

Rapid communication

Molten salt synthesis (MSS) of $\text{Cu}_2\text{Mo}_6\text{S}_8$ —New way for large-scale production of Chevrel phases

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Abstract

The Chevrel phase (CP), Mo_6S_8 , was found to be an excellent cathode material for rechargeable magnesium batteries. Mo_6S_8 is obtained by a leaching process of $\text{Cu}_2\text{Mo}_6\text{S}_8$, which removes the copper. A new method of $\text{Cu}_2\text{Mo}_6\text{S}_8$ production was developed. In contrast to the well-known solid-state synthesis of CP, the method is based on the reaction in a molten salt media (KCl). A fast kinetics of this reaction allows using less active, but more convenient precursors (sulfides instead of sulfur), decreasing temperature and synthesis duration, as well as operation in the inert atmosphere instead of dynamic evacuated systems. It was shown that the composition and the electrochemical behavior of the products obtained by MSS and by the solid-state synthesis are identical. Thus, the molten salt method is extremely attractive for the large-scale production of the active materials for Mg batteries.

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1. Introduction

The ternary Molybdenum Chalcogenides, so-called Chevrel phases (CPs), $\text{A}_x\text{Mo}_6\text{Ch}_8$ ($A = \text{Alkali, transition and rare earth metals, Ch} = \text{S, Se, Te; } 0 < X < 4$), were thoroughly investigated in the past three decades. This family of materials possesses a variety of unusual physical properties like fast ion conduction [1], hydrosulfurization (HDS) catalysis [2]. Thermoelectricity [3] and superconductivity with high upper critical magnetic field H_{c2} [4]. CP also have been intriguing in the eighties as cathode's active materials for Li-ion batteries. Moreover, these unusual compounds allow a fast transport of divalent cations [5]. As a result, in contrast to other hosts, these materials do not need special preparation in the form of nano-materials to be used as practical cathodes in rechargeable Mg battery [6].

At the moment, the most promising cathode is the sulfide, Mo_6S_8 , but in order to use this compound as a practical active mass in the Mg batteries, it is highly important to develop methods, in which this compound

can be produced in a large scale. Unfortunately, Mo_6S_8 is metastable and can be prepared only indirectly by metal removal from stable phases, such as $\text{Cu}_2\text{Mo}_6\text{S}_8$ [7]. Thus, we developed a convenient leaching process to this material [8]. It should be noted that using $\text{Mg}_x\text{Mo}_6\text{S}_8$ obtained by direct high temperature (HT) synthesis seems to be more attractive, but the latter products showed poor electrochemical activity due to passivating MgO film on their surface [9].

Two major ways were proposed to produce $\text{Cu}_2\text{Mo}_6\text{S}_8$. The first one is a HT solid-state synthesis, first reported by Chevrel et al. [7]: A mixture of stoichiometric amounts of the elements was sealed under vacuum in a quartz ampoule, and heated up to 1100 °C. The major disadvantage of this method is a possible evolution of sulfur vapor. The latter results in a high pressure inside the ampoule and in its explosion. This fact limits the use of this method to small amounts.

The second approach was reported by Rabiller-Baudry et al. [10]. CuCP was synthesized from soluble sulfide precursors, such as polythiomolybdates and metal salts, by multi-step heating up to 800 °C. This method allows producing particles with high surface area when needed,

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for instance, in HDS catalysis. However, there are two major disadvantages of this method: (i) the polythiomolybdates themselves have to be pre-synthesized; and (ii) hydrogen is used as a reducing agent in the reaction, and has to be strictly controlled.

An attempt to scale up the CuCP production by the solid-state HT synthesis was reported by Kondo et al. [11]. In order to avoid the sulfur vapor evolution, MoS₂ was used as a non-volatile sulfur source. Small ampoules were replaced by a dynamically evacuated quartz system that was heated up to 985 °C. Due to much lower reactivity of MoS₂ compared to that of elemental sulfur, the heating time had to be very long (200 vs. 75 h in the ordinary method). In addition, the requirement for dynamic vacuum during the heating complicates the operation.

Recently we have proposed the molten salt synthesis (MSS) of Cu₂CP [12]. A great advantage of this method is that the reaction takes place inside a molten salt, which is added to the mixture of precursors. The molten medium serves as an inorganic solvent for the reactants. As a result, the kinetics of the reactions in this medium is essentially higher than that in the solid state. This allows decreasing the temperature and the synthesis duration [13–16]. In the case of CuCP, less reactive sulfides like MoS₂ can be used as precursors, while the heating time needed for the reaction completion is even shorter than that of the solid-state synthesis from the elements. Moreover, the use of a molten medium enables processing with a large amount of the reactants, and prevents the material's oxidation. Thus, in MSS, large furnaces with inert atmosphere can replace small vacuum systems. It means that this method is ideally convenient for a large-scale production.

In this paper, we report the details of the MSS of CuCP from Mo–MoS₂–CuS system. The aim of the work was to compare the composition and the electrochemical properties of the MSS and solid-state products, in order to confirm the validity of the method for a mass production of Cu₂Mo₆S₈ that can be highly important for development of practical rechargeable Mg batteries.

2. Experimental

The CuCP with the intended Cu₂Mo₆S₈ composition was synthesized via MSS (2 g–2.087 mmol). Potassium salts such as KCl (99% Aldrich) and KCO₃ (99.8% Merck) were used as solvents after their drying during 3 h at 150 °C under vacuum. MoS₂ (99% Aldrich) (1 g–6.263 mmol), CuS (99.5% Cerac) (0.398 g–4.175 mmol), and Mo (99% Aldrich) (0.602 g–6.263 mmol), powders were used as received. The reactants mixture (solvent/reactants = 2, by weight) was hand-ground in a mortar and pestle for few minutes, and then was poured into a corundum crucible. In Fig. 1, we present schematic description of the synthesis apparatus. The latter was purged with a very slow flow of argon (99.996%), for 1 h before and during the heating in order to maintain inert atmosphere.

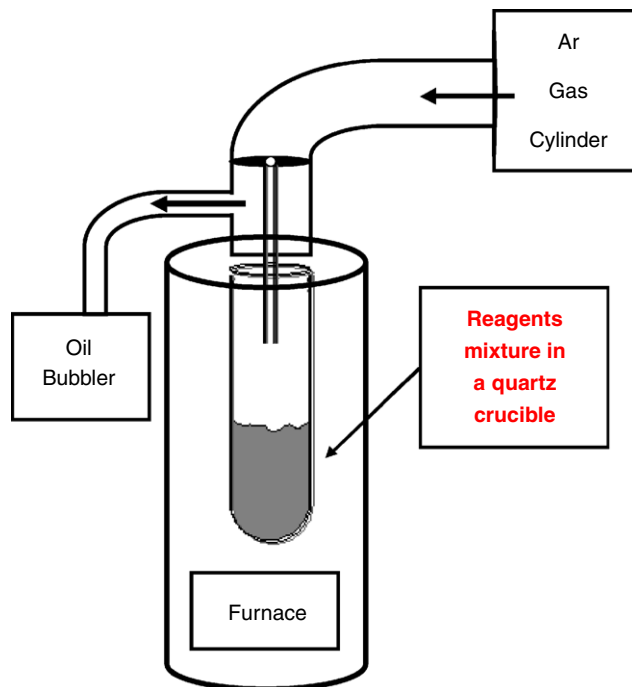
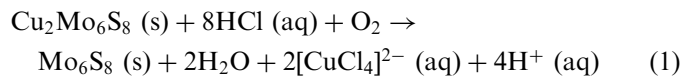


Fig. 1. The layout of the molten salt synthesis system.

The system was heated to 850 °C at a rate of 150 °C/h, held for 60 h, and then cooled to room temperature by shutting down the furnace. The product was washed two times with hot deionized water, and sonicated for 20 min to dissolve any remaining salt and to deagglomerate the particles.

For comparison, Cu₂Mo₆S₈ was also synthesized by solid-state HT reaction: the appropriate powder mixture of the elements was hand-grounded in a mortar and pestle for few minutes and poured into a quartz tube, which was evacuated, sealed and heated up, exactly as published elsewhere [8]. In order to perform the electrochemical experiments, the copper ions were leached out from both MSS and solid-state products, according to Eq. (1):



The remaining CuCP powders were dried in the furnace at 120 °C for 2 h.

X-ray diffraction (XRD) analysis, used to identify the products of syntheses and leaching, was carried out with D8 ADVANCE diffractometer (CuK α radiation), Bruker AXS Inc. (Germany).

Mg ion intercalation into solid-state and MSS CP electrodes was studied using a computerized Arbin Inc. (USA) multi-channel battery tester. The electrode's active mass mixture (about 10 mg of 80% CP, 10% carbon black and 10% PolyVinylidene Fluoride—PVdF) was applied onto a 1 cm² stainless steel mesh. These electrodes were used as working electrodes in a three-electrode cell for the discharge-charge cycles. The electrolyte solution was

0.25 M Mg ($\text{AlCl}_2\text{BuEt}_2$) in THF (Di Chloro Complex—DCC/THF), while strips of Mg foil served as counter and reference electrodes. After each discharge–charge cycle (galvanostatic mode, current 0.1 mA) the electrodes were polarized at a constant potential (1.8 V) until the currents were low ($< 1 \mu\text{A}$), before each next cycle.

3. Results and discussion

One of the most important parameters in the MSS is the choice of the salt that should not react with the synthesis mixture. The use of non-inert media can result in the precursor's consumption and contamination of the synthesis product by the salt ions. In the case of CuCP, such side reactions may cause the substitution of sulfur by the salt anions or copper by the salt cations. It seems that the possibility of the latter exchange in CP depends mostly on the cation size: cations, which are smaller than sodium, can easily diffuse into the vacant sites in the crystal structure of the CuCP and replace the Cu^+ ions. In the anion side, the major contaminants may be oxygen and halides.

The presence of oxygen at elevated temperatures results in the material oxidation, while that of halides may lead to their partial exchange with sulfur. In fact, Sergent et al. [17] succeeded to substitute up to two sulfur anions per formula unit, Mo_6S_8 , with bromine and iodine anions. In contrast, it was shown that such substitution with chlorine or fluorine did not take place. These considerations limit the choice of molten media to potassium chloride or fluoride. KCl may be considered as the optimal medium for this system, because this material is cheap, non-toxic, highly miscible in water, inert to the reactants and has lower melting point comparing to the fluoride (780°C vs. 858°C).

Fig. 2 compares the XRD patterns of $\text{Cu}_2\text{Mo}_6\text{S}_8$ synthesized via solid-state and MSS (KCl as a molten salt). As can be seen, these materials are completely identical, while all the diffraction peaks are related to a pure single rhombohedral phase (space group: $R\bar{3}$) of $\text{Cu}_2\text{Mo}_6\text{S}_8$, which matches well with the reported value (JCPDS-ICDD, 47-1519). Same

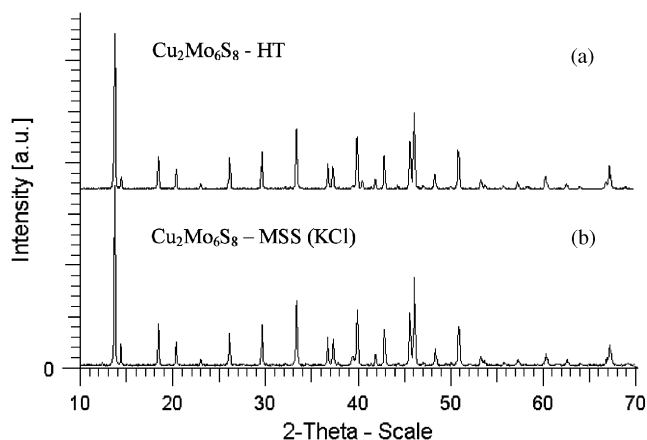


Fig. 2. XRD patterns of $\text{Cu}_2\text{Mo}_6\text{S}_8$, obtained by different ways: (a) HT solid-state synthesis and (b) MSS (KCl).

diffraction pattern was obtained also for the synthesis of 100 g of $\text{Cu}_2\text{Mo}_6\text{S}_8$ (pure single phase) according to MSS procedure that can be extended at least by an order of magnitude. Fig. 3 compares the XRD patterns of the same materials after acid removal of Cu^+ ions. As can be expected, the leached materials are also identical and related to the pure Mo_6S_8 (JCPDS-ICDD 27-0319).

An attempt to decrease the synthesis temperature by addition of K_2CO_3 to create a $\text{KCl-K}_2\text{CO}_3$ eutectic solution (62.1:37.9 mol%, respectively) was unsuccessful. The carbonate anion reacts with the $\text{MoS}_2\text{-CuS-Mo}$ system, forming Mo_2C (similar to JCPDS-ICDD, 35-0787), which is the only phase that remains after washing the product (Fig. 4). This result indicates once again the sensitivity of this system to side-reactions.

Fig. 5 compares the cyclic voltammograms of both MSS and solid-state products. The expected electrochemical behavior was obtained for both products, which indicates reversible insertion of two Mg^{2+} ions per Mo_6S_8 [6]. Thus, the synthetic product prepared by the new route (MSS) can be successfully used as the active cathode material in rechargeable Mg batteries.

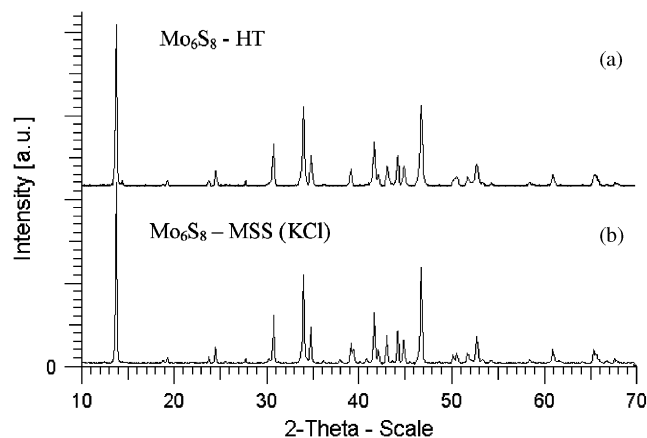


Fig. 3. XRD patterns of Mo_6S_8 , obtained by acid copper removal: (a) HT solid-state synthesis and (b) MSS (KCl).

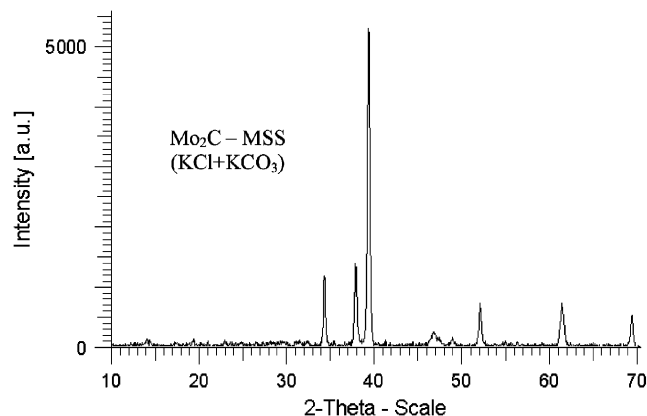


Fig. 4. XRD pattern of the product, obtained by MSS in the $\text{KCl-K}_2\text{CO}_3$ eutectic solution.

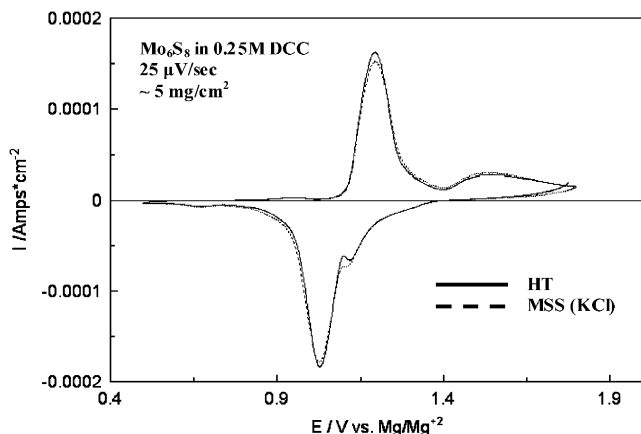


Fig. 5. Cyclic voltammograms of Mo_6S_8 obtained by HT (solid line) and MSS (dotted line) according to Ref. [8].

4. Conclusion

A new synthesis method that can be up-scaled to a mass production of CuCP was developed. This method, based on the molten salt medium, KCl, ensures essentially faster kinetics of the desirable reaction than that of the solid-state synthesis. As a result, the CuCP was obtained from the sulfides at 850°C during 60 h, instead of 985°C during 200 h, and the preparation was performed in an inert atmosphere instead of dynamically evacuated system (the latter parameters were reported previously for the solid-state synthesis). It was shown that the composition and the electrochemical behavior of the products, obtained by MSS

and by the solid-state synthesis, are identical. Thus, the method can be recommended for the mass-production of the active cathode materials for Mg batteries.

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