



Concentration-cell measurement of proton transference number of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$

Je-Yong Yoon, Jung In Yeon, Han-Il Yoo*

WCU Hybrid Materials Program, Department of Materials Science & Engineering, Seoul National University, Seoul 151–744, Korea

ARTICLE INFO

Article history:

Received 24 August 2010
Received in revised form 26 May 2011
Accepted 27 May 2011
Available online 13 July 2011

Keywords:

Proton transference number
Open-circuit voltage
Concentration cell
 $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$
Proton conductors

ABSTRACT

It is not so transparent to determine the proton transference number (t_{H^+}) of a proton-conducting oxide, e.g., $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$, from a concentration-cell open-circuit voltage (U), because in this case U is, in general, no longer a path-independent state property. We clarify this issue to validate the concentration-cell method, and correctly determine t_{H^+} of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$. The experimental values for t_{H^+} are precisely documented in the ranges of oxygen activity $-4 < \log a_{O_2} < 0.1$ and of water vapor activity, $-5 < \log a_{H_2O} < -2$ at 600°, 700°, and 800 °C, respectively, and discussed, in association with the total conductivity at e.g., 800 °C, in the light of defect structure of the oxide.

© 2011 Elsevier B.V. All rights reserved.

1. Introduction

The transference number of protons is a key parameter to characterize for a mixed, protonic oxide-ionic electronic conductor. It determines the open-circuit voltage of a concentration cell involving the mixed conductor as well as its ambipolar conductivity, on which hinge a variety of technological applications of proton conductors, e.g., fuel cells, hydrogen or steam sensors, hydrogen separation membranes, to name only a few. Experimental determination of the proton transference number of a proton-conducting oxide, however, is not trivial at all, and hence, it is not so extensively and precisely documented as other properties, e.g., total conductivity, for most of proton conducting oxides.

One of the simple, classic methods to determine the proton transference number is to resort to the open-circuit voltage of a concentration cell. According to Wagner [1], the open-circuit voltage U of a concentration cell involving a binary compound, e.g., AO, under an activity difference of a component, say, oxygen,

$$a'_{O_2} |AO| a''_{O_2} \quad (1)$$

is given as

$$U = \frac{RT}{4F} \int_{a''_{O_2}}^{a'_{O_2}} (t_{A^{2+}} + t_{O^{2-}}) d \ln a_{O_2} \quad (1)$$

where t_k stands for the transference number of species k and others have their usual significance. The overall ionic transference number $t_{ion} (= t_{A^{2+}} + t_{O^{2-}})$ may, thus, be determined as [1]

$$t_{ion} = \frac{4F}{RT} \left(\frac{dU}{d \ln a''_{O_2}} \right)_{\ln a'_{O_2}} \quad (2)$$

that is, as the instantaneous slope of $4FU/RT$ vs. $\ln a''_{O_2}$. It is mathematically legitimate because t_{ion} is a continuous function of the single variable a_{O_2} at given temperature and total pressure, and hence, U is a path-independent, state property. It remains true even for a ternary or multinary compound providing that there is a single kind of mobile ions under a chemical potential or activity difference of the corresponding mobile component, e.g., a concentration cell involving stabilized zirconia subjected to an oxygen activity difference.

It has recently been reported [2], however, that U is no longer a path-independent, state property for a ternary or multinary compound with two or more mobile ionic species when subjected to multiple chemical potential or activity differences of the corresponding mobile components, e.g., $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_{3-\delta}$ subjected to the activity differences of both oxygen and water. As a consequence, the usual practice, Eq. (2) may not be justified in general.

In this paper, we will clarify this issue, validate the concentration-cell method, and correctly measure the proton transference number t_{H^+} on the system of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ as a function of water vapor activity and oxygen activity at elevated temperatures. The experimental values for t_{H^+} are precisely documented and subsequently discussed, in association with the total conductivity at a temperature, in the light of defect structure of the oxide. We will begin by validating

* Corresponding author.

E-mail address: hiyoo@snu.ac.kr (H.-I. Yoo).

the concentration cell method for a mixed, protonic oxide-ionic electronic conductor.

2. Open-circuit voltage and transference number

Let us consider a concentration cell involving an oxide with protons (H^+), oxide ions (O^{2-}) and electrons (e^-) as mobile charged components, e.g., $SrCe_{1-x}Yb_xO_{3-\delta}$, that is subjected to the differences of oxygen activity $a_{O_2} (\equiv P_{O_2}/atm)$ as well as water vapor activity $a_{H_2O} (\equiv P_{H_2O}/atm)$ across the system oxide:

$$a'_{O_2}, a'_{H_2O} | SrCe_{1-x}Yb_xO_{3-\delta} | a''_{O_2}, a''_{H_2O} \quad (II)$$

In the open-circuit condition, there arises a gradient of electrochemical potential of e^- [2],

$$\nabla \eta_{e^-} = \frac{t_{H^+}}{2} \nabla \mu_{H_2} - \frac{t_{O^{2-}}}{4} \nabla \mu_{O_2} \quad (3a)$$

or due to local equilibrium $2H_2 + O_2 = 2H_2O$,

$$\nabla \eta_{e^-} = \frac{t_{H^+}}{2} \nabla \mu_{H_2O} - \frac{t_{H^+} + t_{O^{2-}}}{4} \nabla \mu_{O_2} \quad (3b)$$

where μ_k denotes the chemical potential of species $k (= H_2, O_2, H_2O)$. By noting that $\nabla \mu_k = RT \nabla \ln a_k$, the open-circuit voltage U of Cell (II) is given as

$$U = -\frac{1}{F} \Delta \eta_{e^-} = \frac{RT}{F} \int_{a'_{H_2}, a'_{O_2}}^{a''_{H_2}, a''_{O_2}} -\frac{t_{H^+}}{2} d \ln a_{H_2} + \frac{t_{O^{2-}}}{4} d \ln a_{O_2} \quad (4a)$$

or equivalently,

$$U = \frac{RT}{F} \int_{a'_{H_2O}, a'_{O_2}}^{a''_{H_2O}, a''_{O_2}} -\frac{t_{H^+}}{2} d \ln a_{H_2O} + \frac{t_{H^+} + t_{O^{2-}}}{4} d \ln a_{O_2} \quad (4b)$$

It has long been widely practiced [3–6] to rewrite Eq. (4) as

$$U = -\frac{RT}{F} \int_{a'_{H_2}}^{a''_{H_2}} \frac{t_{H^+}}{2} d \ln a_{H_2} + \frac{RT}{F} \int_{a'_{O_2}}^{a''_{O_2}} \frac{t_{O^{2-}}}{4} d \ln a_{O_2} \quad (5a)$$

or

$$U = -\frac{RT}{F} \int_{a'_{H_2O}}^{a''_{H_2O}} \frac{t_{H^+}}{2} d \ln a_{H_2O} + \frac{RT}{F} \int_{a'_{O_2}}^{a''_{O_2}} \frac{t_{H^+} + t_{O^{2-}}}{4} d \ln a_{O_2} \quad (5b)$$

that is, U has been regarded simply as additive of voltage by each type of mobile component ions, e.g., H^+ and O^{2-} in the present case.

It should be emphasized here that the wide-spread practice, Eq. (5) can be mathematically justified if and only if the differential $d\eta_{e^-}$ in Eq. (3) is exact or U in Eq. (4) is a path-independent state property. [2] For this differential to be exact,

$$-\left(\frac{\partial t_{H^+}}{\partial \ln a_{O_2}}\right)_{\ln a_{H_2}} = \frac{1}{2} \left(\frac{\partial t_{O^{2-}}}{\partial \ln a_{H_2}}\right)_{\ln a_{O_2}} \quad (5a)$$

or

$$-\left(\frac{\partial t_{H^+}}{\partial \ln a_{O_2}}\right)_{\ln a_{H_2O}} = \frac{1}{2} \left(\frac{\partial (t_{H^+} + t_{O^{2-}})}{\partial \ln a_{H_2O}}\right)_{\ln a_{O_2}} \quad (5b)$$

by necessity and sufficiency [2,7].

It is known [2] that this complete condition can be satisfied only in two special cases: (i) when all the involved transference numbers t_k are constant irrespective of component chemical potentials; (ii) when $[Yb'_C] \approx 2[V_O^{\bullet}] \gg [H_i^{\bullet}], [e^-], [h^{\bullet}]$ (in Kroger-Vink notation) specifically

for the present system. Obviously, these cases are far away from the reality of a mixed conductor oxide with appreciable proton conductivity. In general, this complete condition is not satisfied and hence, U is neither path-independent nor additive. It is path- and even time-dependent, contrary to U for Cell (I): When the oxide in Cell (II), that has previously been fully equilibrated at $a'_{O_2} = a''_{O_2}$ and $a'_{H_2O} = a''_{H_2O}$ with $\nabla \mu_O = 0 = \nabla \mu_H$ internally as well, is suddenly subjected to activity differences, i.e., $a'_{O_2} \neq a''_{O_2}$ and $a'_{H_2O} \neq a''_{H_2O}$, $U(t)$ evolves from $U(t=0) = 0$ to the steady state value $U(t \rightarrow \infty)$ as time elapses. It is because U is dependent on $\nabla \mu_O$ and $\nabla \mu_H$ evolving with time within the system. [2] Such path- and time-dependent nature of U of Cell (II) is quite contrasted with U of Cell (I). For the latter, U would immediately take the steady state value or $U(t=0) = U(t \rightarrow \infty)$ because U is determined only by $\Delta \mu_O$ no matter whether $\nabla \mu_O = 0$ or not internally. Here we, of course, assume that the surface reaction is fast enough.

Therefore, one may determine the proton transference number from U of Cell (II), similarly to Cell (I), as,

$$t_{H^+} = -\frac{2F}{RT} \left(\frac{\partial U}{\partial \ln a_{H_2}} \right)_{a'_{H_2}, a'_{O_2} = a''_{O_2} (\nabla \mu_O = 0)} \quad (6a)$$

or

$$t_{H^+} = -\frac{2F}{RT} \left(\frac{\partial U}{\partial \ln a_{H_2O}} \right)_{a'_{H_2O}, a'_{O_2} = a''_{O_2} (\nabla \mu_O = 0)} \quad (6b)$$

but with one more strict constraint: It is not enough only to keep the oxygen activity in the surrounding uniformly constant or $a'_{O_2} = a''_{O_2}$. One should ensure that the component oxygen chemical potential or activity is kept uniformly constant or $\nabla \mu_O = 0$ internally throughout the system oxide. Then, $d\eta_{e^-}$ in Eq. (3) is rendered exact and hence, the proton transference number can be determined similarly to Cell (I).

3. Experimental

Specimens of $SrCe_{1-x}Yb_xO_{3-\delta}$ with nominal composition of $x = 0.05$ were prepared via a conventional, solid-state route from the starting powders $SrCO_3$ (Aldrich, 99.9% purity), CeO_2 (High Purity Chemicals, 99.9% purity), and Yb_2O_3 (Aldrich, 99.95 Purity). The sintered specimens were found to be of single phase by X-ray diffractometry and 99.2 % dense with a mean grain size of $12 \pm 4 \mu m$ by the Archimedes method and line intercept method, respectively.

The concentration cell was constructed in a conventional design [8] as schematically shown in Fig. 1. A disk specimen, measuring

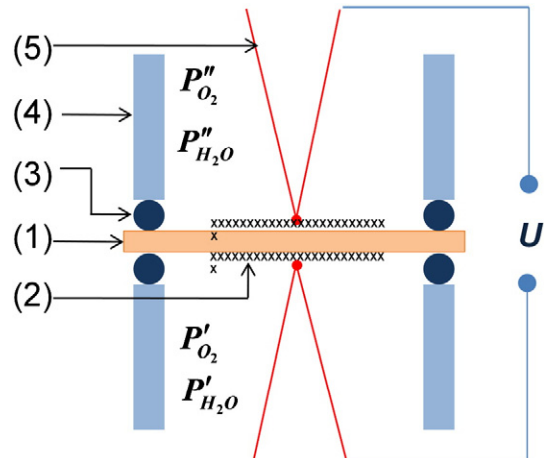


Fig. 1. Schematic of the concentration cell as constructed. 1, Specimen; 2, Reversible electrode; 3, Sealant Pyrex 7740; 4, Alumina tubing; 5, S-type thermocouple.

Download English Version:

<https://daneshyari.com/en/article/1296280>

Download Persian Version:

<https://daneshyari.com/article/1296280>

[Daneshyari.com](https://daneshyari.com)