



Experiment title: **Synchrotron X-Ray Diffraction Studies of Mg Intercalation into Chevrel Phases, as unique cathode materials for Mg battery**

**Experiment number:**  
MA-28

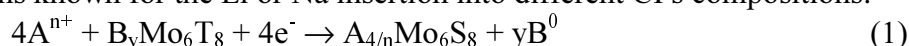
<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 22/07/2006 to: 24/07/2006	<b>Date of report:</b> 12/02/2007
<b>Shifts:</b> 6	<b>Local contact(s):</b> Michaela Brunelli	<i>Received at ESRF:</i>

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**Report:** Chevrel Phases (CPs),  $M_xMo_6T_8$  (M – metal, T = S, Se, Te), are important class of materials with unusual crystal structure and physical properties.<sup>[1]</sup> We are interested in CPs as unique cathodes for rechargeable Mg batteries, where the ability of the hosts to insert fast and reversibly multivalent cations is a crucial parameter for their function. In our previous work<sup>[2]</sup> it was shown that a structural difference between  $MgMo_6S_8$  and  $MgMo_6Se_8$  is responsible for the effectively different electrochemical behavior of the sulfide and selenide hosts at room temperature, namely for the Mg trapping in the sulfide and its absence in the selenide. Mg trapping in  $Mg_xMo_6S_8$  is caused by unique ring arrangement of closely located cation sites with low potential energy. It exists only for  $x = 1$ , because the repulsion between the inserted cations promotes their high mobility in the material.

In order to retain the positive cation repulsion and to avoid trapping, we proposed to use the initial synthetic product,  $Cu_yMo_6S_8$ , instead of the leached material ( $Mo_6S_8$ ). The electrochemical cycling in this case is based on the displacive reactions known for the Li or Na insertion into different CPs compositions:<sup>[3]</sup>



In the electrochemical systems studied previously, such reactions were irreversible. As a result, the phase diagrams were established only for the case of Li insertion into  $Cu_yMo_6T_8$ , while the crystal structure of quaternary compounds was not studied at all. In contrast, according to our experiments, the electrochemical behavior of  $CuMo_6S_8$  in the Mg battery is fully reversible and better than that of pure  $Mo_6S_8$ . Fig. 1 presents slow scan cyclic voltammetry (SSCV) curve for Mg insertion into  $CuMo_6S_8$ . As can be seen, the electrochemical reactions are complicated and depend on the potential range of cycling. Thus, it seems important to study this unusual process in detail.

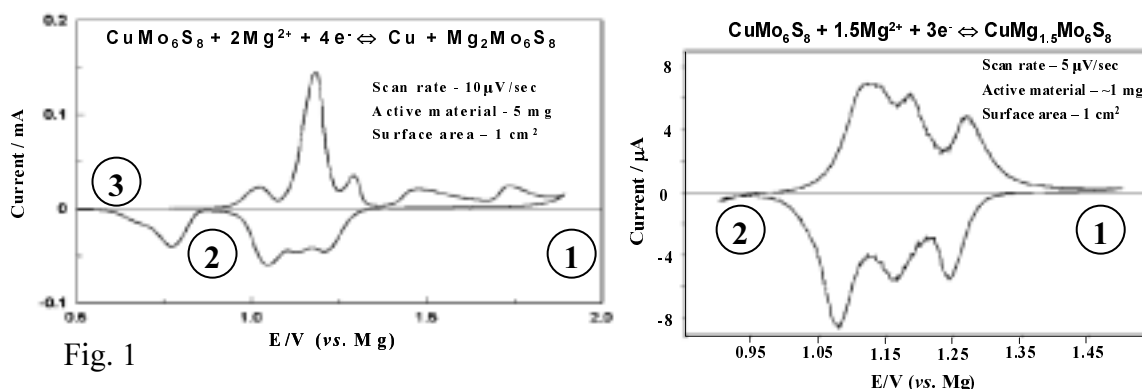


Fig. 1

The aim of the present work was to clarify the phase diagram of Mg insertion into  $\text{CuMo}_6\text{S}_8$  and to study the crystal structure of the intercalation compounds with mixed Mg-Cu-composition.

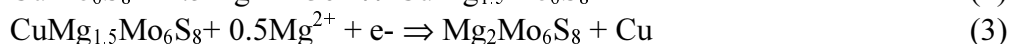
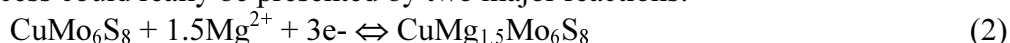
## EXPERIMENTAL

SR experiments were carried out at the beamline ID31 with the wavelength of 0.35 Å and 0.4-mm-diameter glass capillaries loaded mainly in glove-box. The powder materials under study were prepared by three different ways: high-temperature synthesis (sometimes followed by leaching), chemical or electrochemical Mg insertion. In the last case the electrochemical process was stopped at the characteristic potentials corresponding to the minima in Fig.1 (Commonly the redox peaks and the minima in such curves correspond to the phase transitions and to the pure phases, respectively).

## RESULTS AND DISCUSSION

The analysis of the experimental data showed that high quality spectra were obtained only for the samples, stabilized in air, because, in spite of all our efforts to prevent material oxidation, most of the Mg-containing compounds, especially electrochemical products, were unstable and decomposed. Thus, *in-situ* measurements are absolutely required in this case. Nevertheless, the following important results were obtained:

1. The electrochemical process could really be presented by two major reactions:



2. The reaction (3) is not truly reversible, because the process of Cu reduction to  $\text{Cu}^+$  and reinsertion of the latter into the crystal structure occurs mostly at the potentials essentially higher than that of Cu extraction.

3. According to the Rietveld refinements, before Cu extraction (point 2 in Fig. 1), the material seems to be a single phase, but due to the instability of the sample and partial Mg extraction, its composition is extremely heterogeneous. As a result, a satisfactory fitting (Fig. 2) was obtained only in the case when the material was regarded as a mixture of three phases. For the main phase (~70%),  $\text{CuMg}_{1.5}\text{Mo}_6\text{S}_8$ : Space group  $R\bar{3}$ ,  $a_h = 9.721$  Å,  $c_h = 10.394$  Å,  $a_r = 6.596$  Å,  $\alpha = 94.94^\circ$ . Thus, the lattice parameters of this phase are really close to those of  $\text{Mg}_2\text{Mo}_6\text{S}_8$  ( $R\bar{3}$ ,  $a_h = 9.763$  Å,  $c_h = 10.369$  Å,  $a_r = 6.612$  Å,  $\alpha = 95.17^\circ$ ).<sup>[2]</sup> The crystal structure of the quaternary compound is similar to that of other classic CPs with

“small” cations: The latter are distributed randomly between 12 sites per formula unit (6 sites of the inner ring and 6 sites of the outer ring). According to our model, the inner rings in  $\text{CuMg}_{1.5}\text{Mo}_6\text{S}_8$  are occupied only by Mg (one cation per ring), while the composition of the outer rings is mixed: one half of the rings is occupied by Mg (one cation per ring) and another half – by Cu (two cations per ring).

Preparation of a full-length paper related to this work is in progress.

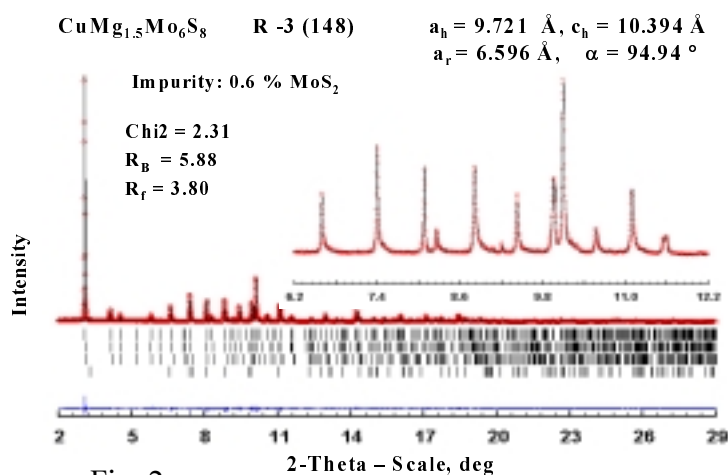


Fig. 2

## References

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