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Transport and electrochemical properties of orthorhombic $LiMnO_2$ cathode material for Li-ion batteries

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The aim of this paper was to determine the temperature range of thermal stability of orthorhombic $LiMnO_2$, together with its electrical and electrochemical characterization. High-temperature studies of the electrical properties of orthorhombic $LiMnO_2$ point to structural instability of the phase at temperatures over 400 °C. Annealing above 400 °C leads to its decomposition into a two-phase mixture (Li_2MnO_3 + $LiMn_2O_4$). Stoichiometric $LiMnO_2$ has a very low conductivity at room temperature, which limits the effectiveness of intercalation at the initial stage. The temperature dependences of the electrical conductivity and thermoelectric power of deintercalated Li_yMnO_2 samples indicate a dominant electronic conductivity over the ionic one. A remarkable increase in electronic conductivity accompanied by a drop of activation energies is observed upon deintercalation. It was shown that the deintercalation of lithium from Li_yMnO_2 makes the structure less stable, leading to a two-phase mixture (Li_zMnO_2 + $Li_xMn_2O_4$).

Key words: *orthorhombic $LiMnO_2$; thermal stability; electrical properties; intercalation; Li-ion battery*

1. Introduction

The present technology of Li-ion batteries is based on $LiCoO_2$ oxide. Manganese oxide, $LiMnO_2$, with its higher capacity (280 mAh/g), lower price, and environmental friendliness, seems to be an attractive alternative cathode material. This material, however, is structurally unstable, which implies insufficient cyclability of manganese oxide-based batteries. There have been numerous attempts to improve its structural stability by manganese substitution with iron or nickel $LiM_xMn_{1-x}O_2$ (M = Fe, Ni) [1, 2]. The studies were limited to the determination of lattice parameters and electrochemical

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characteristics. Transport properties of manganese oxide are not sufficiently known, even though they determine to a great extent functional properties of the cathode material. The first aim of this work was to examine structural and electrical properties of $LiMnO_2$ over a wide temperature range, 230–1070 K, as well as changes in these properties upon lithium deintercalation. The other aim was to find a relationship between the electronic properties of the material and its electrochemical behaviour.

2. Experimental

CH_3COOLi and $(CH_3COO)_2Mn\cdot 4H_2O$ were used as precursors. The substrates in stoichiometric proportions were dissolved in deionised water. The solution was alkalised by dropwise addition of the concentrated ammonia (25%); the amount of ammonia was sufficient for complete precipitation of manganese(II) hydroxide. After condensation, the obtained sol was dried at 90 °C to yield a xerogel, which was subsequently calcined in air, in the temperature range of 250–300 °C, for 24 h. The brownish-black product was powdered, again calcined in argon at 850 °C for 20 h and quenched in order to preserve the structure stable at high temperatures. The calcination parameters (temperature and the composition of the gas atmosphere) were established on the basis of thermogravimetric studies [3].

The structure of the obtained materials was determined using a PHILIPS X'pert X-ray diffractometer (Cu monochromatic radiation, ICDD data base). The electrical conductivity and thermoelectric power were measured at 230–350 K in vacuum. A four-probe AC method was used in the conductivity measurements, and a dynamic method in the thermoelectric power measurements.

The high-temperature measurements of electrical conductivity were performed in air and in argon, using the same methods as mentioned above. The electrochemical behaviour of $LiMnO_2$ was studied with a $Li\,|\,Li^+\,|\,Li_yMnO_2$-type cell using a Kest electronics 32K electrochemical amperostat.

3. Results and discussion

The specimens of $LiMnO_2$ obtained by quenching the high-temperature structure (see experimental) are single-phase and orthorhombic (Fig. 1). Figure 2 presents the electrical conductivity of $LiMnO_2$ in argon ($p_{O_2} = 10^{-5}$ atm) in the temperature range 150–800 °C, measured in heating and cooling cycles. The variations of electrical conductivity are complex. Structural examination of specimens in the characteristic points of the conductivity hysteresis indicates that the orthorhombic structure is unstable at elevated temperatures. In the range 200 – 350 °C, the orthorhombic phase is stable and its conductivity is thermally activated, the activation energy being 0.7 eV. At 350 °C, the conductivity suddenly increases by three orders of magnitude, which is associated with the decomposition of $LiMnO_2$:

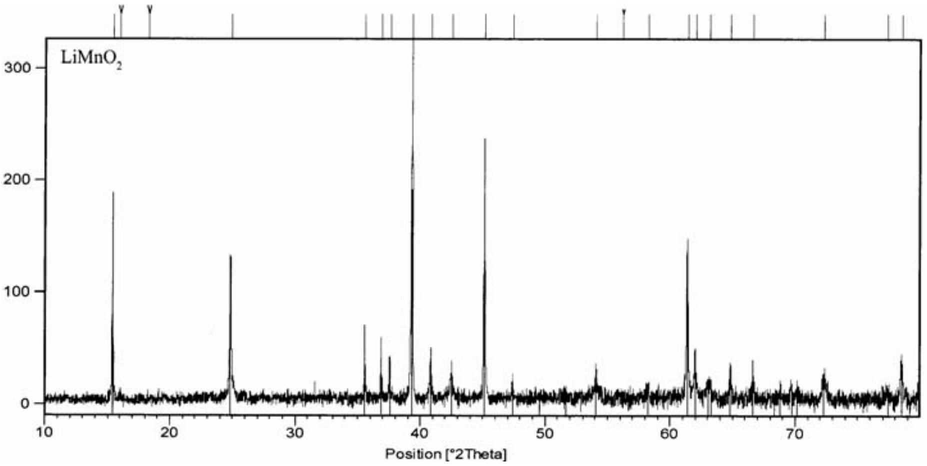

Fig. 1. XRD pattern of lithium manganese oxide $LiMnO_2$

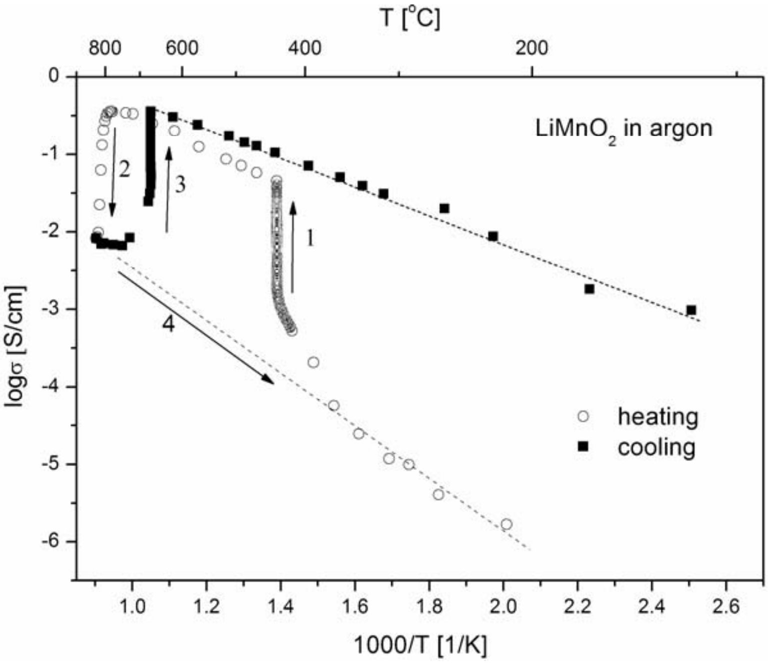

Fig. 2. High-temperature electrical conductivity of $LiMnO_2$ under argon atmosphere

$$3LiMnO_2 + 1/2O_2 = LiMn_2O_4 + Li_2MnO_3 \tag{1}$$

Higher conductivity of the spinel phase ($LiMn_2O_4$) is the reason for the observed significant conductivity increase (Fig. 2, arrow 1). The high conductivity of 10^{-1} S·cm^{-1} and the activation energy of conductivity of 0.1 eV, observed in the temperature range of 400–800 °C, are characteristic of manganese spinel $LiMn_2O_4$ [4] (the conductivity of Li_2MnO_3 is lower by several orders of magnitude). Manganese spinel, however, is not stable at 800 ºC and at low oxygen pressure (10^{-5} atm) [4], and reaction (1) proceeds to the left, which is reflected in a sudden drop of conductivity (arrow 2 in Fig. 2). This drop is related to the formation of $LiMnO_2$, the orthorhombic phase stable

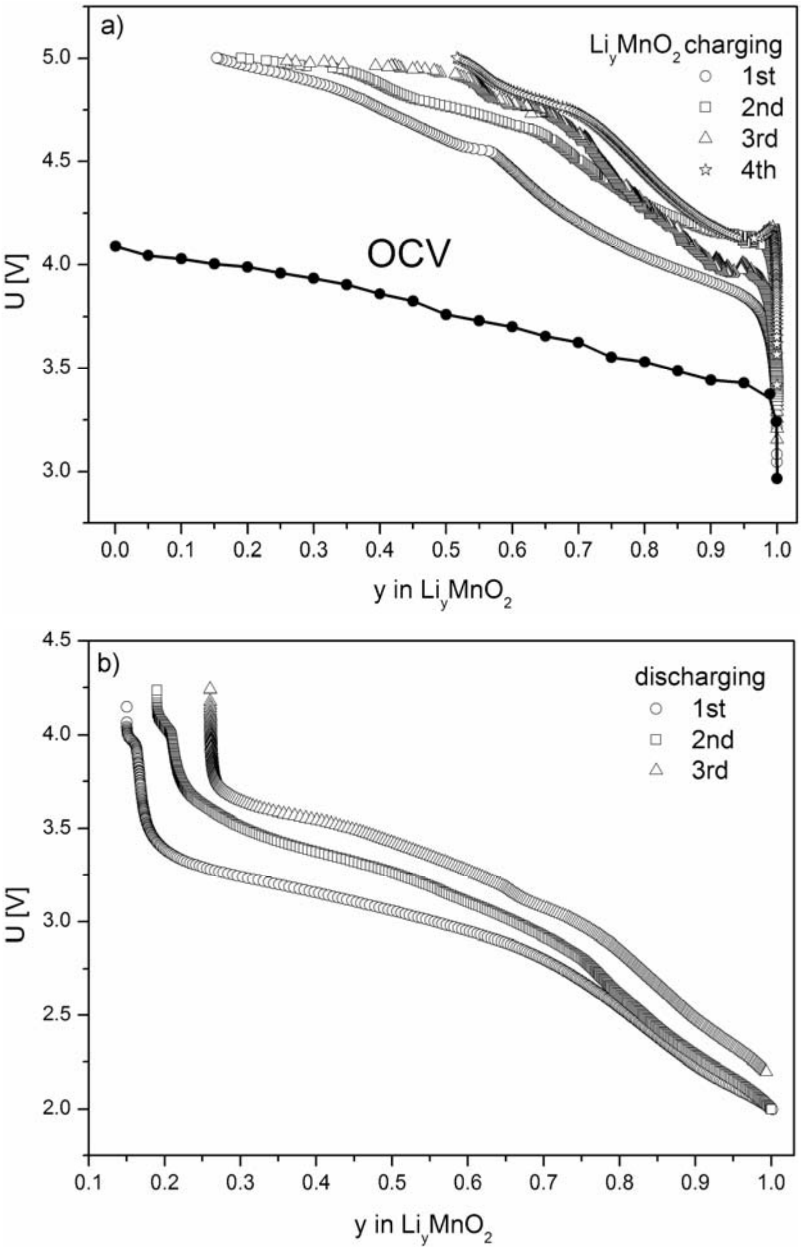

Fig. 3. The charge (a) and discharge (b) curves of the Li | Li^+ | Li_yMnO_2 cell

under these conditions, having much lower conductivity. Quenching of the orthorhombic phase causes the high-temperature structure to be preserved and the conductivity variations to follow arrow 4 in Fig. 2. Slow cooling of the high-temperature orthorhombic phase leads again to the decomposition of $LiMnO_2$ at about 650 °C into manganese spinel $LiMn_2O_4$ and Li_2MnO_3 via reaction (1).

Figures 3a, b show the charge/discharge curves of a $Li | Li^+ | Li_yMnO_2$-type cell at the current density of 100 μA/cm^2. A comparison of the charge curve of the loaded cell with the corresponding OCV curve (Fig. 3a) indicates a significant resistivity of the cathode material Li_yMnO_2. It is worthwhile to note that the discharge curves shift toward higher voltages in consecutive cycles (Fig. 3b). Such behaviour can be explained by a gradual transformation of the orthorhombic $LiMnO_2$ into spinel, with a characteristic voltage of 4 V in a wide range of y_{Li}. X-ray studies confirm the increasing contribution of spinel with progressing lithium deintercalation [3]. This indicates that orthorhombic $LiMnO_2$, unstable at temperatures exceeding 350 °C, is also not stable at room temperature, at which the deintercalation/intercalation of lithium takes place.

High resistivity of the cathode material Li_xMnO_2 implies a low chemical diffusion coefficient of lithium, estimated to be 10^{-9} cm^2/s (Fig. 4).

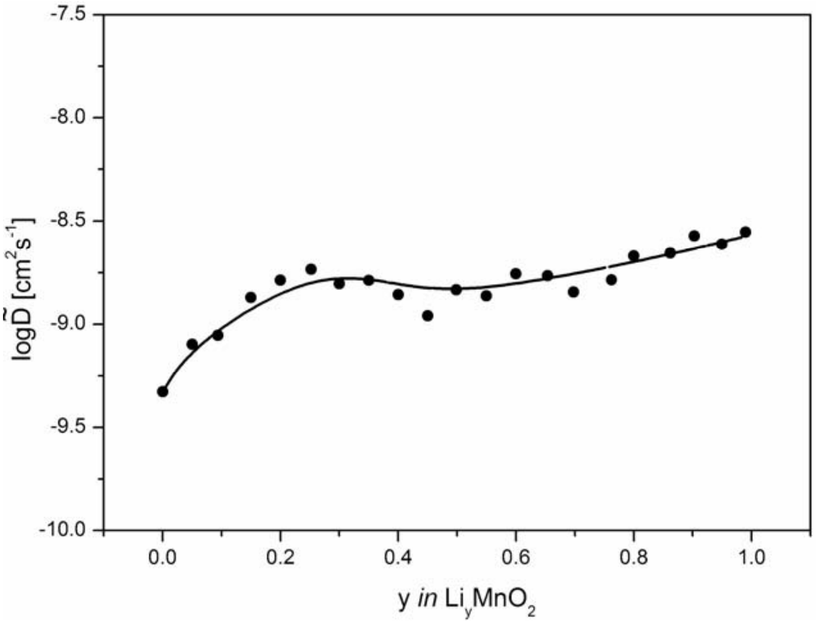

Fig. 4. Chemical diffusion coefficient of lithium in $LiMnO_2$ attained by GITT

Figures 5 and 6 demonstrate the temperature dependences of electrical conductivity and thermoelectric power for the starting compound, $LiMnO_2$, and after the stepwise deintercalation of lithium. Stoichiometric $LiMnO_2$ shows hardly measurable conductivity at room temperature. At 70 °C, its conductivity is 10^{-8} S/cm and rapidly increases during the deintercalation of lithium, reaching 10^{-5} S/cm at room temperature at a composition of $Li_{0.2}MnO_2$.

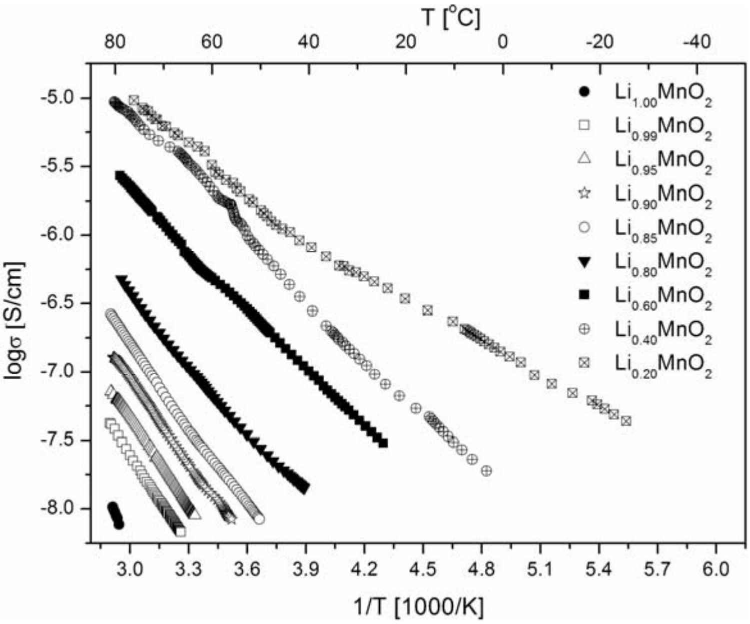

Fig. 5. Electrical conductivity of deintercalated Li_yMnO_2 samples

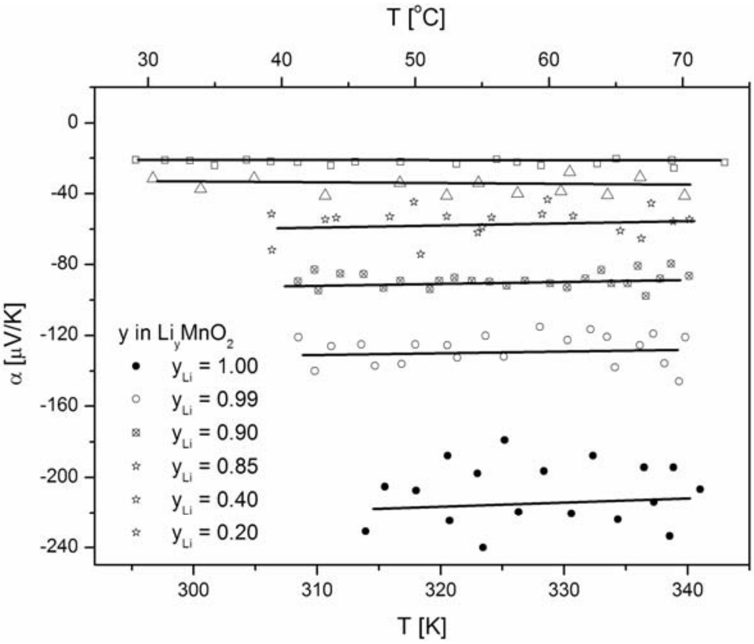

Fig. 6. Thermoelectric power of deintercalated Li_yMnO_2 samples

The activation energy of conductivity decreases in this process from 0.7eV for stoichiometric $LiMnO_2$ to 0.15 eV for $Li_{0.2}MnO_2$ (Fig. 7). The observed temperature characteristics of conductivity and thermoelectric power (Figs. 5 and 6), as well as the high-temperature dependence recorded in argon (Fig. 2) point to dominant electronic conductivity in $LiMnO_2$.

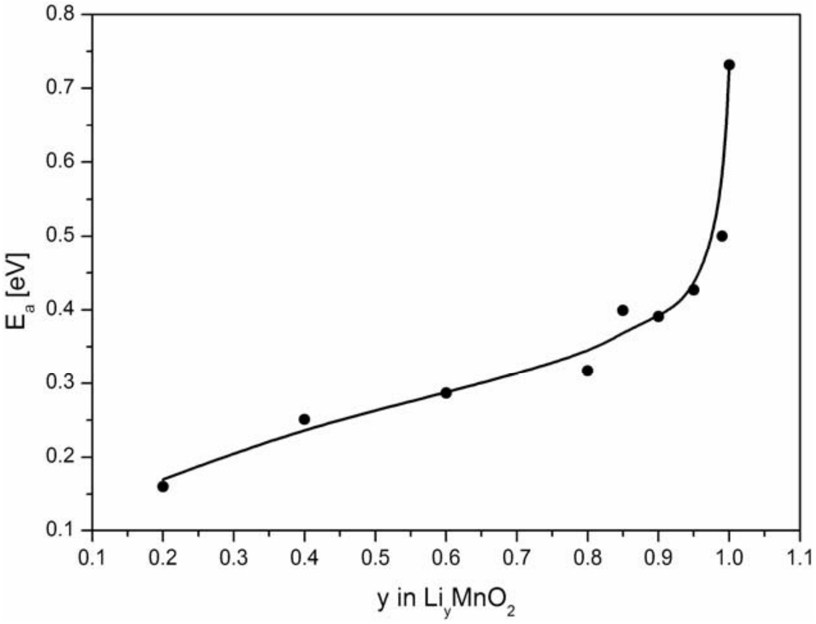

Fig. 7. Conductivity activation energy in deintercalated Li_yMnO_2

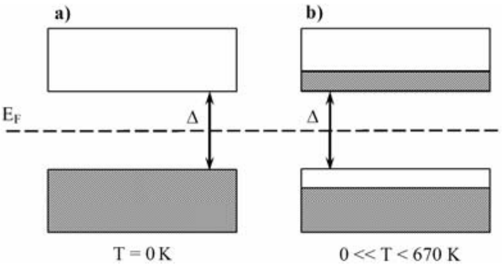

Fig. 8. The electronic structure of $LiMnO_2$ a) at 0 K, b) above 0 K

These results were useful in the elaboration of a qualitative model, which might explain the observed electrical and electrochemical properties. In stoichiometric $LiMnO_2$, a high-spin electron configuration (t_{2g}^3 e_g^1) is favoured. Due to strong interactions between electrons, the effective band e_g^1 splits into two sub-bands with opposite spins (Fig. 8). At 0 K, the lower band is completely filled and the upper one is empty (Fig. 8a). The number of carriers increases with temperature (electrons are generated in the upper sub-band and holes in the lower sub-band). An activation energy of conductivity of 0.7 eV determined for $LiMnO_2$ in the range of 200–350 ºC can be interpreted as the energy gap between the split sub-bands. An analysis of electrical properties of the deintercalated compound Li_yMnO_2 (Figs. 5 and 6) indicates that its electronic structure undergoes modifications at low temperatures (250–350 K). The energy gap becomes smaller, as a consequence of lattice parameter reduction during the deintercalation of lithium (a shortening of the Mn–Mn distance) [3] as is schematically drawn in Fig. 9. The variation in thermoelectric power (Fig. 6) in the direction of positive values with increasing deintercalation degree is consistent with the variation of conductivity (Fig. 5) in so far as the narrowing of the energy gap is concerned. Lack of temperature dependence for thermoelectric power at different compositions y_{Li} indicates that charge transport takes place simultaneously in both split sub-bands (holes in the lower sub-band and electrons in the upper sub-band, Fig. 9).

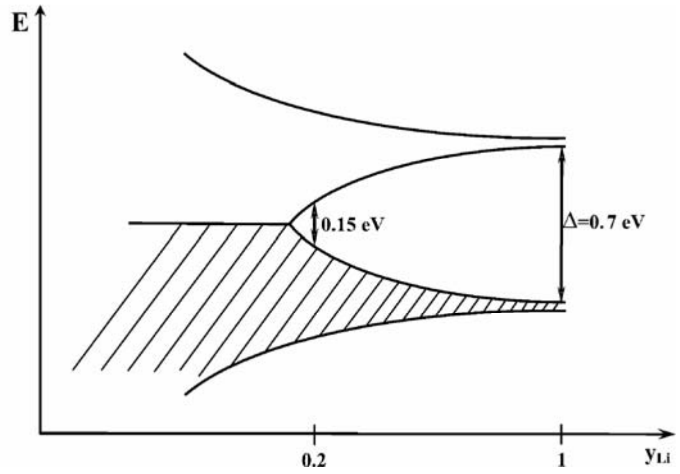

Fig. 9. Modification of the electronic structure of Li_yMnO_2 upon lithium deintercalation

The observed variation in the $Li^+|Li_yMnO_2$ cathode potential (OCV curve in Fig. 3a) of about 0.7 V within the composition range $0.99 < y_{Li} < 0.05$, are quite complex. They can be associated with changes in the electrochemical potential of electrons (Fermi level) due to a decreasing concentration of electrons upon lithium deintercalation, and also with shifts in the Fermi level brought about by a shortening of the Mn–Mn distance in the Li_yMnO_2 structure (Fig. 9). A detailed analysis of correlations between the electronic and electrochemical properties calls for supplementary studies (e.g., XPS, UPS) and an extension of the composition range to lower values of y_{Li}.

Acknowledgements

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