

Thermoelectric Power Measurements of Selected Electrode Materials for Lithium Cells

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Abstract

Electrochemical intercalation / deintercalation of lithium ions into / from host matrix is strongly correlated with transport properties of electrode materials. During the process, these properties of the electrode material are usually modified and sometimes anomalous behaviour is observed. In this work we summarize the results of a thermoelectric power measurement (dynamic technique in variable temperature gradient) together with an electrical conductivity measurement (4 probe AC) of selected spinel type electrode materials for lithium cells. The measurements were conducted on starting materials and on samples with different lithium concentration obtained by a deintercalation in lithium cells.

Introduction

Intercalation / deintercalation process can be described as a topotactic redox reaction during which lithium ions are incorporated into / extracted from host structure (usually transition metal oxide) meanwhile electrons occupy / are removed from their position (in the vicinity of Fermi level) in an electronic structure [1]. Effectiveness of this process is determined by both crystallographic and electronic properties of the material; 2D or 3D structure with a fast diffusion pathways and high density of states near Fermi level are preferable [2]. The above process is a basic concept used in construction of lithium ion cells (i.e. Li_yC_6 / electrolyte containing lithium salt / $\text{Li}_{1-y}\text{CoO}_2$) which are now widely used as a power sources for mobile electronic devices. Construction of an effectively working cell requires many conditions to be fulfilled. For instance for a cathode material high voltage ($>3.5\text{V}$ in relation to a lithium metal anode), high capacity ($>150\text{mAh/g}$), sufficient electrical conductivity, reversibility of the intercalation process and chemical stability seem most important.

Studies regarding possible new materials for lithium cells are being conducted in many laboratories worldwide. Beside the structural studies, the electrical properties measurements seem to be especially important in evaluation of new materials. In this work we present the results of the electrical conductivity and the thermoelectric power measurements of $\text{Li}_y\text{Co}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{Li}_y\text{Cu}_x\text{Mn}_{2-x}\text{O}_4$ spinels.

Experimental

Starting $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ spinels with respectively $0.1 \leq x_{\text{Co}} \leq 0.5$ and $0.1 \leq x_{\text{Cu}} \leq 0.4$ were prepared by high temperature reaction between lithium carbonate, cobalt oxide, copper oxide and manganese carbonate, details can be found elsewhere [3]. Materials with varying lithium concentration (y_{Li}) were obtained by the deintercalation in

$\text{Li} / 1\text{M LiPF}_6$ based electrolyte / cathode material cells. The lithium concentration was calculated using Faraday law. The electrical conductivity was measured by the 4 probe AC method in 220 – 330K temperature range. The thermoelectric power measurements were conducted in 220 – 330K temperature range using the dynamic technique in variable temperature gradient: an rectangular shape sample was placed between two golden electrodes used for collecting thermoelectric voltage (ΔV). An electric heater was used to heat one side of the sample (ΔT of the order of 2K). Two thermocouples were used for collecting temperature from both sides of the sample. The thermoelectric power was calculated using linear regression in $\Delta V - \Delta T$ coordinates.

Results

All of the initial $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ samples as well as the samples with varying lithium concentration were identified to be single phase and possess Fd-3m cubic spinel type structure. Details can be found elsewhere [3].

Lithium manganese spinel LiMn_2O_4 is a mixed ionic – electronic type conductor [4]. The ionic conductivity related to the Li ions movement is believed to be 2 – 3 orders of magnitude lower than the electronic conductivity. The electronic conductivity in LiMn_2O_4 is due to polaron hopping mechanism strictly related to a $[\text{Mn}^{3+}][\text{Mn}^{4+}]$ product. In pure cubic LiMn_2O_4 there are two valence states of manganese: Mn^{3+} and Mn^{4+} (the average Mn valence is +3.5). Structural transition to an orthorhombic structure, which is observed around 280K, is accompanied by so-called “electronic crystallization” and lowers the electrical conductivity [5]. Both Co^{3+} and Cu^{2+} ions substitute Mn ions in octahedral 16d position and therefore change an average valence of manganese ions. In $\text{LiCo}_{0.5}\text{Mn}_{1.5}\text{O}_4$ the average Mn valence is +3.67. Such valence change should have major effect on the electrical conductivity of the materials.

Fig. 1 and fig. 2 show the results of the electrical conductivity and the thermoelectric power measurements of $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ spinels. For comparison, data for pure LiMn_2O_4 spinel is also presented. There is no major change in the electrical conductivity observed for the Co substituted spinels, which is quite surprising, as the $[\text{Mn}^{3+}][\text{Mn}^{4+}]$ product decreases with increasing Co content, which should lower the electrical conductivity. These results can be explained taking into account the effect of Co substitution on a lattice constant of the samples (see [3]). The lattice constant decreases with increasing Co concentration and therefore makes the polaron hopping easier and the total conductivity does not change. The thermoelectric power of $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ materials is in the order of $-100 - -200\mu\text{V/K}$

addition, there are no traces of any structural transition visible on XRD patterns. Similar effects for deintercalated $\text{Li}_y\text{Mn}_2\text{O}_4$, with even higher peak values of TEP are presented elsewhere [1]. The results of the electrical conductivity and the thermoelectric power measurements for deintercalated $\text{Li}_y\text{Co}_{0.2}\text{Mn}_{1.8}\text{O}_4$ and $\text{Li}_y\text{Co}_{0.3}\text{Mn}_{1.7}\text{O}_4$ (Fig. 4 and 5) are similar to the ones obtained for $\text{Li}_y\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$ spinels.

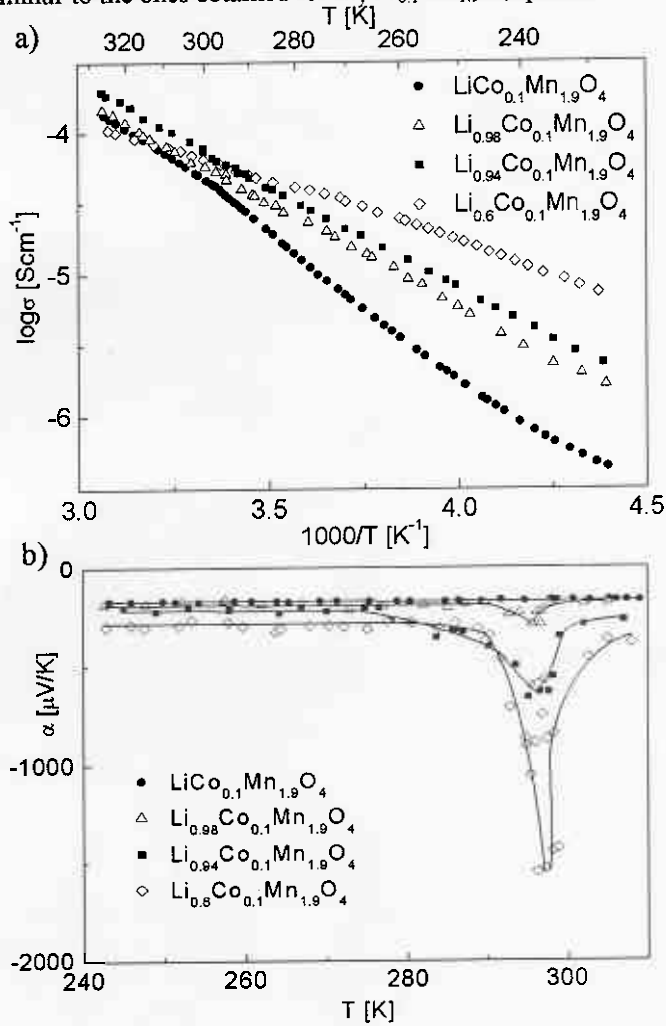


Fig. 3. a) Electrical conductivity, b) thermoelectric power of deintercalated $\text{Li}_y\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$ spinels.

There are no anomalous characteristics observed in the electrical conductivity dependence on the temperature, but in the thermoelectric power dependence relatively sharp peaks appear. These peaks, however, seem to diminish with the increase of cobalt content. The change in the activation energy of the electrical conductivity with the decreasing lithium content is also smaller.

Fig. 5 shows the dependence of the electrical conductivity and the thermoelectric power on temperature for deintercalated $\text{Li}_y\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ samples. With the lithium content decrease, the decrease of the electrical conductivity is observed. The activation energy of the electrical conductivity remains nearly unchanged. The observed dependence of TEP as a function of temperature for deintercalated

$\text{Li}_y\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ samples is anomalous. There are two peaks of TEP present for the $\text{Li}_{0.8}\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ composition and one for the $\text{Li}_{0.91}\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$. The maximum type peak of the order of $500 \mu\text{V/K}$ for the $\text{Li}_{0.91}\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ sample appears near 260K. This peak is different from the ones observed for the other composition or for Co doped samples that are minimum type peaks.

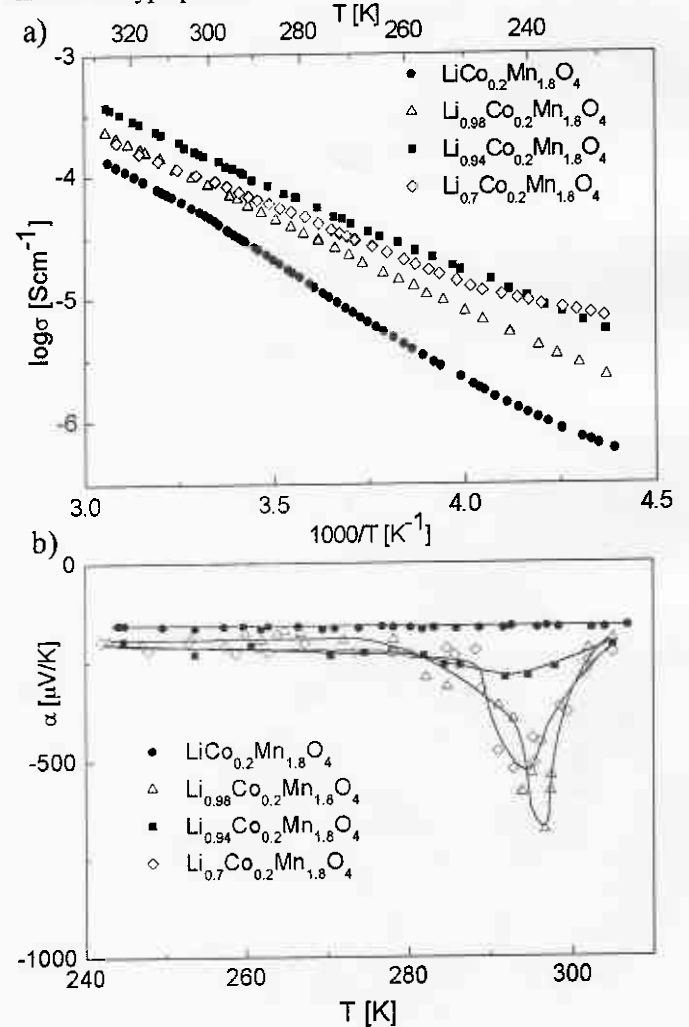


Fig. 4. a) Electrical conductivity, b) thermoelectric power of deintercalated $\text{Li}_y\text{Co}_{0.2}\text{Mn}_{1.8}\text{O}_4$ spinels.

Discussion and Conclusions

The observed anomalous characteristic of the temperature dependence of the thermoelectric power for deintercalated $\text{Li}_y\text{Co}_x\text{Mn}_{2-x}\text{O}_4$ and $\text{Li}_y\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ spinels is similar to the effects observed for the deintercalated $\text{Li}_y\text{Mn}_2\text{O}_4$ [1]. These effects may be also compared to the observed anomalous characteristics obtained for pure LiMn_2O_4 , but there are major differences between them. In LiMn_2O_4 these effects may originate from the phase transition and "electronic crystallization", which appear near 280K. The major difference in the electronic structure and the density of states near the Fermi level between the better conducting cubic

with no major temperature dependence. Negative values of TEP suggest electrons (polarons) as major charge carriers. Contrary to Co substitution (Fig. 1), Cu substituted lithium manganese spinels (Fig. 2) exhibit major changes in both electrical conductivity and thermoelectric power.

attributed to an anomalous density of states near Fermi level and / or anomalous phononic spectra that appear during the transition [1]. There was no structural transformation observed for any of the Co and Cu substituted lithium manganese spinels (see [3]).

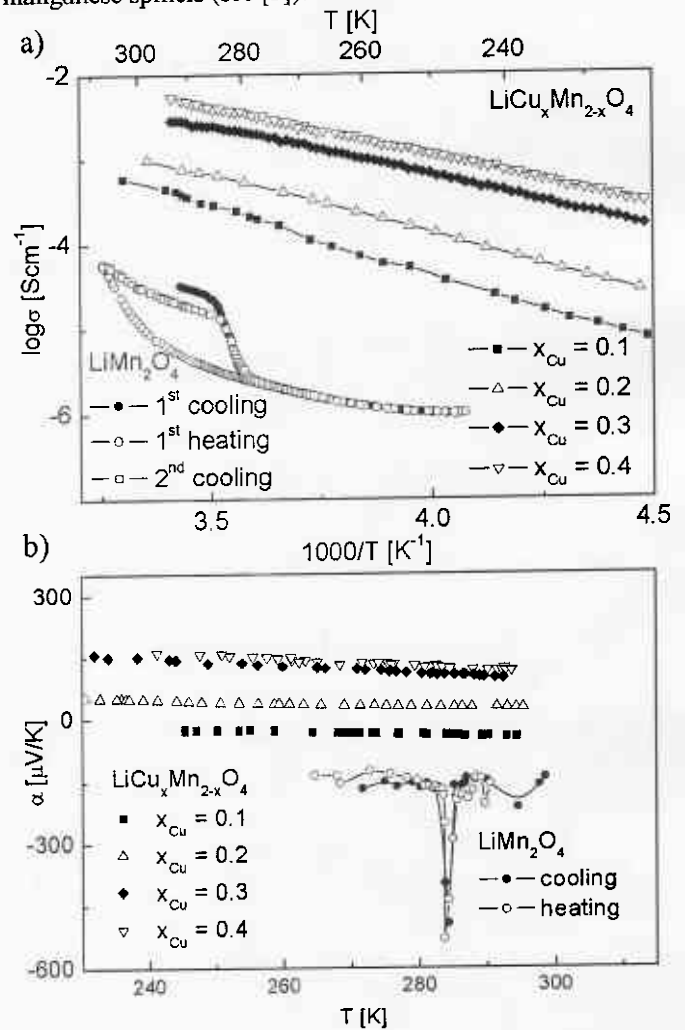
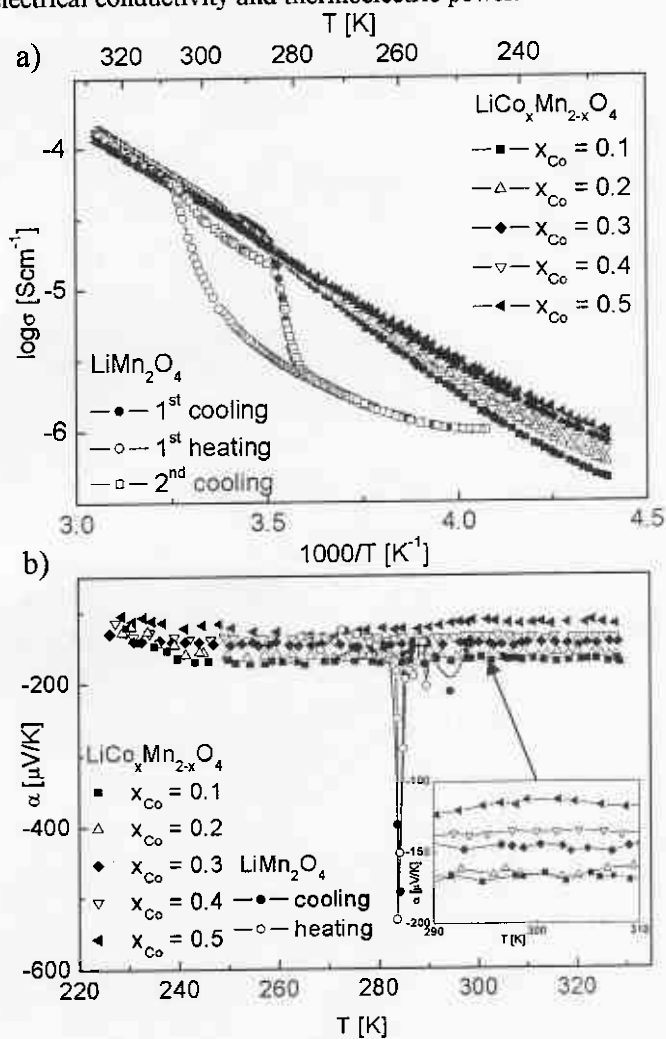


Fig. 1. a) Electrical conductivity, b) thermoelectric power of $\text{LiCo}_x\text{Mn}_{2-x}\text{O}_4$ spinel materials.

Fig. 2. a) Electrical conductivity, b) thermoelectric power of $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ spinel materials.

The electrical conductivity of $\text{LiCu}_x\text{Mn}_{2-x}\text{O}_4$ increases over 2 orders of magnitude with increasing Cu content. Sign of the thermoelectric power changes from negative (for $\text{LiCu}_{0.1}\text{Mn}_{1.9}\text{O}_4$ composition) to positive (for $x_{\text{Cu}} \geq 0.2$). These results suggest that, in contrary to Co substitution, the electrons related to the Cu^{2+} ions participate in charge transport at room temperature. Positive sign of TEP for samples with Cu content ≥ 0.2 suggests that holes are the major charge carries in these materials.

Structural transformation observed for pure LiMn_2O_4 spinel accompanied by the “electronic crystallization” is reflected in its electrical properties: the electrical conductivity drops rapidly around 280K, there is a quite sharp peak of the TEP visible near 280K of the order of $-500\mu\text{V/K}$. It is quite unusual phenomena and probably cannot be easy interpreted as no simple transport mechanism may explain it. It may be

Figs. 3 – 5 show the results of the electrical conductivity and the thermoelectric power measurements for $\text{Li}_y\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$, $\text{Li}_y\text{Co}_{0.2}\text{Mn}_{1.8}\text{O}_4$ and $\text{Li}_y\text{Co}_{0.3}\text{Mn}_{1.7}\text{O}_4$ samples respectively. For decreasing lithium content in $\text{Li}_y\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$ spinels a major decrease of an activation energy (from 0.4eV for starting $\text{LiCo}_{0.1}\text{Mn}_{1.9}\text{O}_4$ to 0.2eV for $\text{Li}_{0.6}\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$) accompanied by an increase of the electrical conductivity at lower temperatures is observed (Fig. 3a). There are peaks in the thermoelectric power dependence on the temperature for the deintercalated $\text{Li}_y\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$ spinels (Fig. 3b). For the $\text{Li}_{0.6}\text{Co}_{0.1}\text{Mn}_{1.9}\text{O}_4$ sample it reaches $-1500\mu\text{V/K}$ that is 3 times higher than the peak observed for pure LiMn_2O_4 . Contrary to pure lithium manganese spinel there is no visible anomalous behaviour observed in the electrical conductivity dependence on the temperature. In

phase and the low temperature orthorhombic phase, that due to "electronic crystallization" possesses lower conductivity, seems to be the major cause of these effects. All of the Co and Cu substituted samples, however, do not undergo the phase transition and there are no anomalous effects observed. These effects appear for the deintercalated samples only, and are only visible on the TEP temperature dependences. It suggests that the nature of these effects is more complicated and may be related to the nature of the deintercalation process.

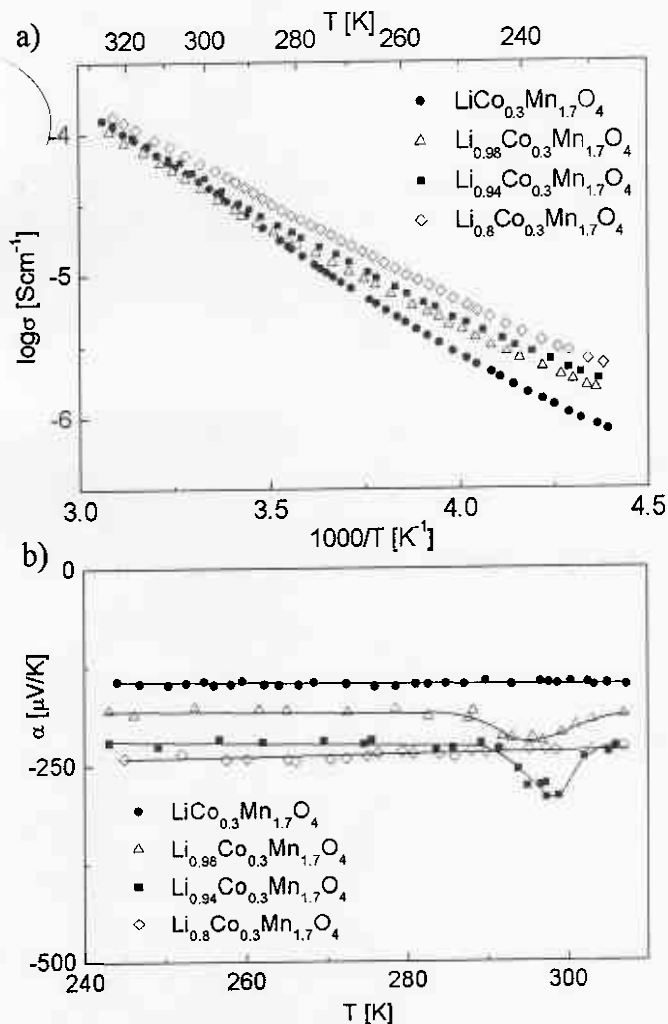


Fig. 5. a) Electrical conductivity, b) thermoelectric power of deintercalated $\text{Li}_x\text{Co}_{0.3}\text{Mn}_{1.7}\text{O}_4$ spinels.

We speculate, that in these materials, locally, at the atomic scale level, similar ordering of charges appears, but as $[\text{Mn}^{3+}]/[\text{Mn}^{4+}]$ ratio is different than in pure LiMn_2O_4 no long range ordering is possible, and therefore no phase transition appears. With increasing Co content observed effects diminish, what can be related to the greater changes in $[\text{Mn}^{3+}]/[\text{Mn}^{4+}]$ ratio. These anomalous effects appear only during the electrochemical deintercalation process, which by its nature is slow and may produce metastable materials, with properties different from the ones obtained by a high temperature synthesis or by a fast chemical deintercalation.

Acknowledgments

One of the authors (K. Ś) would like to thank the Foundation for Polish Science for the financial support in the form of Annual Stipend for Young Scientists.

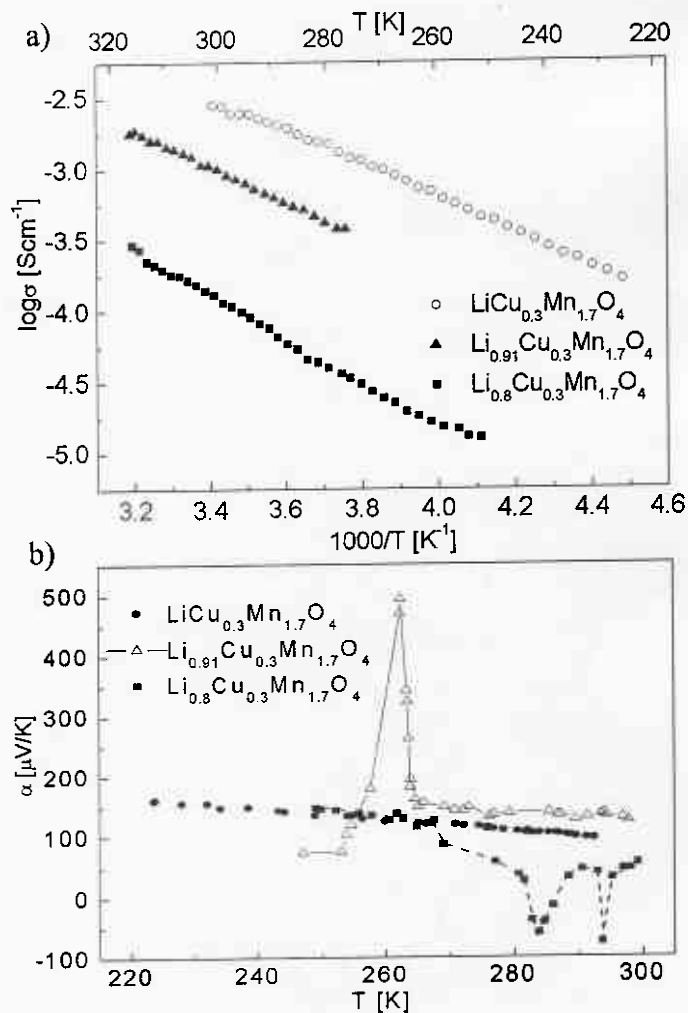


Fig. 6. a) Electrical conductivity, b) thermoelectric power of deintercalated $\text{Li}_x\text{Cu}_{0.3}\text{Mn}_{1.7}\text{O}_4$ spinels.

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