

論文の内容の要旨

論文題目 Polarization and microstructure characteristics of solid oxide fuel cell composite cathodes

(固体酸化物形燃料電池コンポジット空気極の分極特性および電極微細構造に関する研究)

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Fuel cells attract great attention as one of the promising power systems for next generation due to its various merits. Fuel cells can achieve high system efficiency since they directly convert chemical energy to electrical energy. Fuel cells are also environmental-friendly since pollutants do not emit during operation. Especially, solid oxide fuel cells (SOFCs) which operate at high temperature, e.g. 700 ~1000°C, show high efficiency and fuel flexibility compared to other types of fuel cells. The system efficiency can be further improved by combining with waste heat recovery systems.

In SOFC, oxygen is ionized in the cathode, and oxide ion diffuses through the electrolyte and reacts with the fuel in the anode. However, high operation temperature also brings some serious issues. System durability is deteriorated by high thermal stresses in the systems. Furthermore, system cost is increased due to the usage of expensive materials which have durability at high temperatures. If operation temperature of SOFC can be decreased, reliability and system cost are also reduced drastically. However, the efficiency of SOFC will be deteriorated especially for the cathode side. In order to overcome this issue, recent SOFCs employ mixed ionic-electronic conductors (MIECs) for cathode materials. Conventional SOFC cathodes consist of three phases, i.e. pore, electronic and ionic conductors. Electrochemical reaction takes place at triple phase boundary (TPB) where three phases meet at a same position. On the other hand, electrochemical reactions can take place not only at the TPB, but also at the surface for the MIECs. Thus, cathode performance is improved due to the increase of reaction area.

Representative MIEC materials are $\text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_{3-\delta}$ or $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ ($x, y =$ from 0.1 to 0.9). However, ionic conductivity of MIEC materials decreases drastically at low operation temperatures. Therefore, composites of MIEC with high ionic conductors have been investigated in order to improve the cathode performance at low operation temperatures. In fact, performance enhancements of MIEC-ionic conductor composites have been experimentally reported by several researchers. However, MIEC surface area is decreased due to the increase of ionic conducting phase of the composite. Therefore, it is considered that performance is enhanced by not only by the improvement of ionic conduction kinetics, but also by the TPB reactions in the composite. In order to develop efficient MIEC-ionic conductor composite cathodes, it is necessary to investigate concrete electrochemical reaction mechanisms of composite cathodes.

In the present study, electrochemical reaction mechanisms of MIEC-ionic conductor are investigated by both experiments and numerical simulations. $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$ (LSCF) and $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC) were used as the MIEC materials, and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$ (GDC) was used as the ionic conductor. An electrolyte-supported cell was prepared for the experiments. Ni-GDC was used as the anode material and GDC was used as the solid electrolyte material. LSCF-GDC and LSC-GDC composite cathodes with different volume ratios were fabricated onto the GDC electrolyte by screen printing method. Cathode-reference measurements were conducted, and I-V characteristics and electrochemical impedance spectroscopy were measured at 700°C with 100 % of pure oxygen. Activation overpotentials were quantified by extracting ohmic losses. Polarization resistances were obtained from the electrochemical impedance spectroscopy results.

Cathode microstructures were reconstructed by dual beam focused ion beam-scanning electron microscopy (FIB-SEM). Epoxy resin was infiltrated into the post-tested cells in order to distinguish pore phases in the cathodes. Then, the specimens were polished by a cross-section polisher. An energy selective backscattered (EsB) detector was used for the FIB-SEM measurement. Microstructure parameters were calculated, and the results were correlated with cathode polarization characteristics.

Electrochemical reaction mechanisms were investigated by Lattice Boltzmann Method (LBM). In the numerical simulation, both surface reaction and TPB reaction were considered. Exchange current densities for the surface reaction were fitted by the experimental results of pure LSCF and LSC cathodes. Those for the TPB reaction were fitted by the experimental results of composites. Current and oxygen chemical potential distributions were quantified.

For the LSCF-GDC composite cathodes, the best performance is achieved at a volume ratio of LSCF:GDC = 30:70 %. Neither LSCF surface reaction nor TPB reaction can individually explain the performance of LSCF-GDC composites by a single reaction mechanism. As the volume fractions of GDC in the composites increase, reactive thicknesses are elongated. Slight discrepancies between experimental and simulation overpotential results are observed for the volume ratios of LSCF:GDC = 50:50 and 70:30 %. It is considered that improvement of effective ionic conductivity by GDC addition contributes to

the performance enhancement of LSCF-GDC composite cathode. Dependence on ionic conductivity of LSCF is investigated by the numerical simulations. The effective thickness of LSCF:GDC = 30:70 % is achieved at around 40 μm by experiments. Figure 1 shows the experimental overpotential results and the 3D reconstructed microstructures of LSCF-GDC composite cathodes, respectively.

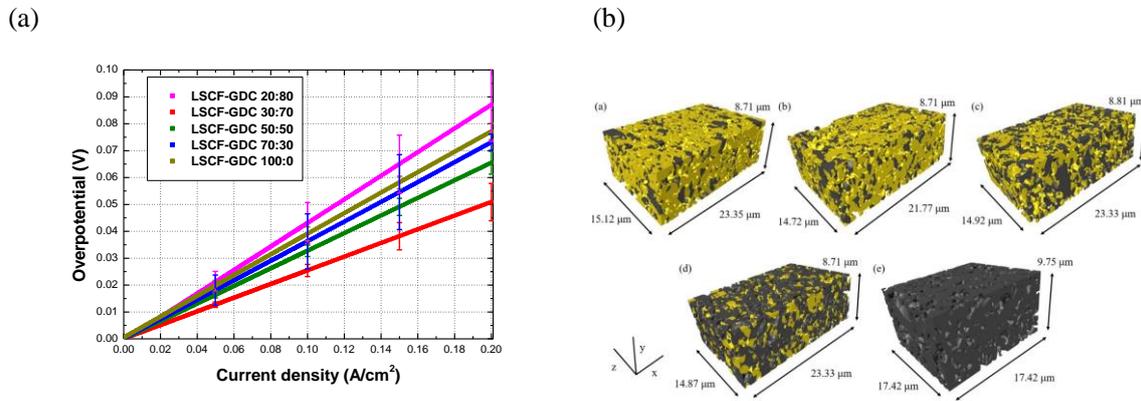


Fig. 1 (a) Experimental results of overpotential and (b) 3D reconstructed microstructures of LSCF-GDC composite cathodes (Yellow: GDC, dark gray: LSCF).

Figure 2 indicates the experimental overpotential results and the 3D reconstructed microstructures of LSC-GDC composite cathodes, respectively. For the LSC-GDC composite cathodes, again a volume ratio of LSC:GDC = 30:70 % shows the best performance. It is considered that reaction mechanisms of LSC-GDC are the same with those of the LSCF-GDC composite. Performances of LSC-GDC composite cathodes are better for all volume ratios than the LSCF-GDC. It is shown that LSC shows high sinterability which leads to small surface area but higher active TPB density at low GDC volume fractions. It is considered that not only the increase of reaction area due to the sintering of LSC, but also the improvement of effective ionic conductivity of the LSC contribute to the performance enhancement of LSC-GDC composite cathodes.

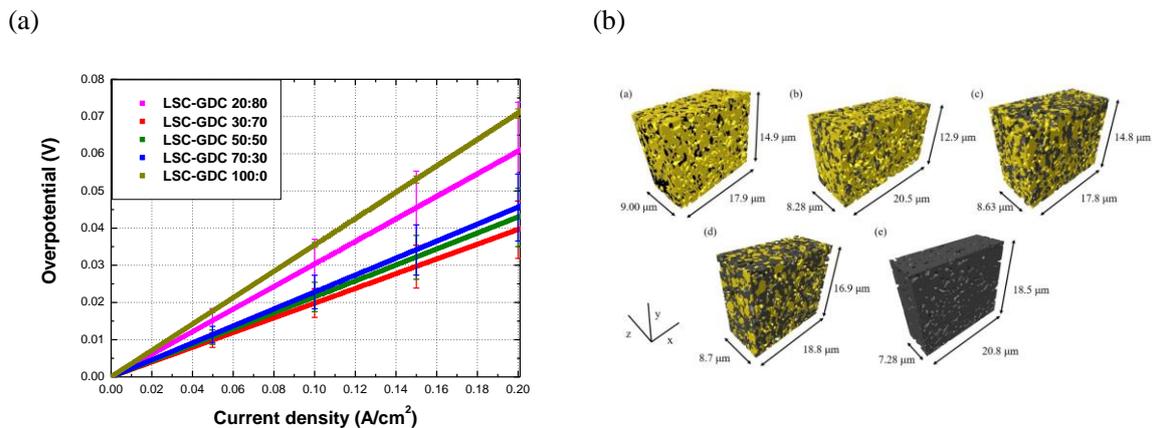


Fig. 2 (a) Experimental results of overpotential and (b) 3D reconstructed microstructures of LSC-GDC composite cathodes (Yellow: GDC, dark gray: LSC).

In order to investigate more deeply the contribution of surface and TPB reactions of the LSC-GDC composite, different sizes of original powder are prepared. LSC of 0.5 μm and GDC of 3 μm (GDC3), LSC of 3 μm and GDC of 0.5 μm (LSC3) are mixed with a volume ratio of 50:50 %. It is assumed that TPB length do not change significantly because the volume ratio is fixed. The GDC3 cathode showed better performance compared to the LSC3 cathode. For the GDC3 cathode, LSC surface area and active TPB density are increased due to higher sinterability of LSC compared to GDC. Tortuosity factor of GDC didn't change with different original particle sizes. However, for LSC, the tortuosity factor is decreased significantly when started from small powder size. It is considered that the increase of reaction area and improvement of ionic conductivity inside the LSC due to the sintering of LSC contributes to the performance enhancement of GDC3 cathode.

LSC-GDC composite cathodes with the volume ratios of 30:70, 50:50 and 70:30 % are discharged with current density of 0.2 A/cm^2 for 100 hrs. As the volume fraction of GDC increases, cathode performance is degraded more significantly. Microstructure parameters before and after operation are investigated. It is shown that performance degradation cannot be explained by microstructural variations. After operation, inhomogeneous microstructures of LSC are observed. It is considered that the LSC-GDC performance is degraded by the morphological change of LSC. Figure 3 represents the morphological change of LSC phases between at initial and after 50 hrs operation. Best performance at initial condition and lower performance degradation rate are achieved for a volume ratio of LSC:GDC = 30:70 %. Therefore, it is expected that a 30:70 % is the most promising volume ratio of LSC-GDC composite for the SOFC cathode material.

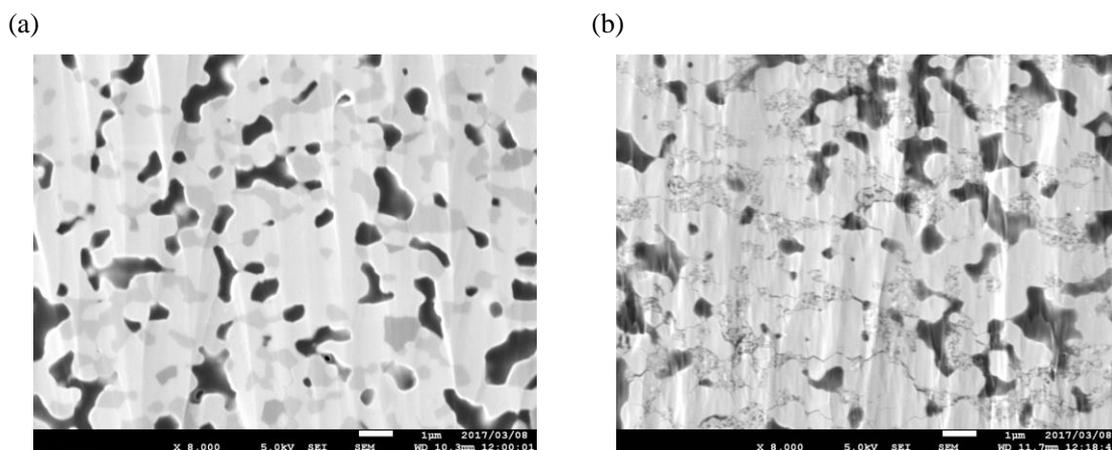


Fig.3 SEM micrographs of LSC:GDC = 30:70 vol. % cathode (a) at initial and (b) after 50 hrs operation (Dark gray: LSC, light gray: GDC).