

Review Article

High-Temperature Electrochemical Hydrogen Pumps and Separators

P. Pasierb and M. Rekas

Faculty of Materials Science and Ceramics, AGH University of Science and Technology, Al. Mickiewicza 30, 30-059 Krakow, Poland

Correspondence should be addressed to P. Pasierb, ppasierb@agh.edu.pl

Received 25 October 2010; Accepted 23 December 2010

Academic Editor: Abel César Chialvo

Copyright © 2011 P. Pasierb and M. Rekas. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

In this work different methods of hydrogen purification were presented and discussed. Special emphasis was given to electrochemical hydrogen pumps and membranes. The general principle of operation of such devices was shown, and the basic criteria for materials selection were formulated. The experimental part shows the example results concerning the pumping efficiency, demonstrating the possibility of application of high-temperature protonic conductors for the construction of pump or membrane for hydrogen purification.

1. Introduction

According to the actual prognoses hydrogen is considered to be the energy carrier of the future [1, 2]. Consequently, there have been intensive efforts in the development of different technologies based on the applications of hydrogen as a fuel instead of fossil carbon-containing fuels. Recent efforts in the development of vehicles fuelled by hydrogen, either in internal combustion engines or through fuel cells, may serve as examples of how close is the “hydrogen age.” Among different types of the fuel cells moderate or low temperature fuel cells (PEMFC—proton exchange membrane fuel cell) are the most promising to be used in automotive applications. Such cells need high-purity hydrogen as a fuel. High-purity hydrogen can be produced now by water electrolysis. However, this process uses the electricity obtained mainly from the combustion of fossil fuels and cannot be considered as a proper choice due to both increase of cost of the fuels and an environmental impact [1].

Hydrogen production is a key component of a hydrogen economy. Several hydrogen production technologies are commercially available but, so far, hydrogen has been produced principally from natural gas using steam reforming [3]. Apart steam reforming of natural gas, hydrogen can also be produced from other fuels and by the gasification of coal or biomass. Unfortunately, all mentioned methods

provide hydrogen contaminated by other gases such as CO₂, CO, water vapor, hydrocarbons, and gaseous compounds of sulfur. Several technologies are available for the separation of hydrogen from CO₂ and other gases [4]. Apart from well known techniques of gases purification such as chemical scrubbing, pressure swing adsorption (PSA), or cryogenic the most promising method is using gas permeable solid membranes. This method can be directly integrated with technological lines for generation of hydrogen by means of reforming or gasification. The following gas permeable membranes may be listed:

- (i) polymer,
- (ii) metallic,
- (iii) nanoporous ceramic or glass,
- (iv) ion transport (solid electrolytes),
- (v) mixed ionic-electronic transport.

Polymer membranes show selective permeability of one or few gases. Gas concentration gradient is a driving force. Their major drawback is susceptibility for destruction caused by aggressive gas components and high temperature [5].

Metallic membranes made from Pd, Zr, Ta, Nb, and their alloys are enabled to separate hydrogen from other gaseous

components at high temperatures (573–873 K) [6]. Mechanism of separation consists in the dissociative absorption of hydrogen molecules as H atoms are dissolved in the metal, their diffusion through the membrane, binding the atoms to H₂ molecules, and their desorption. Assuming fast rates of both the adsorption and desorption processes the local equilibrium state is established at both gas/metal interfaces with equilibrium constant K ,

$$K = \frac{[H_{\text{abs}}]^2}{p(\text{H}_2)}, \quad (1)$$

where $[H_{\text{abs}}]$ denotes local concentrations of absorbed atomic hydrogen in metal at near gas/metal interface; $p(\text{H}_2)$ is partial hydrogen pressure in gas phase. The rate of the process, v_{metal} is equal to the H diffusion flux through the membrane, thus

$$v_{\text{metal}} = D_{\text{H}} \frac{[H] - [H]'}{d} = D_{\text{H}} K^{1/2} \frac{p(\text{H}_2)^{1/2} - p'(\text{H}_2)^{1/2}}{d}, \quad (2)$$

where D_{H} is the diffusion coefficient of hydrogen atoms through the membrane; d is the thickness of the membrane, and $p(\text{H}_2)$ and $p'(\text{H}_2)$ denote hydrogen pressure before and behind of the membrane.

This method provides high-purity hydrogen. The main drawbacks are high cost of material mainly palladium and the need to manufacture thin membrane (with thickness of few micrometers). The attempts of replacement of expensive palladium by other metals were unsuccessful due to embrittlement of membrane material caused by hydrogen dissolution, low hydrogen flux rate, and bad stability of material during operation.

Porous ceramic membranes work as a molecular sieve. Small hydrogen molecules (0.23 nm) migrate through the pores, whereas bigger molecules are stopped. Silica, silicates, aluminosilicates, or zeolites can be used for construction of this type of membranes [7]. The rate of the process, v_{pores} is equal to the H₂ diffusion flux through the pores of the membrane:

$$v_{\text{pores}} = D_{\text{H}_2} \frac{[H_2] - [H_2]'}{d} = D_{\text{H}_2} (RT)^{-1} \frac{p(\text{H}_2) - p'(\text{H}_2)}{d}, \quad (3)$$

where D_{H_2} is the diffusion coefficient of hydrogen molecules through the pores of the membrane; other symbols in (3) have the same meaning as in (2). The main problem is the fabrication of membranes with suitable pore structure. Also, hydrogen selectivity of such membranes is sometimes not sufficient.

Electrochemical hydrogen purification belongs to the most effective and cheap methods. They do not need neither expensive equipment nor use any chemicals. The methods are based on ionic transport of hydrogen through the membrane showing either protonic or protonic-electronic conductivity.

Despite of the mentioned advantages, this method of hydrogen purification is not widely applied so far due to

some drawbacks of proton electrolyte which is the base element of the electrochemical pumps and separators.

In this paper a short review of the hydrogen electrochemical pumps and separators was described. Key protonic materials requirements for their use to the construction of such devices were formulated. Effect of different gas components which may be present in initial gas mixture and particularly the problem of the corrosion used materials by carbon dioxide was discussed.

2. Design and Principle of Operation

The main part of these devices is a ceramic gastight septum separating two chambers. Mixture of gases containing hydrogen is in one chamber, and purified hydrogen is collected in another one.

The construction of electrochemical pumps or membranes requires materials where hydrogen ions (protons) can be transported through the membrane showing either ionic (protonic) or protonic-electronic mixed conductivity.

Depending on the type of electrical conductivity of material two different arrangements may be distinguished: electrochemical pump or membrane. The electrochemical pumps are favourably constructed using the conductors with predominant ionic conductivity (transference number for protonic defects $t_{\text{H}} = 1$). In the case of mixed ionic-electronic conductors the hydrogen membrane is the better choice. The driving force for hydrogen pumping is the external DC voltage supply, while in the case of membranes is the gradient of hydrogen partial pressure. In both cases for practical use, the value of hydrogen flux should be at least 50 cm²/min [8].

The details concerning the construction and operation of hydrogen pumps and membranes, the materials used, and the example results of hydrogen pump operation are given below.

3. Electrochemical Hydrogen Pump

For some applications it is necessary to obtain controlled hydrogen flux (e.g., to feed fuel cells or to keep constant hydrogen partial pressure in the flowing equipment). The hydrogen pumps may be useful in such cases.

According to Figure 1(a), the electrochemical pump is a simple solid cell with the following anode reaction:



Hydrogen molecules from the purified gas mixture take electrons from the electrode forming hydrogen ions (protons). Forming positive potential of the electrode is a thermodynamic factor slowing down the reaction (4).

Formed protons migrate to the right electrode, where the following cathode reaction takes place:



As a result of the reaction (5) cathode assumes negative potential which slows down the reaction (5). So, formed

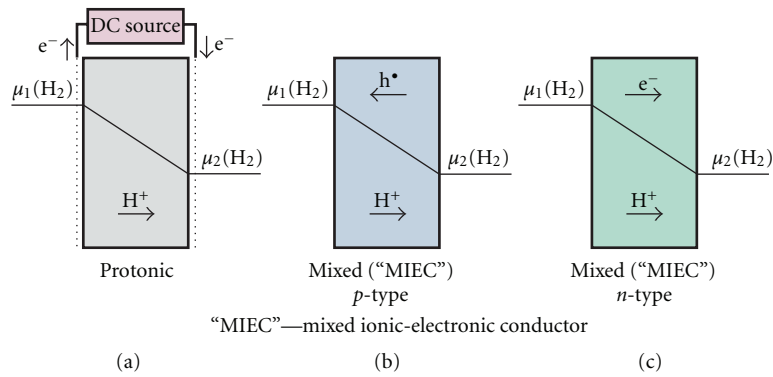


FIGURE 1: Schematic diagrams of electrochemical hydrogen separators: (a) hydrogen pump, (b, c) hydrogen conductive membranes.

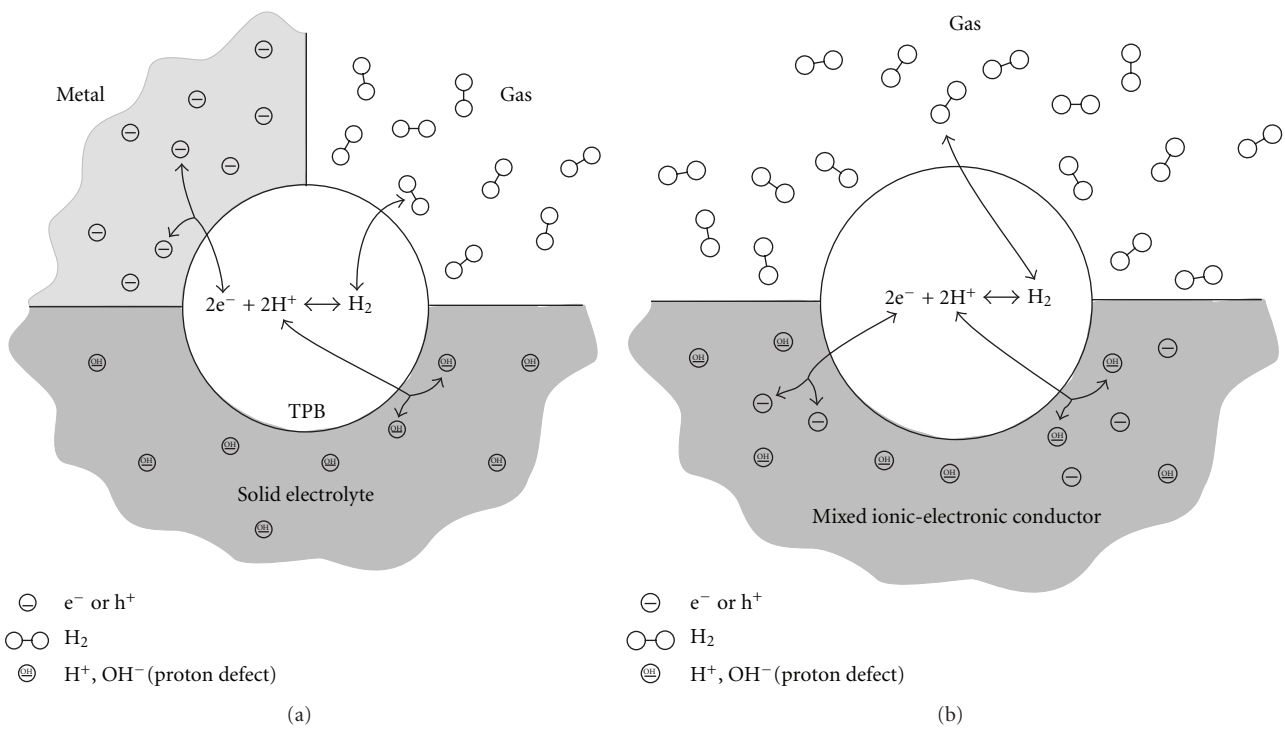


FIGURE 2: Electrode reaction models with contribution of: (a) solid state electrolyte, (b) ionic-electronic conductor.

electrode potentials lead to the establishment of local equilibria at both electrodes.

The device may operate continuously when external electrical Dc Source will be applied to the electrodes. Satisfactory work of such device is determined by

- (i) high efficiency of separation (e.g., expressed amount of pure hydrogen in the time unit),
- (ii) low cost of operation,
- (iii) long lifetime.

Efficiency of separation depends on the rates of the processes occurring at both electrodes and in the solid electrolyte. Applying metal cathode (Figure 2(a)) the reaction

(4) occurs near the junctions of three phases: gas phase (H_2), metal (e'), and solid electrolyte (H^+). Density of such junctions called as three phase boundary (TPB) is low which causes the rate of the anode reaction (4) to be limiting step of the process. Analogous situation exists at the cathode of the cell. There are two ways to overcome this problem. First of them is the use of composite electrodes made from dispersed metal particles in the solid electrolyte matrix (cermet). The main drawback of this solution is gas corrosion of ordinary metals, and on the other hand use of noble metals leads (e.g., Pd, Pt) can be too expensive for membrane manufacture. The second method is to replace the metal as electron source by material exhibiting mixed electronic-ionic conductivity (Figure 2(b)). Also, the increase

of the operation temperature leads to increase of the rates of the electrochemical reactions (4) and (5) as well as increase of the protonic defects transport through the membrane. However, the increase of temperature has negative effect on the cost of device operation and its lifetime. The problem of lifetime and chemical stability will be discussed in the next part of this paper (Section 6).

The first attempt to construct the hydrogen pump based on ceramic protonic conductor was done by Iwahara [9] where either $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ or $\text{BaCe}_{0.9}\text{Nd}_{0.1}\text{O}_{3-\delta}$ was used. He observed that optimal operation temperature of the pump containing barium-based electrolyte (923 K) is lower than that with strontium-based (1173 K). However the barium-based electrolyte undergoes corrosion when CO_2 is presented in the gas mixture.

Many other materials and the methods of modification were proposed and investigated in order to obtain stable materials with high ionic conductivity. The most important groups of materials will be discussed later in Section 5 of this paper.

Another problem which should be taken into account during construction of membrane is the proper selection of sealants to attain hermetic adjoining of the membrane to the walls [10]. Some alloys stable at high temperatures (up to 800°C) used to brazing can be applied [11]. Inconel 600 [10] or gold containing 3% Ni, 0.6% Ti or 16% Ni, 0.75% Mo, 1.25% V alloys [12] can be used.

4. Hydrogen Permeable Membranes

Figures 1(b) and 1(c) illustrate the designs of the hydrogen separators. The membranes show either electron hole-ionic (Figure 1(b)) or electronic-ionic (Figure 1(c)) mixed conductivity. The chemical reactions occurring at two interfaces of gas-membrane are similar to (4) and (5), but electrons come from the membrane material.

When chemical potentials of hydrogen ($\mu(\text{H}_2)$) obey the inequality

$$\mu(\text{H}_2)^{(1)} > \mu(\text{H}_2)^{(2)} \quad (6)$$

which is equivalent to

$$p(\text{H}_2)^{(1)} > p(\text{H}_2)^{(2)} \quad (7)$$

then an ambipolar diffusion of protonic defects and electrons or electron holes proceeds through the membrane.

Overall thermodynamic stimuli determining the separation process are the gradient of chemical potential through the membrane. It is a function of hydrogen partial pressure, temperature, and electrical field. The separation process is composed from the following steps:

- (i) hydrogen diffusion in gas phase through the membrane surface,
- (ii) dissociative adsorption of hydrogen molecules ($\text{H}_2 \rightarrow 2\text{H}$) and ionization of hydrogen atoms ($\text{H} \rightarrow \text{H}^+ + e'$ or $\text{H} + \text{h}^\bullet \rightarrow \text{H}^+$),
- (iii) ambipolar diffusion of the pairs (H^+ , e') or (H^+ , h^\bullet) through the membrane,

(iv) reduction of H^+ ($\text{H}^+ + e' \rightarrow \text{H}$ or $\text{H}^+ \rightarrow \text{H} + \text{h}^\bullet$) at the opposite side of the membrane,

(v) desorption of H atoms and the formation of H_2 molecules.

Depending on the thermodynamic conditions, material structure and its chemical composition each above mentioned step may be rate-limiting process. Generally, rate of the process increases with temperature and decreases with thickness of membrane. Moreover, it depends on a catalytic activity of the membrane surface which is related with the rates of H_2 dissociation and H association.

Rate of the proton transport through the membrane is related with well known ambipolar basis. It depends on total electrical conductivity and transference numbers of electric carriers. It was estimated that both ionic and electronic components of the electrical conductivity should be 0.1 S/cm at least [13]. On the other hand the transference numbers of protons, t_{H^+} and electronic carriers ($t_{e'}$ or t_{h^\bullet}) should assume close values.

Connecting of the external electric sources of two both sides of the membrane (negative polarity to the electrode (1) and positive to the electrode (2)), leads to increase of the hydrogen permeation through the membrane. At suitable high voltage, the hydrogen flux can be achieved even if the relation (7) is not valid. This fact may be used to compress diluted hydrogen, for example, leaving anode compartment in fuel cells [14, 15].

Since the rate of hydrogen separation is proportional to the hydrogen flux through the membrane and to the active surface area, so membrane shape as thin plate with high surface area is preferred. However such membranes are fragile and easily crack due to existing gradients of pressure or temperature. This drawback may be removed by formation of thin dense membranes on a porous support. High open porosity is desirable because it makes easy gas transport through the pores [16, 17]. An important problem in such separators is matching the temperature expansion coefficients of both materials.

There are several forming methods of such membranes. The most popular are spin coating [18, 19], sputtering [20], slip casting [21], sol-gel [22], chemical or electrochemical deposition from the gas phase [23–25], and dry pressing [26].

The last, but not least, problem is surface modification of the membranes in order to achieve suitable catalytic activity in respect to the adsorption-desorption, dissociation of H_2 , association of H, and redox $\text{H}-\text{H}^+$ processes. The modification consists on addition of some promoters of the most sluggish processes (they are usually dissociation-association processes) [26]. Addition of nickel metal particles leads to the increase of electrical conductivity which leads to increase of the dissociation-association rate [26].

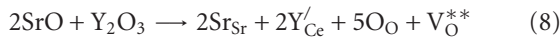
5. Protonic Solid Electrolytes

Practical use of the electrochemical pumps or separators became possible thanks to discovery of high-temperature proton conductivity in oxide perovskites. First of them was KTaO_3 [27, 28]. Then acceptor moped cerates of strontium

and barium: $ACe_{1-x}M_xO_{3-\delta}$, where A is either Sr or Ba, M is trivalent element, usually metal rare, and x is the fraction determining concentration lower than solubility of M acceptor in the cerium sublattice (usually $x < 0.2$ [29]).

These materials exhibit p -type electronic conductivity under oxidizing atmosphere free from hydrogen-containing gases. In the either wet or hydrogen-containing atmosphere the electronic conductivity decreases, and ionic component assumes high value. Studies of electrochemical hydrogen transport revealed that ionic transport is realized by protons. The ionic conductivity is the order 10^{-3} – $10^{-2} \Omega^{-1} \text{cm}^{-1}$ within 873–1273 K. Apart from cerates, the protonic conductivity was stated also in zirconate perovskites, although their conductivities are about ten times lower than those of the cerates [30, 31]. High mechanical and chemical stability of zirconates such as $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-\delta}$ (with respect to carbonate or hydroxide formation [32]) allowed to use them in construction of hydrogen sensor in metallurgy [33].

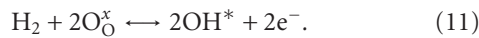
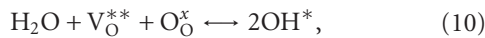
According to the incorporation reaction, given



trivalent ions Y^{3+} substitute tetravalent Ce^{4+} ions, and appropriate amount of oxygen vacancies is formed to maintain the electroneutrality condition

$$x = [\text{Y}'_{\text{Ce}}] = 2[\text{V}_{\text{O}}^{**}]. \quad (9)$$

In presence of either water vapour or hydrogen the protonic defects are formed. Taking into account a small size of protons we can assume that they do not occupy lattice positions but rather attach to oxide ions forming OH^- groups [34]:



The formation of OH^- groups has been confirmed by IR method [35, 36]. Formed in reactions (10) or (11) protonic defects (OH^*) are enabled to move in the perovskite structure.

Undoped SrCeO_3 exhibits only low electronic conductivity [37, 38]. Formed protonic defects OH_{O}^* can move through the solid transporting protons. In order to enforce this process acceptor doping of the perovskite is usually applied. Yttrium or lanthanide elements are used as acceptors. The atoms of acceptor form with the perovskite substitutional solid solution, replacing B position in crystal lattice. During the formation of the solid solution equivalent amount of oxygen vacancies is created.

Barium cerates exhibit the highest total conductivity, but ionic conductivity component is mixed protonic and oxide ions. On the other hand strontium cerates show almost pure protonic conductivity. However both Ba and Sr cerates suffer of instability in CO_2 -containing gas atmospheres. Generally, in both cases, pumps and separators, the thermodynamic stimuli of the protons migration through the membrane

are the difference electrochemical potentials of the protonic defects, η_{H^*} at the both interfaces gas/solid

$$\Delta\eta_{\text{H}^*} = \eta'_{\text{H}^*} - \eta''_{\text{H}^*}, \quad (12)$$

where superscripts are related to left and right sides of the membrane in Figure 1. The electrochemical potential of protonic defects can be expressed as

$$\eta_{\text{H}^*} = \mu_{\text{H}^*} + \varphi, \quad (13)$$

where μ and φ are chemical and electrical potentials, respectively.

Inserting (13) into (12) leads to

$$\Delta\eta_{\text{H}^*} = (\varphi' - \varphi'') + (\mu'_{\text{H}^*} - \mu''_{\text{H}^*}). \quad (14)$$

According to (14) the thermodynamic stimuli are composed from two terms—electrical, V

$$\varphi' - \varphi'' = V \quad (15)$$

and chemical, μ ,

$$\Delta\mu_{\text{H}^*} = \mu'_{\text{H}^*} - \mu''_{\text{H}^*} \quad (16)$$

The electrical term can be controlled by the voltage, V , of the external dc electric source connected to the electrodes. On the other hand the chemical term depends on temperature and the ratio $\log(p'_{\text{H}_2}/p''_{\text{H}_2})$

Taking into consideration that reductive conditions exist at both sides of the membrane the choice of the material of the construction of the membrane is a serious challenge. High-temperature proton conductors such as acceptor-doped cerates or zirconates show mixed conductivity ionic (protons and oxygen ions) and electronic (electrons and electron holes). Acceptor ions of the dopant increase electron hole conductivity. However the reductive atmosphere decreases this conductivity. It leads in some cases the p - n transition. Only few oxide perovskites exhibit sufficiently high protonic conductivity which qualified them as a membrane construction material. Apart from electrical conductivity the second parameter in choice of such material is its stability, mainly resistance against CO_2 corrosion.

Yb-doped strontium cerate, for example, $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ show electrical conductivity 0.005 Scm^{-1} at 800°C and 0.018 Scm^{-1} at 1000°C [18]. These values are too low to use this material. On the other hand doped barium cerate shows sufficiently high protonic conductivity. However, its high chemical reactivity with CO_2 is an important barrier to use it for membrane construction.

Guan et al. studied crystallographic structure [39] and transport properties of $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\alpha}$ [40] and $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\alpha}$ [41]. $\text{BaCe}_{1-x}\text{Y}_x\text{O}_{3-\alpha}$ assumes orthorhombic structure for $x \leq 0.1$ and rhomboedric at $x \geq 0.15$. The rhomboedric form is not susceptible to formation of proton defects [39]. At oxygen/water vapour atmosphere $\text{BaCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\alpha}$ shows proton conductivity within lower temperatures (773–873 K) and oxygen ion conductivity at higher temperatures (973–1073 K). On the other hand at

hydrogen/water vapour the proton conductivity predominates at whole temperature range (773–1073 K). Then at 923 K the transference numbers were 0.77 and 0.23 for ions and electrons, respectively, whereas for $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\alpha}$ they were 0.86–0.90 and 0.14–0.10 within 873–1073 K.

Use of solid solutions of barium cerate with barium zirconate is a known way of modification of these materials [42]. BaZrO_3 shows low electrical conductivity and requires high sintering temperatures in order to obtain unporous, dense material [42].

More complex perovskites such as $\text{M}_2^{2+}(\text{B}_{1+x}^{3+}\text{B}'_{1-x}^{5+}\text{Ln}_x^{3+})\text{O}_{6-\delta}^{2-}$ or $\text{M}_3^{2+}(\text{B}_{1+x}^{2+}\text{B}'_{1-x}^{5+}\text{Ln}_x^{3+})\text{O}_{9-\delta}^{2-}$, where $\text{M}^{2+} = \text{Ba}^{2+}$ or Sr^{2+} ; Ln—trivalent elements such as Nd, Gd, Y, Yb, La were investigated [12, 43–45]. These materials show higher electrical conductivity and high corrosion resistance. For example, $\text{Ba}_3(\text{CaNb}_2)\text{O}_9$ exhibits higher electrical conductivity than $\text{Ba}(\text{Ce}_{1-x}\text{Nd}_x)\text{O}_{3-\delta}$ [43, 44].

Qi and Lin [46] studied membrane formed with z $\text{SrCe}_{0.95}\text{Tm}_{0.05}\text{O}_{3-\delta}$ prepared by the Pechini method. Synthesized powder was calcinated at 1123 K, 10 hrs. After grinding it was pressed under 130 MPa to form cylindrical pellets and then sintered at 1768 K, 48 hrs. Sintered pellets, 25 mm of the diameter and 1–3 mm of the thickness, were soldered to the outlet of an alumina tube using ceramic adhesive (50% $\text{SrCe}_{0.95}\text{Tb}_{0.05}\text{O}_{3-\delta}$, 40% Pyrex glass, and 10% additive). The constructed membrane was tested at 873–1273 K. The highest electrical conductivity was observed at dry oxygen atmosphere (ca. 0.05 S/cm at 1250 K). At dry atmosphere in the same temperature at atmosphere containing 10% H_2/He it decreased to 0.009 S/cm. At the humid atmosphere ($p_{\text{H}_2\text{O}} = 2$ kPa) it was 0.018 S/cm. Applying 10% H_2/He and air at two sides of the membrane the hydrogen flux was $J_{\text{H}_2} = 3 \times 10^{-8}$ mol/(cm²s) at 1173 K.

Hamakawa et al. [47] prepared membranes from $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ 1–20 μm of the thickness on porous support of $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ by the spin coating method from colloidal suspension of the micropowders. Micropowder precursors were prepared by the Pechini method (using citric acid). The membrane of 2 μm thickness exhibits the hydrogen flux equal to $J_{\text{H}_2} = 1 \times 10^{-5}$ mol/(cm²s) at 1123 K. The hydrogen bulk diffusion through the membrane was the limiting process.

In order to improve the hydrogen permeation, Zhan et al. [48] used asymmetrical thin membranes of $\text{SrCe}_{0.95}\text{Y}_{0.05}\text{O}_{3-\delta}$ (SCY) with top layer (in the gas inlet)—coating layer was SCY + NiO + starch (porous maker) 50% SCY, 35% NiO, 15% starch, all have thickness of 1.4 mm, and support layer was made from dense SCY. Hydrogen permeation was controlled by both bulk diffusion and surface kinetics and was 84% higher at 750–950 °C than that of membrane without coating layer.

Song et al. [13, 49] studied hydrogen permeation through membranes made from $\text{SrCe}_{0.95}\text{Eu}_{0.05}\text{O}_{3-\delta}$ and $\text{SrCe}_{0.95}\text{Sm}_{0.05}\text{O}_{3-\delta}$ as a function of temperature and gradients of $p(\text{H}_2)$ and $p(\text{H}_2\text{O})$. In [13] metallic nickel particles (0.08–0.15 μm , 60 vol.%) were added into $\text{SrCe}_{0.8}\text{Yb}_{0.2}\text{O}_{3-\delta}$ in order to enhance electron conductivity component. Such modification of the membrane composition revealed ca. 13

times higher electronic conductivity than initial perovskites oxide material.

Electrochemical hydrogen pump with ceramic proton $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ (SCO) conductor membrane has been proposed by Kawamura et al. [50] to apply for a blanket tritium recovery system of a fusion reactor. Modification of electrodes was done to enhance the hydrogen transportation capability. Electrodes, Pt and Pd, were attached to the SCO sample by the sputtering method. Capability was enhanced when the sputtered electrode was applied. The current density was about 4 or 5 times larger than the usual Pt paste electrode which was observed at 0.1% of H_2 concentration. The electrode reactions occurred at triple phase boundary (TPB) of which is the boundary among the gas phase, the electrode, and the electrolyte as shown in Figure 1(a). The number of TPB was large; that means that the number of the electrode reaction becomes large. Usually, the electrode of the hydrogen pump is porous to let the hydrogen to pass through easily. If the particle size of electrode material is small, the number of TPB per unit area becomes large.

Matsumoto et al. [51] studied hydrogen pumps constructed with the following gas atmospheres:



In the case of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\delta}$ the evolution rate of H_2 at the cathode well agrees with Faraday's law up to around 600 mA/cm². In contrast, the hydrogen pump using $\text{SrZr}_{0.9}\text{Y}_{0.1}\text{O}_{3-\delta}$ has quite poor performance. The hydrogen-pumping rate deviates from the Faradaic one at a current density as low as 20 mA/cm² with quite high overpotentials (>1 V) both at the anode and cathode. Hydrogen-pumping capacity could be enhanced by increasing water vapor supply to the cathode and by reducing operation temperature within the examined range of 700–900 °C. Presence of sufficient water vapor at the cathode would keep the current efficiency of the hydrogen pump [52].

6. Chemical Stability of Protonic Conductors

The application of BaCeO_3 -based protonic conductors for construction of electrochemical pumps or separators will be possible if the electrical conductivity is increased and the chemical stability, especially in gas atmospheres containing CO_2 , is improved. The poor chemical stability of BaCeO_3 -based protonic conductors, especially in the presence of CO_2 , is one of the disadvantages of these materials. Prolonged exposure to CO_2 -containing atmospheres leads to the deterioration of mechanical properties of material, due to formation of secondary barium carbonate and cerium oxide [42, 53]. The formation of solid solutions with chemically stable, isostructural BaZrO_3 is the successful approach to the improvement of corrosion resistance against the CO_2 . Unfortunately, the introduction of Zr leads to the drastic decrease of electrical properties of the material [32]. Recent reports show that simultaneous doping of BaCeO_3 by Zr and Nd leads to the material with good chemical stability (positive effect of Zr) and increased electrical conductivity (influence of Nd) [54]. Also, the improvement of stability may be obtained by introduction of titanium into BaCeO_3

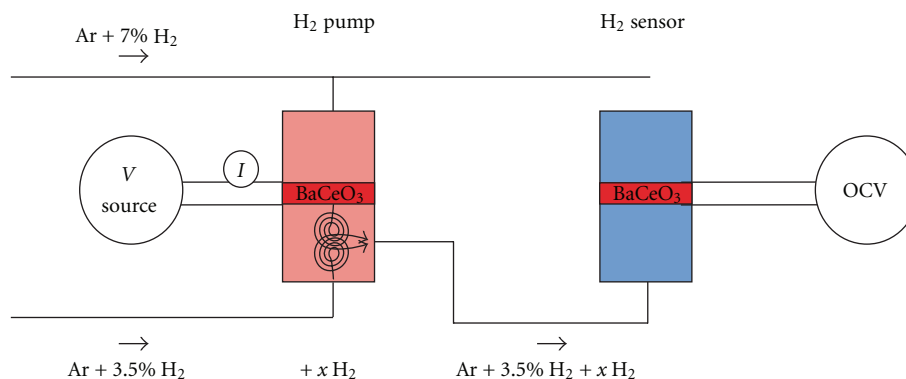


FIGURE 3: Schematic of experimental setup used for the determination of pumping efficiency.

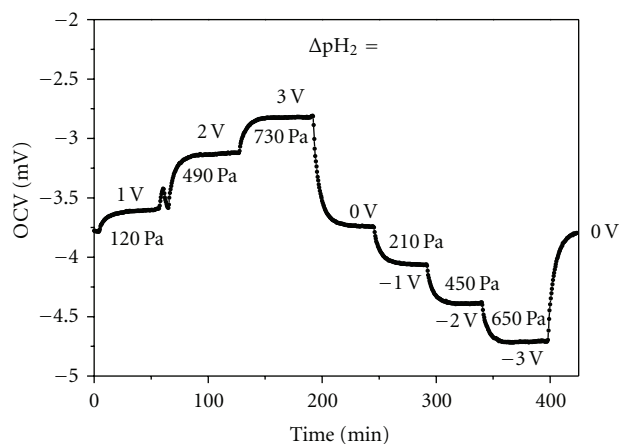


FIGURE 4: The example results of the hydrogen sensor signal due to hydrogen pumping through the electrochemical pump, as function of applied voltage. Pump and sensor worked at 600°C, and gas flow rates at both sides were equal to 20 Scm³/min.

[55, 56]. In this case the total electrical conductivity decreases by ca. 1 order of magnitude comparing to the undoped material. Moreover, the transport properties are also modified; the introduction of titanium led to the decrease of protonic and the increase of electronic transference numbers in the materials. Further modification of these materials by simultaneous doping by Ti and Y was found to be a successful approach to obtain the stable protonic-electronic conductors with relatively high electrical conductivity [56, 57].

Another approach to minimize the effect of secondary reaction of materials with CO₂ is the change of Ba (or Sr)/Ce cationic ratio, as proposed by [58]. It was found that deficiency of Ba in the lattice may improve the stability of material [58, 59].

The observed improvement of chemical stability caused by Zr, Ti doping or by the change of Ba/Ce ratio may be interpreted in terms of modification of crystallographic structure. Namely, the structural parameter S (Goldschmidt

tolerance factor), describing the extent of distortion from ideal perovskite structure, according to the formula

$$t = \frac{(r_A + r_O)}{\sqrt{2}(r_B + r_O)} \quad (18)$$

was correlated with the chemical stability for different pure and doped ABO₃ compounds [60–62].

7. Example of Hydrogen Pump Performance

The determination of the hydrogen pumping efficiency may be done using the experimental setup as shown in Figure 3 by measuring the amount of hydrogen transported through the protonic conductor (pump) as a function of applied voltage and the flowing current in the known period of time.

According to Figure 3, electrochemical pump and the potentiometric H₂ sensor were connected by gas lines in parallel. Both pump and the sensor were the concentration galvanic cells, built from the selected protonic conductors. One side of the cells was purged with gas mixture of argon with 7 vol.% of hydrogen, while the opposite sides of the cells were connected with series and purged with argon containing 3.5 vol.% of H₂. In the case of pump (left cell) the external potential difference was applied, and the flowing current was recorded (Keithley SMU 2400). Forced electrical current led to the flow of protonic defects and pumping of hydrogen by such constructed pump. The right cell was used to detect and measure the additional amount of pumped hydrogen; it was done by measurement of open cell voltage (OCV). The calculation of additional amount of pumped hydrogen was possible basing on the made calibration of the sensor and the Nernst equation.

The comparison of the amount of charge flowing through the material of pump with the amount of hydrogen determined from calibrated sensor measurements allowed to determine the overall efficiency of hydrogen pump.

Figure 4 shows the representative data of the hydrogen sensor signal as a result of hydrogen pumping using the hydrogen pump. The details concerning the experiment are collected in this figure caption.

The determined hydrogen partial pressure gradients (in [Pa]) caused by the pumping are given in red in the figure. Basing on the presented results the pumping efficiency was estimated to be about 40%. The determined efficiency is much lower than 100% which is caused by the mixed electronic-ionic conductivity of the material used for the construction of the hydrogen pump ($\text{Ba}(\text{Ce}_{0.95}\text{Ti}_{0.05})_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$). Also, some aspects of pump construction, equation small leaks caused by the imperfections of the ceramic adhesive used and the hydrogen sensor calibration accuracy, may be partially responsible for the observed lowered hydrogen pumping efficiency. Presented results indicate real possibility to construct such electrochemical hydrogen pumps. Further studies are necessary in order to optimize the properties of materials and the construction and operation details of the pump.

8. Conclusions

State of art concerning hydrogen pumps and separators involving literature data and author's works has been reviewed. Such devices are profitable in various technological applications and especially in the approaching hydrogen era. The principle of operation consists in ionization of hydrogen molecules and pumping formed hydrogen ions through the membrane by either a chemical potential difference of hydrogen or an electric field applied between two electrodes.

The evaluation of different high-temperature protonic conductors was presented in this paper. In spite of considerable progress in the area of optimisation of protonic conductors there is need to solve some problems for wider practical use, especially

- (i) to improve the protonic conductivity of the ceramics in order to attain sufficiently high efficiency of constructed devices,
- (ii) to reduce electrical resistance of the pump by preparation of thin film of protonic solid electrolyte, which is a technologically difficult task,
- (iii) to develop more stable ceramic proton conducting materials operating in real conditions (temperature, pressure, gas contaminants, especially CO_2).

The presented example results concerning the pumping efficiency indicate that construction of different electrochemical devices for hydrogen production or purification will be possible after development of stable, rigid materials with high protonic conductivity.

Acknowledgment

This work was supported by the Polish State Committee with Grants AGH nos. 11.11.160.110 and 11.11.160.799.

References

[1] C. J. Winter, "Into the hydrogen energy economy—milestones," *International Journal of Hydrogen Energy*, vol. 30, no. 7, pp. 681–685, 2005.

[2] T. Bose and P. Malbrunot, *Hydrogen: Facing the Energy Challenges of the 21st*, John Libbey Eurotext, Paris, France, 2007.

[3] A. G. Collot, *Hydrogen the Fuel for the Futurer*, US department of Energy, National Renewable Energy Laboratory, 1995.

[4] O. Bolland and H. Undrum, "A novel methodology for comparing CO_2 capture options for natural gas-fired combined cycle plants," *Advances in Environmental Research*, vol. 7, no. 4, pp. 901–911, 2003.

[5] A. G. Collot, "Prospects for hydrogen from coal," in *IEA Clean Coal Centre Reference*, p. 76, 2003.

[6] J. W. Phair and R. Donelson, "Developments and design of novel (non-palladium-based) metal membranes for hydrogen separation," *Industrial and Engineering Chemistry Research*, vol. 45, no. 16, pp. 5657–5674, 2006.

[7] C. Q. Lu and X. S. Zhao, *Nanoporous Materials: Science and Engineering*, vol. 4 of *Series in Chemical Engineering*, Imperial College Press, London, UK, 2004.

[8] S. Sircar and T. C. Golden, "Purification of hydrogen by pressure swing adsorption," *Separation Science and Technology*, vol. 35, no. 5, pp. 667–687, 2000.

[9] H. Iwahara, "Hydrogen pumps using proton-conducting ceramics and their applications," *Solid State Ionics*, vol. 125, no. 1, pp. 271–278, 1999.

[10] S. P. Simner and J. W. Stevenson, "Compressive mica seals for SOFC applications," *Journal of Power Sources*, vol. 102, no. 1–2, pp. 310–316, 2001.

[11] U. B. Pal and S. C. Singhal, "Electrochemical vapor deposition of yttria-stabilized zirconia films," *Journal of the Electrochemical Society*, vol. 137, no. 9, pp. 2937–2941, 1990.

[12] K. S. Weil, J. S. Hardy, J. P. Rice, and J. Y. Kim, "Braze as a means of sealing ceramic membranes for use in advanced coal gasification processes," *Fuel*, vol. 85, no. 2, pp. 156–162, 2006.

[13] S. J. Song, E. D. Wachsman, J. Rhodes, S. E. Dorris, and U. Balachandran, "Hydrogen permeability of $\text{SrCe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ ($x = .05$, $\text{M} = \text{Eu}, \text{Sm}$)," *Solid State Ionics*, vol. 167, no. 1–2, pp. 99–105, 2004.

[14] K. Onda, T. Araki, K. Ichihara, and M. Nagahama, "Treatment of low concentration hydrogen by electrochemical pump or proton exchange membrane fuel cell," *Journal of Power Sources*, vol. 188, no. 1, pp. 1–7, 2009.

[15] C. Casati, P. Longhi, L. Zanderighi, and F. Bianchi, "Some fundamental aspects in electrochemical hydrogen purification/compression," *Journal of Power Sources*, vol. 180, no. 1, pp. 103–113, 2008.

[16] V. Linkov, "New inorganic proton-conductive membranes for hydrogen separation and electro catalysis," *Membrane Technology*, no. 132, pp. 4–8, 2001.

[17] B. Zhu and B. E. Mellander, "Proton conduction in salt-ceramic composite systems," *Solid State Ionics*, vol. 77, no. C, pp. 244–249, 1995.

[18] H. Iwahara, "Proton conducting ceramics and their applications," *Solid State Ionics*, vol. 86–89, pp. 9–15, 1999.

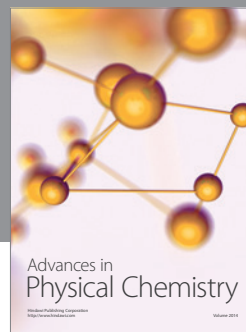
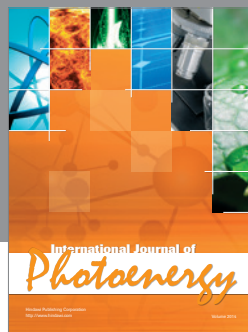
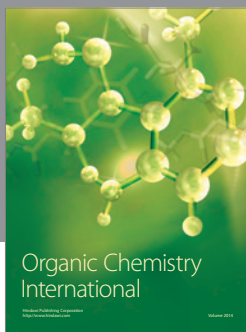
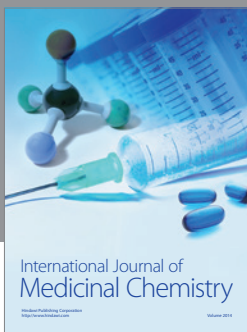
[19] S. Hamakawa, L. Li, A. Li, and E. Iglesia, "Synthesis and hydrogen permeation properties of membranes based on dense $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ thin films," *Solid State Ionics*, vol. 148, no. 1–2, pp. 71–81, 2002.

[20] I. Kosacki and H. U. Anderson, "The structure and electrical properties of $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$ thin film protonic conductors," *Solid State Ionics*, vol. 97, no. 1–4, pp. 429–436, 1997.

[21] Y. Teraoka, T. Fukuda, N. Miura, and N. Yamazoe, "Development of oxygen semipermeable membrane using mixed

- conductive perovskite-type oxides. Part 2. Preparation of dense film of perovskite-type oxide on porous substrate," *Nippon Seramikkusu Kyokai Gakujutsu Ronbunshi/Journal of the Ceramic Society of Japan*, vol. 97, no. 5, pp. 533–538, 1989.
- [22] N. Miura, Y. Okamoto, J. Tamaki, K. Morinaga, and N. Yamazoe, "Oxygen semipermeability of mixed-conductive oxide thick-film prepared by slip casting," *Solid State Ionics*, vol. 79, no. C, pp. 195–200, 1995.
- [23] J. Eschenbaum, J. Rosenberger, R. Hempelmann, D. Nagen-gast, and A. Weidinger, "Thin films of proton conducting SrZrO₃-ceramics prepared by the sol-gel method," *Solid State Ionics*, vol. 77, no. C, pp. 222–225, 1995.
- [24] U. B. Pal and S. C. Singhal, "Electrochemical vapor deposition of yttria-stabilized zirconia films," *Journal of the Electrochemical Society*, vol. 137, no. 9, pp. 2937–2941, 1990.
- [25] U. B. Pal, "Electrochemical vapor deposition of solid oxide films," *Solid State Ionics*, vol. 52, no. 1–3, pp. 227–233, 1992.
- [26] C. R. Xia and M. L. Liu, "Novel Electrode materials for low-temperature solid oxide fuel cells (SOFCs)," *Journal of the American Ceramic Society*, vol. 84, pp. 1903–1905, 2001.
- [27] J. W. Phair and S. P. S. Badwal, "Review of proton conductors for hydrogen separation," *Ionics*, vol. 12, no. 2, pp. 103–115, 2006.
- [28] W. K. Lee, A. S. Nowick, and L. A. Boatner, "Protonic conduction in acceptor-doped KTaO₃ crystals," *Solid State Ionics*, vol. 18–19, no. 2, pp. 989–993, 1986.
- [29] H. Iwahara, T. Esaka, H. Uchida, T. Yamauchi, and K. Ogaki, "High temperature type protonic conductor based on SrCeO₃ and its application to the extraction of hydrogen gas," *Solid State Ionics*, vol. 18–19, no. 2, pp. 1003–1007, 1986.
- [30] H. Iwahara, T. Yajima, T. Hibino, K. Ozaki, and H. Suzuki, "Protonic conduction in calcium, strontium and barium zirconates," *Solid State Ionics*, vol. 61, no. 1–3, pp. 65–69, 1993.
- [31] K. D. Kreuer, "Aspects of the formation and mobility of protonic charge carriers and the stability of perovskite-type oxides," *Solid State Ionics*, vol. 125, no. 1, pp. 285–302, 1999.
- [32] K. D. Kreuer, "On the development of proton conducting materials for technological applications," *Solid State Ionics*, vol. 97, no. 1–4, pp. 1–15, 1997.
- [33] T. Yajima, K. Koide, H. Takai, N. Fukatsu, and H. Iwahara, "Application of hydrogen sensor using proton conductive ceramics as a solid electrolyte to aluminum casting industries," *Solid State Ionics*, vol. 79, no. C, pp. 333–337, 1995.
- [34] DA. Y. Wang, "Electrode reactions at the surface of oxide ionic conductors," *Solid State Ionics*, vol. 40–41, no. 2, pp. 849–856, 1990.
- [35] T. Yajima and H. Iwahara, "Studies on behavior and mobility of protons in doped perovskite-type oxides: (I) in situ measurement of hydrogen concentration in SrCeYbO₃ at high temperature," *Solid State Ionics*, vol. 50, no. 3–4, pp. 281–286, 1992.
- [36] J. F. Liu and A. S. Nowick, "The incorporation and migration of protons in Nd-doped BaCeO₃," *Solid State Ionics*, vol. 50, no. 1–2, pp. 131–138, 1992.
- [37] T. Scherban and A. S. Nowick, "Bulk protonic conduction in Yb-doped SrCeO₃," *Solid State Ionics*, vol. 35, no. 1–2, pp. 189–194, 1989.
- [38] H. Uchida, N. Maeda, and H. Iwahara, "Relation between proton and hole conduction in SrCeO₃-based solid electrolytes under water-containing atmospheres at high temperatures," *Solid State Ionics*, vol. 11, no. 2, pp. 117–124, 1983.
- [39] K. Takeuchi, C. -K. Loong, J. W. Richardson Jr., J. Guan, S. E. Dorris, and U. Balachandran, "Crystal structures and phase transitions in Y-doped BaCeO₃: their dependence on Y concentration and hydrogen doping," *Solid State Ionics*, vol. 138, no. 1–2, pp. 63–77, 2000.
- [40] J. Guan, S. E. Dorris, U. Balachandran, and M. Liu, "Transport properties of BaCe_{0.95}Y_{0.05}O_{3- α} , mixed conductors for hydrogen separation," *Solid State Ionics*, vol. 100, no. 1–2, pp. 45–52, 1997.
- [41] J. Guan, S. E. Dorris, U. Balachandran, and M. Liu, "Transport properties of SrCe_{0.95}Y_{0.05}O_{3- δ} and its application for hydrogen separation," *Solid State Ionics*, vol. 110, no. 3–4, pp. 303–310, 1998.
- [42] S. M. Haile, G. Staneff, and K. H. Ryu, "Non-stoichiometry, grain boundary transport and chemical stability of proton conducting perovskites," *Journal of Materials Science*, vol. 36, no. 5, pp. 1149–1160, 2001.
- [43] K. C. Liang, Y. Du, and A. S. Nowick, "Fast high-temperature proton transport in nonstoichiometric mixed perovskites," *Solid State Ionics*, vol. 69, no. 2, pp. 117–120, 1994.
- [44] A. S. Nowick, Y. Du, and K. C. Liang, "Some factors that determine proton conductivity in nonstoichiometric complex perovskites," *Solid State Ionics*, vol. 125, no. 1, pp. 303–311, 1999.
- [45] H. B. Park, H. Huh, and S. J. Kim, "Structure and bonding of perovskites A(Cu_{1/3}Nb_{2/3})O₃ (A=Sr, Ba and Pb) and their series of mixed perovskites," *Bulletin of Korean Chemical Society*, vol. 13, pp. 122–127, 1992.
- [46] X. Qi and Y. S. Lin, "Electrical conduction and hydrogen permeation through mixed proton-electron conducting strontium cerate membranes," *Solid State Ionics*, vol. 130, no. 1, pp. 149–156, 2000.
- [47] S. Hamakawa, L. Li, A. Li, and E. Iglesia, "Synthesis and hydrogen permeation properties of membranes based on dense SrCe_{0.95}Y_{0.05}O_{3- α} thin films," *Solid State Ionics*, vol. 148, no. 1–2, pp. 71–81, 2002.
- [48] S. Zhan, X. Zhu, B. Ji et al., "Preparation and hydrogen permeation of SrCe_{0.95}Y_{0.05}O_{3- α} asymmetrical membranes," *Journal of Membrane Science*, vol. 340, no. 1–2, pp. 241–248, 2009.
- [49] S. J. Song, T. H. Lee, E. D. Wachsman, L. Chen, S. E. Dorris, and U. Balachandran, "Defect structure and transport properties of Ni-SrCeO_{3- δ} cermet for hydrogen separation membrane," *Journal of the Electrochemical Society*, vol. 152, no. 11, pp. J125–J129, 2005.
- [50] Y. Kawamura, T. Arita, K. Isobe, W. Shu, and T. Yamanishi, "Enhancement of pumping performance of electrochemical hydrogen pump by modified electrode," *Fusion Engineering and Design*, vol. 83, no. 4, pp. 625–633, 2008.
- [51] H. Matsumoto, T. Shimura, H. Iwahara et al., "Hydrogen separation using proton-conducting perovskites," *Journal of Alloys and Compounds*, vol. 408–412, pp. 456–462, 2006.
- [52] H. Matsumoto, S. Hamajima, and H. Iwahara, "Electrochemical hydrogen pump using a high-temperature-type proton conductor: improvement of pumping capacity," *Solid State Ionics*, vol. 145, no. 1–4, pp. 25–29, 2001.
- [53] K. H. Ryu and S. M. Haile, "Chemical stability and proton conductivity of doped BaCeO₃-BaZrO₃ solid solutions," *Solid State Ionics*, vol. 125, no. 1, pp. 355–367, 1999.
- [54] S. Wienströer and H. D. Wiemhöfer, "Investigation of the influence of zirconium substitution on the properties of neodymium-doped barium cerates," *Solid State Ionics*, vol. 101–103, no. 1, pp. 1113–1117, 1997.
- [55] P. Pasierb, "Properties of BaCeO₃ protonic conductors modified by Ti and Y," *Annales de Chimie—Science des Matériaux*, vol. 33, supplement 1, pp. 157–164, 2008.

- [56] P. Pasierb, E. Drozd-Cieśla, and M. Rekas, "Properties of $\text{BaCe}_{1-x}\text{Ti}_x\text{O}_3$ materials for hydrogen electrochemical separators," *Journal of Power Sources*, vol. 181, no. 1, pp. 17–23, 2008.
- [57] P. Pasierb, M. Wierzbicka, S. Komornicki, and M. Rekas, "Electrochemical impedance spectroscopy of BaCeO_3 modified by Ti and Y," *Journal of Power Sources*, vol. 194, no. 1, pp. 31–37, 2009.
- [58] G. Ma, T. Shimura, and H. Iwahara, "Ionic conduction and nonstoichiometry in $\text{Ba}_x\text{Ce}_{0.90}\text{Y}_{0.10}\text{O}_3$," *Solid State Ionics*, vol. 110, no. 1-2, pp. 103–110, 1998.
- [59] K. Przybylski, P. Pasierb, and K. H. Ryu, "Structure and properties of $\text{BaCeO}_{3-\delta}$ -based high temperature protonic conductors," *Proceedings of JCNCS*, pp. 19–22, 2010.
- [60] A. Navrotsky and D. J. Weidner, "A structure of great interest to geophysics and materials science," *Geophysical Monograph*, vol. 45, p. 67, 1987.
- [61] K. Przybylski, P. Pasierb, J. Prazuch, and T. Brylewski, "The properties and chemical stability of $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\delta}$ protonic conductors," in *Proceedings of the European Fuel Cell Forum*, Lucern, Switzerland, July 2009.
- [62] S. M. Haile, G. Staneff, and K. H. Ryu, "Non-stoichiometry, grain boundary transport and chemical stability of proton conducting perovskites," *Journal of Materials Science*, vol. 36, no. 5, pp. 1149–1160, 2001.



Hindawi

Submit your manuscripts at
<http://www.hindawi.com>

