Final Report
On the Project Entitled

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

Sponsored by
U.S. Department of Energy, Contract No. DE-FG02-06ER86280

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Effective Date of Contract: June 28, 2006
Contract Expiration Date: March 27, 2007, Reporting Period: 06/28/2006 – 03/27/2007

June 8, 2007

EXECUTIVE SUMMARY

This STTR Phase I research program was on the development of high temperature (400 to 650°C), secondary batteries with roundtrip efficiency > 90% for integration with a 3 to 10 kW solid oxide fuel cell (SOFC) system. In fulfillment of this objective, advanced planar high temperature rechargeable batteries, comprised of an alkali metal ion conducting, highly refractory, beta" alumina solid electrolyte (BASE) sandwiched between liquid sodium (or potassium) anode and liquid metal salt cathode, were developed at MSRI. The batteries have been successfully demonstrated at a working temperature as high as 600°C. To our knowledge, so far no work has been reported in the literature on planar rechargeable batteries based on BASE, and results obtained in Phase I for the very first time demonstrated the viability of planar batteries, though relatively low temperature tubular-based sodium-sulfur batteries and ZEBRA batteries have been actively developed by very limited non U.S. companies. The results of this Phase I work have fulfilled all the goals and stated objectives, and the achievements showed much promise for further, substantial improvements in battery design and performance.

The important results of Phase I are briefly described in what follows:

1. 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 ionic conductivity than K-BASE, consistence 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 is 22.58 kJ/mol.
2. CuCl_2 , FeCl_2 , ZnCl_2 , and AgCl were identified as suitable salts for Na/metal salt or K/metal salt electrochemical couples based on thermochemical data. Further open circuit voltage measurements matched those deduced from the thermochemical data.
3. Tubular cells with CuCl_2 as the cathode and Na as the anode were constructed. However, it was discovered that CuCl_2 was somewhat corrosive and dissolved iron, an element of the cathode compartment. Since protective coating technology was beyond this Phase I work scope, no further work on the CuCl_2 cathode was pursued in Phase I. Notwithstanding, due to its very high OCV and high specific energy, CuCl_2 cathode is a very attractive possibility for a battery capable of delivering higher specific energy with higher voltage. Further investigation of the Na- CuCl_2 battery can be done by using suitable metal coating technologies developed at MSRI for high temperature applications.
4. In Phase I, FeCl_2 and ZnCl_2 were finalized as the potential cathodes for Na-metal salt batteries for delivering high specific energies. Planar Na- FeCl_2 and Na- ZnCl_2 cells were designed, constructed, and tested between 350 and 600°C. Investigation of charge/discharge characteristics showed they were the most promising batteries. Charge/discharge cycles were performed as many as 27 times, and charge/discharge current was as high as 500 mA. No failure was detected after 50 hours testing.
5. Three-cell planar stacks were designed, constructed, and evaluated. Preliminary tests showed further investigation was needed for optimization.
6. Freeze-thaw survival was remarkably good for planar BASE discs fabricated by MSRI's patented vapor phase process.

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Technical Objectives of the Proposed Work (Phase I)

Technical objectives of the proposed work for this STTR Phase I, as given in the proposal, are given in what follows:

1. To fabricate Na-BASE and K-BASE discs and tubes of high ionic conductivity, high strength, and excellent resistance to moisture attack using a patented, vapor phase process.
2. To identify suitable cathodes based on thermodynamic data, and other physical properties (such as weight, melting point, stability, and compatibility with other cell components), and the measurement of open circuit voltage (OCV) of a number of prospective electrochemical couples.
3. To design and assemble tubular cells with CuCl_2 as the cathode and Na and K as the anodes. In Phase II, cells with other cathodes will be investigated.
4. To measure OCV, and investigate charge-discharge characteristics of the cells over a range of temperatures from 400 to 650°C.
5. To design, construct and evaluate performance of planar cells.

Phase I Work Plan:

- Task 1: Identification and acquisition of prospective cathodes for K and Na/BASE/cathode electrochemical couples through literature search on thermodynamic data
- Task 2: Identification and acquisition of materials for construction of planar cells using BASE electrolyte plates fabricated in-house
- Task 3: Fabrication of BASE plates and tubes using the MSRI patented vapor phase process
- Task 4: Preliminary testing of prospective electrochemical couples using potassium and sodium anodes, prospective cathodes and BASE tubes
- Task 5: Fabrication of cell components for planar cells
- Task 6: Assembly of planar cells with promising cathodes
- Task 7: Electrochemical testing of planar cells
- Task 8: Post-test evaluation of cells
- Task 9: Final report

Phase I Performance Schedule:

The proposed schedule of performance for Phase I followed:

- Task 1 to be completed by the end of second month from start of project
- Task 2 to be completed by the end of second month from start of project
- Task 3 to be completed by the end of third month from start of project
- Task 4 to be completed by the end of fifth month from start of project
- Task 5 to be completed by the end of sixth month from start of project
- Task 6 to be completed by the end of seventh month from start of project
- Task 7 to be completed by the end of eighth month from start of project
- Task 8 to be completed by the middle of ninth month from start of project
- Task 9 to be completed by the end of ninth month from start of project

Work Accomplished: Work done during Phase I is described in what follows.

Task 1: Identification and acquisition of prospective cathodes for Na- and K-BASE cathode electrochemical couples through literature search on thermodynamic data. This task was successfully completed by the end of second month from the start of the project. The prospective electrochemical couples identified and acquired are described in the following paragraphs.

The high temperature rechargeable batteries are comprised of a liquid sodium (or potassium) anode, a sodium (or potassium) ion-conducting beta" alumina solid electrolyte (Na-BASE) (or K-BASE), and a liquid metal salt cathode. The correct choice of a metal salt ensures a large free energy change upon discharge, and thus achieves a high specific energy (Wh/kg). The prospective electrochemical couples used in the proposed batteries must be sufficiently energetic, lightweight, must be neither corrosive nor overly volatile, and must be capable of forming a stable, porous metal structure or a liquid metal in the cathode upon discharge. Since the anode is liquid sodium (or liquid potassium) at the working temperatures ranging from the proposed 400 to 650°C, the possible candidates for the cathode are several metal salts with either low melting temperature and/or forming eutectics with alkali salts, allowing for a deeper discharge and a large enough free energy change upon discharge. The maximum amount of electrical energy that can be derived is $|\Delta G^o|$ (with $\Delta G^o < 0$ for plausible reactions), where the ΔG^o is the free energy of the reaction between sodium (or potassium) and the metal salt to form sodium salt (or potassium salt) and metal. Such reaction is also called as the displacement reaction. The corresponding open circuit voltage (OCV) is given by $E = -\Delta G^o / (nF)$, where n is the number of electrons participating the overall displacement reaction and F is the Faraday constant ($F = 96,485 \text{ C/mol.}$).

Wide-ranging literature [1] searches were conducted by looking at materials thermochemical data and corresponding materials properties. It was discovered that electrochemical couples formed by metal chloride or metal fluoride possessed high OCV and high specific energy. Table 1 lists a few prospective candidates for the electrochemical couples, which are capable of delivering more than 200 Wh/kg specific energies for stationary energy storage applications, and corresponding specific energies calculated at 500°C.

Both OCVs and specific energies at 90% efficiency were also calculated for the potential Na/metal salt and K/metal salt electrochemical couples, identified in Table 1, over the working temperatures from 350°C to 700°C. The results are shown in Figure 1 and Figure 2 for OCVs and specific energies at 90% efficiency, respectively. The calculation results of Na/metal salts and K/metal salts were plotted in the same figures for comparisons. In both figures, the filled symbols represent the Na/metal salts couples, and the unfilled symbols represent the K/metal salts couples. In general, the electrochemical couples comprised of K and metal salts showed higher OCVs than couples comprised of Na and the corresponding metal salts, except K/AgF. On the contrary, K/metal salts have lower specific energies than Na/metal salts due to heavy molecule mass of the electrochemical couples.

Table 1. A list of possible high temperature electrochemical couples capable of delivering 200 Wh/kg

Electrochemical couple Na/Salt	ΔG° for reaction at 500 oC (kJ/mol)	Open Circuit Voltage (V)	Specific energy for the couple at 90% efficiency (Wh/mol)	Specific energy for the couple at 90% efficiency (Wh/kg)	Molar mass of the couple (kg/mol)
Na/AgCl	-252.8	2.620	63.2	380.0	0.1663
Na/CuCl	-222.6	2.307	55.6	456.2	0.1220
Na/CuCl ₂	-571.0	2.959	142.8	791.2	0.1804
Na/FeCl ₂	-434.3	2.251	108.6	628.6	0.1727
Na/NiCl ₂	-490.2	2.540	122.5	697.9	0.1756
Na/ZnCl ₂	-376.3	1.950	94.0	516.1	0.1823
Na/AgF*	-339.3	3.516	84.8	566.0	0.1499
K/AgCl	-275.9	2.860	69.0	378.1	0.1824
K/CuCl	-245.7	2.547	61.4	444.8	0.1381
K/CuCl ₂	-617.2	3.198	154.3	725.6	0.2127
K/FeCl ₂	-480.6	2.490	120.1	586.2	0.2049
K/NiCl ₂	-536.4	2.780	134.1	645.3	0.2078
K/ZnCl ₂	-422.5	2.189	105.6	492.4	0.2145
K/AgF*	-333.9	3.460	83.5	502.9	0.1660

*: The calculation was made at 400°C due to unavailable thermochemical data above 435°C (708K).

Figure 1. Calculations of open circuit voltages based on the electrochemical data for identified electrochemical couples.

Figure 2. Calculations of specific energies at 90% efficiency based on the electrochemical data for identified electrochemical couples.

From the standpoint of the specific energy and OCV, the most preferable selections are K/CuCl₂ and Na/CuCl₂, which possesses a specific energy of 726 Wh/kg (at 90% efficiency) with OCV of 3.198 V and a specific energy of 791 Wh/kg (at 90% efficiency) with OCV of 2.959 V, respectively. These materials set are very attractive for the high specific energy and high voltage applications. In addition, it is unlikely that ion exchange between the Cu⁺² from the salt and Na⁺¹ (or K⁺¹) from the Na-BASE (or K-BASE) would occur, since the ionic radius of Cu⁺² (0.57 Å) is much smaller than Na⁺¹ (0.99 Å) (or K⁺¹ at 1.37 Å) [2]. However, iron, which is the main component of the cathode container, is readily dissolved in the CuCl₂ salt.

At 500°C, the above dissolution reaction between Fe and CuCl₂ has a free energy of -262.5 kJ/mol to form CuCl and FeCl₂. Experimental validations were performed by mixing 7 grams of stainless steel 410 strips with 100 grams of eutectic CuCl₂+NaCl (45 mol% CuCl₂ + 55 mol% NaCl) mixture and heated to 500°C. Within 15 minutes, the SS 410 strips were completely dissolved. Experiments were also performed with SS 316 strips and graphite paper. Similar dissolution was observed for the SS 316, but not for the graphite paper. Thermochemical data show that the available metallic materials that resist liquid CuCl₂ attack are very limited. A possible solution is to apply a protective coating layer to the cathode container. Since the

development of coating technology was beyond this Phase I work scope, the investigation of CuCl_2 as a battery cathode was not pursued, but was elaborated in Phase II proposal.

Other attractive couples were $\text{Na/NiCl}_2 > \text{Na/FeCl}_2 > \text{Na/AgF} > \text{Na/ZnCl}_2 > \text{Na/CuCl} > \text{Na/AgCl}$ for Na-BASE batteries, and $\text{K/NiCl}_2 > \text{K/FeCl}_2 > \text{K/AgF} > \text{K/ZnCl}_2 > \text{K/CuCl} > \text{K/AgCl}$ for K-BASE batteries, listed in the order of preference from high to low. However, AgF salt was not considered in Phase I due to its high vapor pressure when it was in the liquid phase.

In addition to the free energy of the reaction, an important consideration is the attainable depth of discharge, which is central to achieving a high specific energy (Wh/kg). The most important factor determining the depth of discharge is the type of phases formed in the cathode. For NAS batteries, the depth of discharge is limited by deposition of solid, electrically insulating Na_2S_2 . For this reason, the depth of discharge in NAS batteries is limited to about 35%. In contrast, Na-metal salt (or K-metal salt) batteries form a metal in the cathode upon discharge, and the electrical resistance in the electrode actually decreases during discharge.

Figure 3. Phase diagram of ZnCl_2 +NaCl binary system [3]

The choice of liquid electrodes for Na-metal salt batteries (or K-metal salt batteries) ensures excellent mass transport in the cathode allowing for a greater depth of discharge. Therefore, it is desirable that at working temperatures, a liquid phase should span as wide as possible in binary phase diagrams of metal salt and the discharge product sodium salt (or potassium salt) systems. Phase diagrams were studied for Na-salt (or K-salt) and metal salt candidates identified in Table 1. Figure 3 and Figure 4 are the phase diagrams for ZnCl_2 +NaCl (NaCl formed upon discharge)

[3] and (b) $\text{FeCl}_2 + \text{NaCl}$ (NaCl formed upon discharge) [4], respectively. It is observed that both $\text{ZnCl}_2 + \text{NaCl}$ system and $\text{FeCl}_2 + \text{NaCl}$ system stretch widely in liquid phase at temperatures from 400 to 700°C, indicating both ZnCl_2 and FeCl_2 would be very promising cathodes suitable for high specific energy Na- (or K-) metal salt batteries.

Figure 4. Phase diagram of $\text{FeCl}_2 + \text{NaCl}$ binary system [4]

Another attractive candidate of the cathode is NiCl_2 capable of delivering a high specific energy and high OCV based on evaluation of the thermochemical data above. However, phase diagram studies of the $\text{NiCl}_2 + \text{NaCl}$ binary system, shown in Figure 5, suggested it was not suitable for the battery application due to narrow scopes of the liquid phase. The eutectic temperature of $\text{NiCl}_2 + \text{NaCl}$ is around 572°C, which is much higher than the eutectic temperature both $\text{ZnCl}_2 + \text{NaCl}$ system and $\text{FeCl}_2 + \text{NaCl}$ system, and can result in narrow discharge depth. Notwithstanding, it has to be pointed out here that a secondary electrolyte (NaAlCl_4) in liquid phase is introduced in the ZEBRA battery, which uses NiCl_2 as the solid cathode. However, if the ZEBRA battery is overcharged, NaAlCl_4 is decomposed forming NiCl_2 , what results in the loss of the liquid electrolyte permanently.

Figure 5. Phase diagram of NiCl₂+NaCl binary system [4]

Task 2: Identification and acquisition of materials for construction of planar cells using BASE electrolyte plates fabricated in-house. This task was successfully completed by the end of the second month from the start of the project for the identification and acquisition of necessary materials for planar cell constructions.

The criteria of materials selection for the battery construction were based on the attainment of as high a specific energy as possible, but balanced with low materials cost and easy accessibility. The following materials for the construction of batteries have been used and demonstrated successfully in Phase I:

Electrode compartment: Materials for the construction of electrode compartments must sustain moderately high temperatures and somewhat corrosive atmospheres. Inexpensive stainless steel foil (SS316 or SS430) is a suitable candidate, and can be easily stamped into a desired shape. Corrosion tests, similar stainless steel dissolution tests described in Task 1, were performed for all identified cathode candidates. No dissolution was observed, except for the CuCl₂ cathode.

Electrode compartments in cup-shape were designed and the acquisition was made by purchasing commercial products, instead of designing and making a stamping tooling for the metal stamping due to a short period and short funds of Phase I. However, metal stamping approach will be performed in proposed Phase II for a precise design of the electrode compartments. Figure 6 is a

picture of commercial cups for electrode compartments. They were made of stainless steel with 15 mil thickness.

Figure 6. Commercial cups for electrode compartments

Contact aid/wick: The contact aid/wick is a necessary for distributing reactants/products to/from the electrochemical reaction sites, while providing good contact with the BASE and the metal compartments with or without the cathode and anode materials. This is important for electrical contiguity, and the attainment of full discharge. Steel wool with various grades (rated from 000 to 1) and graphite foam were experimentally evaluated for use as the contact aid/wick for the cathode. Both the steel wool with “Grade 0” (fine grade) and graphite foam worked well for metal salt melts. For the anode, it was found that both nickel foam and copper wool had good wicking effect. Therefore, steel wool and copper wool were used as the contact aid/wick for the cathode and anode, respectively, in Phase I.

BASE electrolyte: Both Na-BASE and K-BASE planar discs were fabricated using the tape-casting method, followed by the MSRI patented vapor phase process, which will be discussed in Task 3 in detail. The electrolyte thickness was around 1 mm.

Sealing gasket: Copper gaskets were identified as the seal material for both anode and cathode. The thickness was about 0.254 mm (10 mil).

Figure 7 is a photograph showing the components for a 1” size battery construction identified above. Same materials were used for 2” size battery. Constructions and experimental evaluations are described later in Task 6 and 7.

Figure 7. A photograph showing the components used for a 1" size battery construction

Task 3: Fabrication of BASE plates and tubes using the MSRI patented vapor phase process

Task 3.1: Fabrication of BASE plates and tubes

The goal of making BASE plates and tubes were successfully achieved by the end of the third month from the start of the project, and BASE plates and tubes fabrications were continued until the ninth month of the project.

As it was discussed in the proposal, the conventional process for the fabrication of Na-BASE involves sintering compacts of calcined powder containing BASE (and other sodium aluminates including NaAlO_2) at elevated temperatures ($\sim 1600^\circ\text{C}$) in enclosed MgO containers to suppress vapor phase loss of Na_2O [5]. The necessity of using containers increases cost significantly. Also, since some NaAlO_2 always remains along the grain boundaries, BASE made by the conventional process is susceptible to moisture and CO_2 attack from the atmosphere. In addition, fracture strength of BASE made by the conventional process is generally low – on the order of 200 MPa or less.

MSRI has developed a novel process based on the concept of coupled transport, which has the following advantages over the state-of-the-art [6-9]: (a) The process is conducted at a lower temperature ($\sim 1400^\circ\text{C}$) than the conventional process (~ 1600 to 1650°C). Thus, sintered, dense MgO containers are not required. (b) The process leads to a two phase composite of BASE and zirconia. By using zirconia with a low yttria content ($\sim 3\%$), a two phase composite of BASE + tetragonal zirconia (TZP) can be made with fracture strengths approaching ~ 900 MPa [9]. (c) The process is carried out in such a manner that the thermodynamic activity of Na_2O , $a_{\text{Na}_2\text{O}}$, is always maintained below that required for the formation of NaAlO_2 . Thus, no NaAlO_2 forms,

and the resulting material is resistant to moisture and CO₂ attack. So resistant is the material that it can be boiled in water without any degradation. Materials preparations and processes for the fabrication of BASE by the vapor phase method are described in what follows.

Fabrication of alfa alumina based disks: A tape-casting method was developed to fabricate planar cells. Alfa alumina (α -Al₂O₃) powder was mixed with 8 mol% yttria-stabilized zirconia (8YSZ) powder by the ratio of 70/30 by volume. Adding zirconia to α -Al₂O₃ could enhance the kinetics of the vapor phase conversion process by improving the oxygen transportation through the converted region when the α -Al₂O₃ was converted to beta" alumina. Binder and solvent were added to the powder mixture forming a castable slurry. After de-airing the slurry, a green tape was formed using the tape casting method at a desired thickness. Following a one-day air-drying process, the tape was then laser-cut into circular shape with the desired diameters to fit the size of the electrode compartments. Shrinkage of the tape was studied and taken into account. After bisquing in air to burn out binder and solvent, disks were sintered at 1600°C for 2 hours forming a two-phase material containing α -Al₂O₃ and 8YSZ. The density of the α -Al₂O₃ + 8YSZ composite was measured as high as 99% of theoretical density by the water displacement method.

Fabrication of packing powder: Na-beta" alumina packing powder was prepared by mixing NaAlO₂, LiAlO₂, and α -Al₂O₃ powder in proper ratios in ethanol for 24 hours. The mixed powder was then dried in air followed by calcination at a high temperature. The Na-beta" alumina packing powder was finally made by crushing the calcined powders to break hard agglomerates. The procedure for preparation of K-beta" packing powder followed the same procedure developed for the Na-beta" alumina packing powder, except that KAlO₂ powder was used to replace the NaAlO₂ powder. Both packing powders can be reused numerous times, each time by simply replenishing the NaAlO₂ or KAlO₂ content, thus the cost the materials can be reduced.

Conversion of discs into beta" alumina using packing powder: The sintered discs were placed in an alumina crucible, packed with either Na-beta" alumina packing powder for converting into Na-BASE, or K-beta" alumina packing powder for converting into K-BASE. The conversion process was taken at 1400°C for couple hours. Upon conversion, highly conductive, strong and moisture/CO₂ - resistant BASE formed, and ready for use in battery applications.

In addition to planar discs, one end closed α -Al₂O₃ + 8YSZ based tubes were also fabricated. The process consisted of pressing α -Al₂O₃ + 8YSZ powder mixture in a specially designed die with a steel mandrel, and then cold-isostatic pressing the powder at 30,000 psi to form a tube. The tube was then sintered at 1600°C for two hours. Subsequent vapor phase conversion to BASE followed the exactly same procedure as just described above to form either Na-BASE tubes or K-BASE tubes. This vapor phase process readily allowed for the fabrication of thin, uniform wall thickness tubes, which was not easily achieved by the conventional process due to the warpage associated with liquid phase sintering.

Figure 8 shows a photograph of several BASE tubes and discs, which were fabricated using the MSRI patented vapor phase process. BASE tubes were as long as 8", and discs were as large as 2.5". BASE tubes were used in preliminary electrochemical testing.

Figure 8. A photograph of several BASE tubes and disks made by MSRI's patented vapor phase process.

Task 3.2: Qualification of BASE

Microstructure characterization: After sintering the α -Al₂O₃ + 8YSZ discs and then converting into Na-BASE and K-BASE, microstructures were characterized using a Scanning Electron Microscope (SEM) to determine the morphology of samples before/after conversion. Samples were cross-sectioned and polished, followed by thermally etching. Figure 9, Figure 10, and Figure 11 are the SEM micrographs of an α -alumina + zirconia sample before conversion, after conversion to Na-BASE, and to K-BASE, respectively. In figures, the white grains are zirconia. The dark grains are alpha alumina in Figure 9, Na-beta'' in Figure 10, and K-beta'' in Figure 11. Both Na-beta'' and K-beta'' show unique textured microstructures, which were developed during conversion process and plays an important role in the attainment of good conductivity of the BASE. Similar to Figure 9 and Figure 10, Figure 12 and Figure 13 provide closer looks of the α -alumina + zirconia and Na-BASE, respectively, at a high magnification.

Figure 9. SEM micrographs of alpha-alumina + zirconia before conversion

Figure 10. SEM micrographs of a Na-beta'' alumina + zirconia after conversion

Figure 11. SEM micrographs of K-beta alumina + zirconia after conversion

Figure 12. SEM micrographs of alpha-alumina + zirconia before conversion at a high magnification

Figure 13. SEM micrographs of a Na-BASE at a high magnification

Figure 14. Na-BASE conductivity as a function of temperature

Ionic conductivity measurement: After conversion, BASE samples were characterized by measuring the BASE ionic conductivity with AC impedance measurements. Samples were prepared by painting Pt electrodes that were fired at 900°C for one hour. Figure 14 is an Arrhenius plot of conductivity for Na-BASE. The temperature dependence of conductivity yields an activation energy 22.58 kJ/mol. At 500°C, the Na-BASE conductivity is close to 0.36 S/cm. Similar impedance measurements were also conducted on K-BASE disks, and very high resistivities were observed.

Figure 15. Microwave heating effects comparison between BASE before conversion and BASE after conversion to Na-BASE and K-BASE.

Complimenting the conductivity measurement, the BASE disks can also be qualified by microwave heating for a quick screening. It is well known that materials can be heated with the high frequency electromagnetic waves, which interacts with charged particles in the materials and leads to a heating effect. Since Na-BASE has a high conductivity, it is expected to heat up rapidly in a conventional microwave oven. Tests were performed using regular kitchen microwave (1 kW). Samples were heated for various periods of time in the microwave, up to a maximum of 20 seconds. Between each test, samples were cooled to the room temperature. Figure 15 compares heating characteristics of an $\alpha\text{-Al}_2\text{O}_3+\text{YSZ}$ disk (3.55 grams), a K-BASE disk (4.42 gram), and a Na-BASE disk (4.17 gram). After 20 seconds heating, the Na-BASE disk temperature increased to 485°C, significantly higher than that of the K-BASE disk and the $\alpha\text{-Al}_2\text{O}_3+\text{YSZ}$ disk, which increased only to 50°C and 37°C, respectively. The low heating effect on the K-BASE is consistent with its low conductivity as what is expected. The microwave

heating effect test confirmed the Na-BASE high conductivity characteristics and provided a simple test to affirm the formation of Na-BASE.

Task 4: Preliminary testing of prospective electrochemical couples using potassium and sodium anodes, prospective cathodes and BASE tubes

Preliminary experiments of prospective electrochemical couples were completed successfully by the month originally proposed.

An important point to note here is that the information given in Table 1, that is the OCVs and the specific energies at 90% efficiency plotted in Figure 1 and Figure 2 for the corresponding electrochemical couples, only refers to thermodynamic data. The ability to discharge the cells and to achieve high enough drain rates depends upon polarization characteristics of a given cell. Unfortunately, at the present time, there is no reliable method of making an a-priori judgment on which electrochemical couple will exhibit the best discharge characteristics. The only reliable approach involves experimental testing. This first step is to experimentally measure the OCV, to determine if there is an agreement with the values deduced from thermochemical data. Such tests have been done in this task using the simplest possible geometry using a BASE tube glass-sealed to an alumina tube. The procedure of the OCV measurement is described in what follows. The tests were conducted in a glove box under an oxygen-free and a moisture-free atmosphere filled with argon gas.

The BASE tube was first extended by jointing to an alpha alumina tube using glass seals. Sodium bricks purchased from Alfa-Aesar were heated to 100°C on a hot plat. The molten sodium was then introduced into the BASE tube using a syringe. A nickel rod was inserted into the molten sodium, followed by cooling to a room temperature. The BASE tube was then positioned at the center of a fused quartz or alumina tube. The prospective cathode material, identified in the Task 1, along with a stainless steel felt was placed inside the tube surrounding the BASE tube. In order to lower the polarization and to allow for high discharge currents, a small amount of low melting (m. p. ~150°C) NaAlCl_4 as the molten electrolyte was added to the cathode to enhance ionic conductivity of the cathode. Another metal rod was introduced into the cathode chamber. The selection of metallic materials was made such that there was little tendency for corrosion. Figure 16 is a photograph of the assembly for the OCV measurements to screen prospective electrochemical couples.

Figure 16. Assembly of a BASE tube and a quartz tube for OCV measurements to screen prospective electrochemical couples.

Figure 17. Open circuit voltage (OCV) measurement for Na/AgCl and Na/FeCl₂ electrochemical couples. Symbols are experimental measurements. The lines are calculations based on thermodynamic data. Note excellent agreement between measurements and calculations.

The assembly was then heated in a tube furnace to the temperature between 350 and 700°C. Figure 17 is the OCVs of Na/AgCl and Na/FeCl₂ electrochemical couples. It is clear that the

measured OCVs of both electrochemical couples are in excellent agreement with these deduced from the thermochemical data.

Task 5: Fabrication of cell components for planar cells

This task was completed by the end of sixth month from start of the project. Cell components identified in Task 2 for planar cells were fabricated and acquired. The process is delineated in what follows.

Electrode compartments preparation: Both anode and cathode compartments in cup-shape were commercial products and were readily obtained. The cups were made of 15 mil stainless steel in two sizes, which were 1" and 2" as shown in Figure 6. Flanges of the cups were flattened first, followed by smoothing surfaces by sandpapers. Both current and voltage leads (4 probes) were spot-welded to the electrode compartments for conducting battery current and collecting voltage.

Cathode preparation: The cathode was fabricated using the impregnation method. Cathode powder, a eutectic mixture of dry NaCl salt and the metal chloride salt, was heated on a hot plate and was die-cast in a molten state. Figure 18 is a picture of casting dies machined from graphite rods for casting 1" cell (with electrode size 3/4") and 2" cell (with electrode size 1.5"). The molten salt was then impregnated with a steel wool felt. A graphite piston, also shown in Figure 18, was used to press the felt. This could ensure that the felt was under compression in solid state but was released in liquid state for providing contacts against the BASE. Since the eutectic melting temperatures of NaCl and the metal salts listed in Table 1 were quite low ($< 400^{\circ}\text{C}$), this impregnation method worked very well compared to other approaches, such as hot pressing powders or co-sintering powder mixtures. After cooling, the solid cathode was then pulled out from the casting die and moved into the glove box for cell assembly. It was noticed that both FeCl_2 and ZnCl_2 could be cast in air without absorbing significant moisture. Figure 19 is a photograph a cathode compartment filled with the pre-cast cathode ready for 1" cell assembly.

Figure 18. Casting dies for cathode casting

Figure 19. A cathode compartment filled with pre-cast cathode

Anode preparation: The anode was prepared in the glove box filled with a dry argon atmosphere without oxygen. A metal felt, such as copper or nickel, was positioned inside the anode cup. Sodium was melted in a beaker, and a syringe was used to measure and then to inject the molten sodium into the cavity, which was subsequently cooled to room temperature. Figure 20 shows a picture of an anode with copper mesh.

Figure 20. Picture of an anode of a 1" cell inside the glove box

Even though the approach of the cathode and anode preparation were described as assembly in a partially discharge state, it is possible to assemble the cells in a fully discharged state, so that no metallic sodium needs to be handled.

Spacer ring: Alumina rings were used for the spacers against the BASE ceramic for the support of compression. The rings with the same thickness as the electrode compartments were sliced from an alumina tube, followed by smoothing on edges. Though the alumina rings added extra weight to the battery, resulting in a lower specific energy, the major objective in Phase I was to prove the concept of the planar battery. Optimization of battery designs and using lightweight alumina-silica spacer rings to replace the alumina rings have been proposed in Phase II work.

Figure 21. Components for 1" size planar battery

Figure 21 is a photograph summarizing all components for constructing planar batteries with 1" BASE electrolyte. Components for large batteries with 2" BASE electrolyte are similar.

Task 6: Assembly of planar cells with promising cathodes

Both the FeCl_2 and ZnCl_2 salts have been identified in this Phase I work as the promising cathodes for the Na-metal chloride battery, from the standpoint of specific energy and OCV. Assembly of planar cells with FeCl_2 and ZnCl_2 cathodes was successfully completed by the end of eighth month from start of the project.

Single-cell assembly: Individual cells were assembled in the glove box. A sodium-filled cup was seated on the bottom. The BASE disk with two gaskets on each side was placed on the

anode cup, followed by placing the cathode cup on other side of the BASE disk. In order to improve the sodium wetability on the BASE disk, sodium amide, which melts at 200°C and decomposes at 400°C, was applied on the anode side of the BASE disk. Compression was then applied by bolts over two end plates for thermocompression bonding. The bolts with low thermal expansion were used to apply the compression to the assembly during heat up. The entire assembly was then heated to 400°C. This completed the single-cell assembly. Each battery was attached with four leads: two for conducting current and two for measuring voltage. Figure 22 is a photograph of a single-cell battery assembly ready for testing.

Figure 22. Single-cell battery assembly with compression fixture ready for testing

Multiple-cell battery assembly: Efforts of assembling multiple-cell batteries were also made in Phase I, though the batteries did not survive in tests. Designs of the batteries pack will be engineered in Phase II. Figure 23 is a three-cell stack mockup developed by the subcontractor at the University of Utah under a separate DOE-supported project (DE-FC26-05NT42623). The aforementioned approach of assembling a single-cell battery was repeated to stack multiple cells. In the end, the whole assembly was compressed by low thermal expansion bolts through two end plates on opposite sides, and electrically isolated to prevent short by using insulating sleeves and washers.

Figure 23. A three-cell battery stack developed by the University of Utah under a DOE-funded project with contract No. DE-FC26-05NT42623

Task 7: Electrochemical testing of planar cells

Tests of planar cell batteries were completed successfully by the end of eighth month from the start of project. Tests of cells were conducted in the glove box over a range of temperatures between 350°C and 600°C. Figure 24 is a photograph of the glove box used for battery tests. The glove box was filled with dry argon with oxygen and moisture traps. A split furnace was placed inside the glove box with a temperature controller placed outside the box. A hot plate was used to compensate the heat losses through the bottom of batteries. Thermocouples were also installed to control and monitor the battery temperature. A dual channel Labview-controlled battery tester was designed and built in-house, and was used to carry out current-voltage measurements. When a battery assembly, as shown in Figure 22 or Figure 23, was heated to the testing temperature, a step-wise constant current was applied to the battery through two current leads, and the battery voltage from other two leads was recorded by a PC. In the current-voltage characterization tests, the battery voltage was limited to 105% of OCV during charging and to 95% of OCV during discharging, thus ensuring a 90% of energy efficiency. It was observed that the initial test of a pristine battery with charging would give better performance than that starting with discharging. It was speculated that during the charging step, the sodium moving from the cathode (metal salt side) to the anode (sodium side) helped to wet the BASE electrolyte, resulting in a low contact resistance.

Figure 24. The glove box with controlled atmosphere for Na-metal salt (or K-metal salt) battery tests

Na-FeCl₂ battery: Na-FeCl₂ batteries with electrode area of 2.5 cm² and 10 cm² were tested over a range of temperatures between 400°C and 600°C. Results are presented and discussed in what follows.

Figure 25. Voltage characteristics of a Na-FeCl₂ battery during charge. The charge current was 56 mA.

Figure 25 shows the battery voltage characteristics of a Na-FeCl₂ battery during charge. This battery, initially loaded with the NaCl-FeCl₂ eutectic cathode, had electrode area 2.5 cm² and was tested at 500°C. The OCV was 2.254 V, very close to the calculated value 2.251 based on thermochemical data at 500°C. The discharge voltage limit was set to 2.15V, 95% of OCV. The charge voltage limit was 2.34V, 104% of OCV. As shown in the figure, the battery voltage increased from 2.242 V to 2.34 V over 116 minutes at a constant charge current 56 mA. The total charging capacity was 108 mAh. The area specific resistance was estimated to be 2 Ωcm², which left much room for further optimization of the battery design. In order to identify various losses, including the ohmic losses and activation overpotentials, complex impedance spectroscopy is proposed for use in Phase II.

Similar to the charge curve, the voltage discharge characteristic curve was also recorded for the same battery, as shown in Figure 26. Over 95 minutes of a continuous discharge at the constant current 56 mA, the battery voltage decreased from previous charge limit 2.34 V to 2.154 V. The total discharging capacity was equivalent to 98 mAh. Comparisons between the charging and discharging curves were made, and it was interesting to see that the voltage experienced fast increase/decrease in the first 5 minutes, followed by slow increase/decrease over a long time during the charge/discharge process. It is suspected that the sharp voltage change must correlate to the overpotential change, and AC impedance spectroscopy can be used to identify those various losses in Phase II for optimizing the battery performance.

Figure 26. Voltage characteristics of a Na-FeCl₂ battery during discharge. The discharge current was 56 mA.

Charge/discharge characteristics of Na-FeCl₂ batteries with large active area were also tested. Figure 27 is a performance of a Na-FeCl₂ battery with electrode area 10 cm². At 500°C, tests of charge/discharge cycle were carried out at a constant current 104 mA. The discharge voltage limit was set to 2.157V, 96% of OCV. The charge voltage limit was 2.302V, 102% of OCV. As shown in the figure, no obvious degradation was observed after 6 cycles. Notwithstanding, it is proposed in Phase II to characterize both pristine cells and cells after cycle tests using complex impedance spectroscopy, which can provide the overall cell resistance and the possible origins of resistance change in the batteries after charge/discharge cycles. The charge and discharge capacities of this cell were about 69 mAh and 64 mAh, respectively.

Figure 27. Performance of a Na-FeCl₂ single-cell battery charge/discharge cycles. The cell was charged/discharged with a round trip efficiency of ~94%.

Na-FeCl₂ single-cell batteries were tested successfully at 600°C. The results are presented in the following two figures. Figure 28 is the battery charge/discharge characteristics at a fixed 35 mAh capacity. It was observed that cell voltages were flat for charge/discharge current at both 200 mA and 500 mA. The round trip efficiency was estimated to be 95%. The charge/discharge capacity characteristics are plotted in Figure 29 at the maximum current 500 mA passing through the cell. The battery discharge curve was flatter than the charge curve. At 64 mAh capacity, the battery voltage changed by 90 mV and 44 mV during charge and discharge, respectively. Comparison between the battery performance at 500°C and 600°C showed that operation at higher temperatures was preferred for lowering losses and thus having higher overall efficiency.

Figure 28. Na-FeCl₂ single-cell battery charge/discharge characteristics at 35 mAh capacity. The testing temperature was set to 600°C. The maximum charge/discharge current passed was 500 mA.

Figure 29. Na-FeCl₂ single-cell battery charge/discharge capacity characteristics. The testing temperature was set to 600°C. The charge/discharge current was set to 500 mA.

Planar Na-ZnCl₂ batteries were constructed and tested by the subcontractor at the University of Utah under a separate DOE-funded project. The batteries were assembled either in a partially charged state or in a fully discharged state with ZnCl₂ and NaCl eutectic composition as the cathode. The testing temperatures varied from 350 to 425°C. Figure 30 is the typical voltage response of the charge/discharge cycles of a Na-ZnCl₂ planar cell, which was assembled in a partially charged state at a eutectic composition. This battery was tested at 350°C and 100 mA constant current for 2 hours. The Na-ZnCl₂ battery showed similar voltage characteristics to the Na-FeCl₂ battery, but had relatively high resistances and low capacities.

Figure 30. Voltage response of the charge/discharge of a planar cell assembled in the partially charged state

Long-term tests of Na-ZnCl₂ batteries were performed. Figure 31 shows initial 20 hours test results of a Na-ZnCl₂ battery operated at 425°C. The charge/discharge current varied from 100 mA to 500 mA. A constant current of 100 mA was initially passed through the cell for 5 hours followed by 200 mA cycling tests for couple hours. After tested at 300 mA for 13 hours of charge/discharge cycles, the cell was operated for another 32 hours at 500 mA. No failures were observed after the 50 hours test. As shown in the figure, variable voltage with time during charge and discharge was due to the small capacity of the experimental cell, consequently the depletion of reactants. This cell was charged/discharged at a round trip efficiency of ~ 82%. It can easily be operated at a higher efficiency (>90%) by slightly lowering the current.

Figure 31. Na-ZnCl₂ single-cell battery voltage response during charge/discharge cycles at a temperature of 425°C. The cell was operated for 50 hours. The maximum current passed was 500 mA. The figure shows only a part of it (20 hours). The cell was charged/discharged at a round trip efficiency of ~82%. Data were obtained by the University of Utah under a separate DOE-funded project with contract No. DE-FC26-05NT42623.

Similar to the SOFC, ohmic heating effect on the battery performance is always accompanied along the charge/discharge, due to ohmic losses. Nevertheless, unlike lithium ion batteries, which work only at low temperatures, the Na-FeCl₂ and Na-ZnCl₂ batteries developed in this program can operate over a wide temperature range. For the Na-metal salt battery, increasing the working temperature leads to improvement of the battery performance. This is the distinct advantage of the BASE batteries over the lithium batteries, thus makes it possible to thermally integrate this type of energy storage battery with other high temperature power generation systems, such as SOFC stacks or internal combustion engines. In order to understand the temperature effect, the temperature variation within the battery will be investigated in Phase II as it is proposed. Multiple thermocouples will be embedded in a battery assembly, and the temperature profiles will be recorded during charge/discharge cycles by a data acquisition system. In Phase II, an analytical thermal model will also be set up to correlate the thermodynamic data with the experimental temperature profiles for optimizing the battery operation conditions.

Task 8: Post-test evaluation of cells

This task was completed by the end of the ninth month from start of the project. After testing, each battery assembly was visually inspected for any leaks around the copper seals and the

BASE electrolyte. Figure 32 is a photograph of a typical assembly after testing. No leaks were observed, as shown in the photo. Cells were thereafter disassembled, and remaining metallic Na or K inside the anode compartment was carefully removed by reacting with ethanol alcohol or t-butyl alcohol, respectively. Any potential damage to the electrolyte BASE and the containers were thereafter inspected.

Figure 32. A photograph of a Na-FeCl₂ cell after testing

During the testing of Na-FeCl₂ batteries developed in early Phase I, some of the cells experienced failure after a few charge/discharge cycles. Postmortem analyses of the batteries revealed that thermo-compression bonding between the anode cup and Na-BASE was lost. Further investigation was performed by immersing the BASE electrolyte in water, as shown in Figure 33. Hydrogen bubbles, which were released from the chemical reaction of Na with water, were observed, and the seal gasket was separated gradually from the BASE.

Figure 33. Test of detecting Na remnant deposited on the interfaces of the BASE and the seal gasket

As it was discussed above that Na-BASE was a very good sodium ion conductor, it was suspected that in battery charge mode, sodium ions were reduced to sodium wherever ion transport occurred through BASE and electronic contact existed, including the interfaces between the BASE and the copper gasket. In order to eliminate ions transport in sealing areas, a dielectric layer was spray-coated on the Na-BASE sealing borders to prevent electron flow through the gasket. Notwithstanding, in order to achieve greater uniformity for the BASE, a special design of the BASE has been proposed in Phase II.

Task 9: Final report

Task 9 was the final report, which was completed by the end of ninth month from start of the project.

Summary/Conclusion

This STTR Phase I project was successfully completed on schedule, and all of the principal objectives in the proposed Phase I work were met to a very high degree. The program started from the wide-ranging literature searches to identify suitable electrochemical couples by looking at materials thermochemical data and corresponding materials properties. From the standpoint of the specific energy, open circuit voltage, and depth of discharge, CuCl_2 , FeCl_2 , ZnCl_2 , and AgCl were identified as suitable salts for both Na/metal salt and K/metal salt electrochemical couples. Open circuit voltage measurements, which were conducted in BASE tubes, matched those deduced from the thermochemical data. Further tests of CuCl_2 showed that CuCl_2 was somewhat corrosive and was able to dissolve iron, an element of the cathode compartment. In Phase II, one of the objectives is to explore CuCl_2 by applying an appropriate protective coating technology to the cathode compartment, thus makes it possible to use CuCl_2 cathode for delivering both high energy density and high OCV. In Phase I, both Na-BASE and K-BASE discs and tubes were successfully fabricated using MSRI's patented vapor phase process. SEM studies of Na-BASE and K-BASE showed unique textured microstructures, which was developed during conversion process and played an important role in the attainment of good conductivity of the BASE. Impedance measurements showed that Na-BASE had higher ionic conductivity than K-BASE. At 500°C , Na-BASE conductivity was 0.36 S/cm , which was more than 20 times higher than 8YSZ electrolyte used for SOFC at 800°C . Complimentary measurements of the BASE conductivity through the microwave heating process further confirmed that the Na-BASE possessed much higher conductivity than the K-BASE. Therefore, the Phase I research efforts have been focused on Na-metal salt batteries development. Planar Na- FeCl_2 and Na- ZnCl_2 batteries were designed, constructed, and tested between 350 and 600°C . Charge/discharge characteristic tests showed that both FeCl_2 and ZnCl_2 were favorable cathodes. Charge/discharge cycles were performed as many as 27 times, and charge/discharge current was as high as 500 mA . No failure was detected after 50 hours testing. In order to characterize and identify various losses, the method of complex impedance spectroscopy is proposed for use in Phase II. Optimization of battery designs will thereafter be performed.

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