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## ADVANCED CERAMICS FOR PROTONICS

Hiroyasu Iwahara

Center for Integrated Research in Science and Engineering,  
Nagoya University, Furo-cho, Chikusa-ku, Nagoya, 464 Japan

### ABSTRACT

Protonics deals with the science and technology of protons in motion. A proton conducting ceramic is one of the promising advanced materials for energy saving and environmental conservation in the future. In this paper, the possibilities of protonics as a technology are surveyed and high temperature proton conducting oxide ceramics for them are reviewed with respect to materials, their electrochemical properties and their applications citing mainly the experimental results in the author's laboratory.

### 1. INTRODUCTION

The term "Protonics" means the science and technology of protons in motion. It is analogous to the term "electronics" which covers all science and technology concerning the movement of electrons. "Ceramic protonics" deals with proton movement in good proton-conducting ceramics and their applications. This kind of ceramic will be indispensable to energy saving and the simplification of technological process for the coming century, since it can be applied to many devices for energy conversion, production and separation of hydrogen, synthesis of chemicals and

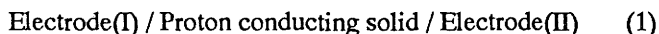
sensing of hydrogen-containing compounds. For these purposes, ceramics usable at elevated temperature are desirable since the electrochemical reactions occurring on the ceramics are fast and efficient.

It is about fifteen years since high temperature proton conducting ceramics based on strontium cerates with relatively high conductivity were reported (Iwahara, Esaka, Uchida and Maeda 1981). A typical example of such a ceramic is  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$ . Since then, a number of studies on proton conduction in various cerate- or zirconate-based perovskite-type oxide ceramics have been carried out by many researchers (Iwahara et al. 1988, Sherban and Nowick 1989, Bonanos, Ellis and Mahmood 1991, 1995, Yajima, Kazeoka, Yogo and Iwahara 1991, Yajima et al 1992, Slade and Singh 1993, Kreuer, Schonherr and Maier 1994, Kreuer 1996).

These ceramics are unique in that they have no protons as a host component but incorporate these via reactions with the atmosphere. In the present paper, after the possibilities of the protonics as a technology are surveyed, proton conducting perovskite-type oxides as an advanced ceramic for protonics are briefly summarized and their defect chemistry, electrochemical properties and experimental trial for several applications performed in our laboratory, are described.

## 2. PROTONICS AS A TECHNOLOGY

One can utilize the motion of protons in solids for many technological applications. Their working principles are based on the utilization of electromotive force or of electrochemical hydrogen transport in the solids. In these applications, the electrochemical cell using a proton conducting solid as an electrolyte diaphragm



is used, where, in many cases, porous electronic conductors are attached to the electrolyte diaphragm as electrodes.

In this cell, fast reactions at both electrodes as well as high conductivity of the electrolyte are

essential for good performance. In general, elevated temperatures are desirable for fast reaction and high conductivity, and, therefore, high temperature type proton conducting ceramics will play an important role in the protonics technology.

**2.1 Sensors.** In the above cell, the difference in the activity (or concentration) of hydrogen between two sides of proton conducting diaphragm gives rise to an electromotive force (emf). This is a kind of hydrogen concentration cell, the principle of which is illustrated in Fig.1. The theoretical emf  $E$  is given by

$$E = \frac{RT}{2F} \ln \left\{ \frac{P_{H_2}(1)}{P_{H_2}(2)} \right\}, \quad (2)$$

where  $P_{H_2}(1)$  and  $P_{H_2}(2)$  are partial pressures of hydrogen at the anode and the cathode, respectively, and  $R$ ,  $F$ ,  $T$  have their usual meanings. We can use this emf as a signal of hydrogen activity, and, thus, the proton conductor can be applied to hydrogen sensor. This type of sensor can be used not only for detecting hydrogen gas but also for water vapor and hydrocarbon gases at elevated temperatures where thermodynamic equilibrium is established with respect to hydrogen activity (Iwahara 1994).

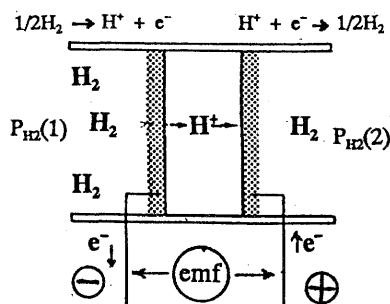


Fig.1 Principle of a hydrogen concentration cell

**2.2 Fuel cells.** If the conductivity of the proton conductor in this electrochemical cell is sufficiently high and if the electrode reaction proceeds smoothly, one can get an appreciable electric power from the cell. As shown in Fig.2 schematically, a hydrogen-oxygen fuel cell can be constructed using a proton conducting solid as an electrolyte. The use of a protonic conductor as a solid electrolyte for fuel cells has distinctive features compared to that of an oxygen ion conductor like a stabilized zirconia. When a protonic conductor is used instead of an oxide ion conductor, fuel circulation is unnecessary in the case of a hydrogen fuel cell because no water molecules are generated at the fuel electrode. Furthermore, in the case of the hydrocarbon fuel cell,

only thermally produced hydrogen is consumed as a fuel and residual parts can be brought out as useful reformed products. For example, one can get ethylene from ethane while generating electric power, as illustrated in Fig.3.

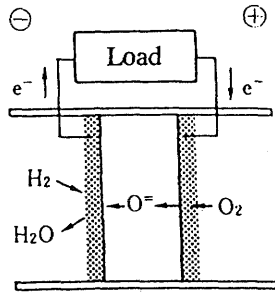


Fig.2 Principles of hydrogen fuel cells

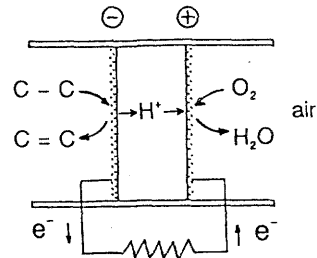
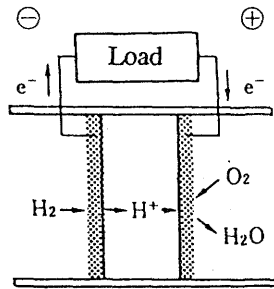


Fig.3 Ethylene production with fuel cell power generation

**2.3 Hydrogen pumps or separators.** When direct current is passed through the electrochemical cell described above on supplying hydrogen to the anode, electrochemical transport of hydrogen in the electrolyte takes place and, as shown schematically in Fig.4, hydrogen evolves at the cathode of this cell consuming hydrogen at the anode. This is a kind of hydrogen pump. Based on this principle, hydrogen can be extracted not only from the mixture containing hydrogen gas but also from compounds of hydrogen. In the former case, the above cell can act as hydrogen gas separator and, in the latter, the cell works as an electrolyzer.

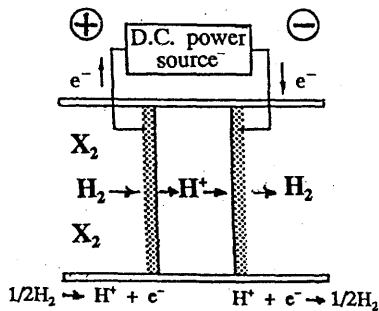


Fig.4 An electrochemical hydrogen pump

**2.4 Electrolyzer and power storage.** Thus, in the case of steam electrolyzer, hydrogen can be taken out from water molecule at the anode of the cell and hydrogen molecules evolve at the cathode as shown in Fig.5, which is the inverse principle of a fuel cell. In this case, pure hydrogen gas is obtained at the cathode in contrast to the case of oxide ion conductor electrolyzer in which water vapor survives at the cathode. Combining the function of fuel cell with that of steam electrolyzer, hydrogen production using excess electric power and power generation using the hydrogen stored are possible. Thus, proton conductors cell may serve as an essential component of electric power storage station.

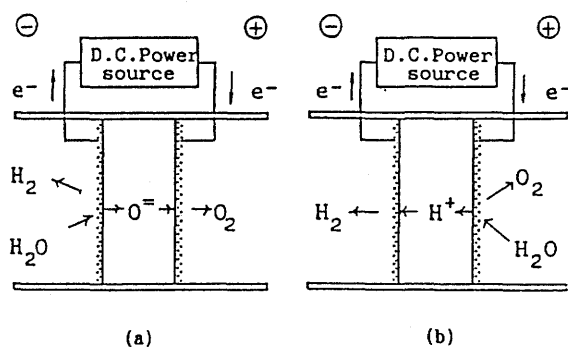


Fig.5 Principles of steam electrolysis

**2.5 Membrane reactors.** The principle of the hydrogen pump can be applied to a kind of membrane reactor. As represented in Fig.6, a proton conducting ceramic cell is able to add the hydrogen atoms electrochemically to organic compounds (hydrogenation) or remove them (dehydrogenation) on sending direct current to it. Dehydrogenation of inorganic compounds such as hydrogen sulfide, chloride etc. may be possible and these reactions can be regarded as electrolysis.

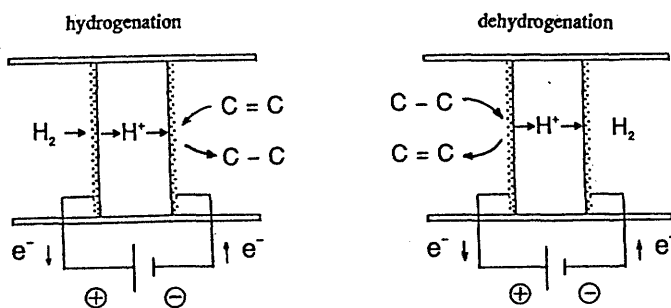


Fig.6 Hydrogenation and dehydrogenation using a proton conductor

**2.6 A steam pump.** A steam pump is one of the modifications of a hydrogen pump. As shown in Fig.7, water vapor in air can be electrolyzed at the anode to form protons, which migrate across the solid electrolyte to the cathode where they react with oxygen in air to form water vapor. Outwardly, steam is pumped from the anode to the cathode although the real pumped species are not water molecules but hydrogen.

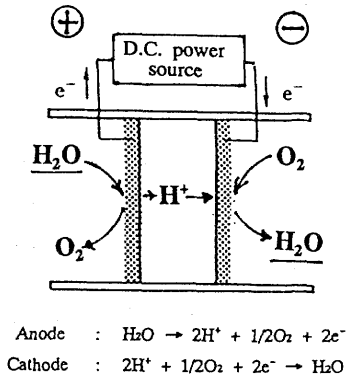


Fig.7 Principle of steam pump

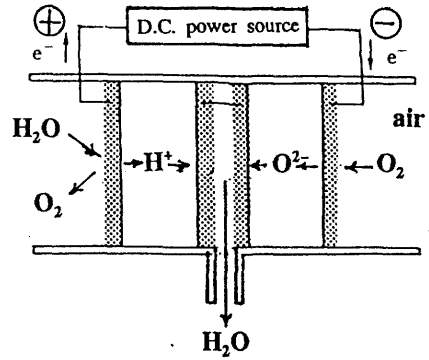


Fig.8 Production of ultra pure water using solid electrolytes

2.7 Deuterium concentrator. Differences in electrochemical transports of hydrogen and deuterium in this kind of electrochemical cell may be used to concentrate the hydrogen isotope by constructing a cascade of the cells.

2.8 Others. There may be other novel applications of protonics using high temperature proton conducting solids. For an example, one can make ultra pure water by using an electrochemical cell composed of both proton conductor and oxide ion conductor as illustrated in Fig.8. Another possibility is a proton launcher, the principle of which is illustrated in Fig.9.

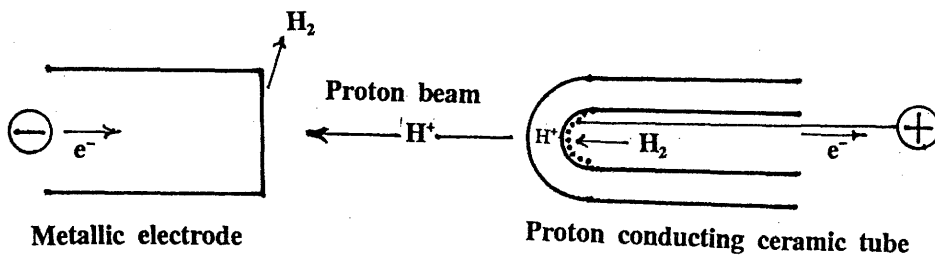


Fig.9 A proton launcher using a proton conducting ceramic.

### 3. PROTON CONDUCTING CERAMICS FOR PROTONICS

**3.1 Required properties for protonics.** Protonics as a technology requires good proton conducting solids which serve as an electrolyte for electrochemical devices. As described above, high temperature type proton conductors are desirable for many devices. The requirements for the conductor are 1) high proton conductivity, 2) low electronic conductivity, 3) high chemical stability at elevated temperatures, 4) high decomposition voltage and 5) good ceramic properties. Moreover, since the protonic conductors are used as a thin diaphragm between two phases with different hydrogen activity, they must be dense enough for preventing the permeation of hydrogen molecules across them. Although ideal materials have not yet been developed, a series of good proton conducting oxide ceramics usable at high temperature has been found since 1981.

**3.2 Proton conducting ceramics.** A typical proton conducting ceramic  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  is a substituted solid solution based on the perovskite-type oxide  $\text{SrCeO}_3$ , in which 5 % of Ce are replaced by Yb (Iwahara et al. 1981). Other perovskite-type oxides based on  $\text{SrCeO}_3$  or  $\text{BaCeO}_3$ , in which some trivalent cations are partially substituted for cerium, are also protonic conductors (Iwahara et al. 1988, Bonanos et al 1991, Slade and Singh 1993). The general formula is written as  $\text{SrCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$  or  $\text{BaCe}_{1-x}\text{M}_x\text{O}_{3-\alpha}$  where M is some rare earth element, x is less than its upper limit of solid solution formation range (usually less than 0.2) and  $\alpha$  is the oxygen deficiency per unit formula.

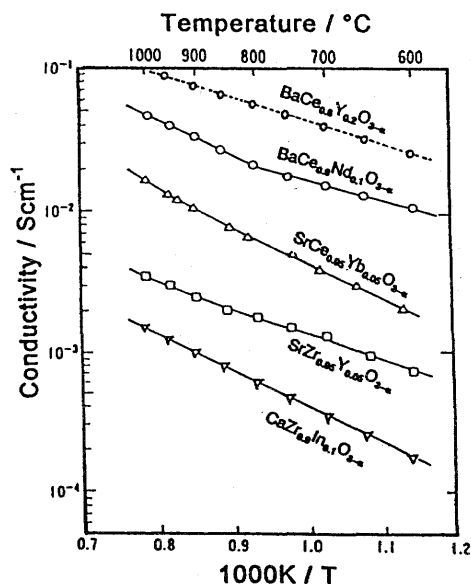


Fig.10 Conductivities of typical proton conducting perovskite-type oxide ceramics under hydrogen gas atmosphere.

The ceramics of these perovskite-type oxide solid solutions exhibit p-type electronic (hole) conduction in an atmosphere free from hydrogen or water vapor at high temperature. However, when they are exposed to hydrogen-containing atmosphere at elevated temperatures, the electronic conductivity decreases and protonic conduction appears. Their protonic conductivities in hydrogen atmosphere are of the order of  $10^{-2} \sim 10^{-3} \text{ Scm}^{-1}$  at  $1000 \sim 600 \text{ }^\circ\text{C}$  as shown in Fig.10. The protonic conduction in these oxides has been verified by electrochemical hydrogen transport experiments under hydrogen- or water-vapor-containing atmosphere at elevated temperatures.

After the discovery of  $\text{SrCeO}_3$ -based protonic conductors,  $\text{KTaO}_3$ -based oxide (Lee, Nowick and Bouatur 1986) and  $\text{Y}_2\text{O}_3$  (Norby and Kofstad, 1984) ceramics were reported to have protonic conduction at high temperatures, although the conductivities were not as high as those of the cerate-based perovskite-type oxide ceramics. Some doped zirconates based on  $\text{CaZrO}_3$ ,  $\text{SrZrO}_3$  or  $\text{BaZrO}_3$  (Yajima et al. 1991, 1992, Iwahara et al. 1993) were also confirmed to exhibit the same behavior as the above cerates although their conductivities were rather low as shown in Fig.10.

Among the oxides described above,  $\text{BaCeO}_3$ -based ceramics show the highest conductivity. However, the contribution of oxygen ions to the conduction grows markedly as the temperature is raised (Iwahara et al. 1988, 1993, Bonanos et al 1991, Taniguchi et al 1992, Kreuer, Schonerr and Maier, 1994). Although the conductivity of  $\text{SrCeO}_3$ -based ceramic is rather low, the transport number of protons is higher than that of  $\text{BaCeO}_3$ -based one. The conductivities of zirconate-based ceramics are lower than those of the cerates, but they are superior with respect to their chemical and mechanical strength. The cerates dissolve easily in the strong acids. For example  $\text{SrCeO}_3$ -based ceramics dissolve into concentrated hydrochloric acid liberating chlorine gas (Uchida, Yasuda and Iwahara 1989). However, zirconates hardly react with acid solution and they are stable against carbon dioxide gas which reacts with cerate ceramics below  $800^\circ\text{C}$  to form carbonates (Yajima et al 1990, 1992).

Recently, Nowick et al. (1995) have reported a series of new protonic conductors in the complex perovskites of the types  $\text{A}_2(\text{B}'\text{B}'')\text{O}_6$  and  $\text{A}_3(\text{B}'\text{B}'')_2\text{O}_9$ , in which the A ions are always charged 2+ and the B' and B'' ions have charges 3+ and 5+ in the former case and 2+ and 5+ in the latter. As an example  $\text{Ba}_3(\text{CaNb}_2)\text{O}_9$  exhibits a conductivity as high as that of  $\text{BaCeO}_3$ -based ceramics.



### 4. PROTONS IN THE OXIDES

These oxides are unique solid electrolytes in that they have no host constituents which liberate conducting ions (protons). The oxides take protons from water vapor or hydrogen molecules in ambient gas as a result of equilibria with defects in the oxide lattice. In these oxides, doping by aliovalent cations is indispensable for the appearance of protonic conduction and gives rise to electron holes and oxygen ion vacancies, which play an important role in the formation of protons. Defect chemistry for proton formation are schematically shown in Fig.11.

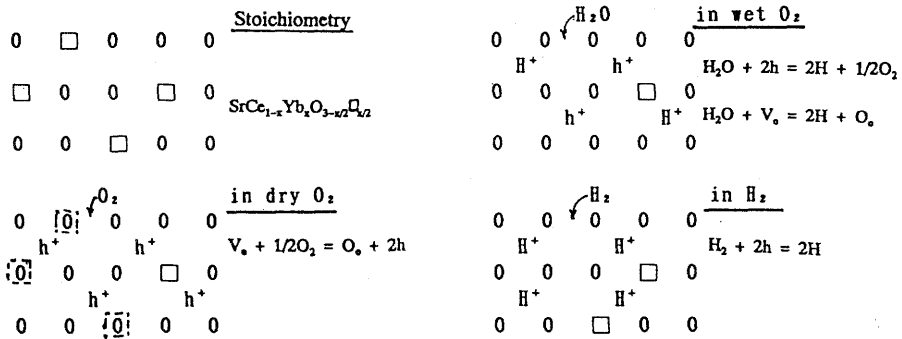
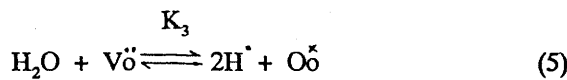
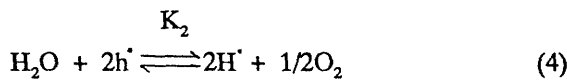
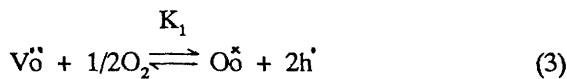


Fig.11 Defect chemistry for proton formation in the oxide

The studies on the electrical conductivity as a function of the dopant content or partial pressures of water vapor and oxygen showed that following three equilibria are simultaneously established between the defects in the oxide and the atmosphere (Uchida et al. 1983)



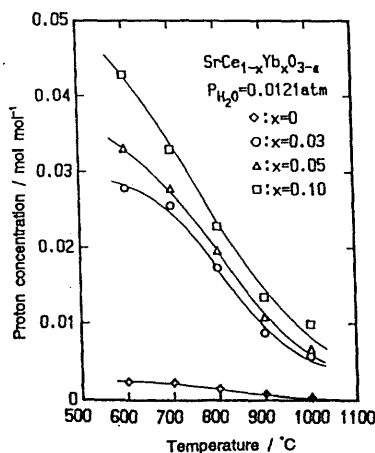
where,  $\text{V}_\text{o}^\bullet$ ,  $\text{O}_\text{o}^\bullet$ ,  $\text{H}^\bullet$ ,  $\text{h}^\bullet$  and  $K$  are oxygen vacancy, oxide ion at normal lattice site, proton, hole and equilibrium constant, respectively, and the relationship between the equilibrium constant of each equation is expressed as

$$K_3 = K_1 K_2 \tag{6}$$

These equilibria have been qualitatively confirmed for  $\text{SrCeO}_3$ -based oxides by measuring the evolution and the absorption of water vapor and/or oxygen on changing their partial pressures or temperature (Uchida et al. 1983, 1989, Yajima et al. 1992).

The solubility of water vapor or hydrogen was studied by several groups reporting comparable values (Uchida et al. 1983, 1989, Yajima et al. 1992). Figure.12 shows an example in which the proton content in  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  under wet air was determined from the solubility of water vapor measured as a function of temperature and a content of dopant (Yajima et al.1992). The content decreases from 0.03~0.045 proton / unit formula of  $\text{SrCeO}_3$  at  $600^\circ\text{C}$  to less than 0.01 at  $1000^\circ\text{C}$ . It is clear from this figure that the content of proton in non-doped oxide is very low indicating the indispensability of doping by aliovalent cations.

Fig.12 Proton concentration  
In  $\text{SrCe}_{1-x}\text{Yb}_x\text{O}_{3-\alpha}$



The mobility of protons can be calculated from the proton concentration thus obtained and the proton conductivity. For  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-\alpha}$  ceramic, the values were  $2 \times 10^{-5} \text{cm}^2 \text{s}^{-1} \text{V}^{-1}$  at  $600^\circ\text{C}$  and  $2 \times 10^{-4} \text{cm}^2 \text{s}^{-1} \text{V}^{-1}$  at  $900^\circ\text{C}$ , and activation energy for proton migration was 0.62 eV which was almost the same as the value of 0.60 eV determined from the temperature dependence of proton conductivity (Yajima et al. 1992).

The oxide ion vacancy relates directly to proton formation and conduction in  $\text{SrCeO}_3$ -based conductors (Yajima et al. 1990). Thus protons from water molecules dissolve in the oxide and behave as charge carriers to form a proton conductor. A protonated oxide of this kind shows some broad IR absorption bands due to OH stretching indicating the existence of somewhat weak OH

bond in the oxide (Huang, Ishigame and Shin 1991, Hibino, Mizutani, Yajima and Iwahara 1992, Yugami, Shibayama, Hattori and Ishigame, 1995). These bands shift toward small wave number on substituting D for H and, accordingly, the conductivity decreases (Iwahara et al. 1993).

According to the neutron scattering study by Sata et al(1996), there exist two equivalent sites for proton between adjacent oxygens in the perovskite-type oxide, one of which can be occupied by the proton. These results suggest hopping mechanism of proton or deuteron changing OH-(or OD-) bond one after another, as illustrated in Fig.13. This mechanism is supported by physical phenomena observed in the experiments on quasielastic photo scattering and a hole burning experiments (Yugami, Matsuo and Ishigame 1995, Yugami et al. 1995). The energy required for proton movement in the oxide and their isotope effect were recently discussed in detail by Kreuer et al. (1995).

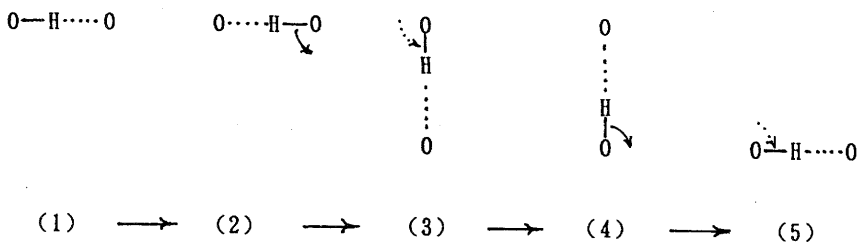


Fig.13 Proton migration in a perovskite-type oxide ( The figures indicate the sequence of migration )

### 5. EXPERIMENTS FOR TECHNOLOGICAL PROTONICS

Technological challenges in the application of high temperature proton conducting ceramics developed by the authors were reviewed in the recent paper (Iwahara, 1995). Some experimental results for technological protonics are introduced in the following, in which perovskite-type oxides are used as proton conducting solid electrolytes.

Galvanic-cell-type hydrogen sensors, steam sensors and hydrocarbon sensors usable at high temperature have been fabricated by way of experiment (Iwahara, 1994). They are essentially based on the principle of hydrogen concentration cell shown in Fig.1. The emf signal of the

hydrogen gas sensor is a linear function of the logarithm of hydrogen partial pressure in the test gas. For the measurement of hydrogen activity in fused aluminum in the casting process, this type of hydrogen sensor has been commercialized by a Japanese company using a  $\text{CaZr}_{0.9}\text{In}_{0.1}\text{O}_{3-x}$  ceramic (Yajima et al. 1995). This sensor may also be applied for other fused metal like zinc or copper.

A laboratory-scale hydrogen fuel cell using  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  ceramic as an electrolyte diaphragm worked stably at  $800 \sim 1000^\circ\text{C}$  (Iwahara et al. 1983). When this cell was discharged, it generated water vapor at the cathode at the theoretical rate calculated from Faraday's law indicating that the conduction in the electrolyte was protonic. The fuel cells using  $\text{BaCeO}_3$ -based ceramic generated much higher power than those using  $\text{SrCeO}_3$ -based ceramic (Iwahara et al 1988, 1989, 1990, 1993, Bonanos et al. 1991, Taniguchi et al. 1992). However, they generated water vapor at both electrodes suggesting that the conduction in the electrolyte was both protonic and oxide ionic.

When a hydrogen fuel cell is operated inversely, this cell works as a kind of steam electrolyzer for hydrogen production as represented schematically in Fig.5. Figure 14 is an example of the experimental results of steam electrolysis using  $\text{SrCeO}_3$ -base solid electrolytes. A bench-scale steam electrolyzer was fabricated using one end closed ceramic tubes made of  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  as a solid electrolyte. The electrolyzer worked stably at  $750^\circ\text{C}$ , and pure and very dry hydrogen (dew point  $< -30^\circ\text{C}$ ) could be extracted at the rate of 3 l/h (Iwahara et al 1986, 1995).

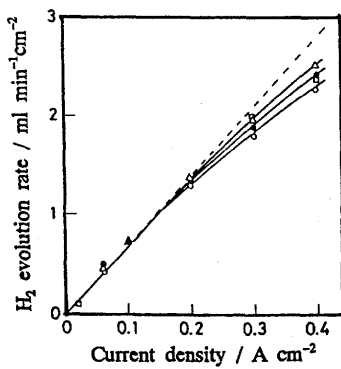


Fig.14 Hydrogen evolution rate in steam electrolysis using  $\text{SrCeO}_3$ -based proton conducting ceramics.

Electrolyte  
 $\text{SrCe}_{0.90}\text{Y}_{0.10}\text{O}_{3-x}$  ; ● 700° △ 800° ○ 900°  
 $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  ; □ 800°

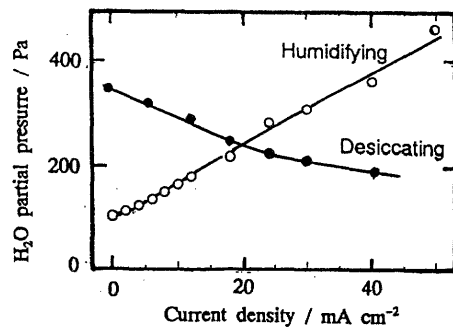


Fig.15 Performance of a steam pump using  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  ( $700^\circ\text{C}$ )

Hydrogen extraction from thermal cracking gas of ethane and hydrogen sulphide at 800°C have been demonstrated in a laboratory scale using a thin disk of  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  ceramic as a solid electrolyte diaphragm (Iwahara et al. 1986, 1991). A proton conducting ceramic membrane can be used, in principle, as a novel chemical reactor for hydrogenation or dehydrogenation of organic compounds (Iwahara 1992). Dehydrogenation of ethane has been tried with this method and found to produce ethylene (Hamakawa, Hibino and Iwahara 1994). Dehydrogenative coupling of methane to get  $\text{C}_2$ -compounds has been studied and observed to enhance the formation of ethane and ethylene on sending an electric current to the cell (Hamakawa et al 1993, Chiang Eng, Stoukides 1993).

The steam pump illustrated in Fig.7 was experimentally verified to work stably (Iwahara 1995). An example of experimental results is represented in Fig.15, in which  $\text{SrCe}_{0.95}\text{Yb}_{0.05}\text{O}_{3-x}$  ceramic was used as a solid electrolyte diaphragm. In this steam pump, an isotope effect was observed, ie. light water was pumped more easily than heavy hydrogen. In the proton conducting electrochemical cell, the behavior of deuterium somewhat differs from that of usual hydrogen due to its large difference in their mass (Sherban and Nowick 1989). This affects both the migration of ions in the electrolyte and the electrode reactions, and marked isotope effect in the electrochemical reaction can be observed (Hibino et al. 1993). This phenomenon may be applied to concentrate heavy hydrogen.

## 6. CONCLUSION

Technological solid state protonics has not yet been made practicable except a hydrogen sensor. However, protonics has many possibilities as shown above. It may contribute to simplification and effectiveness in the technological processes and life systems in future, since the principles of protonics devices are simple and easy to apply if appropriate proton conducting ceramics are developed.

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