GALVANOSTATIC CYCLING OF LITHIUM–TITANIUM DISULPHIDE CELLS IN PROPYLENE CARBONATE AND PROPYLENE CARBONATE–ACETONITRILE ELECTROLYTES

E. J. FRAZER and S. PHANG*

CSIRO Institute of Energy and Earth Resources, Division of Mineral Chemistry, P.O. Box 124, Port Melbourne, Victoria 3207 (Australia)

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Summary

The galvanostatic cycling of Li–TiS$_2$ cells in 1M LiAsF$_6$/propylene carbonate (PC)–acetonitrile (AN), 1M LiAsF$_6$/PC and 1M LiClO$_4$/PC electrolytes is reported. For all electrolytes tested, the discharge capacity was always much larger on the first cycle than subsequent cycles. The capacity was also shown to be dependent on the surface area of the TiS$_2$ and the rate of charge and discharge. The general performance of the cell in LiClO$_4$/PC was a function of the condition of the lithium electrode. The cell performed best in the 1M LiAsF$_6$/PC–AN electrolyte with respect to charge/discharge rate, active material utilisation and cycle life. Although it was possible to cycle the cell in 1M LiAsF$_6$/PC–AN more than 1000 times at current densities $\sim$ 1 mA cm^{-2}, the active material utilisation was $<$ 10% after the first 25 cycles.

Introduction

Recent reviews on metal chalcogenides [1 - 4] indicated that TiS$_2$ was a useful cathode material for nonaqueous lithium batteries. Whittingham [5] reported the shallow galvanostatic cycling of Li–TiS$_2$ cells in LiClO$_4$/tetra-hydrofuran–dimethoxyethane electrolytes. Using only 4% of the cell's theoretical capacity, 1100 cycles at 1 mA cm^{-2} were obtained. Gaines *et al.* [6] achieved 150 - 250 cycles at greater than 60% material efficiency in LiClO$_4$/dioxolane with charge/discharge rates of 2.5 and 10.0 mA cm^{-2}, respectively. Rao *et al.* [7] recently reported the limited cycling of Li–TiS$_2$ cells with an LiSCN/dioxolane–dimethoxyethane electrolyte. While 80 - 90% of the theoretical capacity was obtainable on the first discharge, the overall performance and lifetime were very sensitive to charge/discharge rate and electrode loading.

Holleck and Driscoll [8] reported some galvanostatic and potentiostatic experiments performed on TiS$_2$ electrodes in 1M LiClO$_4$/PC, 1M LiAlCl$_4$/PC

*Now at Karratha College, P.O. Box 315, Karratha, Western Australia 6714, Australia.

and 1M $LiAlCl_4$/PC containing TEAP (tetraethylammonium perchlorate). As far as we can ascertain, only PC electrolytes were used in their galvanostatic experiments and current densities were quite low, being limited to 0.3 mA cm^{-2}. (It should be noted that recent studies of Trumbore and Auborn [9] on the purification of nonaqueous electrolytes using molecular sieves suggest that lithium ion concentrations reported by Holleck and Driscoll [8] may be in error.) A later report by Holleck *et al.* [10] has shown that the Li–TiS_2 cell can withstand extended cycling (100 - 200 cycles) between preselected voltage limits (1.6 and 3.0 V) using an $LiAsF_6$/2-methyltetrahydrofuran electrolyte. However, the current densities used and active material utilisation obtained were not reported.

For a cell to be acceptable for traction purposes it must be capable of being cycled in excess of 1000 times at high current densities [11]. Although extended cycling of Li–TiS_2 cells at high current densities with large active material utilisation has been reported [6], further work in this direction appears desirable. One of our objectives is to screen various electrolyte systems for Li–TiS_2 cells with the above requirements in mind. In this paper we report some results obtained from the galvanostatic cycling of Li–TiS_2 cells in 1M $LiClO_4$/PC, 1M $LiAsF_6$/PC and 1M $LiAsF_6$/PC–AN electrolytes. The choice of the PC–AN electrolyte was based on preliminary studies made by Parker *et al.* [12] and Cedzynska *et al.* [13] who suggested its use in lithium cells.

Experimental

Titanium disulphide was prepared using the method described by Whittingham [14]. Elemental titanium sponge (Hopkin & Williams Ltd., England) and powdered sulphur (Alfa, USA, t5N5), in almost stoichiometric proportions, were sealed, under vacuum, in a quartz tube and slowly heated to $\sim$ 300 °C for 36 h and then $\sim$ 600 °C for 48 h. The sulphur was always in very slight excess. The product was analysed gravimetrically by conversion to TiO_2 [15], and for all samples prepared, the value of x in Ti_xS_2 was 1.005 ± 0.005. A sample of commercially produced TiS_2 was also obtained for testing (Laporte Industries Ltd., England). Surface areas were determined using the BET technique (Carlo Erba Sorptomatic Model 1800). The TiS_2 prepared in this laboratory had a surface area of 2.52 m^2 g^{-1} whereas the commercial sample was 9.04 m^2 g^{-1}.

Propylene carbonate (Aldrich Chemical Company, Inc., USA, 99%) was first dried with 4A molecular sieves and then vacuum distilled at $\sim$ 5 Torr with a reflux ratio of $\sim$ 5:1. The water content as indicated by Karl Fischer titrations was $\sim$ 70 ppm or less. Technical grade AN was distilled from $KMnO_4$, dried over calcium hydride for a week, and then triply-distilled from calcium hydride. Lithium hexafluoroarsenate (USS Agrichemicals, electrochemical grade) and lithium perchlorate (ICN, 99.8% pure) were vacuum dried at $\sim$ 200 °C and then used without further purification [16].

The TiS_2 electrodes were made by hot-pressing (at ~ 150 °C, 5000 psi) a mixture of 50 - 100 mg of TiS_2 (50% w/w), powdered carbon (38% w/w) and polyethylene (12% w/w) onto a 2 cm square nickel grid. Pure lithium foil (Alfa, USA, m3N) or lithium–aluminium (90/10 at.%) foil (Foote Mineral Company, USA) was also pressed on a nickel grid of similar dimensions. The TiS_2 electrode was sandwiched between two lithium electrodes and separated from each using a microporous polypropylene film (Celgard 2400, Celanese Corporation, USA). The electrodes were then held firmly together in parallel plate configuration inside a Teflon cell filled with electrolyte. The cells were cycled galvanostatically between the preset voltages of 1.5 and 2.6 V using an Amel Model 545 Galvanostat–Electrometer coupled with a YEW Model 3066 Y–t recorder. Since the lithium was normally present in large excess (5 - 10 times) in these cells, the term "active material utilisation" refers to utilisation of the TiS_2. The electrochemical experiments were conducted at room temperature (~ 23 °C) under an argon atmosphere in a Vacuum Atmospheres Corporation dry box (Model HE-43) equipped with a Model HE-493 Dri-Train.

Results and discussion

(i) Influence of TiS_2 surface area and the lithium electrode on cell performance

In Fig. 1, we show the discharge curves obtained for TiS_2 electrodes fabricated from two different surface area materials. Curves A_1, A_2 and B_1, B_2 represent the first and second discharge curves for the laboratory and commercial samples, respectively. Comparison of curves A_1 with B_1, and A_2 with B_2, shows that TiS_2 electrodes fabricated with larger surface area material gave better active material utilisation. The same observation was reported by Whittingham [14] for TiS_2 with surface areas of 0.3 m^2 g^{-1} and 2.7 m^2 g^{-1} in an $LiClO_4$/dioxolane electrolyte. Figure 1 also shows a typical feature of these cells, viz., the capacity obtained from the initial discharge is always much larger than that from subsequent cycles (compare A_1 with A_2 and B_1 with B_2). This may be explained by the loss of active material during discharge and/or by incomplete recharge of the electrode. Holleck and Driscoll
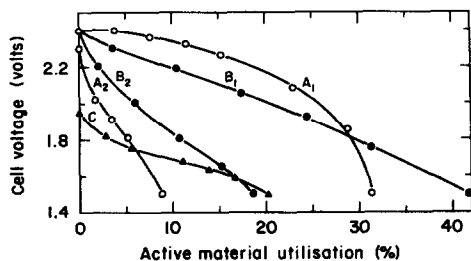
Fig. 1. Discharge characteristics of Li–TiS_2 cells in 1M $LiClO_4$/PC (i_C = 0.06 mA cm^{-2}). A = laboratory sample; B, C = commercial sample. $\circ$, i_D = 0.012 mA cm^{-2}, TiS_2 = 109 mg; $\bullet$, i_D = 0.06 mA cm^{-2}, TiS_2 = 60.3 mg; $\blacktriangle$, i_D = 0.12 mA cm^{-2}, TiS_2 = 50.3 mg.

[8] observed a similar decrease in capacity when cycling Li–TiS$_2$ cells in 1M LiAlCl$_4$/PC.

In LiClO$_4$/PC, the maximum active material utilisation we achieved was only 40% at 0.06 mA cm^{-2}, and much lower figures were obtained at larger current densities. The dependence on discharge rate is illustrated in Fig. 1 (see curve C) where only about 20% active material utilisation was obtained from the initial discharge at 0.12 mA cm^{-2}. On cycling, large decreases in discharge capacities were observed and this behaviour may be associated with the poor cycling efficiency of the lithium electrode in PC reported by other workers [17 - 21]. It has now been shown that cells containing LiAsF$_6$ electrolytes give improved performance of the lithium electrode compared with those containing other lithium salts [20 - 26]. In LiAsF$_6$/2-methyltetrahydrofuran lithium cycling efficiencies approaching 98% have been obtained [25, 26]. Although not shown in Fig. 1, we have also cycled cells using a 1M LiAsF$_6$/PC electrolyte. As observed in LiClO$_4$/PC, large voltage drops were observed even at low discharge rates. For the first discharge, 30 - 40% active material utilisation could only be obtained at very low current densities (0.1 mA cm^{-2}). On extended cycling (> 150 cycles) the active material utilisation fell to < 1.5%.
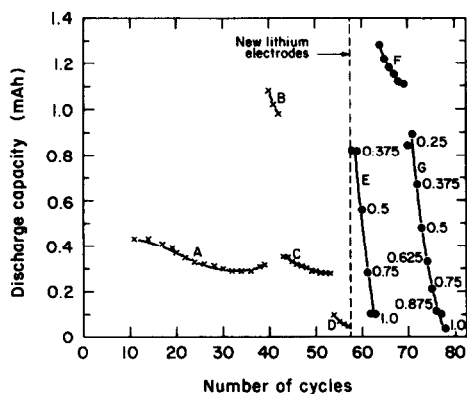

Fig. 2. Discharge characteristics of Li–TiS$_2$ cells in 1M LiClO$_4$/PC (commercial TiS$_2$ = 125 mg). Curve A (i_D = i_C = 0.12 mA cm^{-2}); Curve B (i_D = 0.12 mA cm^{-2}, i_C = 0.025 mA cm^{-2}); Curve C (i_D = i_C = 0.12 mA cm^{-2}); Curve D (i_D = 0.25 mA cm^{-2}, i_C = 0.06 mA cm^{-2}); Curve E (i_D = as shown, i_C = 0.06 mA cm^{-2}); Curve F (i_D = i_C = 0.12 mA cm^{-2}); Curve G (i_D = as shown, i_C = 0.12 mA cm^{-2}).

Figure 2 shows the typical effects of charge/discharge rate and condition of the lithium electrode on the performance of the Li–TiS$_2$ cell in 1M LiClO$_4$/PC. Between cycles 1 and 10, the cell was discharged at 0.12 mA cm^{-2} and charged at various current densities ranging from 0.05 to 0.12 mA cm^{-2}. This procedure was carried out to minimize the variations in capacity normally observed in the first few cycles. The cell was then cycled at a constant charge/discharge rate of 0.12 mA cm^{-2} and the discharge capacities so obtained are shown in curve A. Although discharge capacities normally

decrease with cycle number, a slight increase in capacity was evident after the 34th cycle. This behaviour has also been observed by Murphy *et al.* [27] when cycling the Li–NbSe$_{4.0}$ cell in 1M LiClO$_4$/PC. When the cell was charged at a lower rate (0.02 mA cm^{-2}), much larger discharge capacities were obtained and these are shown in curve B. When the cell was returned to the charging rate of 0.12 mA cm^{-2} (see curve C), discharge capacities comparable with those in curve A were obtained. Finally, the discharge rate was increased to 0.25 mA cm^{-2} while the charging rate was decreased to 0.06 mA cm^{-2} (see curve D). Despite the lower charging rate, somewhat smaller discharge capacities were obtained at the increased discharge rate.

The lithium electrodes were then replaced with fresh ones, and the discharge rate was systematically increased while keeping the charging rate constant at 0.06 mA cm^{-2}. As shown in curve E, larger discharge rates were now possible without as severe a penalty on the discharge capacity as experienced previously. On subjecting the cell to the original charge–discharge rate of 0.12 mA cm^{-2}, the discharge capacities shown in curve F were obtained. These values indicate a four-fold increase in discharge capacity when compared with those obtained using the original lithium electrodes, as shown in curves A and C. The cell was then subjected to a series of large discharge rates while maintaining a charging rate of 0.12 mA cm^{-2} (see curve G). A comparison of curves E and G shows that larger capacities could be obtained when the cell was charged at a lower rate. This behaviour is consistent with that described above for curves A, B and C. It is also worth noting, by comparing curve G with curves A and C, that the same discharge capacity could now be obtained at $\sim$ 0.6 mA cm^{-2}, which is some five times the previous discharge rate. Overall, these results suggest that the cycling behaviour and the discharge capacity of the Li–TiS$_2$ cell in 1M LiClO$_4$/PC are markedly influenced by the general condition of the lithium electrodes. It is thus interesting to note that Dampier [28] also reported poor active material utilisation when cycling Li–CuS and Li–MoO$_3$ cells in 1M LiClO$_4$/PC electrolyte.

(ii) Cell performance in 1M LiClO$_4$/PC and 1M LiAsF$_6$/PC–AN electrolytes

In Fig. 3 it is shown that the Li–TiS$_2$ cell performs better in 1M LiAsF$_6$/PC–AN (50–50 vol%) than in the pure PC electrolyte. The cell was initially discharged at 0.12 mA cm^{-2} in 1M LiClO$_4$/PC, and as shown by curve A only $\sim$ 20% active material utilisation was obtained. The cell was then charged at 0.06 mA cm^{-2} and again discharged at 0.12 mA cm^{-2}. As shown by curve B, there was a large drop in cell voltage and thus a substantial decrease in active material utilisation (to $\sim$ 1%). The electrolyte was then changed to 1M LiAsF$_6$/PC–AN, the cell being carefully rinsed with the new electrolyte before being reassembled. The cell was charged and discharged at 0.06 mA cm^{-2} and 0.12 mA cm^{-2}, respectively, and curve C shows the improved performance obtained. Comparison of curve B with curve C shows that the cell experienced less voltage drop and a large increase in the active material utilisation in 1M LiAsF$_6$/PC–AN.
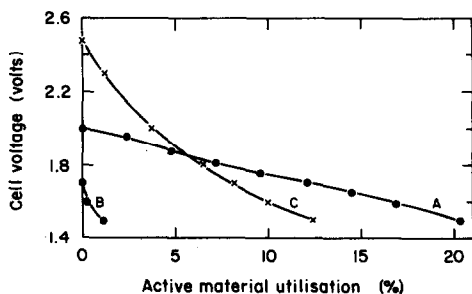
Fig. 3. Discharge curves for Li–TiS$_2$ cells in two different electrolytes: ●, 1M LiClO$_4$/PC; ×, 1M LiAsF$_6$/PC–AN. Curves A, B, and C represent first, second, and third discharge, respectively. (i_D = 0.12 mA cm^{-2}, i_C = 0.06 mA cm^{-2}, commercial TiS$_2$ ≈ 57.8 mg.)

TABLE 1

Performance of TiS$_2$ electrodes in 1M LiClO$_4$/PC and 1M LiAsF$_6$/PC–AN electrolytes under various charge/discharge regimes

Electrolyte	Discharge rate (mA cm^{-2})	Discharge capacity (mA h)	Active material utilization (%)	Charge rate (mA cm^{-2})	Charge capacity (mA h)	Percentage recharged (%)
A	0.012	5.59	32	0.012	2.74	49.0
A	0.012	8.16	31	0.06	1.50	18.4
A	0.06	2.19	24	0.06	0.014	0.6
A	0.12	2.54	21	0.06	0.02	0.8
B	0.62	5.83	51	0.06	0.825	14.2
B	1.0	8.27	54	0.12	1.06	12.8
B	1.2	8.42	52	0.06	1.23	14.6
B	1.2	4.92	49	0.25	0.67	13.6

A, 1M LiClO$_4$/PC; B, 1M LiAsF$_6$/PC–AN.

The performance of the Li–TiS$_2$ cell in 1M LiAsF$_6$/PC–AN was also investigated using various charge–discharge regimes. The data obtained for the first cycle were compared with those for 1M LiClO$_4$/PC, and the results are presented in Table 1. Since the capacities shown in columns 3 and 6 were calculated on the first cycle, they therefore represent the best values obtained in the life of each electrode. As shown in Section (i), active material utilisation of ~ 30% could only be obtained at low discharge rates (< 0.1 mA cm^{-2}) in 1M LiClO$_4$/PC. While the active material utilisation decreased with increasing current density (see column 4) as expected in 1M LiClO$_4$/PC, this behaviour was not apparent in 1M LiAsF$_6$/PC–AN. Column 7 indicates the charge that can be put back into the TiS$_2$ electrode after the initial discharge. The results obtained in 1M LiClO$_4$/PC showed that low discharge rates followed by high charge rates produced poor percentage rechargeability (compare rows 1 and 2). A large discharge rate also produced poor percentage rechargeability (compare rows 3 and 4 with row 2). Thus, the Li–TiS$_2$ cell containing 1M LiClO$_4$/PC only gave adequate rechargeability at very low

charge/discharge rates, and such behaviour must limit its practical application. On the other hand, better charge/discharge rates could be obtained from the cell containing the 1M $LiAsF_6$/PC–AN electrolyte. As shown in rows 6 - 8, active material utilisation in excess of 50% could be obtained at $\sim$ 1 mA cm^{-2}. While only average rechargeability values ($\sim$ 14%) were obtained under these conditions, there was no appreciable dependence on charging rate. The apparent superiority of the 1M $LiAsF_6$/PC–AN electrolyte over the 1M $LiClO_4$/PC electrolyte can best be seen by comparing rows 7 and 8 with rows 1 and 2.
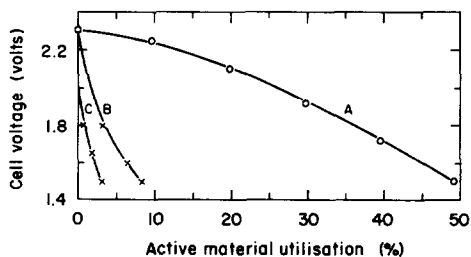

Fig. 4. Discharge characteristics of Li–TiS_2 cells in 1M $LiAsF_6$/PC–AN. Curves A, B, and C represent first, second, and 26th discharge, respectively. (i_D = 1.2 mA cm^{-2}, i_C = 0.25 mA cm^{-2} and commercial TiS_2 = 42.3 mg.)

(iii) Cycling behaviour in 1M $LiAsF_6$/PC–AN electrolyte

Figure 4 shows the discharge characteristics of the Li–TiS_2 cell in the 1M $LiAsF_6$/PC–AN electrolyte for various cycles. The initial discharge gave $\sim$ 50% active material utilisation (curve A). However, on the second discharge (after charging at 0.25 mA cm^{-2}) the active material utilisation decreased to < 10% (curve B). The subsequent discharge capacities did not decrease so drastically and this behaviour is exemplified by curve C (26th cycle). As already observed in 1M $LiClO_4$/PC, and as also reported by Holleck and Driscoll [8] in 1M $LiAlCl_4$/PC, a substantial decrease in capacity after the initial discharge is a common feature of the Li–TiS_2 cell.

Because of the promising behaviour of the Li–TiS_2 cell in the 1M $LiAsF_6$/PC–AN electrolyte, some extended cycling was also performed and the results are presented in Fig. 5. Curve A shows the variation of active material utilisation with cycle number at a charge/discharge rate of 0.12/1.0 mA cm^{-2}. While a loss of electrolyte through evaporation was observed during cycling, the addition of fresh electrolyte only slightly improved the discharge capacity. Curve B shows the variation of active material utilisation with cycle number at a higher charge/discharge rate of 0.25/1.2 mA cm^{-2}. One of the cells was fabricated using a lithium–aluminium (90–10 at.%) alloy anode and also cycled at a charge/discharge rate of 0.25/1.2 mA cm^{-2} (see curve C). Comparison of curves B and C reveals a better performance for the cell using the lithium–aluminium alloy as the anode material. This observation is consistent with the work of Rao *et al.* [29, 30] who reported the cycling of Li(Al)–TiS_2 cells in $LiClO_4$/dioxolane and found that the alloy anode con-
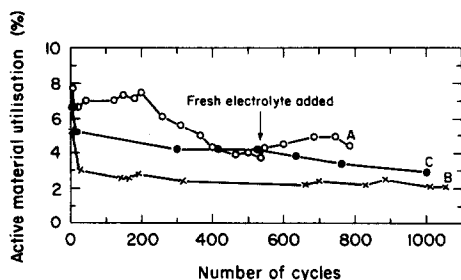
Fig. 5. Cycling behaviour of Li–TiS$_2$ cells in 1M LiAsF$_6$/PC–AN. (A, B = lithium anode, C = lithium–aluminium anode) ○, i_D = 1.0 mA cm^{-2}, i_C = 0.12 mA cm^{-2}, commercial TiS$_2$ = 64.4 mg; ✕, i_D = 1.2 mA cm^{-2}, i_C = 0.25 mA cm^{-2}, commercial TiS$_2$ = 36.7 mg; ●, i_D = 1.2 mA cm^{-2}, i_C = 0.25 mA cm^{-2}, commercial TiS$_2$ = 42.3 mg.

tributed to the improvement of cell performance. The encouraging feature in Fig. 5 is that while the active material utilisation was very low, the Li–TiS$_2$ cell could be cycled ∼ 1000 times without failure. After the first 25 cycles the cells showed only a gradual decline in capacity which may have been partly due to the deterioration of the electrolyte.

Conclusions

It has been confirmed that surface area is important when fabricating TiS$_2$ electrodes. Electrodes composed of high surface area materials gave better active material utilisation. The Li–TiS$_2$ cell showed poorer cycling characteristics in 1M LiClO$_4$/PC than in 1M LiAsF$_6$/PC–AN. Poor performance in 1M LiClO$_4$/PC was normally associated with the lithium electrode. In 1M LiAsF$_6$/PC–AN higher charge/discharge rates could be used while maintaining the same capacity. In addition, Li–TiS$_2$ cells containing LiAsF$_6$/PC–AN could be cycled ∼ 1000 times with only a gradual decrease in the discharge capacity after the first 25 cycles. However, rates of 5 - 10 mA cm^{-2} with large active material utilisation, as reported by workers using other electrolytes, were not achieved. Overall, our results indicate that Li–TiS$_2$ cells containing the 1M LiAsF$_6$/PC–AN electrolyte may be most suitable for primary or very limited secondary applications.

Acknowledgements

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