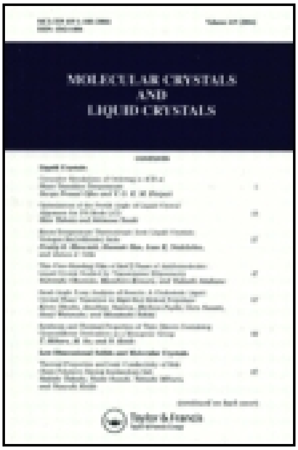

Molecular Crystals and Liquid Crystals Science and Technology. Section A. Molecular Crystals and Liquid Crystals

Electronic Properties and Reactivity of Intercalation Compounds

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Electronic properties and reactivity of intercalation compounds

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The paper presents the results of electrical and electrochemical measurements of intercalation compounds (Li_xCoO_2, Li_xVO_2, Li_xWO_3). A close correlation has been shown between the electronic structure of transition metal compounds and the reactivity in relation to lithium.

Keywords: electrical properties, intercalation process, transition metal oxides

INTRODUCTION

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 $A/A^+/ A_xM_aX_b$ 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 intercalation process the basic structural elements do not undergo any significant changes except some small reversible deformations. Structural stability during the intercalation is related to the existence of strong ionic-covalent bonds between M and X atoms. The ionic transport in these systems is related to appreciable mobility of alkaline ions in two-dimensional interlayer spaces or tunnels whereas the electronic transport is related to *d* electrons. The properties of *d* electrons in these compounds are variable, starting from insulator properties of VO_2 and TiO_2 through semiconducting ones of MoS_2 and WSe_2 to the metallic ones of TiS_2 and Na_xCoO_2. This complex behavior of *d* electrons is enhanced by nonstoichiometry which sometimes exceeds ten atomic percent. From the viewpoint of electronic structure the nonstoichiometry introduces local dopant centers which on ionization produce additional charge carriers in the system. Nonstoichiometry occurring in such systems can lead to insulator-metal transition similarly as in the case of Mott's transition in doped semiconductors.

The investigations on defect structure and transport properties (deviation from stoichiometry, electrical conductivity, thermoelectric power) carried out under the conditions of thermodynamic equilibrium at elevated temperatures enable to determine the ionic and electronic defect structure, charge transport mechanism and optimum thermodynamic parameters (T, pX_2) for the synthesis of electrode materials with desired transport properties.

The author of this work after her own investigations on $A_xM_aX_b$ (A=Li, Na; M=3*d*, 4*d*, 5*d*; X=O, S, Se) has pointed out that the electronic structure of these materials plays an important role in the intercalation process [1]. 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 valency.

Variations of emf of the $A/A^+/\ A_xM_aX_b$ cell, accompanying the intercalation reaction, correspond to those of electrochemical potential of electrons (Fermi level) of the cathode material brought about by alkaline metal doping. High density of states near the Fermi level is associated with wide range of alkaline metal concentration and weak compositional dependence of the cathode potential, whereas the existence of delocalized electronic states guarantees rapid relaxation of the cathode material and good useful properties. The investigations of physico-chemical 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 structure, composition, disorder and reactivity of solids which remains an open question in materials science.

The following paragraphs will present selected electrode materials emphasizing correlation between their electronic and electrochemical properties.

Li_xCoO_2 system

Fig. 1 presents a discharge curve of a $Li/Li^+/\ Li_xCoO_2$ cell in the OCV system. Points A, B, C, D, E, denote compositions at which the work of the cathode material was broken up in order to examine its physical properties.

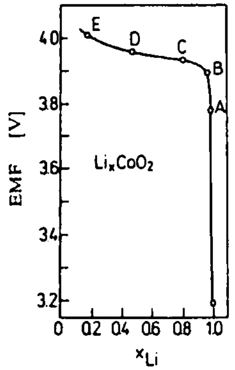

FIG. 1 Charge curve EMF for Li_xCoO_2

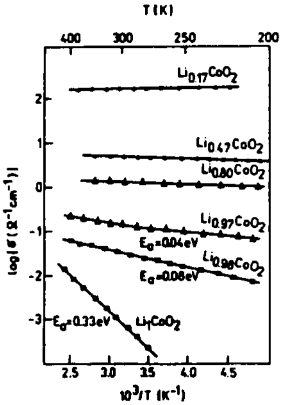

FIG. 2 Temperature dependence of electrical conductivity for Li_xCoO_2

Fig. 2 show electrical conductivity of the cobalt bronze Li_xCoO_2 as a function of desintercalation degree. Comparison of figs. 1 and 2 confirms close correlation between the electronic and electrochemical properties of the cathode material. Cobalt bronze with compositions A and B (fig. 1) situated within the potential jump exhibits semiconducting properties, energy gap corresponding to the height of the jump (0.7eV) whereas at compositions situated on the potential plateau (points C, D, E, in fig. 1) it shows metallic properties. The analysis [2] indicates that good electrochemical properties of Li_xCoO_2 within the composition range $0.1 < x_{Li} < 0.97$ are due to the existence of the effective energy band and delocalization of electronic states near the Fermi level.

Li_xVO_2 system

Vanadium dioxide is a system which ability to intercalate lithium ions can be controlled by modifying electronic structure. At 340K it shows a typical Mott-Hubbard semiconductor-metal transition [3]. The temperature of this transition is very sensitive to the presence of impurities and dopants. At the transition temperature VO_2 undergoes structural rearrangement (monoclinic ⇄ tetragonal lattice) accompanied by abrupt change of electrical and magnetic properties. Fig. 3 illustrates temperature dependence of electrical conductivity of VO_{2-y} at different oxygen nonstoichiometry ($y_{III} > y_{II} > y_I$). The observed discontinuity of electrical properties can be explained on the basis of a qualitative model of its electronic structure, shown in fig. 4 [4]. Charge transport on the non-metallic side of the transition ($T<T_t$) proceeds via localized states. On the metallic side of transition the charge transport takes place in the effective band with carriers near the Fermi level, electronic gas is correlated. Extensive studies [5] have shown that localization of electronic states is the reason why pure VO_2 does not accept lithium ions at room temperature (kinetic limit). It has been shown [5] that high purity vanadium dioxide which at room temperature did not undergo any intercalation at all, after doping with tungsten (due to weaker electronic correlation) acquired high

capability of intercalating lithium ions even at lower temperatures which indicates that the electronic structure of the cathode material is decisive for the electrochemical behavior.

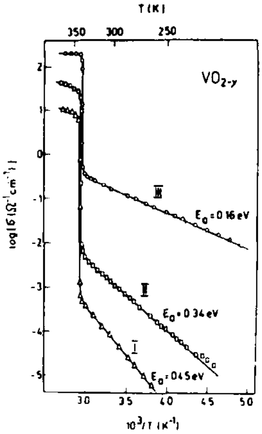

FIG. 3 Temperature dependence of electrical conductivity of VO_{2-y} ($y_{III}>y_{II}>y_{I}$)

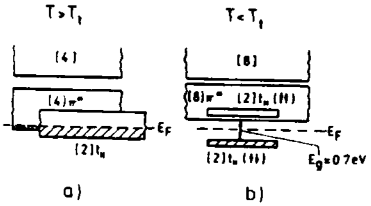

FIG. 4 Qualitative scheme of the electronic structure of vanadium dioxide [4]: a)$T>T_t$ and b) $T<T_t$

Li_xWO_3 system.

To demonstrate that electronic structure of the cathode material determines its capability of intercalating lithium, certain electronic parameters of Li_xWO_{3-y} were referred to chemical diffusion coefficient of lithium, being responsible for the effectiveness of the intercalation. Fig. 5 shows variation of physicochemical properties of spectrally pure tungsten trioxide upon intercalation with lithium in the region where electrochromic effect is observed. The observed growth of chemical diffusion coefficient of lithium at $x_{Li}<0.12$ is related to increasing delocalization degree of carriers, i.e. lowering of their effective mass and of the activation energy of conductivity.

To verify a hypothesis that the nature of electronic states implies the effectiveness of intercalation, the measured chemical diffusion coefficients of lithium were referred to electronic properties of the cathode material in critical points. Fig. 6 shows a dependence of chemical diffusion coefficient of lithium and emf of the Li/Li$^+$/Li$_x$WO$_{3-y}$ cell in the x_{Li} range where the characteristic jump of the cathode potential takes place for tungsten trioxide.

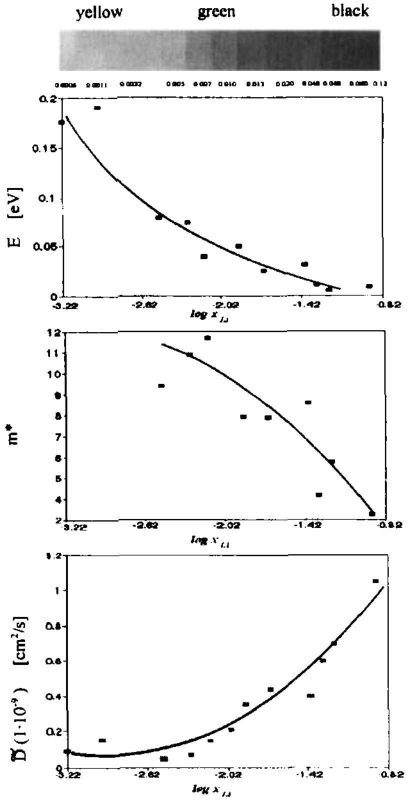

FIG. 5 Variation of physico-chemical properties (colour, activation energy of electrical conductivity E, effective mass of carriers m* and chemical diffusion coefficient of lithium

From the viewpoint of electronic structure the potential jump is related to filling-up of the π^* band with electrons and subsequent sudden rise of the Fermi level to the σ^* band. It can be noticed that the chemical diffusion

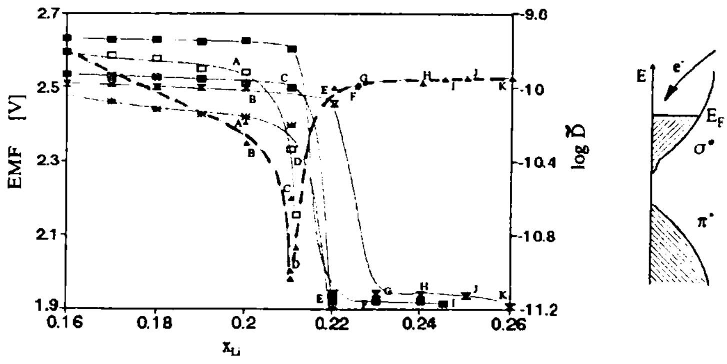

FIG.6 Variation of chemical diffusion coefficient of lithium $\tilde{D}$ in Li_xWO_3 in function of intercalation degree x_{Li} (dashed line)
-EMF of the $Li/Li^+/Li_xWO_3$ cell - solid lines A-A, B-B...K-K denote equilibrium potential of the cathode and related $\tilde{D}$.

coefficient of lithium decreases upon approaching the upper edge of the π^* band. If it were empirically possible to catch the moment of filling-up of the band, the resistivity of the cathode material would be extremely high and the chemical diffusion coefficient of lithium would be extremely low. As follows from fig.6 injection of electrons to the empty σ^* band brings about increase of chemical diffusion coefficient of lithium related to its increasing concentration and mobility of carriers.

Presented results prove that the chemical diffusion coefficient of lithium ($\tilde{D}$) in Li_xWO_{3-y} is determined by transport properties of electrons.

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