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RECHARGEABLE HIGH-VOLTAGE LOW-TEMPERATURE MOLTEN-SALT CELL Na/β"-ALUMINA/SCl_3^+ IN $AlCl_3$-NaCl
Final Report

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December 1985

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RECHARGEABLE HIGH-VOLTAGE LOW-TEMPERATURE MOLTEN-SALT CELL

Na/β''-ALUMINA/SCl_3^+ IN $AlCl_3$-NaCl

Final Report

December 1985

by

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ABSTRACT

This report deals with the rechargeable molten salt cell: Na/β"-alumina/SCl_3^+ in $AlCl_3$-NaCl, and its underlying chemistry. This cell is operated at 180-250°C, and is characterized by two discharge plateaus:

$$4Na + SCl_3AlCl_4 + 3AlCl_3 = S + 4NaAlCl_4$$

$$2Na + S + AlCl_3 = AlSCl + 2NaCl$$

The $AlCl_3$-NaCl melt is important in stabilizing several sulfur species formed in charge/discharge processes and in maintaining a conducting liquid positive mixture. The cell voltage in the fully charged state is $\geq$4.30 V for the first step and 2.75 V for the second step. The theoretical capacity is in excess of 190 Ah kg^{-1}, corresponding to a theoretical specific energy in excess of 700 Wh kg^{-1}, based on the electrode active materials. High energy and power densities have been achieved. Hundreds of deep charge/discharge cycles have been obtained for several cells using Reticulated Vitreous Carbon or tungsten positive current collectors.

INTRODUCTION

The development of new batteries for load-leveling, electric-vehicle and other applications has received considerable attention in recent years. Such batteries should ideally involve low cost materials, have high energy and power densities and long lifetimes. Aqueous, organic, molten salt and solid electrolytes and various electrode systems have been investigated in the past [1-6].

To date, no molten-salt battery system has become commercially available. Probably the most developed system is the Na/β"-alumina/S cell. It was introduced by Kummer and Weber in 1967 [7] and has since been under development in several laboratories throughout the world [8]. It has a theoretical energy density of 758 Wh kg^{-1} and typical working temperatures of 350°C [9]. Energy densities of ~150 Wh kg^{-1} have been demonstrated for finished cells [8]. Levine and coworkers at Dow Chemical Company have taken a different approach by replacing the β"-alumina tube with thousands of hollow Na^+- conducting glass fibers in each cell [10]. The much lower specific conductivity of this glass compared to that of β"-alumina is compensated by the very small wall thickness (~10 μm) and the fact that much lower current densities can be employed because of the much larger area of the Na^+- conducting glass fibers.

The LiAl/LiCl-KCl/FeS and Li_4Si/LiCl-KCl/FeS_2 cells are operated at ~450°C. The second cell has a much higher theoretical energy density (944 Wh kg^{-1}) than the first (458 Wh kg^{-1}) due to the much lower equivalent weight of the electrodes [9]. Large battery modules have been tested although a number of problems remain.

Several positive electrodes for secondary cells using molten chloroaluminates (mainly $AlCl_3$-NaCl melts) as electrolytes and aluminum or sodium as negative electrodes have been examined [11-30]. Molten chloroaluminates offer several advantages such as low liquidus temperatures and reasonably high conductivity [31,32]. The chemical and physical properties and the chemistry of numerous solutes in these melts are well characterized [33]. Secondary cells that have involved chloroaluminate melts include the Al/Cl_2 [20,21], Na/Cl_2 [17], Al/S [22,23], Al/MCl_x [24], Na/MCl_x [17-19,25,26], and the Na/S_2Cl_2 [30] cells. Most of these cells exhibit very high theoretical energy densities, for instance ~1400 Wh kg^{-1} for the Al/Cl_2 cell [20]. However, the problems associated with the use of chlorine (normally adsorbed on carbon powder) and with the dendrite formation and passivation of aluminum electrodes [34,35] make most of these cells somewhat less desirable.

The most developed battery using chloroaluminates involves the $Na/SbCl_3$ system. A theoretical energy density of 825 Wh kg^{-1} and an open circuit voltage (OCV) of 2.83 V have been reported for this system [17,26]. This cell operates typically at 220°C. Some of the problems encountered with this cell include corrosion of positive current-collectors, short seal life, and a low probability of achieving load-leveling battery cost targets [19].

The Na/SCl_3^+ chloroaluminate cell and its chemistry were under investigation in our laboratory during the period 1976-1984. This report summarizes the underlying chemistry and the results obtained for many laboratory cells during 1979-84.

CHEMISTRY OF THE Na/SCl_3^+ CHLOROALUMINATE SYSTEM

The cell: Na/β"-alumina/SCl_3^+ in $AlCl_3$-NaCl melts exhibits two major discharge steps corresponding to the simplified overall reactions

$$SCl_4 + 4Na = S + 4NaCl$$

and

$$S + 2Na = Na_2S$$

when the chloroaluminate solvent is not included. During discharge, the Lewis acidity of the positive mixture decreases until eventually the melt becomes saturated with NaCl near the $AlCl_3$-NaCl (50-50 mol % ≡50/50) composition at typical operating temperatures of 180-250°C. The main features of $AlCl_3$-MCl (M = alkali metal) melts are summarized in Table 1. The dominant complex ion in basic melts ($\leq$ 50 mol % $AlCl_3$) is $AlCl_4^-$. The acidic mixtures (> 50 mol % $AlCl_3$) have low liquidus temperatures. A miscibility gap is observed in very acidic melts (36,37). Potentiometric [38-40], vapor pressure [41,42], Raman [43,44] and infrared [45] spectroscopic studies have shown that $AlCl_4^-$, $Al_2Cl_7^-$, $Al_nCl^-_{3n+1}$ ($n \geq 3$) and Al_2Cl_6 are present in acidic melts. It is expected that some properties of chloroaluminate melts are affected by high concentrations of the different sulfur species present in the positive electrode mixture of the Na/SCl_3^+ chloroaluminate cell.

The Lewis acidity has a pronounced effect on the complexation and stability of several sulfur species formed in the chloroaluminate melt. Elemental sulfur is present in the melt predominantly as S_8 [46]. It can be oxidized or reduced in both basic and acidic melts [47-53]. The reduction results in polymeric sulfides present as either $(AlSCl)_n$ in acidic melts or $(AlSCl_2^-)_n$ in basic melts [52,54]. The values of n are believed to be ~3-4 in dilute melts [54]. When sulfur is oxidized in basic melts,

TABLE 1.

Main features of $AlCl_3$ - MCl melts (M = alkali metal).

X_{AlCl_3}	0	0.50	0.667	0.75	0.8-0.9	1.00
Bonding	———	———	Ionic	———	———	Immiscibility → Covalent
Increasing Acidity[a]	→	→	→	→	→	
Increasing Liquidus Temp.[b]	←	→	- - -	→	→	193°C
Stoichiometric Composition	MCl	$MAlCl_4$	MAl_2Cl_7	(MAl_3Cl_{10})		$AlCl_3$
Melt Equilibria	$Cl^- \underset{MCl}{\overset{AlCl_3}{\rightleftharpoons}}$	$AlCl_4^- \underset{MCl}{\overset{AlCl_3}{\rightleftharpoons}}$	$Al_2Cl_7^- \underset{MCl}{\overset{AlCl_3}{\rightleftharpoons}}$	$(Al_3Cl_{10}^-) \underset{MCl}{\overset{AlCl_3}{\rightleftharpoons}}$		Al_2Cl_6

[a]Lewis acid is a Cl^- ion acceptor.

[b]Eutectic melt compositions depend on alkali metal counter ion. $LiAlCl_4(s)$ and $NaAlCl_4(s)$ melt incongruently.

monovalent sulfur species present as S_2Cl_2 result [48,51]. Further oxidation results in chlorine evolution since SCl_3^+ is unstable in basic melts [51].

In acidic melts, the oxidation of sulfur involves three voltammetrically distinguishable steps. The first of these steps leads to S_8^+ and other sulfur cationic species as evidenced by the apparent n-value per sulfur atom which ranges from 0.13 to 0.22, depending on the temperature (175-250°C) and the concentration of sulfur. Additional evidence for this behavior has been obtained from spectroelectrochemical results [49,55]. The second step results in the formation of monovalent sulfur as S_2Cl_2 or S_2Cl^+ [47,48] which is oxidized to SCl_3^+ in the third step [49,55,56]. The presence of tetravalent sulfur as the complex ion SCl_3^+ has been confirmed by Raman spectroscopy [52,57]. Formal potentials estimated from voltammetric data for various sulfur redox couples in both acidic and NaCl-saturated melts at 250°C *vs* three different reference electrodes are summarized in Table 2 [27]. The last column gives the expected OCV for the Na/β"-alumina/SCl_3^+ cell at the quoted conditions. These OCV values will be somewhat altered when acidity and sulfur concentrations are different as in practical cells. For instance, we have observed an OCV of 4.35 V in very sulfur-rich cells in the fully charged state (this OCV is higher than for any other rechargeable cell). We usually denote a cell as sulfur-rich when the S/Al molar ratio in the positive mix is larger than 0.15.

THEORETICAL ENERGY AND CAPACITY DENSITIES

The theoretical energy density is the product of the OCV and the capacity density. The latter is determined by the Al/Na composition range that can be utilized in the six-electron reduction/oxidation of sulfur. Because of the instability of tetravalent sulfur in basic melts, the positive mixture is adjusted to complete the first step of discharge (i.e., S(+4) → S(0)) within the acidic melt composition range (Al/Na > 50/50). The maximum theoretical energy density then corresponds to a positive mix where in the fully charged state sulfur is in the +4 state and all of the sodium is in the elemental state. The overall cell reactions (including the solvent), and the corresponding theoretical capacity and energy densities are as follows:

First step

$$SCl_3AlCl_4 + 1.5Al_2Cl_6 + 4Na = S + 4NaAlCl_4 \quad (3)$$

OCV : 4.35V

Capacity density: 126.8 Ah kg^{-1}

Energy density: 552 Wh kg^{-1}

TABLE 2

Formal potentials of various sulfur redox couples at 250°C

Redox couple	Melt composition	Potentials		
		E°' *vs.* Al(III)/Al in $NaCl_{sat}$ melt (V)	E°' *vs.* Al(III)/Al in 63/37 melt (V)	E°' *vs.* Na (V)[c]
$S(IV)/S_2^{2+}$	63/37	2.57[a]	1.95[a]	4.17
S_2^{2+}/S_8^{2+}	63/37	2.52[a]	1.90[a]	4.12
S_8^{2+}/S_8	63/37	2.14[a]	1.52[a]	3.74
S_8/S^{2-}	63/37	1.77[b]	1.15[b]	3.37
S_2^{2+}/S_8	$NaCl_{sat}$	1.92[b]	-	3.52
S_8/S^{2-}	$NaCl_{sat}$	1.15[b]	-	2.75

[a]Values obtained from the plots E_p (differential pulse voltammograms) vs. log C_{S_8} for log C_{S_8} = 0.

[b]Values estimated from cyclic voltammetric peak potentials and differential pulse peak potentials.

[c]Values obtained by adding 1.60V to the values in the third column.

Second step

$$S + NaAlCl_4 + 2Na = NaAlSCl_2 + 2NaCl \quad (4)$$

OCV : 2.75V

Capacity density: 63.4 Ah kg^{-1}

Energy density: 174 Wh kg^{-1}

Total

$$SCl_3AlCl_4 + 1.5Al_2Cl_6 + 6Na = NaAlSCl_2 + 3NaAlCl_4 + 2NaCl \quad (5)$$

Capacity density: 190.2 Ah kg^{-1}

Energy density: 726 Wh kg^{-1}

The energy and capacity densities are based on the weight of the active materials for the process, excluding, however, the mass of β"-alumina, cell casing, electrodes and current collectors.

A fully charged state corresponding to $SCl_3AlCl_4 + 1.5Al_2Cl_6$ is probably not practical due to the expected low conductivity and high vapor pressure. The $SCl_3AlCl_4 + 1.5Al_2Cl_6$ positive mixture composition corresponds to an 80 mol % $AlCl_3$ - 20 mol % hypothetical $SCl_3^+Cl^-$ composition. The conductivity of such a melt should be lower than that of the corresponding 80 mol % $AlCl_3$ - 20 mol % NaCl melt. The effects of exchanging Na^+ with SCl_3^+ upon vapor pressure, immiscibility, and other parameters are not known. It is worth noting that the presence of stoichiometric amounts of sulfur and sodium prevents chlorine evolution on overcharge. The decreasing conductivity of the positive mix and the corresponding increasing cell voltage on charging indicates approach to full charge.

CELL PERFORMANCE

More than 40 laboratory cells were tested during this subcontract. With a few exceptions they have all been constructed of Pyrex. A typical cell is shown in Fig. 1. Either tungsten or Reticulated Vitreous Carbon (RVC) have been used as positive electrodes. Only with RVC can the second step be satisfactorily utilized [29]. The cells were usually equipped with a Al(III)/Al in $AlCl_3$ - $NaCl_{sat}$ reference electrode to monitor the potential of each electrode. Some cells have been "inside-out" cells, i.e., the sodium was placed on the outside of the β"-alumina tube.

The cells have been operated between 165 and 250°C. The lower temperature limit is determined by the liquidus temperature of the positive mixture (see, however, the partial phase diagram in [29]) and the decreasing conductivity of β"-alumina. The upper temperature limit is mainly determined by

the expected high vapor pressure of the positive mixture, especially at very high charge levels.

Because of the relatively small size (OD 10.5-24 mm) of β"-alumina tubes employed in the laboratory cells, there are substantial differences between the inside and outside areas of the β"-alumina tubes. For instance, the outside area is ~40% larger than the inside area for tubes of 10.5 mm OD. This results in a substantial difference in current and power densities depending on whether these properties are expressed with respect to the inside or outside area. The effect is most pronounced for small diameter tubes. As noted later, the main effective cell resistance results from polarization at the melt/β"-alumina interface. Therefore it is best to express power and current densities with respect to the melt side of β"-alumina.

Sulfur can be introduced into the cell either as SCl_3AlCl_4 [57] or as elemental sulfur. No difference in cell performance was found between these two methods of adding sulfur [27] and thus the simpler approach of using elemental sulfur was usually employed.

Figure 2 shows the galvanostatic charge-discharge curves for the first step for one of the earlier cells [27]. The Al:Na ratio in the fully charged positive mixture was 69:31. It was not possible to utilize effectively the second step in this cell, which was equipped with a tungsten positive electrode. Figures 3 and 4 show the temperature and current-density dependence of cell voltage (CCV), utilization, energy density, and energy efficiency. This cell achieved 476 deep charge-discharge cycles.

In recent cells, higher energy densities were achieved by introducing higher concentrations of sulfur and employing RVC electrodes to utilize the second step [29]. Typical charge-discharge curves for a sulfur-rich cell with an RVC electrode are shown in Fig. 5. The S:Al ratio was 0.21 and the Al:Na ratio in the fully charged state was 86.4:13.6 for this cell. It should be noted that the second step is quite reversible in this case (in contrast with Figs. 1 and 2, in [29]).

Achieved energy densities (expressed with respect to active materials for a $6e^-$ process), for several sulfur-rich cells (Al:Na ratio $\geq$ 71.4:28.6 in the charged state) are given in Table 3. It may be seen that an energy density of ~440 Wh kg^{-1} has been achieved for several cells. The very high values for the one-step JH-8-83 cells using tungsten electrodes are due to a combination of a very high charge level (Al:Na ratio ~100:0) and a fairly low cell resistance (~12 Ω cm^2).

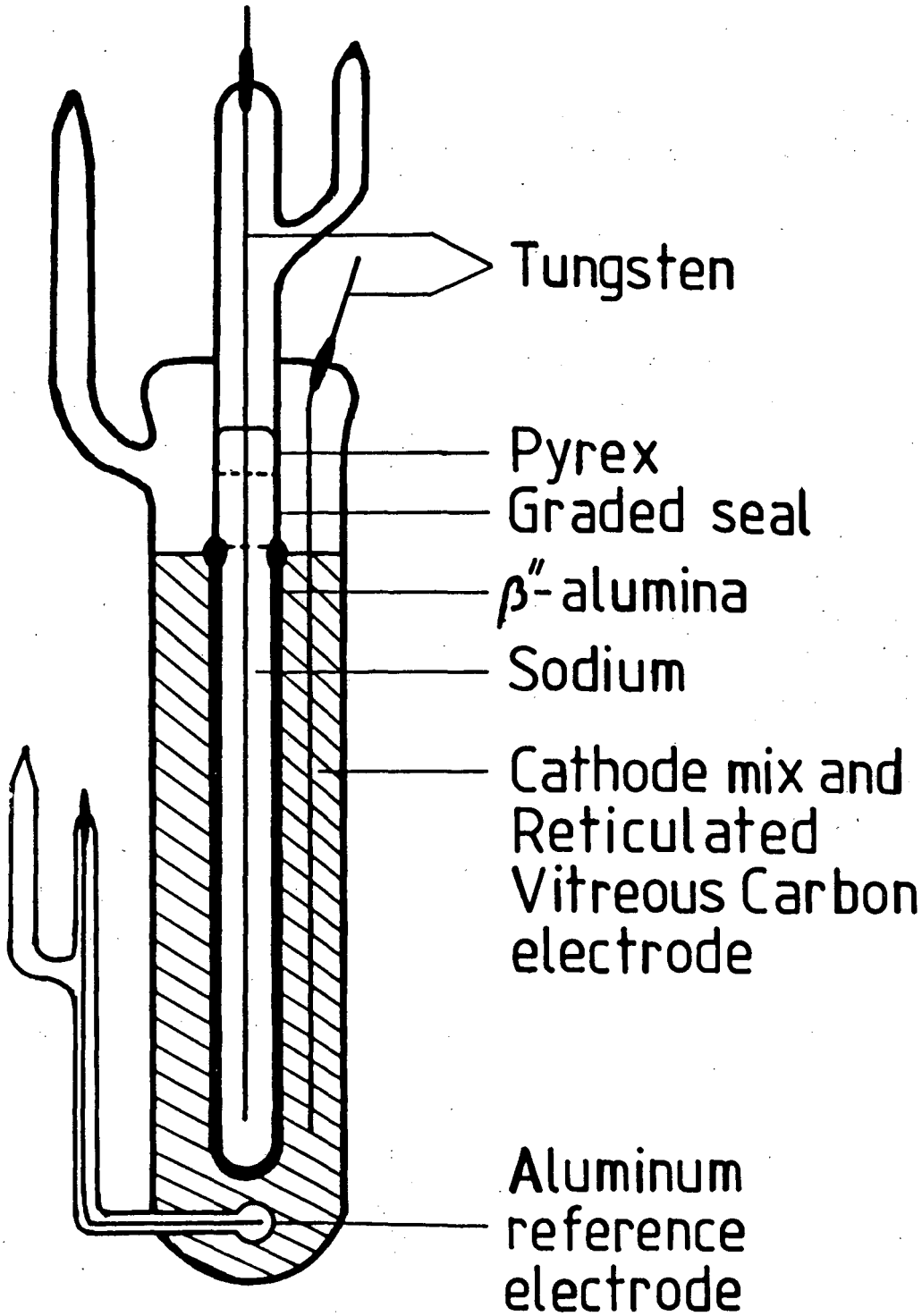

Fig. 1. A Na/β"-alumina/SCl_3^+ chloroaluminate laboratory cell

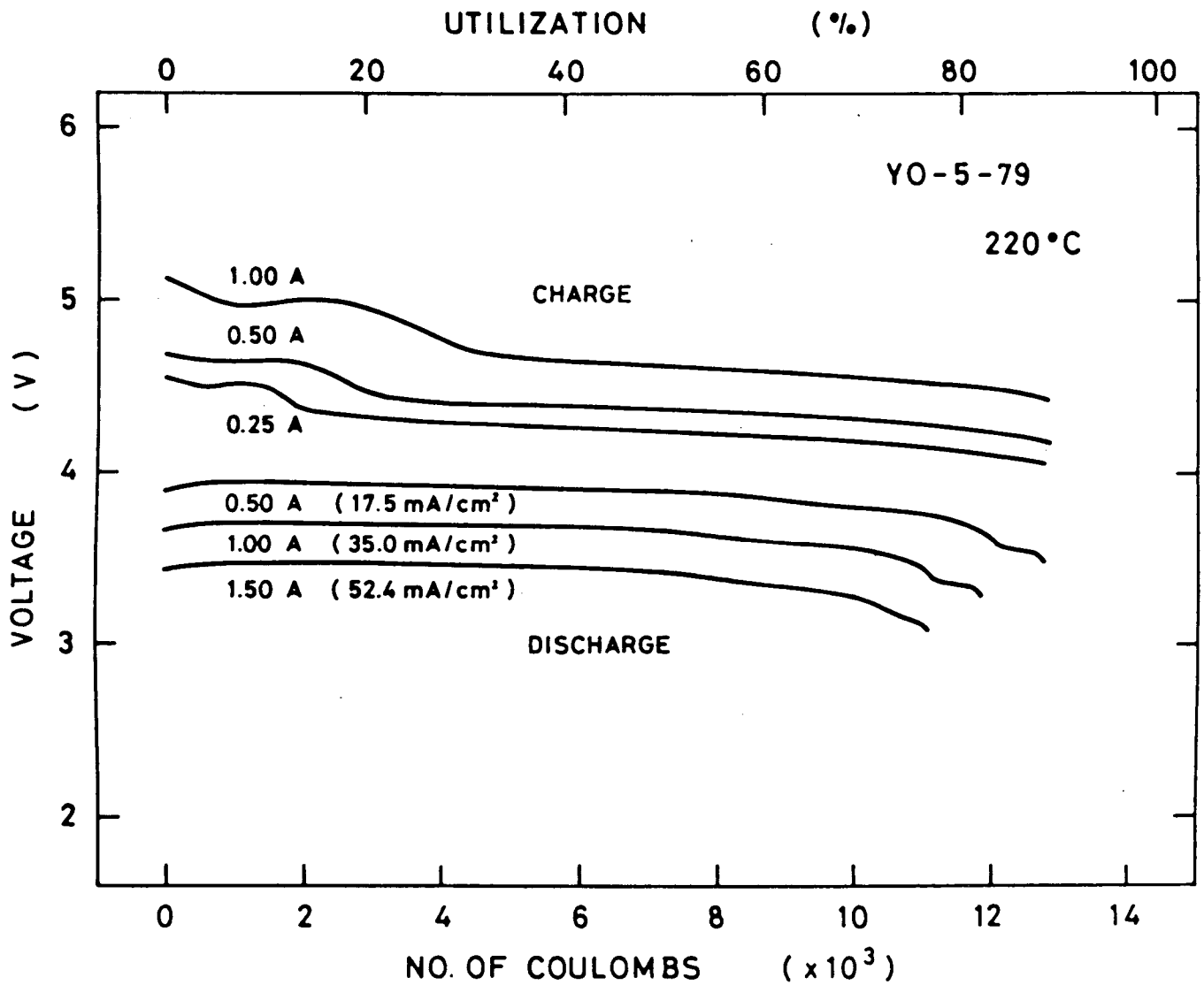

Fig. 2. Galvanostatic charge-discharge curves for cell YO-5-79 at several current densities at 220°C.

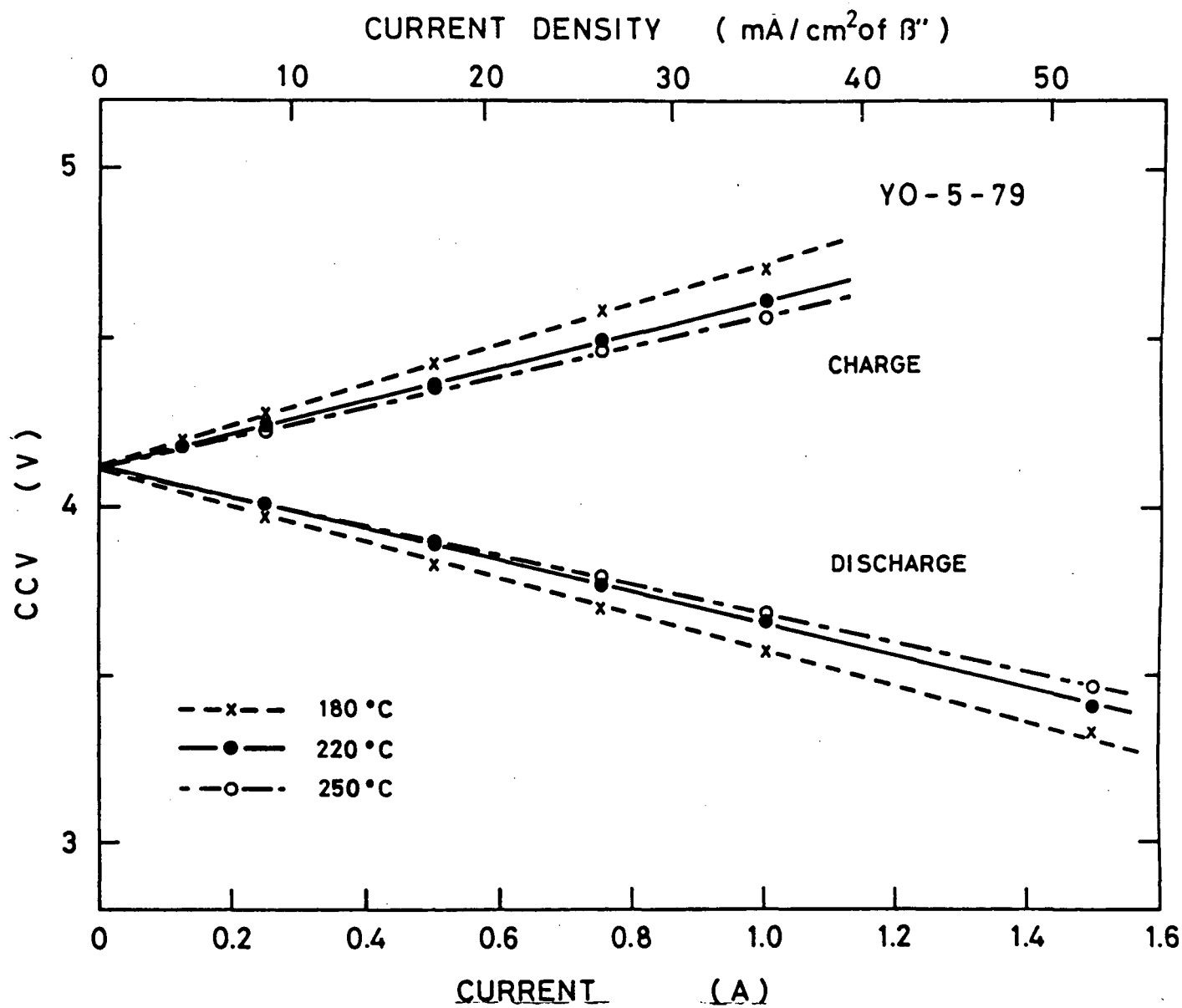

Fig. 3. Current dependence of the CCV measured at the midpoint of discharge at three temperatures for cell YO-5-79.

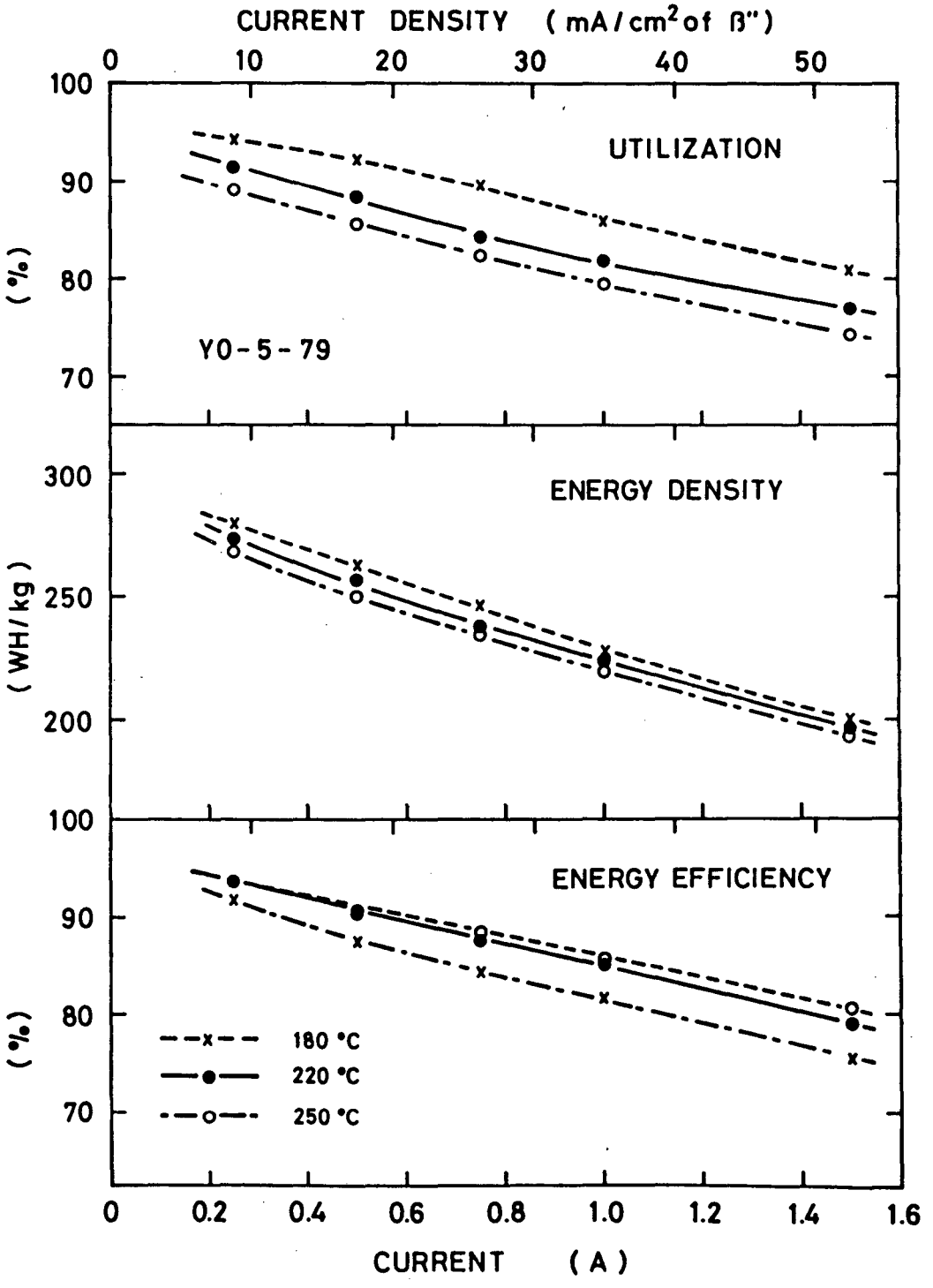

Fig. 4. The dependence of the utilization, the energy efficiency and the energy density on the current density at three temperatures for cell YO-5-79.

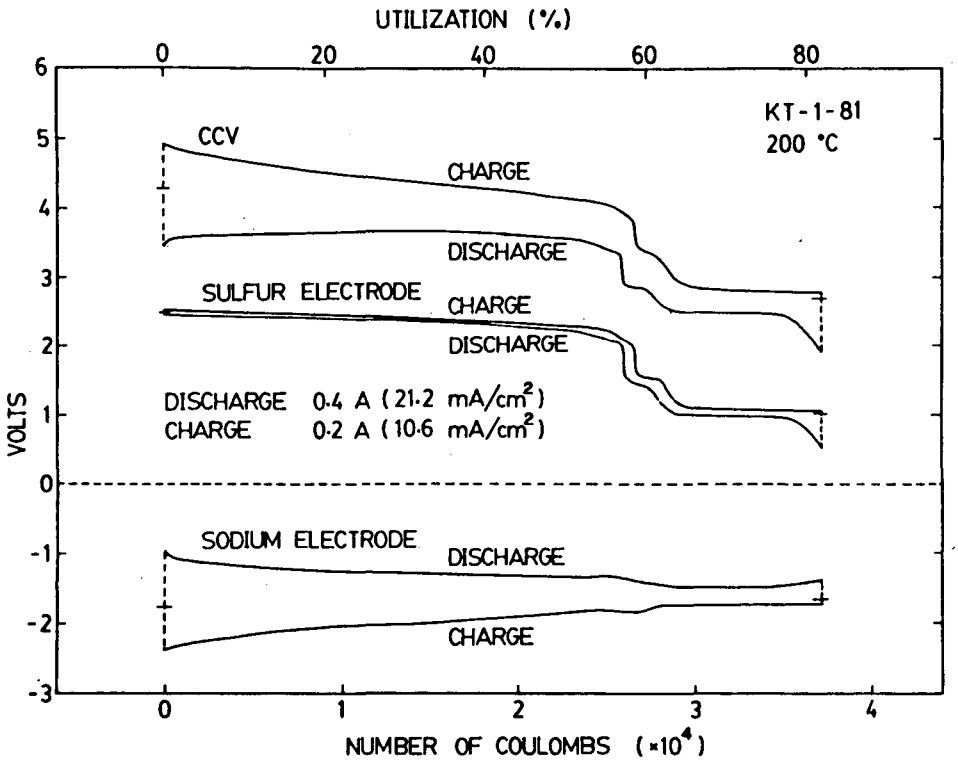

Fig. 5. Galvanostatic charge-discharge curve and potentials of sulfur and sodium electrodes *vs.* Al(III)/Al (in $NaCl_{sat}$ melt) reference electrode at 200°C for cell KT-1-81. Reticulated vitreous carbon used as positive current collector.

TABLE 3

Achieved energy densities for some cells

Cell No.	Electrode material	Current density (mA cm^{-2})		Energy density (Wh kg^{-1} active material)		
		Na side	Melt side	1st step	2nd step	Total
KT-1-81	RVC	21.2	14.7	336	103	439
JH-10-82	RVC	20.0	13.6	284	46	330
JH-1A-83	RVC	24.0	16.7	305	132	437
JH-1B-83	RVC	24.0	16.7	307	135	442
JH-5-83	RVC	17.9	20.0	294		
JH-6-83	RVC	13.9	20.0	340	Inside-out cells. Poor second step performance	
JH-8A-83	W	15.2	20.0	430		
JH-8B-83	W	15.2	20.0	439		
JH-9-83	W/RVC	15.2	20.0	390		

Another important performance parameter is the power density. Achieved power densities are given in Table 4. It may be seen that the Na/β"-alumina/SCl_3^+ cell is capable of power densities greater than 500 mW cm^{-2}. It should be noted that using RVC positive electrodes, both high energy and power densities have been achieved with the same cells. The JH-6-83 cell had a very high mass power density of 1579 W kg^{-1} active material due to the high surface-area/inside-volume ratio of this inside-out cell furnished with a 10.5 mm OD β"-alumina tube. In the inside-out configuration, the active surface area of β"-alumina is proportional to the ID while the active mass is proportional to $(ID)^2$. Thus doubling the ID reduces the mass power density by 50%, but, on the other hand, increases the capacity and discharge time by a factor of 4.

At this stage of development, cycle life testing has not been carried out extensively. However more than 100 deep charge-discharge cycles have been achieved for 5 cells. For one cell, 1370 cycles were achieved (Fig. 6). The cell testing has often been terminated because of leaks in the glass-tungsten seals.

FACTORS AFFECTING THE PERFORMANCE

As stated in the introduction, high energy and power density, high energy efficiency, and long cycle life are desirable performance properties. Factors resulting in the improvement of some of these properties may have a negative effect on the other properties and compromises may be necessary for a given application of any battery system.

Effective cell resistance

The effective cell resistance, R $|OCV-CCV|/i$ [Ω cm^2], is an important parameter that affects the cell performance. This quantity may be readily obtained from the linear plot of cell voltage *vs* current density, i (see Fig. 3). The cell resistance affects the cell performance in several ways.

Fig. 7 shows the charge-discharge curves and the corresponding OCV's and cell resistances for a two step sulfur-rich cell of intermediate performance. It should be noted that the cell resistance varies during the cycle. The changes in cell resistance during the cycle are mainly due to the polarization at the positive mixture/β"-alumina interface [58,59].

For the best performing cells, the cell resistances were as low as 12 Ω cm^2 at 200°C and 20 mA cm^{-2}. However, for all sulfur-rich cells, the cell resistance increased at high charge levels, i.e., when the formal oxidation state of sulfur was above approximately +3 and the Al:Na ratio was above

TABLE 4

Achieved power densities for the first step at 250°C

Cell No.	Electrode	Current density ($mA\ cm^{-2}$)		Power density ($mW\ cm^{-2}$)	
		Na side	Melt side	Na side	Melt side
KT-3-82	W	125	103	286	235
KT-6-82	W	200	138	430	297
JH-10-82	RVC	300	203	627	425
JH-1B-83	RVC	360	250	788	545
JH-6-83[a]	RVC	174	250	352	505
JH-12-83[a]	RVC	175	250	380	543

[a]inside-out cells.

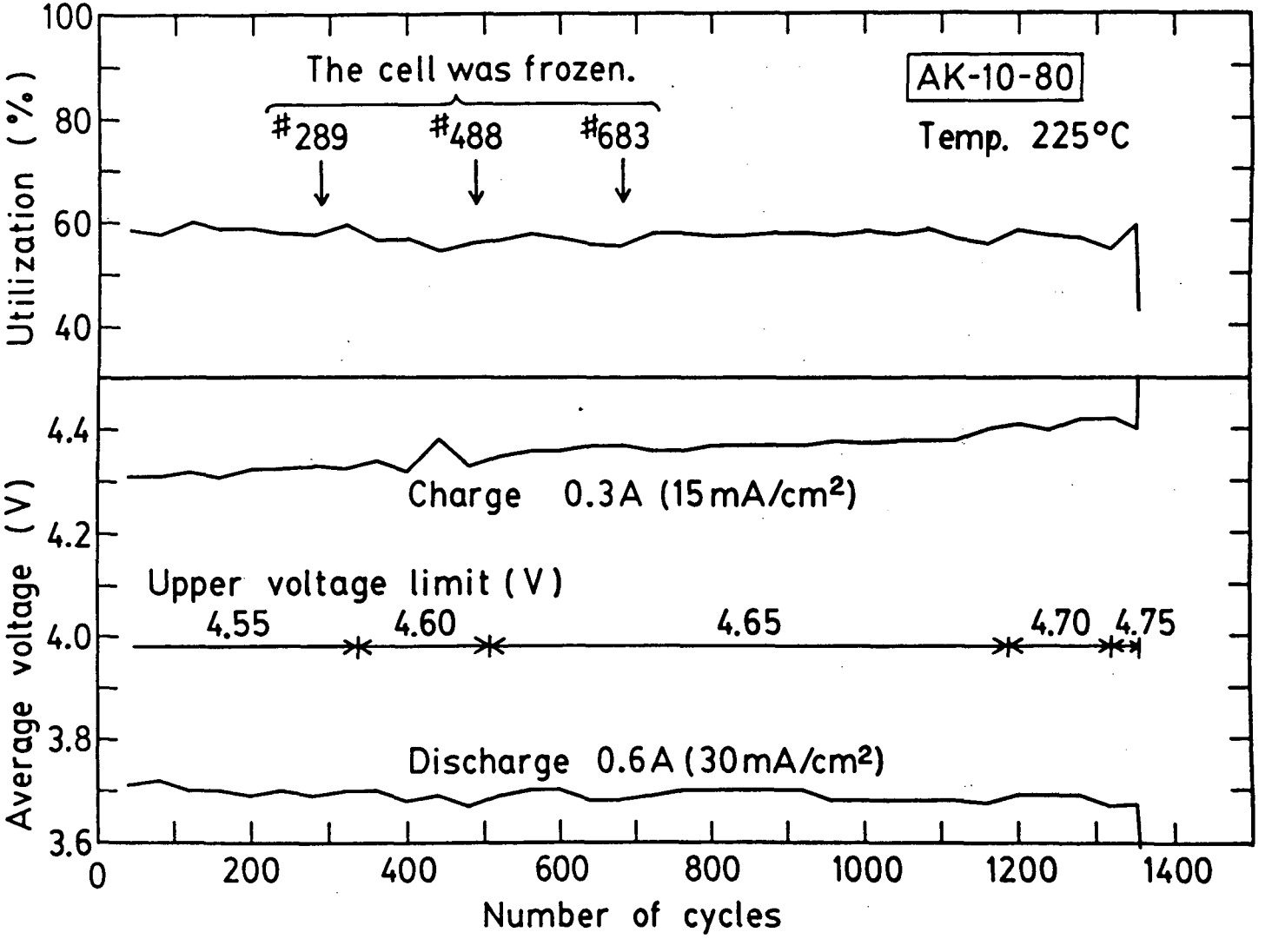

Fig. 6. Performance of cell AK-10-80.

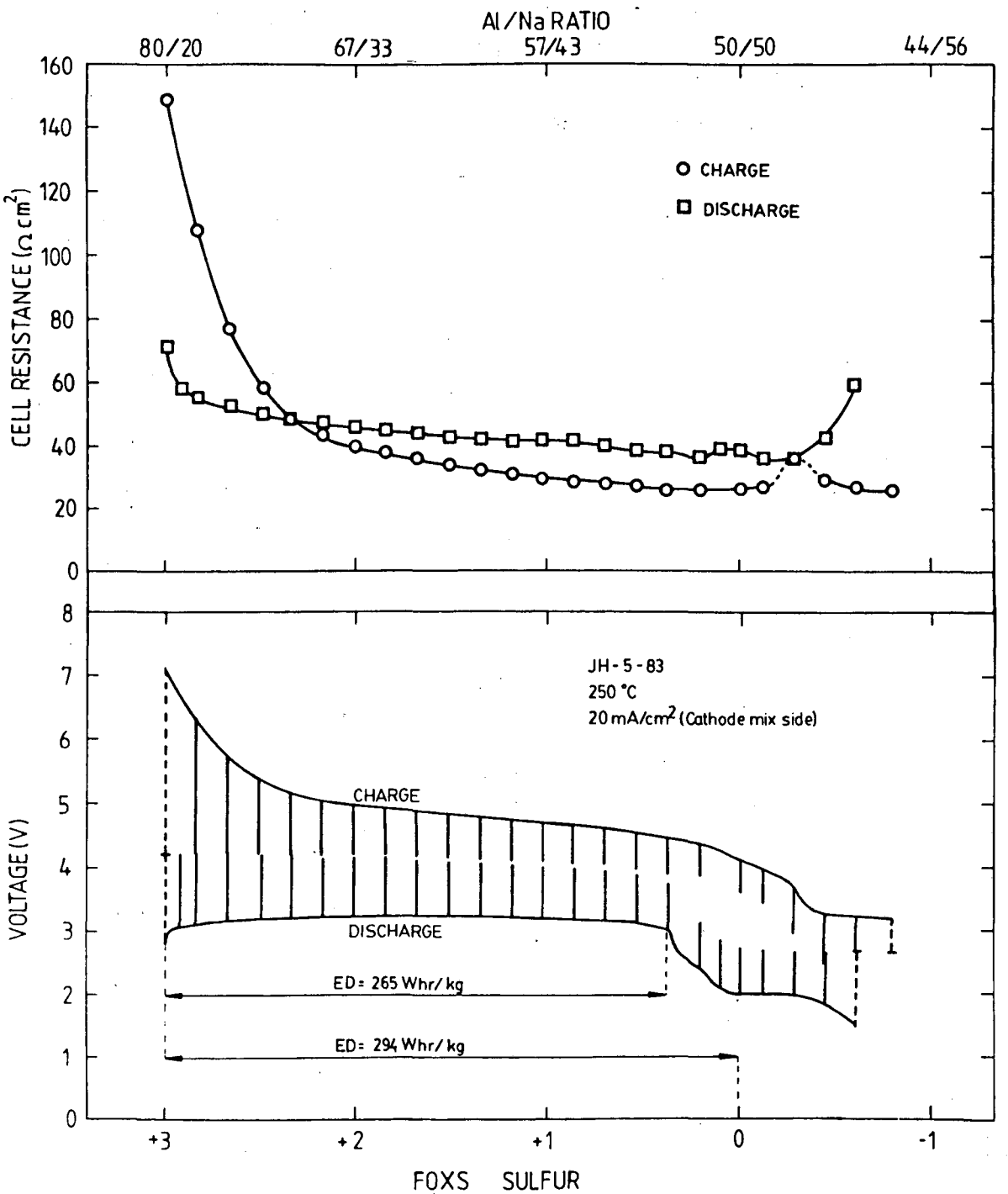

Fig. 7. Variation of effective cell resistance and cell voltage during a charge-discharge cycle of a two-step sulfur-rich cell.

~80:20. The cell resistance did not always decrease to the same level upon discharge; it gradually increased with the number of cycles. The reasons for this behavior are not clear yet. It seems likely that at high charge levels, the very acidic melts may cause a reaction at the β"-alumina surface which is only partly reversible.

At high power densities, cell resistances have been as low as 6 $\Omega\ cm^2$ at 150 - 300 mA cm^{-2} and ~250°C. This effect may be caused by an increase in temperature due to i^2R heating.

The conductivity of β"-alumina increases with temperature [60]. For a typical wall thickness of 1.5 mm, the contribution to cell resistance from the β"-alumina tube at 200°C is ~1 $\Omega\ cm^2$ [60], i.e., much less than the total observed cell resistance.

Typical cell resistance for a Na/β"-alumina/S cell operating at 350°C is ~2 $\Omega\ cm^2$ [8], while ~20 $\Omega\ cm^2$ is typical for the Na/β"-alumina/$SbCl_3$ cell at 220°C [19]. These differences cannot be explained by a temperature change in β"-alumina conductivity alone. It seems that the higher cell resistances for the Na/SCl_3^+ and Na/$SbCl_3$ chloroaluminate cells compared to the Na/S cell may be due to the lower conductivity of the chloroaluminate solvent and a temperature-dependent polarization at the β"-alumina/melt interface [59].

It should be noted that because of the very high voltage of the Na/SCl_3^+ chloroaluminate cell compared to other cells, the effect of cell resistance upon CCV and energy and power densities is somewhat less critical.

Utilization

Another factor limiting the energy density is utilization of theoretical capacity. A full theoretical charge is impractical due to the low conductivity and the high vapor pressure of Al_2Cl_6 of the fully charged positive mixture. At present, however, these limitations are of less concern than the rapid increase in cell resistance when high charge levels are applied. This results in only a few cycles with high energy density performance. Therefore, a compromise between longer cycle life and high energy density may be necessary.

Incomplete utilization observed on discharge at high current densities may be due to non-equilibrium conditions within the cell. The active sulfur species are present in three different phases during the charge-discharge process. The solubility of elemental sulfur in $AlCl_3$-$NaCl_{sat}$ melt is low [46]; therefore it is likely that elemental sulfur will be present as a separate liquid phase which has a very high viscosity around 200 °C [61].

The ionic sulfur species as well as S_2Cl_2 and minor amounts of S_8 are present in the ionic electrolyte. S_2Cl_2 is also present as a yellow gas which disappears on both high charge and deep discharge. Fig. 4 illustrates the effect of temperature and discharge rate upon first-step utilization. It is clear that a better cell design is needed to optimize the utilization.

CONCLUSIONS

The Na/β"-alumina/SCl_3^+ cell has several advantages, such as high cell voltage, high theoretical energy density, good utilization, relatively low operating temperatures, and cheap raw materials. High energy and power densities and long cycle life have been demonstrated for laboratory cells. Problems involving polarization at the β"-alumina/melt interface may be minimized by predischarge and the adjustment of the initial melt composition. The corrosion of the cell should be minimal in an "inside-out" arrangement. Further work is required on the development of a good seal for the positive compartment of a practical cell.

REFERENCES

1 D. A. J. Swinkels, in J. Braunstein, G. Mamantov, and G. P. Smith (Eds.), Advances in Molten Salt Chemistry, Vol. 1, Plenum, New York, 1971, pp. 165-223.

2 E. J. Cairns and R. K. Steunenberg, in C. A. Rouse (Ed.), Progress in High Temperature Physics and Chemistry, Vol. 5, Pergamon, New York, 1973, pp. 63-124.

3 K. V. Kordesch, in J. O' M. Bockris and B. E. Conway (Eds.), Modern Aspects of Electrochemistry, No. 10, Plenum, New York, 1975, pp. 339-443.

4 J. R. Birk and N. P. Yao, in N. P. Yao and J. R. Selman (Eds.), Proceedings of the Symposium on Load Leveling, The Electrochemical Society Softbound Proceedings Series, Princeton, N.J., 1977, pp. 229-250.

5 R. J. Brodd and A. Kozawa, in E. Yeager and A. J. Salkind (Eds.), Techniques of Electrochemistry, Vol. 3, J. Wiley, New York, 1978, pp. 200-290.

6 G. Halpert, in Ref. 5, pp. 291-368.

7 J. T. Kummer and N. Weber, Proc. SAE Congr., 1967, Paper 670179.

8 J. L. Sudworth and A. R. Tilley, in R. P. Tischer (Ed.), The Sulfur Electrode, Academic, New York, 1983, pp. 235-325.

9 E. J. Cairns, G. Mamantov, R. P. Tischer and D. R. Vissers, in M. Blander (Ed.), Proc. Fourth Int. Symp. Molten Salts, The Electrochemical Society, Pennington, N.J., 1984, pp. 284-312.

10 C. A. Levine in Ref. 8, pp. 327-338.

11 G. Mamantov, R. Marassi and J. Q. Chambers, High Energy Cathodes for Fused Salt Batteries, Technical Report ECOM-0060-F, April, 1974.

12 G. Mamantov, R. Marassi and J. Q. Chambers, Ext. Abs. No. 8, Electrochem. Soc., Proc. Vol. 74-2, New York, 1974, p. 24.

13 G. Mamantov, R. Marassi and J. Q. Chambers, U.S. Pat. 3,966,491 (1976).

14 G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer and E. J. Frazer, Ext. Abs. No. 89, Electrochem. Soc., Proc. Vol. 77-2, Atlanta, Georgia, 1977, p. 243.

15 G. Mamantov and R. Marassi, U.S. Pat. 4,063,005 (1977).

16 G. Mamantov, R. Marassi, J. P. Wiaux, S. E. Springer and E. J. Frazer, in Ref. 4, pp. 379-383.

17 J. J. Werth, U.S. Pat. 3,847,667 (1974); U.S. Pat. 3,877,984 (1975).

18 J. J. Werth, EPRI Report EM-230, December 1975.

19 A. M. Chreitzberg, EPRI Report EM-751, April 1978.

20 J. Giner and G. L. Holleck, NASA Report CR 1541, March 1970.

21 G. D. Brabson, A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, Ext. Abs. No. 26, Electrochem. Soc., Proc. Vol. 73-1, Chicago, Illinois, 1973, p. 61.

22 L. Redey, I. Porubszky and I. Molner, 9th International Power Sources Symposium, Brighton, England, September 17-19, 1974.

23 J. Greenberg, U.S. Pat. 3,573,986 (1971); 3,635,765 (1972).

24 G. D. Brabson, J. K. Erbacher, L. A. King, and D. W. Seegmiller, FJSRL Technical Report 76-0002, January 1976.

25 R. O. Miller, NASA Tech. Memo. TMS-3245 (1975).

26 W. P. Sholette, I. S. Klein and J. Werth, in Ref. 4, pp. 306-317.

27 G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux and E. J. Frazer, J. Electrochem. Soc., 127 (1980) 2319-2325.

28 G. Mamantov, R. Marassi, Y. Ogata, M. Matsunaga, and J. P. Wiaux, in Proc. 15th Intersoc. Energy Conv. Eng. Conf., American Institute of Aeronautics and Astronautics, Seattle, Wash., 1980, p. 569.

29 G. Mamantov, K. Tanemoto and Y. Ogata, J. Electrochem. Soc., 130 (1983) 1528-1531.

30 J. J. Auborn and S. M. Granstaff Jr., J. Energy, 6 (1982) 86-90.

31 P. V. Clark, Fused Salt Mixtures-Specific Conductivity Tables, Report SC-R-69-1386, National Bureau of Standards, U.S. Department of Commerce, October 1969, p. 58.

32 R. C. Howie and D. W. MacMillan, J. Inorg. Nucl. Chem., 33 (1971) 3681-3686.

33 G. Mamantov and R. A. Osteryoung, in G. Mamantov (Ed.), Characterization of Solutes in Non-Aqueous Solvents, Plenum, New York, 1978, pp. 223-249.

34 R. C. Howie and D. W. MacMillan, J. Appl. Electrochem., 2 (1972) 217-222.

35 B. Gilbert, D. L. Brotherton, and G. Mamantov, J. Electrochem. Soc., 121 (1974) 773-776.

36 A. A. Fannin, Jr., L. A. King, D. W. Seegmiller and H. A. Øye, J. Chem. Eng. Data, 27 (1982) 114-119.

37 R. A. Carpio, A. A. Fannin, Jr., F. C. Kibler, Jr., L. A. King and H. A. Øye, *ibid.*, 28 (1983) 34-36.

38 G. Torsi and G. Mamantov, Inorg. Chem., 11 (1972) 1439.

39 A. A. Fannin, Jr., L. A. King and D. W. Seegmiller, J. Electrochem. Soc., 119 (1972) 801-807.

40 L. G. Boxall, H. L. Jones and R. A. Osteryoung, *ibid.*, 120 (1973) 223-231.

41 H. A. Øye and D. M. Gruen, Inorg. Chem., 3 (1964) 836-841.

42 E. W. Dewing, J. Am. Chem. Soc., 77 (1955) 2639-2641.

43 G. Torsi, G. Mamantov and G. M. Begun, Inorg. Nucl. Chem. Lett., 6 (1970) 553-560.

44 E. Rytter, H. A. Øye, S. J. Cyvin, B. N. Cyvin and P. Klaeboe, J. Inorg. Nucl. Chem., 35 (1973) 1185-1198.

45 J. Hvistendahl, P. Klaeboe, E. Rytter and H. A. Øye, Inorg. Chem., 23 (1984) 706-715.

46 R. Huglen, F. W. Poulsen, G. Mamantov, R. Marassi and G. M. Begun, Inorg. Nucl. Chem. Lett., 14 (1978) 167-172.

47 R. Marassi, G. Mamantov and J. Q. Chambers, *ibid.*, 11 (1975) 245-252.

48 R. Marassi, G. Mamantov and J. Q. Chambers, J. Electrochem. Soc., 123 (1976) 1128-1132.

49 R. Marassi, G. Mamantov, M. Matsunaga, S. E. Springer and J. P. Wiaux, *ibid.*, 126 (1979) 231-237.

50 K. A. Paulsen and R. A. Osteryoung, J. Am. Chem. Soc., 98 (1976) 6866-6872.

51 K. Tanemoto, R. Marassi, C. B. Mamantov, Y. Ogata, M. Matsunaga, J. P. Wiaux and G. Mamantov, J. Electrochem. Soc., 129 (1982) 2237-2242.

52 K. Tanemoto, A. Katagiri and G. Mamantov, *ibid.*, 130 (1983) 890-892.

53 R. Marassi and G. Mamantov, in Ref. 8, pp. 191-217.

54 R. W. Berg, S. von Winbush and N. J. Bjerrum, Inorg. Chem., 19 (1980) 2688-2698.

55 V. E. Norvell, K. Tanemoto, G. Mamantov and L. Klatt, J. Electrochem. Soc., 128 (1981) 1254-1261.

56 N. J. Bjerrum in Ref. 33, pp. 251-271.

57 G. Mamantov, R. Marassi, F. W. Poulsen, S. E. Springer, J. P. Wiaux, R. Huglen and N. R. Smyrl, J. Inorg. Nucl. Chem., 41 (1979) 260-261.

58 A. Katagiri and G. Mamantov, Yoyuen, 25 (1982) 201-217.

59 A. Katagiri, J. Hvistendahl, K. Shimakage and G. Mamantov, J. Electrochem. Soc., 133 (1986), in press.

60 R. W. Minck, Ford Motor Co., private communication.

61 R. F. Bacon and R. Fanelli, J. Am. Chem. Soc., 65 (1943) 639-648.

Publications that have resulted from this Subcontract

1. G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux and E. J. Frazer, "The Use of Tetravalent Sulfur in Molten Chloroaluminate Secondary Batteries," J. Electrochem. Soc., 127, 2319 (1980).

2. G. Mamantov, R. Marassi, Y. Ogata, M. Matsunaga and J. P. Wiaux, "A New Rechargeable High Voltage Low Temperature Molten Salt Cell," Proceedings of 15th Intersociety Energy Conversion Engineering Conference, Vol. 1, 809107, American Institute of Aeronautics and Astronautics, Seattle, Wash., August 18-22, 1980.

3. G. Mamantov, "Molten Salt Electrolytes in Secondary Batteries," in Materials for Advanced Batteries, D. W. Murphy, J. Broadhead and B. C. H. Steele, eds., Plenum Press, 1980, pp. 111-122.

4. V. E. Norvell, K. Tanemoto, G. Mamantov and L. Klatt, "UV-Visible and Electron Spin Resonance Spectroelectrochemical Studies of Sulfur Oxidation in $AlCl_3$-NaCl (63/37 mole %) Melt," J. Electrochem. Soc., 128, 1254 (1981).

5. G. Mamantov, V. E. Norvell, L. Klatt, K. Tanemoto, R. Marassi, Y. Ogata, M. Matsunaga, J. P. Wiaux and C. B. Mamantov, "Spectroelectrochemical and Other Studies of Sulfur and Its Halides in Chloroaluminate Melts: Application to a New Rechargeable High Voltage Low Temperature Cell," in Proceedings of The Third International Symposium on Molten Salts, G. Mamantov, M. Blander, and G. P. Smith, eds., pp. 158-166, The Electrochem. Soc. Inc., Pennington, N.J., 1981.

6. Y. Ogata and G. Mamantov, "Sodium/Sulfur(IV) Molten Cell and the Chemistry," Yoyuen, 1981, 24, 7-31.

7. K. Tanemoto, R. Marassi, C. B. Mamantov, Y. Ogata, M. Matsunaga, J. P. Wiaux, and G. Mamantov, "Oxidation of Sulfur in Chloroaluminate Melts of Intermediate pCl," J. Electrochem. Soc., 129, 2237 (1982).

8. A. Katagiri and G. Mamantov, "Polarization Phenomena at the β"-Alumina Separator in the Molten Aluminum Chloride-Sodium Chloride Secondary Battery," Yoyuen, 1982, 25, 201-17.

9. K. Tanemoto, A. Katagiri, and G. Mamantov, "In Situ Raman Spectroscopic Studies of the Rechargeable Low Temperature Molten Salt Cell Na/β"-alumina/S(IV) in $AlCl_3$-NaCl," J. Electrochem. Soc., 130, 890 (1983).

10. G. Mamantov, K. Tanemoto and Y. Ogata, "Two-Plateau Rechargeable Sodium/Sulfur(IV) Molten Chloroaluminate Cell," J. Electrochem. Soc., 130, 1528 (1983).

11. R. Marassi and G. Mamantov, "Electrochemistry of Sulfur in Strongly Acidic Media," in The Sulfur Electrode, R. P. Tischer, ed., Academic Press, 1983, pp. 191-217.

12. E. J. Cairns, G. Mamantov, R. P. Tischer, and D. R. Vissers, "The Chemistry and Status of Rechargeable Molten Salt Batteries," in Proceedings of the Fourth International Symposium on Molten Salts, The Electrochemical Society, Inc., Pennington, NJ, 1984, pp. 284-312.

13. G. Mamantov and J. Hvistendahl, "Rechargeable High Voltage Low Temperature Molten Salt Cell Na/β"-Alumina/SCl_3^+ in $AlCl_3$-NaCl," J. Electroanal. Chem., 168, 451 (1984).

14. R. Marassi, T. M. Laher, D. S. Trimble and G. Mamantov, "Electrochemical and Spectroscopic Studies of Sulfur in Aluminum Chloride-N-(n-Butyl)Pyridinium Chloride," J. Electrochem. Soc., 132, 1639 (1985).

15. G. Mamantov, "Sodium-Tetravalent Sulfur Molten Chloroaluminate Cell" U.S. Patent 4,508,795, April 2, 1985.

16. A. Katagiri, J. Hvistendahl, K. Shimakage, and G. Mamantov, "A Study of Polarization at the β"-Alumina Interfaces in the Rechargeable Sodium/Sulfur(IV) Molten Chloroaluminate Cell", J. Electrochem. Soc. (in press).

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