Journal of Solid State Chemistry 242 (2016) 151–154

Contents lists available at ScienceDirect

Journal of Solid State Chemistry

journal homepage: www.elsevier.com/locate/jssc

Short communication

Express and low-cost microwave synthesis of the ternary Chevrel phase $Cu_2Mo_6S_8$ for application in rechargeable magnesium batteries

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ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form
20 July 2016
Accepted 21 July 2016
Available online 22 July 2016

Keywords:
Magnesium battery
Chevrel phase
Microwave synthesis

ABSTRACT

The ternary Chevrel phase $Cu_2Mo_6S_8$ was successfully synthetized using a simple and cost-effective solid-state microwave-assisted reaction. While solid-state routes require days of high-temperature treatment under inert atmosphere, highly pure and crystalline $Cu_2Mo_6S_8$ could be obtained in only 400 s from this precursor, the Chevrel binary phase Mo_6S_8 was then obtained by copper removal through acidic leaching, and was evaluated as a positive electrode material for Mg-battery. The electrochemical performance in half-cell configuration shows reversible capacity exceeding 80 mAh/g, which is comparable to previous works carried out with materials synthesized by conventional high-temperature solid-state routes.

1. Introduction

Since their discovery in early 70's, ternary molybdenum chalcogenides $M_xMo_6T_8$ – known as Chevrel phases – continues to fascinate the research community for their wide range of physical and chemical outstanding properties [1]. They were firstly under the light for their superconducting behavior and for the richness of the available chemical compositions [2–4]. Indeed, the crystal structure exhibits an open array of Mo_6T_8clusters (a chalcogen T_8cube surrounding a distorted Mo_6octahedron) that offers large channels for various M cations. The high mobility of M guest atoms in this open framework enables preparing new metastable compositions through low-temperature chemical or electrochemical reactions [5]. Consequently, Chevrel phases $M_xMo_6T_8$ and Mo_6T_8 have been widely investigated as electrode materials in rechargeable lithium or sodium batteries [6–11]. However, their relatively low operating voltages and reduced specific capacities have prevented their use as positive electrode materials in commercial cells as they cannot compete with layered or polyanionic compounds. In 2000, Chevrel phases were put back on stage as the positive electrode material of the first prototype of rechargeable magnesium battery (MB) by the group of Pr. Aurbach. In this pioneering work, Mo_6S_8-based electrodes showed a stable capacity during reversible Mg^{2+} ions intercalation (60 mAh/g for almost 600 cycles of discharge/charge) [12]. Further improvements led to reversible capacities around 80–100 mAh/g [13–19]. Magnesium batteries are considered as a reliable alternative to the current Li-ion technology, in the light of the limited lithium resources and also thanks to the high theoretical capacities of Mg metal (2.2 Ah/g and 3.8 Ah/cm^3) [20]. However, magnesium electrochemistry is challenging especially because of the sluggish diffusion of Mg^{2+} cations in solid oxide hosts [21–24]. Searching for enhanced ion mobility involves weaker coulombic attraction and thus leads to compounds with soft anion lattice such as sulfur [25]. Today the Chevrel phase Mo_6S_8 still remains the benchmark for cathode materials in magnesium battery and also starts to be pointed out for calcium- and aluminum-ion cells [26–28].

According to the literature, binary compound Mo_6S_8 is often obtained from the ternary Chevrel phase $Cu_xMo_6S_8$ [5,6]. This precursor was originally synthesized by high-temperature solid state reaction from native elements in a sealed silica tube under vacuum [1]. As gaseous sulfur might be generated in the process, this route is not suitable for upscaling. Replacing sulfur by more stable chemicals such as molybdenum sulfide improves the safety; however, the reaction still lasts more than 100 h [29]. Alternative strategies using either molten salts or self-propagating techniques enable decreasing the reaction time as well as the temperature [30,31]. However, in most cases the ternary Chevrel phase is obtained with a significant amount of impurities. A facile synthesis of Mo_6S_8 nanocubes was recently reported; however, such protocol might not be transferable for large batch production [32].

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http://dx.doi.org/10.1016/j.jssc.2016.07.022
0022-4596/

Therefore, in this context of using Mo_6S_8 as electrode material, it seems important to develop cost-effective and efficient new protocol to synthesize the Chevrel phase $Cu_2Mo_6S_8$ with a high degree of purity.

Microwave heating is a promising technology allowing softer reaction conditions in aqueous or organic media. It was recently shown to be also very efficient even in solid-state reactions for the preparation of oxides and intermetallic compounds [33–35]. Herein, a fast, cost-effective and high-yield microwave synthesis of the Chevrel phase $Cu_2Mo_6S_8$ is presented. Classical copper removal through acidic leaching leads to the binary Mo_6S_8 that is then successfully tested as positive electrode in rechargeable Mg batteries.

2. Experimental

In a typical synthesis of $Cu_2Mo_6S_8$, as received powders of MoS_2 (99%, Sigma-Aldrich, < 2 μm), Mo (99.95%, Alfa-Aesar, 3–7 μm) and Cu (99.9%, Alfa-Aesar, 100 mesh) were mixed in stoichiometric quantities and pressed together at 1.5 bar. The compacted pellet was then put into a graphitized quartz tube positioned in an alumina crucible filled with carbon powder (C-NERGY Super C45, Timcal) and covered by mineral wool (5–30 μm, Sodipro). In order to avoid any possible reaction with the carbon, an alumina disk protected the pellet (Fig. 1). The thermal treatment was carried out in a Startsynth laboratory microwave (Milestone) for 400 s at 1200 W. Then the quartz tube was rapidly taken out and cooled down in water.

The resulting ingot was manually ground in an agate mortar to obtain a homogeneous powder. X-ray diffraction (XRD) was carried out using an Empyrean 2theta/omega diffractometer (PANalytical), equipped with Cu Kα radiation. Powder morphology was investigated by scanning electron microscopy (SEM) with a Hitachi S-4800 microscope equipped with a field emission gun. Following the literature [36], copper removal was performed by acidic leaching (1 night of stirring in 6 M HCl solution with oxygen bubbling).

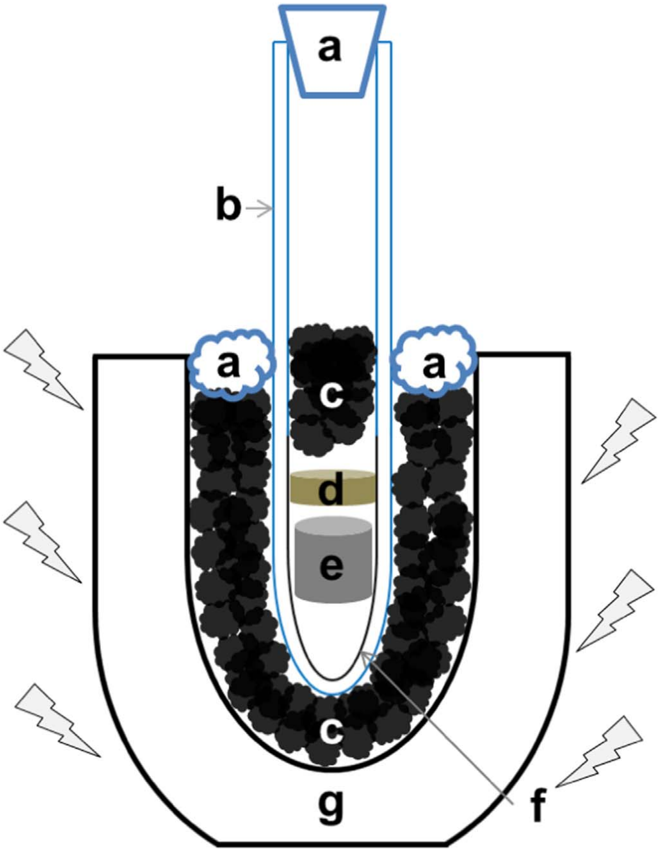

Fig. 1. Schematic representation of the microwave-assisted synthesis. a) mineral wool; b) quartz tube; c) carbon; d) alumina disk; e) sample ingot; f) graphitized inner layer; g) alumina crucible.

Electrodes were prepared by mixing the active powder with 10 wt% carbon black (Y50A, Saft), 10 wt% vapor ground carbon fibers (VGCF, Showa Denko K.K., VGCF-H) and 10 wt% polytetrafluoroethylene (PTFE, DuPont, 6 N). Electrodes were tested in 2-electrode Swagelok-type cells against a magnesium disk (99.9%, Goodfellow) as both the reference and the negative electrode. Whatman GF/A borosilicate glass fiber sheets were used as separators. The electrolyte consisted on a mixture of ethylmagnesium chloride (EtMgCl, 2.0 M in tetrahydrofuran, Sigma-Aldrich) and diethylaluminum chloride (Et_2AlCl, 97%, Sigma-Aldrich) solubilized in anhydrous tetrahydrofuran (THF, $\geq 99.9\%$ Sigma Aldrich). The final concentration of the organohaloaluminate complex "EtMgCl-Et_2AlCl" was estimated to be 0.35 mol/L. All the necessary operations of cell assembly were carried out in an Ar-filled glovebox. Galvanostatic tests were performed at room temperature using research-grade battery testers (BioLogic) in the [0–2 V *vs.* Mg^{2+}/Mg] window. The C/*n* constant current rate means that 1 mol of Mg reacts with 1 mol of active material in *n* hours.

3. Results and discussion

The product of the microwave synthesis is an ingot that can be easily pulverized in an agate mortar. The powder XRD pattern (Fig. 2a) can be indexed with a rhombohedral space group (R-3). Refined cell parameters through Le Bail method ($a=9.679(1)$ Å; $c=10.217(1)$ Å) perfectly match with the literature and confirm the formation of $Cu_2Mo_6S_8$ [1,29]. The Chevrel phase is highly crystallized. Even though very small residuals of the precursor MoS_2 are sometimes found from one synthesis to another, the phase is usually obtained with a very high degree of purity, especially when compared to other fast reaction routes for which significant amounts of Mo, MoS_2 or Mo_2O_3 are often detected [31]. In microwave-assisted synthesis, carbon acts as a susceptor (*i.e.*, a material able to absorb the magnetic radiation and to convert it into heat). Here it also prevents any oxidation of the starting metallic powders.

SEM evidences the formation of cuboidal micrometric particles (from 0.5 to 2 μm) that can be sometimes aggregated together. Well-faceted particles with defined morphologies are rather commonly obtained in solid-state microwave synthesis, and can be found for instance in intermetallic compounds prepared in similar conditions [34,35].

An acidic leaching treatment with concentrate HCl is necessary to remove the copper from the Chevrel phase to obtain the electrochemically active Mo_6S_8. This topotactic chemical oxidation does not impact the overall structure of the Chevrel phase but only slightly modifies the cell parameters. The XRD pattern collected after the powder leaching evidences a weak shift of the peaks (Fig. 2b). The refined values of the new cell parameters ($a=9.190(1)$ Å; $c=10.883(1)$ Å) match with the literature and confirm the formation of the binary Chevrel phase Mo_6S_8 [5]. The acidic treatment does not change the powder grains size, but slightly alters the surface of the particles with a partially loss their regular and faceted shape.

The first galvanostatic cycles at C/20 of a Mo_6S_8/Mg battery are shown in Fig. 3. The initial discharge evidences a sloppy plateau from 1 to 0.6 V before a final drop to 0 V. A very high capacity of 123 mAh/g is obtained and corresponds to the reaction of more