

Synthesis, characterization and properties of metastable lamellar MoO₃ hydrate

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Abstract Molybdenum oxide hydrate with high purity was synthesized via a simple sol-gel approach. The oxide crystallizes in a lamellar structure consisting of needle-like particles with 150–300 nm of width and length up to five μm . An interesting feature is the stability of the electrochemical response, *i.e.*, the decrease in total after successive reduction/oxidation cycles is negligible.

Molybdenum oxide and its derivatives are used in industry as catalysts, display devices, sensors, smart windows, or battery electrodes. Accordingly, efforts have been devoted to designing novel methods for the synthesis of nanomaterials with different characteristics, aiming at exploiting their potentials [1]. It is well known that MoO₃ is a lithium insertion compound and it was investigated during the early years of lithium battery research [1,2]. However, high capacity reversible cycling was not demonstrated. In this context, herein we describe sol-gel synthetic route of lamellar MoO₃ consisting of needle-like particles, as well as characterization and electrochemical properties.

Powder X-ray diffraction pattern exhibits peaks characteristic of a layered structure (12.96° and 25.86° attributed to 001 and 002 planes, with interlayer distance of 0.70 nm), evidencing that the product is a molybdenum oxide hydrate, MoO₃.0.3H₂O, which is confirmed by thermal analysis. In fact, thermogravimetric curve indicates a weight loss of ca. 3% up to 650 °C, related to the release of adsorbed water molecules (~2%) and strongly bonded water molecules (~1%). In addition, FTIR spectrum shows bands at 1050, 975 cm⁻¹ and attributed to stretching of Mo=O bond and a peak at 600 cm⁻¹ related to O-Mo-O stretching. Besides, the broad bands around 1620 and 3445 cm⁻¹ were related to adsorbed water and OH groups. Therefore, the phase of the molybdenum oxide hydrate synthesized is MoO₃.0.3H₂O.

SEM images show that the material exhibits a lamellar arrangement, corroborating the diffraction results. In addition, the images show the presence homogeneous needle-like particles forming the oxide layers, in which the width is found to be ca. 150–300 nm, and length up to five micrometers.

Ultraviolet/visible spectrum shows absorption bands in the 500 and 900 nm range, indicating d-d transitions (Mo (d¹) → Mo (d⁰)), and a intense LMTC charge transfer band at 210 nm.

Voltammetric studies showed reversible electrochemical intercalation/de-intercalation reaction (MoO_x + ye⁻ + yLi⁺ ↔ Li_yMoO_x) as well as electrochromic properties. In addition, the electrochemical response is dependent on support electrolyte solution varying the cation species. An interesting feature is the stability of the electrochemical response, *i.e.*, the decrease in total charge in aqueous medium even after eighty successive reduction/oxidation cycles is negligible. Thus, the molybdenum oxide hydrate is structurally stable, in such a way that upon cycling, the insertion and de-insertion of lithium ions and solvent molecules do not provoke significant mechanical stress, leading to a lower capacity fade.

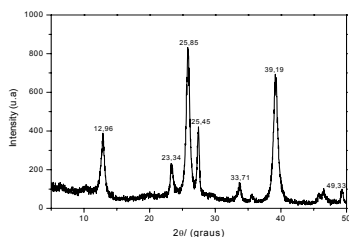


Figure 1: X-ray diffraction pattern of MoO₃.0.3H₂O.

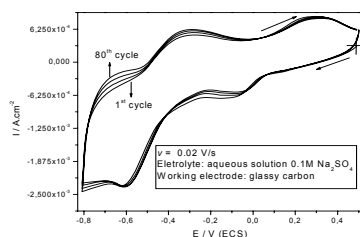


Figure 2: Cyclic voltammograms of MoO₃ xerogel composite.

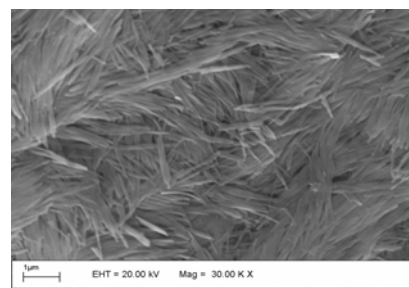


Figure 3: SEM image of MoO₃.0.3H₂O.

References:

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- [2] R.F. Farias; M. S. Refat; H. A. Hashem; J Incl Phenom Macrocycl Chem (2008) 61:113–118.

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