Moving boundary diffusion problem for hydration kinetics evidenced in non-monotonic conductivity relaxations of proton conducting perovskites

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ABSTRACT

A high temperature van der Pauw method using a bulk disk sample was applied for a more reliable kinetic investigation in a protonic ceramic conductor, barium zirconate doped with 20 m/o yttrium. Similarly activated faster hydrogenation and slower oxygenation process can be explained by the moving boundary diffusion mechanism previously evidenced by in-situ optical spectroscopy where the hydrogenation kinetics is limited by the hydration front. The mechanism generally applies to all protonic ceramic conductors exhibiting non-monotonic conductivity relaxations. Defect-chemical consideration on the humidity, oxygen activity and temperature dependence of chemical diffusivities is provided.

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1. Introduction

Bar geometry is usually employed for 4-probe conductivity measurements of bulk samples, whereas the van der Pauw (vdP) method [1] is applied for thin samples of a finite size. For both cases the position, geometry, and the reversibility of the electrodes are important for accurate conductivity measurements. The vdP method can provide an accurate conductivity for the thick samples as long as the electrodes are applied along the entire thicknesses [2,3].

The average conductivity perpendicular to the direction of the concentration gradients has been used to monitor in-situ the integral variation in the charge carrier concentrations by the oxygen or water incorporation, which is known as the electrical conductivity relaxation (ECR) method. Bar geometry samples have been so far mostly employed where the mass transport can be approximated as two-dimensional diffusion in the rectangular cross section.

ECR by the vdP method for the planar samples has been previously reported by Preis et al. [4]. In the present work a high temperature vdP setup for the ECR experiments using disk shape samples was designed. As-prepared disk samples can be directly used with minimal machining. The four symmetrically positioned lateral electrodes were securely attached using alumina parts connected with springs at cold ends, thus infinitely small size of electrodes at the periphery was ensured. Two gas outlets close to the sample surface at both sides should ensure the symmetrical one-dimensional diffusion process as close as possible. A large surface area also allows a surface modification for the facile surface reaction control, as long as the sheet resistance of the coated layer is sufficiently large. The measurements were automated so that the eight resistance measurements for more reliable average conductivity effects were made within 36 s. The method can be thus used for the oxidation/reduction kinetics in nonstoichiometric oxides, which has been so far mostly performed using conventional bar-geometry samples, with prospects of better controlled surface reactivity and diffusion path. Au paste and wires were applied to minimize the in/excorporation at the electrodes.

Since the first reports on water incorporation kinetics in an Fe–SrTiO$_{3-\delta}$ single crystal by Yu et al. [5,6], and in Yb-doped ScCeO$_{3-\delta}$ polycrystal [7], non-monotonic conductivity relaxations have been confirmed as general phenomena for the proton ceramic conductors in perovskite or related structure in *p*-type oxidized regime [8–15]. The relaxation has been modeled as the superposition of the decoupled hydrogen and oxygen diffusion, although the spatially-resolved optical spectroscopy on Fe–SrTiO$_{3-\delta}$ single crystals revealed, a rather involved but realistic moving boundary diffusion phenomena [5,6], viz., the faster hydrogen in-diffusion proceeding from the hydration front developing into the sample, not from the sample surface.

In this work the high temperature vdP method was applied for the hydration/dehydration kinetics in a 20 m/o yttrium-doped $BaZrO_{3-\delta}$ (BZY) system in oxygen atmosphere. Dense BZY disk samples were obtained by reactive sintering with NiO additive after Tong et al. [16,17]. The non-monotonic conductivity relaxation in BZY has been also recently performed by a conventional 4-probe method using bar geometry samples [9,10,18]. The present contribution reports that the non-monotonic kinetics observed by ECR measurements can be straightforwardly explained by such a moving boundary diffusion mechanism.

2. Experimental

Dense ceramic pellets of 20 mol% Y-doped $BaZrO_3$ (BZY) were prepared after Refs. [16,17]. Commercial powder $BaCO_3$ (99.8%, Alfa Aesar, USA), ZrO_2 (98%, Kojundo, Japan), Y_2O_3 (99.9%, Kojundo, Japan) and NiO (99%, Alfa Aesar, USA) were used. Raw powder mixtures with 1 wt.% of NiO were cold-isostatically pressed and sintered at 1400 °C for 24 h. The SEM image of Fig. 1 shows the dense microstructure with the grain size of ca. 2 μm and XRD indicates the presence of the small amount of the secondary phase, Fig. 2, as in the previous reports. The lattice constant of the as-sintered pellet was estimated as 0.4219 (± 0.0001) nm using XLAT software [19].

An as-prepared disk sample of diameter 15.5 mm was mirror-polished in a plane parallel of the thickness 1.3 mm. Four symmetrical grooves were made at the lateral side vertically along the thickness as shown in Fig. 3(a), thus ensuring the infinitely small size of the electrodes at the periphery required for the accurate estimation of the vdP conductivity [1]. The inner areas of the diameter ca. 10 mm of the top and bottom surfaces were thinly coated using a SEM Pt coater.

The disk sample was mounted on the high temperature van der Pauw setup. Two alumina disks with inner holes with four slits of the total extension slightly smaller than the BZY sample were used to hold securely the vdP disk sample together with the Au wire and paste across the sample thickness on the lateral side (Fig. 3(b)). The holder and sample disk stacks were pressed together using the three alumina support rods through the support disks. They are fixed mechanically using alumina stubs into the holes punched at the end of the rods on the sample side and by the springs at the cold side fixed on the stainless steel flange. The disk sample was exposed to the gas flow blown perpendicular to the surface symmetrically (Fig. 3(c)). A K-type thermocouple (TC) with an insulating sheath was put close to the sample and the four gold wires were carried by two 2-bore alumina tubes which are connected with the gold wires by tweezing near the sample. (The TC and alumina tubes are not shown in Fig. 3(c) for clarity.) As indicated in Fig. 3(b) six holes of the alumina support disks are used for aligning the TC and 2-hole tubes for the lead wires as well as the support rods.
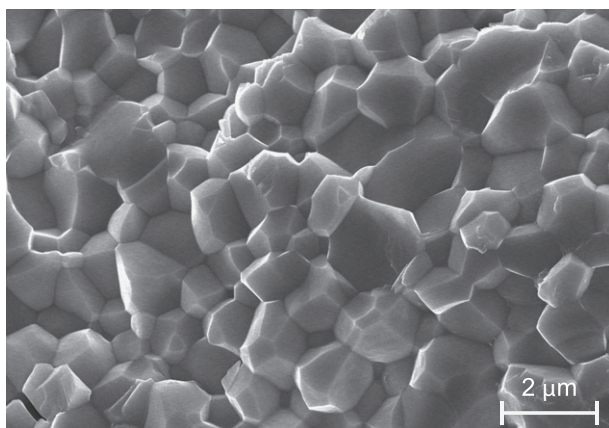

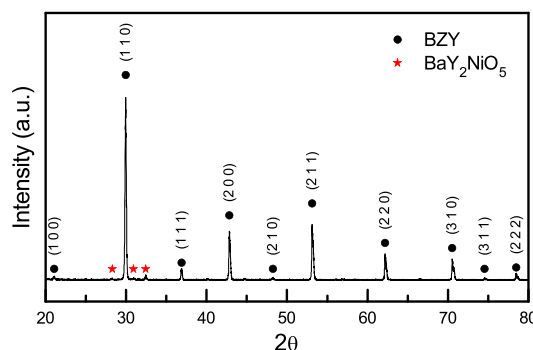**Fig. 1.** SEM image of BZY by reactive sintering with NiO additive.

Fig. 2. XRD of BZY by reactive sintering with NiO additive.

The conductivity was estimated by the automated full permutation of current and voltage probes and reversed polarity according to the standard van der Pauw method. A DMM with a scanner (Keithley 2700, 7700 channel card) and a current supply (Keithley 2400) was controlled by a Labview program. The single conductivity measurement takes 36 s. The conductivity was monitored as a function of time upon the change of the humidity in oxygen atmosphere at 700, 650, 600 °C. The humidity was controlled by flowing 50 sccm oxygen gas controlled by a mass flow controller (TSC210, NFS, Korea) through a bubbler with a glass filter in the water bath set at 17 °C as wet condition (2% H_2O) and by flowing dry oxygen (0.005% H_2O). The stainless steel tubes (1/8 in.) carrying the humid gas were heated above 30 °C using heating tapes. The humidity was in-situ monitored by a hygrometer (MI70, Vaisala, Finland). The gas line was divided before the measurement cell and directed symmetrically to the top and bottom of the disk sample as illustrated in Fig. 3(c).

3. Result and discussion

3.1. vdP conductivity measurements

For the cylindrical sample and symmetrical electrode geometry shown in Fig. 3(a), in an ideal situation, a single resistance measurement should be sufficient to evaluate the sheet resistance as

$$R_S = \frac{\pi R_{ij,kl}}{\ln 2} \tag{1}$$

where

$$R_{ij,kl} = V_{ij}/I_{kl} \tag{2}$$

with i, j, k, l being 1, 2, 3, 4 or 2, 3, 4, 1 etc. Since the current level is fixed at 0.1 mA, the resistance values correspond to the measured voltage values as $V = 0.1 \times R$ in mV, which are less than kT and should be considered small enough for the ohmic behavior. The symmetric geometry thus allows the faster monitoring of the accurate conductivity.

Fig. 4 shows, however, that the resistance values using the different combinations of the current leads and voltage probes and at different polarities are substantially different. The differences are much larger for the transient points of "d^*" or "w^*" indicated in Fig. 5(b) and (d) than for the equilibrated state in dry and wet conditions indicated by "d" and "w" indicated in Fig. 5(a) and (c). Such a large difference between measurements would not be acceptable for the accurate conductivity measurements of semiconductors or metallic conductors. However, for the high temperature mixed proton, oxygen, hole conductors as in the present work, substantially different contact resistances depending on the different blocking and catalytic degrees and due to the temperature inhomogeneity and the electrode geometry may not