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LITHIUM INTERCALATION INTO TRANSITION METAL DICHALCOGENIDES

GEORGETA ŢARĂLUNGĂ*, SILVIA FEŞNIC, L.D. BOBOŞ,
CS. BOLLA, L. ONICIU

"Babeş-Bolyai" University, Faculty of Chemistry and Chemical Engineering, 3400 Cluj-Napoca, Romania
**University of Agricultural Sciences and Veterinary Medicine, 3400 Cluj-Napoca, Romania*

ABSTRACT. The electrochemical processes of the lithium batteries are based on the intercalation phenomenon of the lithium ions into a host lattice of transition metal dichalcogenides.

This paper presents some theoretical aspects concerning the intercalation of Li^+ into TiS_2 electrodes. The physical and structural characteristics and the electrochemical behaviour of the TiS_2 electrodes were investigated by X-ray diffraction, and charge-discharge curves in galvanostatic regime.

INTRODUCTION

It is well known that lithium batteries are one of the most promising devices for light and compact power sources because of their high power, high energy density and long cycle life.

Various types of active materials for rechargeable lithium batteries have been investigated by research groups worldwide. Among these, titanium disulphide has been thought to be one of the desirable cathode materials for a high energy density secondary battery [1-6]. Its high current characteristics and good reversibility are due to the fact that the electrochemical reaction is an intercalation reaction of lithium into the van der Waals layer of titanium disulphide [7-11].

The disulphides are formed by two hexagonally close-packed sulphur layers between which reside the transition metal ions. These metal ions are found either in sites of octahedral symmetry or in ones of trigonal prismatic symmetry. The transition metals of the group IV B (Ti, Zr, Hf) are in octahedral symmetry, the group VI B (Cr, Mo, W) in the trigonal prismatic sites, but Nb and Ta of the group V B are found in both [12-14].

In Fig. 1 is shown the ordering of the Ti and S layers, as well as the octahedral symmetry sites. The S and Ti atoms are covalent bonded, but the sandwich-type building units are maintained together by van der Waals forces.

The compound is nonstoichiometric, the titanium or sulphur excess founding in the van der Waals layer. The titanium excess stabilized the compound, but a subsequent intercalation becomes more difficult, and sulphur excess led to the moulding of the titanium trisulphide, which has been unable for reversible intercalation.

The cell reaction, which results in the moulding of the intercalation compounds, is given by:

$$x\,Li + xe^- + TiS_2 \rightarrow Li_xTiS_2 \qquad (1)$$

where $0 < x < 1$.

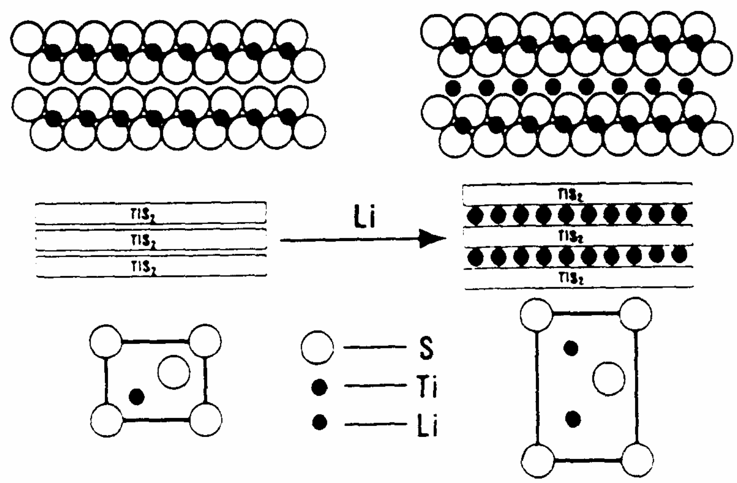

Fig. 1. Diagram representing intercalation of lithium ions in TiS_2 layered crystalline structure.

The diffusion of the lithium ions takes place only in the van der Waals layer, there being non-significant mobility perpendicular to these places. Therefore, the diffusion is bidimensional and there is not diffusion through the sulphide layers [15].

The structure of the Li_xTiS_2 intercalation compound is about the same with the crystalline structure of the host dichalcogenide.

The Li/TiS_2 cell consists of an elemental lithium anode (negative electrode), a titanium disulphide cathode (positive electrode), and a lithium salt dissolved in an aprotic nonaqueous solvent as the electrolyte. During discharge of the cell, lithium ions intercalate in the TiS_2 cathode forming Li_xTiS_2 and elemental lithium at the anode is oxidized to lithium ions.

In this paper are presented:

a) the preparation and the physical and structural characterization of TiS_2 active mass;
b) the electrochemical behaviour of TiS_2 electrodes.

In literature [16,17] there are several methods for obtaining TiS_2:

- by direct reaction between titanium and sulphur at 600^0C;
- by disproportion reaction of TiS_3 at 600^0C;
- by reaction of $TiCl_4$ and H_2S at 550^0C;

The first two methods are not advantageous because the temperature in the reaction zone must be kept rigorously. In addition, titanium disulphide obtained presents crystalline imperfections, which determine a structural reduction of the Li^+ mobility during the intercalation.

EXPERIMENTAL

We obtained TiS_2 by the third method, based on the reaction between $TiCl_4$ and H_2S:

$$TiCl_4 + 2H_2S \xrightarrow{475-550^0 C} TiS_2 + 4HCl \qquad (2)$$

The reaction occurred in a tubular quartz reactor, placed vertically and having external heating system. The temperature in the reactor was rigorously maintained in 475-550^0 C range to avoid the decomposition of H_2S and the formation of undesired compounds (TiS_2, $TiOCl_2$).

The physical characteristics of prepared TiS_2 powder were determined by gravimmetric analysis [18].

The structural characteristics of TiS_2 active mass were investigated by X-ray diffraction (XRD) with a Dron 3 powder diffractometer, using CuK_α radiation.

TiS_2 electrodes were realized from prepared TiS_2 as active mass, graphite as electronic conductor, and teflon as binder, having different compositions.

The electrochemical behaviour of these electrodes has been investigated by charge-discharge curves in galvanostatic regime, at room temperature. The charge-discharge curves were performed for Li/ TiS_2 button batteries.

RESULTS AND DISCUSSION

The gravimmetric analysis of TiS_2 powder, having a dark tint and golden lustre, is presented in Table 1.

Table 1.

Titanium content of TiS_2 samples.

Sample	Ti (%wt)	S (%wt)
1	39.68	60.32
2	41.08	58.92
3	40.12	59.88
4	39.20	60.80
5	40.06	59.94

It can be seen that the values for titanium content are very near of theoretical value (42.76%wt) [18].

The X-ray diffraction pattern of TiS_2 prepared powder is showed in Fig. 2. and is evidenced that the X-ray diffractogram contained the specific diffractional lines of titanium disulphide.

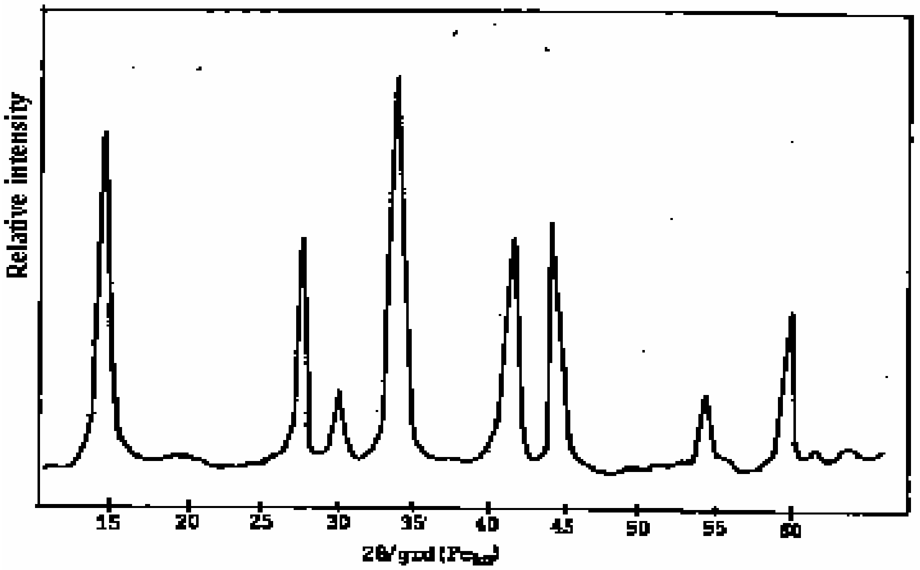

Fig. 2. X-ray diffractional patterns of TiS_2.

The electrochemical behaviour of TiS_2 electrodes was studied by testing in Li/TiS_2 cells. The discharge and charge curves presenting the voltage (U) vs. specific masic capacities (C) are illustrated in Fig. 3.

From the slopes of performance curves it comes out that Li/TiS_2 cells are reversible systems; the charge and discharge processes unfold in one stage.

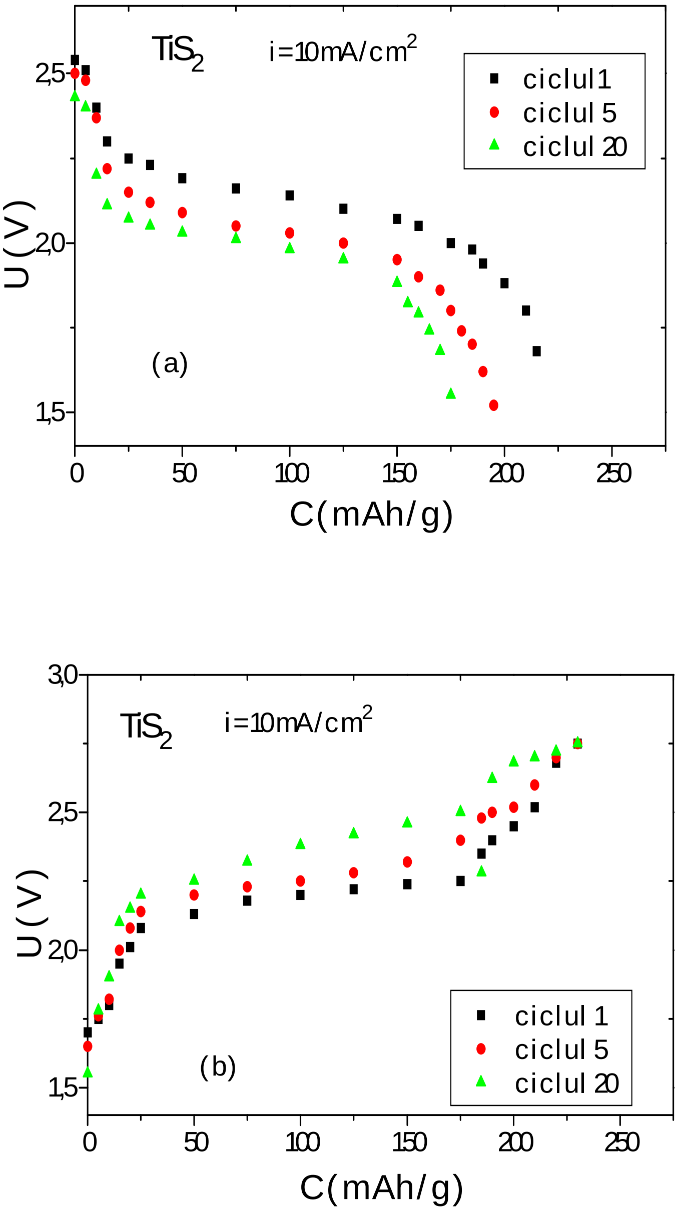

Fig. 3. Performance curves of Li/TiS_2 cell with 93.33%wt TiS_2, 0%wt graphite, and 6.67%wt teflon cathode composition; (a) discharge curves, and (b) charge curves.

The discharge curves have a slight downwarded plateau, therefore intercalation of lithium ions takes place in a larger voltage domains (2.10 - 1.90 V vs. Li/Li$^+$). The voltage for lithium intercalation depends on cathodic composition and on number of charge-discharge cycles.

Because the titanium disulfide is characterized by a very high electronic conductivity, it was possible to prepare electrodes without graphite or with a very small amount of graphite.

In accordance with the cathode composition, were realized three Li/TiS$_2$ button batteries. The opencircuit voltage cells is situated at 2.4 - 2.5 V vs. Li/Li$^+$, and the batteries are considered entirely discharged for 1.7 - 1.8 V vs. Li/Li$^+$ open circuit voltage. This value corresponds to a maximum intercalation degree of lithium ions in TiS$_2$ crystalline structure (x = 1).

The charge of batteries was made until the open circuit voltage was arrived at 2.7 V vs. Li/Li$^+$. The discharge and charge processes were performed at the same current density (i = 10 mA/cm^2).

From the experimental data, corresponding to the different cycles, were calculated the discharge capacities, C_{disch}, charge capacities C_{ch}, the utilization coefficient of active material, u, and efficiency of batteries r_F. The electrochemical characteristics of TiS$_2$ depolarisants are shown in Table 2.

Table 2.

Electrochemical characteristics of TiS$_2$ electrodes.

Cycle	C_t [mAh/g]	t_{disch} [h]	C_{disch} [mAh/g]	t_{ch} [h]	C_{ch} [mAh/g]	r_F [%]	u [%]
Electrode composition: 93.33 %wtTiS$_2$; 0%wt graphite; 6.67%wt teflon							
1	223	7.5	210.26	8	224.28	93.74	96.28
5	223	7	196.25	8	224.28	87.50	88.00
20	223	6.2	173.83	8	224.28	77.50	77.94
Electrode composition: 89.2 %wtTiS$_2$; 4.47%wt graphite; 6.33%wt teflon							
1	213.18	7	205.42	8	234.76	87.49	96.36
5	213.18	6	176.07	8	234.76	74.99	82.59
Electrode composition: 85.4 %wtTiS$_2$; 8.53%wt graphite; 6.08%wt teflon							
1	204.08	6.7	205.44	7.5	229.98	89.32	**100.66**
5	204.08	6	183.98	7.5	229.98	79.89	90.15
12	204.08	5	153.32	7.5	229.98	66.66	75.12

As can be seen from Table 2, the best performance was obtained with the batteries without graphite in composition of the cathode. For these cells were obtained 20 charge-discharge cycles, with good efficiencies (77-94%) at high utilized degree of active mass.

The displacement between the discharge and charge curves is due almost solely to resistance losses in the electrolyte, except at the extreme values of x, where polarization becomes important.

CONCLUSION

From the obtained results it can be establish that TiS_2 electrodes present good electrochemical characteristics, the intercalation phenomenon taking place by diffusion of the lithium ions only in the van der Waals layer, there being non-significant mobility through the sulfide layers.

The electrochemical behaviour of the electrodes is influenced by the crystalline structure of active material, TiS_2, by preparation conditions, and by electrode composition (graphite and teflon ratio).

The galvanic system with TiS_2 cathodes is reversible, observing plateau regions on charge-discharge curves, which corresponds to intercalation and deintercalation of lithium ions.

The reversibility of the electrode processes descrease with the number of charge-discharge cycles, because the oxidation process becomes more difficult in the presence of lithium ions.

REFERENCES

1. L. Aselage, E.E. Hellstrom, *J. Electrochem. Soc.,* 1987,**134**, 1932.
2. S.S. Wang, *J. Electrochem. Soc.,* 1988, **135**, 1675.
3. M. Eisenberg, *Electrochim. Acta,* 1981, **26**, 955.
4. Z.I. Takemara, Z. Ogumi, *J. Electrochem. Soc.,* 1991, **138**, 1574.
5. R.H. Friend, A.D. Yoffe, *Adv. Phys.*, 1987, **36**, 1.
6. E.J. Plichta, W.K. Behl, D. Vujic, W.H.S. Chang, D.M. Schleich, *J. Electrochem. Soc.,* 1992, **139**, 1509.
7. T. Jacobsen, K. West, S. Atlung, *Electrochim. Acta*, 1982, **27**, 1007.
8. M.A. Santa-Ana, V. Sanchez, G. Gonzales, *Bol. Soc. Chil. Quim.*, 1992, **37**, 157.
9. G.L. Henriksen, D.R. Wissers, A.A. Chilenskas, *J. Power Sources*, 1995, **54**, 134.
10. M.S. Whittingham, *Prog. Solid State Chem.,* 1978, **12**, 41.
11. K. Kanehori, F. Kirino, T. Kudo, K. Miyauchi, *J. Electrochem. Soc.,* 1991, **138**, 2217.
12. K. Kanehori, F. Kirino, T. Kudo, K. Miyauchi, *J. Electrochem. Soc.*, 1991, **138**, 2216.
13. S.A. Safran, *Solid State Phys.*, 1987, **40**, 183.
14. O. Tillement, J. Angenault, J.C. Couturier, M. Quarton, *Solid State Ionics,* 1992, **53-56**, 391.
15. S.R. Narayanan, D.H. Shen, S. Surampudi, A.I. Attia, G. Halpert, *J. Electrochem. Soc.,* 1993, **140**, 1854.

16. M.B. Armand, *Materials for Advanced Batteries*, Edited by D.W. Murphy and J. Broadhead, p. 145, 1984.
17. E.J. Frazer, S. Phang, *J. Power Sources,* 1981, **6**, 307.
18. Georgeta Țarălungă, *Ph. D. Thesis,* "Babeş-Bolyai" University Cluj-Napoca, Romania, 1998.