Direct Oxidation of Methane by Pd–Ni Bimetallic Catalyst over Lanthanum Chromite Based Anode for SOFC

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Steady generation of electricity with dry CH_4 fuel, 150 mW·cm^{-2} at 1073 K and 360 mW·cm^{-2} at 1173 K, was successfully performed by a low loading of Pd–Ni bimetallic catalyst on a lanthanum chromite based porous-composite anode for solid oxide fuel cells (SOFC). The amounts of carbon deposition were quite small under the open and closed circuit conditions. The electrocatalytic activity of the Pd–Ni catalyst was significantly higher than that of Pd or Ni catalysts.

Direct utilization of hydrocarbon fuels in solid oxide fuel cells (SOFC) is received a great attention for effective energy conversion to electric power. In particular, direct oxidation of hydrocarbons, not through internal steam reforming, is strongly desired because of an increase in energy conversion efficiency and a reduction of operation costs. There are, however, major problems of (i) carbon deposition and (ii) low electrocatalytic activity to achieve the direct oxidation of hydrocarbons over the typical (Ni + YSZ) cermet anode. Some attractive works were reported to suppress carbon deposition using new anode materials, Cu–ceria cermet[1] and lanthanum chromite-based anode.[2] Since these materials have low electrocatalytic activity for the oxidation, the additions of Rh,[3] Ni,[4] and Pd[5] catalysts were reported. However, theses electrocatalytic activities are not enough, especially for the CH_4 fuel. Further acceleration of electrocatalysis is essential to develop active anodes for the CH_4 oxidation. We have investigated active elecrocatalysts for the CH_4 oxidation and found a synergy of Pd and Ni catalysts over a porous-composite anode ($La_{0.8}Sr_{0.2}CrO_3$ and $Ce_{0.8}Sm_{0.2}O_{1.9}$). We report the performance of the direct oxidation of CH_4 over the Pd–Ni bimetallic catalyst in this work.

A solid electrolyte used in this work was $La_{0.83}Sr_{0.17}Ga_{0.8}Mg_{0.2}O_3$ electrolyte[6] disk (diameter 14 mm, thickness 0.5 mm, Japan Fine Ceramics Co.). The porous-composite anode which consists of two layers, first layer: $Ce_{0.8}Sm_{0.2}O_{1.9}$ (SDC) and second layer: SDC and $La_{0.8}Sr_{0.2}CrO_3$ (LSCr) (50:50 wt %). LSCr powder was synthesized by the Pechini method and finally calcined at atmosphere for 8 h at 1423 K. One side of the LSGM electrolyte disk was painted with the first ink prepared from SDC powder (Toshima MFG Co.), ethyl cellulose (Aldrich Co.) and benzyl alcohol (Wako Co.). After drying up at 343 K, the second layer painting was carried out with the second ink prepared from SDC powder, LSCr powder, ethyl cellulose and benzyl alcohol. The LSGM painted double layer was sintered at 1573 K for 5 h. The both thicknesses of the first and second layer were about 15 µm. LSCr works as an electronic conductor, therefore loading of metal can be reduced compared with conventional Ni cermet anodes.[4,5] A cathode was prepared from $La_{0.8}Sr_{0.2}CoO_3$ (Japan Pure Chemical Co.). The geometric areas of both electrodes were 0.28 cm^2. Pd and Ni were loaded on the porous-composite anodes by the impregnation method.[7] Typical loadings of Pd and Ni were 5.8 µmol·cm^{-2} corresponding to about 9 wt % for Pd and 5 wt % for Ni, respectively.

Au paste (TR-1301, Tanaka Precious Metals Co.) was coated on the anode to connect a current collector of Au mesh. Pt paste (TR-7601, Tanaka Precious Metals Co.) and Pt mesh were used for cathode connection. An activation treatment for the anode was carried out to reduce Pd and Ni with H_2 of 34 kPa for 30 min at 1073 K before the fuel-cell reaction. SOFC performance experiments were carried out by using dry H_2 and CH_4 fuel gases of 101 kPa. Cell voltages were controlled by an electrochemical instrument system (Electrochemical Interface 1287, Solartron). Oxidation products of CH_4 over the anode were CO, CO_2, H_2, and H_2O. The formation rates of the products were determined by an online gas chromatograph (GC-8A, Shimazu) with a TCD and He carrier gas. CO_2 and H_2O were analyzed by a Gaskuropack 54 column ($3\phi \times 2$ m) and CO was done by an AC column ($3\phi \times 2$ m). H_2 was analyzed by another GC-8A with a TCD, Ar carrier gas and an AC column.

We have studied the electrocatalysis of the bimetals (Pd, Rh, Pt, Ni, Co, Cu, Fe, and Mn) from the view point of the activation of C–H bond, and found the synergy of Pd and some co-additives (Ni, Rh, Fe, and Mn). In these combinations, the Pd–Ni catalyst was the best for the anodic oxidation of CH_4. Figure 1 shows time courses of current density over the Pd–Ni/, Pd/, Ni/ and

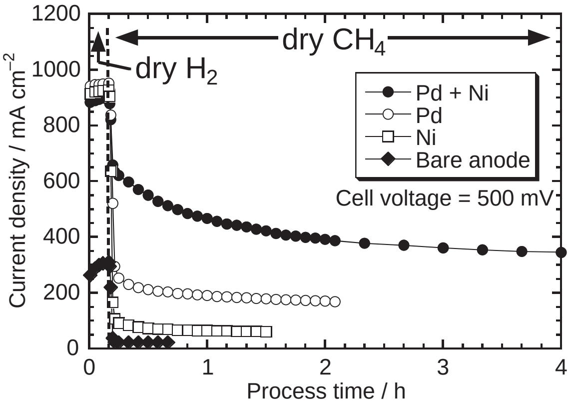

Figure 1. Time courses of current densities for the Pd–Ni/(LSCr + SDC)/SDC, Pd/(LSCr + SDC)/SDC, Ni//(LSCr + SDC)/SDC and (LSCr + SDC)/SDC anodes at 500 mV and 1073 K. Pd and Ni loadings; 7.7 µmol·cm^{-2}.

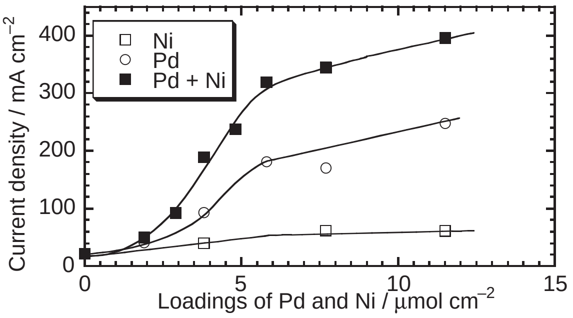

Figure 2. Effects of catalysts loadings on current densities in steady states for the CH_4 oxidation over the (LSCr + SDC)/SDC anode at 500 mV and 1073 K. The horizontal axis indicates each loading of Pd and Ni. The Pd–Ni/anode of *x* µmol cm^{-2} includes Pd of *x* and Ni of *x* µmol cm^{-2}.

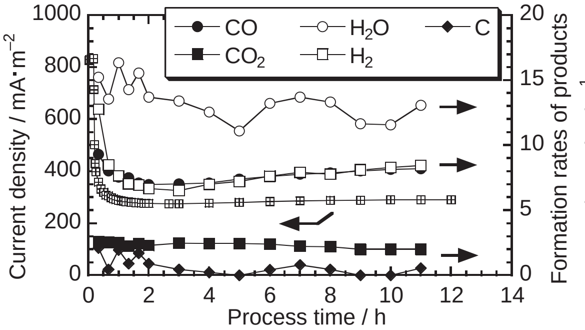

Figure 3. Time courses of current density and formation rates of products for the CH_4 oxidation over the Pd–Ni/(LSCr + SDC)/SDC anode (5.8 µmol·cm^{-2} loadings) at 500 mV and 1073 K. Formation rate of carbon was estimated from the rates of CO, CO_2, H_2O, and H_2.

bare (LSCr + SDC) composite anodes at 1073 K and 500 mV. The loadings of the Pd/ and Ni/ande were 7.7 µmol·cm^{-2}, respectively. The Pd–Ni/anode includes both Pd and Ni of 7.7 µmol·cm^{-2}. At first, H_2 fuel was introduced and almost similar current densities (≈900 mA·cm^{-2}) were observed for theses anodes except for the bare anode (≈300 mA·cm^{-2}). After H_2 was replaced with CH_4 at 10 min, the current density for the Pd–Ni/anode gradually decreased from 600 to 350 mA·cm^{-2} in 4 h. The Pd/anode also showed the oxidation activity for CH_4 (≈180 mA·cm^{-2} at 2 h) but was less active than the Pd–Ni/anode. On the other hand, the Ni/anode was not active for the CH_4 oxidation. The obvious synergy of Pd and Ni was observed.

Figure 2 shows effects of the catalyst loadings on the current densities in steady states for the CH_4 oxidation over the Pd–Ni/, Pd/ and Ni/anodes at 1073 K and 500 mV. Loadings of each metals were varied from 2 to 13 µmol·cm^{-2}. The current density over the bare composite anode was 20 mA·cm^{-2} in this condition. Ni catalyst was not active for the CH_4 oxidation (max. 40 mA·cm^{-2} at 13 µmol·cm^{-2}). For the Pd–Ni and Pd catalysts, the current densities significantly increased with loadings. The current densities for the Pd–Ni/anodes were about twice as large as those for the Pd/anodes at all loadings.

Stability of the Pd–Ni/anode (5.8 µmol·cm^{-2} loading) was examined in the CH_4 fuel at 500 mV and 1073 K. Figure 3 shows time courses of current density and formation rates of CO, CO_2, H_2O, and H_2, which were determined by gas chromatograph. Constant current density of 300 mA·cm^{-2} was observed for 12 h. The deposition rate of carbon estimated from material balance was quite low during the oxidation at least for 12 h. Continuous current and very low-carbon deposition suggest that most of carbon atoms from the converted CH_4 were exhausted as gaseous products. Therefore the continuous operation of the SOFC was possible with dry CH_4 fuel over the Pd–Ni/composite anode.

Stability of the Pd–Ni/anode under the open-circuit conditions was also examined in the CH_4 fuel at 1073 K because the destruction of cell is often observed for the conventional Ni cermet anodes.[9] When the circuit was opened in CH_4, the H_2 formation was temporarily observed but immediately decreased to a negligible value in 30 min. This result suggests that the Pd–Ni catalyst catalyzed the CH_4 decomposition to H_2 and C but was immediately deactivated.[7] Therefore, the amount of the carbon was limited and the cell destruction did not occur. When the circuit was closed at 500 mV after the exposure to CH_4, the current density of 60% was observed compared to that for the fresh anode. This decreased current suggests that some deposited carbon still remained. This residual carbon on Pd–Ni catalysts could be removed by the methanation with H_2. After the methanation procedure, the Pd–Ni/anode showed a good oxidation activity for CH_4 as well as the fresh anode. This result shows that Pd–Ni bimetallic catalyst is stable over the composite anode.

I–V polarization curves were measured for the Pd–Ni/anode (5.8 µmol cm^{-2} loading) in CH_4 at 1073 and 1173 K. The maximum power densities of 150 and 360 mW·cm^{-2} were obtained at 1073 and 1173 K, respectively, at 500 mV.

Pd–Ni, Pd and Ni catalysts showed significantly different oxidation activities for CH_4, in contrast, those for H_2 were similar. Activation of C–H bond over catalysts should be a key factor for the anodic CH_4 oxidation. However, details of the synergy mechanism between Pd and Ni catalysts have not been clear yet. Additional studies should be done to reveal the detailed reaction scheme and synergy mechanism of Pd and Ni catalysts for the electrochemical oxidation of CH_4.

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