Titanium Disulfide Cathode Prepared Directly on the Titanium Plate¹⁾

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1 Introduction

Recently, Li/TiS₂ cell is attracting attentions of many workers in the field of high energy density secondary batteries²⁾. All the TiS₂ cathodes reported in the literature have been prepared exclusively by hot-pressing a mixture of powdery TiS₂ and some binders. However, the use of binders of organic polymers not only increases the internal resistance of a TiS₂ cell but also leads to a decrease of energy density. In order to overcome these disadvantages, it is desirable to prepare the TiS₂ cathode directly on the substrate of metallic titanium without using any binders.

In the previous paper, we prepared a thin layer of titanium sulfides by anodic oxidation of titanium plates in molten Na₂S·9H₂O³⁾. The main product obtained there was, however, titanium monosulfide and the expected product, TiS₂, was not obtained. As a result, the output voltage of the lithium cell prepared by this method was one-half of the ordinary Li/TiS₂ cells.

In the present study, an attempt was made to prepare TiS₂ directly on the surface of titanium plate by means of the thermal reaction. If this is possible, TiS₂ cathodes can be prepared in one-step operation omitting the hot-press process and the resistance of the resultant electrode should be smaller.

2 Experimental

For the purpose of comparison, TiS₂ was prepared in two different ways. One was prepared by reacting titanium plates (5×5×0.5 mm) directly with sulfur at 700°C in a sealed quartz tube. In order to form the surface film only on one side of the titanium specimen,

Table 1 Preparation of TiS₂ electrodes

Sample No.		Molar ratio (Ti : S)	Heat treatment at 700°C (h)
MSE	1 ^{a)}	1 : 1	18
	2 ^{b)}	5 : 1	12
	3 ^{b)}	10 : 1	6
PE	4 ^{c)}	1 : 2	18
	5 ^{c)}	1 : 2	12
	6 ^{c)}	1 : 2	6

a) Product film peeled off the substrate body spontaneously. The film was directly mounted on one end of a brass rod to make the electrode, b) Base plate of Ti served as the collector electrode, c) Powdery product was hot-pressed at 300°C with 10% Teflon powder.

the other side of specimen was covered by asbestos during the heat treatment. The reaction time and the amount of sulfur to be reacted were varied to control the thickness of the TiS₂ film as listed in Table 1. In order to avoid confusion, we shall call this as the metal supported electrode (MSE). In this way, the 1st sample was prepared by the reaction of titanium plate with equimolar amount of sulfur for 18 hours. A thick film (approximately 0.5 mm) produced by this treatment was however readily peeled off from the substrate body without degrading the film structure. The film peeled off was used as it was for the cathode electrode (MSE 1) by mounting it directly on the brass rod lead. MSE's 2 and 3 were prepared by reducing both the molar ratio of sulfur to titanium and the reaction time. These two products were tightly attached to the substrate body and did not peel off. The thickness of TiS₂ layer of MSE 3, which was the thinnest in the present study, was calculated to be 0.1 mm from the weight gain.

For all the three MSE's, X-ray diffractometry revealed the reaction product to be TiS₂ mainly. Besides this, a small amount of dimeric form

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Key Words: Titanium Disulfide Cathode, Lithium Cell

(Ti_2S_4) was also detected. Scanning electron microscopy indicated that the crystal size of metal supported TiS_2 was almost the same as powdery TiS_2 .

The other type of electrodes were made with the ordinary procedure to produce powdery TiS_2 . A given amount of spongy titanium was mixed with the stoichiometric amount of sulfur and heated in a quartz tube at 700°C for three different reaction times, which were made the same as in the preparation of MSE. Powdery TiS_2 thus obtained was mixed with Teflon powder (10% in weight) and pressed at 300°C with pressure of $2 \times 10^4 \text{ g}\cdot\text{cm}^{-2}$ to form a pellet. We shall call this as the pellet electrodes (PE).

Either propylene carbonate (PC) or equivolume mixture of γ -butyrolactone (BL) and tetrahydrofuran (THF) were used as the solvent and LiClO_4 ($1 \text{ mol}\cdot\text{dm}^{-3}$) as the supporting electrolyte. These solvents and electrolyte were purified and dried in a usual manner⁴⁾. All experiments were done in a glove box under the argon atmosphere at room temperature.

3 Results and Discussion

Figure 1 shows the steady state polarization curves of two types of TiS_2 electrode observed in two different solvent systems. Measurements were made galvanostatically. Results in

Fig. 1 Steady state polarization curves in PC (curve *b*, *d*) and BL-THF (curve *a*, *c*)
Curves *a* and *b* were obtained with MSE 2, Curves *c* and *d* were obtained with PE 5

this figure exhibits typically a solvent effect on the cell performance with TiS_2 electrodes. When PC was used as the solvent, active material began to detach from the electrode surface at a certain current density (curves *b* and *d*). This phenomenon is attributed to the expansion of the layer distance of TiS_2 as a result of intercalation of PC itself⁵⁾. The threshold current density for the degradation was 2×10^{-4} and $10^{-3} \text{ A}\cdot\text{cm}^{-2}$ for the pellet and metal supported electrodes, respectively. It is worth noting that the metal supported electrode is more resistant for the layer expansion than the pellet electrode. The threshold current density of the pellet electrode depends on both the amount of binder and pressing conditions. The degradation of electrode was inherent to the PC solvent system. Different behaviors are observed when solvent was changed. Curves *a* and *c* show this. In the equivolume mixture of BL and THF both the two types of electrodes, metal supported and pellet, were stable and no breakdown was observed upto $10^{-2} \text{ A}\cdot\text{cm}^{-2}$.

Curves in Fig. 2 show the effect of the nature of TiS_2 electrodes prepared under several different conditions on the actual cell performance. In this measurement, cells were constructed

Fig. 2 Effect of nature of TiS_2 cathodes on the cell performance

Discharge was made at constant load ($10 \text{ K}\Omega$), Solution: 1 M LiClO_4 in BL-THF, *a*: MSE 1, *b*: MSE 3, *c*: PE 4, *d*: PE 6, Curve *e* was obtained with a pellet electrode made of the same material as PE 6 but contained no Teflon binder

with Li-anode and several types of TiS_2 cathode. Solution was 1 M LiClO_4 in BL-THF solvent. The change in output voltage was recorded with time during the discharge through a constant load (10 K Ω) and plotted against the fractional utilization of the cathodic active material, TiS_2 . In this figure, curves *a* and *b* were recorded with two different MSE's (MSE's 1 and 3), while *c*, *d* and *e* were with three kinds of pellet electrode. It is obvious from the figure that better performance is obtained with cells of MSE. The difference in voltage characteristics between MSE and PE may be attributed to the higher internal resistance of PE which contains organic binder. This is to some extent confirmed by comparing curves *d* and *e*, which were obtained with two PE's made of the same TiS_2 material (PE 6). Only difference was the use (curve *d*) and non-use (curve *e*) of binder. It is seen that the non-use of binder certainly improves the output voltage to some extent but the improvement is still insufficient. It should be noted that the curve *a* was obtained with MSE 1, which was made of the film peeled off from the Ti-substrate and did not contain any binder either.

These results indicate that the use of binder in the preparation of TiS_2 electrodes is quite undesirable. However, the disadvantage of using PE is not only related with this problem but also related with some other factors. As are represented by curves *b* and *e*, the performance of a PE cell is still inferior even with an electrode free from binder. The reason of this may partly be attributed to that the intergranular contact resistance is still not negligible in PE. Another reason is probably attributed to the porous structure of PE. Because of the granular structure of a pellet the voidage is thought to be greater in PE than in MSE.

Usually, TiS_2 powder is synthesized by reacting metallic titanium and sulfur for several days at 700°C. On the other hand, the pellet electrodes examined here were all prepared with TiS_2 which was heat treated only for 18

hours at the longest. This might be a reason of inferiority of the pellet electrodes. In order to make sure this point, we studied the effect of the duration of heat treatment. No improvement of the discharging characteristics was, however, observed upon increasing the reaction time from 18 to 48 or even to 168 hours. This shows that, as far as the practical use is concerned, the heat treatment can be reduced considerably. A 18 hours treatment, which is almost one-tenth of the time of usual heat treatment, seems to be sufficient.

In conclusion, metal supported electrodes have superior characteristics than the pellet electrodes made of powdery TiS_2 . Advantages can be summarized as follows.

1. Metal supported electrode can be prepared in one-step operation omitting the hot-press process.
2. Output voltage of a cell with this electrode is higher than that with the pellet electrode. This is probably due to the higher density of MSE than PE, which is made from powder by hot-press.
3. Since the use of any binder is unnecessary, the internal cell resistance becomes smaller.
4. It is also superior in the sense of the mechanical strength against the expansion of layer distance.

Acknowledgement :

This work was financially supported by the Ministry of Education (Grant No. 57850257).

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(Received Mar. 14, 1983; Accepted May 4, 1983)