V.3 A High Temperature (400 to 650°C) Secondary Storage Battery Based on Liquid Sodium and Potassium Anodes

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Objectives

- Develop an energy storage device based on an alkali metal ion conducting beta" alumina solid electrolyte (BASE) (high temperature battery).
- Investigate materials for suitable electrochemical couples.
- Fabricate both tubular and planar BASE possessing high strength, high conductivity, and high moisture-resistance.
- Design and construct planar batteries.
- Evaluate the charge/discharge and freeze/thaw capability of batteries at elevated temperatures.

Accomplishments

- Both Na-BASE and K-BASE discs and tubes have been successfully fabricated using MSRI's patented vapor phase process. Ionic conductivity measurements showed that Na-BASE had higher conductivity than K-BASE. At 500°C, Na-BASE conductivity is 0.36 S/cm. The activation energy is 22.58 kJ/mol.
- $CuCl_2$, $FeCl_2$, $ZnCl_2$, and AgCl were identified as suitable materials for electrochemical couples used for Na-metal salt batteries from thermochemical data. Further open circuit voltage (OCV) measurements matched these deduced from the thermochemical data.
- Tubular cells with $CuCl_2$ as the cathode and Na as the anode were constructed. It was discovered that $CuCl_2$ was somewhat corrosive and dissolved iron, an element of the cathode compartment.
- $FeCl_2$ and $ZnCl_2$ were acquired as the potential cathodes for Na-metal salt batteries for delivering high specific energies.
- Planar cells were designed. Na-$FeCl_2$ and Na-$ZnCl_2$ batteries were constructed and tested between 400 and 650°C. Charge/discharge characteristics showed these as the most promising types of batteries. Charge/discharge cycles were performed as many as 27 times, and the current was as high as 500 mA. No failure was detected after 50 hours tests.
- Freeze-thaw cycling tests were carried out and the survival was remarkably good for planar BASE disks fabricated by MSRI's patented vapor phase process.

Introduction

The solid oxide fuel cell (SOFC) is an energy conversion device, which efficiently converts chemical energy of hydrocarbon fuels directly into electricity at a high efficiency without the need for moving parts, except those for auxiliary pumps and blowers. As an electricity generator, its most efficient, practical and realistic use is in combination with an efficient energy storage device for electric-power generation and distribution application, particularly for utility load leveling and peak shaving. However, the associated energy storage devices of the integrated energy conversion-storage system must be capable of a very high roundtrip efficiency. Suitable batteries and reversible SOFC (or so-called solid oxide electrolysis cell – SOEC) could be the candidates serving as the energy storage devices in different energy forms, which are electrical energy and chemical energy carried by hydrogen, respectively. Due to the inherent limitations, such as hydrogen gas storage and parasitical losses, the SOEC doesn't have high enough roundtrip efficiency. In addition, the high cost of hydrogen storage and infrastructure also confines the reversible SOFC application. Instead, load leveling batteries (such as the sodium-sulfur battery, a.k.a. NAS), which have been under development widely outside of U.S., are capable of achieving a high roundtrip efficiency. An advanced high-temperature energy storage battery, based on an alkali metal ion conducting BASE and a non-corrosive metal salt, is proposed in this project to demonstrate a roundtrip efficiency in excess of 90%. The similar applications of BASE is NAS batteries, with as large as 8 MW power rating (64 MWh capacity), have been developed and installed by NGK Insulators, Ltd. and

Tokyo Electric Power Company (TEPCO) in Japan, and have demonstrated life in excess of 7 years with projected cost less than $140/kWh for annual installed capacity of >3,200 MWh. The NAS battery is by all indications close to commercialization.

An alkali metal-metal salt battery to be developed in the project comprises an alkali metal ion conducting BASE sandwiched between an alkali metal as the anode and a metal salt as the cathode. At elevated temperatures, during discharge, the alkali metal is oxidized at the anode forming metal ions, which migrate through the alkali metal ion conducting BASE and react with the metal salt at the cathode. Consequently, electrical power is generated by the battery. During charge, the above processes are reversed, and electrical power is stored in the battery. In addition to the inherent advantage of its high roundtrip efficiency, the high-temperature battery to be developed can be thermally integrated with intermediate temperature SOFC (IT-SOFC) stacks, forming an economical, compact, lightweight hybrid system with very high system efficiency.

Approach

This project is directed toward the development of a planar, high temperature (400~650°C) secondary storage battery based on alkali metal – metal salt battery technology. Both Na-BASE and K-BASE were fabricated using the methods of cold isostatic-pressing and tape-casting of α-Al_2O_3 + 8YSZ for tubes and planar discs, respectively, followed by MSRI's patented vapor phase process. Packing powders for conversion of K-BASE and Na-BASE were prepared in-house and could be reused each time by replenishing the K_2O and $NaAlO_2$ contents. Material properties of BASE were qualified by measuring the density and the ionic conductivity at various temperatures. Microstructures of the discs were characterized using a scanning electron microscopy (SEM) to determine the morphology of BASE before/after conversion.

Electrochemical couples comprised of an alkali metal (Na and K) and a transition metal salt were investigated through literature search on thermochemical data. Open circuit voltages and specific energies were calculated based on the thermochemical data over temperatures from 350°C to 700°C to determine prospective couples suitable for electrodes of the proposed battery. Dissolution tests of iron, an element of electrode compartments, were carried out for metal salts to exclude any corrosive salt from the candidates. Phase diagrams of the metal salt and the alkali metal salt were also studied to assist the choice of the cathode, thus ensuring excellent mass transport in the liquid cathode and allowing for a greater depth of discharge. OCVs of the interested electrochemical couples were measured in BASE tubes at elevated temperatures. Planar cells were designed, and correlative cell components, including electrode compartments, seals and wicks, were identified and acquired. Planar cells in two sizes, either with 2.5 cm^2 or 10 cm^2 active areas, were constructed in the partially discharged state. The planar battery characteristic tests of the charge/discharge cycles and thermal cycles were conducted in an oxygen-free and moisture-free glove box over a range of temperatures between 400 and 650°C. After tests, batteries were dissembled and inspected for any potential damage to BASE, electrode compartments, and seals. 1 kWh battery designs and BASE optimization designs were proposed for further development, and preliminary investigations were also carried out.

Results

Important results and accomplishments were summarized in what follows.

1. From the standpoint of high specific energy and open circuit voltage, the prospective cathodes were $FeCl_2$, $ZnCl_2$ and AgCl, listed in the order of preference from high to low. In addition, they were not corrosive and the corresponding eutectic temperatures were lower than the working temperatures ensuring a greater depth of discharge. OCV measurements of the Na/$FeCl_2$ and Na/AgCl electrochemical couples between 350 and 700°C, as presented in Figure 1, show excellent agreements with these deduced from the thermochemical data.
2. A tape-casting method was developed to fabricate planar cells. Green tapes were laser-cut into desired shapes, either in a circular or in a square shape. Tubes were fabricated in a specially designed mold with a steel mandrel followed by a cold-isostatic

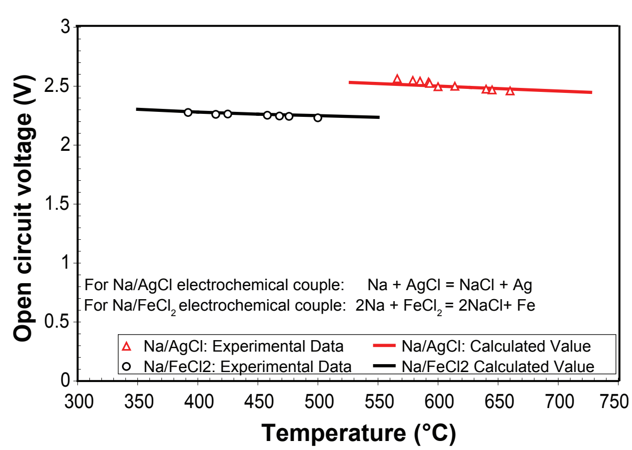

FIGURE 1. OCV measurements for Na/AgCl and Na/$FeCl_2$ electrochemical couples. Symbols are experimental data. The lines are calculations based on thermodynamic data. Note excellent agreement between measurements and calculations.

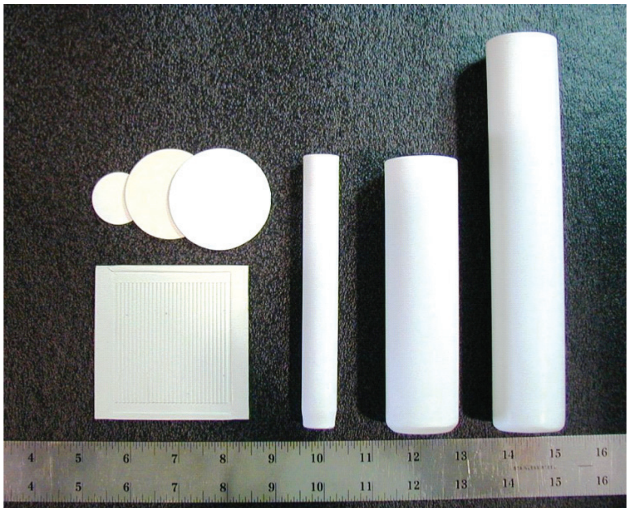

FIGURE 2. A Photograph of Several BASE Tubes and Discs Made by MSRI's Patented Vapor Phase Process

press at 30,000 psi. Figure 2 is a photograph of the BASE tubes and disks made by the MSRI patented vapor phase process. BASE tubes were made as long as 20 cm, and disks were as large as 6 cm in diameter, or plates 9 cm in length. Typical BASE tubes fabricated by the conventional process for use in NAS batteries were well in excess of 1 to 1.5 mm in thickness leading to a high ohmic area specific resistance (ASR). In contrast, the BASE made by MSRI's novel, patented process exhibits excellent properties, unmatched by BASE made using conventional processes.

3. Ionic conductivities of Na-BASE and K-BASE were measured using AC impedance method at elevated temperatures. The experimental results showed that Na-BASE had higher ionic conductivity than K-BASE, consistent with the literature. At 500°C, Na-BASE conductivity is 0.36 S/cm, which is more than 20 times higher than 8YSZ electrolyte used for SOFC at 800°C. The activation energy of Na-BASE is 22.58 kJ/mol. Microstructures of the discs after thermally etching were characterized using the SEM to determine the morphology of BASE before/after converting into Na-BASE and K-BASE. Unique textured microstructures, which were developed during the conversion process and played an important role in the attainment of good conductivity of the BASE, were observed.
4. Planar batteries were designed. Stainless steel cups were acquired as the electrode compartments. Cathodes, in a partially discharged state at a eutectic composition of $FeCl_2$+NaCl or $ZnCl_2$+NaCl, were fabricated by the impregnation method. In order to provide reactants/products to/from the electrochemical reaction sites, and to make good contacts with the BASE and the metal compartments, steel wool and copper wool were used as the wick for the cathode and anode, respectively. Copper gaskets were used as the seals for both the anode and cathode. The final assembly of the batteries was carried out in the glove box. Compression was applied by low thermal expansion bolts over two end plates. Figure 3 is a photograph of a battery assembly.
5. Planar single-cell batteries were tested over the temperature range between 400°C and 650°C. Figure 4 shows the Na-$FeCl_2$ battery voltage characteristics obtained at 500°C and 104 mA constant current. The discharge voltage limit was set to 2.157 V, 96% of OCV (2.254 V). The charge voltage limit was set to 2.302V, 102% of OCV. The roundtrip efficiency was about 94%. No obvious degradation was observed after 6 cycles over 7 hours of testing. Na-$FeCl_2$ batteries were also

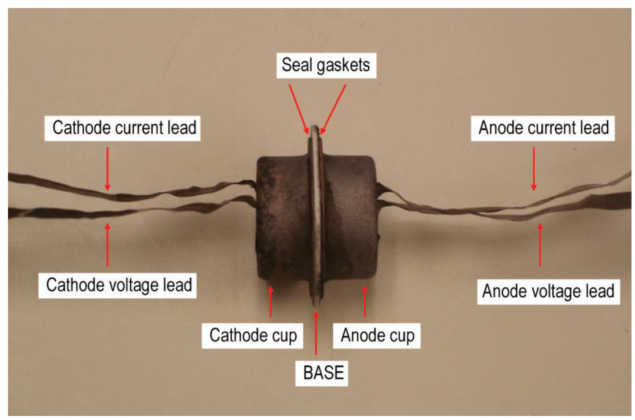

FIGURE 3. A Photograph of a Na-$FeCl_2$ Battery Assembly

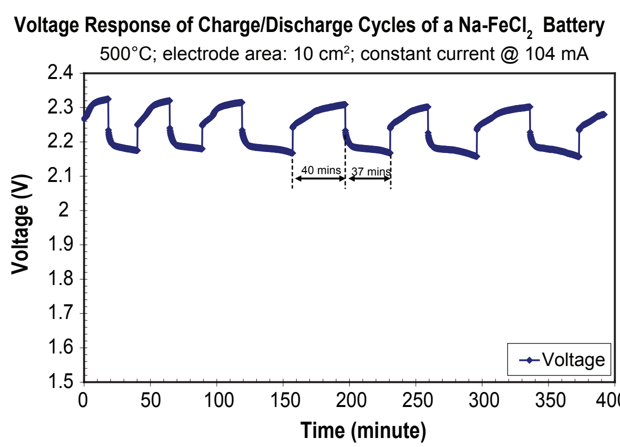

FIGURE 4. Voltage characteristics of a Na-$FeCl_2$ single-cell battery tested at 500°C and 104 mA constant current. The cell was charged/discharged with a round trip efficiency of ~94%.

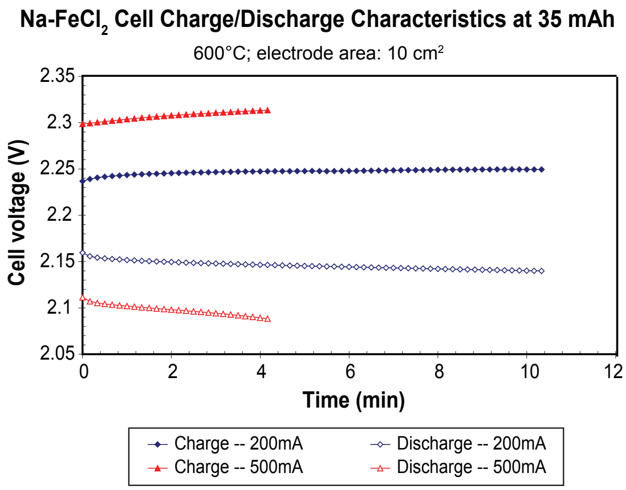

FIGURE 5. Voltage characteristics of a Na-$FeCl_2$ single-cell battery tested at 600°C and 35 mAh capacity. The charge/discharge currents were 200 mA and 500 mA.

tested at 600°C, and the typical charge/discharge characteristics at a fixed 35 mAh capacity are shown in Figure 5 at 200 mA and 500 mA constant currents. The roundtrip efficiency was estimated to be 95%.

Conclusions and Future Directions

- Both Na-BASE and K-BASE discs and tubes were made using MSRI's patented vapor phase process. The BASE is free of moisture and CO_2 attack. Impendence measurements showed that Na-BASE had much higher ionic conductivity than K-BASE. Therefore, Na-BASE electrolyte favors batteries for delivering high specific energy.
- Due to its very high OCV and high specific energy, $CuCl_2$ is a promising cathode and investigation of $CuCl_2$ cathode is proposed to be performed in Phase II by using suitable coating technologies.
- Na/$FeCl_2$ and Na/$ZnCl_2$ electrochemical couples were identified as the prospective electrodes from the standpoint of high specific energy, high OCV, and none dissolution of electrode compartments. OCV measurements of the identified electrochemical couples matched these deduced from the thermochemical data.
- Planar cells were designed, constructed, and tested successfully between 400 and 650°C. The roundtrip efficient was demonstrated as high as 95%.
- Charge/discharge cycles were conducted as many as 27 times without failures after 50 hours of testing on the Na-$ZnCl_2$ battery at 425°C, which was performed by the subcontractor under a separate DOE-funded project.
- Freeze-thaw survival was remarkably good after numerous thermal cycling tests for planar BASE disks fabricated by MSRI's patented vapor phase process.
- Preliminary studies of BASE optimization and the 1 kWh battery design were applicable to high specific energy batteries.

FY 2007 Publications/Presentations

1. G. Tao, N. Weber, A. Virkar and P. Parthasarathy, "A secondary battery based on liquid anode for energy storage", 16^{th} International Conference on Solid State Ionics, July 1-6, 2007, Shanghai, China.