of high energy density, but with serious drawback – insulating properties (~$10^{-10}$ S/cm at 300 K). Practically advantageous operational parameters of a battery, like high current density, require electronically conductive cathode material, therefore efforts are concentrated on significant improvement of conductivity by selective doping of $LiFePO_4$ with other metals (*e.g*. Zr, Nb, W).

First reports by Y-M. Chiang [13] on metallic type conductivity of $LiFePO_4$ achieved by doping emerged great attention and intensified studies on the influence of dopants on electrical conductivity of this material. According to the presented by the author in the previous chapters descriptions of factors determining features of intercalation process the low concentration of electronic carriers in stoichiometric $LiFePO_4$ is a kinetic limitation of lithium extraction process leading to the appearance of the two phase mechanism in $Li/Li^+/LiFePO_4$ cell:

$$LiFePO_4 - xLi^+ - xe^- = (1-x)LiFePO_4 + xFePO_4 \qquad (6)$$

Y.-M. Chiang [13] showed spectacular increase in electrical conductivity of factor $10^7$ obtained by introducing $Nb^{5+}$, $Zr^{4+}$ or $Mg^{2+}$ ions into lithium sublattice. The activation energies were of the order of 0.05 eV at around room temperature. Few attempts of this substitution reported in literature [14] yield however ambiguous results. On the other hand theoretical approach and band structure calculations of stoichiometric $LiFePO_4$ bring surprising results indicating metallic or semiconducting properties with narrow energy gap 0.3 eV being at odds with observed low conductivity ($10^{-9}$ S/cm) of the system [15,16]. Similar calculations performed for the material doped with chromium, titanium or niobium indicated peaked density of stated at the Fermi level, what could explain the observed metallic type conductivity [14,17]. Figs. 5 and 6 present obtained results of electrical conductivity and thermoelectric power of the phospho-olivine samples doped with $W^{6+}$, $Ti^{4+}$ and $Al^{3+}$. The observed values of conductivity $10^{-2}$–$10^{-3}$ S/cm together with low values of activation energies in the 0.02 to 0.1 eV can be interpreted as appearance of metallization at the border ofcarrier localization. Low absolute values of thermoelectric power of the order of 10 $\mu$V/K and practically no dependence on temperature are characteristic of a metallic state. This could be related to the formation of a narrow band created by the dopant. Such a mechanism of semiconductor – metal transition upon doping is know in semiconductors as Mott's type transition [18]. For critical $N_c$ concentration an overlapping of electronic wave functions of dopant occurs leading to the formation of dopant conduction band. However systematical analysis of determined electrical properties of the phospho-olivine doped with different concentration of W, Ti and Al gives rise to doubts whether the conductivity mechanism is a bulk one. The minor and rather random influence of the dopant type and its content on the conductivity and the observed no critical concentration of the dopant for which the dopant band could be formed are the basic objections. Moreover sometimes observed inhomogeneous dopant distribution (as seen by EDS microprobes) also leads to the same "metallic" behavior of the material and even for the high-conductive samples deintercalation proceeds *via* two phase mechanism as in the case of pure $LiFePO_4$. The results obtained by Nazar *et al.* [19], where no dopants were added, but by use of specific synthesis route the obtained phospho-olivine samples with lithium deficiency $Li_{1-x}FePO_4$ and even the stoichiometric $LiFePO_4$ showed metallic type of conductivity, are remarkable arguments against the picture of bulk metallic conductivity caused

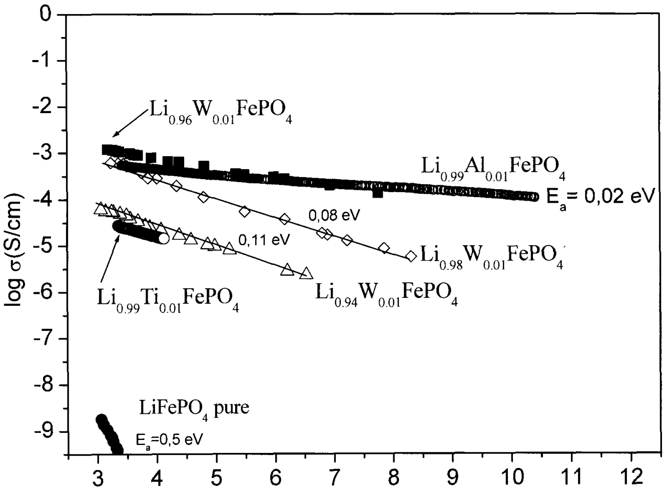

**Figure 5.** Temperature dependence of electrical conductivity for doped phospho-olivine.

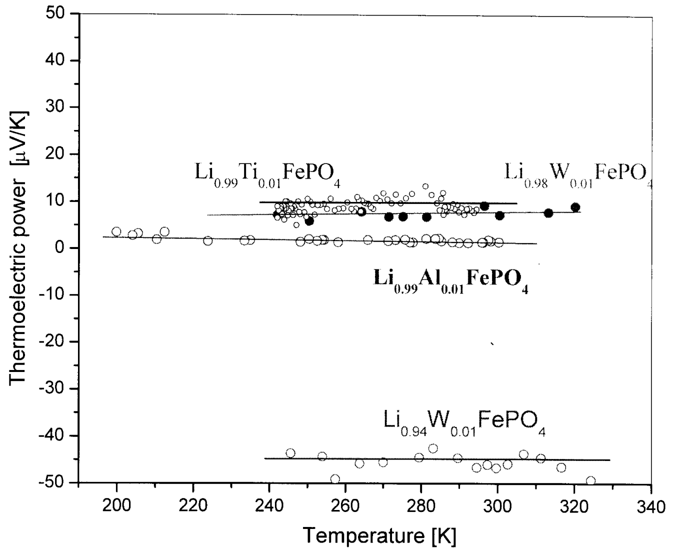

**Figure 6.** Temperature dependence of thermoelectric power for doped phospho-olivine.

by the presence of dopant atoms. Providing that even the obtained stoichiometric sample may probably has a slight lithium deficiency leading to the presence of mixed valency state of iron, the existence of the $Fe^{2+}$ – $Fe^{3+}$ pair cannot cause the observed high electronic conductivity, as the iron–iron distance (~4 Å) in the olivine structure is too large. In numerous M–O oxides a metallic type conductivity appears for M–M distances smaller than 3 Å. Then, what is actual reason for the observed increase in conductivity by seven orders of magnitude? According to the author two possibilities should be considered: a conductive path created by residual carbon originating from organic precursors used in synthesis or formation of iron phosphides on the phosphate grains forming thin, conductive path. Traces of the iron phosphides (content estimation ~4%) were observed by surface sensitive CEMS technique [20] or TEM [19]. So, we deal with a composite material with highly resistive bulk and electronically conductive surface of the grains as covered by iron phosphides, what creates conductive path over the whole sample. The origin of the iron phosphides formation on the surface of the grains may be related to presence of the internal reducing agents, as from substrates such as $FeC_2O_4 \cdot H_2O$, $NH_4H_2PO_4$ and $Li_2CO_3$ during the synthesis process few internal reducing agents are released like: Fe, $Fe_x(CO)_y$, C, CO and $NH_3$. Therefore partial reduction of phosphate to iron phosphides should be considered. For that reason the real influence of the dopant seems to restrict only to the assumed lithium deficiency during synthesis of the doped compound, what leads to the presence of the $Fe^{2+}/Fe^{3+}$ redox couple which catalyzes the reduction of the $LiFePO_4$ into $Fe_2P$, forming thin conductive layer over the sample.

**Summary**. At an early stage of lithium battery technology only these cathode materials were used , which without any additives exhibited high efficiency of the intercalation process. This high efficiency was assumed by high ionic and electronic conductivity in their layered structures. The development of technology of new reactive cathode oxides or phosphates requires some conductivity improving additives, enabling technological application of the novel cathode materials with high potential of intercalation reaction but with insulating properties. In the case of the discussed phospho-olivine cathode material, the phosphides which are created on the grain surfaces during synthesis routh, are an extraordinary "additive" forming in situ a, par excellence, composite material.

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## REFERENCES

1. Whittingham M.S., *J. Electrochem. Soc*., **123**, 315 (1976).
2. Nagelberg A.S. and Worrell W.L., *J. Solid State Chem.*, **38**, 321 (1981).
3. Ohzuku T., in Lithium Batteries, New Materials, Developments and Properties, ed. By G. Pistoia, Elsevier 1994.
4. Than Do, Molenda J. and Stoklosa A., *Electrochim. Acta*, **36**, 1555 (1991).
5. Molenda J., Stoklosa A. and Bak T., *Solid State Ionics*, **36**, 53 (1989).
6. Molenda J. and Kubik A., *Solid State Ionics*, **117**, 57 (1999).
7. Molenda J. and Stoklosa A., *Solid State Ionics*, **36**, 43 (1989).
8. Molenda J., Bak T. and Stoklosa A., *Physica C*, **207**, 147 (1993).
9. Molenda J., *Phys. Stat. Sol.(b)*, **165**, 419 (1991).
10. Molenda J., Marzec J., Swierczek K., Ojczyk W., Ziemnicki M., Molenda M., Drozdek M. and Dziembaj R., *Solid State Ionics*, **171**, (2004).
11. Molenda J. and Marzec J., Nanostructured Materials, Selected Synthesis Methods, Properties and Applications, Kluver Academic Publishers, Boston 2002, eds. P. Knauth, J. Schoonman.
12. Marzec J., Swierczek K., Przewoznik J., Molenda J., Kimon D.R., Kelder E.M. and Schoonman J., *Solid State Ionics*, **146**, 225 (2002).
13. Chung S.-Y., Bloking J.T. and Chiang Y.-M., *Nature Materials*, vol. 1, October 2002.
14. Lampe-Onnerund C., Dalton S., Onnerud P., Novikov D., Shi J., Treger J. and Chamberlain R., 203rd Meeting of The Electrochemical Society, April 27-May 2, 2003.
15. Tang P. and Holzwarth N.A.W., *Physical Review B*, **68**, 165107 (2003).
16. Yamada A., Lithium battery discussion electrode materials, Bordeaux-Arcachon, France, 14–19 September, 2003.
17. Shi S., Liu L., Ouyang Ch., Wang D., Wang Z., Chen L. and Huang X., *Physical Review B*, **68**, 195108 (2003).
18. Mott N.F. and Davis E.A., Electronic processes in noncrystalline materials, Clarendon Press, Oxford 1971.
19. Herle P.S., Ellis B., Coombs N. and Nazar L.F., *Nature Material*, Advance On Line Publication, www.nature.com/naturematerials.
20. Molenda J. and Marzec J., (in preparation).