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

To cite this article: Hiroshige Matsumoto et al 2007 Sci. Technol. Adv. Mater. 8 531

View the article online for updates and enhancements.

Related content
- A New Method for Producing Fine Platinum Particles
  Akihito Kumamoto and Chihiro Kaito
- Phase-field model for deposition process of platinum nanoparticles on carbon substrate
  S Yamakawa, K Okazaki-Maeda, M Kohyama et al.
- Effect of Proton Irradiation Dose on the Gettering Efficiency of Platinum and the Performance of Local Lifetime-Controlled Power Diodes
  Dongping Hu, Baodong Han, Shushan Xie et al.

Recent citations
- High-Efficiency Direct Ammonia Fuel Cells Based on BaZr0.1 Ce0.7 Y0.2 O3–Pd Oxide-Metal Junctions
  Yoshitaka Aoki et al
- Review on nanoperoevskites: materials, synthesis, and applications for proton and oxide-ion conductivity
  Bradha Madhavan and Anuradha Ashok
- Conduction Electron Resonance used to Determine Size of Palladium Nanoparticles in Proton Conducting Ceramics
  Brian J. Simonds et al
Nanoionics phenomenon in proton-conducting oxide: Effect of dispersion of nanosize platinum particles on electrical conduction properties

Hiroshige Matsumoto\textsuperscript{a,b,*}, Yoshihisa Furuya\textsuperscript{a}, Sachio Okada\textsuperscript{a}, Takayoshi Tanji\textsuperscript{c}, Tatsumi Ishihara\textsuperscript{a,b}

\textsuperscript{a}Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
\textsuperscript{b}Center for Future Chemistry, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan
\textsuperscript{c}Department of Electronics, Graduate School of Engineering, Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan

Received 2 May 2007; received in revised form 7 August 2007; accepted 12 September 2007

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

Contents

1. Introduction ................................................................. 532
2. Experimental ............................................................. 532
3. Results and discussion .................................................. 533
  3.1. Electrical conduction properties of Pt/SZO composites. ...................... 533
  3.2. Percolation model ..................................................... 534
4. Summary ................................................................. 535
Acknowledgment .......................................................... 535
References ................................................................. 535

*Corresponding author. Department of Applied Chemistry, Faculty of Engineering, Kyushu University, 744 Motooka, Nishi-ku, Fukuoka 819-0395, Japan. Tel.: +81 92 802 2869; fax: +81 92 802 2871.
E-mail address: matsumoto@cstf.kyushu-u.ac.jp (H. Matsumoto).

1468-6996/$ - see front matter © 2007 NIMS and Elsevier Ltd. All rights reserved.
doi:10.1016/j.stam.2007.09.008
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, Ysup+sup3+ is substituted for Zrsup+sup4+ in SrZrOsub3 to yield SrZr0.9Y0.1O3~3. 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 oxide vacancies and generates electron holes with the equilibrium:

\[ V_{O}^{\cdot\cdot}\cdot + \frac{1}{2} O_2 \rightarrow O_{2}^{\cdot\cdot} + 2h^{\cdot\cdot} \]

where \( V_{O}^{\cdot\cdot}\cdot \), \( O_{2}^{\cdot\cdot} \), and \( h^{\cdot\cdot} \) 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:

\[ H_2O + 2h^{\cdot\cdot} \rightarrow 2H^{\cdot\cdot} + \frac{1}{2} O_2 \]

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

\[ H_2O + V_{O}^{\cdot\cdot\cdot} \rightarrow 2H^{\cdot\cdot} + O_{2}^{\cdot\cdot} \]

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, 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.

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; SrZr0.9Y0.1O3~3 (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
powders containing SZO and finely dispersed platinum using either nitrate or chloride precursors. The composite powders were cold-isostatically pressed and sintered in air at 1600 °C. The X-ray diffraction (XRD) patterns of the sintered composites are shown in Fig. 2. Most of the peaks originate from the platinum or SZO, although a small peak arises from zirconia. For comparison purposes, Pt/SZO samples were also prepared by mixing fine powders of SZO (fired in air at 1350 °C for 10 h then ball milled) and platinum (Tanaka Kikinzoku, AY-1020) by a wet ball-mill process and then sintered at 1600 °C. The oxygen partial pressure dependence of the electrical conductivity was measured by a direct-current four-probe method at 800 °C. Atmospheric control was obtained by using a mixture of oxygen–argon or argon–hydrogen gas, both of which were moistened with water vapor ($p_W = 1.9 \times 10^3$ Pa).

Percolation threshold was estimated numerically by employing a cubic cell containing $500 \times 500 \times 500$ cubic elements that were initially assigned to be conductive. Spherical resistive particles with a given radius were introduced randomly into the cell without prohibiting their overlapping under a periodic boundary condition. The cubic elements contained within the spheres were reassigned to be resistive, and the number fraction of the resistive cube elements to the total number of cubic elements was obtained as a function of the number of introduced resistive spheres.

3. Results and discussion

3.1. Electrical conduction properties of Pt/SZO composites

The results from the electrical conductivity measurements of the Pt/SZO composites [1] are shown in Fig. 3. The electrical conductivities of the sintered samples containing no platinum (◇) are roughly $2 \times 10^{-3}$ S cm$^{-1}$, while the composite prepared by combustion synthesis and containing 4 vol% platinum (●) exhibited an electrical conductivity that was 3–4 orders of magnitude lower. On the other hand, the Pt/SZO composites prepared by mixing fine powders of SZO and platinum and sintered at the same temperature showed electrical conductivities typical of high-temperature proton conductors containing no platinum (□ and +). The TEM images of the samples are shown in Figs. 4a and b. The samples prepared by combustion synthesis (Fig. 4a) contained platinum particles in the size range of approximately 0.5 to several nanometers, while the sample that showed no drop in electrical conductivity (Fig. 4b) contained platinum particles in the size range of a few tens of nanometers that were scattered throughout the oxide matrix. From these observations, it is thought that the decrease in electrical conductivity of the Pt/SZO composites prepared by combustion synthesis is due to the effect of the finer dispersion of the platinum particles.

Fig. 5 shows the dependence of the volume fraction of platinum on the electrical conductivity of the Pt/SZO composite prepared by combustion synthesis [1]. The decrease in the electrical conductivity of the proton conductors is not linear with respect to the volume fraction of platinum. The decrease is minimal when the volume fraction of platinum is 0.5% or 1%, and the electrical conductivity is close to the value for bulk SZO containing no platinum. On the other hand, the electrical conductivity decreases markedly when the volume fraction of platinum is 2% or higher. The electrical conductivity varies nonlinearly with the volume fraction of platinum and depicts a sigmoid curve with a threshold at approximately 1.5%.

![Fig. 2. XRD patterns of Pt/SrZr$_{0.9}$Y$_{0.1}$O$_{3-\theta}$ composite samples with different amount of platinum prepared by combustion synthesis method (Cu-Kα radiation X-ray used) [1].](image-url)
3.2. Percolation model

The change in electrical conductivity as a function of the volume fraction of platinum particles can be explained in terms of a percolation model [6,10]. Platinum particles are assumed to change the oxide with which they are in contact into a resistive phase, resulting in the formation of a resistive oxide layer on the surface of the platinum particles; the entire volume (resistive shell and platinum core) of each particle acts as a resistive particle. The situation shown in Fig. 1b can be supposed for the formation of the resistive oxide, where both electron–hole and protonic charge carriers disappear in the oxide phase at the metal interface; no new resistive phase is generated but the proton–hole conducting phase is assumed to change into a resistive phase at the interface with platinum. As illustrated in Fig. 6, the high-resistance particles thus formed are dispersed throughout the conductive matrix. When the high-resistance particles are sparsely scattered, a conduction pathway remains (i.e., percolating), whereas when the high-resistance particles are packed, electrical conduction is blocked. Percolation theory suggests that there is a transition between the percolating and blocking situation with respect to the volume fraction of the resistive phase to the total volume of the solids. There will be a threshold for the transition and Sigmoid behavior like Fig. 5 is observed as a result.

Mathematically, the threshold for the percolating/blocking transition, calculated from a three-dimensional model, is roughly 0.3 for the fraction of the conducting matrix. The remaining 0.7 is the resistive part, comprising resistive particles consisting of a platinum core and a resistive oxide shell in this case. These figures allow us to estimate the thickness of the resistive oxide layer formed on the surface of Pt particles, as follows.

Let us consider an oxide matrix of volume $V$ containing dispersed resistive particles with a mean volume of $v_p$. The number of particles dispersed in the oxide matrix is expressed as $Vn_p$, when the number density of resistive particles is written as $n_p$. Accordingly, the volumetric summation of the resistive particles introduced into the oxide matrix is $Vn_pv_p$. If the overlapping of the resistive particles is not allowed, the volumetric fraction of the resistive part to the total oxide matrix, $f_r$, is $f_r = n_pv_p = Vn_pv_p/V$; thus, the percolation transition occurs when $f_r = n_pv_p = 0.7$. In the previous report, this assumption was employed, i.e., $n_pv_p$ was taken to be 0.7 to obtain the estimated thickness of the resistive layer as 0.7–4 nm [1]; mean diameters of 0.5–3 nm was presumed for platinum particles and 1.5 vol% was used as the threshold volume fraction of platinum. However, as shown in Fig. 6, the resistive particles naturally overlap each another. If the
overlapping among the resistive particles is considered, the fraction of the resistive part, \( f_r \), must be smaller than \( n_p v_p \). Fig. 7 shows the result of the numerical simulation showing the relation between \( n_p v_p \) and \( f_r \); all the resistive particles were assumed to be spheres of a uniform size. It is notable that when \( n_p v_p \) is 0.7, \( f_r \) is 0.5, i.e., the composite is still conductive. For \( f_r \) to be 0.7, that is, the normally assumed threshold for percolation transition, the value of \( n_p v_p \) should be 1.2, i.e., the total volume of the resistive particles should be 120% of the original oxide volume.

The estimation of the thickness of the resistive layer should, therefore, be altered from that in the previous report [1]. On assuming that all the introduced platinum is dispersed in spherical particles with a mean diameter of 2\( r \), the following equations hold, which allow us to estimate the thickness of the resistive layer, \( \ell \):

\[
r^3 : (r + \ell)^3 = 0.015 : 1.2, \tag{4}
\]

\[2r = 0.5 - 3 \text{ nm}. \tag{5}\]

The resulting thickness, \( \ell \), is 0.8–5 nm. Although the thickness is slightly larger than that obtained by the previous estimation, only the existence of a thin layer can explain the conductivity behavior shown in Fig. 5.

In our recent investigations, it was also found from TEM observation that larger platinum particles on the order of 100 nm coexist with the nanometer-size platinum particles, suggesting that not all the platinum was finely dispersed.

Thus the high-resistance layer should be thicker than that estimated above. However, even if it is assumed that only 1% of the platinum is within the 0.5–3 nm size range, the high-resistance layer is estimated to be as thin as 5–29 nm. Therefore, the conductive behavior shown in Fig. 5 can be explained by the generation of a very thin high-resistance layer.

4. Summary

We found that a marked reduction in electrical conductivity took place in a proton-conducting oxide when fine platinum particles were dispersed. A threshold amount of platinum was observed to induce the reduction in the conductivity. These results can be explained in terms of percolation theory, i.e., a resistive layer forms in the oxide on the surface of the platinum particles. The present results suggest that the concept of nanoionics will become a new basis for obtaining markedly enhanced and controlled ionic conductivity in solid oxides. In particular, the use of heterointerfaces will result in the effective creation of new ionic functions in solids.

Acknowledgment

This study was supported by a Grant-in-Aid for Scientific Research on Priority Areas “Nonoionics (No. 439)” by the Ministry of Education, Culture, Sports, Science and Technology, Japan.

References

[1] H. Matsumoto, Y. Furya, S. Okada, T. Tanji, T. Ishihara, Electrochem. Solid-State Lett. 10 (2007) P11. (Figs. 1, 2, 3, 5 and 6 are reproduced from the article.)
[2] H. Iwahara, T. Esaka, H. Uchida, N. Maeda, Solid State Ionics 3–4 (1981) 359.
[3] K.D. Kreuer, Annu. Rev. Mater. Res. 33 (2003) 333.
[4] T. Norby, Solid State Ionics 40–41 (1990) 857.
[5] N. Bonanos, K.S. Knight, B. Ellis, Solid State Ionics 79 (1995) 161.
[6] P. Knauth, Solid State Ionics 177 (2006) 2495.
[7] F. Ye, T. Mori, D.R. Ou, M. Takahashi, J. Zou, J. Drennan, J. Electrochem. Soc. 154 (2007) B180.
[8] J. Maier, Nat. Mater. 4 (2005) 805.
[9] S. Bredikhin, T. Hattori, M. Ishigame, Phys. Rev. B 50 (1994) 2444.
[10] A. Bunde, W. Dieterich, J. Electroceram. 5 (2000) 81.