

# Synthesis of sulfide cathodic materials and study of their physicochemical properties and electrochemical activity

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## Abstract

A relationship has been ascertained between the conditions of synthesis, physicochemical properties and electrochemical activity of sulfide cathodic materials ( $\text{TiS}_2$ ,  $\text{V}_2\text{S}_2$ ,  $\text{MoS}_3$ ) in lithium batteries with an aprotic electrolyte. The existence of two forms of titanium disulfide has been shown for the first time, a 'soft' and 'hard' form ( $\text{TiS}_{2(s)}$  and  $\text{TiS}_{2(h)}$ ) that differ essentially in their structure, conductivity, electrochemical activity and mechanism of intercalation.  $\text{TiS}_{2(s)}$  synthesized under non-stationary conditions with a considerable disorderliness has greater specific capacity (210 mAh/g) and better lithium transport properties than  $\text{TiS}_{2(h)}$  synthesized under long stationary conditions. It has been shown that the effectiveness of solid-phase cathodic materials in lithium batteries is caused by their macro- and microstructure and depends on their preparation conditions, the stoichiometry of active cathodic substances is not the basic criterion. The other cathodic materials obtained by the methods of non-stationary synthesis also possess extremely high specific properties:  $\text{MoS}_3$ : ~400 mAh/g and  $\text{V}_2\text{S}_2$ : 240–260 mAh/g.

*Keywords:* Cathodes; Sulfide; Lithium batteries

## 1. Introduction

The main criteria of cathodic materials in promising lithium batteries are their high rechargeability and power intensity, thermal stability, conductivity, and electrochemical compatibility with the electrolyte. These properties are largely due to not only the nature of the active cathodic materials but to their manufacturing conditions.

Analysis of data available in literature [1–5] and our results show that the effectiveness of solid-phase cathodic materials in lithium batteries is caused by their macro- and microstructure and depends on the preparation conditions, the stoichiometry of active cathodic substances is not the main criterion. By governing the conditions of the thermosynthesis one can obtain cathodic materials with good electrophysical and electrochemical properties.

The present work gives results of the study concerning the effect of the conditions of the  $\text{TiS}_2$  synthesis on its stoichiometry, lattice parameters, conductivity, thermal stability and electrochemical activity in lithium batteries. Results of the electrochemical testing of  $\text{TiS}_2$ ,  $\text{MoS}_3$  and  $\text{V}_2\text{S}_2$ , as active cathodic materials obtained by various methods, have also been shown.

## 2. Experimental

To synthesize sulfides of 99.9% titanium, molybdenum and vanadium different fraction sizes, but no more than +8 mesh, were used. Sulfur was of 99.999% purity grade. More than 200 samples, titanium sulfides of the  $\text{Ti}_x\text{S}_2$  composition ( $1 \leq x \leq 1.2$ ),  $\text{V}_2\text{S}_2$  and  $\text{MoS}_3$  have been obtained. The synthesis was carried out at various temperatures in the 600–1050 °C range and at different rates of heating or cooling of the reaction products within the above temperature range. The composition of these materials was ascertained by burning in oxygen at 1100 °C, as well as by photometry. The structure was investigated by X-ray diffraction analysis and scanning electron microscopy. The conductivity was measured with alternating current (1–10 kHz). The thermal stability of the materials was studied by differential thermal analysis and thermogravimetry. The electrochemical testing of the sulfide materials was carried out by cyclic voltammetry in a four-electrode cell (lithium reference electrode versus silver–silver chloride) at various scanning rates, 1 to 10 mV/s.

The working electrode was prepared by pressing the active cathodic mass onto a platinum grid with a 7 wt.% addition of acetylene black.

The galvanostatic cycling was carried out in lithium batteries, of a prismatic design, at a current density of 0.5 mA/cm<sup>2</sup> and an electrode area of 1.25 cm<sup>2</sup>. The electrolyte used was 1 M LiClO<sub>4</sub> in propylene carbonate:dimethoxyethane (1:3). The electrodes were prepared by the method of flexible cathode with polytetrafluoroethylene as binder.

### 3. Results and discussion

#### 3.1. Synthesis of materials and their characterization

Two forms of titanium disulfide can be synthesized depending on the preparation method: a 'hard' TiS<sub>2(h)</sub> and a 'soft' TiS<sub>2(s)</sub>. The synthesis of the 'hard' form proceeds at any temperature between 600 and 900 °C due to a long interaction between titanium and sulfur. As a result well-ordered crystals of a practically stoichiometric product are formed. The optimum lattice parameters are  $c = 5.695 \text{ \AA}$  and  $a = 3.407 \text{ \AA}$  [1].

The other form, TiS<sub>2(s)</sub> has a non-stable (varying) parameter of the interplanar distance  $5.695 < c \leq 5.725 \text{ \AA}$ , whereas the  $a$ -parameter is almost constant. In other words, the TiS<sub>2(s)</sub> structure can be characterized as soft and mobile in comparison with TiS<sub>2(h)</sub> which is rigidly fixed and stable. The TiS<sub>2(s)</sub> form is synthesized under non-stationary conditions due to a change in the rate of heating and cooling within the 600–1050 °C range, i.e., due to a combination of high-temperature and low-temperature synthesis methods. A peculiarity of TiS<sub>2(s)</sub> consists in its decreased conductivity, by 10 to 50%, in comparison with TiS<sub>2(h)</sub>, which seems to be due to a distortion of the extended structure, at the semiconductor's type of  $\sigma$  versus  $t^\circ$  dependence remained. The TiS<sub>2(h)</sub> form has higher thermal stability and electrochemical activity.

Both forms are of the same olive colour with golden luster, but differ in size and shape of their crystals. The described properties of the two TiS<sub>2</sub> forms are shown in Fig. 1.

The V<sub>2</sub>S<sub>2</sub> and MoS<sub>3</sub> samples were prepared by non-stationary synthesis in the 500–800 °C temperature range.

#### 3.2. Electrochemical results and discussion

Comparative analysis of the electrochemical behaviour of the two forms of TiS<sub>2</sub> shows that TiS<sub>2(s)</sub> has higher values of maximum currents of the cathodic and anodic branches in cyclic voltammograms (CVA) in comparison with those of TiS<sub>2(h)</sub> (Fig. 2). The position of cathodic and anodic maxima in the CVA curve of TiS<sub>2(h)</sub> does not change in repeated potential scanning (Fig. 2(a)). The CVA for TiS<sub>2(s)</sub> (Fig. 2(b)) shows a shift of the cathodic maximum towards more positive

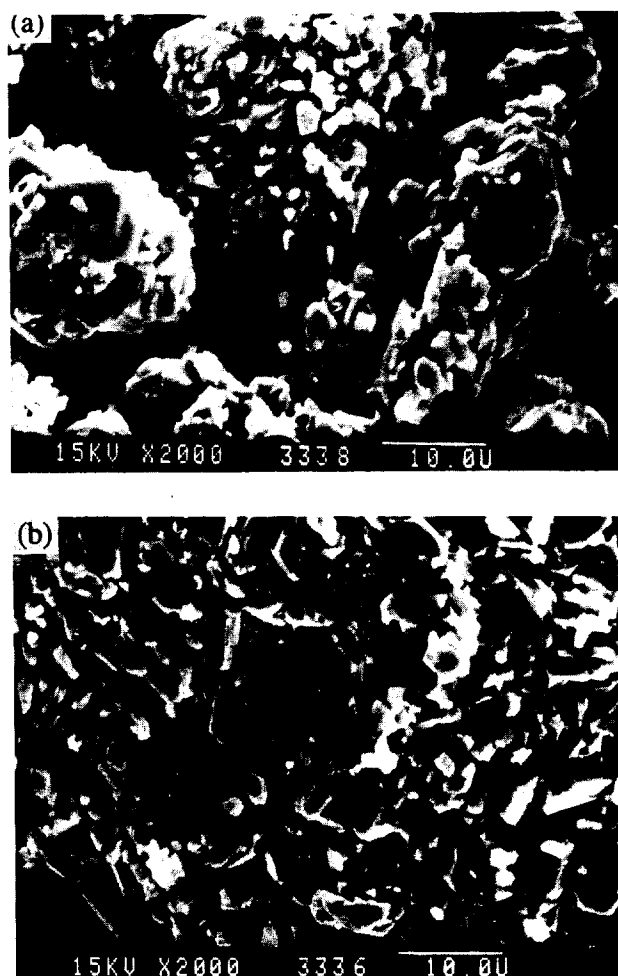


Fig. 1. Scanning electron microscopy pictures (a) TiS<sub>2(h)</sub>:  $c = 5.695 \text{ \AA}$ ,  $\sigma_{20^\circ\text{C}} = 25.2 \text{ S/cm}$ ,  $t_{\text{synth}}^\circ = 700 \text{ }^\circ\text{C}$ , time of the synthesis  $\tau = 30 \text{ h}$ ; (b) TiS<sub>2(s)</sub>:  $c = 5.711 \text{ \AA}$ ,  $\sigma_{20^\circ\text{C}} = 16.6 \text{ S/cm}$ ,  $t_{\text{synth}}^\circ = 600\text{--}1000 \text{ }^\circ\text{C}$ ,  $\tau = 8 \text{ h}$ .

potentials by repeated potential scanning, which evidences a decrease in the general overvoltage of the reaction. The anodic CVA curve of TiS<sub>2(s)</sub> has one more maximum (about 3.0 V) preceding the increase in electrochemical activity in addition to the de-intercalation maximum (2.2–2.3 V). Such 're-oxidation' of TiS<sub>2</sub> causing the increase in currents, and the change in potential differences between cathodic and anodic maxima can be explained by the macro- and micro-structure of TiS<sub>2(s)</sub>.

The increase of electrochemical activity of TiS<sub>2(s)</sub> in comparison with TiS<sub>2(h)</sub> has been also verified by cycling the lithium batteries (Fig. 3).

The specific capacity of TiS<sub>2(s)</sub> ranges from 200 to 210 mAh/g (cf. 150 mAh/g for TiS<sub>2(h)</sub>). The electrochemical tests have also shown that for the titanium sulfides Ti<sub>x</sub>S<sub>2(s)</sub> ( $1 \leq x \leq 1.2$ ) a deviation from the stoichiometry towards titanium slightly affects the capacity and cycleability of the active cathodic material.

In our opinion, the improvement in electrochemical characteristics of TiS<sub>2(s)</sub> is due to the presence of defects

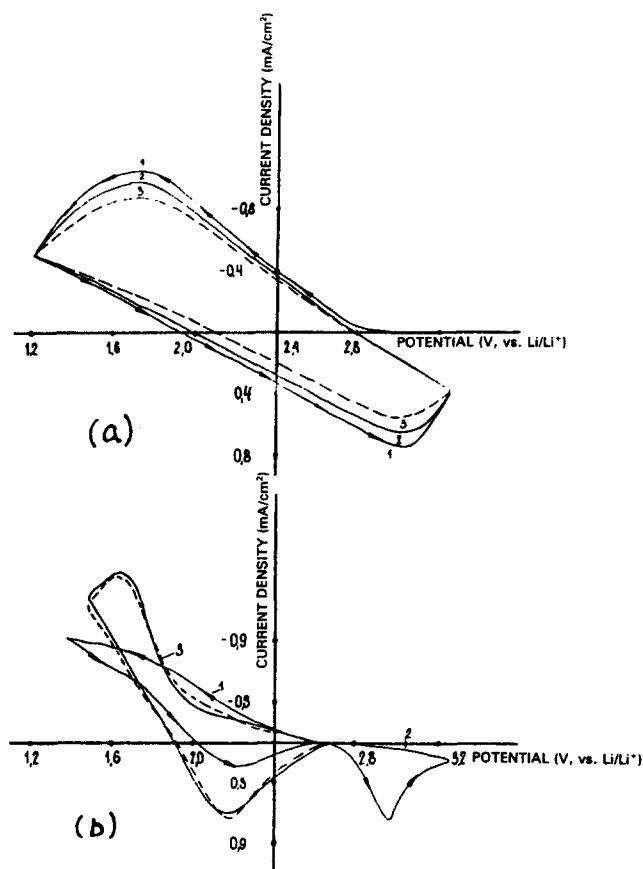


Fig. 2. Cyclic voltammograms for (a)  $\text{TiS}_{2(\text{h})}$  and (b)  $\text{TiS}_{2(\text{s})}$ . Potential scanning rate = 1 mV/s.

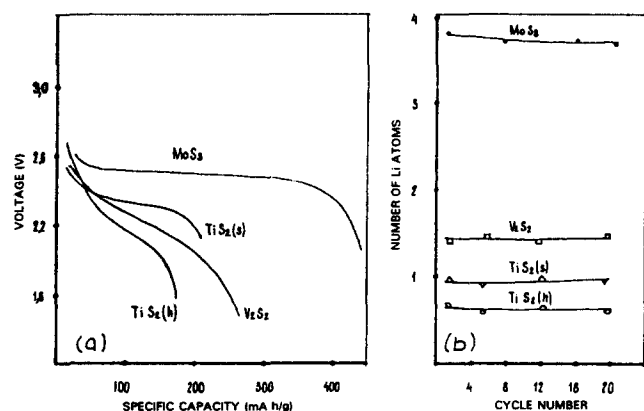


Fig. 3. Galvanostatic cycling (a) discharge curves of the first cycle; (b) lithium intercalated vs. number of cycles.

in its crystal structure. This results in the van der Waals layers sliding apart more readily and, hence, in a more effective lithium intercalation. Step-by-step electrochemical modification of the  $\text{TiS}_{2(\text{s})}$  structure seems to take place at the initial stages of cycling during the intercalation and de-intercalation processes, the modification being towards a more considerable increase in 'c'. This leads to improved kinetics of  $\text{Li}^+$ -ion intercalation. The above statement finds its verification when comparing the values of volume expansion of the

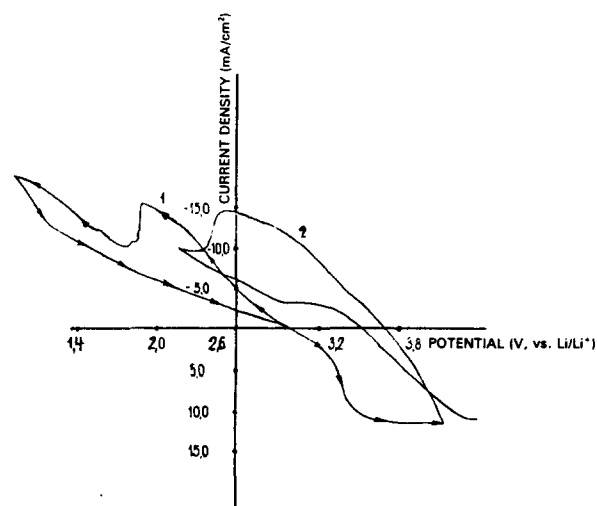


Fig. 4. Cyclic voltammograms for  $\text{MoS}_3$ . Potential scanning rate = 5 mV/s.

cathodes based on  $\text{TiS}_{2(\text{h})}$  and  $\text{TiS}_{2(\text{s})}$ . These average values were 10% and 2%, respectively, for each  $\text{TiS}_2$  modification after 100 deep cycles in the lithium batteries.

The application of the principles of non-stationary synthesis to  $\text{MoS}_3$  and  $\text{V}_2\text{S}_2$  gives more considerable results. The specific capacity of  $\text{V}_2\text{S}_2$  ranges from 240 to 260 mAh/g, and that for  $\text{MoS}_3$  from 400 to 420 mAh/g. These values have been never reported in the literature. These data have been verified by voltammetric studies of  $\text{MoS}_3$  (Fig. 4). In this case, an increase in cathodic and anodic current densities and a considerable shift in cathodic potentials after 're-oxidation' are also observed during initial CVA cycles.

#### 4. Conclusions

The synthesis conditions markedly affect the physicochemical properties and electrochemical activity of sulfide cathodic materials.

The substances obtained under non-stationary synthesis conditions, and hence possessing greater disorderliness, show high specific and cycle-life characteristics in lithium batteries.

An essential feature of the mechanism of intercalation of these materials is a decrease in total overvoltage in the electrochemical system during lithium intercalation.

The findings reported allow us to conclude that non-stationary methods of synthesis of other cathodic materials in lithium batteries are of great effectiveness and practical importance.

#### Acknowledgements

The authors would like to thank Professor A. Tkalenko, Dr V. Kutcz and Professor V. Prisyajny from

the National Ukrainian Academy of Sciences for their helpful discussion and to Mrs S. Tovpeko for her technical support.

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