

Proton-conducting oxide and applications to hydrogen energy devices*

Hiroshige Matsumoto^{1,2,3,‡}, Takaaki Sakai¹, and Yuji Okuyama¹

¹INAMORI Frontier Research Center (IFRC), Kyushu University, 744, Motoooka Nishi-ku 819-0395, Japan; ²International Institute for Carbon-Neutral Energy Research (WPI-I2CNER), Kyushu University, 744, Motoooka Nishi-ku 819-0395, Japan; ³Next-Generation Fuel Cell Research Center (NEXT-FC), Kyushu University, 744, Motoooka Nishi-ku 819-0395, Japan

Abstract: The change of the primary energy source from fossil fuels to the so-called renewable energies, such as solar and wind energy, is a major and necessary trend. The use of these energies needs efficient methods of energy storing and restoring, and hydrogen can serve for an effective conversion between the electricity and the chemical energy. This paper describes the ion-conducting materials applicable to the so-called “hydrogen energy system”. Since hydrogen works as an energy medium in this system, hydrogen-ion-transporting materials are beneficial. Proton-conducting oxides will work for this purpose and will be introduced here, viewing from material designing and working mechanism. Application of the proton-conducting oxide materials to water electrolysis is another topic, and how the materials work in principle for conversion between electricity and chemical energy and how their performances could/can be improved will be described.

Keywords: electrochemistry; energy conversion; hydrogen; hydrogen energy; perovskite; proton conductors; solid-state chemistry; steam electrolysis.

INTRODUCTION

The Earth is warming, and the rise of the global temperature results in changes in weather and climate. Increase in the concentration of carbon dioxide in the air, resulting in the strengthening of the greenhouse effect, is considered to cause the rise of the temperature. In order to keep the global temperature within an acceptable range, we should obviously reduce the use of fossil fuels so as to reduce the emission of carbon dioxide, and we should increase the use of renewable energies, such as solar and wind power, taking the place of fossil fuels. However, sunlight and winds are unstable and fluctuate daily, monthly, and yearly, so that the use of these energies needs redundancy in the capacity and efficient methods of energy storing and restoring. For the latter necessity, hydrogen is one of the most suitable energy mediums: Hydrogen can be produced via water/steam electrolysis that uses electricity generated from renewable energies, and fuel cells can convert the hydrogen energy into electricity, as depicted in Fig. 1.

Pure Appl. Chem.* **85, 315–462 (2013). A collection of invited papers based on presentations at the 12th Eurasia Conference on Chemical Sciences, Corfu, Greece, 16–21 April 2012.

‡Corresponding author

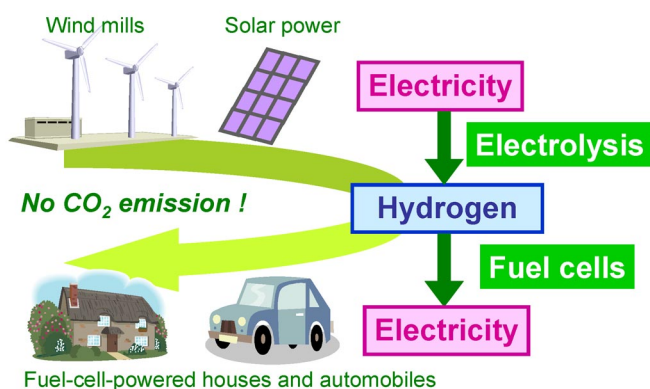


Fig. 1 Schematic illustration of a hydrogen energy system, water/steam electrolysis and fuel cells being combined based on sustainable energies.

Ion-conducting solids are useful for applications in relation to energy and the environment. For example, secondary batteries, fuel cells, etc. utilize ion conduction in solids effectively to convert chemical energy to electrical energy. Gas sensing is also important for controlling energy devices and ensuring safe operation. Particularly for a hydrogen energy system in which hydrogen serves as an energy medium, hydrogen-ion-transporting materials will play an important role, and proton-conducting oxides will work for the purpose. On the other hand, we should pay attention to the fact that these materials need electrochemistry to work, i.e., electrochemical cells are the essential mechanism for operation. For example, water electrolysis is an electrochemical process.



We should notice that this reaction can proceed only in an electrochemical manner; in other cases, the water-splitting will never proceed spontaneously under ordinary conditions. Gibbs free energy, $\Delta_r G$, is the minimal energy required to be given from the outside for the water-splitting reaction. Accordingly, $\Delta_r G/nF$, in which n is 2 for reaction 1 and F is the Faraday constant, is the minimal (reversible) electrolysis voltage. In the actual electrolysis, additional voltage, η , is necessary, totally $\Delta_r G/nF + \eta$ to apply to the electrochemical cell, where η is called overvoltage (or overpotential). The opposite will be true for fuel cells: $\Delta_r G$ is the maximum work a fuel cell can give to the outside and the actual energy derived from the cell must be lost by $nF\eta$ (i.e., we can get $\Delta_r G - nF\eta$ as electrical energy). The overpotential is originated from ohmic loss and electrode resistance coming mostly from the ionic conductivity of the electrolyte and electrocatalytic activity of electrodes, respectively. Therefore, highly conductive electrolytes and catalytically active electrodes are essential for the energy efficiency of the electrochemical devices.

In this paper, some proton-conducting oxides will be reviewed briefly with a proton-conducting mechanism, and applicability to the devices and the energy-converting applications is introduced. It is demonstrated how the overpotentials can be reduced with respect to the electrolyte conductivity within the limitation of acceptable chemical stability and optimization of electrode materials and structures.

PROTON-CONDUCTING OXIDES

Perovskite-type oxides such as SrCeO_3 - or SrZrO_3 -based oxides (Fig. 2a) exhibit protonic conductivity in moist atmospheres at around 400–900 °C; this type of material is often referred to as high-temperature proton conductors (HTPCs) [1–9].

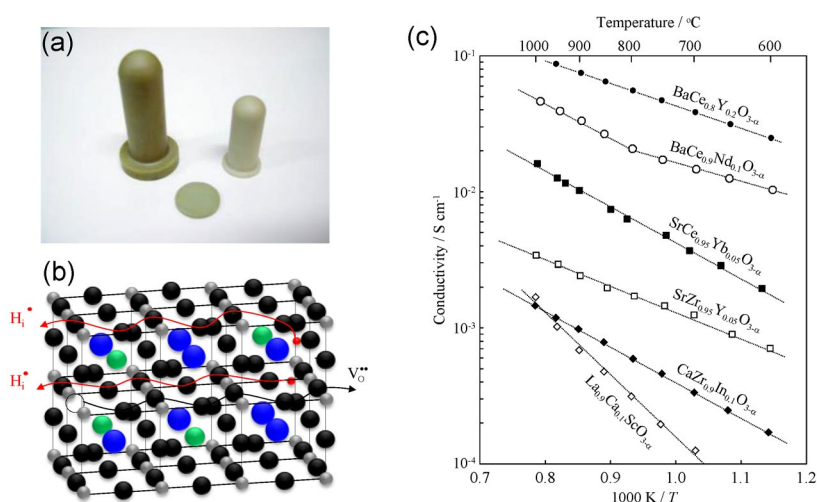


Fig. 2 (a) Appearance of proton-conducting oxide sinters, (b) ABO_3 perovskite structures and proton diffusion, and (c) the electrical conductivity of typical proton conductors in moist hydrogen.

Basic characters of proton-conducting perovskites

ABO_3 is a general chemical formula of perovskite-type oxides and aliovalent cation doping, e.g., partial substitution of trivalent yttrium for tetravalent B site cation, is essential to give proton conductivity to the materials. $SrCe_{0.95}Yb_{0.05}O_{3-\alpha}$, $SrZr_{0.9}Y_{0.1}O_{3-\alpha}$ are the examples of the proton-conducting perovskite oxides. They are designed to have oxide ion vacancies by the lower-valent cation doping; α in the above chemical formulae indicates the molar amount of oxygen vacancies. In moist environments, ambient water molecules are incorporated into the oxide ion vacancies to form protons that make hydrogen bonds to the lattice oxygen (Fig. 2b).

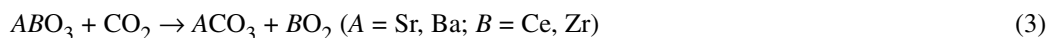


The proton can move from the oxygen atom to another by breaking and forming the hydrogen bonds with the oxygen atoms.

The electrical conductivity of typical proton conductors is represented in Fig. 2c. One of the characteristics of the proton-conducting perovskite-type oxides is the low-temperature dependence of the proton conductivity. Activation energy of proton hopping between adjacent oxide ions is low, e.g., typical values of the activation energy of the proton conductivity are around 0.6 eV in doped- $SrCeO_3$, 0.3–0.5 eV in doped $BaZrO_3$, and 0.5–0.6 eV in $BaCeO_3$ -based electrolytes [10]. Accordingly, the proton-conducting perovskite oxides are advantageous in intermediate-temperature use. “Intermediate temperature” differs from person to person. From a commercialization point of view, 500–700 °C will be a target temperature range [11]. The authors are targeting the operation temperature as low as 600 °C for steam electrolysis as described later.

Conductivity and stability

As shown in Fig. 2c, either cerium or zirconium is typically chosen as the B site cation. Cerates have high protonic conductivity, but are thermodynamically less stable and reactive with carbon dioxide to decompose into cerium oxide and alkaline earth carbonates [12].



Zirconates are characterized by high chemical stability as well as good mechanical strength, but are not so conductive as cerates. In other words, the proton-conducting oxides primarily have a trade-off relationship between the conductivity and stability. The chemical stability is explained by thermodynamics. Figure 3 shows the standard free energy for reaction 3 [13], revealing that cerates will react with carbon dioxide at 1 bar below around 1000 °C. Reversely, the cerates can be used under condition that carbon dioxide can be minimized. For practical compromise, solid solutions of cerates and zirconates have been investigated and several compositions were reported [14–16].

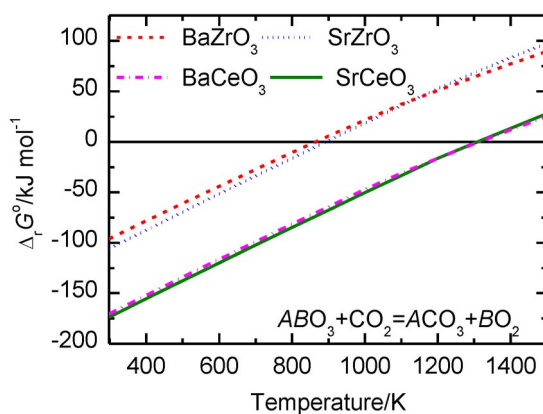


Fig. 3 Standard Gibbs free energy of carbonation reactions of ABO_3 as a function of temperature calculated from a thermodynamic database [13].

The authors examined the strontium-based solid solutions, $SrZr_{0.9-x}Ce_xY_{0.1}O_{3-\alpha}$ ($x = 0-0.9$). The conductivity isotherm is shown in Fig. 4a. It was found in this solid solution system that the conductivity showed a maximum at $x = 0.4$. This feature is unusual since the solid solutions usually show monotonous change of the conductivity from the lowest zirconate to the highest cerate. The reason for the appearance of maximum in the present case is unclear; the dopant level of Y should be lower than 10 % for $SrCeO_3$. $SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-\alpha}$ (SZCY-541) was found to have the highest conductivity. As shown in Figs. 4b and c, this compound was not reactive with carbon dioxide at 600 °C. Therefore, this composition can be determined as an optimized composition and was employed for steam electrolysis explained in the next section.

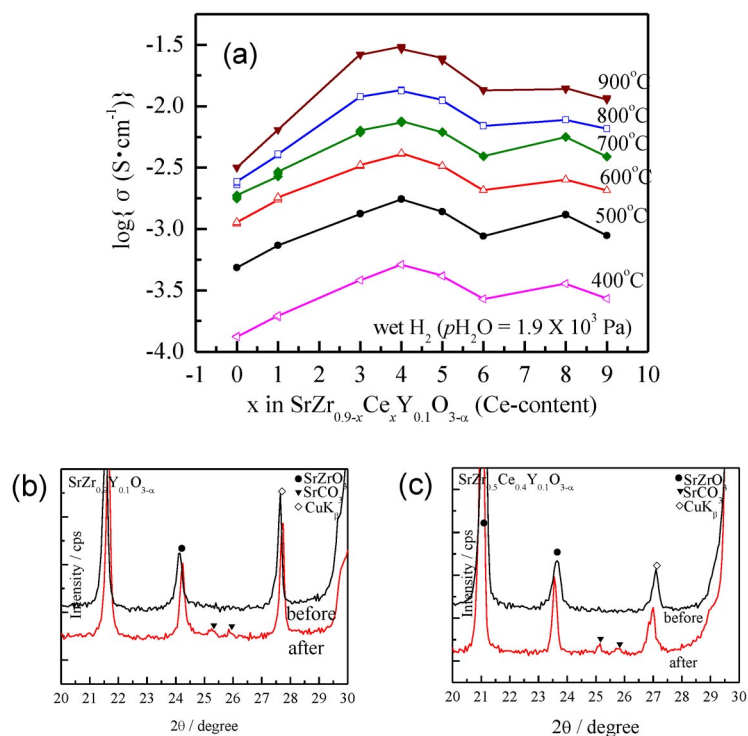


Fig. 4 (a) Conductivity isotherms of $\text{SrZr}_{0.9-x}\text{Ce}_x\text{Y}_{0.1}\text{O}_{3-x}$ ($x = 0\text{--}0.9$). (b) and (c) compare the X-ray diffraction (XRD) patterns at $x = 0$ and 0.4 before and after exposure to 1 bar carbon dioxide at 600 °C.

STEAM ELECTROLYSIS

Steam electrolysis is a reverse operation of solid oxide fuel cells (SOFCs), and thus either a proton or oxide ion conductor can be used. A schematic principle of the steam electrolysis using a proton-conducting oxide is shown in Fig. 5. By sending a direct current to the electrochemical cell made of a proton-conducting solid electrolyte, water vapor at the anode (left-hand side) is split into oxygen and proton, accompanied by the evolution of hydrogen at the cathode (right-hand side) by the following electrode reactions:



The choice of a proton conductor has an advantage that steam is introduced to the anode and hydrogen is produced at the cathode of the electrolysis cell, so that the separation of hydrogen from steam is not needed in principle. Intermediate-temperature operation (600 °C) is assumed, so that fast electrode kinetics can be expected and thus there is no need of precious metal electrodes (platinum, palladium, etc.). As stated above, the perovskite-type proton-conducting oxide has been employed as the electrolyte assuming a benefit of high conductivity at the intermediate-temperature region in comparison with other type of solid electrolyte; e.g., stabilized zirconia works only at 800–1000 °C.

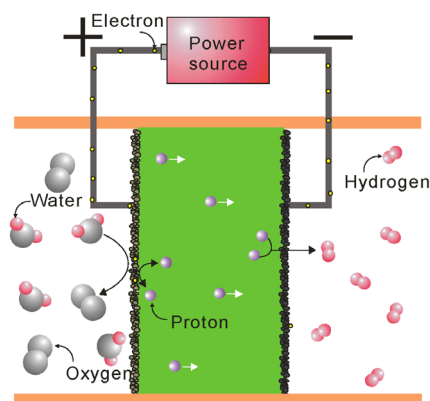
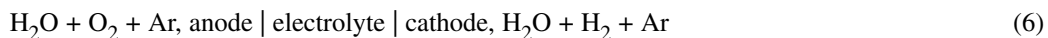


Fig. 5 Schematic illustration showing the working principle of steam electrolysis.

Investigation of electrode materials

As stated in the former section, $\text{SrZr}_{0.5}\text{Ce}_{0.4}\text{Y}_{0.1}\text{O}_{3-\alpha}$ (SZCY-541) is an optimized composition, possessing acceptable conductivity and chemical stability for steam electrolysis application. $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\alpha}$ (SZY-91) was also used as another electrolyte. In order to reduce the electrode overpotentials for steam electrolysis, different types of electrode materials and structures have been examined [17]. The following electrochemical cell was employed for the steam electrolysis test:



A disk-shaped sintered body of SZCY-541 or SZY-91 with a thickness of 0.5 mm and a diameter of ca. 13 mm was used as the electrolyte on which the anode and cathode were attached with a diameter of 8 mm on the faces and the reference electrode was attached on the side of the disk electrolyte to fabricate the three-electrode cell configuration. The anode gas contained H_2O at 20 % and O_2 at 1 % diluted with Ar, and the cathode gas contained H_2O at 1.9 % and H_2 at 1 % diluted with Ar, respectively. The cell was operated at 600 °C. The electrode overpotentials were measured by a current interrupt method, and the evolution rates of hydrogen and oxygen were measured by gas chromatography [17]. Figures 6a and b compare the anode and cathode overpotentials, respectively, with different electrodes and electrolytes. For the anode, it is notable to see in Fig. 6a that $\text{Sm}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (SSC-55) was found to have much higher electrocatalytic activity than platinum. This result suggests that SSC-55 works better than the noble metal electrode. SSC-55 is known so far to work as a good oxygen electrode in the operation of fuel cells with a lanthanum-gallate-based oxide ion conductor [18] and a barium-cerate-based proton conductor [19]; that is the reason for the choice of the material in the present experiment. Although further optimization will be possible, it is conclusive that the transition-metal-containing oxide is a good electrocatalyst for proton conductor cells. Figure 6b shows the cathode overpotentials of nickel electrode. Note that the nickel cathode works better with SZCY-541 electrolyte than with SZY-91 electrolyte. The introduction of zirconium free perovskite ($\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$) interlayer in-between SZCY-541 and nickel cathode further reduces the cathode overpotential. These results imply that the electrode activity depends not only on the electrode material, but also on the electrolyte. In this case, the introduction of cerium into the zirconium site of the electrolyte, which increases the conductivity as shown in Fig. 4a, also enhances the electrode performance. Thus, for the choice of electrolyte material we should consider not only the ionic conductivity but also the compatibility with the electrode. In the present case, it seems that zirconium contained in the electrolyte reduces the catalytic activity of nickel cathode.

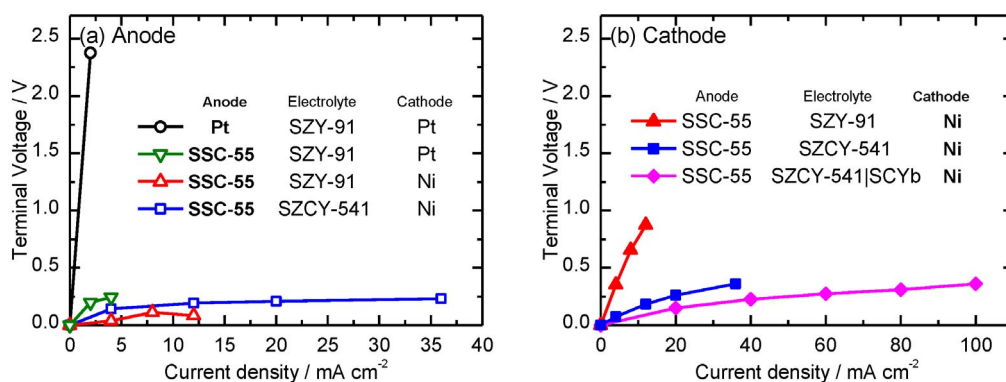


Fig. 6 The (a) anode and (b) cathode overpotentials of steam electrolysis operated at 600 °C with different electrodes and electrolytes. The combinations of the electrodes and electrolytes are shown inside the graphs. “SZCY-541|SCYb” in (b) means that SrCe_{0.95}Yb_{0.05}O_{3-α} interlayer (about 4 μm thick) in-between SZCY-541 and nickel cathode. The data were corrected from ref. [17].

Thin-film electrolyte cell

In order to reduce the electrolyte resistance, thin-film electrolyte is effective [18,19] and was prepared as follows. A paste of SZCY-541 was screen-printed on a composite substrate of NiO/electrolyte-oxide mixture, and co-fired at 1400 °C. After applying a paste of SSC-55 as the anode, the specimen was set to the electrochemical cell and hydrogen was introduced to the cathode compartment to reduce the nickel oxide; this post-reduction allows the oxide substrate to become porous Ni/SZCY-541 cermet cathode. Figure 7 shows the top view and cross-section of the specimen. A thin and dense electrolyte film was successfully prepared on the porous cathode.

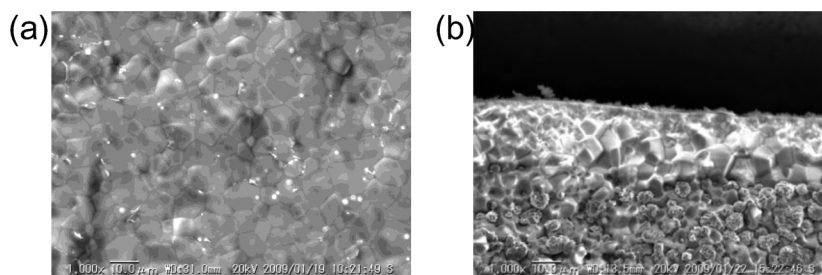


Fig. 7 Scanning electron microscope (SEM) observation: (a) Top view and (b) cross-section of the SZCY-541 thin-film electrolyte cell (about 22 μm thick) prepared on Ni/SZCY-541 cermet substrate; the pictures are of the sample after post-annealing in hydrogen for the cathode side so that the nickel contained in the substrate is in the porous metal form as seen in (b).

Figure 8 shows the current–voltage characteristics of the cell above prepared and operated at 600 °C; the result of the electrolyte-supported cell (electrolyte thickness: 0.5 mm) is also shown as a comparison. The thin-film electrolyte cell has reduced overvoltage, and the electrolysis voltage was as low as 1.2 V at 0.1 A cm⁻². For the production of 100 % hydrogen at 1 bar, the voltage is translated to be 1.4 V. Conventional alkaline water electrolysis typically needs around 2 V or higher, and even polymer electrolyte cells are operated at 1.6–1.8 V for water electrolysis. It is conclusive that the present steam electrolyzer made of a proton-conducting electrolyte will be energetically effective for the production of hydrogen. A problem of the present cell is the limitation of current density. Application of

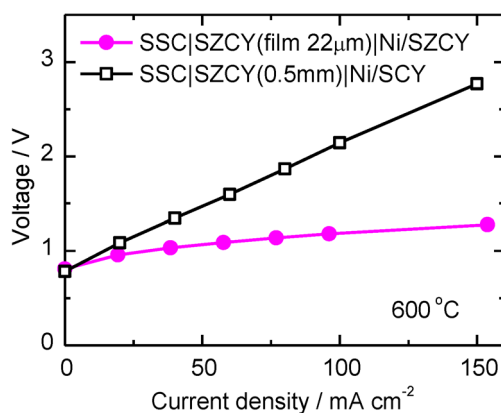


Fig. 8 *I*-*V* characteristics of steam electrolysis using SZCY-541 electrolyte, SSC-55 anode, and Ni/SZCY-541 cermet cathode with different electrolyte thickness operated at 600 °C. The anode gas contained saturating water vapor at 81.4 °C ($p_{\text{H}_2\text{O}} = 5.1 \times 10^4$ Pa) and was supplied at 100 ml min⁻¹, the cathode gas was humidified by saturating water vapor at 17 °C ($p_{\text{H}_2\text{O}} = 1.9 \times 10^3$ Pa) and flowed at 30 ml min⁻¹.

high current density would cause the reduction in the current efficiency from unity, due to the generation of a partial electronic conduction in the electrolyte, and 0.1 A cm⁻² was the highest current density for the present steam electrolysis (Fig. 8). The mechanism for the partial electronic conduction to take place under application of high current densities is not clear at present. On the other hand, the overpotential was 0.4 V (i.e., open-circuit voltage was 0.8 V) 0.1 A cm⁻². The authors consider that further reduction of the overpotential will be possible, by reducing the electrolyte thickness and tuning the cathode and anode materials and structures.

SUMMARY

Intermediate-temperature steam electrolysis using proton-conducting oxides has been considered as a means to convert electricity to hydrogen, being an important procedure in hydrogen energy systems. Proton-conducting oxides have been introduced here with material designing, formation mechanism of protonic charge carriers, and proton conduction properties in relation to the chemical stability. For the steam electrolysis, 600 °C was assumed as a practical operation temperature and how the electrode and electrolyte materials affect the performance of electrolysis. It is conclusive at present that SrZr_{0.5}Ce_{0.4}Y_{0.1}O_{3-α} (SZCY-541) is an optimized electrolyte and Sm_{0.5}Sr_{0.5}CoO₃ (SSC-55) is a suitable anode. Introduction of zirconium free interlayer in-between the nickel cathode and electrolyte was found to be effective in reducing the cathode overpotential. Fabrication and operation of a thin-film electrolyte cell was demonstrated: the electrolysis voltage was 1.4 V for 1 bar hydrogen production at 600 °C. This voltage is much lower than the conventional water electrolysis, and thus the intermediate temperature steam electrolysis can be considered as a candidate method to produce hydrogen from renewable energies.

ACKNOWLEDGMENTS

Part of this paper has been conducted under financial support from Industrial Technology Research Grant Program (06A41502c and 08C46583c) from NEDO and Grants-in-Aid for Scientific Research (21360481) from JSPS. This work was supported by World Premium International Research Center Initiative (WPI-I2CNER), MEXT, Japan.

REFERENCES

1. H. Iwahara, T. Esaka, H. Uchida, N. Maeda. *Solid State Ionics* **3–4**, 359 (1981).
2. H. Iwahara, T. Esaka, H. Uchida, T. Yamauchi, K. Ogaki. *Solid State Ionics* **18–19**, 1003 (1985).
3. H. Iwahara, T. Shimura, H. Matsumoto. *Electrochemistry* **68**, 154 (2000).
4. H. Iwahara, T. Yajima, T. Hibino, K. Ozaki, H. Suzuki. *Solid State Ionics* **61**, 65 (1993).
5. K. D. Kreuer. *Solid State Ionics* **97**, 1 (1997).
6. K. D. Kreuer. *Annu. Rev. Mater. Res.* **33**, 333 (2003).
7. T. Norby. *Solid State Ionics* **125**, 1 (1999).
8. T. Norby. *Nature* **410**, 877 (2001).
9. T. Schober. *Solid State Ionics* **162–163**, 277 (2003).
10. H. Matsumoto. *Perovskite Oxide for Solid Oxide Fuel Cells* (Series: Fuel Cells and Hydrogen Energy), T. Ishihara (Ed.), Chap. 12, Springer (2009).
11. A. Tarancón. *Energies* **2**, 1130 (2009).
12. H. Matsumoto, T. Shimura, H. Iwahara, T. Higuchi, K. Yashiro, A. Kaimai, T. Kawada, J. Mizusaki. *J. Alloys Compd.* **408–412**, 456 (2006).
13. Thermodynamic-database-MALT-group. Thermodynamic database for Windows, Kagaku Gijyutu-sha (2005).
14. K. Katahira, Y. Kohchi, T. Shimura, H. Iwahara. *Solid State Ionics* **138**, 91 (2000).
15. J. Lü, L. Wang, L. Fan, Y. Li, L. Dai, H. Guo. *J. Rare Earths* **26**, 505 (2008).
16. S. W. Tao, J. T. S. Irvine. *Adv. Mater.* **18**, 1581 (2006).
17. T. Sakai, S. Matsushita, H. Matsumoto, S. Okada, S. Hashimoto, T. Ishihara. *Int. J. Hydrogen Energy* **34**, 56 (2009).
18. J. Yan, H. Matsumoto, T. Akbay, T. Yamada, T. Ishihara. *J. Power Sources* **157**, 714 (2006).
19. H. Matsumoto, I. Nomura, S. Okada, T. Ishihara. *Solid State Ionics* **179**, 1486 (2008).