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Na-Zn liquid metal battery

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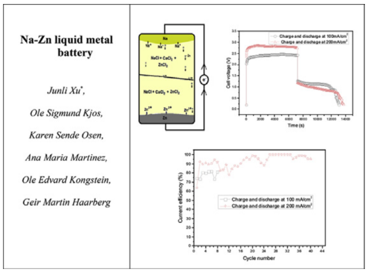
HIGHLIGHTS

- Na-Zn liquid metal battery which can be assembled in discharge state is developed.
- The discharge flat voltage is 1.1 V with about 90% cycle efficiency at 100 mA/cm^2.
- The cost of the battery electrode materials is very low (4.3 $ per KWh).

GRAPHICAL ABSTRACT



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ABSTRACT

A new kind of membrane free liquid metal battery was developed. The battery employs liquid sodium and zinc as electrodes both in liquid state, and NaCl-$CaCl_2$ molten salts as electrolyte. The discharge flat voltage is in the range of about 1.4 V–1.8 V, and the cycle efficiency achieved is about 90% at low discharge current densities (below 40 mA cm^{-2}). Moreover, this battery can also be charged and discharged at high current density with good performance. The discharge flat voltage is above 1.1 V when it is discharged at 100 mA cm^{-2}, while it is about 0.8 V with 100% cycle efficiency when it is discharged at 200 mA cm^{-2}. Compared to other reported liquid metal battery, this battery has lower cost, which suggests broad application prospect in energy storage systems for power grid.

1. Introduction

Rechargeable molten salt batteries are promising technologies for energy storage to balance out renewable energy technologies such as solar and wind, and it has received much attention since 1960s because molten salts have been expected to have low-cost and long-life. Today, the sodium sulphur battery (NAS) has been commercially available for grid application, with some 200 installations world-wide [1]. However, this kind of battery requires a sodium ion selective membrane (β-Al_2O_3) which adds a great deal of expense to the cell. Moreover, β-Al_2O_3 is brittle, and the crack of the β-Al_2O_3 membrane will result in a vigorous reaction occurring between the electrode materials, releasing large amounts of heat which may result in a severe explosion [2]. On September 21st, 2011, the sodium-sulfur (NAS) batteries installed at Mitsubishi Materials Corp's Tsukuba Plant of Japan, caught on a severe fire disaster because of the crack of the β-Al_2O_3 membrane [3].

Another commercial molten salt battery is the so-called ZEBRA battery which is based on sodium-nickel chloride chemistry, is also at a commercial level. ZEBRA cells use excess transition metal and

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transition metal chlorides as the cathode, Na metal as the anode, and solid β-Al_2O_3 and liquid $NaAlCl_4$ as electrolyte. Compared to the NAS battery, the ZEBRA battery has the advantages of less corrosive nature of the cathode materials and safe cell failure mode [1,4,5]. However, the use of solid β-Al_2O_3 still inhibits the use of high current density.

In 2009, Professor Sadoway's research group at MIT developed a new kind of molten salt battery which was called "liquid metal battery" [6]. This battery technology utilizes three liquid layers as electroactive components. It consists of a self-assembling stratified system of an antimony-magnesium liquid metal alloy at the bottom, a chloride molten salt mixture as electrolyte in the middle and liquid magnesium metal at the top. These three layers float on top of one another naturally due to their density differences and immiscibility [7]. This three liquid layer structure makes it possible to apply high current densities and slight polarization during charge and discharge because of quick diffusion kinetics in the liquid. It was reported that this cell showed a 97% coulombic efficiency and a voltage efficiency of 71% at 50 mA cm^{-2}. However, the cell voltage is quite low, i.e. about 0.4 V at 50 mA cm^{-2}, and about 0.2 V at 200 mA cm^{-2}, which is impractical for commercial applications [8]. Recently, Li//Sb—Pb and Ca-Mg//Bi liquid metal batteries have also been developed by Professor Sadoway's research group [9,10]. In these cases, more than 98% coulombic efficiencies were reported. The discharge flat potential increases compared to the Sb-Mg liquid metal battery. It is about 0.69 V at 275 mA cm^{-2} for Li//Sb—Pb cell, while it is about 0.8 V at 100 mA/cm^2 for Ca-Mg//Bi cell. These potentials seem to be somehow low, since a cell voltage above 1 V is commonly required for the practical application.

In this paper, a new kind of liquid metal battery is studied, which employs liquid sodium as anode at the top of the cell, liquid zinc as cathode at the bottom of the cell, and NaCl-$CaCl_2$-$ZnCl_2$ molten salts as electrolyte between the zinc cathode and the sodium anode. Fig. 1(a) shows a simple sketch of the battery. By utilizing the immiscible nature of liquid Zn and Na at the operating temperature, the ion selective membrane can be substituted by a diaphragm. The diaphragm will ensure a physical separation between the two cell compartments, and will be considerably less resistive than a membrane giving lower voltage losses, and higher currents densities. The function of calcium chloride is to lower the operating temperature and Na solubility. During charging, zinc could, to a certain extent, be codeposited at the Na electrode. In order to maintain a low concentration of $ZnCl_2$ in the electrolyte, it is of outmost importance to decrease the deposition competition of Zn with Na, thus gaining a high coulombic efficiency. However, even though Zn is produced at the Na electrode during charging, it will sink to the bottom and then be recovered in the Zn pool. This due to Na-Zn immiscibility at temperature above 556 °C (see Fig. 1(b)) and different densities. Likewise, any Zn formed by spontaneous reaction between Na and $ZnCl_2$ is expected to sink to the bottom.

The aim of this paper is to study the performance of the Zn-Na battery by determining cycle efficiencies and discharge flat voltage at different current densities.

2. Experimental

The Na||Zn battery cell was assembled in an argon filled glove box at a fully discharged state. The cell comprised a graphite crucible, sintered alumina insulating liner, and Mo current leads. Magnesia stabilized zirconia with 0.3 cm thickness and porosity equal to 30 ppi (30 pores per linear inch) was used as diaphragm materials. The electrolyte was NaCl: $CaCl_2$ (50:50 mol %), with a melting point of ca. 500 °C. At the working temperature of 560 °C, the electrolyte density is about 1.92 g cm^{-3}.

NaCl was dried at 120 °C for several days, and $CaCl_2$ was dried at 250 °C for 24 h before being transferred to the glove box. Zinc was placed at the bottom of the cell, and the corresponding amounts of salts were filled on the top of it. The cell was introduced in a quartz container and placed inside a vertical tube furnace attached to a glove box filled with argon, and it was heated up to 560 °C. The electrical connection to the Zn electrode was made through the graphite container, whereas that to the Na electrode was made solely through a Mo wire. Mo wire was inserted into the melting salts for about 2 cm, and the bottom of Mo wire to the Zn anode surface is about 5 cm. Fig. 2 shows the schematics of an assembled Na||Zn cell at a fully discharged state.

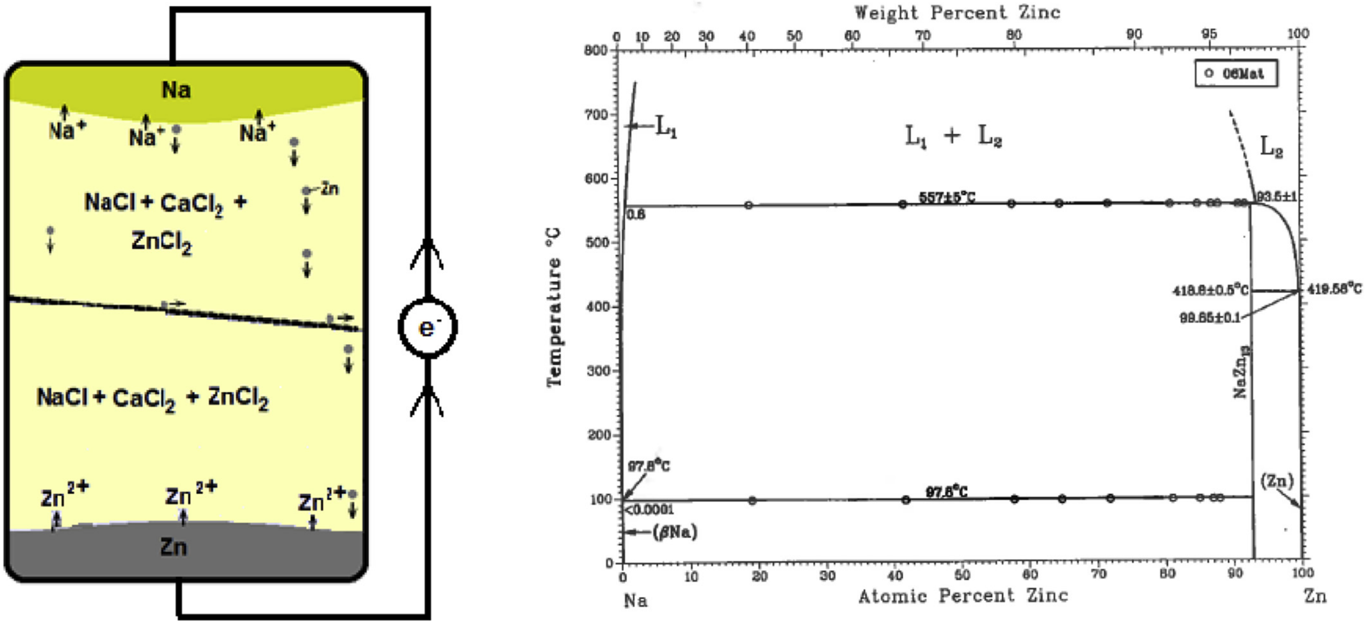

Fig. 1. Left: Drawing of battery operation (charging); Right: Na-Zn phase diagram [11].