SHORT COMMUNICATION

Effective conductivities of FeS positives in LiCl–LiBr–LiF electrolyte at different states of charge

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1. Introduction

In order to provide better understanding of the charge–discharge behaviour of LiAl/FeS high-temperature secondary cells, we measured effective conductivities of both the positive and negative electrodes separately. The results for porous positive FeS electrodes reported in previous papers [1, 2] indicated that the LiCl concentration in the LiCl–KCl electrolyte strongly affects the electrode resistance behaviour. The discharge performance is greatly improved by the use of LiCl-rich electrolytes. In this study we measured electrode conductivities of FeS positives during charge and discharge cycles using the LiCl–LiBr–LiF system as the electrolyte. Since the salt system is free of K^+ ions, containing Li^+ ions as the only cations, it can be considered as a case of the LiCl-rich electrolyte. The following merits might be expected [3, 4] when the LiCl–LiBr–LiF electrolyte is used:

(a) higher ionic conductivity than LiCl–KCl electrolytes because of the higher Li^+ ion concentration,

(b) simple electrode reactions, and good chargeability and dischargeability because of the lack of interaction with the K^+ ion,

(c) ease of analysis of the experimental results because of no change in the electrolyte composition in the electrode pores during charge and discharge.

2. Experimental procedure

The experimental set-up was identical to that reported previously [1], consisting of a working electrode which was the positive, a counter electrode which was an Li–Al negative, and a cell container. The positive electrode potentials were measured against an $Ni-Ni_3S_2$ reference electrode [5]. The electrolyte mixture was prepared from 31 mol % LiCl, 47 mol % LiBr and 22 mol % LiF (polarographic grade), supplied by Anderson Physics Laboratories, Inc. This salt has a liquidus temperature of 430° C. The FeS test electrode of 1 cm diameter and 0.4 cm thickness was prepared by pressing a mixture of FeS (-60, $+145$ mesh) and the electrolyte. The initial loading density was 1.30–1.35 A h cm^{-3}. The impedance measurements were made by a vector impedance meter (Hewlett-Packard Model 4800A) with a 10 μF capacitor blocking direct current. The accuracy of the instrument was $\pm 5\%$.

3. Results and discussion

3.1. Effective electrode resistance in the LiCl–LiBr–LiF electrolyte

Typical electrode resistance profiles during a discharge–charge cycle at 10 and 100 mA cm^{-2} are shown in Figs 1 and 2, respectively. At 10 mA cm^{-2} the electrode resistance increases gradually up to 40% utilization and starts to rise rather rapidly up to 60% utilization. At about 70% utilization it begins to decrease as observed in the LiCl-rich electrolyte. The decline in the electrode resistance in the last stage of discharge can be attributed to the increase of coarse iron particles formed during this period of discharge. A similar phenomenon has been discussed in a previous paper [1]. The discharge voltage curve is very flat with a slight cathode potential drop (about 30 mV) at about 50% utilization, corresponding to the potential difference between
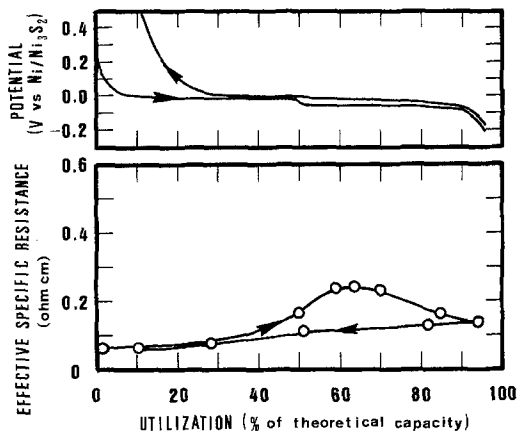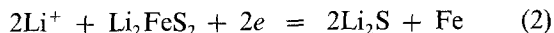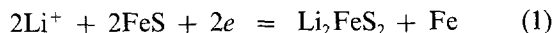
Fig. 1. Change in effective specific resistance of a 4 mm-thick FeS electrode during a cycle at $10\,mA\,cm^{-2}$ in LiCl–LiBr–LiF electrolyte. Loading density, $1.35\,A\,h\,cm^{-3}$; operating temperature, $450°\,C$.

FeS–Li_2FeS_2 and Li_2FeS_2–Li_2S. The discharge reactions in the all lithium cation electrolyte have been identified as follows [6, 7]:

$$2Li^+ + 2FeS + 2e = Li_2FeS_2 + Fe \qquad (1)$$

$$2Li^+ + Li_2FeS_2 + 2e = 2Li_2S + Fe \qquad (2)$$

When the FeS electrode is discharged at $100\,mA\,cm^{-2}$, the electrode resistance starts to increase at about 30% utilization and it remains at a high resistance level to the end. On charge it returns to the low resistance level of the fully-charged state. The effect of current density on the resistance profile during discharge is shown
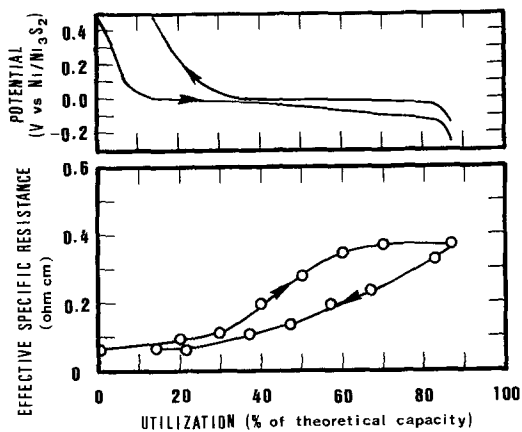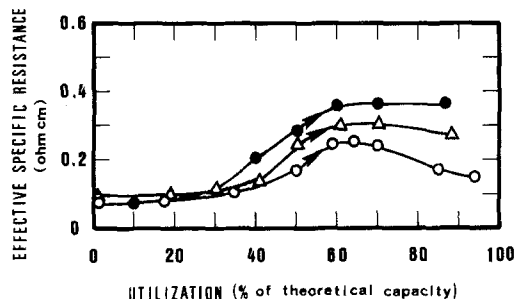

Fig. 3. Effect of current density on electrode resistance profile of a porous FeS electrode during discharge in LiCl–LiBr–LiF electrolyte. Loading density, $1.35\,A\,h\,cm^{-3}$; operating temperature, $450°\,C$. O, 10; △, 50; ●, $100\,mA\,cm^{-2}$.

in Fig. 3. A slight decline in the resistance at the last stage of discharge was observed at a current density as high as $50\,mA\,cm^{-2}$. The changes in resistance profile with discharge current density can be attributed to the difference in electrode porosities at the reaction front of the positive electrode. During the cell discharge, reductions in electrode porosity occur, resulting from the formation of Li_2S, which leads to high effective resistivity [1, 2]. At the high current density, the pores of the electrode are quickly choked, causing the high effective electrode resistance.

3.2. Comparison of results obtained in the LiCl–LiBr–LiF and the LiCl–KCl electrolytes

The electrode resistance profiles obtained for

Fig. 2. Change in effective specific resistance of a 4 mm-thick FeS electrode during a cycle at $100\,mA\,cm^{-2}$ in LiCl–LiBr–LiF electrolyte. Loading density, $1.35\,A\,h\,cm^{-3}$; operating temperature, $450°\,C$.
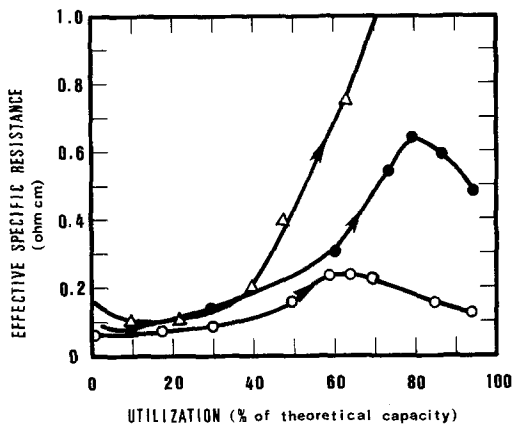

Fig. 4. Electrode resistance profiles of porous FeS electrodes during discharge at $10\,mA\,cm^{-2}$ in three different composition electrolytes. △, eutectic; ●, LiCl-rich; O, LiCl–LiBr–LiF electrolyte.
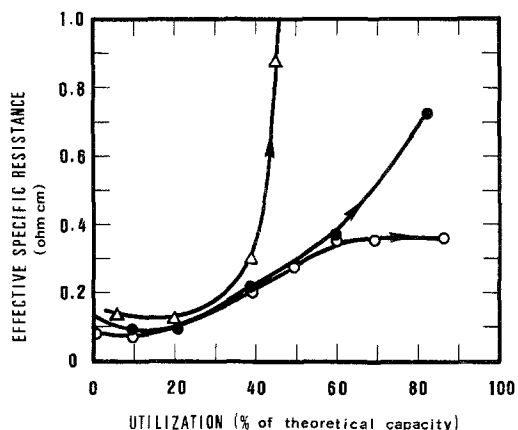
Fig. 5. Electrode resistance profiles of porous FeS electrodes during discharge at $100\,mA\,cm^{-2}$ in three different composition electrolytes. $\triangle$, eutectic; $\bullet$, LiCl-rich; $\bigcirc$, LiCl–LiBr–LiF electrolyte.

FeS positive electrodes in the LiCl–LiBr–LiF electrolyte, an LiCl-rich (67.4 mol % LiCl, 32.6 mol % KCl) electrolyte and the eutectic electrolyte (58.2 mol % LiCl, 41.8 mol % KCl) are shown in Figs 4 and 5. The detailed results obained in these LiCl–KCl electrolytes are described in previous papers [1, 2].

At all discharge current densities studied, the changes of the effective specific resistance in the LiCl–LiBr–LiF electrolyte were the smallest, particularly toward the end of the discharge. This can be attributed to the lack of the intermediate phases such as J-phase ($LiK_6Fe_{24}S_{26}Cl$) during discharge [6]. In addition, because of the absence of the K^+ ion, neither deposition of KCl or local electrolyte freezing could occur during discharge. When the LiCl–KCl electrolyte was employed, a high resistance increase was

observed and is attributed to the separation of a solid phase due to the local formation of excess component — KCl on discharge and LiCl on charge [2, 8]. The use of the LiCl-rich electrolyte would alleviate the deposition of KCl on discharge, but the use of the all-lithium cation electrolyte would completely remove the problem. Electrolyte composition gradients and separations of the salt under applied potentials have been analysed both theoretically [9–11] and experimentally [12, 13]. The low electrode resistance of the LiCl–LiBr–LiF electrolyte makes the system an attractive alternative to the LiCl–KCl system.

References

[1] M. Hiroi and H. Shimotake, *J. Electrochem. Soc.* **130**(1983) 12.
[2] *Idem, J. Appl. Electrochem.* **14** (1984) 341.
[3] R. K. Steunenberg, US. DOE. REP. CONF-821211-6 (1982).
[4] G. Barlow, P. Dand and B. Askew, 'Power Sources 9' (edited by J. Thompson), Academic Press, London, (1983) p. 534.
[5] L. Redey and D. R. Vissers, *J. Electrochem. Soc.* **128** (1981) 2703.
[6] Z. Tomczuk, S. K. Preto and M. F. Roche, *ibid.* **128** (1981) 760.
[7] Z. Tomczuk, M. F. Roche and D. R. Vissers, *ibid.* **128** (1981) 2255.
[8] M. J. Willars, J. G. Smith and R. W. Glazebrook, *J. Appl. Electrochem.* **11** (1981) 335.
[9] R. Pollard and J. Newman, *J. Electrochem. Soc.* **128** (1981) 491.
[10] C. E. Vallet and J. Braunstein, *J. Phys. Chem.* **81** (1977) 2438.
[11] *Idem, J. Electrochem. Soc.* **125** (1978) 1193.
[12] C. E. Vallet, D. E. Heatherly and J. Braunstein, *J. Electrochem. Soc.* **130** (1983) 2366.
[13] C. E. Vallet, D. E. Heatherly, L. Heatherly, Jr. and J. Braunstein, *ibid.* **130** (1983) 2370.