Effect of NiO sintering-aid on hydration kinetics and defect-chemical parameters of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\triangle}$

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ABSTRACT

The influence of NiO, used as a sintering aid, on the transport properties of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\triangle}$ was investigated by monitoring electrical conductivity relaxation of specimens with and without NiO during hydration in atmospheres of different oxygen activities at 700 and 800 °C. The chemical diffusivities of H and O governing the kinetics were precisely evaluated from the transient conductivity, and all the defect-chemical parameters — the two external equilibrium constants and mobilities of all the carriers, $V_O^{\cdot\cdot}$, $H_i^{\cdot}$ and $h^{\cdot}$ — were determined from the steady-state equilibrium conductivity. It is found that the processing benefits afforded by NiO are accompanied by a significant reduction in ionic mobilities and hydration reaction constant. These factors, in turn, result in a smaller electrolytic regime in the presence of NiO than when it is absent.

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1. Introduction

Y-doped BaZrO$_3$, often dubbed BZY, displays the highest protonic conductivity of any known proton conducting oxide, along with excellent chemical stability. These characteristics render it highly attractive for fuel cell and other electrochemical applications [1]. The material is, however, notorious for its poor sinterability, and sintering temperatures in the 1600 to 1700 °C range along with long sintering times are typically required to achieve materials with high density and sufficiently large grains that the high impedance grain boundaries do not dominate the overall material resistance [2]. Sintering aids, specifically NiO, CuO and ZnO [3], have been shown to permit densification at substantially reduced temperatures. For example, introduction of just 1 wt.% NiO enables sintering to almost full density at a temperature as low as 1500 °C. In combination with reactive sintering approaches [2], sintering temperatures can be further reduced to ~1400 °C [4], effectively eliminating high-temperature processing and grain boundary resistance as obstacles to utilization of BZY in technological applications [1]. However, the effects of the sintering aid on transport properties and defect-chemical parameters, probably the most important aspects of protonic oxides, are not well known.
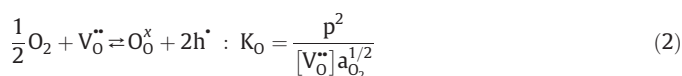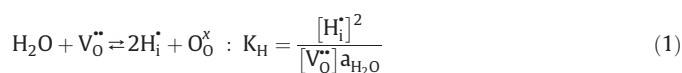
As a precursor to understanding the role of sintering aids, we recently examined the hydration kinetics and evaluated the diffusion coefficients of BaZr$_{0.8}$Y$_{0.2}$O$_{3-\triangle}$(BZY20) [5]. Here, from analogous hydration relaxation experiments performed on BZY20 prepared using 1 wt.%(=4.4 mol%) NiO, we determine not only the chemical diffusivities, but also all the defect-chemical parameters including hydration and oxidation reaction equilibrium constants and electrochemical mobilities of all the charge carriers of interest, and finally the electrolytic domain. These experiments and analyses permit a direct comparison of the impact of the NiO sintering aid. We begin by briefly introducing the methodology of determining the kinetic and defect-chemical parameters.

2. Methodology

2.1. Defect chemical parameters

The equilibrium defect structure of BZY20 may be described in the standard Kroger–Vink system of notation [6] as:

$$H_2O + V_O^{\cdot\cdot} \rightleftharpoons 2H_i^{\cdot} + O_O^x \quad : \quad K_H = \frac{[H_i^{\cdot}]^2}{[V_O^{\cdot\cdot}]a_{H_2O}} \tag{1}$$

$$\tfrac{1}{2}O_2 + V_O^{\cdot\cdot} \rightleftharpoons O_O^x + 2h^{\cdot} \quad : \quad K_O = \frac{p^2}{[V_O^{\cdot\cdot}]a_{O_2}^{1/2}} \tag{2}$$

$$2[V_O^{\cdot\cdot}] + [H_i^{\cdot}] + p \approx [Y_{Zr}'] \tag{3}$$

Here the K_R terms denote the equilibrium constants for the hydration ($R = H$) and oxidation ($R = O$) reactions. The defect $H_i^\bullet$ is an interstitial proton recognized to reside within the electron cloud of the oxygen ion and, accordingly, is often also denoted as $OH_O^\bullet$.

In the charge neutrality constraint, Eq. (3), the hole concentration p is typically neglected in the ranges of thermodynamic variables, temperature (T), water activity (a_{H_2O}) and oxygen activity (a_{O_2}), of practical interest [7–13]. However, it is now well-established [5] that, if the surroundings are not sufficiently reducing (e.g., $log a_{O_2} \leq -15$ at 700 °C), the hydration of barium zirconate proceeds via the decoupled two-fold chemical diffusion of H and O with mediation by holes. This indicates that the normal practice of neglecting p in Eq. (3) is not, in the general case, justified. Thermogravimetric measurements comparing weight gain under hydration by H_2O vs. that by D_2O also point to the importance of holes in the electroneutrality condition [14].

Given the concentration of the acceptor dopants $[Y_{Zr}'](=0.20)$, one can solve Eqs. (1)–(3) simultaneously to obtain a closed analytical solution for each defect concentration, [s] as a function of K_H, K_O, a_{O_2}, and a_{H_2O}. The partial conductivities are then, by definition, these concentrations multiplied by the corresponding electrochemical mobilities $\{u_s\}$ and charge. From the sum of these partial conductivities, one finally obtains the total conductivity σ in closed form as

$$\sigma = \sigma\left(a_{O_2}, a_{H_2O}; K_H, K_O, u_v, u_i, u_h\right) \qquad (4)$$

where the notation has been simplified by denoting the defect identities in the subscripts as $v(=V_O^{\bullet\bullet})$, $i(=H_i^\bullet)$ and $h(=h^\bullet)$.

This equilibrium total conductivity is easily determined as the steady state (final) value of the transient conductivity $\sigma(a_{H_2O}, a_{O_2}; t)$ as time $t \to \infty$, or $\sigma(a_{H_2O}, a_{O_2}; \infty)$ from the relaxation experiment. By spanning wide ranges in a_{H_2O} and a_{O_2} at a given temperature, one can evaluate the 5 defect-chemical parameters $\{K_H, K_O, u_v, u_i, u_h\}$ separately with satisfactory precision.

2.2. Kinetic parameters

As described elsewhere [5,15], the hydration kinetics of a protonic, mixed conducting oxide exposed to water chemical potential gradient $\nabla \mu_{H_2O}$ in a surrounding of uniform oxygen chemical potential ($\nabla \mu_O = 0$) are completely described by the thermodynamic equations of motion, given as:

$$J_s = -\widetilde{D}_{sH} \nabla c_s (s = v, i), \qquad (5)$$

where $\widetilde{D}_{sH}$ is the chemical (or ambipolar) diffusivity of species s exposed to a gradient in a_{H_2O}, indicated by the second subscript H; J_s and c_s denote, respectively, the chemical (or ambipolar) diffusion flux and concentration (in #/unit volume) of the defect species, s ($v = V_O^{\bullet\bullet}$; $i = H_i^\bullet$). Site and mass balance considerations require $J_O = -J_v$ (the flux of oxygen is opposite that of the flux of vacancies) and $J_H = J_i$ (the flux of hydrogen is equal to the flux of protons). The relevant chemical diffusivities are defined as

$$\widetilde{D}_{iH} \equiv \frac{\sigma_i(1-t_i)}{2F^2}\left(\frac{\partial \mu_{H_2O}}{\partial c_i}\right)_{\nabla \mu_O = 0} ; \quad \widetilde{D}_{vH} \equiv \frac{\sigma_v t_i}{4F^2}\left(-\frac{\partial \mu_{H_2O}}{\partial c_v}\right)_{\nabla \mu_O = 0} \qquad (6)$$

Where t_s is the transference number of the carrier species, s, and F is Faraday's constant. The quantities in parentheses in Eq. (6) are the thermodynamic factors, which can be evaluated from $[s] = [s](a_{H_2O}, a_{O_2})$ at a given temperature.

During hydration, the carrier concentrations, c_s (s = v, i), vary with time (t) and position (x,y,z) in accord with the continuity equation,

$$\frac{\partial c_s}{\partial t} = \widetilde{D}_{sH} \nabla^2 c_s (s = v, i). \qquad (7)$$

For a conductivity specimen with a typical parallelepiped geometry, the analytic solutions, $c_s = c_s\left(x, y, z; t; \widetilde{D}_{iH}, \widetilde{D}_{vH}\right)$, have been made available for a step-wise change of a_{H_2O} in infinite series form [15,16] and accordingly c_h due to Eq. (3). Letting σ_0 and $c_{s,0}$ denote the uniform total conductivity and uniform concentration of $s(=i,v)$ at $t = 0$, respectively, the spatial mean of total conductivity $\overline{\sigma}(t)$ takes an analytic form, specifically:

$$\overline{\sigma}(t) - \sigma_0 = -\lambda_{h,i}\left(\overline{c}_i - c_{i,0}\right) - \lambda_{h,v}\left(\overline{c}_v - c_{v,0}\right) \qquad (8a)$$

where

$$\lambda_{h,s} = e_o(u_h - u_s) \ (s = i, v). \qquad (8b)$$

And e_o is the fundamental charge. By fitting Eq. (8a and 8b) to the measured transient conductivity, one can extract $\widetilde{D}_{sH}(s = i, v)$ as has now been shown from multiple measurements [17].

In passing, it is pointed out that the information content of these kinetic parameters $\widetilde{D}_{sH}(s = i, v)$ is frequently misunderstood to be different from that of the defect-chemical parameters. As is seen from Eq. (6),
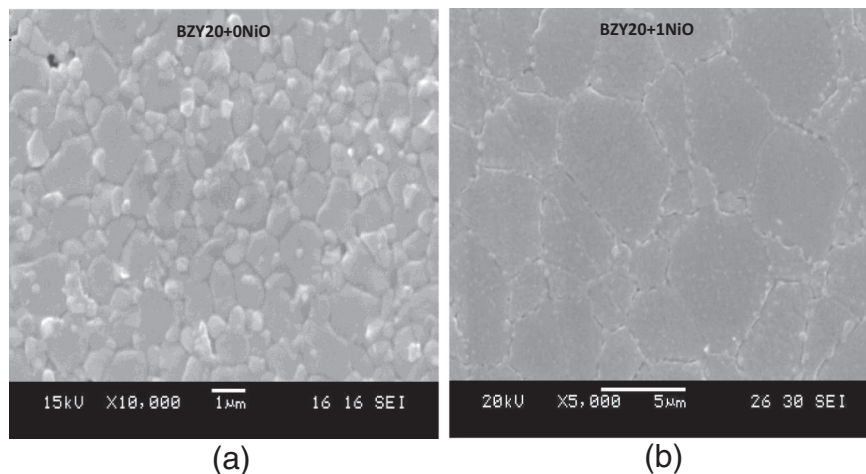

Fig. 1. Microstructures of BZY + 0NiO (a) and BZY + 1NiO (b) as sintered, both taken from the as-polished surfaces by SEM (JEOL, JSM-6360). From Ref. [22].