学 位 論 文 内 容 の 要 旨

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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 demonstrate high oxygen selectivity and high permeability. 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 stabilities, 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. 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. 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 °C, 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 °C. 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. 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. A platinum 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 have to be tried more. The experimental factors should investigated 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. 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. The 8YSZ-SS45vol% dual-phase membrane achieved good percolation structure of the 8YSZ and SS phases. 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 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (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. 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 were 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, 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.