PERFORMANCE OF A SODIUM-SELENIUM(IV) MOLTEN CHLOROALUMINATE CELL FOR AN ELECTRIC VEHICLE

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ABSTRACT

Performance of a molten salt cell, sodium/beta"-alumina/selenium(IV) in a basic chloroaluminate melt, has been studied to develop the battery for electric vehicles. Results on the response to the load, the cell resistance and the current distribution in the positive current collector are presented.

INTRODUCTION

The development of advanced batteries for electric vehicles has recently a lot of attention. These batteries require several severe properties such as high power density, high energy density, quick response, long cycle life, maintenance free, capability at wide temperature range, rapid charging and low cost. A rechargeable cell, sodium/beta"-alumina/tetravalent selenium in a basic chloroaluminate melt, is one of the most attractive batteries, since this shows high emf, 3.8V at 423-523K (1) and high energy density as high as 415Wh/kg based on the weight of active components (2). Although this cell possesses high potential, a lot of properties should be improved to apply for the electric vehicles. Recent results on the response to the load, cell resistance, and current distribution in the positive current collector are presented in this paper.

EXPERIMENTAL

Three kinds of cell design have been prepared to investigate the behavior of a single cell. Typical arrangements of experimental cells are shown in Figures 1 and 2. These cells consist of a Pyrex glass compartment filled with the positive melt which is separated from the liquid sodium electrode by means of a beta"-alumina tube.
The sizes of beta"-alumina tubes obtained from NGK Spark Plug or Mitsubishi Heavy Industry are 16mm or 15mm OD, 13mm ID, and 100mm length. A graphite felt (GF-20 from Nippon Carbon) is used in these cells as the positive current collector. Tungsten wire and sheet are used to get electric contact between the graphite felt and terminal. These three kinds of cells have different design of the positive electrode. Type-A shown in Figure 1 has two tungsten wire to eliminate the resistance of tungsten wire, of which one is used for current flow and the other is for voltage measurement. Type-B is similar to type-A, in which only one tungsten lead is used for current flow and voltage measurement. The other cell, type-C, shown in Figure 2 has four tungsten microelectrodes set in the graphite felt. The position of these microelectrodes is also shown in this figure. The inner one (I) is between the beta"-alumina and the graphite felt, and the outer one (O) is between the graphite felt and the tungsten sheet. The other two (MI and MO) are between graphite felt sheets. In this type cell the lower graphite felt was used as quasi-reference electrode. The chemicals, AlCl₃, NaCl and Na, were used after purified with usual methods. SeCl₄ (4N) was used as received. Each experimental cell was prepared as fully charged state.

RESULTS AND DISCUSSION

The load curves of electric vehicles show the abrupt change of power, and the pulsed output power continues from several seconds to a few minutes. This load pattern requires the batteries to respond quickly and to supply constant power at least for a few minutes. To study the response to the quick change of the load, a type-B cell (No. CS-1002, theoretical capacity 20.1Ah) was discharged with high current pulses. Figure 3 shows typical transient observed in this cell with 5A (0.1 A/cm²-beta") pulses at the early stage of discharging at 433K. Quick response to the load was surely observed, and voltage change within 10s was negligible. This stable voltage could continued at least for several minutes except for the end of discharging. These results suggest that the charge transfer in both electrodes and ionic conduction in the solid electrolyte and molten salts must be fast enough for the response to the abrupt change of the load. The average voltage at discharging calculated from closed and open circuit voltage was little influenced by the value of pulsed current density, if the average discharging current density was the same. This suggests that the polarization mainly consists of the resistance of the components such as melts and beta"-alumina.
The resistance of this cell, No.CS-1002, at the early stage of the discharging was 15 ohm·cm²-beta" at 433K and 7 ohm·cm²-beta" at 473K. This resistance at 473K is almost the same as those for previous cells with graphite felt current collector. This value is, however, larger than that estimated from the specific resistance of the cell components, such as beta"-alumina and molten salts, which might be at most 3 ohm·cm²-beta" at 473K. To study this discrepancy between the experimental and estimated values, type-A cell (No.HC-1109, theoretical capacity 30.1Ah) was prepared, in which we can eliminate the resistance of tungsten lead as mentioned above. In our experimental cell made with Pyrex glass, long tungsten wire should be used to connect the current collector to the terminal. The resistance of long tungsten wire at 473K cannot be negligible. Figure 4 shows the typical charge and discharge curves observed for the cell No.HC-1109, where the solid and broken lines indicate the voltages measured with voltage terminals and current flow terminals, respectively. The difference measured with two methods, about 2 ohm·cm², corresponds to the resistance of tungsten wires, which changes with the height of sodium and melt in the cell. The minimum cell resistance without tungsten wires was 3.6 ohm·cm²-beta" at the discharging at 473K, and similar values was observed at the charging as shown in Figure 4. The wall thickness of the beta"-alumina tube used in this cell was 1.5mm, which indicates the resistance of the ceramic tube is 1.7 ohm·cm²-beta" at 473K. Since the thickness of the graphite felt with positive mix was about 9mm, the rest of the cell resistance except the beta"-alumina is mainly due to the melt resistance. Therefore, we can conclude the polarization of the Na/Se(IV) battery must be ohmic. In the cell No.HC-1109 three layers of graphite felt was used, the another cell (type-A) with two layers of graphite felt was recently prepared. This cell showed lower resistance such as 3.0 ohm·cm²-beta" at 498K. On these grounds we have come to the conclusion that thin-wall beta"-alumina as 1.0 mm and two layers of graphite felt should be adopted for the practical cells of which resistance is lower than 3.0 ohm·cm²-beta".

The effects of current density on the charge and discharge curves are depicted in Figure 5. The cell voltage even with 5A (0.1 A/cm²-beta") was flat at the discharging, which suggests high power density can be obtained from the Na/Se(IV) cell. At the charging, however, the voltage with high current densities often fluctuated as shown in Figure 5. The evolution gaseous compounds may cause these voltage fluctuation.

It is well known for Na/S battery that the electrochemical reaction rate is high at the solid electrolyte
surface and container surface, when one kind of graphite is used for the current collector. It is likely that similar phenomenon occurs in the sodium/molten chloride cells which use porous materials as the current collector. In order to estimate the reaction rate during charging and discharging, the potential of four microelectrodes in a type-C cell was measured. Figure 6 shows the open circuit voltage just after the break of the current at the charging. The inner electrode (I) usually showed higher potential than those of other electrodes. The outer electrode (O) showed higher value at the first half of the charging. On the other hand, these electrodes showed lower potential during the discharging. The potential of these microelectrodes measured at the closed circuit also exhibited the similar tendency. The higher potential at the charging and lower value at the discharging of the inner and outer electrodes suggest that the electrochemical reaction rates near these two microelectrodes are high near the beta"-alumina surface and near the container surface. This ununiform current distribution in the graphite felt would cause the serious problem especially at the discharging. In sodium/molten chloroaluminate cells which utilize the basic melts, solid NaCl deposits on the current collector during the discharging. When the reaction rate is high near the solid electrolyte, deposited NaCl will fill up the pore of the graphite felt. This indicates the volume occupied by the melts becomes narrow, and the cell resistance increases with discharging. It is assumed that this ununiform current distribution may be one of the reason of an increase in the cell resistance with the number of cycles. We now plan to adopt the dual mat design for the current collector in order to suppress high rate near the beta"-alumina surface.

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REFERENCES

1. M.Matsunaga and K.Hosokawa, Yoyuen (Molten Salt), 30, 83 (1987)
2. M.Matsunaga and K.Hosokawa, Proc. Joint Intern. Symp. Molten Salts, pp.669 (1987)
Figure 1 Schematic Representation of a Type-A Cell

Figure 2 Schematic Representation of a Type-C Cell

Figure 3 Change of Cell Voltage of a Type-B Cell (No.CS-1002) with Pulsed Current at the Early Stage of Discharging

Figure 4 Charge and Discharge Curves for a Type-A Cell (No.HC-1109)
Figure 5 Charge-Discharge Curves with Several Current Densities at a Type-A Cell (No.HC-1109)

Figure 6 Open Circuit Potential of Four Microelectrodes during Charging