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Electronic limitations of lithium diffusibility. From layered and spinel toward novel olivine type cathode materials

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Abstract

The ability and efficiency of lithium intercalation into transition metal compounds have 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 that is controlled 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 following it.

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.

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1. Introduction

Transition metal compounds with a general formula $A_x M_a X_b$ (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 $M_a X_b$) already at room temperature, without significant changes in their crystallographic structure. In the numerous group of MaXb 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 $A_x M_a X_b$ 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

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

2. Electronic aspect of intercalation process

The author of this work basing on her own, numerous investigations on $A_x M_a X_b$ compounds has pointed out that the electronic structure of these materials plays an important role in the intercalation process [4–8,10,12–15]. The

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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 $M_a X_b$ lattice proceeds via simultaneous introduction of alkaline ions A⁺ and the equivalent number of electrons:

$$xA^{+} + xe^{-} + M_a X_b \leftrightarrow A_x M_a X_b \tag{1}$$

Variations of the EMF of the $A/A^+/A_xM_aX_b$ cell, accompanying the intercalation reaction, corresponds to those of electrochemical potential of electrons (Fermi level) of the cathode material brought about by alkaline metal doping [10]. Wide range of alkaline metal concentration and weak compositional dependence of the cathode potential are assured by high density of states near the Fermi level, whereas the existence of delocalized electronic states enables rapid relaxation of the cathode material and good useful properties. The analysis of the electrochemical properties of A_xMO₂ oxides indicates correlations between the character of the discharge curves and microscopic electronic parameters such as the metal-metal distances. The $A_x MO_2$ layered oxides may be included in the class I of oxides according to the classification given by Goodenough [9], in which strong interactions between the electrons are linked with the direct cation-cation (M-M) interactions due to small interatomic distances. In such a case, the electronic structure is formed mainly from the d orbitals of a transition metal and it depends on the M-M distance. The critical parameter R_c for which a transition metal-isolator occurs can be calculated on the basis of a formula given by Goodenough [9], which for the 3d oxides with octahedral coordination of 3d metal has the following form:

$$R_{\rm c} = 3.20 - 0.05m - 0.03(Z - Z_{\rm Ti}) - 0.04s(s+1) \left[\mathring{A}\right]$$
(2)

where *m* is the valency of M^{m+} , *Z*—the atomic number of the transition metal and *s*—the effective spin. This formula







Fig. 2. Electronic structure of the cathode material (a) and related changes of the EMF of the Li/Li⁺/Li_x $M_a X_b$ cell (b); R_{M-M} —effective M–M distance, R_c —critical M–M distance for insulator-metal transition [9].

can be applied to $A_x MO_2$ oxides, since in these compounds the electronic structure is dependent on the 3d electrons of transition metal ions in octahedral coordination. Figs. 1 and 2 show the expected cathode potential variations in function of electronic structure of the cathode material $A_x M_a X_b$. 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 curves. Systems with $R_{M-M} > R_c$ correspond to the Mott insulators, while those with $R_{M-M} < R_c$ represent correlated metals. Under such a classification scheme, there is principal difference between the two kinds of systems after intercalation.

It follows from the presented approach that examination of the $A_x M_a X_b$ compounds potential by measuring the EMF of $A/A^+/A_x M_a X_b$ cells is an excellent tool of solid state physics, which permits direct observation of the Fermi level changes during the intercalation process. The investigations of physicochemical properties of the intercalated systems in function of alkaline metal concentration have an important cognitive 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 what still remains an open question in materials science.

3. Correlations between electronic and electrochemical properties of A_xMO_2 oxides

Fig. 3 shows R_c values calculated from (2) for A_xMO_2 oxides (0<*x*<1) (hatched regions) as well as the range of actual R_{M-M} changes during electrochemical intercalation

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