Transport and electrochemical properties of orthorhombic LiMnO₂ 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 LiMnO₂, together with its electrical and electrochemical characterization. High-temperature studies of the electrical properties of orthorhombic LiMnO₂ 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 (Li₂MnO₃ + LiMn₂O₄). Stoichiometric LiMnO₂ 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 LiₙMnO₂ 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 LiₙMnO₂ makes the structure less stable, leading to a two-phase mixture (LiₓMnO₂ + LiₓMn₂O₄).

Key words: orthorhombic LiMnO₂; thermal stability; electrical properties; intercalation; Li-ion battery

1. Introduction

The present technology of Li-ion batteries is based on LiCoO₂ oxide. Manganese oxide, LiMnO₂, 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 LiₙMₙₓO₂ (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$_3$COOLi and (CH$_3$COO)$_2$Mn·4H$_2$O 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$_x$MnO$_2$-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$_2$: 
Higher conductivity of the spinel phase (LiMn₂O₄) 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 LiMn₂O₄ [4] (the conductivity
of Li₂MnO₃ is lower by several orders of magnitude). Manganese spinel, however, is not stable at 800 °C 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 LiMnO₂, the orthorhombic phase stable

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Fig. 3. The charge (a) and discharge (b) curves of the Li[Li⁺][Li,MnO₂] 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 LiMnO₂ at about 650 ºC into manganese spinel LiMn₂O₄ and Li₂MnO₃ via reaction (1).

Figures 3a, b show the charge/discharge curves of a Li|Li⁺|LiₓMnO₂-type cell at the current density of 100 μA/cm². 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 LiₓMnO₂. 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 LiMnO₂ into spinel, with a characteristic voltage of 4 V in a wide range of yMn. X-ray studies confirm the increasing contribution of spinel with progressing lithium deintercalation [3]. This indicates that orthorhombic LiMnO₂, unstable at temperatures exceeding 350 ºC, is also not stable at room temperature, at which the deintercalation/intercalation of lithium takes place.

High resistivity of the cathode material LiₓMnO₂ implies a low chemical diffusion coefficient of lithium, estimated to be 10⁻⁷ cm²/s (Fig. 4).

Fig. 4. Chemical diffusion coefficient of lithium in LiMnO₂ attained by GITT

Figures 5 and 6 demonstrate the temperature dependences of electrical conductivity and thermoelectric power for the starting compound, LiMnO₂, and after the step-wise deintercalation of lithium. Stoichiometric LiMnO₂ shows hardly measurable conductivity at room temperature. At 70 ºC, 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$_2$MnO$_2$.

Fig. 5. Electrical conductivity of deintercalated Li$_y$MnO$_2$ samples

Fig. 6. Thermoelectric power of deintercalated Li$_y$MnO$_2$ samples
The activation energy of conductivity decreases in this process from 0.7 eV 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$_y$MnO$_2$](image)

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 en-
ergy 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$_y$MnO$_2$ (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$_y$MnO$_2$ upon lithium deintercalation](image)

The observed variation in the Li$^+$|Li$_y$MnO$_2$ 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$_y$MnO$_2$ 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 $y_{Li}$.

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References


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