



Short communication

Low temperature electrochemical cells with sodium β'' -alumina solid electrolyte (BASE)

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ABSTRACT

Cells of Daniell-type with copper–zinc electrochemical couples and sodium β'' -alumina solid electrolyte (BASE) were constructed. The cathode consisted of copper in contact with its ions (Cu/Cu^{2+}) while zinc in contact with its ions (Zn/Zn^{2+}) constituted the anode. Dimethyl sulfoxide (DMSO) containing 1 M NaBF_4 was used as the liquid electrolyte. The configuration of the cell constructed can be written as follows:

$$\text{Zn(s)}/\text{ZnCl}_2(\text{DMSO})(0.1 \text{ M}), \text{NaBF}_4(1 \text{ M})/\text{BASE}/\text{NaBF}_4(1 \text{ M}), \text{CuCl}_2(\text{DMSO})(0.1 \text{ M})/\text{Cu(s)}$$

The cell was subjected to charge–discharge cycles at 100 °C. The BASE discs were found to be stable even after the cell was subjected to several electrochemical charge–discharge cycles. Cells were also constructed using BASE discs with porous BASE surface layers introduced to lower the interfacial resistance. Cells with surface modified BASE exhibited a lower resistance in comparison to those using unmodified BASE. XRD and SEM analyses indicated that no detectable degradation of BASE discs occurred after cell testing. Preliminary cell tests were also conducted with NaCF_3SO_3 in place of NaBF_4 .

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1. Introduction

In recent years, the growing interest in new aspects of energy technology has provided a strong stimulus for the investigation and development of high temperature batteries. Rechargeable high-temperature battery technologies with metallic sodium anode are being explored for many large-scale energy-storage applications such as electric power generation and distribution (e.g. load leveling and peak shaving), powering motive devices (e.g. electric cars and buses) and space power [1]. The first high temperature battery near commercialization is the sodium/sulfur battery [2] which uses liquid sulfur as the positive electrode, liquid sodium as the negative electrode and sodium β'' -alumina solid electrolyte (BASE). Later developments included the ZEBRA battery [3] which uses nickel chloride as cathode. The operating temperature of both these systems is about 300 °C.

BASE is a sodium aluminate of approximate composition $\text{Na}_2\text{O}\cdot 6\text{Al}_2\text{O}_3$. It has a rhombohedral structure which, indexed as a hexagonal unit cell, comprises three aluminum–oxygen spinel blocks separated by loosely packed layers of oxygen and sodium ions [4]. These layers are linked to the blocks by bridging oxygen ions. In these planes are found the vacant sites available for the

migration of sodium ions, giving rise to a high two-dimensional conduction. The sodium ion conductivity of BASE at 300 °C is around $\sim 0.25 \text{ S cm}^{-1}$ while at 50 °C it is $\sim 0.01 \text{ S cm}^{-1}$. Because of the high sodium ion conductivity of BASE, it has become an important solid electrolyte for applications in high temperature batteries (sodium/sulfur, ZEBRA, etc.) and other devices such as the Alkali Metal Thermo Electric Converter (AMTEC). Also, BASE is stable in contact with a number of cathode materials as well as with liquid or solid or gaseous sodium.

The room temperature conductivity of BASE is higher than that of NASICON ($\text{Na}_{1+x}\text{Zr}_2\text{Si}_x\text{P}_{3-x}\text{O}_{12}$, with $0 < x < 3$), a well-known sodium superionic conductor [5]. The conductivity of NASICON of composition corresponding to $x = 2$ is $\sim 0.14 \text{ S cm}^{-1}$ at 300 °C, which is comparable to that of Na- β'' -alumina. However, NASICON is not stable in contact with molten Na. Good low temperature sodium ion conductivity coupled with good stability of BASE in oxidizing and reducing atmospheres makes possible many potential electrochemical devices including batteries.

In this communication, we report an electrochemical cell consisting of BASE with metal electrodes (copper–zinc electrochemical couples) in a polar aprotic solvent (DMSO). The cell was designed such that BASE functioned both as a separator and as a solid electrolyte between the anode and the cathode. The cell was subjected to charge–discharge cycling experiments at 100 °C. XRD and SEM analysis was performed to assess the stability of BASE before and after cell testing.

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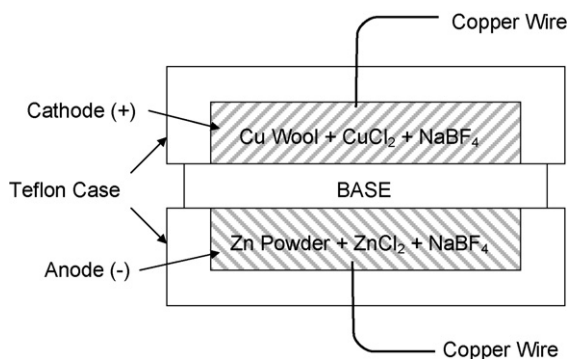


Fig. 1. Schematic representation of the cell.

2. Experimental

Sodium β'' -alumina discs were prepared using a vapor phase synthesis method [6]. Alpha alumina (CR 30 Baikowski International Corporation) 70% by volume and yttria stabilized zirconia (TZ-3Y, Tosoh corporation, 3 mol% Y_2O_3 -partially stabilized tetragonal zirconia) 30% by volume were mixed and dispersed in an aqueous medium of pH 10. The powder mixture was dried followed by ball milling in ethanol for 8 h. Subsequently, ethanol was removed by evaporation. The dried powder (Al_2O_3 + TZ-3Y) was ground, sieved and compacted to form circular discs by die-pressing uniaxially at ~ 70 MPa. The discs (0.15 cm thickness, 4.7 cm diameter) were sintered in air at $1600^\circ C$ for 1 h. The Al_2O_3 + TZ-3Y discs were then converted into β'' -alumina using a vapor phase process by placing the discs in a BASE packing powder (7.6% $NaAlO_2$, 1.2% $LiAlO_2$, 91.2% $\alpha-Al_2O_3$) in a ceramic 4-YSZ crucible and heat treating to $1450^\circ C$ for 2 h [6]. Yttria stabilized zirconia (TZ-3Y)

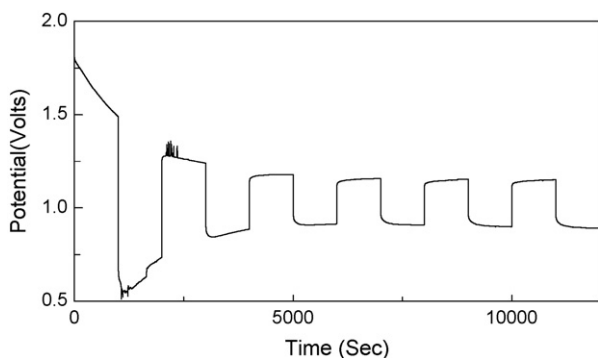


Fig. 2. Charge–discharge cycles for a cell with BASE at a constant current of 1.0 mA. Temperature = $100^\circ C$.

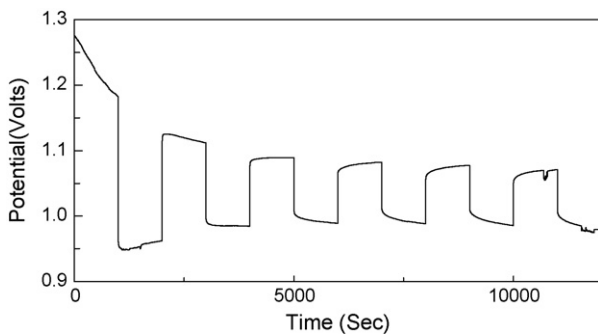


Fig. 3. Charge–discharge cycles for a cell using BASE modified with a porous BASE layer at a constant current of 1.0 mA. Temperature = $100^\circ C$.

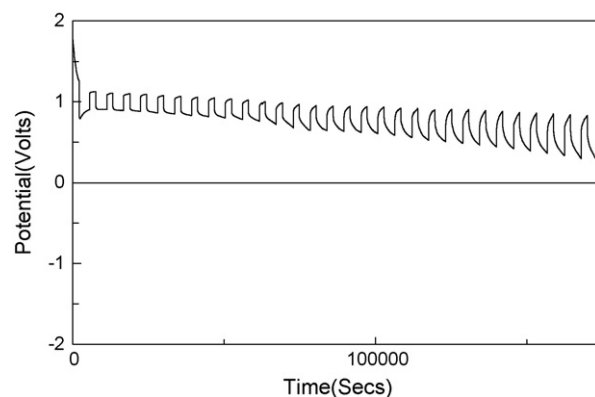


Fig. 4. Cycling behavior of a cell constructed using BASE modified with a porous BASE surface layer for 48 h at a constant current of 1.0 mA. Temperature = $100^\circ C$.

in the composite provides a path for oxygen ion diffusion during the vapor phase conversion of $\alpha-Al_2O_3$ to β'' -alumina [6]. It has been observed that in the vapor phase conversion of alpha alumina into β'' -alumina, no stabilizer such as Li_2O or MgO is required

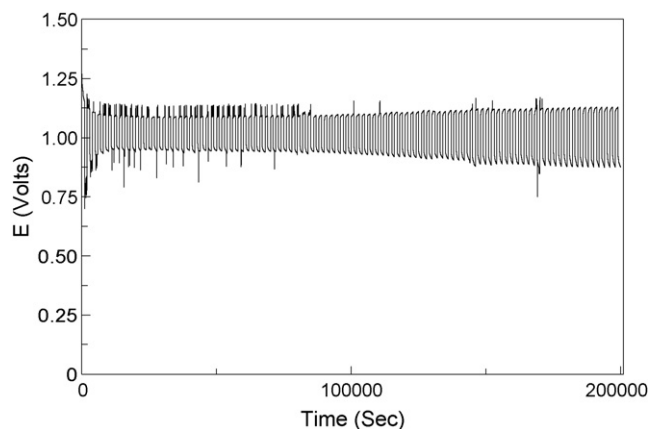


Fig. 5. Cycling behavior of a cell using BASE modified with a porous BASE surface layer and using 1 M $NaCF_3SO_3$ for 55.5 h at a constant current of 1.0 mA. Temperature = $100^\circ C$.

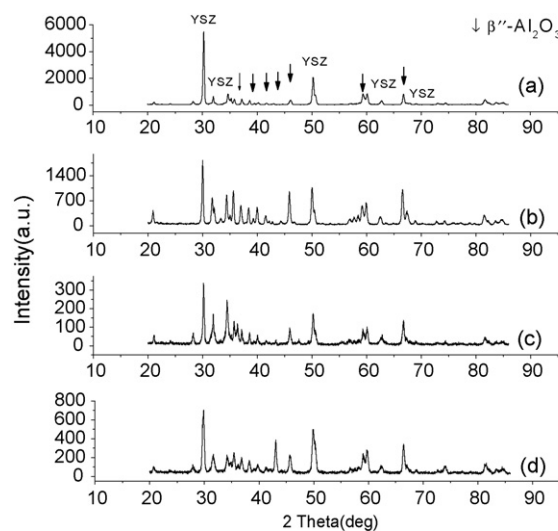


Fig. 6. XRD patterns of (a) BASE, (b) surface modified BASE, (c) surface of BASE in contact with Cu electrode and (d) surface of BASE in contact with Zn electrode.

unlike high temperature conventional processes [6]. This also suggests that perhaps the need for Li_2O or MgO as a stabilizer in the high temperature, conventional process may be related to processing rather than a structural requirement. The surfaces of some of the $\text{Al}_2\text{O}_3 + \text{TZ-3Y}$ discs were modified by applying a layer of 60% $\text{Al}_2\text{O}_3 + 40\%$ carbon. The discs were sintered at 1600°C in air for 1 h. The surface modified discs were also then converted to β'' -alumina by the procedure mentioned earlier. This leads to the formation a surface porous Na- β'' -alumina (BASE) layer on the BASE disc. This porous layer increases the electrolyte surface area per unit projected area, which effectively decreases activation polarization resistance. All chemicals, viz., Zn powder, Cu powder, ZnCl_2 , CuCl_2 , NaBF_4 , NaCF_3SO_3 and dimethyl sulfoxide (DMSO) (Alfa Aesar, USA) were used as received.

Two circular Teflon plates consisting of cavities containing cathode and anode materials with a BASE disc between the Teflon plates

as a separator, constituted the cell assembly. O-rings were used for sealing. The lower Teflon plate (anode) consisted of 25 g of Zn powder ($6\ \mu\text{m}$ median size) and 4 ml of 0.1 M ZnCl_2 (1 M NaBF_4 in DMSO) was the liquid electrolyte used to prepare the ZnCl_2 solution). The upper Teflon plate (cathode) consisted of 0.5 g of copper powder (-625 mesh), 4 ml of 0.1 M CuCl_2 (1M NaBF_4 in DMSO) and 2.75 g of copper wool. The BASE disc was placed between the upper and lower Teflon plates. Copper wires attached to the cathode and anode cavities served as electrical contacts. The schematic of the cell is shown in Fig. 1.

Galvanostatic charge–discharge experiments were performed using a Solartron electrochemical analyzer (model SI-1287). X-ray diffraction studies were carried out on a Philips X'Pert PW3040 diffractometer with $\text{Cu K}\alpha$ radiation and a graphite monochromator at 45 kV and 40 mA. Scanning electron micrographs were obtained using a Hitachi S-3000 N scanning electron microscope (SEM).

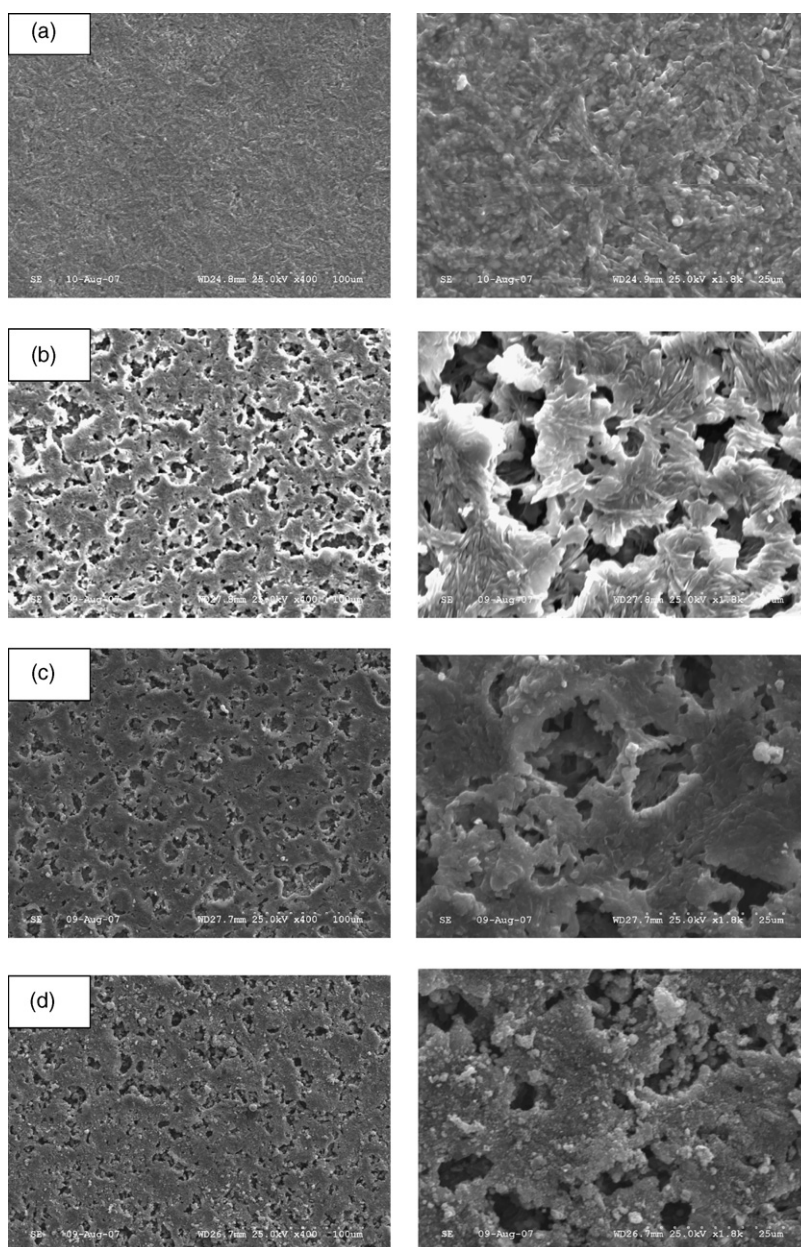


Fig. 7. SEM images of (a) BASE, (b) surface modified BASE, (c) surface of BASE in contact with Zn electrode, and (d) surface of BASE in contact with Cu electrode. SEM images on the left side are at a magnification of 400 \times . The figures on the right side are the corresponding images at a magnification of 1800 \times .

3. Results and discussion

The configuration of the electrochemical cell used is given as:

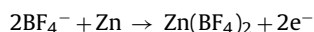
Zn(s)/ZnCl₂(DMSO)(0.1 M), NaBF₄(1 M)/BASE/NaBF₄(1 M),

CuCl₂(DMSO)(0.1 M)/Cu(s)

The corresponding open circuit voltage of the cell at 25 °C was $E = 1.05$ V.

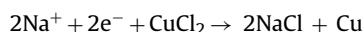
The half cell reactions are as follows:

Zn electrode:

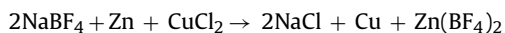


2Na⁺ transport through the BASE, 2e⁻ transport through the external circuit.

Cu electrode:



The net cell reaction is:



NaBF₄ was used as the salt because of good thermal stability of tetrafluoro borate anions. The cell was subjected to constant current charge–discharge cycling at 100 °C. Fig. 2 shows the cycling behavior of the cell with BASE disc at a constant current of 1.0 mA for 3.3 h at 100 °C. The charge and discharge voltage profiles are symmetrical indicating that sodium ion insertion and de-insertion through BASE is essentially reversible. A total cell resistance of ~130.0 Ω was calculated at an applied constant current of 1.0 mA at the end of 3.3 h for a contact area of 7.50 cm² of BASE. The high cell resistance in comparison to the resistance of BASE (2.0 Ω calculated from the area, thickness and conductivity of the BASE disc) is mainly attributed to the interfacial resistance for transfer of Na⁺ ions across non-aqueous solvent (DMSO)/BASE interface and also possibly due to the insufficient contact at the solid electrolyte/electrode interface, a problem associated with battery systems employing solid electrolytes [7,8].

The contact area between BASE and the electrodes was increased by modifying surfaces of both sides of BASE by incorporating porous BASE layers. A cell with a surface modified BASE was constructed and subjected to charge–discharge cycling experiments at 1.0 mA. Fig. 3 shows the cycling behavior of the cell constructed with surface modified BASE. The shapes of charge and discharge curves are similar to those in Fig. 2. A cell resistance of ~50.0 Ω was obtained at an applied current of 1.0 mA at the end of 3.3 h for a contact area of 7.5 cm² of BASE. This appreciable decrease in cell resistance compared to that obtained for the cell employing unmodified BASE indicates that contact at BASE/electrode interface was improved due to the porous BASE layer on the surface of BASE. Several analyses of the role of porous surfaces in improving electrocatalysis have been reported [9–11]. The present results are in accord with these predictions on the role of porous surface layers.

A cell with surface modified BASE was subjected to long-term cycling at a constant current of 1.0 mA for 1 h discharge time at 100 °C (Fig. 4). A resistance of ~100 Ω was obtained at the end of second cycle (after 3 h). At the end of ~25 h, the cell resistance increased to ~150 Ω. After 48 h of cycling, the cell resistance was ~290 Ω. The increase in resistance is primarily attributed to extraneous factors such as loss of contact in the electrodes or the

leakage/evaporation of the liquid from the electrodes through the seals.

In a preliminary investigation with 1 M NaCF₃SO₃ (sodium trifluoromethanesulfonate) in DMSO as liquid electrolyte instead of 1 M NaBF₄ in DMSO, it was found that the cell resistance was ~120.0 Ω at the end of 48.0 h of cycling (Fig. 5). Also the cell resistance was ~130.0 Ω at the end of 55.5 h. Fig. 5 shows that the cell exhibited stable performance over the duration of the test.

The stability of BASE after long term cycling was examined using XRD analysis and SEM. Fig. 6(a) shows an XRD pattern of BASE before cycling. Peaks corresponding to the β'-alumina phase are identified in the figure. Fig. 6(b) shows an XRD pattern of porous BASE layer of the modified BASE before cycling. Fig. 6(c) and (d) are the XRD patterns of surface modified BASE exposed to Cu and Zn electrodes, respectively. Absence of any additional peaks shows that BASE remained stable even after cycling for 48 h and also that BASE did not undergo any reaction with the electrodes and DMSO.

SEM images were obtained to determine whether BASE had undergone any morphological changes after cell testing. Fig. 7(a) and (b) are SEM images of the surfaces of BASE discs without and with porous surface layers prior to cell testing. It is seen that surface modified BASE has a porous structure (40% porosity) when compared to unmodified BASE. Fig. 7(c) and (d) correspond respectively to the images corresponding to Cu and Zn electrodes exposed surfaces of BASE after cycling. The images show that no detectable morphological changes occurred on either side of the BASE discs. XRD and SEM studies thus showed that BASE exhibits excellent stability.

4. Conclusions

Electrochemical cells with copper–zinc couples and BASE were designed, constructed and tested at 100 °C. The cells exhibited good cycling behavior. Also, BASE was found to be stable even after 48 h of cycling. The high cell resistance in comparison to the resistance of BASE was attributed to the interfacial resistance for transfer of Na⁺ ions across non-aqueous solvent/BASE interface. The surface modified BASE comprising porous BASE layers exhibited lower cell resistance indicating that porous BASE surface layers decreased the interfacial resistance. The present work shows that BASE may be used as a solid electrolyte for electrochemical cells such as the Daniell-type cell in which the active species, copper and zinc, are different from mobile ion in BASE namely sodium.

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