

Lithium insertion into TiS_2 from various electrolytes

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Abstract

The quasi-equilibrium behaviour of TiS_2 electrodes in various electrolytes was studied, and the galvanostatic switch-on transients in those were measured. It was found, that both the potential of the intercalate Li_xTiS_2 with fixed x values and the diffusivity of the intercalating species are dependent on the nature of the electrolyte.

Introduction

It is generally acknowledged that the cycling behaviour of the lithium electrode in nonaqueous electrolytes is strongly dependent on the nature of the solvent and of the anion. The electrolyte influence on the performance of Li electrodes is usually considered as the key problem of the choice of the electrolyte for rechargeable batteries [1]. Meanwhile, some examples of electrolyte influence on the behaviour of the positive electrodes can be found in the literature [2]. This may be connected with the fact that not fully dissolved Li^+ ions but more complex species are intercalated into the positive electrode during discharge. In principle, the nature of intercalating species can influence the equilibrium behaviour of the insertion compounds as well as the diffusion kinetics. The behaviour of TiS_2 electrodes in various electrolytes — 1 M LiClO_4 in propylene carbonate (PC) and in γ -butyrolactone (BL), 1 M LiBF_4 in BL, and 1 M LiAsF_6 in a mixture of 2-methyltetrahydrofuran (MeTHF) with 2-methylfuran (MeF) — was studied in the present work.

Experimental

Positive electrodes ($3\text{ cm} \times 2\text{ cm}^2$) were made from 0.4 g mixture of TiS_2 powder (80 wt.%), carbon black (10 wt.%), and polytetrafluoroethylene (PTFE) binder (10 wt.%). The particle size distribution of the TiS_2 powder is presented in Table 1. The specific area of the TiS_2 powder estimated from this distribution was about 1000 to $1500\text{ cm}^2/\text{cm}^3$. The mixture was pressed onto a nickel mesh. The positive electrode was wound with a nonwoven polypropylene separator. One positive and two negative (Li sheet) electrodes were placed into a prismatic cell made from PTFE. A separate small Li reference electrode was also inserted into the cell.

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TABLE 1

Particle size distribution in TiS_2 powder

Size range (μm)	%
> 300	0.22
160–300	23.8
100–160	38.7
80–100	9.33
60–80	0.17
40–60	4.47
< 40	23.3

Quasi-equilibrium discharge curves were obtained at current density $8 \mu\text{A}/\text{cm}^2$. Previously, it was shown that these curves were practically reversible – the IR drop was less than 1 mV.

Chronopotentiometric measurements were performed at current densities from 0.4 to $2.5 \text{ mA}/\text{cm}^2$.

Results and discussion

Quasi-equilibrium discharge

Quasi-equilibrium discharge curves, i.e., dependences of potential (E) on intercalation degree (x) for Li_xTiS_2 in various electrolytes are shown in Figs. 1(a)–(c). Curves for LiBF_4 in PC [3], for LiClO_4 in dioxolane [4], and for LiAsF_6 in a mixture MeTHF + ethylene carbonate [5] are also shown. It is clear that the equilibrium E - x curves are dependent on the nature of the electrolyte especially on that of the anion. The most positive potentials (i.e., the least activity of Li in the intercalate) were obtained for LiBF_4 in BL. The difference between equilibrium potentials at $x=0.5$ for this solution and for LiClO_4 in PC is about 0.2 V.

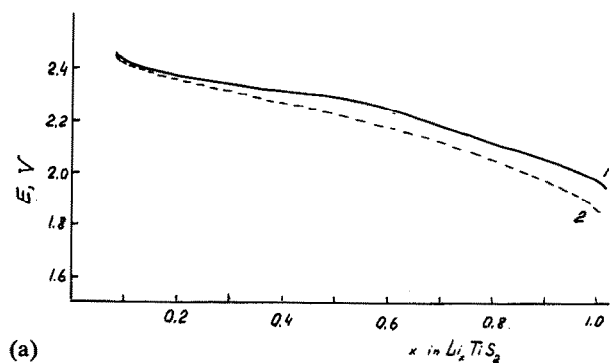
The important feature of the curves in Fig. 1 is their almost linear shape in some intervals of x . On the whole, these curves may be considered as consisting of two linear parts at $0.1 < x < 0.5$ and at $0.5 < x < 0.9$. Therefore, the E - x dependency in an analytical form may be written as:

$$\left. \begin{aligned} E &= E_1^0 - \gamma_1 x & (\text{for } 0.1 < x < 0.5) \\ E &= E_2^0 - \gamma_2 x & (\text{for } 0.5 < x < 0.9) \end{aligned} \right\} \quad (1)$$

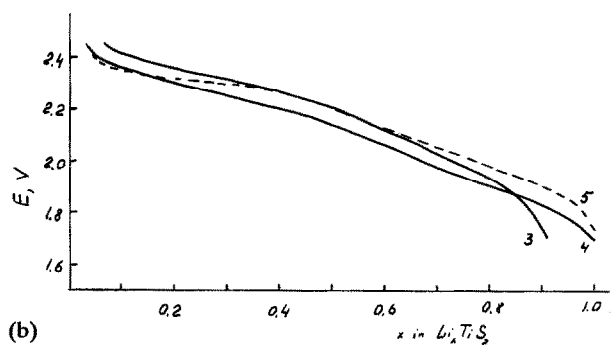
It may be seen from Fig. 1, that the curves slope in the region of high x -values (i.e., γ_2) are almost 1.5 to 2 fold in comparison with the one in the region of low x values.

Chronopotentiometric measurements

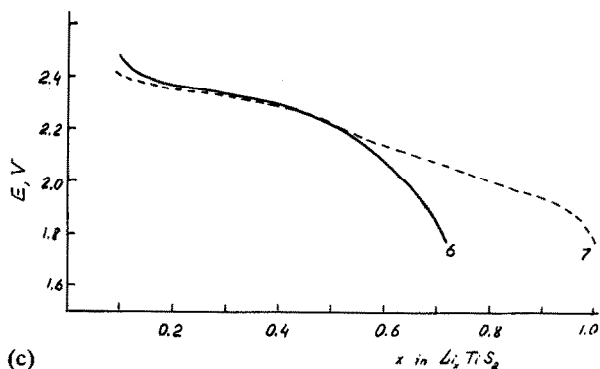
Galvanostatic switch-on transients for LiClO_4 in PC are shown in Fig. 2(a). There is a sharp jump in these curves and then a slow transient. The jump, proportional to the current is due to both IR drop and activation polarization. The slow transients are linearized in the coordinates $E - \sqrt{t}$ (t : time after switch-on), Figure 2(b), shows that diffusion is the limiting step in the whole process.



(a)



(b)



(c)

Fig. 1. (a) Quasi-equilibrium discharge curves for Li_xTiS_2 in LiBF_4 in (1) BL and in (2) PC (according to ref. 3); (b) quasi-equilibrium discharge curves for (3) Li_xTiS_2 in LiClO_4 , in BL, (4) in PC, and (5) in dioxolane (according to ref. 4); (c) quasi-equilibrium discharge curves for (6) Li_xTiS_2 in LiAsF_6 in MeTHF/MeF, and (7) in a mixture MeTHF/ethylene carbonate (according to ref. 5).

Figure 3 shows that the slopes of lines in Fig. 2(b) are proportional to current I . This fact confirms that the current distribution on the TiS_2 surface was uniform, and solid-state diffusion of Li is the limiting step of the process in this case.

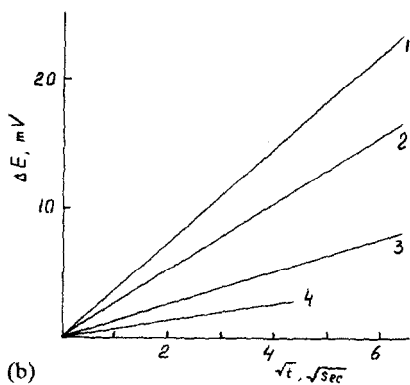
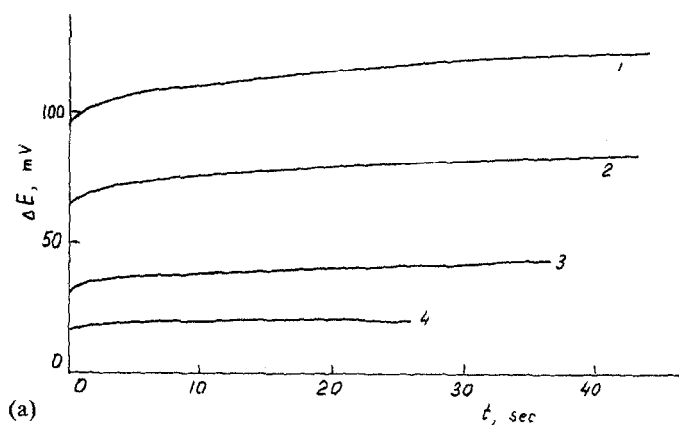


Fig. 2. (a) Galvanostatic switch-on transients for LiClO_4 in PC; current: curve (1) 30 mA, curve (2) 20 mA, curve (3) 10 mA and curve (4) 5 mA; electrode area 12 cm^2 ; (b) the same transients in coordinates E, \sqrt{t} (initial jump is omitted).

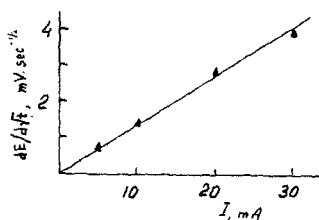


Fig. 3. $dE/d\sqrt{t}$ vs. I for LiClO_4 in PC.

According to the theory of chronopotentiometry the concentration of diffusing species at the surface in the case of linear semi-infinite diffusion obeys the following equation:

$$c_t = c_0 + \frac{2i}{nF} \sqrt{\frac{t}{\pi D}} \quad (2)$$

where c_0 and c_t are the concentrations at the first moment and at the time t , D is the diffusion coefficient.

A good approximation for Li_xTiS_2 is:

$$x = Mc/\rho \quad (3)$$

when ρ and M are density and molecular weight of TiS_2 , therefore

$$x_t = x_0 + \frac{2iM}{nF\rho} \sqrt{\frac{t}{\pi D}} \quad (4)$$

The true current density i is connected with the current I :

$$i = I\rho/sm \quad (5)$$

where m is the weight of TiS_2 in the electrode, and s the specific area. Combining eqns. (1), (4) and (5) one can obtain:

$$E = E_0 - \gamma x_0 - \frac{2IM\gamma}{nFsm\sqrt{\pi}} \frac{\sqrt{t}}{\sqrt{D}} \quad (6)$$

It can be seen that the curves in Fig. 2 are consistent with eqn. (6).

The curves in Fig. 2 were obtained by means of an electrode with an intercalation degree $x = 0.10$. The corresponding curves for other electrodes in the range $0.1 < x < 0.9$ were almost the same. The values of $\beta = d^2E/d\sqrt{t} dI$ (i.e., slopes of the lines as in Fig. 3) were equal to 1.60, 2.31, 2.14, and 2.00 $\Omega \text{ cm}^2 \text{ s}^{-1/2}$ for x values of 0.10, 0.17, 0.45 and 0.70.

Eqn. (6) gives a possibility to calculate the diffusion coefficient of the inserting species in the intercalate:

$$D = \left(\frac{2M\gamma}{nFsm\beta\sqrt{\pi}} \right)^2 \quad (7)$$

The diffusion coefficient of species intercalated from LiClO_4 in PC was estimated as high as $10^{-10} \text{ cm}^2/\text{s}$.

Keiichi *et al.* [6] reported some other data concerning diffusion coefficients of lithium in titanium disulfide. They found that the diffusion coefficient of species intercalated from 1 M LiClO_4 in PC into single crystal sample of TiS_2 is strongly depended on the intercalation degree x : for x values of 0.1, 0.5, and 0.8 D is equal to 2×10^{-9} , 2×10^{-7} , and $5 \times 10^{-8} \text{ cm}^2/\text{s}$. The reason of disagreement with our data is unclear, but one may assume, that it is connected with nonstoichiometry of TiS_2 . Keiichi *et al.* [6] note especially, that D values decrease with increasing excess of stoichiometric titanium in TiS_2 .

Galvanostatic switch-on transients for Li_xTiS_2 samples with $x < 0.1$ are not linearized in $E-\sqrt{t}$ coordinates, Fig. 4. This effect is due to nonlinearity of the $E-x$ curve in this case, and consequently impossible to use eqn. (6).

Transients for LiBF_4 in BL are shown in Fig. 5. From these curves it is apparent that the solid-state diffusion is rather fast in this case, and the transients are almost the same as the quasi-equilibrium $E-x$ curves shown in Fig. 1. One can conclude that the diffusion coefficient for species intercalating from LiBF_4 in BL is much higher than for a LiClO_4 -PC solution.

The transients for LiClO_4 in BL, and for LiAsF_6 in the MeTHF/MeF mixture were almost the same as those for LiBF_4 in BL.

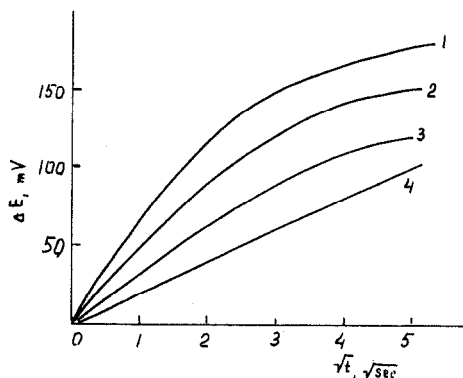


Fig. 4. Galvanostatic switch-on transients for LiClO_4 in PC at electrode with $x=0.02$ (initial jump is omitted); current: curve (1) 30 mA; curve (2) 20 mA; curve (3) 10 mA, and curve (4) 5 mA (electrode area: 12 cm^2).

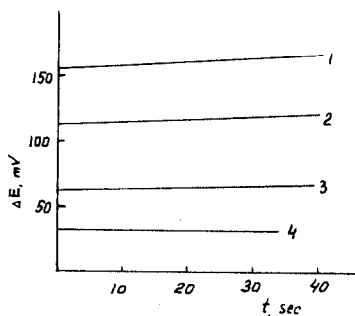


Fig. 5. Galvanostatic switch-on transients for LiBF_4 in BL; current: curve (1) 30 mA, curve (2) 20 mA, curve (3) 10 mA and curve (4) 5 mA (electrode area 12 cm^2).

It is interesting that the transport properties of intercalating species are correlated with their activity. The species intercalating from LiBF_4 in BL have the highest values of D , and the least activity, whereas the ones intercalating from LiClO_4 in PC have the lowest values of D and the highest activity.

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