

Ionic conductivity of undoped BaTiO_{3-δ} with electron transfer suppressed

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Abstract

Ionic conductivity has been directly measured on “undoped” BaTiO_{3-δ} over a temperature range of 550 to 1000 °C with the aid of a modified electron-blocking cell. The modified cell could eliminate or greatly suppress or circumvent the haunting annoying artifacts associated with gas leak, reaction of a sample with an electron-blocking electrode or sealing glass, and large interfacial resistances in a conventional two-probe electron-blocking cell. The ionic conductivity of undoped BaTiO_{3-δ} in the stoichiometric regime ($\delta \approx 0$) may best be represented depending on temperature range as:

$$\sigma_{\text{ion}} / \text{Scm}^{-1} = (6.6 \times 10^5 / T) \exp(-1.58 \text{ eV} / kT) \quad \text{for } T \geq 1073 \text{ K};$$

$$\sigma_{\text{ion}} / \text{Scm}^{-1} = (1.20 \times 10^7 / T) \exp(-1.83 \text{ eV} / kT) \quad \text{for } T < 1073 \text{ K}.$$

It is indicated that association (with an association enthalpy of 0.25 eV) occurs between carrier oxygen vacancies and the charge compensating acceptor species, whether extrinsic or intrinsic, at temperatures below 1073 K. The higher temperature result is in good agreement with those obtained indirectly from the identical quality specimens. The chemical diffusivity has been determined from the temporal change of the cell voltage under a galvanostatic condition and is also in satisfactory agreement with the earlier study.

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1. Introduction

Perovskite-type oxides ABO₃ have been attracting lots of attention due to their wide variety of interesting properties such as ferroelectricity [1], electrical conductivity [2], magnetic property [3], and catalytic property [4] to name only a few. They are now in use or further development as dielectrics, ferroelectrics, piezoelectrics, superconductors, thermoelectrics, oxide ion and/or proton conductors, mixed ionic electronic conductors, etc.

BaTiO₃ (abbreviated henceforth as BT) is a representative prototype of this family, which turns to a mixed ionic electronic conductor at elevated temperatures. Due to its

technological importance, e.g., as the basic substance of multilayer ceramic capacitors (MLCC) and positive temperature coefficient resistors (PTCR), its defect structure and mass/charge transport properties have been extensively investigated during the past three decades [5]. Nevertheless, the information on its partial ionic conductivity is still very sparse: the ionic conductivities have so far been reported on undoped and Al-doped BT by two research groups [6–9]. Furthermore, all these data were obtained in an indirect manner, i.e., by fitting the total conductivity data against oxygen activity to a defect-chemical model. Such fitting is unavoidably based on assumptions, e.g., the majority type of disorder and hence, likely affected by the choice of adjustable defect-chemical parameters. One may, thus, wish to directly measure the partial ionic conductivity of this mixed conducting oxide.

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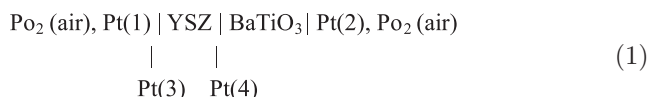
Direct measurement of the partial conductivity of minority charge carriers has been an important subject of solid state electrochemistry: Hebb [10] and Wagner [11] proposed a polarization technique in a dc field, in which only the minority carriers are allowed to migrate while the majority carriers are blocked by appropriate semi-blocking electrodes. This technique has since been widely applied to measure partial electronic conductivities of predominantly ionic conducting oxides, e.g., stabilized ZrO_2 [12] and most recently $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_{3-\delta}$ [13]. However, its application to the reciprocal case, i.e., measurement of the partial ionic conductivity of a predominantly electronic conductor oxide, is quite often subjected to complications mainly due to mechanical or electrochemical leak of gas oxygen, and interfacial reactions between the oxide specimen and blocking electrode material or glass that is used for sealing to prevent parasitic oxygen transport.

The purpose of the present work is to directly measure the ionic conductivity of undoped BaTiO_3 over as wide a temperature range as possible by the electron-blocking polarization technique. To this end, we have first modified the conventional two-probe electron-blocking cell in order to eliminate or if not, minimize or circumvent all those disturbing artifacts mentioned above. In this paper, we will report on the modifications of the conventional electron-blocking cell, the cell performance, the ionic conductivity, and a byproduct therefrom, chemical diffusivity. The latter will be exhaustively compared with the literature data.

2. Experimental

2.1. Cell modifications

Fig. 1 illustrates schematically the electron-blocking cell used in the present work, which may be represented as:



A conventional electron-blocking cell normally employs only two electrodes, say, Pt(1) and Pt(2), across which a current is passed as well as voltage monitored simultaneously or vice versa. In the present cell, two additional, potential probes Pt(3) and Pt(4) are attached across the electron-blocking electrode, YSZ (yttria-stabilized zirconia): Pt(3) is located on the same side of the YSZ as Pt(1), but spatially apart from it and Pt(4) between the specimen BT and the YSZ. By using these potential probes, one can measure the open-circuit voltage across the YSZ, which may be the least disturbed by IR -drops due to the current passing through the current probes, Pt(1) and Pt(2) (see below).

A porous Pt-paste is to be applied at the interface between the YSZ and BT in order to keep an intimate stick

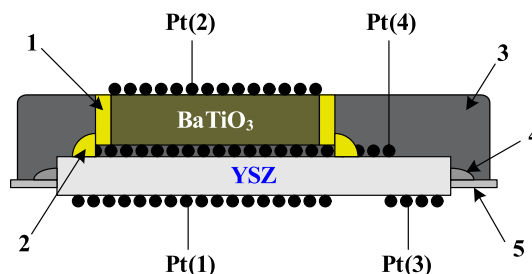


Fig. 1. Modifications of a conventional two-probe electron-blocking cell by employing two additional potential probes, Pt(3) and Pt(4), a porous Pt-layer between the specimen BaTiO_3 and electron-blocking YSZ. 1, Au-layer sputter-deposited; 2, Au-paste; 3, sealing glass; 4, alumina cement; 5, alumina plate.

between them while preventing possible reaction as well as facilitating the oxygen transfer between them. Furthermore, in order to prevent possible chemical reaction between the BT specimen and surrounding sealing glass, a thick layer of Au is to be sputtered onto the lateral surface of the BT, and then encapsulated with the sealing glass.

2.2. Cell preparation

The specimens were prepared from undoped BT powder of 99.995% purity (Lot 0517BW, Aldrich), the same powder which was used for the earlier study of chemical diffusivity [7,14]. According to the manufacturer's product information, the powder bears 5 ppm Fe, 5 ppm Si, and 1 ppm Al as the nonvolatile impurities. The powder, with 3 w/o PVA (poly-vinyl-alcohol) added, was pressed into disks, measuring 10 mm diameter \times 3 mm thickness, under a pressure of 200 MPa, followed by sintering at 1320 °C in air for 3 h. The as-sintered sample was ca. 96% dense with grains in a range of 30–50 μm and pure by X-ray diffractometry.

A sintered BT disk and a YSZ disk were polished to a fineness of 1 μm with assorted diamond pastes. Pt-paste (Engelhard, No. 5542) was lightly applied onto a polished face of the BT disk entirely that was to be in contact with the YSZ, and a Pt-mesh was attached to cover entire other surface with the aid of Pt-paste as a current probe, Pt(2). As the current probe Pt(1), Pt-paste was applied onto a polished surface of the YSZ and spatially apart from it a potential probe Pt(3).

Cell (1) was then constructed as follows: at first, the BT disk and YSZ disk as such were brought into intimate contact by firing together at 1000 °C for 6 h. A thick dense layer of Au was subsequently sputtered onto the lateral sides of BT. A thick layer of Au-paste was then applied additionally along the periphery of the interface between the BT and YSZ. This supplement of Au-paste has turned out to be crucial to the appropriate performance of the cell (see Section 3.4). A 0.2 mm thick Pt wire acting as the potential probe Pt(4) was attached to an extension of the Pt paste located between the BT and YSZ with the aid of Pt-paste by firing at 900 °C for 3 h. Finally all the space in the surrounding of the BT and YSZ was completely filled with a sealing glass.

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