

Copper (II) sulfide as cathode active material in secondary lithium batteries

I. Exnar and J. Hep

RENATA S.A., 4452 Itingen (Switzerland)

Introduction

Copper (II) sulfide is known to be a useful high-energy density cathode material for primary organic electrolyte Li batteries [1-3]. Transition-metal chalcogenides such as TiS_2 , MoS_2 , NbS_3 are found to have good rechargeability. On that basis, we have investigated the use of CuS as a positive material for secondary batteries. For low-drain memory backup applications we have developed a rechargeable battery module with a nominal voltage of 4 V. This module can be recharged directly with feed current at 5 V.

Experimental

Copper sulfide preparation

Copper metal powder (99.0% Baudier France) and sulfur (E. Merck) in equivalence ratio were stirred in *p*-xylene at 90 °C for 4 h. The obtained CuS was leached with 1.2 M HCl, followed by washing with water and 1,3-dioxolane. Finally, the powder was dried in vacuum and stored under argon to prevent auto-oxidation of CuS to $CuSO_4$.

Electrolyte preparation

All experiments and preparations of solutions were carried out in dry boxes filled with argon (Braun, Munich, Germany). Propylene carbonate (PC) was distilled under vacuum (2 Torr, 82 °C). Dimethoxyethane (DME) and 1,3-dioxolane were dried over 4 Å molecular sieves and distilled.

Cell preparation

The cell used was a crimp-sealed coin type (1225 and 2025) as shown in Fig. 1. The anode was pressed from the Lithco high purity Li-Al alloy powder. The pressed cathode was supported by a stainless-steel current collector. The electrolyte was 1 M $LiCF_3SO_3/1,3$ -dioxolane.

Electrochemical measurements

A PAR 173 potentiostat/galvanostat and its associated equipment were employed for the cyclic voltammetric experiments. A 1 cm² CuS pellet on fine Ni mesh was used as working surface, Pt plate, 2 cm², as the counter electrode and Li wire as a reference.

X-ray diffraction data (XRD) were obtained using the Enraf Nonius Guinier camera system with Mo $K\alpha$ radiation, 40 kV/30 mA.

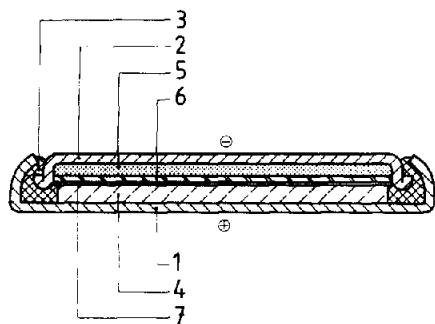


Fig. 1. Cross-section view of secondary Li-CuS cell: (1) cathode can; (2) anode cap; (3) insulating ring; (4) CuS cathode; (5) Li-Al alloy anode; (6, 7) separators and electrolyte.

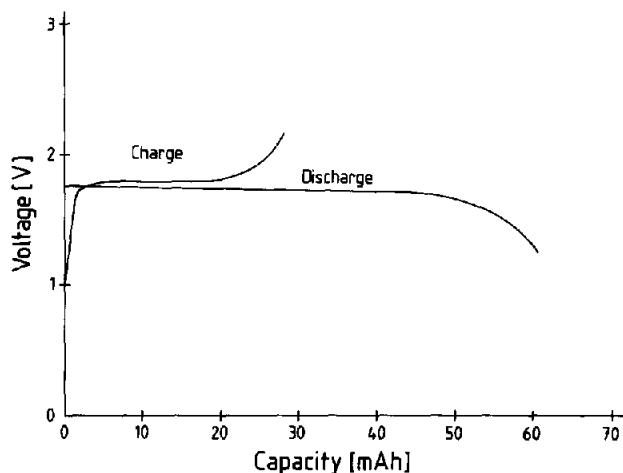


Fig. 2. Discharge/charge profiles of 1225 Li/CuS cell at 0.1 mA constant current.

A two-cell battery module was cycled according to the following method: discharge with a constant load of 43.2 k Ω for 16 h and a charge with a constant voltage of 4.45 V (5 V feed current minus diode loss) for 8 h.

Results and discussion

Figure 2 shows a discharge profile for a 1225-size Li/CuS cell. The overall cell reaction is given as:



and represents 100% depth-of-discharge (DOD). At 0.1 mA discharge rate, 60 mA h are delivered to 1.25 V. Charging rate was 0.1 mA.

Due to the volumetric growth of the cathode which is caused by the conversion of CuS to reaction products [4], the deintercalation is not well defined and results in poor cycling properties. In other words, after a charge following a 100% discharge

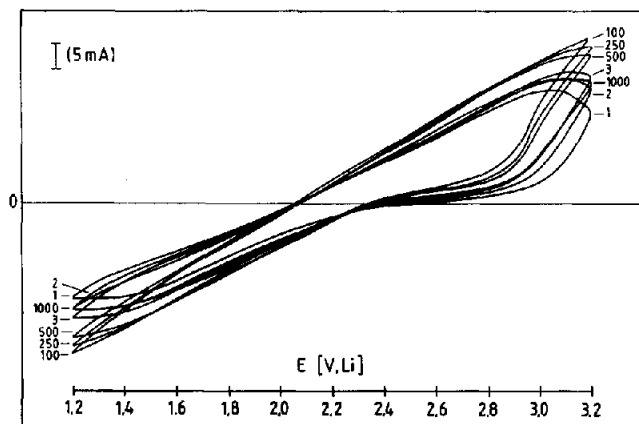


Fig. 3. Cyclic voltammograms of CuS in 1 M $\text{LiClO}_4/\text{PC-DME}$ electrolyte, 1–1000 cycles; sweep rate 100 mV s^{-1} .

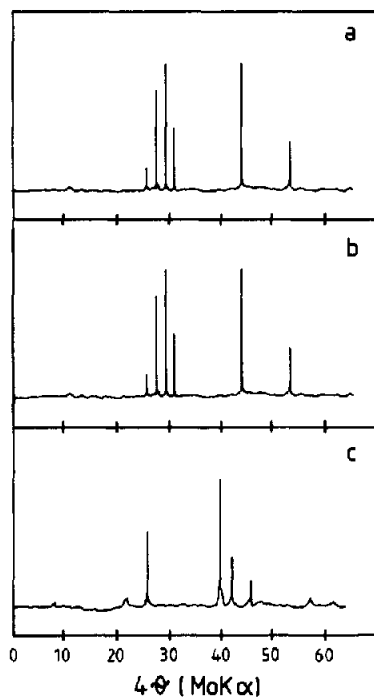


Fig. 4. X-ray diffraction patterns of CuS cathode: (a) fresh, (b) after 100 cycles 5% DOD, and (c) 100% discharged.

some Li remains in the cathode which explains why the recharge capacity is smaller than the discharge capacity. By comparison, if the DOD is limited at $\sim 5\%$ (meaning 3 mA h in the case of 1225 cell as shown in Fig. 2), the insertion of Li ions and

electrons into the CuS a crystal lattice for low DOD is reversible and can be written as:



Figure 3 shows the cyclic voltammogram of CuS in 1 M LiClO₄/PC-DME for 1 to 1000 cycles. The voltammogram shows that in addition to the intercalation of Li into CuS no other reactions occur.

Figure 4 shows XRD patterns of the (a) fresh CuS cathode and (c) patterns of Cu₂S obtained by 2CuS + 2Li → Cu₂S + Li₂S discharge reaction. Curve (b) shows XRD after 100 cycles with 5% DOD. The patterns return to those of the original CuS and do not show any Cu₂S patterns. This indicates good rechargeability for low depth (5% DOD) cycling.

The specifications of the two-cell battery module employing our CuS-cathode, LiCF₃SO₃/1,3-dioxolane electrolyte and Li-Al alloy anode are given in Table 1.

Figure 5 shows the cycle life versus DOD. Discharge depth is calculated from nominal capacity.

Figure 6 shows a basic circuit for the application of the battery module. This module can be recharged directly with a feed current at 5 V. Figure 7 illustrates the discharging/charging curves for an 81225 module at room temperature. After 1000 cycles we still reach 22 mA h, if the cell was completely discharged as primary battery. Nevertheless, the cell was no longer rechargeable. Following complete discharge of new cells the cycle life was limited to ~50 cycles 5% DOD. Curve 4 in Fig. 7 shows the end of cycle life with a complete two-plateau reduction to Cu.

TABLE 1

Specification of two-cell modules

Cell type	Dimension (mm)	Nominal capacity ^a (mA h)	Nominal voltage (V)	Cycles (10% DOD)
2 × 81225	16 × 16 × 7.5	40	4	1500
2 × 82025	22 × 22 × 8.5	140	4	1500

^aNominal capacity is defined as capacity if discharged as a primary battery.

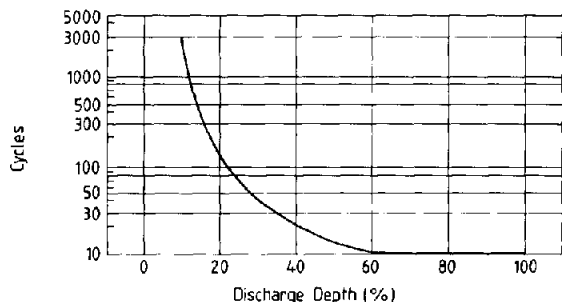


Fig. 5. Charge/discharge characteristics in relation to DOD; charge: 0.05 mA, discharge: 0.1 mA, temperature: 23 °C.

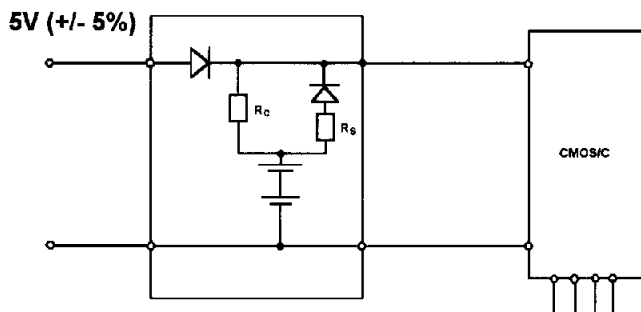


Fig. 6. Basic circuit of rechargeable two-cell battery module; longitudinal diode maximum 100 mA; R_c : limitation of charging current, and R_s : limitation of discharge current.

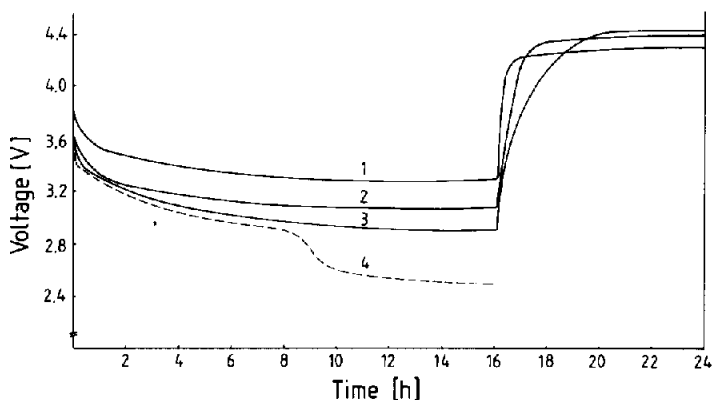


Fig. 7. Discharge/charge curves of 81225 two-cell module; discharge: constant load 43.2 k Ω ; charge constant voltage 4.45 V; (1) 1 cycles; (2) 500 cycles; (3) 100 cycles, and (4) 3000 cycles.

Conclusion

We found that the CuS cathode shows good reversibility in 1,3-dioxolane/electrolytes for low discharge depth. Our cycleability study emphasizes the practical application for memory backup. The cells show high-energy density as primary batteries and moderate cycle life. Further investigations are in progress.

References

- 1 J. P. Gabano, V. L. Dechenaux, G. M. Gerbier and J. Jammitt, *J. Electrochem. Soc.*, 114 (1972) 489.
- 2 *The Cordis Lithium Battery*, Cordis Co., Miami, FL, USA, May 1978.
- 3 J. P. Gabano (ed.), *Lithium Batteries*, Academic Press, New York, 1983.
- 4 N. Margalit, *Proc. Symp. Battery Design and Optimization*, The Electrochemical Society, Princeton, NJ, 1979, pp. 320–326.