

# Electrochemical intercalation of lithium in ternary metal molybdates $M\text{MoO}_4$ (M: Cu, Zn, Ni and Fe)

N.N. Leyzerovich\*, K.G. Bramnik, T. Buhrmester, H. Ehrenberg, H. Fuess

*Institute of Materials Science, University of Technology Darmstadt, D-64287 Darmstadt, Germany*

## Abstract

Ternary oxides with general formula  $M\text{MoO}_4$  (where M is a 3d-transitional metal) were characterized as cathode materials for lithium rechargeable batteries by galvanostatic charge–discharge technique and cyclic voltammetry. The significant capacity fading after the first cycle of lithium insertion/removal takes place for different copper molybdates ( $\alpha\text{-CuMoO}_4$  and high-pressure modification  $\text{CuMoO}_4\text{-III}$ ) corresponding to the irreversible copper reduction and formation of  $\text{Li}_2\text{MoO}_4$  during the first discharge. X-ray powder diffraction data reveal the decomposition of pristine  $\text{ZnMoO}_4$  by electrochemical reaction, lithium zinc oxide with the NaCl-type structure and  $\text{Li}_2\text{MoO}_3$  seem to be formed. Lithium intercalation into nickel and iron molybdates is shown to proceed without phase transitions, but at unsatisfactory low operating voltages.

© 2003 Elsevier B.V. All rights reserved.

*Keywords:* Batteries; Lithium intercalation; Molybdates

## 1. Introduction

Among the systems which are intriguing in the rechargeable lithium ion technology molybdenum(VI) compounds remain of significant potential. The idea to take an advantage of the charge couple  $\text{Mo}^{6+}/\text{Mo}^{4+}$  where the metal-redox oxidation state can change by two units is very attractive for the development of batteries with high capacity and consequently, with high energy density. Since more than 20 years the various molybdenum oxides have been tested as cathode materials in lithium rechargeable batteries [1–5]. However, the significant capacity fading after several cycles accompanied with irreversible structure transformations during the first discharge (lithium insertion) has been reported.

Mixed-molybdenum oxides are interesting as “hosts” for lithium insertion while the combination of two metals in oxide-matrices produces the materials with new structure and chemical properties compared to that of binary oxides. Additionally, because in many cases the bimetallic oxides can form different crystal structures or phases depending on the synthetic conditions and compositions, a large variety

of systems could be modeled and tested. Vanadium-based compounds like  $\text{MVO}_4$  (M: In, Cr, Fe, Al, Y and Ni) were shown to be good candidates for anode materials in lithium batteries [6,7]. However, up to now there are very few investigations concerning lithium intercalation into the same type of molybdenum compounds. Quite early the copper molybdate was probed as cathode for primary lithium battery, but the reversibility of intercalation was not discussed [8,9]. Recently, the low potential lithium insertion in manganese-molybdenum oxide and its potential application as anode material in lithium batteries has been described [10].

In this work, we report our results of electrochemical insertion of lithium into ternary molybdates  $\alpha\text{-MMoO}_4$  (M: Cu, Zn, Ni and Fe).  $\alpha\text{-CuMoO}_4$  is known to crystallize in the triclinic system (space group  $P\bar{1}$ ), where three molybdenum atoms on different sites are tetrahedrally coordinated by oxygen [11]. For comparison, the high pressure modification  $\text{CuMoO}_4\text{-III}$  (space group  $P\bar{1}$ ) [12,13] with molybdenum atoms octahedrally coordinated by oxygen was included in this investigation.  $\text{ZnMoO}_4$  is isotypic with  $\alpha\text{-CuMoO}_4$ . The  $\alpha$ -phases of  $\text{NiMoO}_4$  and  $\text{FeMoO}_4$  crystallize in the monoclinic space group  $C2/m$ , where both Ni and Mo ions are localized in oxygen octahedra [14,15].

This investigation is focussed on the testing and characterization of these compounds as cathode materials for lithium

\* Corresponding author.

*E-mail address:* [natascha@steno.st.mw.tu-darmstadt.de](mailto:natascha@steno.st.mw.tu-darmstadt.de) (N.N. Leyzerovich).

rechargeable batteries. At the same time data presented here can provide better insight into the operating mechanisms of lithium intercalation into mixed molybdenum oxides.

## 2. Experimental

Ternary metal  $\alpha$ -molybdates were synthesized by solid-state reaction of a stoichiometric mixture of  $\text{MoO}_3$  (99.99% Aldrich) and MO (M: Fe, Ni, Cu and Zn) (99.99% Aldrich) as described previously [11]. The reactants were thoroughly mixed in agate mortar under acetone, sealed in a platinum crucible and heated at  $700^\circ\text{C}$  for 72 h. Afterwards the reaction product was cooled down at a rate of  $120^\circ\text{C/h}$  to room temperature. The high pressure modification  $\text{CuMoO}_4\text{-III}$  was prepared following the procedure described by Tali et al. [12]. Phase identification was performed by X-ray powder diffraction.

Electrochemical studies were carried out with a multichannel potentiostatic–galvanostatic system VMP (Perkin-Elmer Instruments, USA). Swagelok<sup>TM</sup>-type two-electrode cells were assembled in an argon filled glove box using lithium negative electrode and glass-fibre separator soaked with a electrolyte solution. The electrolyte was Selektipur-30 (Merck, Germany, 1 M  $\text{LiPF}_6$  in EC:DMC, 1:1 vol.%), which was used as received. The composite cathode was fabricated as follows: 80% active material, 15% acetylene carbon black and 5% polyvinylidene fluoride as polymer binder were intimately mixed, ground in an agate mortar and pressed into a pellet of about 30 mg. A three electrode glass-cell with lithium as reference and counter electrodes was used for the cyclic voltammetry experiments. In this case the cathode was prepared by pressing of the cathode mix ( $\sim 3$  mg) onto Ni-mesh. Then, the cell was mounted and operated in a dry argon atmosphere. All the experiments were performed at room temperature.

We conducted our electrochemical experiments either in current-controlled or in potential-controlled mode. Galvanostatic cycling was carried out with  $0.5\text{ mA/cm}^2$  current density between the selected voltage limits. The amount of intercalated lithium was calculated based on the charge passed through the cell and cathode mass. Electrochemical potential spectroscopy experiment (EPS) [16] conditions were set at 5 mV potential step with  $I_{\text{lim}} = 0.15\text{ mA/cm}^2$ .

Structure characterization of cathode materials was made after galvanostatic charge–discharge of the cells to the desired depth of intercalation. The cathode was picked out from the cell and studied by X-ray powder diffraction. The data were collected with a STOE STADI/P powder diffractometer (Co  $K\alpha_1$  radiation, curved Ge monochromator, transmission mode, step  $0.02^\circ$  ( $2\theta$ ), linear PSD counter). For structure refinements the RIETAN-97 program was used [17], based on the Rietveld method with a modified pseudo-Voigt profile function.

## 3. Results and discussion

### 3.1. $\alpha\text{-CuMoO}_4$ and $\text{CuMoO}_4\text{-III}$

The evolution of cell voltage with composition ( $x$  mol Li per formula unit of copper molybdate) was obtained for two modifications of  $\text{CuMoO}_4$  from the galvanostatic cycling in the potential range 0.5–3 V at the current density of  $0.5\text{ mA/cm}^2$  (Fig. 1). During the first discharge down to 0.5 V both compounds intercalate the same number of lithium ions ( $\sim 5$ ) per formula unit, that corresponds to about 600 mAh/g deliverable capacity. Nevertheless, the character of the first discharge curves is quite different. The first lithium insertion into the  $\alpha$ -form proceeds through four flat areas at the  $E = f(x)$  curve in the ranges 2.9, 2.7, 1.6 and 1–0.5 V, respectively. For  $\text{CuMoO}_4\text{-III}$  the first and second plateau are identified at lower voltage (2.7 and 2.4 V) and, then, after insertion of 1 Li equivalent per mol  $\text{CuMoO}_4\text{-III}$ , the voltage changes to 1 V with the reasonably high slope  $dV/dx$ . For both compounds, about 3 mol Li per formula unit cannot be removed from cathode upon the following charge up to 3 V. This indicates that the cathode material undergoes an irreversible structure transformation at the first lithiation.

The incremental capacity versus voltage plots shown in Fig. 2 exhibit several peaks which can be correlated quite well with the voltage plateau in the range 3.5–1.2 V at the voltage–composition curves. In the beginning of the first discharge two adjacent peaks were detected at 2.83 and 2.77 versus  $\text{Li}^+/\text{Li}$  for  $\alpha\text{-CuMoO}_4$ , 2.72 and 2.52 for  $\text{CuMoO}_4\text{-III}$ . These sharp peaks are known to be characteristic of structural phase transitions [16]. At that time, no appropriate peaks were observed during charging. Therefore, EPS-experiment reveals, that the irreversible behavior of these systems results from the two-step transformations of cathode compounds occurring at the initial stage of discharge. Relatively broad and weak peaks detected at about 1.6 V seem to be attributed to the continuous changing of the stoichiometry of the system inside the single-phase region.

In order to obtain the information about structural changes of pristine copper molybdates we performed XRD study for cathodes after 8 cycles in the charged state. No difference in the phase compositions of the samples ( $\alpha\text{-CuMoO}_4$  and  $\text{CuMoO}_4\text{-III}$ ) could be observed, both diffraction patterns containing diffraction peaks of metallic copper and  $\text{Li}_2\text{MoO}_4$ . Metallic copper can be visually identified at the surface of the sample after extracting cathodes from the cell. Thus, during the first lithiation the irreversible reduction of the copper, accompanied with the formation of  $\text{Li}_2\text{MoO}_4$  takes place for both copper molybdates. XRD-study for two samples of  $\alpha\text{-CuMoO}_4$  with different depths of the first discharge ( $x = 0.9$  and 2.5) shows the presence of metallic Cu,  $\text{Li}_2\text{MoO}_4$  and some amount of pristine  $\text{CuMoO}_4$  at the potential 2.7 V (the end of the second plateau at the voltage–composition curve) (Fig. 3). If the system is discharged to  $x = 2.5$  (the third plateau) metallic Cu and  $\text{Li}_2\text{MoO}_4$  were

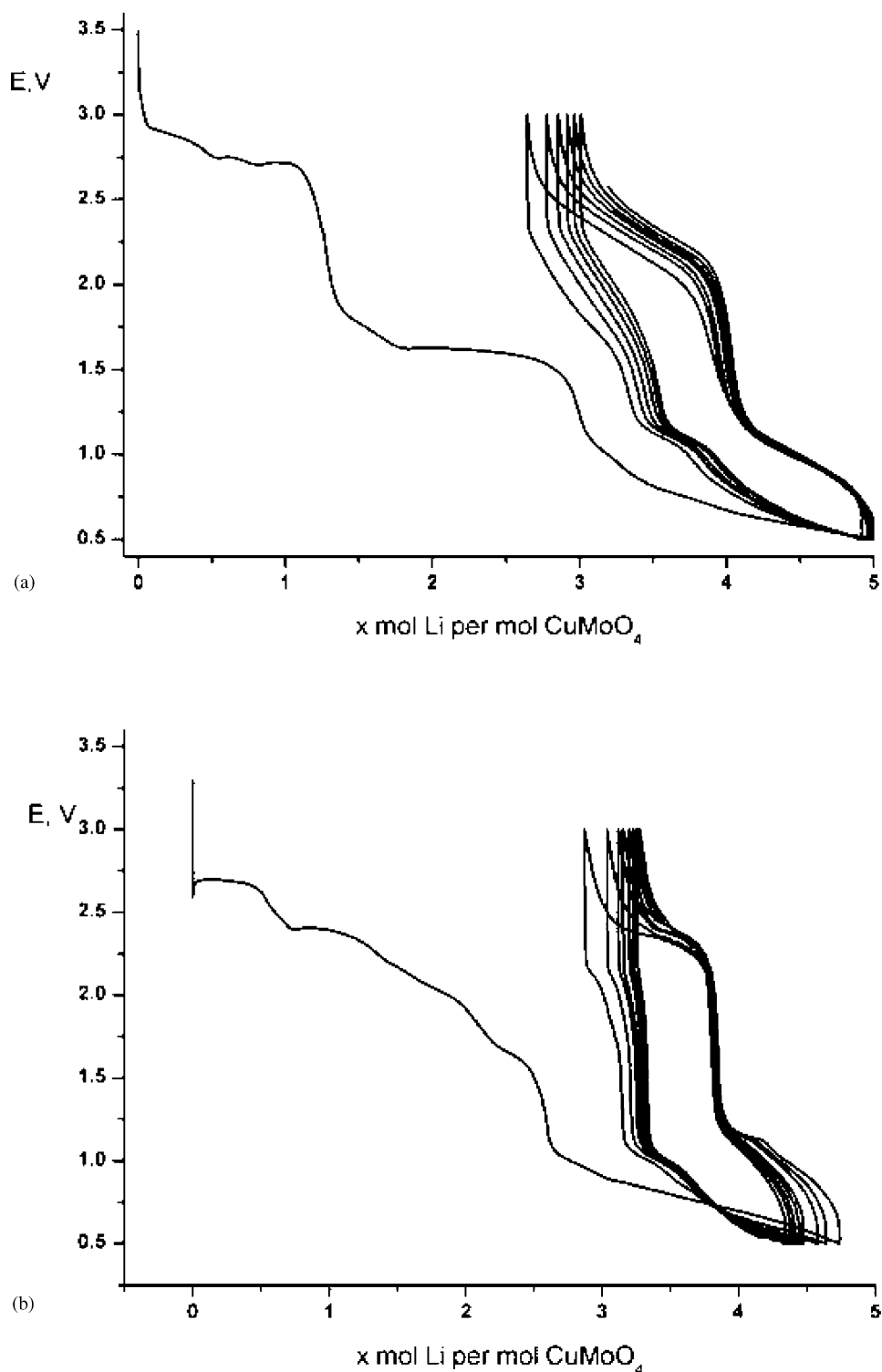


Fig. 1. Charge–discharge curves of the cells with  $\alpha$ -CuMoO<sub>4</sub> (a) and CuMoO<sub>4</sub>-III (b) as cathode materials at the rate 0.5 mA/cm<sup>2</sup> (cut-off voltages 0.5 and 3 V).

identified only. Consequently, after reduction of Cu the following insertion of Li into Li<sub>2</sub>MoO<sub>4</sub> proceeds via changing of stoichiometry without any structural phase transition.

The behaviour of the two forms of CuMoO<sub>4</sub> after the first discharge is quite similar. It is not surprising, because the

initial reduction leads to the formation of the same insertion compound Li<sub>2</sub>MoO<sub>4</sub> in both cases. Lithium intercalation occurs here at relatively low voltages so that copper molybdates cannot be assumed as good cathode materials for lithium rechargeable batteries.

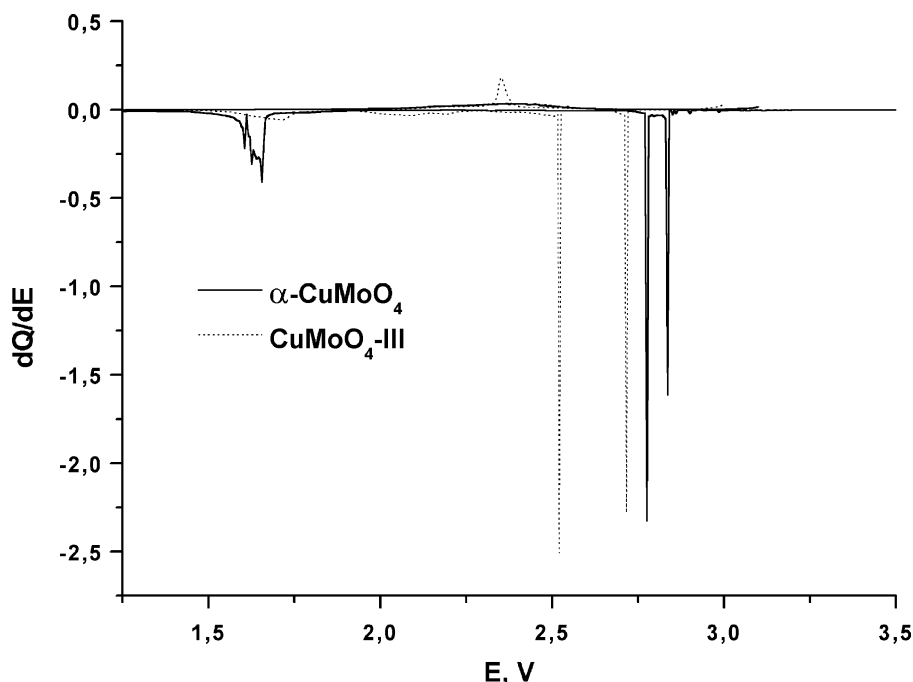


Fig. 2. First cycle differential capacity plot for Li/copper molybdate cells.

### 3.2. ZnMoO<sub>4</sub>

While zinc is a stronger reduction agent in comparison to copper ( $E_{\text{Cu}^{2+}/\text{Cu}} = 0.345 \text{ V}$ ,  $E_{\text{Zn}^{2+}/\text{Zn}} = -0.762 \text{ V}$ ), one can expect that the intercalation of lithium into mixed zinc-molybdenum oxide occurs without participation of zinc in the redox reaction. We characterized this cathode material by cyclic voltammetry and galvanostatic cycling. ZnMoO<sub>4</sub> demonstrates different charge–discharge profiles compared

to the copper molybdates (Fig. 4). After intercalation of 0.02 Li per ZnMoO<sub>4</sub> the cell voltage drops from 3.2 V (open-circuit voltage) to 1.6 V and, then, the voltage plateau is identified up to  $x$  approximately 0.8. This plateau was not observed in further charge–discharge operations. Being cycled in the range of 0.6–3 V the cell shows significant capacity fading from 260 and 255 mAh/g in the first and second cycle, respectively, to 70 mAh/g in the seventh cycle.

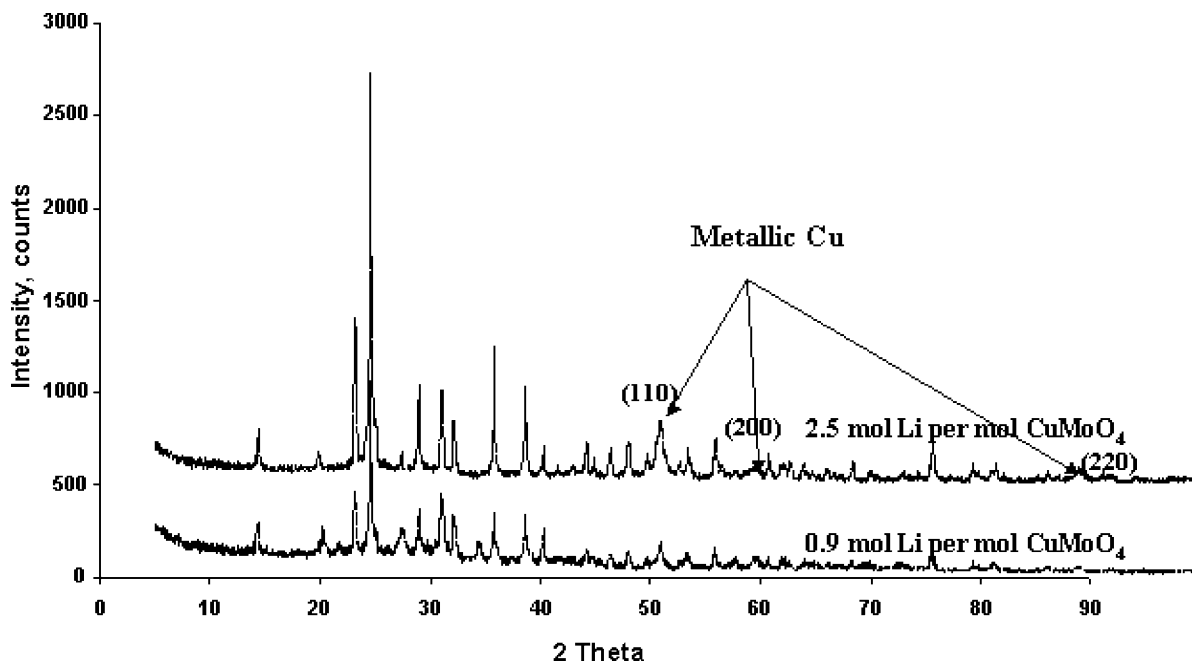


Fig. 3. X-ray powder diffraction patterns of composite  $\alpha$ -CuMoO<sub>4</sub> cathodes discharged to  $x = 0.9$  and 2.5.

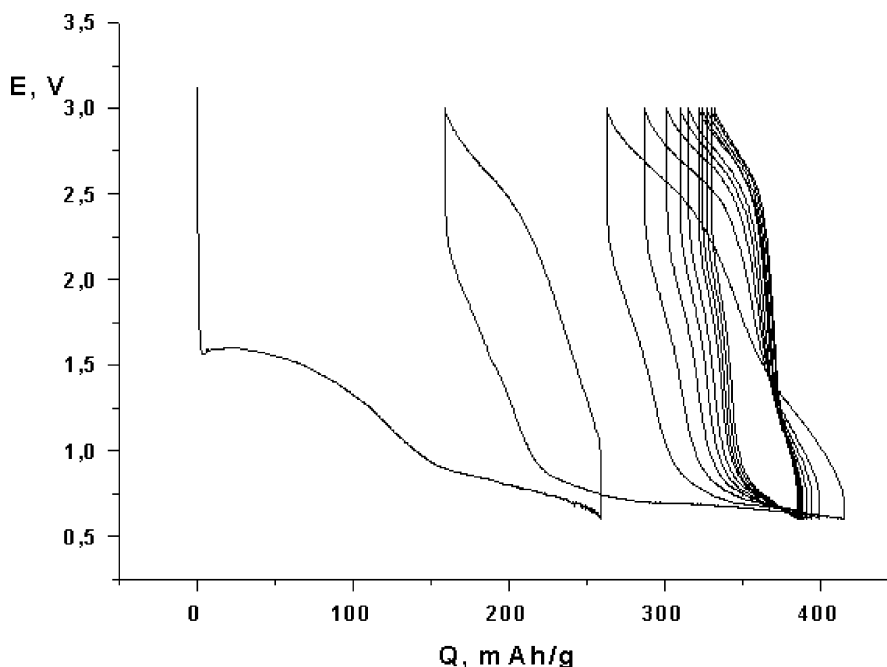


Fig. 4. Galvanostatic cycling for  $\text{ZnMoO}_4$  at the current density  $0.5 \text{ mA/cm}^2$  in the voltage range  $0.6\text{--}3.0 \text{ V}$ .

In cyclic voltammetry experiment a wider voltage range between the potential limits  $0.0$  and  $3.2 \text{ V}$  versus  $\text{Li/Li}^+$  was chosen and the series of scans was performed at a slow scan rate of  $0.1 \text{ mV/s}$ . Comparing the curves shown in Fig. 5, one can see immediately the difference between the first and following cycles. The broad peak at  $1.5 \text{ V}$  and partially overlapped peaks at  $0.52$  and  $0.33 \text{ V}$  were observed at the first potential sweep in the cathodic direction. However, the anodic branch contains only very broad peaks at  $0.7$  and  $1.6 \text{ V}$

with small intensity. Such behavior of  $\text{ZnMoO}_4$ -cathode is indicative for irreversible electrode reaction. In the second scan the intensity of cathodic peaks decreases dramatically and anodic peaks are not visible. Moreover, after 5 cycles the cathodic peaks disappear almost completely.

The XRD-data obtained for a cathode after the first discharge to  $x = 0.4$  (Fig. 6) reveal the presence of three phases: pristine  $\text{ZnMoO}_4$ ,  $\text{Li}_2\text{MoO}_3$  and an unknown compound. All diffraction peaks, which did not belong to  $\text{ZnMoO}_4$  and

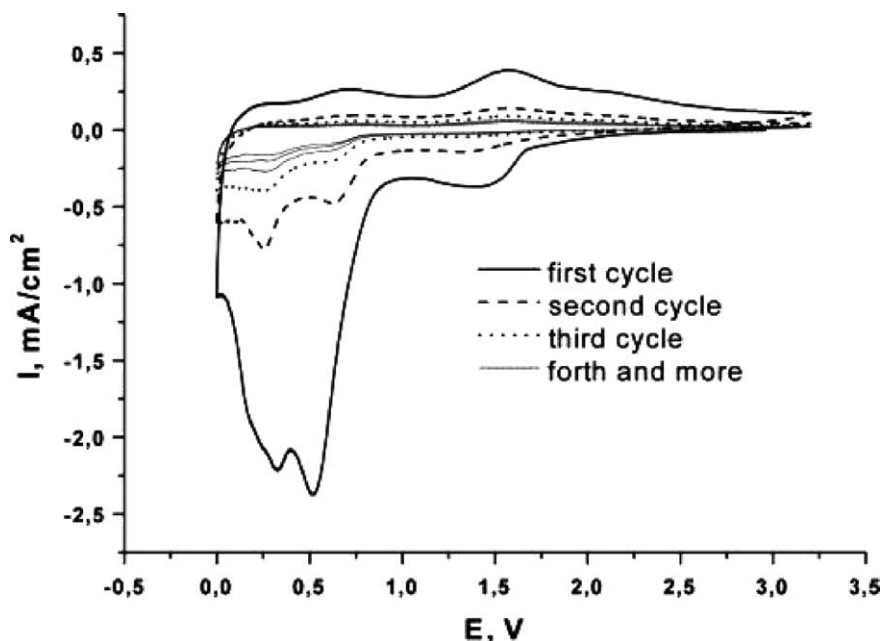


Fig. 5. Cyclic voltammogram of  $\text{ZnMoO}_4$  at the scan rate  $0.1 \text{ mV/s}$  (electrolyte  $1 \text{ M LiPF}_6$  in EC-DMC, reference, counter electrodes—metallic Li).

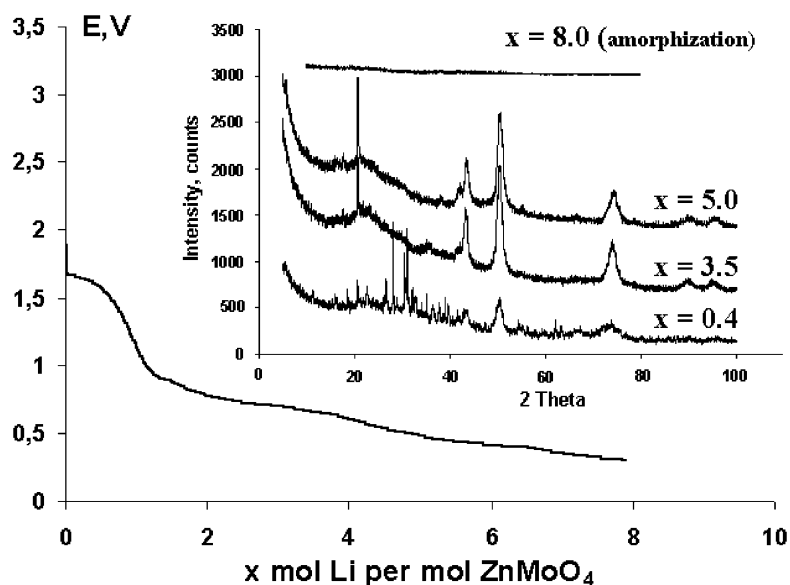


Fig. 6. Voltage–composition profile during galvanostatic ( $0.5 \text{ mA/cm}^2$ ) intercalation of 8 Li per  $\text{ZnMoO}_4$  unit and X-ray diffraction patterns at different depths of discharge.

$\text{Li}_2\text{MoO}_3$ , could be indexed on the base of  $F$ -centered cubic cell with cell parameter  $a = 4.197(2) \text{ \AA}$ . The Bragg peaks of  $\text{ZnMoO}_4$  completely disappear in the X-rays diffraction pattern for the cathode discharged to  $x = 3.5$ . A deeper discharge of the cell to  $x = 5$  does not change the positions of the peaks attributed to unknown compound significantly. However, after the intercalation of approx. 8 mol Li per mol  $\text{ZnMoO}_4$  the XRD-pattern is typical for a completely amorphous sample. To date, the amorphization of several molybdates upon the deep lithiation has already been repeatedly reported [6,10].

Two-phase Rietveld refinement of X-ray powder data for the sample obtained at the intercalation of 5 Li per pristine

$\text{ZnMoO}_4$  was also carried out (Fig. 7). Due to the similarity between the cell parameters of the unknown compound and the already described compound  $\text{Li}_{0.21}\text{Co}_{0.79}\text{O}$  [18], which has NaCl-type structure (space group  $Fm\bar{3}m$ ), the crystal structure of  $\text{Li}_{0.21}\text{Co}_{0.79}\text{O}$  was used as the initial structure model for the refinement. The atomic parameters for the second phase,  $\text{Li}_2\text{MoO}_3$ , were taken from [19]. After sequential iterations, good agreement between experimental and calculated patterns was achieved:  $R_1 = 0.028$ ,  $R_p = 0.039$ ,  $R_{wp} = 0.051$ . ( $R_1 = 0.047$  for  $\text{Li}_2\text{MoO}_3$ ).

To resume, the electrochemical intercalation of Li into  $\text{ZnMoO}_4$  leads to the formation of a two-phase system:  $\text{Li}_2\text{MoO}_3$  and a Zn-containing phase, which possesses the

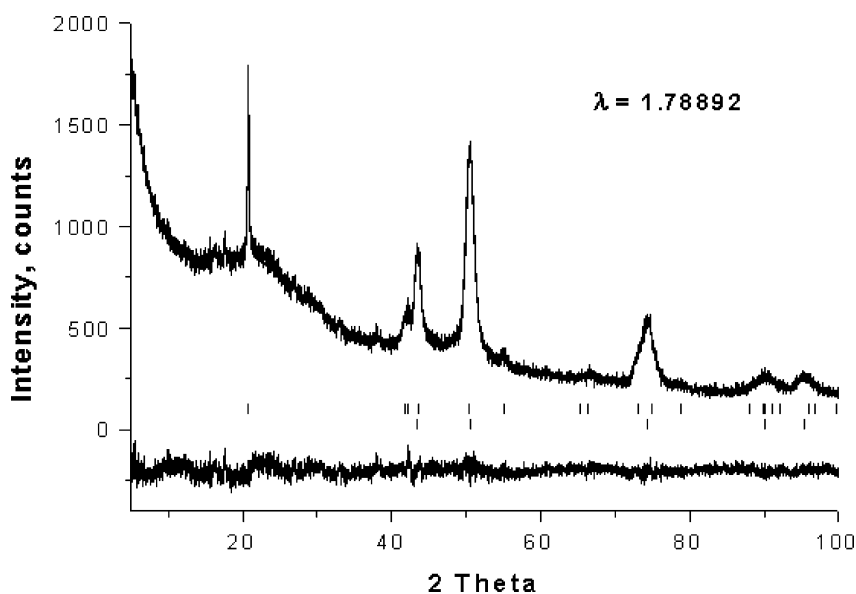


Fig. 7. Experimental, calculated and difference X-ray powder diffraction pattern for cathode intercalated 5 Li per mol pristine  $\text{ZnMoO}_4$ .

rock salt structure and was not previously described. Recently, the formation of the intermediate compound with NaCl-type structure during electrochemical lithiation of  $\text{MnMoO}_4$  was reported by Kim et al. [10]. The authors observed this compound as the only product at transformation of the pristine  $\text{MnMoO}_4$  upon the discharge down to 0.25 V, after that the amorphization of the sample occurs. It was shown [10], that the lattice constant of this compound was 4.30 Å and this value is in good agreement with the theoretical lattice constant of  $\text{Li}_2\text{MnMoO}_4$  (4.27 Å) calculated

based on the ionic radii reported by Shannon [20]. In our case, the presence of  $\text{Li}_2\text{MoO}_3$  and an unknown compound with NaCl-structure was established in the discharged sample. It is difficult to imagine the simultaneous formation of  $\text{Li}_2\text{MoO}_3$  and  $\text{Li}_2\text{ZnMoO}_4$  during lithium intercalation. One of the possible mechanisms can include the destruction of pristine  $\text{ZnMoO}_4$  leading to the formation of lithium zinc oxide ( $\text{Li}_x\text{Zn}_{1-x}\text{O}$ ) with NaCl-type structure and molybdenum oxide. In this case the intercalation could proceed into these two phases simultaneously.

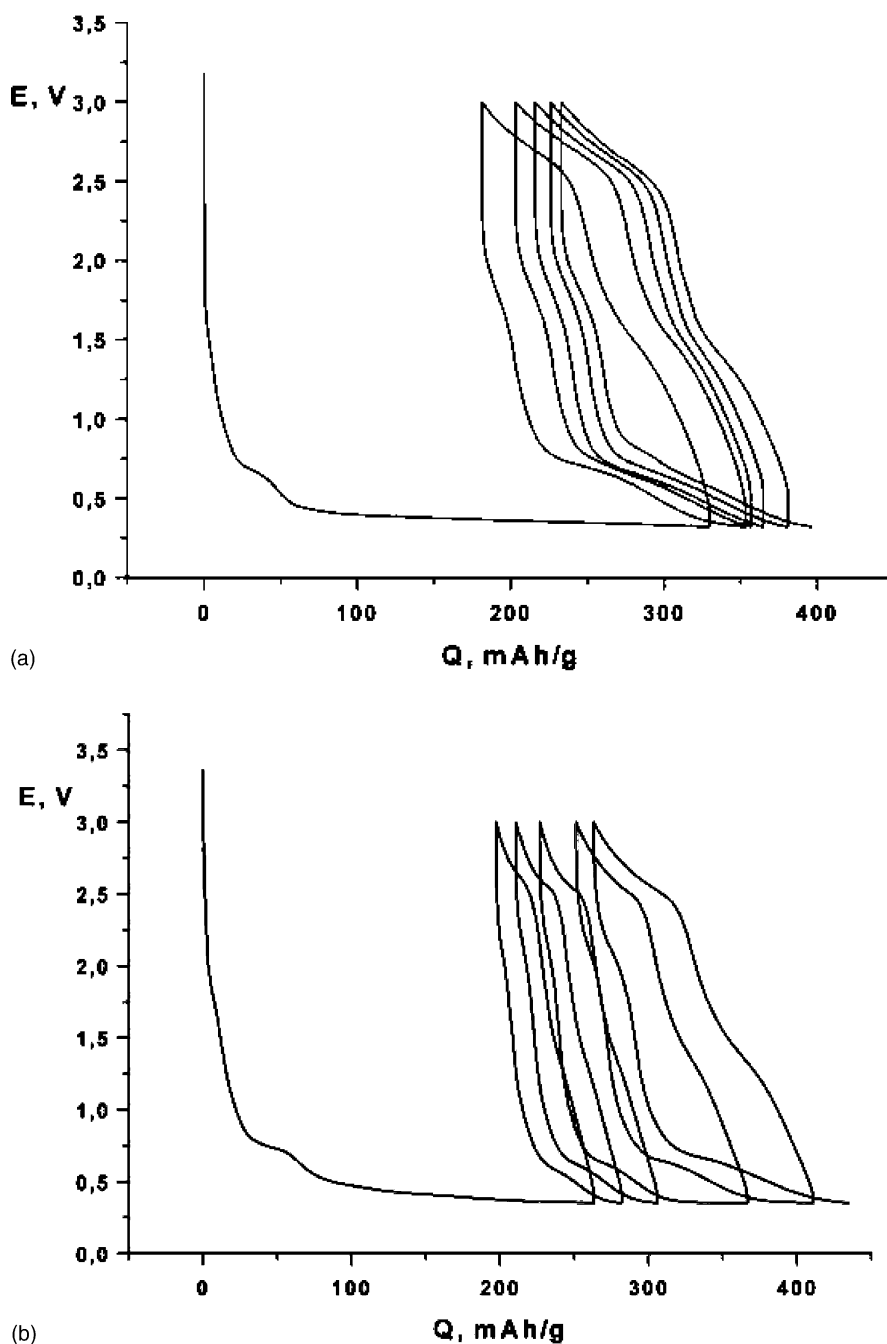


Fig. 8. Galvanostatic charge–discharge curves for  $\text{NiMoO}_4$  (a) and  $\text{FeMoO}_4$  (b) at current density  $0.5 \text{ mA/cm}^2$ , cut-off voltages 3–0.35 V.

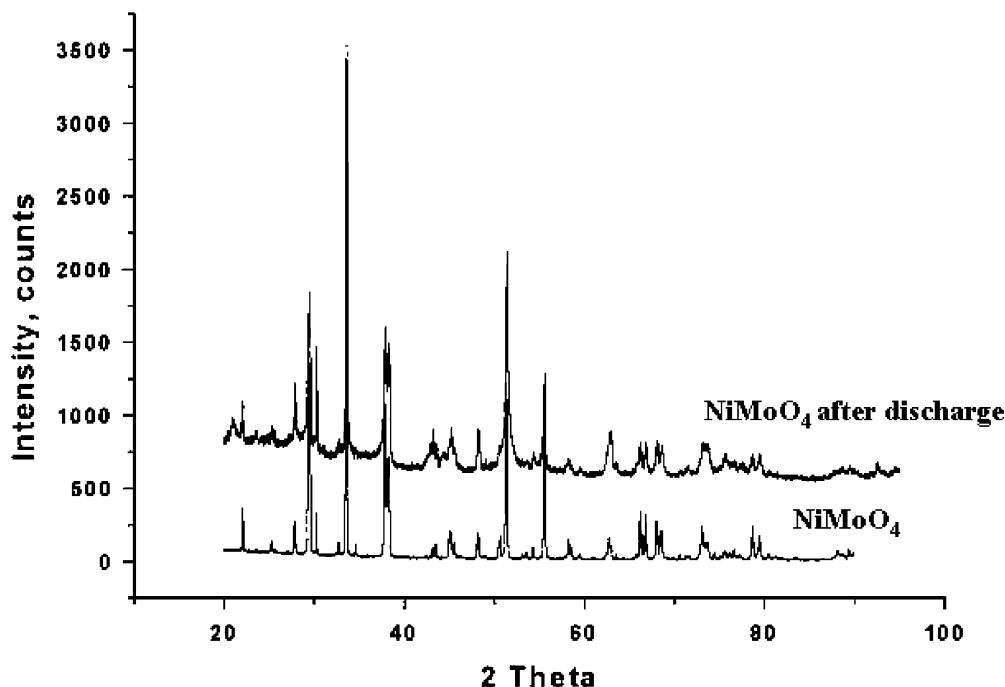


Fig. 9. X-rays diffraction patterns for pristine NiMoO<sub>4</sub> and intercalated sample containing 2 mol Li per mol NiMoO<sub>4</sub>.

### 3.3. NiMoO<sub>4</sub> and FeMoO<sub>4</sub>

Nickel and iron molybdates exhibit a similar voltage–composition profile at the first discharge of the cell, the intercalation proceeding mainly in the low voltage region (0.7–0.3 V) (Fig. 8). After the discharge to  $x = 2$  (245 mAh/g), no difference was detected in diffraction patterns of pristine NiMoO<sub>4</sub> and the intercalated sample,

containing 2 Li per NiMoO<sub>4</sub> (Fig. 9, the data obtained for FeMoO<sub>4</sub> are very similar and are therefore not shown here). Obviously, insertion of lithium does not lead either to the formation of a new phases or to shifts of the peak positions in the X-ray diffraction pattern. On the other hand, the fact, that the intercalation does not cause any change of pristine compound is quite surprising. It is possible, that during the redox-reaction Li-ions are not incorporated into the

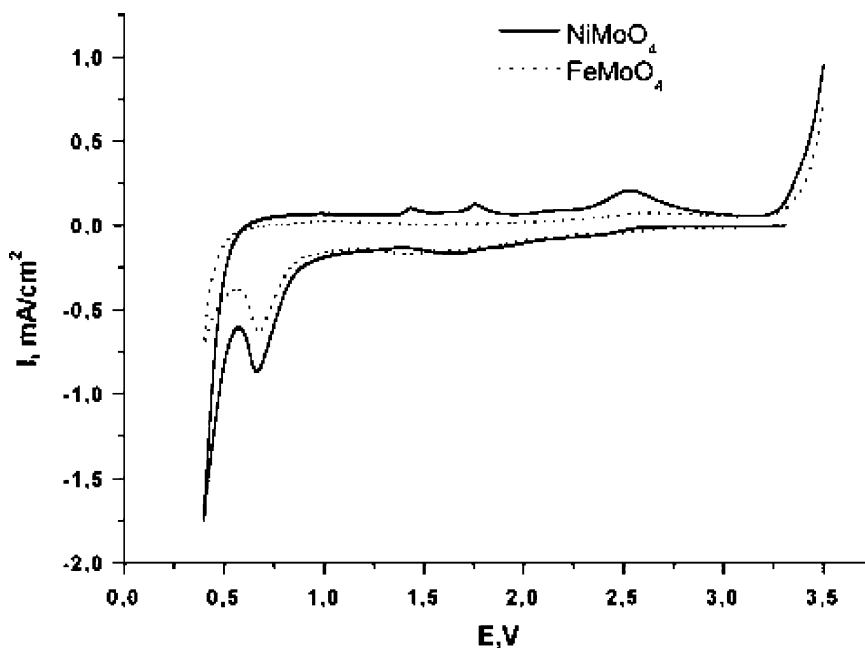


Fig. 10. Cyclic voltammogram of NiMoO<sub>4</sub> and FeMoO<sub>4</sub> at scan rate 0.1 mV/s (electrolyte 1 M LiPF<sub>6</sub> in EC-DMC, counter, reference electrodes—metallic Li).



structure of the cathode materials and, in this case, the use of the term “intercalation” is not appropriate. Considering the cycling behavior of both compounds implies the irreversibility of the first lithiation. The cyclic voltammograms for NiMoO<sub>4</sub> and FeMoO<sub>4</sub>-cathodes (Fig. 10) illustrate that the reduction in the first cycle starts at a potential below 0.7 (the first peak at 0.6 V and the following increase of the potential at 0.5 V). Then, the appropriate oxidation process could be ascribed to the increase of the potential at 3.3 V in the anodic range. Therefore, although lithium intercalation does not decompose the structure of NiMoO<sub>4</sub> and FeMoO<sub>4</sub>, the electrochemical reaction proceeds in these cases with extremely high overvoltage, so that these compounds seem to be unsatisfactory as cathode materials in lithium batteries applications.

#### 4. Conclusions

For two out of four studied cathode materials, copper and zinc molybdate, an irreversible phase transformation during the first lithiation was observed. Lithium intercalation into copper molybdates proceeds through the irreversible copper reduction and the formation of Li<sub>2</sub>MoO<sub>4</sub>. The further lithium intercalation into Li<sub>2</sub>MoO<sub>4</sub> is possible, but galvanostatic cycling reveals, that this process occurs at relatively low voltages. On the other hand, the lithium insertion into ZnMoO<sub>4</sub> results in formation of Li<sub>2</sub>MoO<sub>3</sub> and an unknown compound with NaCl-type structure. We suppose, that this compound can be considered as mixed lithium zinc oxide Li<sub>x</sub>Zn<sub>1-x</sub>O, but, to confirm this assumption, additional methods have to be applied. The testing of nickel and iron molybdates showed that the low voltage lithium intercalation takes place without the destruction of the “host” structure at least up to an intercalation of two Li atoms per formula unit. All studied compounds were shown to be unsatisfactory as cathode materials in lithium rechargeable batteries, but may be of

interest for general aspects of decomposition of ternary oxides induced by intercalation.

#### References

- [1] P.A. Christian, J.N. Carides, F.J. DiSalvo, J.V. Waszczak, *J. Electrochem. Soc.* 127 (11) (1980) 2315.
- [2] J.O. Besenhard, J. Heydecke, E. Wudy, H.P. Fritz, W. Foag, *Solid State Ion.* 8 (1983) 61.
- [3] T. Tsumura, M. Inagaki, *Solid State Ion.* 104 (1997) 183.
- [4] A. Yu, N. Kumagaj, Z. Liu, J. Lee, *Solid State Ion.* 106 (1998) 11.
- [5] R.H. Sanchez, L. Trevino, A.F. Fuentes, A. Martinez-de la Cruz, L.M. Torres-Martinez, *J. Solid State Electrochem.* 4 (2000) 210.
- [6] S. Denis, E. Baudrin, M. Touboul, J.-M. Tarascon, *J. Electrochem. Soc.* 144 (1997) 4099.
- [7] F. Orsini, E. Baudrin, S. Denis, L. Dupont, M. Touboul, D. Guomard, Y. Piffard, J.-M. Tarascon, *Solid State Ion.* 107 (1998) 123.
- [8] B. Di Pietro, B. Scrosati, F. Bonino, M. Layyari, *J. Electrochem. Soc.* 126 (5) (1979) 729.
- [9] F. Bonino, M. Lazzari, B. Scrosati, *J. Electrochem. Soc.* 131 (3) (1984) 610.
- [10] S.-S. Kim, S. Ogura, H. Ikuta, Y. Uchimoto, M. Wakihara, *Solid State Ion.* 146 (2002) 249.
- [11] H. Ehrenberg, H. Weitzel, H. Paulus, M. Wiesmann, G. Wltschek, M. Geselle, H. Fuess, *J. Phys. Chem. Solids* 58 (1) (1997) 153.
- [12] R. Tali, V.V. Tabachenko, L.M. Kovba, L.N. Dem'janets, *Russ. J. Inorg. Chem.* 36 (1991) 927.
- [13] M. Wiesmann, H. Ehrenberg, G. Mieke, T. Peun, H. Weitzel, H. Fuess, *J. Solid State Chem.* 132 (1997) 88.
- [14] J.A. Rodriguez, J.C. Hanson, S. Chatuverdi, A. Maiti, J.L. Brito, *J. Chem. Phys.* 112 (2000) 935.
- [15] A.W. Sleight, B.L. Chamberland, J.F. Weiter, *Inorg. Chem.* 7 (1) (1968) 1093–1099.
- [16] A.H. Thompson, *J. Electrochem. Soc.* 126 (4) (1979) 608.
- [17] F. Izumi, in: R.A. Young (Ed.), *The Rietveld Method*, Oxford University Press, Oxford, 1993 (Chapter 13).
- [18] W.D. Johnston, R.R. Heikes, D. Sestrich, *J. Phys. Chem. Solids* 7 (1958) 1.
- [19] A.C.W.P. James, J.B. Goodenough, *J. Solid State Chem.* 76 (1988) 87.
- [20] R.D. Shannon, *Acta Crystallogr. Sect. A* 32 (1976) 751.