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Journal of Power Sources 97–98 (2001) 555–556

JOURNAL OF
POWER
SOURCES

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Degradation of cathodic sulphide materials in melted electrolytes

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Received 11 July 2000; accepted 4 January 2001

Abstract

The dissolving of various sulphide cathodic materials in melted halogenides at 460–500°C was investigated. A role of quantitative electrolyte composition on corrosion of cathodes was demonstrated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Lithium batteries; Cathodic sulphide materials; Role of corrosion

1. Introduction

Transition metal chalcogenides, in particular ferric sulphides, are of great interest for secondary lithium power sources with melted electrolytes. The merits of the electrochemical cells are stemming from high power capacities, the stability of basic electrochemical characteristics and from their relatively low cost [1,2]. However, the usage of melted salts dictates some problems in exploitation of high-temperature batteries, such as the corrosion of the cathode materials in hostile medium.

The objective of the study was to examine the interaction peculiarities of Fe, Ti, Cu, Al sulphides with melted electrolytes, namely mixed (LiCl–KCl) or monocationic ones (LiF–LiCl–LiBr) at 350–500°C range and to determine the solubility of these substances depending on the composition of the cathodic materials.

2. Experimental

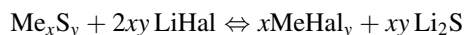
The investigation was carried out by isothermal holding of metal sulphide powders in contact with melted electrolyte. The samples of the electrolyte were quenched and analyzed for sulphides and for Fe ions (if ferric sulphides were used). The analysis for sulphide ions was conducted by iodometry techniques and for Fe-ions by measuring electromotive force in concentration circuits.

3. Results and discussion

The data for solubility of Li_2S – FeS_2 – FeS_5 samples in eutectic mixture of LiCl–KCl are given in Table 1.

The results for measurements of metal sulphides solubility in melted monocationic electrolyte are summarized in Table 2.

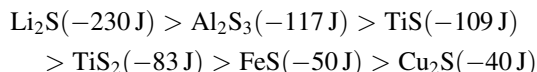
The values obtained make it clear that the samples with Li_2S , which contains the same cation as the electrolyte, possess the highest solubility. The relatively high solubility of different metal sulphides and their distinctive changes with temperature are likely to be caused by ionic double exchange reactions of cathodic material with electrolyte



where Me = Ti, Al, Fe, Cu, Hal = F, Cl, Br.

In effect, the proceeding of the exchange reaction leads to dissolving of Li_2S and MeHal_y in the electrolyte. It seems reasonable that the similarity in properties of metal sulphide with those of lithium sulphide (e.g. ionicity of the bonds, the charge and ionic radius of the ions) favors the run of the reaction above, thus, increasing the solubility of metal sulphides.

According to Pauling, the heat of formation per equivalent weight can be taken as a measure of bond ionicity. Using this criterion, the ionicity of sulphides is supposed to decrease in the order



As a consequence, Al_2S_3 possess the greatest similarity in bond ionicity with Li_2S , and so do their cationic radii. The tendency to form a stable hexafluoroaluminate complex (Li_3AlF_6) also favors the proceeding of the ion exchange reaction between monocationic electrolyte and Al_2S_3 . As the exchange reaction is supposed to be exothermal, a raise

Table 1
Solubility of Li_2S – FeS_2 – FeS samples in eutectic mixture of LiCl – KCl

No.	Composition of the samples	Solubility of ferric sulphides	
		at 350°C, $S \times 10^4$	at 460°C, $S \times 10^4$
1	FeS_2	5.0	8.0
2	$\text{Li}_2\text{S} + 9\text{FeS}_2 + \text{FeS}$	6.0	5.0
3	$\text{Li}_2\text{S} + 7\text{FeS}_2 + \text{FeS}$	3.0	3.0
4	$\text{Li}_2\text{S} + 5\text{FeS}_2 + \text{FeS}$	6.0	2.0
5	$\text{Li}_2\text{S} + 3\text{FeS}_2 + \text{FeS}$	10.0	10.0
6	$\text{Li}_2\text{S} + \text{FeS}_2 + \text{FeS}$	20.0	25.0
7	$\text{Li}_2\text{S} + \text{FeS}$	60.0	70.0

Table 2
Solubility of metal sulphides in melted LiF – LiCl – LiBr

No.	Composition	Solubility of sulphides, wt. %		
		at 460°C	at 500°C	at 550°C
1	Li_2S	1.15	1.35	1.77
2	TiS	0.028	0.026	0.023
3	TiS_2	0.051	0.047	0.037
4	$\text{Li}_2\text{S} \cdot \text{TiS}_2$	0.29	0.39	0.50
5	FeS	0.033	0.027	0.030
6	Al_2S_3	1.15	1.19	0.67
7	Cu_2S	0.155	0.195	0.21

in temperature should adversely affect the equilibrium, thus, lowering the sulphide solubility.

The match in ionic charges (+1), which ultimately can counterbalance the effect of bond ionicity, might explain a relatively high solubility of Cu_2S .

Furthermore, one should take into account the role of some other factors or the equilibrium of the exchange reactions, namely, fugacity of metal halides and the formation of metal thiosalts Li_xMeS_y .

4. Conclusion

To summarize briefly, the phenomenon of cathodic materials' solubility in melted electrolytes is of major importance for the usage of high-temperature lithium batteries. The deterioration of cathodic materials may be a principal cause for power sources self-discharge, and consequently, the above mentioned lend impetus to a search for efficient separators used in lithium batteries.

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