

ELECTROCHEMICAL BEHAVIOUR OF METAL SULPHIDES AS CATHODES IN PRIMARY LITHIUM BATTERIES

F. BONINO, S. MORZILLI and B. SCROSATI

Dipartimento di Chimica, Università di Roma 'La Sapienza', Rome (Italy)

Summary

As part of a research program on the electrochemical behaviour of solid materials which may be used as cathodes in voltage-compatible lithium-organic electrolyte batteries, we have considered here cuprous sulphide, cadmium sulphide and lead sulphide.

The discharge reaction of these sulphides involves the replacement of the metal by lithium, with the formation of copper, cadmium, and lead, respectively, and of lithium sulphide. The characteristics of the discharge curves and the values of the specific energy contents make the three metal sulphides very promising cathode materials for the development of lithium voltage-compatible batteries of practical interest.

Introduction

Following the development of popular microelectronic devices, a continuing interest has developed relating to high-energy, long-life lithium batteries having working voltages around 1.5 V. Such 'voltage-compatible' lithium batteries may be directly interchanged with conventional zinc dry cells, with great advantages in terms of reliability and longevity [1].

In previous papers we have described the characteristics of lithium-copper molybdate [2] and of lithium-copper sulphide [3] systems, and in this work we extend the series by examining the properties of lithium-cadmium sulphide and lithium-lead sulphide voltage-compatible batteries.

Experimental

Lead sulphide has been synthesized from the elements using powdered Pb and S (Reagent Grade chemicals). Cadmium sulphide, Alfa Reagent Grade product, was used as received. The purification of the solvent, propylene carbonate (PC), the solute, lithium perchlorate, and the preparation of the electrolyte solution, 1M LiClO₄-PC, have been described previously [2, 3].

Typical two-electrode, button-type laboratory cells were used for discharge tests. These cells consisted of a lithium pellet, a glass-wool separator soaked with the electrolyte solution and a cathode pellet (supported on a copper substrate), housed in a plastic container having stainless steel terminals. This cell had an electrode surface of 1.12 cm^2 .

Results and discussion

The Li-CdS system

A typical 0.25 mA/cm^2 constant current discharge curve of the Li/LiClO₄-PC/CdS cell is shown in Fig. 1. The reduction of CdS is a single process consuming 2 F/mole of sulphide. After the complete discharge, the cathodic mass was analyzed by X-rays. The spectrum, shown in Fig. 2(B), revealed only the presence of cadmium and of lithium sulphide. Comparison with the spectrum of the starting CdS, shown in Fig. 2(A), indicates that the electrochemical reaction had proceeded to completion.

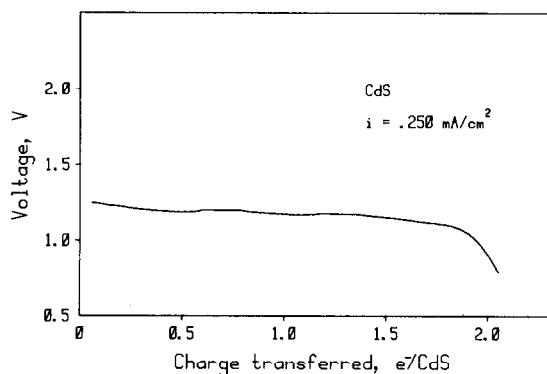


Fig. 1. 0.25 mA/cm^2 constant current discharge of Li/LiClO₄-PC/CdS cell at room temperature.

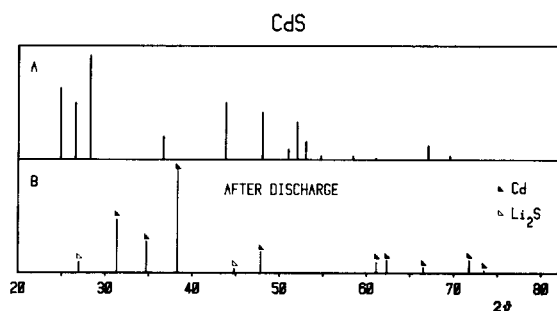


Fig. 2. (a) X-ray diagram of undischarged CdS cathode; (b) X-ray diagram of discharged CdS cathode.

From the above results, the discharge reaction of the Li/CdS cell may, then, be identified as



The resistivity of CdS is sufficiently low to allow its use as a cathode without the addition of inert conductive materials (such as graphite). Furthermore, the production during discharge of finely-dispersed cadmium helps to keep the resistance of the cathodic mass low throughout cell life. This is further indicated in Fig. 3, which shows that the discharge curves of the Li/CdS cell remain flat even at high rates.

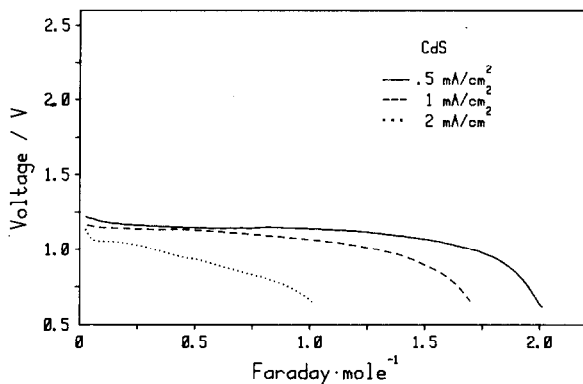


Fig. 3. Constant current discharge curves of Li/LiClO₄-PC/CdS at 0.5, 1 and 2 mA/cm² at room temperature.

The Li-PbS system

A typical 0.25 mA/cm² constant-current discharge curve of the Li/LiClO₄-PC/PbS cell is shown in Fig. 4. In this case also, the cell reaction may be described as a single process involving the reduction of the sulphide. However, the process is less efficient than in the case of the CdS cathode,

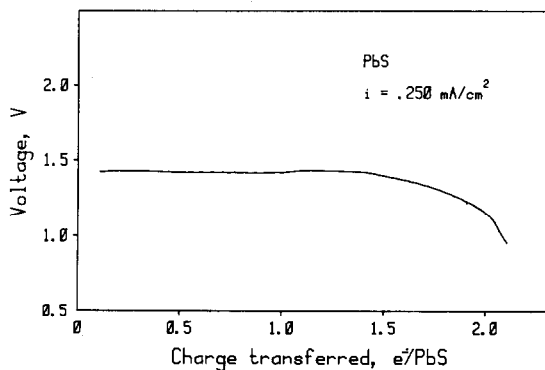


Fig. 4. 0.25 mA/cm² constant current discharge of Li/LiClO₄-PC/PbS cell at room temperature.

since full capacity of 2F/mole is reached only if graphite (10% by weight) is added to the PbS cathodic mass to increase its conductivity.

An X-ray analysis of the completely discharged cathode of the Li/PbS cell is illustrated in Fig. 5(B). Surprisingly, although the peaks of Pb metal are easily detectable, no Li_2S peaks could be identified. However, these peaks could be masked by the rather complicated and crowded spectrum of the discharged cathodic mass, of which Fig. 5(B) is only a schematic representation. Therefore, considering the shape of the discharge curve of Fig. 4 and the certain identification of lead in the X-ray spectrum of Fig. 5(B), one may propose the following:



as the most probable discharge process of the Li/PbS cell.

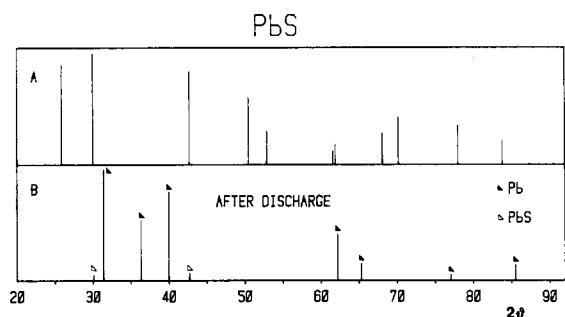


Fig. 5. X-ray analysis of the PbS cathode in a lithium cell (A) before, and (B) after discharge.

Characteristics of lithium-metal sulphide batteries

In Fig. 6 the discharge curves of lithium cells using the cadmium and lead sulphides described here, are compared with that of a similar cell using cuprous sulphide, whose basic electrode behaviour has been described previ-

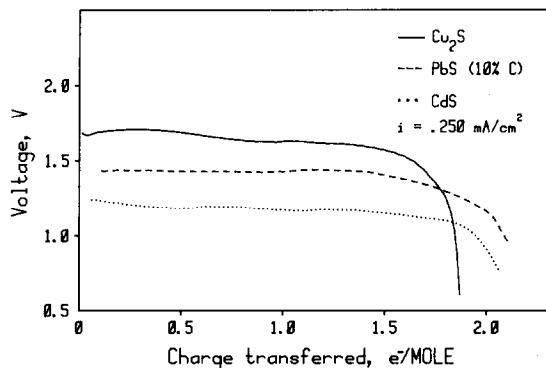


Fig. 6. Constant current discharge curves of lithium-organic electrolyte batteries using Cu_2S , CdS and PbS , respectively, as cathode materials.

TABLE 1

Characteristics of lithium-metal sulphide cells discharged at 0.25 mA/cm² *

Cell system	Average voltage (V)	Specific capacity		Specific energy	
		(A h/g)	(A h/cm ³)	(W h/g)	(W h/cm ³)
Li/Cu ₂ S	1.60	0.309	1.73	0.497	2.78
Li/CdS	1.18	0.363	1.75	0.428	2.06
Li/PbS	1.38	0.209	1.56	0.289	2.16

*In the above calculations only the cathodic mass was considered.

ously [3]. The energetic parameters of the three metal sulphides derived from these discharge curves are reported in Table 1.

There are no drastic differences between the three cathodic materials. The cuprous salt is able to sustain the highest regimes [3] and is thus, perhaps, preferable for high power applications. However, in the ranges usually required by the most popular electronic devices, all three materials perform satisfactorily. Long-term discharge tests of flat button batteries of practical sizes and capacities are currently under way in our laboratory.

Acknowledgement

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