



Experiment title:

Study in-situ of the electrochemical intercalation of cations in molybdenum clusters for sensors and metal recovery.

Experiment number:
MA-3149

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to:

Date of report:

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Shifts:

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Local contact(s):

Catherine Dejoie

Received at ESRF:

Names and affiliations of applicants *

Dr. Carmelo Prestipino* ISCR (univ rennes 1)

Jose Barbosa* IJL (univ Lorraine)

Dr. Olivier Hernandez* ISCR (univ rennes 1)

Serge Paofai* ISCR (univ rennes 1)

Report:

.Operando coupled XRPD and electrochemistry study has been carried during the intercalation of Chevrel phases. The setup used is composed of an self sustaining electrode inside a teflon cell, equipped with a Ag/AgCl reference electrode, in which concentration of the cation is maintained constant by a continues refreshed by a closed circuits moved by a peristaltic pump. The setup used is visible in figure 1

This approach had the benefit of both techniques allowing a clear identification of phase creating during the

reaction. However the limited thickness of the electrode strongly limited the quality of acquisition, effectively due the small amount of material presents on the optical path the grain orientation statistics where very low with a consequence effect on the relative intensity of the pics that are no more directly related to crystallographic phase. Such inconvenience has make vane a fully accurate analysis of in situ data as sequential Rietveld refinements or Maximum Entropy Method (MEM), but the data has been still treated semi-quantitatively by the use of Le Bail fit .

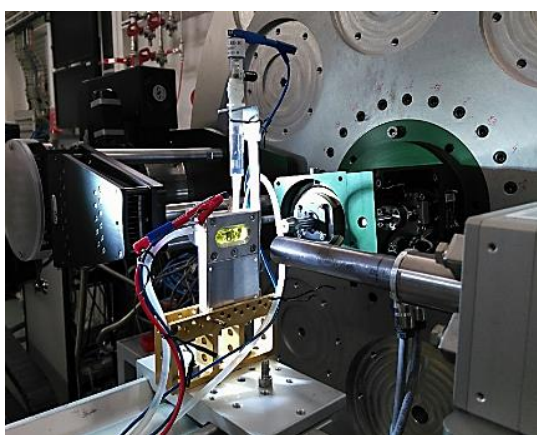


Figure 1 : ESRF experimental setup

Three cationic system in water solution has been studied for Sulphur based and selenium base Chevrel phases : Cd⁺⁺ alone , Cd⁺⁺ and Co⁺⁺, nd finally the Cd⁺⁺ Co⁺⁺ and Ni⁺⁺. The combined data show without a doubt that

Chevrel phases intercalates preferentially Cd^{++} in respect to the other cation tested both for Selenium and Sulphur although in the cyclic voltammetry small cation as Co and Ni presents lower intercalation voltage.

The complementarity of electrochemical and diffraction technique has allows to single out a complex kinetic equilibrium between the intercalated phase and the existence of two kind of Cd phase ($\text{Cd}_2\text{Mo}_6\text{S}_8$ and CdMo_6S_8) although cyclic voltammetry shows only one intercalation peak

As already said the semi-quantitative approach with Le Bail fit has allows to evaluated the phase kinetic

and to associate them with electrochemistry as visible for instance in figure 3, for the intercalation of Mo_6S_8 in a tri-cation solution of Ni, Co, Cd. The intercalation reaction is semi-reversible with a two phases

mechanism, indeed during the intercalation the potential remain constant and cell parameter for the involved phase are also constant the chevrel phase form directly a rich $\text{Cd}_2\text{Mo}_6\text{S}_8$ avoiding to the poor ternary phase CdMo_6S_8 which is form only along the de-intercalation, however during further intercalation the rich $\text{Cd}_2\text{Mo}_6\text{S}_8$ is formed by direct intercalation of Mo_6S_8 and for intercalation of CdMo_6S_8

Finally ex situ data collected on capillary filled with electrochemistry intercalated chevrel phases has allows to define the crystal structure of the Cd phases

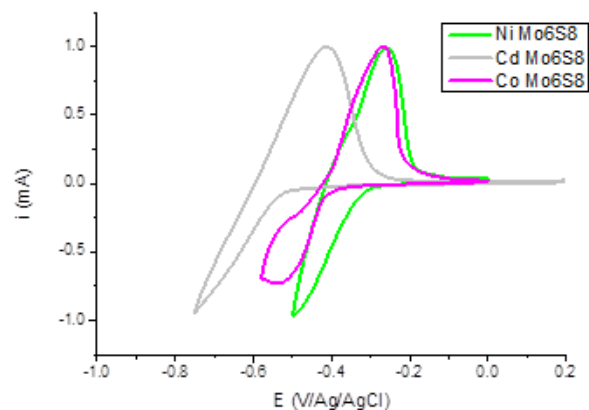


Figure 2 cyclic voltammetry of an chevrel phase electrode in Ni Cd Co solution green grey and red curves respectively

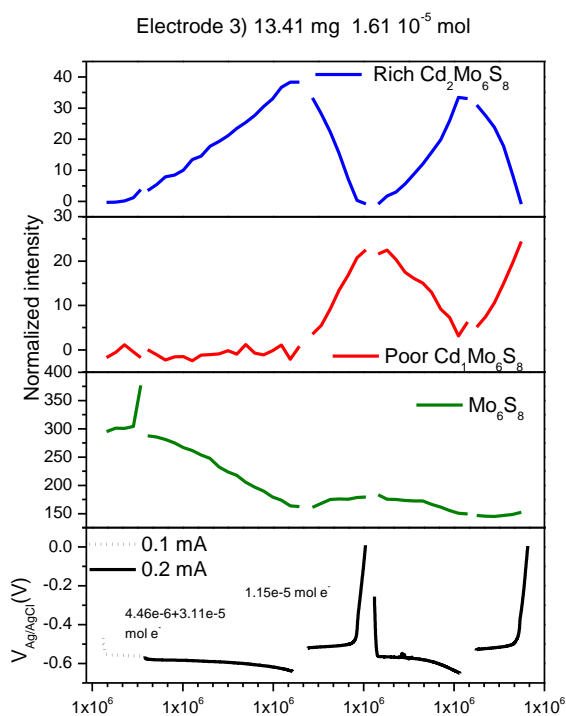


Figure 3 electrochemistry and associate phase evolution during intercalation reaction