

CATHODIC PERFORMANCE OF SOME SULFIDE ELECTRODES IN LIQUID AMMONIA

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Summary

The cathodic performance of some metal sulfide electrodes has been investigated in a liquid ammonia solution of NH_4SCN . In dry liquid ammonia, the polarization of the CuS electrode was the smallest, and that of the Ti_2S_3 electrode was the greatest. The utilizations of the sulfides on continuous discharge were 35% at 0 °C and 45% at 20 °C for NbS, and 25% at 20 °C for FeS (2 mA/1.33 cm²). In the presence of a small amount of water in the electrolyte, the polarization increased, though the cell resistance decreased.

Introduction

In the field of high energy density batteries, the use of non-aqueous solvents as the electrolyte has been a subject of recent interest. Many investigators have reported the use of non-aqueous organic solvents [1, 2], molten salts [3 - 5] and others as the electrolyte of the batteries. Among the non-aqueous solvents, the conductivity of liquid ammonia containing an electrolytic salt is very high [6], and this solvent can be used as the electrolyte at low temperatures also. The adoption of liquid ammonia for the electrolyte of a battery may enable a high energy density battery working at low temperatures to be realized. Adlhart [7] and Minnick [8] reported in 1960 on magnesium anode batteries with liquid ammonia electrolyte and HgSO_4 , PbSO_4 , S or S compounds as cathodes. Their batteries worked over a wide temperature range, 74~ - 62 °C, but the duration of discharge was a period of only several minutes. In 1963 Wood and Doan [9] examined some experimental problems of ammonia batteries and Minnick [10] described the construction of a complete battery. Later, Comyn and Nelson [11] reported that the addition of methanol to liquid ammonia reduced the vapor pressure of ammonia and they adopted amalgamated zinc as the anode and organic depolarizers and lead dioxide as cathodes. Saito and coworkers [12] examined some oxides and chlorides as cathodes in ammonia batteries, but the discharge durations were short. During these investigations, the supporting

electrolyte in liquid ammonia was the thiocyanates, KSCN or NH_4SCN . In the course of these investigations, Matsuda and coworkers [13] have shown that CuS shows a stable cathodic performance during a long discharge period. The purpose of the present work was to investigate the cathodic characteristics of CuS and the other metal sulfides (Ti_2S_3 , TaS_2 , FeS, NbS and NiS) as the positive electrode in liquid ammonia and to clarify the matters relating to their performance.

Experimental

The liquid ammonia system with pressure bottles and electrolytic cell was the same as that used in a previous work [13].

A working electrode consisting of a pellet (area 1.33 cm^2) was prepared by pressing a mixture of pure commercial metal sulfide, graphite, acetylene-black (AB) and polyethylene (PE) powder. This electrode was mounted at the bottom of a glass tube with glass frit at the end of it, and graphite powder and a carbon rod were used to make electrical contact. The counter electrode was a platinum plate of dimensions $2.0 \times 3.0 \text{ cm}$, and the reference electrode was a $\text{Ag}/\text{AgCl}/\text{Cl}^-$.

Any slight moisture and impurities in the ammonia were removed by drying with metallic sodium and by redistillation, respectively. Ammonium thiocyanate and ammonium chloride were JIS special grade reagents, and the metal sulfides used were of greater than 99.9% purity. These reagents were used after drying under reduced pressure.

A potentiogalvanostat was used for measurements of polarization and efficiency during continuous discharge. A current pulse generator and an oscilloscope were used for measurements of i.r. loss. However, the value of i.r. loss measured was that between the test electrode and the reference electrode because it was not structurally possible to use a Luggin capillary. Therefore, these i.r. losses contained the resistances of the test and reference electrodes, and that of the electrolyte solution between both electrodes. These i.r. losses are represented as cell resistance in this paper.

The utilization of the electrodes was estimated from the point of inflexion of the curve showing discharge time *versus* electrode potential where diffusion polarization appeared.

The operating temperature was controlled by immersing the electrolytic cell in organic solvent-dry ice bath, water-ice bath etc., and the potential relationships were measured at constant temperature.

Results and discussion

Cathodic polarization characteristics

Potential-current curves for some metal sulfide electrodes at various temperatures are plotted in Fig. 1 (Ti_2S_3 electrode), Fig. 2 (CuS electrode),

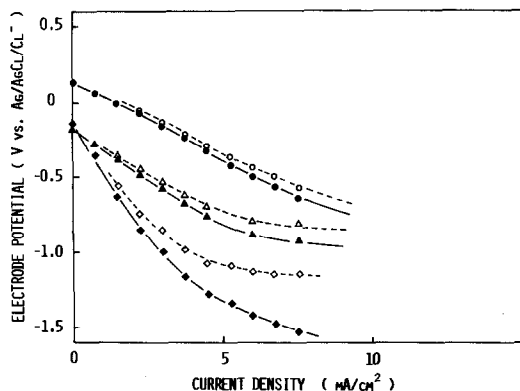


Fig. 1. Cathodic polarization curves for a Ti_2S_3 electrode at various temperatures. The solid curves (—) correspond to the polarization including the i.r. loss and the dotted curves (.....) correspond to the polarization free of i.r. Electrode composition: Ti_2S_3 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: \circ , \bullet , 20 °C; \triangle , \blacktriangle , 0 °C; \diamond , \blacklozenge , -65 °C.

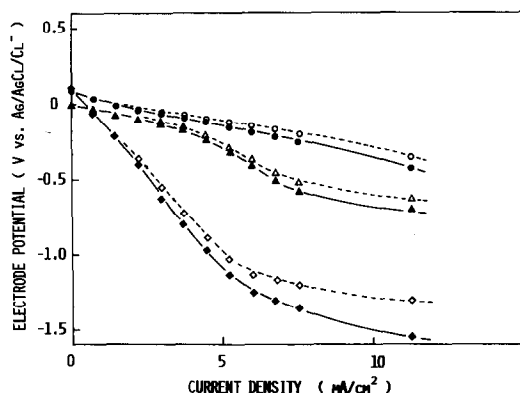


Fig. 2. Cathodic polarization curves for a CuS electrode at various temperatures. The solid curves (—) correspond to the polarization including the i.r. loss and the dotted curves (.....) correspond to the polarization free of i.r. Electrode composition: CuS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: \circ , \bullet , 20 °C; \triangle , \blacktriangle , 0 °C; \diamond , \blacklozenge , -65 °C.

Fig. 3 (FeS electrode) and Fig. 4 (NbS electrode). These Figures show that the values of the polarization and i.r. loss increased as the temperature was lowered. This phenomenon could be caused by increase of the viscosity [14] and decrease of the conductivity of the electrolyte at lower temperatures; analogous to the behavior of aqueous electrolytes.

The current densities observed with these electrodes at constant potentials of -0.25 and -0.50 V (*vs.* $\text{Ag}/\text{AgCl}/\text{Cl}^-$) and the rest potential of each electrode are shown in Table 1. This Table shows that the polarization of the CuS electrode is the smallest among the metal sulfide electrodes, and

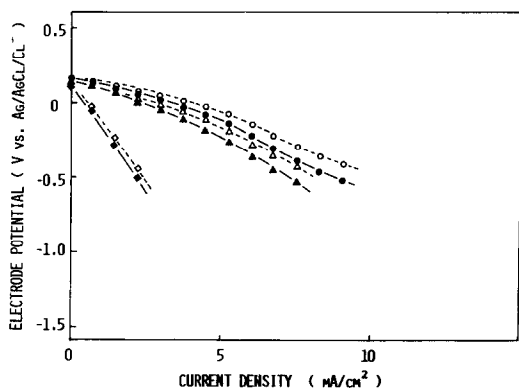


Fig. 3. Cathodic polarization curves for a FeS electrode at various temperatures. The solid curves (—) correspond to the polarization including the i.r. loss and the dotted curves (.....) correspond to the polarization free of i.r. Electrode composition: FeS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: $\circ \bullet$, 20 °C; $\triangle \blacktriangle$, 0 °C; $\diamond \blacklozenge$, -65 °C.

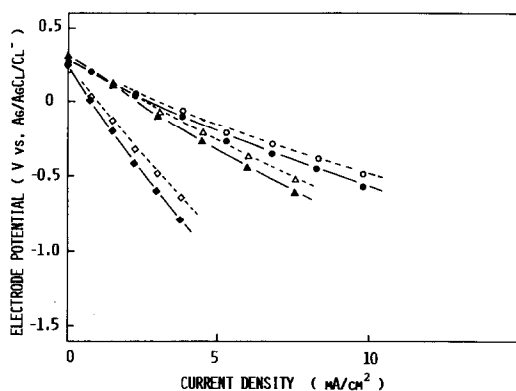


Fig. 4. Cathodic polarization curves for a NbS electrode at various temperatures. The solid curves (—) correspond to the polarization including the i.r. loss and the dotted curves (.....) correspond to the polarization free of i.r. Electrode composition: NbS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: $\circ \bullet$, 20 °C; $\triangle \blacktriangle$, 0 °C; $\diamond \blacklozenge$, -65 °C.

that of the Ti_2S_3 electrode is the greatest. The Ti_2S_3 electrode showed self-discharge and this pellet electrode could not maintain its shape in liquid ammonia.

Continuous discharge characteristics

The FeS electrode and NbS electrode were continuously discharged at constant current ($2 \text{ mA}/1.33 \text{ cm}^2$), and were compared with the CuS electrode [13]. Discharge curves for the NbS electrode and FeS electrode are shown in Figs. 5 and 6, respectively. The cathodic discharge mechanisms of these sulfide electrodes have not been clarified except that of CuS. On the

TABLE 1

Relations between electrode potentials and current densities (mA/cm^2) for metal sulfide electrodes

Electrode potential		Temp. ($^{\circ}\text{C}$)	NiS	TaS ₂	Ti ₂ S ₃	CuS	FeS	NbS
-0.25 V	Contained	20	5.2	4.0	3.9	7.9	6.2	5.6
	i.r. loss	0	3.2	3.4	0.6	4.5	5.1	4.3
		-65	0.9	1.9	0.4	1.6	1.3	1.6
<i>vs.</i>								
Ag/AgCl/Cl ⁻	i.r. free	20	6.0	4.6	4.2	9.2	7.0	6.4
		0	—	—	0.7	5.0	5.2	4.9
		-65	—	—	0.3	1.7	1.5	2.0
-0.50 V	Contained	20	9.1	7.0	6.2	12.5*	8.8	9.2
	i.r. loss	0	5.1	5.2*	2.4	6.7	7.2	6.7
		-65	1.8	2.8	1.2	2.6	2.1	2.6
<i>vs.</i>								
Ag/AgCl/Cl ⁻	i.r. free	20	9.6*	7.5	6.9	15.5*	10.2*	10.5
		0	—	—	2.8	10.0	8.1*	7.6
		-65	—	—	1.4	2.8	2.4	3.2
Rest potential			+0.16	+0.13	+0.13	+0.10	+0.17	+0.31
(V <i>vs.</i> Ag/AgCl/Cl ⁻)			}	}	}	}	}	}
			-0.04	+0.08	-0.18	-0.02	+0.14	+0.25

*Extrapolated value.

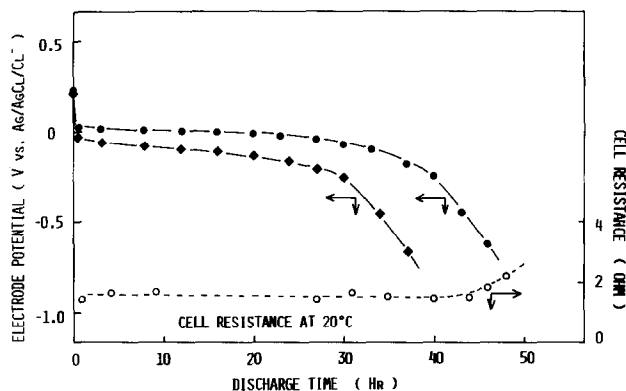


Fig. 5. Discharge curves at constant current. Electrode composition: NbS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Current density: 2 mA/1.33 cm^2 . Temperature: ●, 20 $^{\circ}\text{C}$; ◆, 0 $^{\circ}\text{C}$.

CuS cathode, the CuS changed progressively into Cu during the course of discharge. Therefore, the utilization of the electrodes was calculated by assuming that every sulfide cathode was reduced and finally changed into its metal.

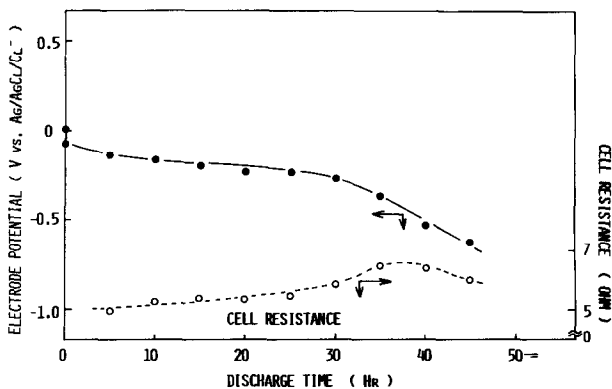


Fig. 6. Discharge curves at constant current. Electrode composition: FeS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Current density: 2 mA/1.33 cm^2 . Temperature: 20 °C.

The utilization of the NbS electrode was 35% for 30 h discharge at 0 °C and 45% for 38 h discharge at 20 °C, and that of the FeS electrode was 25% for 30 h discharge at 20 °C; assuming that the electrode reactions on these electrodes involved two electrons. In the case of the CuS electrode, it was 71% at 5 mA/1.33 cm^2 and 67% at 10 mA/1.33 cm^2 (at 0 °C) [13]. In comparison with the utilization of the CuS electrode, the values for the NbS and FeS electrodes were rather low.

During the continuous discharges (curves shown as broken lines in Figs. 5 and 6), all resistances tended to increase as the electrode potential decreased. After the continuous discharge of the FeS electrode, the electrolyte was analyzed colorimetrically (thiocyanate method). The result showed that the quantity of Fe dissolved into the electrolyte was about 54 mg (the quantity of FeS in the electrode was 400 mg before discharge), which was about 57% of the Fe discharged.

Cell resistance

In Fig. 6, the cell resistance gradually increased with duration of discharge and then decreased slowly. This small decrease after a discharge time of 35 h could be caused by the dissolution of Fe formed through the cathodic discharge and the deterioration of the electrode. This kind of phenomenon was observed only with the FeS electrode.

Figure 7 shows the relationship between cell resistance R , which was calculated from i.r. loss, and discharge current on NiS, TaS₂ and FeS electrodes, respectively. The measurements were repeated three times, and similar results were obtained in the 2nd and 3rd runs. These results showed good reproducibility. From the Figure, it can be seen that the values of the resistance were relatively constant for the NiS and TaS₂ electrodes (4.4 and 7.2 ohm, respectively), but the value decreased from a large initial resistance to a small constant value for the FeS electrode. This phenomenon was assumed to be due to the formation of some compounds with low conductivity on

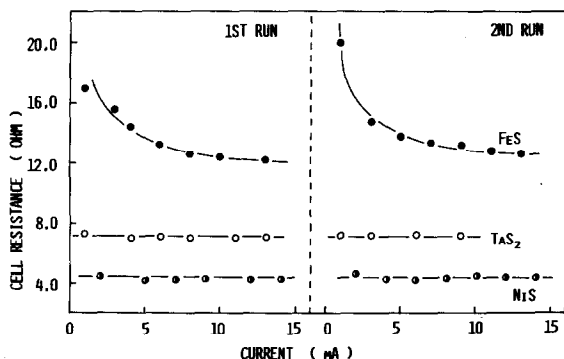
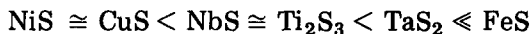


Fig. 7. Relationship between cell resistance and discharge current of metal sulfide electrodes at 20 °C.

the electrode surface in liquid ammonia during each break in the discharge. Therefore, the initial value of resistance after closing the discharge circuit was rather large, but was reduced as the film dissolved after current flowed again.

The resistance contains that of the test electrode and the reference electrode and of the electrolyte between both electrodes, but the resistances of the reference electrode and the electrolyte were almost the same in each cell, but not the resistance of the test electrode. From Table 2, the order of the resistances is as follows:



This order corresponds to the order of the relative conductivities of the metal sulfides.

TABLE 2

The cell resistances of the system
(calculated from i.r. loss) at 20 °C.

Metal sulfide	Cell resistance (ohm)
CuS	4.7
NiS	4.4
TaS ₂	7.2
NbS	6.2
Ti ₂ S ₃	6.5
FeS	12.5 ~ 20.0

Influence of water on the polarization characteristics

A small amount of water (1% vol.) was added to the electrolyte, and potential-current curves were measured, and the effect of water on polarization and cell resistance was determined.

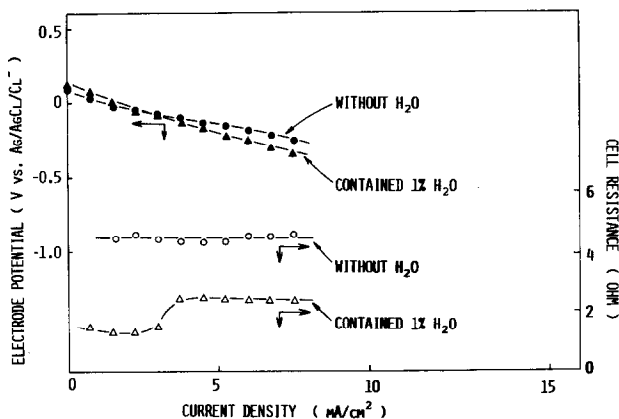


Fig. 8. Influence of water in the electrolyte on cathodic polarization characteristics. Electrode composition: CuS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: 20 °C.

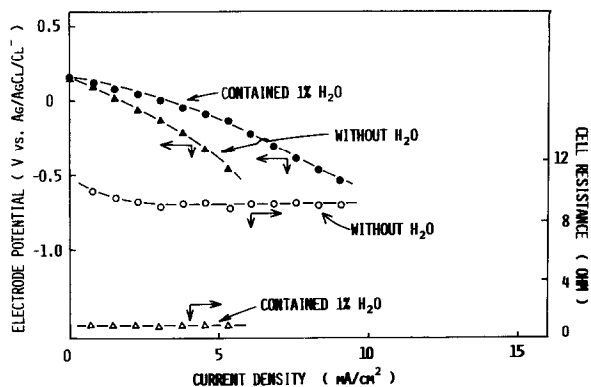
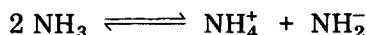


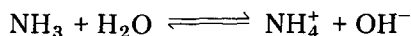
Fig. 9. Influence of water in the electrolyte on cathodic polarization characteristics. Electrode composition: FeS 80%, PE 5%; Graphite 13%, AB 2%. Solution: 4 mol/l NH_4SCN + 0.5 mol/l NH_4Cl . Temperature: 20 °C.

The effect of the addition of water on the performance of CuS and FeS electrodes is shown in Figs. 8 and 9, respectively. In the case of the addition of 1% water, reproducible potential-current curves were obtained. The Figures show that the polarization was increased and the cell resistance decreased by the addition of water. The influence of water was more pronounced on the FeS electrode than on the CuS electrode.

The effects of the addition of water to the electrolyte may be considered as follows. Firstly, the dielectric constant of water (79 at 25 °C) is larger than that of liquid ammonia (17 at 25 °C). Secondly, the dissociation of liquid ammonia without water is shown in the following equation:



However, in the presence of water in liquid ammonia the ionization is as shown in the following equation:



As the mobility of the hydroxyl ion would be larger than that of the other ion species, the i.r. value of the system might be smaller than that in dry liquid ammonia.

Conclusions

The cathodic polarization characteristics of CuS, NbS and NiS were excellent in liquid ammonia containing thiocyanates and ammonium chloride, but the discharge product of the FeS cathode was soluble in the electrolyte solution and the Ti_2S_3 cathode showed self-discharge. The performance of the sulfide cathodes was in the same order as their relative conductivities. The utilization of the NbS electrode was 35% at 0 °C and 45% at 20 °C, and that of the FeS electrode was 25% at 20 °C. These values were smaller than that of the CuS electrode. Except for the case of the FeS electrode, cell resistance remained almost constant during discharge, increasing only in the final stage. By adding water to the liquid ammonia, the cathodic polarization was generally increased, but the cell resistance was decreased.

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