

Study on flowerlike ceria-zirconia as a catalyst support for solid oxide fuel cell directly fed by biogas

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(バイオガスの直接供給で作動する固体酸化物形燃料電池への適用を目的とした花びら形状セリア-ジルコニア触媒担体に関する研究)

区 分 : 甲

論 文 内 容 の 要 旨

Biogas, the mixture of CH_4 and CO_2 , is regarded as a promising renewable energy source that can be produced by anaerobic digestion of organic wastes such as agricultural residues, garbage, etc. Solid oxide fuel cell (SOFC), high temperature electrochemical conversion device, can accept the direct supply of biogas. In feeding biogas to SOFC anode (Ni-stabilized zirconia composite), dry reforming of methane (DRM: $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{CO} + 2\text{H}_2$) takes place within the anode to produce syngas (the mixture of H_2 and CO) which is electrochemically oxidized to generate electricity. In this concept called direct internal reforming SOFC (DIR-SOFC), any hydrocarbon fuels other than biogas can be directly converted to electricity.

The main roadblocks to the realization of DIR-SOFC are the coking on the anode material and the thermal shock due to the strong endothermicity of DRM, resulting in cell performance deterioration. These issues can be solved by the application of paper-structured catalyst (PSC) technology based on the ceramic fiber network in which Ni-loaded catalyst supports are dispersed. When the PSC is mounted on the anode, DRM primarily takes place within the catalytically active PSC domain to mitigate coking within the porous anode and the thermal shock to SOFC.

This study tried to create a new catalyst support to be dispersed in the ceramic fiber network for the enhancement of the catalytic activity of PSC for DRM. For this purpose, ceria (CeO_2) with oxygen storage capacity (OSC) was selected as a basic material. OSC, in other words lattice oxygen in an oxide, can contribute to the surface reaction such as the removal of carbonaceous species deposited on a catalyst surface. The challenges were how to enhance the OSC of ceria as much as possible and how to suppress Ni agglomeration loaded on the ceria-based oxide support. An idea to meet both requirements is to develop the ceria-zirconia (ZrO_2) solid solution (abbreviated by CZ) with flowerlike morphology denoted as CZ(F).

After the optimization of the hydrothermal process to obtain flowerlike CeO_2 (C(F)) in Chapter 3, $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ (x is the molar ratio of $\text{Zr}/(\text{Ce} + \text{Zr})$ in the precursor) was synthesized by the one-step hydrothermal process (Chapter 4). OSC value of the $\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ monotonously increased with x . $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ (CZ0.5) exhibited OSC value of $517 \mu\text{mol-O}_2 \text{ g}^{-1}$ corresponding to the OSC utilization rate of 61%, whereas those of pure CeO_2 (CZ0) were only $284 \mu\text{mol-O}_2 \text{ g}^{-1}$ and 20%, respectively. However, unfortunately, flowerlike morphology could not be formed for the composition of $x \geq 0.3$, because Zr^{4+} without redox ability in the precursor solution may hinder the production of N-containing graft copolymers and subsequent

self-assembly of these copolymers during the hydrothermal process.

To solve this issue, a novel process, the two-step hydrothermal process was developed, which enables to obtain the CZ(F) particles even at $x = 0.5$. In the first hydrothermal process (1st-step), the precursor of flowerlike ceria, C(F), was prepared as a core. Then, the Zr^{4+} -containing solution was added to the slurry after the 1st-step with $x = 0.5$, followed by the second hydrothermal process (2nd-step) and subsequent calcination at 600°C . $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ particles synthesized by the two-step process had the flowerlike morphology (denoted as CZ(F)0.5), and its OSC value was $536 \mu\text{mol-O}_2 \text{ g}^{-1}$, corresponding to the OSC utilization rate of 63%.

$\text{Ce}_{1-x}\text{Zr}_x\text{O}_2$ prepared by the one-step process at $x = 0, 0.2$, and 0.5 and by the two-step process at $x = 0.5$ were loaded with Ni, and then dispersed in the ceramic fiber network to prepare PSCs, which were utilized for the DRM tests at 750°C for 15 h. The one with the flowerlike $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ obtained by the two-step process (CZ(F)0.5) exhibited the highest catalytic activity, and the highest coking tolerance among the tested PSCs, because, in addition to the highest OSC, the size of the pores surrounded by the flower petals may be most appropriate for Ni metal particles to penetrate into the pores and settle on the flat surface of the petals, resulting in greater metal-support interaction to enhance the ability to burn off the carbonaceous species accumulated on the catalyst surface.

DRM tests performed at 650°C with Ni/CZ(P)-PSC (synthesized by co-precipitation) and Ni/CZ(F)0.5-PSC (developed in this study) under the same gas hourly space velocity (GHSV) clearly demonstrated the advantage of the flowerlike morphology of CZ. Non-flowerlike CZ-dispersed PSC (Ni/CZ(P)-PSC) was intolerant to coking at this temperature, however for the flowerlike CZ-dispersed PSC (Ni/CZ(F)0.5-PSC) nearly no coking took place.

PSC with high mechanical flexibility and ease of handling allows us to provide any types of cell stack with catalytic function by just inserting PSCs between single cells, eliminating an external reformer to realize downsizing and cost reduction of SOFCs. In Chapter 5, Ni-PSC (PSC without the dispersion of ceria-based support) and Ni/CZ(F)0.5-PSC (Ni-loaded flowerlike $\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2$ -dispersed PSC) were mounted on the porous anode of electrolyte-supported cell (ESC), and 100 h galvanostatic tests of DIR-SOFC fueled by simulated biogas ($\text{CH}_4/\text{CO}_2 = 1$) were performed at 750°C under 0.1 A cm^{-2} for the assemblies of Ni-PSC|ESC and Ni/CZ(F)0.5-PSC|ESC, and for the ESC without PSC as well. By the application of PSCs on the anode, performance of the DIR-SOFC was remarkably elevated as a result of the enhancement of open circuit voltage (OCV) over 100 mV. However, during the 100 h test, significant coking occurred within the Ni-PSC and the porous anode of Ni-PSC|ESC, resulting in large increases in both charge transfer and mass transfer resistances. On the other hand, the Ni/CZ(F)0.5-PSC|ESC exhibited considerably stable performance without changes in both resistances due to the inhibition of coking, demonstrating that Ni/CZ(F)0.5-PSC is a promising structured-catalyst for realizing DIR-SOFC.