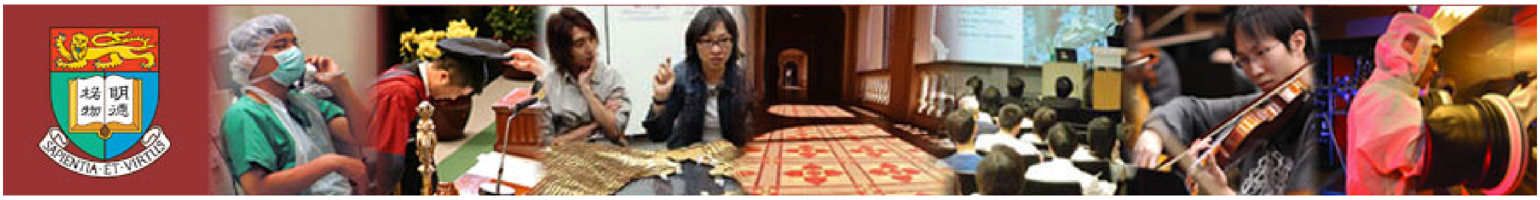

STUDY ON ELECTROCHEMICAL PROPERTIES OF FES_2 IN ROOM TEMPERATURE MOLTEN SALT

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ABSTRACT

In this paper, FeS_2 electrodes have been prepared by using reactive codeposition methods. The electrochemical performances of FeS_2 were studied in LiCl buffer Lewis neutral 1-methyl-3-ethylimidazolium chloride (MeEtImCl)/$AlCl_3$ (room temperature molten salt) melts. The results show that FeS_2 electrodes possess reversible Li ion intercalation and deintercalation behavior in the first step two electron processes.

INTRODUCTION

Metal sulfide has been widely used as cathodes in lithium batteries, This system appears particularly attractive because of high energy density, low cost and environmental safety.

The possibility of developing rechargeable lithium/FeS_2 in a room temperature molten salt (RTMS) electrolyte is currently being explored in both industrial and academic laboratories.

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This paper reports on the electrochemical studies of FeS_2 electrodes in RTMS electrolyte.

EXPERIMENTAL

All experiments involving moisture-sensitive materials were performed in a MBRAUN comp. glove box containing a dry argon atmosphere. FeS_2 electrodes were prepared by using reactive codeposition methods[1,2] at Ni foam substrate in 0.25M $FeCl_2$ + 0.1M $Na_2S_2O_3$ +0.02M $N_2H_2{<}2HCl$ solution. Electrochemical experiments of FeS_2 electrodes were performed in *LiCl buffer Lewis neutral* 1-methyl-3-ethylimidazolium chloride(MeEtImCl)/$AlCl_3$ melt[3]. The addition of small amount of $SOCl_2$ (20μL/L) in order to promote the reversible reduction and oxidation behavior of lithium. All potentials are referenced to an Aluminum wire immersed in acidic melt (0.6 mol fraction $AlCl_3$) and separated from the bulk melt via a fine porosity frit. A lithium strip was served as a counter electrode.

RESULTS AND DISCUSSION

Cyclic voltammograms obtained on FeS_2 electrodes in RTMS melts are given in Figure 1. It can be seen that two anodic peaks appear at 1.30V, 1.67V and two cathodic peaks at 1.35V, 0.43V respectively. It was concluded that most likely mechanism involved a two-step process. Namely,

$$FeS_2 + 2\,Li \rightarrow Li_2FeS_2 \quad \text{(upper plateau)} \quad (1)$$

$$Li_2FeS_2 + 2\,Li \rightarrow 2\,Li_2S + Fe \quad \text{(lower plateau)} \quad (2)$$

The upper two electron plateau is utilized for normal charge-discharge for Li/FeS_2 batteries. In this case, the lithium ions are intercalated and deintercalated during charge-discharge processes. It is unlike the behavior found in the molten salts that the FeS_2 is not regenerated during full recharge. In the lower plateau, the reaction proceeds by discharge of the Li_2FeS_2 to metallic iron. However, the actual cathodic discharge mechanism has been found to be much more complex than this case. In anodic charge processes, it yields FeS_y according to the following reactions[4,5]:

$$Fe + 2\,Li_2S \rightarrow 2\,Li + Li_2FeS_2 \quad (3)$$

$Li_2FeS_2 \rightarrow Li_{2-x}FeS_2 + x\ Li \quad (0<x\leq 0.8)$ (4)

$Li_{2-x}FeS_2 \rightarrow FeS_y + (2-y)S + (2-x)Li \quad (y=1.064)$ (5)

The charge-discharge characteristics of FeS_2 electrodes under various current-densities are shown in Figure 2. For discharge current densities below 0.75mA/cm^2 , the FeS_2 electrodes exhibit flat discharge profiles and, hence , have a utility in lower current drain applications. At higher discharge current densities (1.25mA/cm^2), the electrode potential decreases rapidly in the first few minutes and then the profile appears two quasi-plateaus, it is related to the two step process as shown in equations (1) and (2).

The cycle life characteristics of Li/FeS_2 cell are shown in Figure 3. As discussed above, the major one limited the positive discharge to the upper plateau to improve power density(via higher voltage) and cycle life performance of the cell. In 1975 CoS_2 was first used as a conductive additive in rechargeable FeS_2 electrodes[6]. Adding a small amount of $CoCl_2$ in the electrodeposition electrolytes, it was found that the cell resistance was decreased and the capacity utilization was increased respectively.

CONCLUSIONS

In summary, FeS_2 electrodes were prepared by using reactive codeposition methods possess good performance in RTMS melts. FeS_2 was not regenerated during full recharge.

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REFERENCES

1. A.C.C. Tseung, S.P. Jiang, Y.Z. Chen, J.K. You, J. of Materials Science Letters , 9, 1294 (1990).

2. S.P. Jiang, Y.Z. Chen, J.K. You, T.X. Chen, A.C.C.Tseung, J. Electrochem. Soc.,

137, 3374 (1990).
3. David M. Ryan, Eric R. Schumacher, and Thomas L. Riechel, J. Electrochem. Soc., 143, 908 (1996).
4. R. Fong, J.R. Dahn and C.H.W. Jones, J.Electrochem. Soc., 136, 3206, (1989).
5. R. Fong, C.H.W. Jones, and J.R. Dahn, J. Power Sources, 26, 333, (1989).
6. C.C. McPheeters, W.W. Schertz, and N.P. Yao, Abstract 25, Extended Abstracts. The Electrochemical Society, Vol.75-2 (1975).

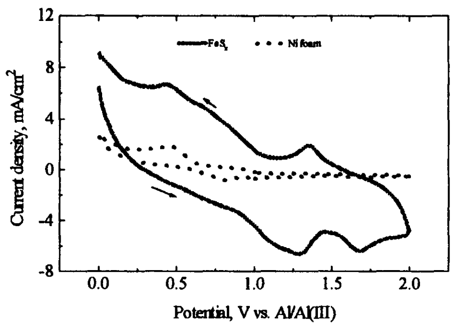

Fig. 1 Cyclic voltammograms of FeS_2 (—) and Ni foam(...) electrodes in RTMS melts at scan rate 25mV/s.

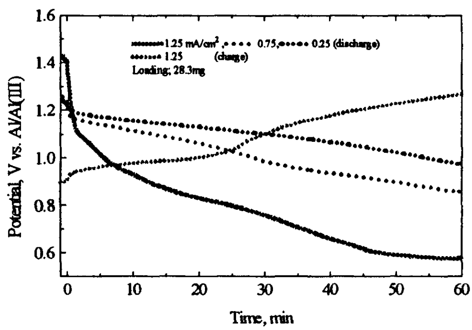

Fig. 2 Charge-discharge curves for FeS_2 electrodes (obtained with reactive codeposition) in RTMS melts at various current densitues

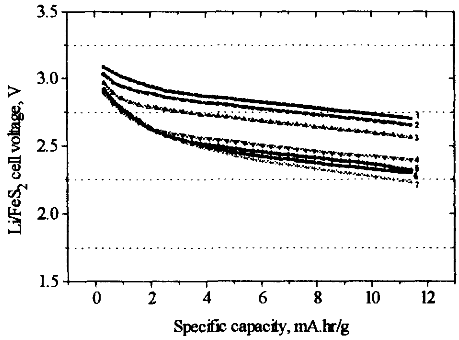

Fig.3 Discharge curves of Li/FeS_2 cell in RTMS melts at 0.2mA/cm^2. The cycle number as indicated in the figure.