学 位 論 文 の 要 約

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学 位 論 文 題 名

Study on dual-phase oxygen separation membrane with percolation structures of oxide ionic and electronic conductors
(酸化物イオン・電子伝導体のパーコレーション構造を持つ二相酸素分離膜に関する研究)

Oxygen separation membrane has attracted attention for a small-scale oxygen producing device which is suitable for developing for the household oxygen generator. Mixed ionic-electronic conducting (MIEC) membrane demonstrates high oxygen selectivity and high permeability. The theoretical oxygen permeation mechanism in single-phase MIEC membranes is illustrated in Figure 1.　MIEC material development is one of the most important issues to improve performance. However, it is difficult to improve both oxide ionic and electronic conductivities in single-phase materials. The dual-phase membrane, which is composed of an oxide ion conductive phase and an electronic conductive phase, has an advantage over a single-phase membrane. Those two phases combine the best characteristics of the used materials to achieve both a high oxygen permeability with good chemical and mechanical stability, at elevated temperatures and under harsh conditions. In this research work, the fabrication of novel dual-phase membranes was achieved by varying materials combination, fabrication process and modification to obtain oxygen separation performance. This dissertation consists of six chapters:
Chapter 1 presents the current status of oxygen separation membranes and the significance of this study; Chapters 2-5 describe the results obtained in this study; and Chapter 6 presents a summary. Chapter 1 is an introduction to this research. The background and essential information for understanding the basics of oxygen separation membrane is explained, and the current situation of this research field is conveyed.
In Chapter 2, a new facile fabrication method using vacuum infiltration and spark plasma sintering (SPS) processes for a dual-phase membrane with a co-continuous structure has been presented. A schematic showing the preparation process of the YSZ-carbon felt dual-phase membranes is shown in Figure 2. The slurry of 8 mol% yttria-stabilized zirconia (8YSZ) was filled in the void of a porous body of carbon felt by a vacuum infiltration process. Spark plasma sintering (SPS) process was adopted as sintering method, a schematic of the SPS is shown in Figure3. The process conditions such as sintering temperature and applied pressure were optimized. The YSZ-based dual-phase membrane with gas-tight and co-continuous structures, high chemical compatibility and good phase stability was successfully fabricated. YSZ-C felt dual phase membrane has an ability to separate the oxygen at 550 ℃, suggesting that this new processing route can be used to fabricate oxygen separation membranes. However, oxidation of the carbon felt occurred at temperatures up to 600 ℃. Searching for a suitable electronic conductor was discussed in the next research chapter.

In Chapter 3, several electronic conducting phases (nickel, nickel-chromium alloy, 316L stainless steel and silicon carbide) were investigated to determine suitable materials against 8YSZ. Figures 4 indicate the structures of the various metal foams. The use of open-cell metal foam (or metal foam with 3D porous structure) as the electronically conductive phase was attempted. 8YSZ was filled into the voids of the metal foam by a vacuum filtration process. Aplatinum coating was applied to the sample surface after SPS sintering. The platinum coating process was expected to prevent oxidation of the metal phase during oxygen separation characterization and promote gas exchange reactions at the membrane surface. Among the electronic conducting phases used, 316L stainleess steel (SS) showed good oxidation resistance and non-reactivity with YSZ. However, there was a limit to improving the oxygen separation performance. The optimization has to be tried more. The experimental factors should investigate more deeper to determine the optimal condition.

In Chapter 4, 8YSZ-316L SS dual phase membrane was fabricated with a variation of stainless steel powder contents. The SS content was varied from 15 vol% to 55 vol% to achieve a percolation structure for obtain the oxygen transport activity as shown in figure 5. The surface modification was done by applying silver paste on both side of the membrane. In this research study, a free-standing dense 8YSZ-SS membrane with a thickness of 0.5 mm was successfully fabricated by SPS. Figure 6 shows the internal structure images of the YSZ-SS45vol% dual-phase membrane observed by X-ray CT. The 3D images of the YSZ and SS phases suggested that both phases have percolation structures. YSZ-SS45vol% dual-phase membrane with a silver coating exhibited the oxygen permeation flux (j_{O2}) of 1.38 ml (STP)/min cm^2 at 900 ℃. With a silver coating, 8YSZ-SS45vol% dual-phase membrane exhibited the high oxygen permeation flux among the performance of dual-phase membrane reported so far.

In Chapter 5, further improvement of the oxygen separation performance of the 8YSZ-45vol% SS dual phase membrane was studied. In order to improve the oxygen flux by improving the oxygen exchange rate, both sides of the YSZ-SS dual-phase membrane surface were coated with Ba0.5Sr0.5Co0.8Fe0.2O3-δ (BSCF), which is an excellent mixed oxide ionic electronic conductor (MIEC). To prevent the reaction between YSZ and BSCF, a thin GDC-SS buffer layer was formed on both sides of the YSZ-SS dual phase membrane before the coating of BSCF. In this study, electrophoretic deposition (EPD) was selected as a method to deposit BSCF on the membrane surface. In Figure 7, shows the preparation of the multi layered membrane. The EPD conditions such as the suspension condition, the applied voltage and the deposit time were investigated. The applied voltage and the deposition time at 150 V and 10 min achieved the most homogeneous coating. After the coating process, the multi layered membrane was fired at 800 °C to obtain the BSCF porous layers. In this study, fabrication of a membrane with a five-layer sandwich structure was achieved. The microstructure of the membrane is shown in Figure 8, but evaluation of the oxygen separation properties was left as future work.

In Chapter 6, the results obtained in this study were summarized, and the effectiveness of the dual-phase membrane for oxygen separation application, and the importance of the fabrication process and materials selection were concluded.

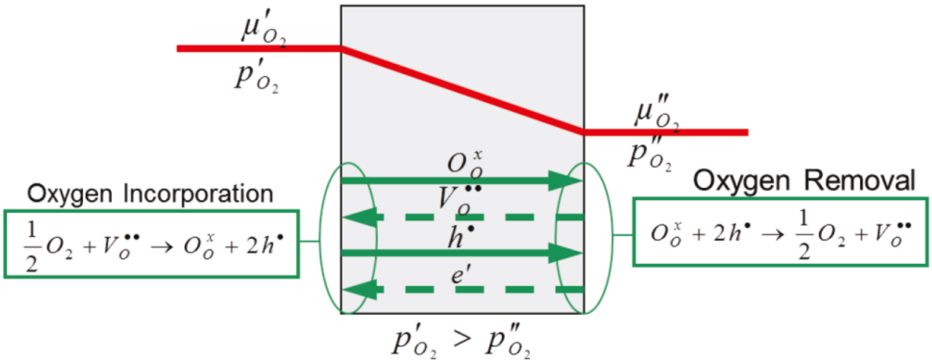

Fig. 1 Oxygen separation mechanism of the oxygen separation membrane [Santos J.C., Cruz P., Regala T., Magalhães F.D., and Mendes A., Industrial & Engineering Chemistry Research, 46(2007) 591-599.]

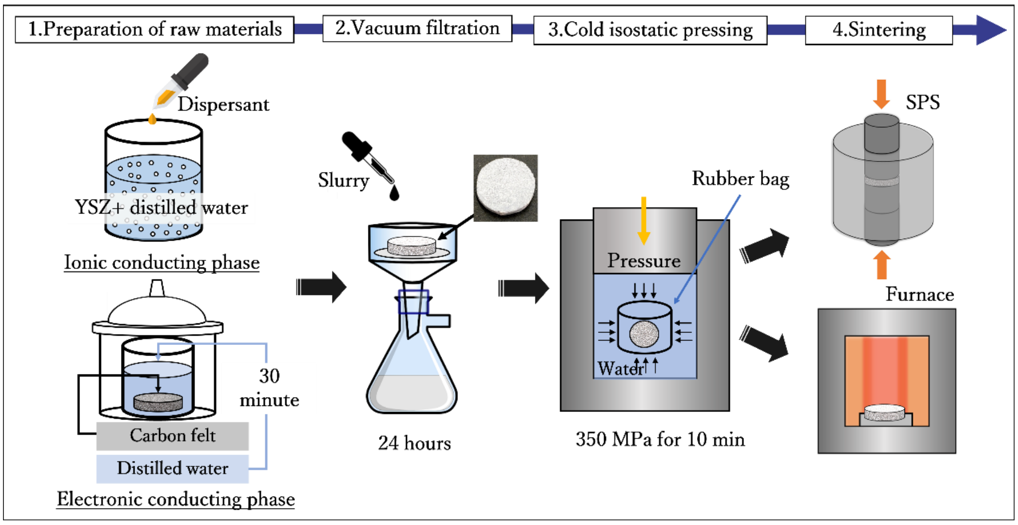

Fig. 2 Schematic showing the preparation process of YSZ-based dual-phase membrane

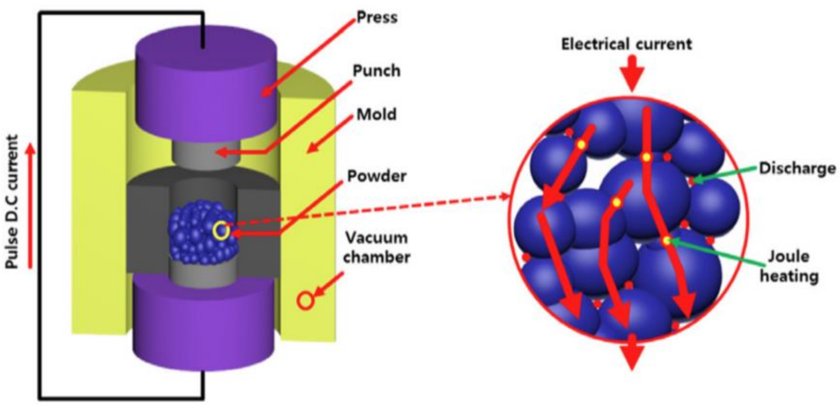

Fig. 3 Schematic diagram of Spark Plasma Sintering process [Lee S., Ceramist, 22(2019) 170-181.]

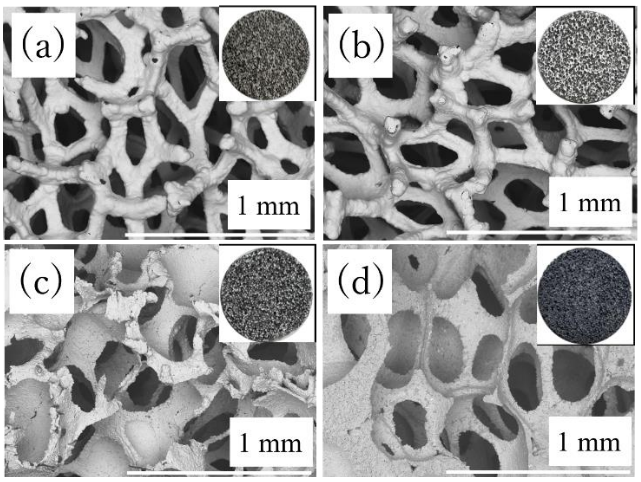

Fig. 4 Microstructure of (a) nickel foam, (b) nickel chromium foam, (c) 316L stainless steel foam and (d) silicon carbide foam.

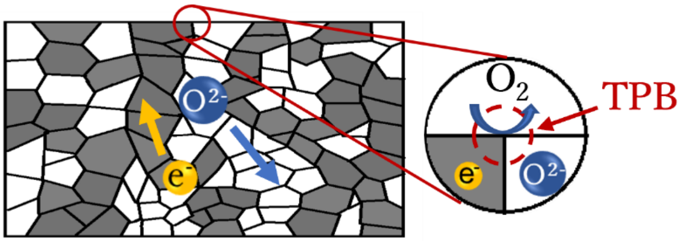

Fig. 5 Schematic overview of triple phase boundary (TPB) in a dual-phase membrane material. The white and grey regions indicate the oxide ion and electron-conducting phases, respectively.

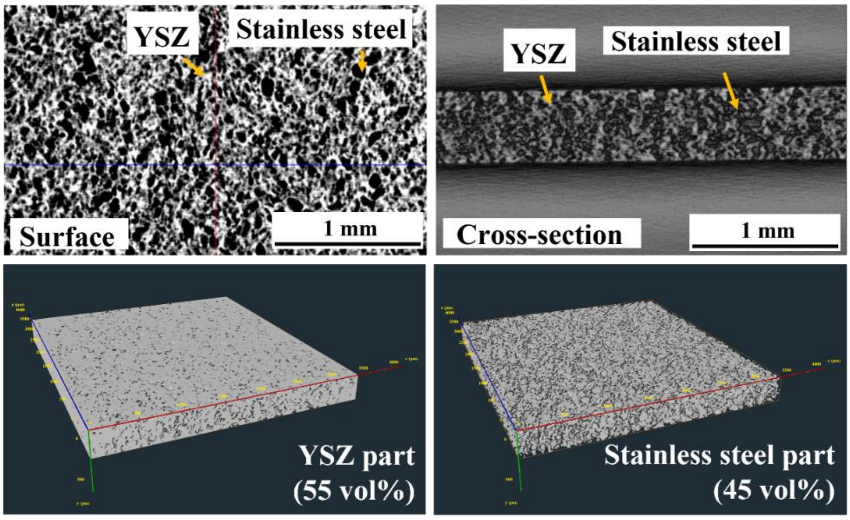

Fig. 6 X-ray CT image of YSZ-SS45vol% dual-phase membrane. The white and black regions indicate the YSZ and SS phases, respectively.

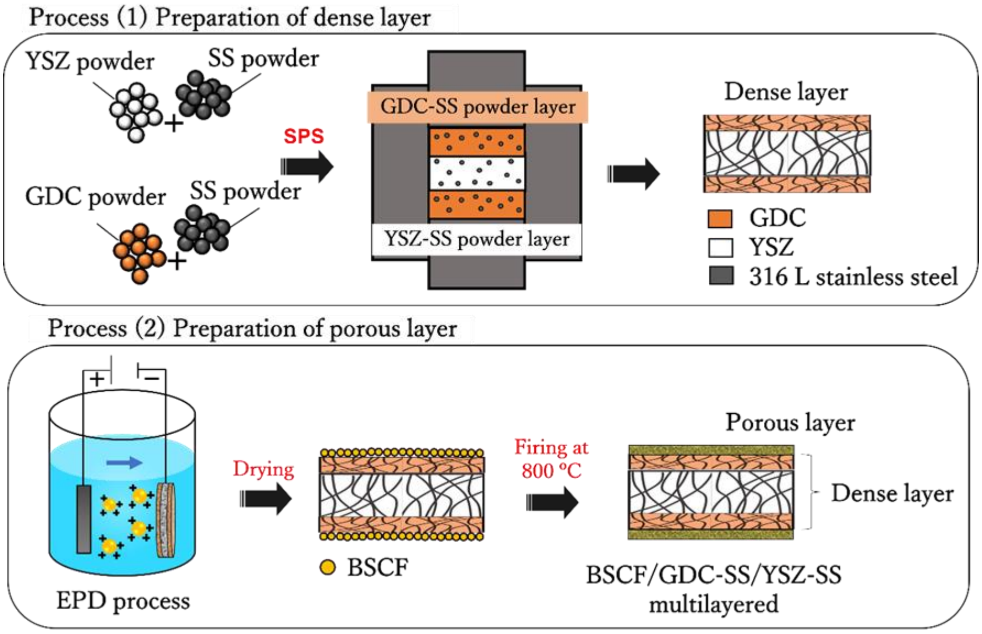

Fig. 7 Schematic showing the preparation process of multi-layered dual-phase membranes.

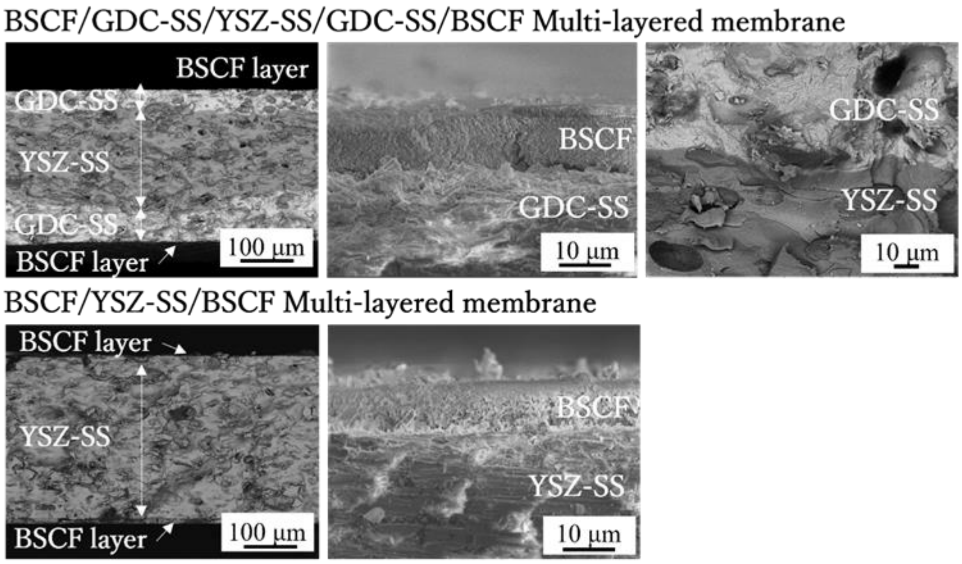

Fig. 8 Cross section images of the microstructures of multi-layered membrane