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Review

Nanoionics phenomenon in proton-conducting oxide: Effect of dispersion of nanosize platinum particles on electrical conduction properties

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Abstract

High-temperature proton conductors are oxides in which low-valence cations are doped as electron acceptors; the incorporation of water molecules into the oxides results in the formation of protonic defects that act as charge carriers. Since the protons thus formed are in equilibrium with other electronic defects, electrons and holes, the oxides possibly have different proton-conduction properties at and near boundaries when they are in contact with another phase. In this paper, we present our recent experimental observation of a marked change in the electrical properties of a proton conductor upon the dispersal of fine platinum particles in the oxide. First, the material shows extremely low electrical conductivity in comparison with the original proton-conducting perovskite. Second, there was a threshold amount of platinum at which such a drop in conductivity occurred. A percolation model is employed to explain these experimental results; the fine platinum particles dispersed in the proton-conducting oxide wears highly resistive skin that is formed due to shifts in defect equilibriums, which prevents ionic/electronic conduction. The experiments suggest that the ion-conducting properties of oxides can be varied by introducing interfaces at a certain density; nanoionics is a key to yielding enhanced and/or controlled ionic conduction in solids.

Keywords: Nanoionics; Proton conductor; Platinum; Heterointerface; Metal–oxide interface; Band bending; Defect chemistry

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Contents

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1. Introduction

This paper presents a recent experimental observation, a marked change in the electrical properties taking place in a proton conductor upon dispersal of fine platinum particles [1].

Perovskite-type high-temperature proton conductors are designed to have oxide ion vacancies by doping low-valence cations as acceptors; for example, Y^{3+} is substituted for Zr^{4+} in $SrZrO_3$ to yield $SrZr_{0.9}Y_{0.1}O_{3-\alpha}$. As a result, the oxides show protonic conduction at high temperatures [2–5], and are governed by the following defect equilibriums. An excess of oxygen enters the oxygen vacancies and generates electron holes with the equilibrium:

$$V_O^{\bullet\bullet} + \frac{1}{2}O_2 \rightleftharpoons O_O^{\times} + 2h^{\bullet}, \quad K_1 = \frac{[O_O^{\times}][h^{\bullet}]^2}{[V_O^{\bullet\bullet}]p(O_2)^{1/2}}, \tag{1}$$

where $V_O^{\bullet\bullet}$, $O_O^{\times}$, $h^{\bullet}$ and $H_i^{\bullet}$ represent oxygen vacancies, lattice oxygen, holes and protons, respectively, and [ ] is used to show the concentration of the species written inside the brackets. Holes and protons are in equilibrium by the following equation:

$$H_2O + 2h^{\bullet} \rightleftharpoons 2H_i^{\bullet} + \frac{1}{2}O_2, \quad K_2 = \frac{[H_i^{\bullet}]^2 p(O_2)^{1/2}}{p(H_2O)[h^{\bullet}]^2}. \tag{2}$$

From Eqs. (1) and (2), the equilibrium equation of proton generation with respect to the equilibrium between oxygen vacancies and the surrounding water can be written as

$$H_2O + V_O^{\bullet\bullet} \rightleftharpoons 2H_i^{\bullet} + O_O^{\times}, \quad K_3 = K_1K_2 = \frac{[H_i^{\bullet}]^2}{p(H_2O)[V_O^{\bullet\bullet}][O_O^{\times}]}. \tag{3}$$

Generally, in ionic conductors, lattice defects act as charge carriers for ionic conduction. In high-temperature proton conductors, proton conduction occurs through interstitial protonic defects. Since lattice defects are defined with respect to the periodicity of a three-dimensional crystal lattice, ionic conduction is usually considered to be a bulk property. The interfaces of crystallites, or grain boundaries, however, have atomic-scale structures that differ from the bulk and should possess a unique defect equilibrium. Therefore, the concentration and mobility of the ionic charge carriers at and near the grain boundaries are thought to be different from those of the bulk. Such phenomena are termed nanoionics in association with the length scale of the interface regions [6–9]. In particular, the heterointerfaces of two coexisting phases are expected to have defect states that are disparate from homointerfaces due to the inherent differences in the Fermi level resulting in the occurrence of electronic/ionic charge redistribution; the dissimilarity of the structural order between the grain boundaries and the bulk is another factor that causes the different state of charge carriers between the bulk and grain boundary.

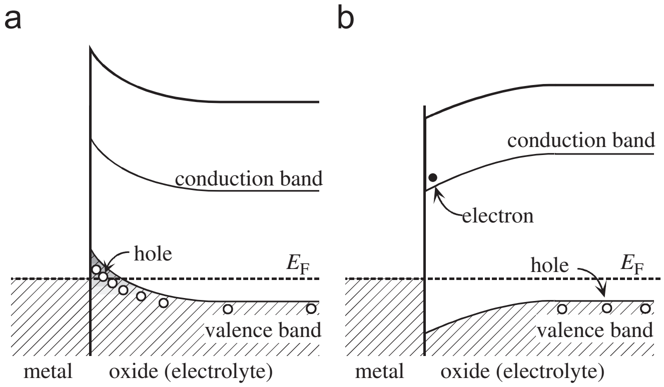

Fig. 1. Schematic illustration of band bending in oxide at an interface with metal: (a) the work function of the oxide is smaller than that of the metal so that the oxide is positively charged; (b) opposite band bending resulting in reduced electron hole concentration at the interface [1].

In high-temperature proton conductors, the protons, which are the charge carriers, are in equilibrium with holes, as shown in Eqs. (1)–(3). Band bending occurs in the proton conductors at the heterointerface with a metal due to differences in the Fermi level and the corresponding generation of space charge. At the interface of a metal with a large work function, as shown in Fig. 1a, the oxide will be positively charged, and thus the concentration of holes will increase and the concentrations of protons that are in equilibrium with the holes are also expected to increase. On the other hand, when the Fermi level of the oxide is lower than that of the metal, band bending occurs such that the concentration of the holes and protons decreases, as shown in Fig. 1b [1].

Taking into account the aforementioned discussion, a composite of a proton-conducting oxide with platinum was formed; $SrZr_{0.9}Y_{0.1}O_{3-\alpha}$ (SZO) was chosen as the high-temperature proton conductor. The electrical conductivity characteristics of the composites were investigated and interesting experimental results were obtained, whereby the electrical conductivity decreased dramatically upon the dispersal of fine platinum particles in the oxide [1]. These experimental results are thought to be a result of nonionic phenomena occurring between the proton conductor and the platinum. We summarize the experimental results and the investigation of the characteristics of the Pt/SZO interface [1]. In our previous paper, a percolation model was applied to explain the results; the thickness of the resistive layer formed on the platinum particles was estimated to be of nanometer order. However, the volume fraction of the resistive particles thus formed was estimated by their number density and volume, and their overlapping was neglected. To take into account the probable spatial overlapping of the resistive particles, numerical simulation was performed and a threshold value for the occurrence of percolation in the present system was estimated.

2. Experimental

A Pt/SZO composite containing 0–4 vol% platinum was prepared. Combustion synthesis was used to prepare