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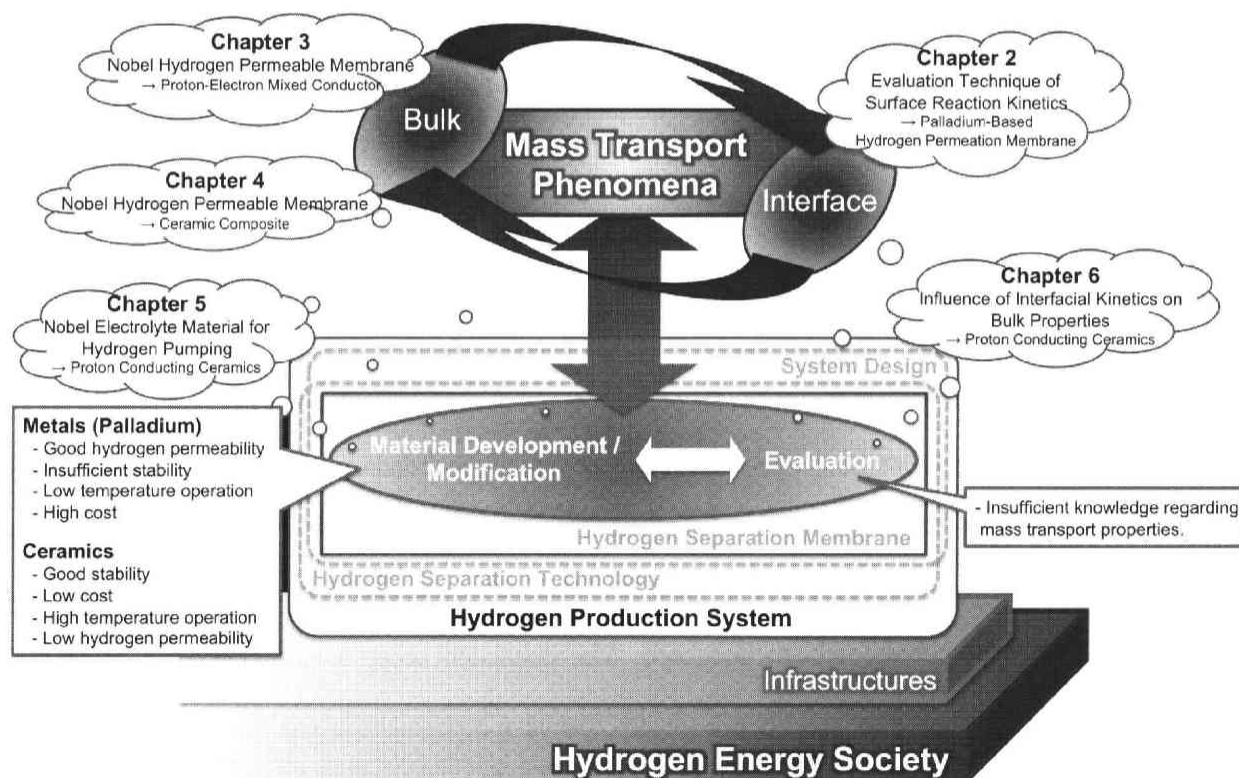
## 論文内容要旨

Continuous increase in demands on fossil fuels of today, which is expected in the future as well, will shortly bring about the exhaustion of the fuel resources. Thus, we have a necessity to reconsider the way to use of and have alternatives of fossil fuels. One possible scheme to overcome the above situation is to use hydrogen as an energy carrier in combination with polymer electrolyte fuel cells (PEFCs) as an energy converter. However, in the case that such an energy system spreads, demands on hydrogen is expected to explosively increase, and thus, infrastructures including hydrogen production, transport and storage need to be constructed. Figure 1 shows a schematic illustration of the key technological elements of hydrogen production with red square. In the illustration, hydrogen production from fossil fuels through the chemical processes is considered. Although hydrogen production from renewable resources is preferable in the long run, installing the system of hydrogen production from fossil fuels is a realistic strategy for the first step.

As described in Fig. 1, in hydrogen recovery from fossil fuels, hydrogen separation is one of the key technologies. Whereas various kinds of the candidate materials for the hydrogen separation membranes are proposed so far, the individual materials have advantages and disadvantages. For instance, palladium-based membranes are of particular interest due to its high and selective hydrogen permeation properties. Therefore, a compact system based on the abovementioned merits is expected. Meanwhile, cost reduction and improvements of durability are issues need to be addressed. Proton conducting ceramics having high chemical and mechanical stability better than palladium membranes can be a candidate for use in hydrogen separation. Since a

typical working temperature of this kind of materials is higher than palladium, thus, efficient use of waste heat is expected. However, the weakness is quite low hydrogen permeability. Thus, the ceramics having high hydrogen permeability need to be developed. The variety of the materials for the hydrogen separation membranes allows offering multiple options for hydrogen production system. Thus, making efforts on developments and modifications of the candidate materials for hydrogen separation membranes is important although there remain challenges on their performances.

From the viewpoint of materials science, hydrogen separation process is the mass transport phenomena through high temperature materials. Hydrogen permeation flux across the materials is based on the bulk properties, while interfacial reaction often governs the transport kinetics. Mixture of kinetics both in bulk and at the interfacial leads the mass transport phenomena to be complicated, and sometimes brings difficulties to design the hydrogen separation systems. Therefore, knowledge on mass transport phenomena will be helpful to design the systems and will



**Fig. 1** A schematic illustration of the key technological elements for hydrogen production system. Correlation between the purpose of the present thesis and hydrogen separation technology is provided.

be fed back to developments and modifications of the hydrogen permeation membranes. Developments of the hydrogen permeation membranes by this circulation will lead to practical uses of the hydrogen production technologies. As suggested above, in order to have the hydrogen permeation membranes with desired performances, not only seeking the materials but also having guidelines for developments and modifications of the materials are quite important. Based on this point of view, the present thesis aimed to provide suggestions for the developments of hydrogen separation membranes. The framework of the thesis can be divided into two parts: (i) To propose the concept of analytical technique of the mass transport phenomena (Chapter 2 and 6). Based on the proposed analytical technique, it was shown that the knowledge on the interfacial reaction can be reflected to design the hydrogen separation equipments. (ii) To propose concepts for developments and modifications of the hydrogen separation membranes. With model materials, the validities of the concepts have been examined (Chapter 3 to 5).

Among the materials considered for hydrogen separation membranes, palladium and its alloy membranes have gained particular attentions. That is because, not only significantly high hydrogen permeability but also high selectivity is attractive as a hydrogen separation membrane. When we look at the hydrogen permeation process, bulk diffusion is known to govern the hydrogen permeation kinetics across the membranes in a pure hydrogen system. However, the hydrogen permeation flux is reported to decrease by the interference effect of co-existing gases such as methane, carbon monoxide, carbon dioxide and/or methane on the surface reaction of hydrogen. Means, contribution of the surface reaction needs to be taken into consideration in order to describe the hydrogen permeation flux across the palladium-based membranes in practical systems. In chapter 2, in order to examine how a co-existing gas affects the hydrogen permeability of the palladium alloy membrane, hydrogen permeation measurements were carefully carried out. Based on the continuity of the surface reaction rate and bulk diffusion flux, the effect of co-existing gas on surface reaction has been quantitatively evaluated. The simulation using the empirical rate expression obtained in this thesis could fairly describe the hydrogen permeation flux in an actual module of the hydrogen production system. In addition, surface state of co-existing gas species were examined via an in-situ polarization modulated infrared reflection absorption spectroscopy. In mixture gas of hydrogen, water vapor and carbon monoxide, infrared absorption peak due to C-O stretching due to the surface adsorbed CO on the palladium-silver surface appeared. The peak intensity increased with

decreasing temperature. This tendency of the in-situ polarization modulated infrared reflection absorption spectroscopy was in consistent with that of the hydrogen permeation measurements in which the interference effect of the co-existing gas species was remarkable as temperature decreased. It suggests that the decreased permeation flux of hydrogen across the palladium-alloy membrane was attributed to the surface adsorbed co-existing gas species.

A membrane of hydrogen permeable ceramics, (Ce,Sr)PO<sub>4</sub>, was fabricated in chapter 3. In cerium-phosphate, CePO<sub>4</sub>, the substitution of lower valent cation, Sr<sup>2+</sup>, into Ce<sup>3+</sup>-site is expected to have two meanings: (i) Formation of protonic defect. Oxygen vacancy in the crystal lattice is introduced by the substitution and accepts ambient water vapor in the ceramics, resulting in introduction of protonic defect. (ii) Inducing mixed valence state of Ce<sup>3+</sup>/Ce<sup>4+</sup>, resulting in introduction of electronic defect. Thus, mixed proton and electron hole conduction is expected in Sr-substituted CePO<sub>4</sub>. The mixed conductivity of proton and electron hole, leads to the hydrogen permeability across the ceramic membranes. Electrical conductivity and hydrogen permeability of a mixed proton and electron (hole) conductor, (Ce,Sr)PO<sub>4</sub>, are evaluated in reducing conditions. From the electrical conductivity measurements under various partial pressures of oxygen and water vapor, contributions of proton and electron (hole) are separately evaluated based on a simplified defect equilibrium model. As was expected from the nature of defect chemistry, hydrogen has successfully permeated across the above ceramic membranes. This is, to the best of author's knowledge, the first report of hydrogen permeable ceramics in which any alkaline earth metals are not included as main components. Thus, compared to the hydrogen permeable perovskite type oxide, high chemical stability against ambient gas such as carbon dioxide and water vapor is expected in the class of the above materials. It was also found from the hydrogen permeation measurements that loading the surface catalysts such as platinum and palladium on the ceramic membranes improved the hydrogen permeation flux obviously. This means, contribution of the surface reaction kinetics to the total is significant. The hydrogen permeation flux of the cerium phosphate was found to be comparable to or slightly lower than those of the oxide materials reported in the preceding papers.

The ambipolar conductivity, consisting of proton and electron (hole) conductivities, is one of the key factors to determine the hydrogen permeation flux in the case of the solid solutions. However, it is quit difficult for the materials to satisfy both high proton conductivity and high electron (hole) conductivity due to thermodynamic reasons. Thus, a novel concept of the hydrogen

permeation membrane developed in chapter 4 is to use the composite materials in order to separately guarantee the pathways for protons and electrons. In the composite materials, it is expected to be free from the limitations on the partial conductivities mentioned above, possibly resulting in highly hydrogen permeable membranes. As a model of this concept, a composite material which consists of  $\text{SrZrO}_3$  and  $\text{SrFeO}_3$ ,  $(1-y)(\text{SrZrO}_3) - y(\text{SrFeO}_3)$ , were prepared for hydrogen separation membrane. In this system, it is expected that  $\text{Sr}(\text{Zr,Fe})\text{O}_3$  and  $\text{Sr}(\text{Fe,Zr})\text{O}_3$  phases individually provide pathways for protons and electrons, respectively. Electrical conductivity and hydrogen permeability of the above composite materials were evaluated in humidified reducing conditions. As expected, hydrogen was successfully permeated across the membranes of the composite materials for  $y = 0.05 - 0.2$  in which porous platinum was used as a surface catalyst. Based on the correlation between the hydrogen permeation flux and the electrical conductivity, it was found that the hydrogen permeation flux is well described by assuming the ambipolar diffusion-like kinetics for  $y = 0.1$  and  $0.2$  at  $1173 \text{ K}$  although the ceramic membranes does not consist of a single phase. However, as temperature and/or the content of  $\text{SrFeO}_3$ -based phase decreased, the hydrogen permeation fluxes were smaller than those estimated assuming the ambipolar diffusion mechanism. It suggested that the contribution of the surface reaction became large as temperature and/or the amount of  $\text{SrFeO}_3$ -based phase decreased.

Pure protonic conductors are also candidates for materials of hydrogen separation membranes. When current is supplied via the external circuit, hydrogen permeates across the ceramic membranes, adhering to the Faraday's law. In order to apply the pure protonic conductors as hydrogen separation membranes, the materials essentially need to have high bulk conductivity. In the preceding works, it was revealed that the conductivity of  $\text{LaP}_3\text{O}_9$ -based ceramics was higher than that of  $\text{LaPO}_4$ -based one. From the crystal structural point of view, difference in density of  $\text{PO}_4^{3-}$  in their crystal lattice may provide a possible explanation. That is because increased density of  $\text{PO}_4^{3-}$  may create more pathways for protonic defects. It may lead higher electrical conductivity. In chapter 5, based on the interpretations, ultra-phosphate,  $\text{La}_{1-x}\text{Sr}_x\text{P}_5\text{O}_{14-\delta}$  (nominally  $x = 0, 0.01, 0.03, 0.05$ ), has been prepared with expectation to show higher protonic conductivity than other phosphate-based proton conductors. It was found from the electrical conductivity measurements in both oxidizing and reducing atmospheres that the electrical conductivity slightly increased with increasing partial pressure of water vapor while it was almost independent on oxygen partial pressure. Since the

electrical conductivity showed isotopic effect of H<sub>2</sub>/D<sub>2</sub>, proton is concluded to be the major carrier in the ceramics. In addition, it was found that the electrical conductivity of porous specimen was smaller than that of the dense one while the activation energies were found to be almost the same. It suggests that the bulk is the conduction path for carrier species. Contrary to expectation, the electrical conductivity of the ultra-phosphate was smaller than that of La<sub>0.99</sub>Sr<sub>0.01</sub>P<sub>3</sub>O<sub>9-δ</sub>. The total conductivity was almost independent on the content of dopant, Sr. It suggested that the ceramics was saturated enough with small amount of dopant such as 1 mol%.

SrZrO<sub>3</sub>-based perovskite, is known to show mixed protonic and oxide ionic conduction in humidified hydrogen at high temperatures. When the material is used for electrochemical hydrogen pump, the overpotential at the interface is known to be significant. Thus, clarifying the interfacial kinetics is an emerging task to have directions to use this class of materials for a practical system. Chapter 6 aimed to evaluate the gas/solid interfacial reaction mechanism by ac and dc measurements. The electrochemical cell consisting of platinum and SrZr<sub>0.9</sub>Y<sub>0.1</sub>O<sub>3-δ</sub> as electrode and electrolyte, respectively, was tested in humidified hydrogen. From the steady state dc polarization measurements and ac impedance measurements under dc biases, the electrolyte resistance was found to vary by application of dc biases: the conductivity of the oxide increased by the anodic bias, while it decreased by the cathodic bias compared to that under open circuit voltage. In order to explain the variation of the electrolyte resistance, potential profiles and carrier distribution has been calculated by assuming that the gas/solid interface blocks oxygen or hydrogen. From the calculation results, it was found that the variation of the electrolyte resistance could be well described when oxygen is assumed to be partially blocked at the interface.

At the last of this thesis, based on the pieces of knowledge on the mass transport phenomena through the hydrogen separation membranes, the validities of the proposed concepts on analysis of the mass transport phenomena and on material developments and modifications were emphasized in Chapter 7.



# 論文審査結果の要旨

化石燃料の消費と地球温暖化ガスの排出を低減させるために、再生可能エネルギーを基盤とした水素エネルギーシステムの構築が急がれている。現実的なコストで水素を大量に製造するには現状では石油や天然ガスを原料とせざるを得ないが、これらを効率よく改質して高純度の水素を分離する手法を確立することは、水素ステーションの設置など水素をエネルギーキャリアとする社会基盤の整備を促すこととなり、水素エネルギーシステムの早期実現に向けた効果的な戦略となる。本論文はこのためのキーテクノロジーである水素の膜分離技術を取りあげ、システムを最適化する解析手法の確立と、高性能化のための材料設計指針の確立を目指したものであり、全7章からなる。

第1章は緒論であり、本研究の背景と目的を述べている。

第2章では、開発が進められているパラジウム合金系水素分離膜について、水素透過能に及ぼす表面過程の影響を評価し、改質残留ガスを含む現実のシステムで想定される水素透過流量を定式化する手法を提案している。これは、膜表面直下の固相中の水素の活量を、水素透過速度の精密解析から明らかにし、これにより表面反応に消費されるエネルギーと流束との関係式を得て、そのパラメータとして共存ガスの影響を定量化するものである。本章ではさらに、表面反応阻害の発生と共存ガス吸着との相関を偏光変調高感度赤外吸収分光法により実証している。これらの成果は、膜分離改質システムの最適設計を行う上で非常に重要な成果である。

第3章では、合金系水素分離膜に比べて形状安定性に優れる、プロトン導電性セラミックスを用いた水素透過膜の設計について述べている。プロトン導電材料を水素透過膜として利用するためには、プロトンが運ぶ電荷を中和する電子の導電性を付与することが必要となる。本章では化学的安定性の高いリン酸塩系材料を取りあげ、希土類サイトにセリウムを用いることで、その混合原子価により電子導電性を発現させることを提案している。実際に、 $(\text{Ce,Sr})\text{PO}_4$ において、リン酸塩系材料としては世界で始めて水素透過能を確認しており、重要な成果である。

第4章は、プロトン-電子混合導電性セラミックスを、より高い自由度で設計する手段として、2相共存状態として存在する電子導電体とプロトン導電体を利用することを提案している。具体例として、プロトン導電相である $\text{SrZrO}_3$ と電子導電相である $\text{SrFeO}_3$ の混合相を取り上げ、安定性と相関係を明らかにした後、その水素透過性能の測定を行っている。その結果、この混合相は各相の導電特性を均質化した混合導電体として振る舞うことを明らかにしている。これは高性能な水素透過膜材料の設計に関する重要な成果である。

第5章では、外部回路に電子を通すことで水素を分離する、所謂水素ポンプの電解質として使用されるプロトン導電性材料の探索を行っている。改質残留ガスに対して化学的に安定な材料系の中から、ウルトラリン酸と称される一連の化合物群 ( $\text{La}_{1-x}\text{Sr}_x\text{P}_5\text{O}_{14d}$ ) について導電挙動と  $\text{H}_2/\text{D}_2$  同位体効果を測定し、プロトン導電性を明らかにしている。高い導電率を持つプロトン導電材料の設計指針を与える重要な成果である。

第6章は、水素ポンプにおけるバルクと界面の輸送特性の相関について述べている。 $\text{SrZrO}_3$ 系のプロトン導電性材料では、通電下で電解質のバルク輸送特性が変化することが知られているが、これが界面での酸化物イオンのブロック現象に起因することをシミュレーションにより明らかにしている。界面輸送がバルクの物性を変調することを示すもので、基礎科学的にも応用分野においても重要な成果である。

第7章は結論であり、本論文を総括している。

以上要するに、本論文は、水素エネルギーシステムの早期構築に向けて、水素の膜分離技術に利用される種々の

材料を、それぞれの開発段階に応じて解析・設計する手法を示したものであり、環境科学および機械システムデザイン工学の発展に寄与するところが少なくない。

よって、本論文は博士（環境科学）の学位論文として合格と認める。