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Interfacial electric properties of beta″-alumina and electrode by AC impedance

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Abstract

In order to enhance cell power density and to study the interfacial electric property between beta″-alumina and an electrode, test cells of Na(l)/beta″-alumina/M, where M = TiN or TiB_2 or Na–Sn or Na–Pb molten alloys as electrode materials, were set up and run within the temperature range of 400°–800°C. The performance of the test cells and the interfacial electric properties were investigated by measuring current–voltage characteristics and AC impedance. The maximum power density of 0.18 W cm^{-2} for TiN and 0.24 W cm^{-2} for TiB_2 could be achieved with a large electrode-area of 30 cm^2 at 800°C. A simplified model and equivalent circuit were given, based on the impedance data. The effect of microstructure of the porous electrode and roughness of the beta″-tube on the cell electric performance and impedance has been studied and discussed. The electron-transport through the porous electrode to the interface of the electrode and the beta″-tube surface is the control step for the electrode reaction, $Na^+ + e \rightarrow Na$, rather than the mass-transport step, for a cell of Na(l)/beta″-alumina/porous thin film electrode. The AC impedance data demonstrated that wetting of the beta″-alumina electrolyte plays an important roll in reducing the cell resistance for the molten Na–Sn or Na–Pb electrode, and the molten alloy electrodes have a smaller cell-resistance, 0.3–0.35 Ω cm^2, at 700°C after 10–20 h. The comparison with sputtered thin, porous film electrodes, showed that the microstructure and thickness of electrode, and the interfacial resistance between electrode and the surface of the beta″-alumina is crucial to enhance cell power density.

Keywords: Beta″-alumina; AC impedance; Interfacial electric properties

1. Introduction

Beta″-alumina has been extensively studied in the last three decades due to its potential applications such as electrochemical sensors, and particularly, as a high energy battery—sodium sulphur battery for electric vehicles [1,2]. Another application for heat–electricity converter is the Alkali Metal Thermoelectric Converter (AMTEC). AMTEC is a system, in which beta″-alumina acts as a solid state electrolyte and sodium is used as working medium, for direct conversion of heat into electricity [3–6]. Its main advantages are high efficiency, high power density, modular design, low maintenance and low manufacturing cost. An AMTEC cell with an efficiency of 19% [7,8], lifetimes to 10,000 h [4,5], and cell power destiny to 1 W cm^{-2} [9] has been reported.

The AMTEC essentially consists of two compartments (Fig. 1): a high-pressure compartment, where sodium is heated by suitable heat source to 500 to 1000°C and a low-pressure compartment, where sodium vapour is condensed at a temperature of about 300°C, corresponding to a saturated vapour pressure of about 10^{-5} bar. In principle, electricity is generated in the AMTEC based on sodium ions transport from the high-pressure to the low-pressure compartment through beta″-alumina electrolyte, while electrons flow through the load, delivering suitable electric power. The driving force for this process is the pressure difference between the two compartments. Separation and recombination of ions and electrons take place at electrodes on both sides of the solid state electrolyte.

The electrodes play a very important role in electrochemical process of the AMTEC. The anode is normally liquid sodium metal itself, and the cathode is often prepared using materials with high melt point, good electric conductivity and high electrochemical corrosion resistance. In order to improve the stability of electric power output

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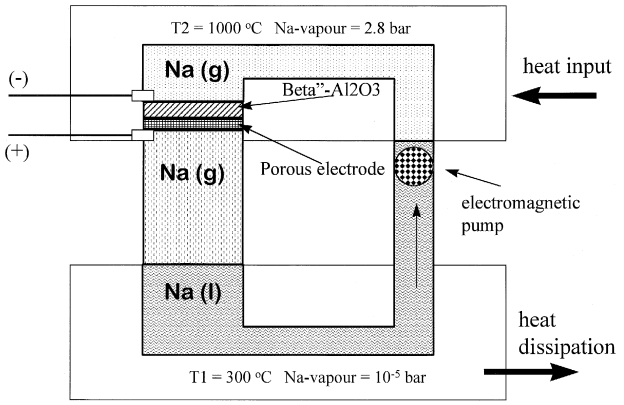

Fig. 1. Schematic diagram of the principle of the AMTEC.

and electrochemistry, the AMTEC study with TiN, TiB_2 thin films as electrodes has been carried out [10–12]. The results from sputtered Mo, TiN or TiB_2 thin-film electrodes indicated that the power density of a AMTEC cell depends not only on thickness, porosity and electric conductivity of the thin film used, but also on the contact between the electrode and the electrolyte, and the connection of the electrode and the electricity collector [13,14]. The contact-interface resistance has a strong influence on the electric power density for the AMTEC cell.

Use of the polycrystalline sodium beta″-alumina ceramic as a solid state electrolyte for the sodium sulphur battery or AMTEC, requires consideration of not only the effects of the interior of the grains and grain boundaries, but also the effects of the electrode and interface between the electrode and the ceramic materials. This work is an attempt to determine the electrical properties of a sodium/beta″-alumina/electrode test cell and the contributions of the electrolyte, electrode and interface between the electrode and the beta″-alumina ceramic by impedance spectroscopy and current–voltage curves. Previous work using molten alloy Na–Sn and Na–Pb as electrode materials in order to study the contact- and interface-impedance of an AMTEC cell has been reported [15]. The aims of this work are mainly to investigate the impedance data and electric properties of different electrode materials, to assess the performance of AMTEC-cells with different electrode materials, to determine the influence of the contact- and interface-impedance between the electrode and the electrolyte and of the electrode itself and to look for a new route to enhance AMTEC-cell power density.

2. Experimental details

2.1. Beta″-alumina ceramic electrolyte tubes

The beta″-alumina tube of 25-mm diameter and 200-mm length, with a 1.3-mm wall thickness were obtained from BAT, ABB, Germany.

2.2. Electrode materials

TiN and TiB_2 were chosen as electrode materials for investigating a sodium gas cell. The TiN and TiB_2 electrode thin films were deposited onto the beta″-alumina tube using a magnetic sputtering technique with a TiN and a TiB_2 target, respectively. The sputtering power was 500 W at an Ar pressure of 8×10^{-3} mbar. The two sputtered electrode thin films show a similar columnar microstructure, which is important for sodium flow through the cathode. The thickness was varied from 0.2 to 10 μm for TiN and from 0.5 to 4 μm for TiB_2, and the area on to which the electrode materials were sputtered was 30 cm^2.

The sodium alloys were prepared by the following two methods: (1) ex situ using pure sodium and tin or lead in a nitrogen atmosphere and; (2) in situ by a coulometric transfer of sodium through the cell into pure molten Sn or Pb metal.

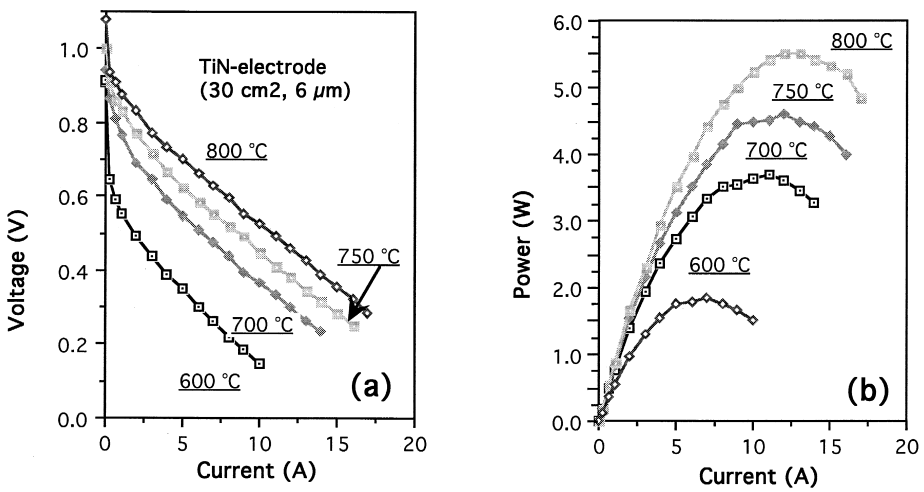

Fig. 2. Current–voltage and current–power curves of TiN electrode at different temperatures.

2.3. Test cells

The tubes with different electrodes were tested in special cell arrangements. The details of the test cells can be found elsewhere [10–15]. Current–voltage curves were measured under steady state condition in a temperature range from 500–800°C. The cell impedance was determined by a commercial impedance spectrometer with potentiostatic control (Zahner Electronic IM 5d, Germany).

3. Results and discussion

3.1. Na(l) / beta″-Al_2O_3 / porous thin film electrode

The current–voltage relationship and the corresponding current–power curves at different temperatures for the TiN electrode are shown in Fig. 2. It can be seen that a maximum power density of 0.18 W cm^{-2} could be achieved with a large electrode-area of 30 cm^2 at 800°C.

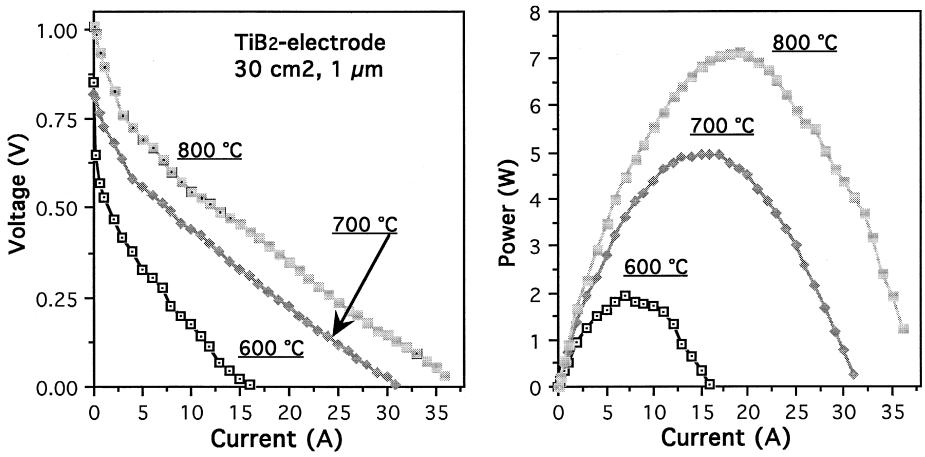

Fig. 3. Current–voltage and current–power curves of TiB_2 electrode at different temperatures.

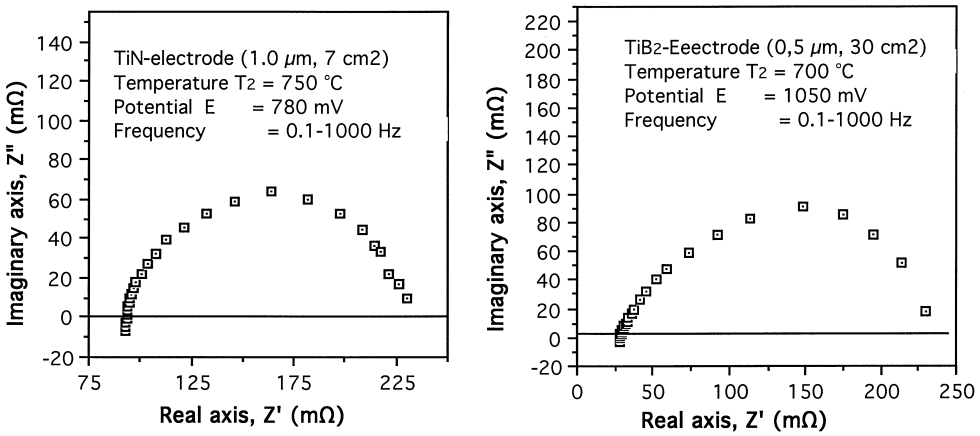

Fig. 4. Typical complex plane plots of impedance data of TiN and TiB_2 electrodes.

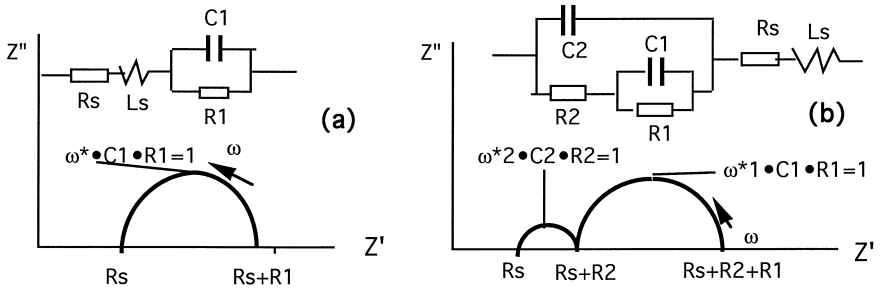

Fig. 5. Equivalent circuit for AMTEC Na–gas cell: (a) four parameters; (b) six parameters.

Fig. 3 shows the current–voltage and the corresponding current–power curves for the TiB_2 electrode at different temperatures. Maximum current density and maximum power density were 1.3 A cm^{-2} and 0.24 W cm^{-2}, respectively.

The impedance measurements were carried out for test cells with different electrode materials. Fig. 4 shows typical complex plane plots of impedance data for TiB_2 and TiN electrodes at open circuit. These complex plane plots have similar features in that the impedance spectrum consists of a flatted half-circle, which can be considered as an RC-loop with a resistance and an inductance (Fig. 5a). This series inductance, which results from the electrode as well as the wrapped Mo-wire used as a current collector, is independent of the measuring potential. According to the impedance measurements of the test cell, an equivalent circuit for the Na–gas cell is shown in Fig. 5b, where L_s is a series inductance, R_s is a series resistance. Sodium ionic charge is considered to pass easily through the grain and the grain boundaries in beta″-alumina, the resistance and dielectric properties of the interface between beta″-alumina and electrode are described by C_2, R_2. The R_1C_1-loop represents the impedance contribution from a porous electrode. As a simplified model of this work, it is convenient to ignore the contribution of the crystal grain interior and the interface between electrode and current collector, but in practice, the contact between electrode and current collector plays an important role to enhance the cell performance [13,14].

Values of interfacial capacitance and both kinetic and mass-transport parameters were obtained from the impedance data of two thin, porous TiN and TiB_2 electrodes and of Na–M melted alloy electrodes over large temperature ranges. Using the simplified model of the equivalent circuit above, impedance data was fit to Bode or complex plane plots. Typical impedance data of TiN and TiB_2 are shown in Fig. 6. Data for TiB_2 are shown in Table 1. The results reveal that the frequency and potential dependence are useful in evaluating detailed models of the properties of the electrode/beta″-ceramics interface and of the porous electrode itself.

Table 1
Impedance data of TiB_2-electrode (3.9 cm^2; 1 μm; T_2 = 750°C)

Potential (V)	1.043	0.843	0.740	0.710
Voltage (V)	1.043	0.800	0.600	0.500
Current (A cm^{-2})	0.0003	0.0411	0.1328	0.2002
R_s (Ω cm^2)	0.600	0.588	0.582	0.577
L_s (μH cm^2)	1.4	1.4	1.4	1.4
R_1 (Ω cm^2)	1.920	0.504	0.208	0.158
C_1 (mF cm^{-2})	29.00	27.59	19.51	15.82
R_2 (Ω cm^2)	12.195	1.533	0.486	0.337
C_2 (mF cm^{-2})	65.31	82.59	90.31	87.59

The magnetic sputter parameters such as sputtering power, Ar pressure and the morphology of the beta″-alumina surface have a strong influence on the microstructure of the porous electrode [11]. The effect of microstructure of the electrode on the electric performance can be investigated by AC impedance measurements and current–voltage curves. Table 2 shows the measured data for TiB_2 thin electrodes, which were prepared in different Ar-pressures from 5×10^{-3} mbar to 1.6×10^{-2} mbar, the thickness of the TiB_2 electrode films were 0.5 μm. The resistances R_1, R_2, and the capacitance decrease with the decreasing Ar-pressure. Suppose the resistance and the capacitance here are directly stated to the microstructures (grain size, porosity and interface area) of the electrodes and thus, to the interface of the electrode and the beta″alumina-tube surface, then the fact that the poorer cell electric performance comes with an electrode sputtered at a higher sputtering pressure, in which the electrode thin film with higher porosity is deposited, shows that the electron-transport through the porous electrode to the interface of the electrode and the beta″alumina-tube surface is the control step for the electrode reaction, $Na^+ + e \rightarrow Na$, rather than mass-transport step. It has been reported that the maximum thickness of TiB_2 and TiN thin film for

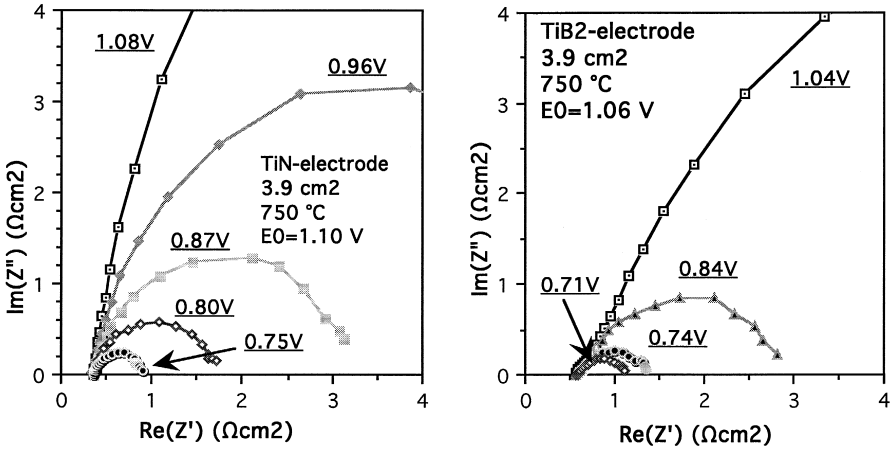

Fig. 6. Complex plane plots of impedance data of TiN and TiB_2 electrodes using different measuring voltages.

Table 2
Impedance data of the test cell with TiB_2-electrode sputtered under different Ar-pressures

Cell number	B-9	B-6	B-8
Ar-pressure (mbar)	1.6×10^{-2}	8×10^{-3}	5×10^{-3}
R_s (Ω cm^2)	0.93	0.87	0.89
L_s (μH cm^2)	3.09	3.29	3.04
R_1 (Ω cm^2)	2.12	1.51	0.84
C_1 (mF cm^{-2})	26.00	11.42	6.11
R_2 (Ω cm^2)	5.85	4.17	2.65
C_2 (mF cm^{-2})	79.50	27.6	22.86
Maximum power density (W cm^{-2})	0.13	0.17	0.18

maximum power output is up to 3.0 μm and 10 μm, respectively [12].

The effect of roughness of beta″alumina-tube on the cell electric performance is shown in Table 3. 'As-received' beta″-alumina (B6) tube has a roughness of about 15 μm. One cell test was also carried out with a TiB_2 thin film (0.5 μm) on a polished beta″alumina-tube. The roughness of the polished beta″alumina-tube (B11) was about 2–3 μm. The result shows that the maximum power output of the polished beta″alumina-tube cell is smaller than that of normal one. Though the polished beta″alumina-tube can reduce the surface resistance (from 36 to 30 Ω cm^{-1}), the decreased interface contact area between electrode and electrolyte leads to bigger resistances R_1, R_2, and smaller capacitances C_1 and C_2, which result in a smaller power output from the test cell.

3.2. Na(l) / beta″-alumina / Na–M (M = Sn, Pb) cells

It is worth noting that the wetting of the solid state electrolyte by molten metals (Sn or Pb) or molten alloys is of highest importance. The relatively high impedance of the cell which is measured immediately after set-up of the cell shows that in the beginning the beta″-alumina tube is only poorly wetted. A better wetting of the electrolyte tube and a lower contact-resistance between electrolyte and molten electrode would be obtained by longer heating or by flowing current for a longer time of cell operation. Table 4 shows the wetting effect, in which the cell-impedance measurements were carried out at 700°C after the new cell was set up.

Table 3
Impedance data of the test cell of TiB_2-electrode with different roughness

Number	B-11	B-6
Ar-pressure (mbar) (mbar)	8×10^{-3}	8×10^{-3}
R_s (Ω cm^2)	0.90	0.87
L_s (μH cm^2)	3.02	3.29
R_1 (Ω cm^2)	1.53	1.51
C_1 (mF cm^{-2})	10.67	11.42
R_2 (Ω cm^2)	5.87	4.17
C_2 (mF cm^{-2})	21.14	27.16
$R_{surface}$ (Ω cm^{-1})	30	36
Maximum power density (W cm^{-2})	0.153	0.17

Table 4
Contact-resistance of the cell with molten Na–Sn and Na–Pb electrode by 700°C

Time (min)	5	30	60	120	180	240	300
R_c of Sn (Ω cm^2)	1.10	0.80	0.65	0.58	0.50	0.48	0.48
R_c of Pb (Ω cm^2)	1.20	1.00	0.85	0.76	0.68	0.65	0.64

The electrode process with Na–Me molten electrode is relatively simple, compared with the electrode process in a porous, thin film electrode, which includes interfacial transfer of Na^+ ions, electrochemical reaction and diffusion of Na–gas in the holes of the electrode. The impedance spectrum of a test cell with a molten Na–M electrode is also simple. Since the interface capacitance is very small, the impedance is only an ohmic resistance. This resistance is the sum of the ohmic resistance of the electrolyte and the interfacial charge transfer resistance. The resistance (impedance) depends on the temperature and the current density, but is almost independent of the Na concentration in the Na–M alloy. The cell resistance for various molten alloy electrodes are definitely different at lower temperature but they become practically the same in all cases by 700°C (resistance range 0.3–0.35 Ω cm^2).

The maximum power density and cell-resistance for an AMTEC cell with an Na–M electrode are strongly dependent on the Na-concentration in the Na–M electrode. The maximum power density for 0.5 mol% Na and 700°C for Na–Pb electrode reaches 0.30 W cm^{-2}, while for Na–Sn electrode the maximum power density for 0.5 mol% Na and 700°C is 0.21 W cm^{-2}. The maximum power densities decrease with the increasing Na-concentration. These maximum power densities for Na–Me alloy electrodes are comparable with, or better than, that for the sputtered Mo and TiB_2 electrodes, in which it is just 0.13 W cm^{-2} and 0.17 W cm^{-2} at 700°C, respectively. The fact, that AMTEC with a molten alloy electrode has good power density, is mainly due the lower interface resistance. Cell resistances of 0.75, 0.66 and 0.51 Ω cm^2 for TiN, Mo and TiB_2 sputtered porous electrodes at 800°C have been reported [11,12].

4. Conclusions

Test cells Na(l)/beta″-alumina/M, where M = TiN or TiB_2 with Na–Sn or Na–Pb, as electrode materials, were set up and run with temperature range of 400°–800°C. The performance of the test cell and the interfacial electric properties were investigated by measuring current–voltage characteristics and AC impedance. The maximum power density of 0.18 W cm^{-2} for TiN and 0.24 W cm^{-2} for TiB_2 could be achieved with a large electrode-area of 30 cm^2 at 800°C. A simplified model and equivalent circuit

was given, based on the impedance data. The effect of microstructure of the porous electrode, roughness of beta″alumina-tube on the cell electric performance and impedance has been studied and discussed. Electron-transport through the porous electrode to the interface of the electrode and the beta″alumina-tube surface is the control step for the electrode reaction, $Na^+ + e^- \rightarrow Na$, rather than mass-transport step for a cell of Na(l)/beta″-alumina/porous thin film electrode. The AC impedance data demonstrated that wetting of the beta″-alumina electrolyte plays an important roll in reducing the cell resistance for molten Na–Sn or Na–Pb electrodes, and the molten alloy electrodes have a smaller cell-resistance, 0.3–0.35 Ω cm^2 at 700°C after 10–20 h. The comparison with the sputtered thin, porous film electrodes, showed that the microstructure and thickness of the electrode, and the interfacial resistance between the electrode and the surface of beta″-alumina is crucial to enhance cell power density.

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