

## STUDIES ON 1.5V LITHIUM-IRON SULPHIDE BUTTON CELLS

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Existing electronic gadgets operating with 1.5V power source will be benefited by using lithium-iron sulphide nonaqueous cells of longer shelf-life. Investigations on the discharge behaviour, internal resistance and impedance response of this type of cells have been carried out.

**Key words:** Li-FeS cells, Impedance studies

### INTRODUCTION

Lithium cells are widely known for their use in many electronic gadgets like wrist watches, calculators and pace makers. Many of the lithium cells have voltages between 3.0 and 3.6. Li/MnO<sub>2</sub>, Li(CF)<sub>n</sub> and other cells come under this category and they are being used in a large number of miniature electronic equipments. However, the existing gadgets which operate with 1.5V power source, cannot utilize the above lithium cells. Hence it is necessary to develop 1.5V lithium cells in place of the Leclanche, alkaline Zn/Ag<sub>2</sub>O, Zn/HgO and other cells. Lithium cells have specific advantage of longer shelf life (5 years) over other cells. This paper reports our investigations on lithium-iron sulphide cells [1-4].

### MATERIALS

**Anode:** Pure lithium metal (Foote Mineral Co., USA) was used as anode. The metal was rolled into sheet from the ingot and then cut to the required size.

**Cathode:** Specially synthesised iron sulphide was used as cathode material. Acetylene black (AB), and colloidal teflon (Du Pont, USA) were used as conductor and binding agent respectively. The cathode mix consisted of 10% AB and 90% iron sulphide. Cathode pellets were made at a pressure of 1000 kg/sq.cm. using this mix.

**Electrolyte:** LiClO<sub>4</sub> (Fluka) was heated in vacuum for 72 hours. Propylene carbonate (PC) (Fluka) was dried in calcium oxide for 24 hours and then distilled under reduced pressure. Then it was dried over Linde 4A molecular sieves. One molar solution of LiClO<sub>4</sub> in PC was prepared in the glove box.

**Cell:** Cells of 20 mm dia and 2mm thickness were fabricated using lithium as anode, iron sulphide as cathode, 1M PC (LiClO<sub>4</sub>) as electrolyte and cellulose as separator.

All operations like preparation of electrolyte and fabrication of anode were done inside a glove box.

### EXPERIMENTS

Cells were discharged at 50, 100 and 200 microampere currents

and the cell voltages were measured periodically. Voltage vs time plots were constructed.

The cells were drained at different currents and voltage at each load was measured and voltage vs current plots were drawn. Internal resistance of the cell was calculated from the slope of the straight line obtained.

The iron sulphide samples were subjected to x-ray analysis, using Perkin Elmer instrument and the 'd' values were calculated. SEM analysis of the iron sulphide samples was also done using a JEOL - JM 35 scanning electron microscope.

Impedance measurements of the cell was made using a Solartron 1174 Frequency Response Analyser. Frequencies ranging from 10 mHz to 10 kHz were used in galvanostatic mode on a 100 kilo ohm load over the cell.

### RESULTS AND DISCUSSION

The discharge curves are given in Fig. 1.

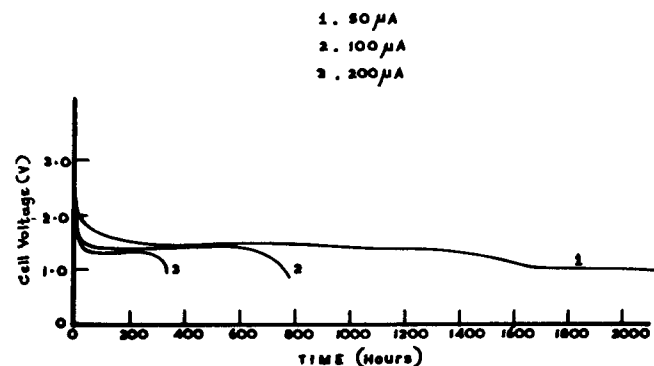


Fig.1. Discharge curves of Li/iron sulphide cell with 1 MPC/LiClO<sub>4</sub>

The curves are flat indicating that iron sulphide is reduced smoothly at low rates of discharge. At lower rates 90% efficiency of the utilization of cathode material was realised. It was also observed that cells of dimensions 6.5mm x 2.5mm thick could not reach efficiencies as high as the presently investigated cells i.e. 20mm x 2mm. Hence, it be useful to investigate the cell design and its effect on discharge characteristics in detail.

The internal resistance of the cell was found to be 220 ohms (Fig. 2). There is a steep fall of voltage during withdrawal of current which indicates that the cell cannot meet heavy current drains.

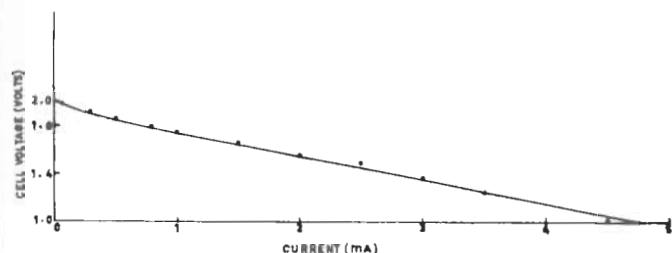


Fig.2. i - e behaviour of Li/FeS cell with 1 MPC/LiClO<sub>4</sub>

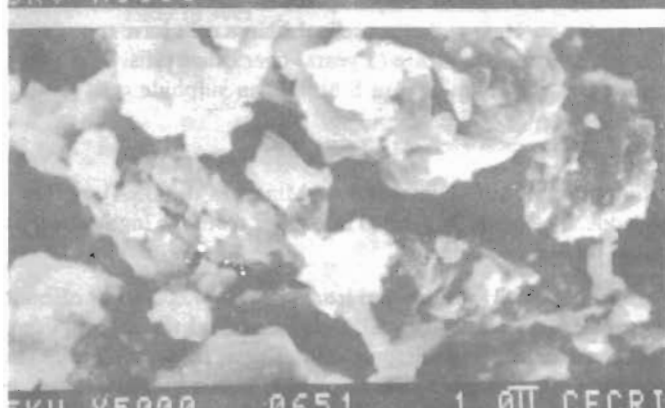
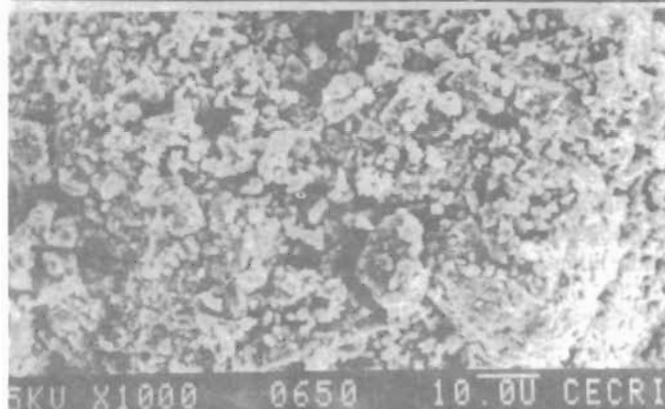
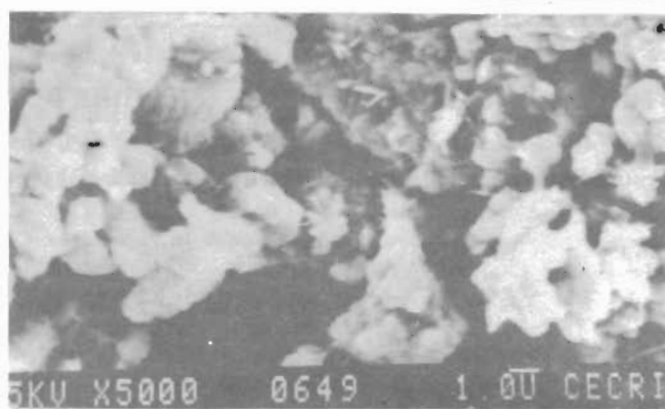
The 'd' values calculated by X-ray study for the samples are 0.4779 and 0.3676. Hence the two iron sulphide samples which are used for investigations are different and it is to be expected that the performance characteristics of the samples also will be different. The SEM photographs of the two types of iron sulphide synthesised in the laboratory are given in photographs bearing the numbers 649, 650, 651 and 652.

The photographs bearing Nos. 649 and 650 are for the first sample at x5000 and x1000 magnifications. The latter two photographs are for the second sample with the same magnifications. The first sample of iron sulphide is more uniform in grain size and has more surface area than the second one. Hence this sample has been used in our studies.

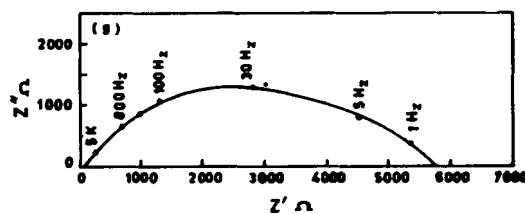
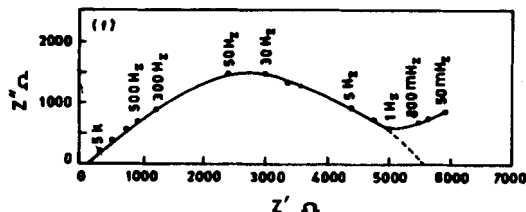
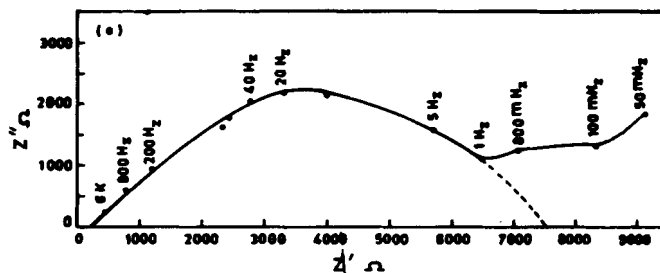
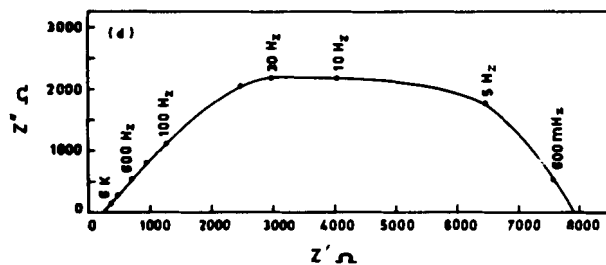
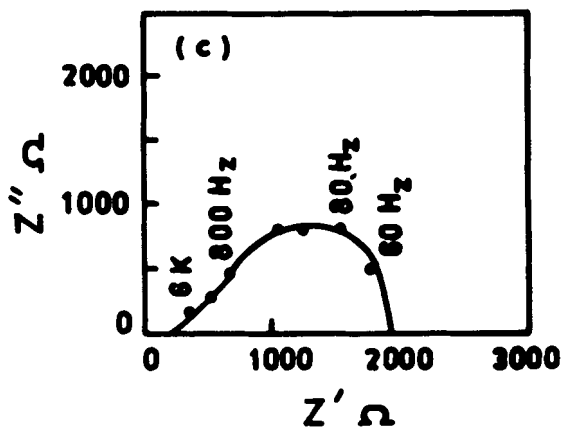
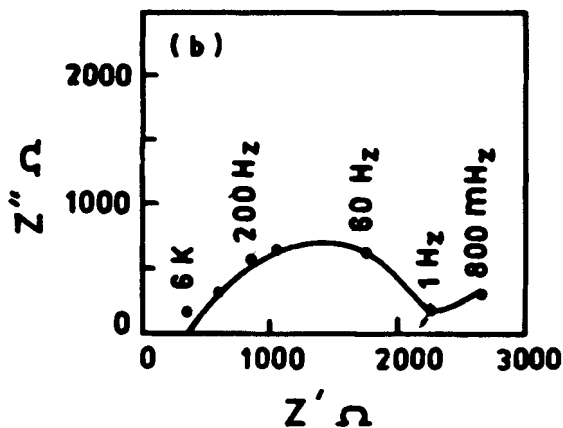
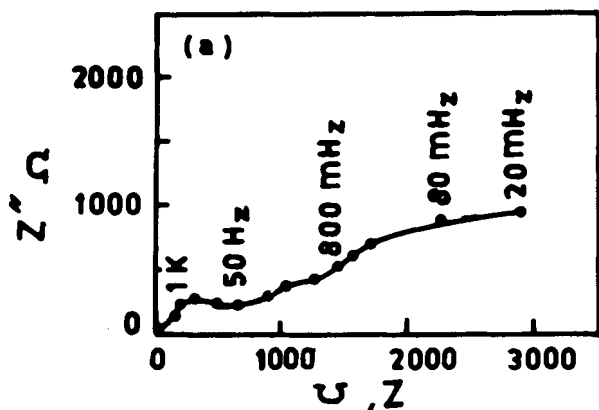
Impedance measurements for the cell were made immediately after the fabrication of the cell and at various periods of storage. Cole-Cole plots were constructed for these measurements, Table I shows the variation of solution resistance values (R<sub>sol</sub>) and charge transfer resistance (R<sub>act</sub>) values at different intervals.

Table I: Variation of solution resistance and charge transfer resistance

Period of storage hours	R <sub>sol</sub> ohms	R <sub>act</sub> ohms
0	—	—
25	250	2750
95	250	1750
142	150	7700
192	150	7350
240	75	5425
571	50	5700



Figs. 3(a) to 3(g) show the general shape of the impedance plots.



It is observed from the plots that the solution resistance decreases with storage. However, the  $R_{act}$  values first increase and then decrease. The general shape of the semicircle for the fresh cell is only a line. Then this shape alters during storage and turns into a semicircle and finally becomes a distorted figure. From the impedance plots of a battery, it can be concluded that the semicircular area as corresponding to the anode and the low frequency area to the cathode [5]. The variations are mostly observed in the anode region and therefore lithium metal is believed to form a solid electrolyte film in  $PC(LiClO_4)$  solution [6]. The variation in  $R_{act}$  values suggests that the charge transfer characteristics of the lithium anode are getting altered and hence the reaction characteristics are

altered. The film formation on lithium surface probably takes time for completion. The entire system needs time to get stabilized. The geometry of the semicircle is determined by the electrode area, the electroactive concentrations and the state of roughness of the electrode [7,8]. Hence it is clear that film formation takes place slowly and this influences the cell characteristics.

### CONCLUSION

Two methods were used to synthesize iron sulphide. The samples were subjected to X-ray and SEM studies, one of the samples having large 'd' value and large surface area has been used as cathode material in lithium/iron sulphide cells and the cells were discharged

at different rates. Impedance studies show that the cell takes time to stabilise. The other sample with small 'd' value and less roughness of surface could not discharge properly as expected.

#### REFERENCES

1. W E Aker, N Margolit, D P Johnson, R J Ekern, N A Fleischer and R J Brodd, *J Electrochem Soc*, **131**-8 (1984) 1839
2. Y Uetani, K Yokoyama and T Kawai, *Proc. 28th Power Sources Symp. 1978*, Electrochem Soc Inc, Princeton, p 219
3. N A Fleischer, R J Ekern, D P Johnson, *Proc Symp on Li battery* - Ed. A N Dey, **84**-1 (1984)p 353
4. H Ikeda, S Narukawa and Shinjiso, *Proc. 30th Power Sources Symp* (1982) p 179
5. J R Sandifer, M R Suchanski, *J Appl Electrochem Soc*, **14** (1984) 329
6. S A G R Karunathilaka, N A Hampson, M Hughes, W G Marshall, R Leek and T J Sinclair, *ibid*, **13** (1983) 577
7. M Hughes, S A G R Karunathilaka, N A Hampson and T J Sinclair, *ibid*, **13** (1983) 669
8. Y Geronov, F Shwager and R H Muller, *Proc. of Workshop on Li-nonaqueous battery*, Electrochem. Ed. E.B.Yeager et al, Electrochem. Soc, N.J.(1980) p 115