Cathode Catalysts of Solid Oxide Electrolysis Cells for Direct Methane Synthesis

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Abstract: Direct methane synthesis in solid oxide electrolysis cells (SOEC) is an emerging method of energy carrier production. To demonstrate the concept, SOEC cathode materials were investigated both catalytically and electrochemically. Typical Ni-GDC and Ru-loaded Ni-GDC were compared, and the modified cathode showed superior performances under H_2O existing conditions. The results may be ascribed to the hydrogen spillover from Ru metal to adjacent Ni species, which was supported by the TPR study.
Keywords: SOEC, methane, ruthenium.

1. Introduction

Electrochemical methane synthesis from carbon dioxide and water provides an energy conversion pathway from electrical energy to chemical energy, which makes energy transportation and storage easier. Furthermore, CO_2 reduction to CH_4 can contribute to carbon-neutral fuel cycle. Solid oxide electrolysis cells (SOEC) can be used to convert CO_2 and H_2O into H_2 and CO at temperature around 800°C (co-electrolysis). If operation temperature is lowered, exothermic CO methanation reaction ($CO + 3H_2 \rightarrow CH_4 + H_2O$) will also take place on the cathode and direct CH_4 synthesis will be realized. Since most of the recently published works on direct CH_4 synthesis in SOEC were focused on systems design[1-3], research on cell materials is necessary to demonstrate this concept.

In the present study, SOEC cathode materials were investigated for direct CH_4 synthesis. Typical Ni-GDC composite (GDC: gadolinium-doped ceria) was modified by ruthenium impregnation, then catalytic and electrochemical activities were measured. Effects of the modification are discussed along with characterization results such as temperature programmed reduction (TPR) profiles.

2. Experimental

GDC ($Ce_{0.9}Gd_{0.1}O_{1.95}$) was prepared by co-precipitation method from nitrate precursors. Then GDC and NiO were ball-milled for 24 h and calcined at 1300°C for 5 h to form NiO-GDC cermet. Ni content was set to 60wt%. Obtained sample was further heat-treated to duplicate SOEC cathode thermal history. After that, NiO-GDC powder was impregnated with ruthenium nitrate solution and calcined at 500°C for 3 h. Ru amount was 3wt%. Existence of RuO_2 phase was confirmed by XRD.

SOECs were prepared by using zirconia-based Hionic™ electrolyte substrates. NiO-GDC cathode and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$-GDC anode (LSCF 50wt%) were attached to the electrolyte. Thin GDC interlayer was placed between the electrolyte and the anode to prevent them from reacting each other. Ruthenium was loaded on the NiO-GDC cathode in the same manner as in the catalyst preparation.

CO_2 methanation ($CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O$) activity tests were conducted in a fixed-bed reactor. This reaction can be regarded as a combination of reverse water gas shift reaction ($CO_2 + H_2 \rightarrow CO + H_2O$) and CO methanation reaction. Pelletized NiO-GDC or RuO_2/NiO-GDC was reduced at 800°C for 1 h by 5%H_2/Ar, then the reaction was conducted. To evaluate the effects of H_2O in the feed gas, composition was varied as CO_2:H_2:H_2O:N_2 = 15:60:x:(25-x). Total flow rate was set to 2.0 L min^{-1} $g_{\text{Ni-GDC}}^{-1}$. In electrochemical tests at 600°C, cathode gas composition was set to CO_2:H_2O:H_2:N_2 = 15:30:30:25. The flow rate was the same as in the catalytic tests. Air was supplied at 30 mL min^{-1} to the anode.

TPR measurements were conducted at heating rate of 5°C min^{-1}. 5%H_2/Ar gas was supplied at 50 mL min^{-1}, and hydrogen consumption was monitored by a thermal conductivity detector.

3. Results and discussion

Figure 1 shows the results of CO_2 methanation activity tests with H_2O in the feed stream. Both CO_2 conversion and CH_4 selectivity were higher for the Ru-loaded catalyst. After the tests with humidified feeds, catalytic activity of the catalyst was measured again in dry feed (results shown by open marks). The results indicate that degradation was suppressed by the Ru addition. Under high H_2O concentrations, surface of Ni metal can be oxidized and deactivated[4]. It is considered that, in the modified case, Ru remained in the metal form and provided hydrogen to adjacent Ni species through the spillover effect, which prevented the deactivation. Figure 2 shows the TPR profiles of the cathode materials. Low temperature peak (< 200°C) observed in the Ru-added sample was attributed to the reduction of RuO_2 to Ru metal. The second peak around 270°C may be accounted for the reduction of NiO in the proximity of Ru, which indicates the hydrogen spillover from Ru metal to the NiO. This consideration is also supported by the decrease in the peak area at around 600°C. Ruthenium impregnation to Ni-GDC also affected the electrochemical test results. With the Ru-loaded cathode, methane formation rates were about five times larger than those in the non-modified case (Figure 3). Possibly Ru suppressed the catalyst deactivation in polarized conditions.

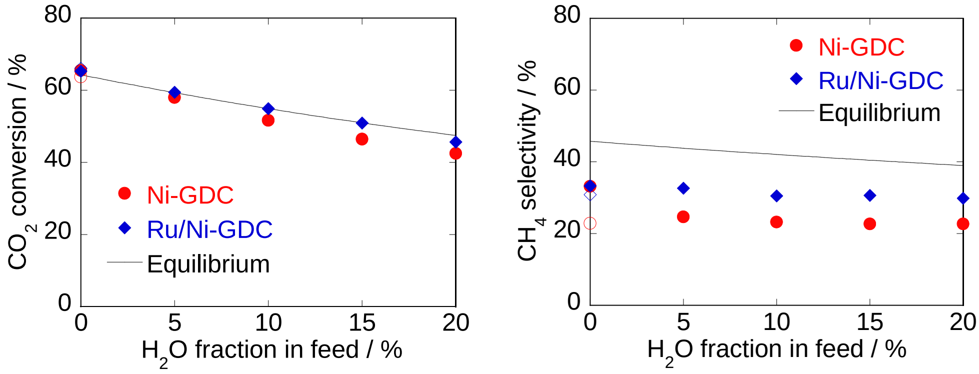

Figure 1. CO_2 methanation catalytic activity tests at 600°C with H_2O in the feed (open marks: 2nd time).

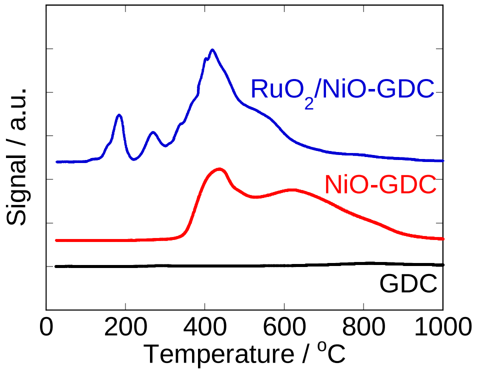

Figure 2. TPR profiles of cathode materials.

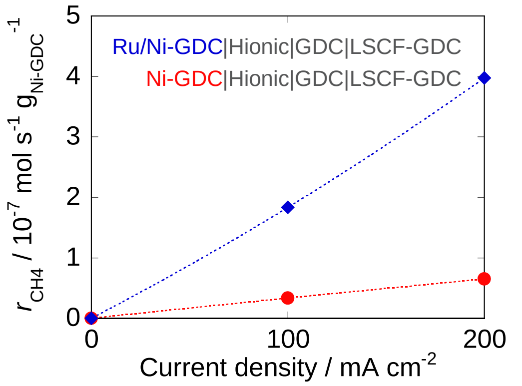

Figure 3. Methane formation rates in electrochemical tests.

4. Conclusions

Ni-GDC and Ru/Ni-GDC were tested as cathode materials of SOEC for direct CH_4 synthesis. The Ru-loaded cathode showed superior performances under H_2O existing conditions. The results may be explained by the hydrogen spillover from Ru metal to adjacent Ni species.

References

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