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RECHARGEABLE LITHIUM-TITANIUM DISULPHIDE CELLS OF SPIRALLY-WOUND DESIGN

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Summary

A thin and flexible TiS_2 electrode is being developed. The electrode is made without carbon via a non-aqueous process, thus avoiding some of the earlier difficulties encountered with TiS_2 electrodes. Cylindrical, spirally-wound Li–TiS_2 cells were fabricated. An AA-size cell delivers 1.08 A h at an average discharge voltage of 2.12 V (200 mA rate). Cycle life at over 80% depth of discharge varies between 50 and 200 cycles depending on cell fabrication parameters. These include: type and amount of electrolyte, Li to TiS_2 capacity ratio, and type of separator.

Introduction

The rechargeable Li battery is a promising candidate to power portable devices. In spite of 15 years of laboratory research [1], only very limited data on actual cell performance are available [2]. We are developing a TiS_2 electrode that is made from commercially available materials via a practical manufacturing process [3]. Spirally-wound AA Li–TiS_2 cells were fabricated with these electrodes. Their performance is reported in this publication.

Experimental

TiS_2 powder was supplied by Degussa Corp. The powder was mixed with a proprietary binder to form a thin sheet. The sheet was pressed onto an expanded Ni screen. This process yields very reproducible electrodes. Our electrolyte solution contains $LiAsF_6$ (1.2 - 1.5 M) in mixture of 2-methyltetrahydrofuran (2-MeTHF) with tetrahydrofuran (THF) [4]. The ethers were refluxed and then distilled over benzophenone ketyl to remove water. The water content of the ethers was typically 40 ppm after treatment.

Cell internals were spirally wound in an argon-atmosphere glove-box with a home-made rolling setup. The separator employed in the cells was a microporous polyolefin, 1 - 2 mil thick. These rolls were inserted into metal

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cans. Electrolyte filling, top welding, and cell closure were carried out in a dry-room environment. Cells were typically cycled between 1.6 and 2.6 V via a computerized cycler.

Results

Discharge profiles for an AA Li–TiS_2 cell are shown in Fig. 1. At a 200 mA discharge rate, 1 A h is delivered to 1.7 V (Fig. 1(a)). Charging rate was 100 mA. The Figure demonstrates the excellent reversibility of the cell with low polarization, high energy efficiency, and a coulombic efficiency of 100.0 ± 0.4% per cycle. The voltage profile of the cell is modestly sloped. At the 200 mA rate, 90% of the capacity is available between 2.3 and 1.8 V. Though a flat voltage profile is preferred for some applications, the modest slope allows the direct reading of the state-of-charge of the battery by noting the cell voltage. The average discharge voltage at the 200 mA rate is 2.12 V. The cell weighs approximately 19 g. This translates to an actual gravimetric energy density of an AA cell of 110 W h kg^{-1}.

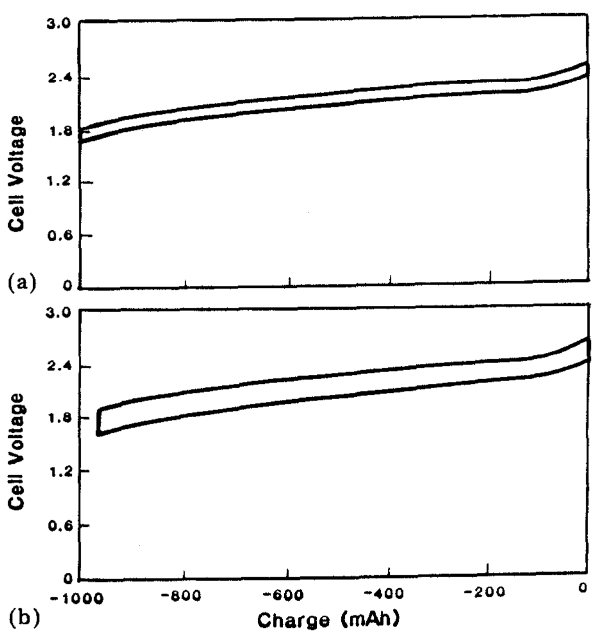

Fig. 1. Voltage profiles for AA size Li–TiS_2 cells. (a) Discharge/charge rates 200/100 mA; (b) discharge/charge rates 500/100 mA.

At the 500 mA discharge rate (Fig. 1(b)), 0.96 A h capacity is available to 1.6 V. The average discharge voltage drops to 2.03 V as a result of the expected overall increase in polarization. This moderately high-rate performance will satisfy the power requirements of numerous commercial portable devices as well as several military and aerospace applications. At even higher rates, the polarization increases and deliverable capacity drops sharply.

Figure 2 displays capacity *versus* discharge rate for three unoptimized AA cells of different design. Capacity is measured to 1.7 V on discharge rates up to 500 mA and to 1.6 V for discharge rates above 500 mA. Curve (a) displays the capacity of a low-rate cell. Curve (b) displays the capacity *versus* discharge rate of a cell fabricated with a thinner electrode of higher geometric surface area. The cell of curve (b) delivered over 85% of its 200 mA capacity at rates as high as 1000 mA. Curve (c) displays data for standard surface area electrodes with improved cathode (binder) composition. Significant capacity drops occur only at rates higher than 800 mA.

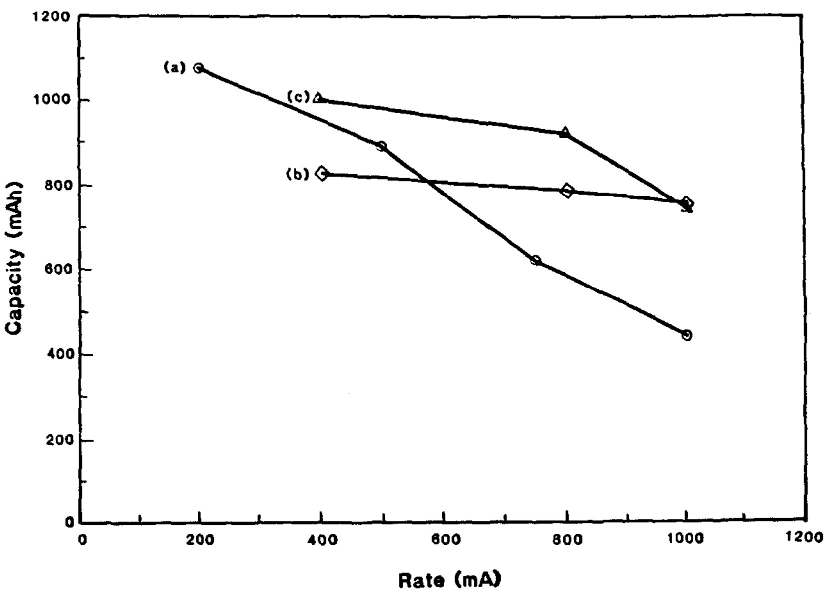

Fig. 2. Capacity–rate data for AA Li–TiS_2 cells. (a) High capacity–low rate design; (b) high electrode surface area design; (c) improved cathode (binder) design.

At lower temperatures, electrode thickness becomes even more crucial. Figure 3 displays data for the above three cells measured at −20 °C. Evidently, the capacity of the cells with standard surface area, curves (a) and (c), drops significantly at rates higher than 200 mA. The high surface area, thin electrode cell, curve (b), delivers 680 mA h at 400 mA which is nearly 80% of its theoretical capacity.

The cell's cycle life is limited by irreversible reactions at the Li/electrolyte interface. Current cells will deliver 75 - 200 cycles at over 80% depth of discharge. Cycle life depends on the cell design parameters. In particular, increasing the Li to TiS_2 capacity ratio increases cycle life. For cycle life of over 200 cycles, a new electrolyte system will most likely have to be developed.

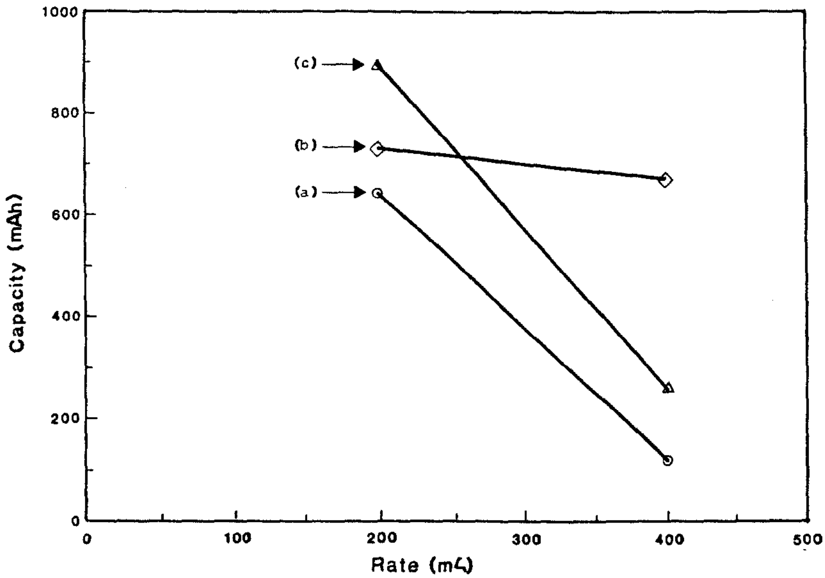

Fig. 3. Capacity–rate data for AA Li–TiS_2 cells at −20 °C. (a) High capacity–low rate design; (b) high electrode surface area design; (c) improved cathode (binder) design.

Storage tests demonstrate excellent shelf life. An uncycled cell that was stored at room temperature for 8 months lost only 7% of its charge on the first cycle. Upon further cycling, this cell delivered full capacity. Other cells were cycled 20 times and then stored at 72 °C for 48 h. Their voltage profile and deliverable capacity following the high-temperature storage was essentially unchanged compared with the pre-storage data. Although more storage tests are underway, the shelf life of fresh and cycled cells appears to be adequate even when stored at above-ambient temperatures.

Conclusion

An AA-size, rechargeable Li cell is being developed. At present, its capacity at 400 mA rate is 1 A h at 2.1 V mid-discharge voltage. The cell shows high energy density, moderately high rate capabilities, moderate cycle life, and good charge retention.

References

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