SODIUM-SELENIUM(IV) MOLTEN CHLOROALUMINATE CELLS WITH POROUS NICKEL AND VITREOUS CARBON CURRENT COLLECTORS

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ABSTRACT

The charge-discharge behaviors of sodium/β”-alumina/tetravalent selenium in a basic chloroaluminate melt have been investigated with porous vitreous carbon and nickel as the positive current collector. The discharging capacity of the cells with the vitreous carbon current collector was limited by the deposition of solid sodium chloride, which often caused the breakage of reticulated vitreous carbon. The redox reaction of Se(IV)/Se(0) could occur on the nickel current collector covered with nickel chloride film. Thick nickel chloride film, however, made the polarization higher at discharging, whereas the voltage at charging unchanged.

INTRODUCTION

A rechargeable cell, sodium/β”-alumina/tetravalent selenium in chloroaluminate melt, is one of the most attractive batteries for the load leveling and electric vehicle applications, since this cell has high voltage such as 3.8V at 150-250°C, and high energy density higher than 400Wh/kg (1-3). The composition of AlCl3-NaCl melt changes with charging and discharging in this cell, which indicates the cell operates within wider range of melt composition to obtain high energy density (2,4). When the melt is basic, it is necessary to use porous materials as the positive current collector, since sodium chloride deposits and covers the electrode at discharging (2,3). The degradation of the percent utilization and energy efficiency was, however, usually observed after several decades cycles in the cells with the carbon felt current collector (2,3). In this study porous nickel and vitreous carbon have been utilized for the positive current collector to improve the cell performance, especially life time.

EXPERIMENTAL

Commercial reagents of AlCl3 and NaCl were purified as follows. AlCl3 was sublimed through a glass filter after reaction with aluminum metal (m5N) for one day. NaCl was dried under vacuum for a few days at 400°C. Commercial grade of selenium(m6N) was used without pretreatment. Salt mixtures were prepared with purified chemicals in a glove
box filled with high-purity nitrogen. Sodium metal was purified by double filtration.

A schematic representation of an experimental cell is shown in Fig.1. The cell consisted of a Pyrex glass compartment filled with positive mixture, which was separated from sodium electrode by mean of a $\beta^\infty$-alumina tube (NGK Spark Plug Co.). Open pore "foam" nickel (Sumitomo Denko Co.) or reticulated vitreous carbon (Fluoro-carbon Ltd.) was used as a positive current collector, which was bound with tungsten spiral lead. An experimental cell was kept under vacuum at 400-450°C for a few weeks before the loading of sodium and positive mixture in order to remove moisture adsorbed on the $\beta^\infty$-alumina tube.

RESULTS AND DISCUSSION

Typical charge-discharge curves of a cell, No.RS-807, are shown in Fig.2, which utilized reticulated vitreous carbon (RVC) as a positive current collector, of which specific surface area was $6700m^2/m^3$. In this cell the molar ratios of AlCl$_3$/NaCl in the melt were prepared to be 50/50 and 30/70 at fully charging and discharging, respectively. The voltage during charging and discharging in this cell was quite stable, comparing to those with a carbon felt current collector (2,3). The RVC electrode has uniform open pore structure, and better electronic contact to tungsten lead because of its hardness. Therefore, the current distribution might be uniform on the current collector, which would make the charging and discharging voltages stable. In the cells with a RVC current collector the second voltage plateau was usually observed at the end of the discharging. This second plateau corresponds to the reduction of lower oxidized selenium (5,6), whereas the first long plateau is the discharging of tetravalent selenium. The oxidation number of this low oxidized species might be less than unity, since the coulombs passed for the second plateau was much less than those for the first step.

Three kinds of RVC were utilized in this study to investigate the effects of the surface area on discharging capacity. Typical charge-discharge curves observed in the cells, No.RS-901 and RS-808, are shown in Fig.3 and Fig.4. The specific surface areas of RVC were 4000 and $1100m^2/m^3$, respectively. In these cells the specifications were the same of the cell No.RS-807, such as the volume of RVC current collectors, the weight of melt and the melt compositions at fully charging and discharging. These results suggested the discharging capacity depended on the surface area of the RVC current collector. It has become apparent that the discharging capacities in these three cells were almost identical with same current densities for the unit surface area of the RVC current collector as shown in Fig.5. These results suggest the discharging limit in these cells relates to the coverage of the RVC with solid sodium chloride, like that in the carbon felt current collector (2). The values of polarization in these three cells were quite different as shown in Figs.2, 3 and 4, which
mainly depended on the resistivity of the RVC current collector.

Although Na/Se(IV) cells with the RVC current collector showed high energy density and high energy efficiency at early cycles, the abrupt change of performance was often observed especially for the cells with high capacity as shown in Fig.6. It has become apparent that the RVC electrodes were partially or wholly fractured after the degradation of performances. The observation of segments by SEM indicated the mechanical stress caused the breakage of vitreous carbon. In high capacity cells larger amounts of sodium chloride deposited during the discharging in a basic chloroaluminate melt. This deposit occupied the open pores in the RVC, and the compressive stress by the deposit might cause the cracking. These troubles suggest the elastic materials are preferred for the positive current collector of a sodium/tetravalent selenium cell which utilizes the basic chloroaluminate melts.

It is well known that nickel chloride is insoluble in basic chloroaluminate melts, which is utilized as the positive of a Na/NiCl$_2$ battery (7,8). It will be possible to use nickel for the positive current collector of a sodium/tetravalent selenium cell, since no higher oxidation state than divalent is stable in AlCl$_3$-NaCl melts. Fig.7 shows the first charge-discharge curve of an experimental cell with a porous nickel current collector of which specific surface area is 2500m$^2$/m$^3$. The cell voltage at discharging was clearly divided into two region. One corresponded to the reduction of tetravalent selenium above 3.5V, the other to the reduction of nickel chloride at 2.5V. This result suggests that redox reaction between Se(IV) and Se(0) can reversibly occur on the nickel electrode covered with nickel chloride film.

The discharging capacity above 3.5V, however, decreased with charge-discharge cycles as shown in Fig.8. In 73rd cycle new plateau at 3.2-3.3V appeared, although the charging curve changed little. This second plateau was different from those observed in the cells with the RVC current collector, since the cell voltage was not the same and the discharging period of this plateau increased with the number of cycles. To explain the cause of this low voltage at discharging, selenium was loaded into the cell which had operated more than one hundred cycles as a Na/NiCl$_2$ cell. The typical charge-discharge curves of this cell No.NS-905 are shown in Fig.9. In this type of experimental cells the discharging period of the high voltage region, first plateau, was quite short even at the early cycles. The charge-discharge curves observed in this cell have changed little at cycles more than one hundred. The discharging capacity at the first plateau decreased with an increase of current density and with lowering the temperature, whereas the voltage drop was less than the cells with carbon current collectors.

The ohmic drop and polarization at discharging were measured with current pulses to elucidate the change of the discharging curve. Fig.10 depicts typical results measured with 1A pulses, of which on-
time and off-time were 10ms. The ohmic drop measured from the abrupt voltage change at switching off was constant during the discharging. The polarization increased with the change of cell voltage, which was determined as the difference of the cell voltage at the ends of on-time and off-time. The dashed line in the discharge curve indicates the cell voltage compensated by the ohmic drop, which could not explain the polarization at the second plateau. The values of polarization measured with longer pulses were quite different from those shown in Fig.10. The variation of cell voltage with 1min pulses are shown in Fig.11. The voltage drastically changed except the early stage of discharging. The cell voltage observed at the ends of on-time and off-time are depicted in Fig.12. These results suggest the open circuit voltage measured at the end of off-time gradually changed, which corresponds to the reduction of tetravalent selenium for both plateaus. The difference between the voltages at on-time and off-time in Fig.12 is the polarization at discharging, which has never been observed in the cells with carbon current collectors. The reason of this large polarization would depend on the nickel chloride film which covered the nickel current collector. The diffusion of tetravalent selenium ions in this solid film must be the rate determining step at the discharging of the cell, which induced the large polarization.

The variations of turnaround energy efficiency and percent utilization of tetravalent selenium with the number of cycles are shown in Fig.13. In spite of the larger polarization at discharging, the performance of Na/Se(IV) cells changed little with the number of cycles in the cells prepared with the same manner as No.NS-905. These results suggest the porous nickel will have longer life as the current collector of Na/Se(IV) cells, although the polarization due to the nickel chloride film should be reduced.

SUMMARY

Charge-discharge behaviors of sodium/tetravalent selenium cells with reticulated vitreous carbon or nickel as the current collector have been described. The discharging capacity of the cells with vitreous carbon depends on the surface area of the current collector, and is limited by the deposition of sodium chloride on the current collector in basic AlCl₃-NaCl melts. The vitreous carbon has, however, often broken by deposited sodium chloride especially in the cells with high capacity. The redox reaction of Se(IV)/Se(0) can occur on nickel electrode covered with nickel chloride film. Thick nickel chloride film induces higher polarization at discharging, since the diffusion of tetravalent selenium species in the film is the rate determining step. The performance of the cells with a porous nickel current collector changes little with the number of cycles, when the nickel chloride film becomes relatively thick.
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Fig. 1 Schematic Diagram of an Experimental Na/Se(IV) Cell
(A) Tungsten Wire (B) Sodium Inlet
(C) Positive Mixture Inlet (D) Pyrex Glass (E) Sealing Glass
(F) Sodium (G) B"Alumina Tube (H) Reticulated Nickel or RVC
(I) Tungsten Spiral (J) Molten Salt MIxture
Fig. 2: Charge-Discharge Curves of a Cell No. RS-807 with a RVC Current Collector at 200°C

Fig. 3: Charge-Discharge Curves of a Cell No. RS-901 with a RVC Current Collector at 200°C

Fig. 4: Charge-Discharge Curves of a Cell No. RS-808 with a RVC Current Collector at 200°C

Fig. 5: Relations between Surface Area of RVC and Discharging Capacity of Na/Se(IV) Cells
Fig. 6 Effect of the Number of Cycles on Discharging Capacity of a Na/Se(IV) cell with a RVC Current Collector at 200°C

Fig. 7 First Charge and Discharge Curves of a Cell No. NS-904 with a Nickel Current Collector

Fig. 8 Change of Charge-Discharge Curves of a Cell No. NS-902 with Cycles

Fig. 9 Charge-Discharge Curves of a Na/Se(IV) Cell with a Nickel Current Collector, Which Has Operated as a Na/NiCl₂ Cell for More Than 100cycles
Fig. 10 Voltage Transient at Discharging Observed with Current Pulses

Fig. 11 Polarization and Ohmic Drop of a Cell with a Nickel Current Collector at Discharging Measured with Current Pulses

Fig. 12 Cell Voltages at the Ends of On-Time and Off-Time with 1A Pulses at Various Discharging States

Fig. 13 Effect of the Number of Cycles on Performance of a Cell with a Nickel Current Collector