TEMPERATURE DEPENDENCES OF ELECTRICAL AND ELECTROCHEMICAL PROPERTIES OF TITANIUM DISULFIDE

J. Molenda

INSTITUTE OF MATERIAL SCIENCE, ACADEMY OF MINING AND METALLURGY, 30–059 CRACOW, POLAND

The electrical conductivity and thermoelectric power of titanium disulfide were measured at temperatures ranging from 77 to 300 K on samples exhibiting different deviations from stoichiometry. It was found that $Ti_{1+y}S_2$ has metallic properties at the temperatures studied, the effective mass of the carriers varying with the deviation from stoichiometry. It was shown that the character of the discharge curve for the $Li/Li^+/Li_xTi_{1+y}S_2$ cell was correlated with the electronic structure of titanium disulfide.

Keywords: electrical, electrochemical properties, titanium disulfide

Introduction

Titanium disulfide belongs in a large group of layered compounds of A_xMX_2 type (A = alkali metal; M = transition metal; X = O, S or Se), which can reversibly incorporate foreign atoms into their lattice without any essential modification of the crystallographic structure [1, 2]. It has been stated that titanium disulfide has quite a significant nonstoichiometry range, since the S/Ti ratio can vary from 2 to 1.8 or even less [3, 4]. However, the defect structure and the mechanism of charge carrier transport in this material remain unclear.

The purpose of the present work was to demonstrate a relation between the electronic and the electrochemical properties of the cathode material $Li_xTi_{1+y}S_2$.

Experimental

Electrical and electrochemical measurements were carried out on samples of $Ti_{1+y}S_2$ obtained by direct synthesis from titanium and sulfur. A detailed description of the sample preparation and the measuring procedure has been given elsewhere [5, 6].

Results and discussion

Titanium disulfide exhibits a significant deviation from stoichiometry, which may reach 0.2 moles/mole TiS_2 and which is associated with excess titanium atoms in the interlayer spaces. The reported results of electrical conductivity and thermoelectric power measurements at thermodynamic equilibrium and at high temperatures (970–1220 K) as functions of temperature and sulfur vapor pressure (280 Pa – 95 kPa) have shown that the electrical conductivity is the following function of sulfur vapor pressure [7]:

$$\sigma = const \ ps_2^{1/3.5} \tag{1}$$

Analysis of the dependence indicates that the predominant defects are interstitial Ti^+ and Ti^{2+} ions. The negative sign of the thermoelectric power in the temperature range studied [7] supports such a defect structure model and indicates that electrons are the predominant charge carriers in $Ti_{1+y}S_2$. From the viewpoint of electronic structure, the interstitial titanium atoms are donor centers formed as follows:

$$TiS_2 \rightleftharpoons Ti_i^{n+} + S_2 + n \ e^- \tag{2}$$
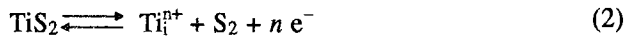
Analysis of high-temperature measurements of the electrical conductivity and the deviation from stoichiometry indicates that at these temperatures the intrinsic conductivity, i.e. the generation of carriers through the energy gap ($E_g = 0.7$ eV), should also be considered in $Ti_{1+y}S_2$. The total conductivity is the sum of a component relating to the deviation from stoichiometry, σ_y, and another intrinsic component, σ_o:

$$\sigma = \sigma_y + \sigma_o \tag{3}$$

Analysis of the temperature dependence of the mobility indicates that the mobility decreases with increasing temperature ($\mu = AT^{-5.5}$). Moreover, the dependence of the thermoelectric power on the carrier concentration appears to be of the type $\alpha = f(n^{-2/3})$, which implies metallic properties of the charge carriers at high temperatures. The effective mass of the carriers, determined from thermoelectric power measurements, varies from 2 to 1.5 m_e [7].

Low-temperature (77–300 K) electrical measurements [5] on quenched $Ti_{1+y}S_2$ samples with a fixed deviation from stoichiometry indicate that the metallic properties are preserved at low temperatures. Figures 1 and 2 show the temperature dependences

of the electrical conductivity and the thermoelectric power for several values of y. It can be seen that the properties change continuously with increasing deviation from stoichiometry. Figure 3 presents the experimental dependence on the thermoelectric power on the carrier concentration (y in $Ti_{1+y}S_2$) at 300 K (points). In this figure, the solid line shows the theoretical dependence of the thermoelectric power on the carrier concentration in the metallic state, resulting from the equation.

$$\alpha = \frac{2}{3}\left(\frac{\pi}{3}\right)^{\frac{2}{3}}\left(\frac{m^{*}k^{2}T}{eh^{2}}\right)n^{-\frac{2}{3}} \qquad (4)$$
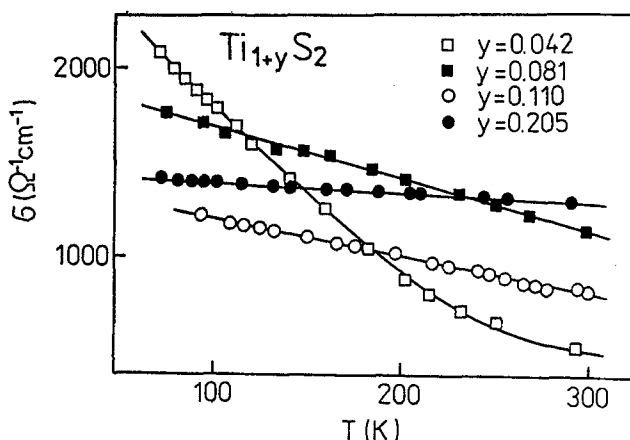

Fig. 1 Temperature dependence of electrical conductivity for $Ti_{1+y}S_2$ of different y
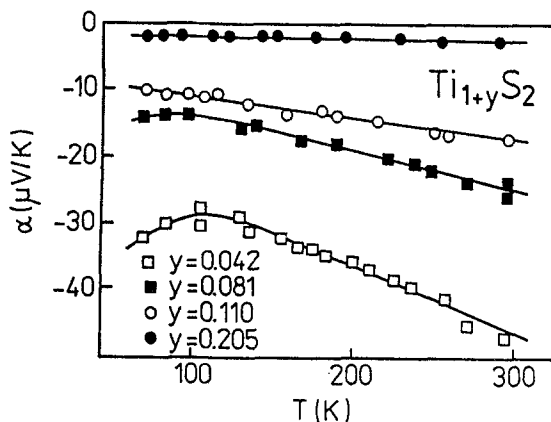

Fig. 2 Temperature dependence of thermoelectric power for $Ti_{1+y}S_2$ of different y

where h is Planck's constant, m^* is the effective mass of the carriers, and n is the carrier concentration. A comparison of the experimental points with the theoretical dependence indicates that in the range of low deviations from stoichiometry a good approximation can be obtained when the effective mass of the carriers m^* is equal to 5 m_e whereas for the highest deviations from stoichiometry the effective mass approaches, m_e.
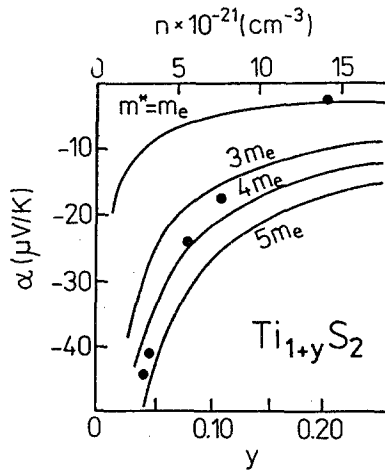

Fig. 3 Dependence of thermoelectric power on carrier concentration for $Ti_{1+y}S_2$ at 300 K (points). Solid line — a theoretical dependence (Eq. 4)

Analysis of the high- and low-temperature electrical properties permits the proposal of a qualitative model of the electronic structure in nonstoichiometric titanium disulfide, which is shown schematically in Fig. 4. At room temperature (i.e. at the working temperature of a $Li/Li^+/Li_xTi_{1+y}S_2$ battery), the charge transport in titanium disulfide with a low deviation from stoichiometry (Fig. 4a) takes place in a narrow donor band formed from the overlapping wave functions of $3d$ electrons belonging to titanium interstitials. Formation of the donor conduction band can be anticipated on the basis of Mott's criterion [8] for a transition from localized electronic states to the metallic state in the case of a doped semiconductor (y in $Ti_{1+y}S_2$ plays the role of a dopant). If it is assumed that the ionization energy of donor centers, E_D, is 0.01 eV and that the dielectric constant χ is 10, it is possible to estimate m^*/m_e from the following relation:

$$E_D = -\frac{13.52}{(\chi^2 n^2)}\left(\frac{m^*}{m_e}\right) \qquad (5)$$

The critical concentration of donor centers, N_c, at which a donor conduction band forms can be calculated from an expression given by Mott [8]:

$$N_c^{1/3}\, a_H \cong 0.25 \qquad (6)$$

where a_H is a hydrogen-like radius of a dopant, for which the following condition is satisfied:

$$a_H = 0.53 \left(\frac{m_e}{m^*} \right) \chi \, n^2 \qquad (7)$$

The N_c value thus estimated for $Ti_{1+y}S_2$ is $4.2 \cdot 10^{19}$ cm^{-3} which corresponds to the deviation from stoichiometry $y = 0.0003$ moles. Consequently, for the lowest deviations from stoichiometry studied, i.e. $y = 0.042$, the donor conduction band has already been formed. Further increase in dopant concentration (y) leads to this band becoming wider, and it finally overlaps the conductivity band (Fig. 4b). Simultaneously, the effective mass of the carriers decreases. It has been found from thermoelectric power measurements that the effective mass of the charge carriers decreases from 5 m_e to 1 m_e with increasing deviation from stoichiometry.
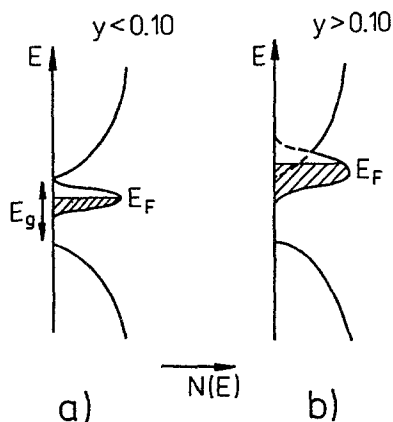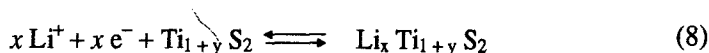

Fig. 4 Scheme of the electronic structure of $Ti_{1+y}S_2$, a) $y < 0.10$ and b) $y > 0.10$

Electrons introduced in the electrochemical intercalation (together with Li^+ ions)

$$x \, Li^+ + x \, e^- + Ti_{1+y} S_2 \rightleftharpoons Li_x \, Ti_{1+y} S_2 \qquad (8)$$

occupy the available electronic states and raise the Fermi level in accordance with the state density function, $N(E)$ (Fig. 4).

Figure 5 shows a discharge curve for the $Li/Li^+/Li_x Ti_{1.081}S_2$ cell, reflecting the Fermi level variations of the cathode material with the concentration of electrons introduced into $Ti_{1.081}S_2$ (points). This Figure also shows the theoretical curve (solid line) representing the Fermi level variations with the carrier concentration calculated for the metallic state from the equation.

$$E_F = \left(\frac{h^2}{2m^*}\right)(3\pi^2)^{2/3}\, n^{2/3} \qquad (9)$$

Figure 5 reveals the good approximation of the experimental curve (discharge curve) to the theoretical curve ($\Delta E_F = f(n)$) when the effective mass of the carriers is $m^* = 4.5 - 3.6\, m_e$. This change in the effective mass for $Li_xTi_{1+y}S_2$ ($0<x<1$) indicates that the modification of the electronic properties of titanium disulfide due to its doping with lithium in the electrochemical process differs from that due to the increasing deviation from stoichiometry (compare Fig. 3: $m^* = 5 - 1\, m_e$). This is associated with a significant increase in the Ti–Ti distance in the electrochemical intercalation.
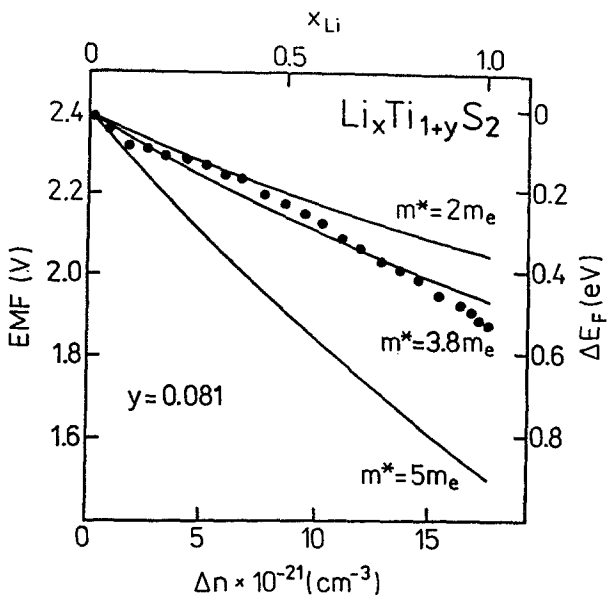

Fig. 5 Discharge curve illustrating the variations of the Fermi level as a function of electron concentration introduced in the intercalation process in $Li_xTi_{1+y}S_2$ (points). Solid line — a theoretical dependence (Eq. 9)

Measurements [5] with gradually intercalated $Li_xTi_{1+y}S_2$ samples indicate that the modification of the electronic structure of $Ti_{1+y}S_2$ that occurs in the intercalation process proceeds toward Anderson's localization.

*   *   *

References

1 M. S. Whittingham and F. R. Gamble, Mater. Res. Bull., 10 (1975) 363.
2 D. A. Winn, J. M. Shermilt and B. C. H. Steele, Mater. Res. Bull., 11 (1976) 559.
3 M. Saeki, J. Crystal Growth, 35 (1976) 77.
4 D. A. Winn and B. C. H. Steele, Mater. Res. Bull., 11 (1976) 551.
5 J. Molenda, A. Stoklosa, Do Than and T. Bak, Phys. Status Sol. (a), 119 (1990) 221.
6 Do Than, J. Molenda and A. Stoklosa, Electrochim. Acta, 36 (1991) 1555.
7 J. Molenda, A. Stoklosa, S. Mrowec and Do Than, Phys. Status Sol. (a), 119 (1990) 1571.
8 N. F. Mott and E. A. Davis, Electronic processes in noncrystalline materials, Clarendon Press, Oxford 1971.

Zusammenfassung — An Proben mit unterschiedlich starken Abweichungen von der stöchiometrischen Zusammensetzung wurde im Temperaturbereich von 77 bis 300 K die elektrische Leitfähigkeit und die thermoelektrische Kraft von Titandisulfid gemessen. Man konnte feststellen, daß $Ti_{1+y}S_2$ bei den fraglichen Temperaturen metallische Eigenschaften aufweist. Es wurde weiterhin gezeigt, daß die Entladungskurve für eine $Li/Li^+/Li_xTi_{1+y}S_2$ Zelle mit der Elektronenstruktur von Titandisulfid korelliert.