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(Received 7 November 1990)

AMBIENT TEMPERATURE LITHIUM BATTERIES WITH LAYER TYPE CATHODES: PERFORMANCE

OF TiS_2 CELLS

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SUMMARY

A titanium disulphide cathode has been used in a coin cell in which one molar solution of $LiClO_4$ in propylene carbonate was the electrolyte. The cell was charged and discharged for one hour each at 0.1mA. Cycling between voltage limits of 4 and 1.4 was also carried out.

INTRODUCTION

The positive electrode material for a secondary lithium cell should have high energy density, stability in the electrolyte, good electrical conductivity and withstand moderate to high rates of discharge. Transition metal chalcogenides have these qualities and hence are being widely used as cathodes in these cells. TiS_2 , a material with layered structure, has good rate capability and a high theoretical specific energy when coupled

with lithium anode (480Wh Kg^{-1}) [1]. It is almost insoluble in most of the organic solvents, has an electrical conductivity of $2 \times 10^2 \text{ S cm}^{-1}$ and good intercalation of lithium between TiS_2 layers. It is often described as semimetallic [2]. On intercalation with lithium TiS_2 is converted into $\text{Li}_x \text{TiS}_2$ a single phase product with $0 < x \leq 1$ [3]. This system has been studied successfully by several workers [4-8]. In several of these investigations, solvents other than propylene carbonate [PC] have been used. Acetonitrile, tetrahydrofuran, 2 - methyl tetrahydrofuran, 1,3 - dioxolane and 1, 2 - dimethoxyethane are some of the solvents studied [5,8]. $\text{PC}(\text{LiClO}_4)$ solution owing to its high conductivity, boiling point and other properties is still a candidate [6,9,10]. Poor cycling efficiency of lithium is the main cause of failure of these cells. The formation of surface film, dendrite growth and poor active material utilization are some of the problems that are to be contended with. Excess lithium is usually incorporated in such cells to overcome these problems to a certain extent [4]. In this work, $\text{PC}(\text{LiClO}_4)$ solution was used in a coin cell.

EXPERIMENTAL

Anode: Lithium ingots (Foote, USA) was used for making thin sheets from which circular anodes were prepared in a dry box.

Cathode: TiS_2 (CERAC) was mixed with 10 w/o acetylene black and PTFE binder and pellets were made at 9.81 K Pa.

Separator: Celgard 2402 (immediately above the cathode) and Tata polypropylene 421 C (India) were used.

Electrolyte: LiClO_4 was fused in vacuum at 150°C for 24 hours.

PC was stored over CaO for 24 hours, then distilled under reduced pressure and then stored over 4 \AA molecular sieves 1 molar solution of LiClO_4 in PC was prepared in a dry box.

20 mm dia coin cells were fabricated in a dry box under argon atmosphere. Anode to cathode ratio was 2:1 only for reasons of close packing in the cell.

The cells were discharged at 0.1mA and the capacity was determined as 1mAh. Cycling was done under two modes:

1. Discharge : 0.1mA for 1 hour
Charge : 0.1mA for 1 hour
2. Discharge : 0.1mA upto 1.4V
Charge : 0.1mA upto 4.0V

In mode 1, cell voltages were measured at the end of charge and discharge. In the case of mode 2, the capacity was calculated for each discharge upto 1.4V

RESULTS AND DISCUSSION

The results of cycling under mode 1 are given in Fig.1. The depth of discharge is 10%. The cycling was abandoned at 234 cycles since the charge voltage rose beyond 4.5V. At this point the cell end of discharge voltage was only 2, well above the cut off voltage of 1.4V. The end of discharge voltage was measured in this study to determine the usability of the cell at various stages, since in most equipments, operating voltage is the main criterion. In the second mode (Fig.2) the depth of discharge was 45%. Here again cycling was discontinued not due to reaching cutt off voltage at discharge. The charge voltage increased and only 15 cycles could be studied. If we are to go by the earlier works in this field, the failure is due to the lithium electrode only. Lithium forms a surface film in PC[11 to 13]. It is well known that the poor cyclability of lithium electrode reduces the life of these cells. The nature and characteristics of these films are still being explored. Usually an anode to cathode ratio of 6:1 is employed[4]. Incorporating additives to retard film formation on lithium, use of LiAsF_6 in 2Me THF and other solvents, and alloying of lithium are some of the ways being studied. We believe that by continuous work in this line, a Li/TiS_2 rechargeable cell of several thousand

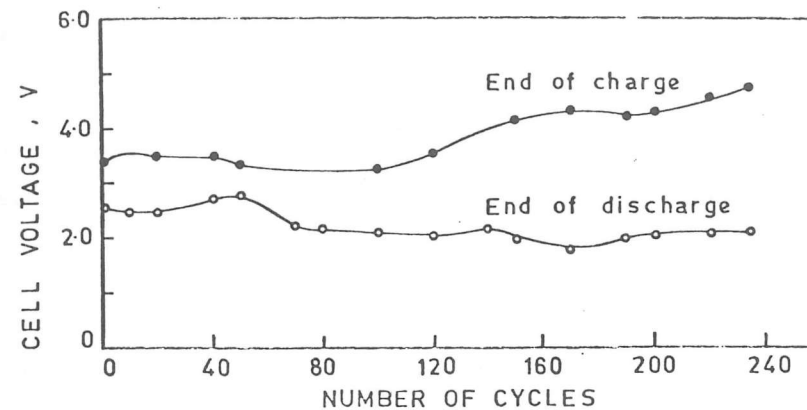


Fig. 1. Cell voltage at end of discharge and charge and charge vs. number of cycles for Li/TiS_2 cell

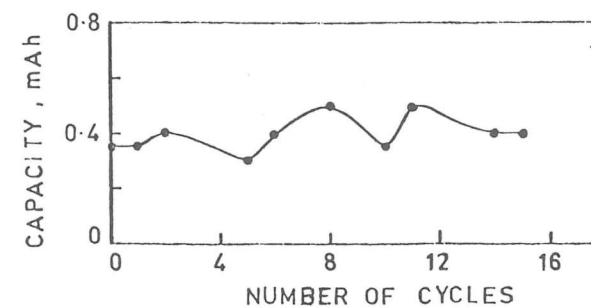


Fig. 2. Capacity vs. number of cycles for Li/TiS_2 cell.

cycles can be made to reality.

Acknowledgement

The authors wish to thank Prof.S.K. Rangarajan, Director, Central Electrochemical Research Institute, Karaikudi for his kind permission to publish this work.

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(Received 12 November 1990

Revised form 12 January 1991)