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Enhancement of anode activity and stability by Cr addition at Ni/Sm-doped CeO_2 cermet anodes in NH_3-fueled solid oxide fuel cells

Michihiro Hashinokuchi*, Mengjia Zhang, Takayuki Doi, Minoru Inaba

Department of Molecular Chemistry and Biochemistry, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan

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ABSTRACT

Chromium was added to nickel/Sm_2O_3-doped ceria (Ni/SDC) cermets by a $CrCl_3$ impregnation method, and the activity of the resulting Ni-Cr/SDC cermets was evaluated as anodes in ammonia-fueled solid oxide fuel cells (SOFCs) in the temperature range of 773 to 1173 K. It has been revealed that the addition of Cr was effective for the catalytic activity for NH_3 reforming, followed by hydrogen oxidation. The optimum amount of Cr was 3 at.% of the total metal in the Ni-Cr/SDC cermets. In addition, we demonstrated the improved stability of the Ni_{97}-Cr_3/SDC cermets in NH_3 atmosphere at 873 K. The addition of Cr suppressed the agglomeration of Ni, and promoted the anode durability. XRD analysis suggested the formation of a nitride CrN during operation in the Ni_{97}–Cr_3/SDC anode, and the role of the nitride was discussed in detail.

1. Introduction

Solid oxide fuel cells (SOFCs) are one of promising candidates for power generation systems because of their high energy conversion efficiency with various fuels containing hydrogen, such as hydrocarbon and ammonia (NH_3) [1–14]. However, the high operating temperatures (973–1273 K) cause some problems concerning chemical and thermo-mechanical stabilities of cells and stacks. Lowering operation temperature of SOFCs is one of keys to solve these problems, while the kinetics of catalytic reactions at the electrodes (e.g. fuel reforming) becomes a rate limiting factor.

Recently, NH_3 has attracted much attention as a fuel for SOFCs. NH_3 is electrochemically oxidized at an anode through NH_3 reforming reaction ($2NH_3 \rightarrow N_2 + 3H_2$), followed by hydrogen oxidation [11]. The enthalpy change of NH_3 reforming is significantly lower than those of hydrocarbons (e.g. CH_4). Furthermore, NH_3 is free of carbon. Therefore, SOFCs can be operated directly with NH_3 fuels even at low temperatures (< 773 K). Direct NH_3-fueled SOFCs have been developed by several groups [4–14]; however, the activity for NH_3 oxidation at the conventional Ni cermet anode drops at around 973 K. Furthermore, the degradation in the anode performance due to the agglomeration of Ni catalyst at temperatures lower than 973 K is a matter of concern [14].

In previous work [15,16], we investigated the activity of Ni-Fe alloy anode cermets for direct NH_3-fueled SOFCs in the temperature range of 973 to 1173 K. We found that the activity of the anode for NH_3 oxidation strongly depended on the metal composition, and was the highest at Ni:Fe = 4:6 (in atomic ratio) [15]. The density functional theory studies for NH_3 reforming on single crystal Fe and Ni surfaces have suggested that Fe (heat of N_2 adsorption, $\Delta H^0_{M\text{-}N} = -205\,\mathrm{kJ\,mol^{-1}}$) accelerates dissociative NH_3 adsorption process, while Ni ($\Delta H^0_{M\text{-}N} = -138\,\mathrm{kJ\,mol^{-1}}$) enhances N_2 desorption process, both of which would be the rate-determining steps in NH_3 reforming on catalyst [17,18]. Therefore, we concluded that the synergetic effect of Ni and Fe enhances the catalytic activity of the Ni_{40}-Fe_{60}/SDC anode for NH_3 reforming, resulting in the observed enhancement of the cell performance. In a further study, we prepared the Ni-Mo/SDC anodes by the impregnation of $MoCl_5$ solution into the Ni/SDC cermets, and investigated their anode performance in direct NH_3-fueled SOFCs [19]. Mo binds to N atoms ($\Delta H^0_{M\text{-}N} = -335\,\mathrm{kJ\,mol^{-1}}$) more strongly than Fe. The Ni_{97}-Mo_3/SDC anode exhibited a high activity for NH_3 oxidation, which was comparable to the Ni_{40}-Fe_{60}/SDC in the temperature range of 973 to 1173 K.

The catalytic activities of several transition metals for NH_3 reforming were investigated [20]. The $\Delta H^0_{M\text{-}N}$ of typical transition metals is tabulated in Table 1. The catalytic activity for NH_3 reforming on metal catalysts has been well correlated with metal-nitrogen (*M*-N) binding energy of metals [21]. Mo-based binary catalysts have attracted much attention as a catalyst for NH_3 reforming due to their high activity [22]. Co-Mo, Ni-Mo and Fe-Mo binary catalysts exhibited the activity much better than that of the constituent atoms [23], suggesting that there is an optimum of the *M*-N binding energy for NH_3 reforming, which can be realized by combining two kinds of metals with a strong and a weak *M-N* binding energy that accelerate dissociative NH_3 adsorption and N_2 desorption, respectively. It seems to be applicable to

* Corresponding author.
E-mail address: mhashino@mail.doshisha.ac.jp (M. Hashinokuchi).

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Table 1
Heat of N_2 adsorption of typical transition metals.

	Co	Ni	Fe	Mo	Cr	V	W
$-\Delta H^0_{M\text{-}N}$ (kJ mol^{-1})	134	138	205	335	410	469	536

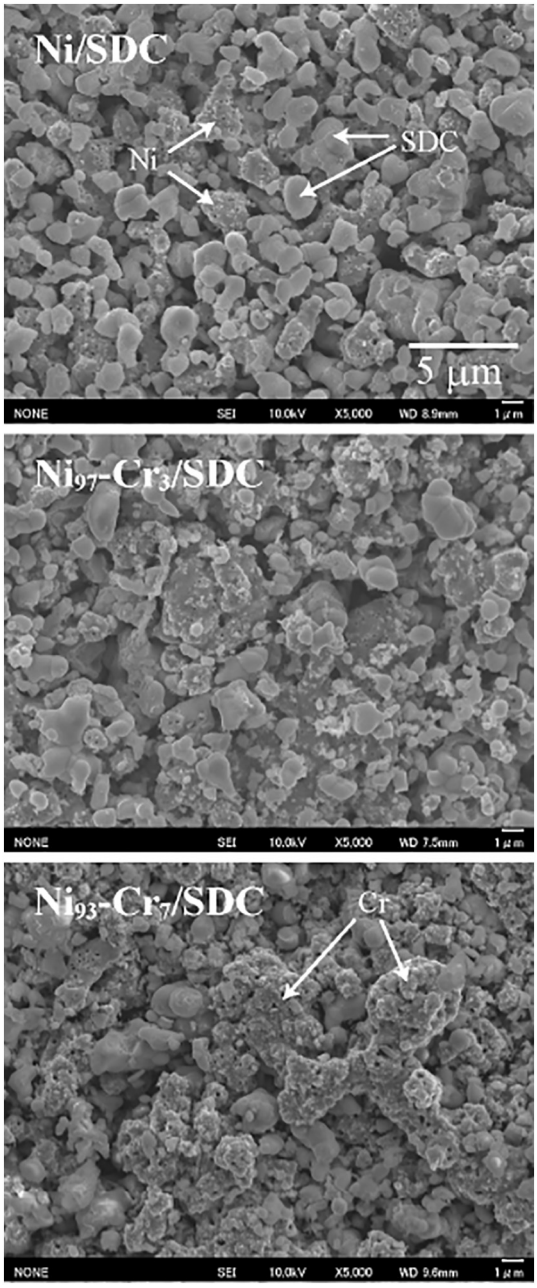

Fig. 1. SEM images of the anode surfaces of Ni-Cr/SDC|LSGM|SSC cells of different Cr contents, C_M = 0, 3 and 7% after electrochemical measurements at 973 K with dry NH_3 and air.

the catalytic activity for NH_3 reforming on the Ni-based binary anodes.

On the other hand, it has been also reported that the agglomeration of Ni catalyst particles causes significant degradation in the anode performance at temperatures below 973 K [14]. This might be resulted from a volume change of Ni catalyst induced by nickel nitride (Ni_3N) formation under the conditions of NH_3 reforming. It is known that metal oxides with a low surface free energy enhance the wettability of Ni particles by anchoring them with the interface and suppress the

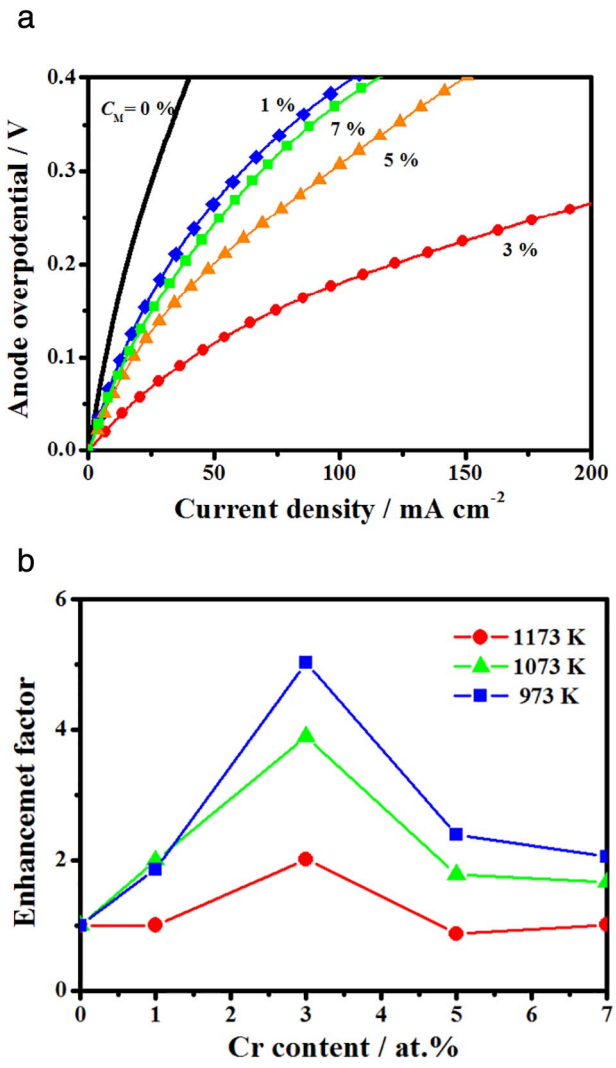

Fig. 2. (a) Anode polarization curves for Ni-Cr/SDC|LSGM|SSC cells of different Cr contents at 973 K with dry NH_3 and air. (b) Enhancement factors plotted against Cr content in the anode for Ni-Cr/SDC|LSGM|SSC cells operated at different temperatures with dry NH_3 and air.

agglomeration of Ni in the SOFC anodes [24]. Moreover, it was reported that the agglomeration of transition metals (Ni, Co and Fe) catalysts dispersed in the alumina matrix was significantly suppressed in NH_3 reforming [25]. The agglomeration of Ni in the Ni-based anode would be suppressed by the modification with stable metal oxides (or nitrides) of a low surface free energy in NH_3 reforming.

In this study, we selected chromium (Cr) as an added metal in Ni/SDC cermets from to improve the catalytic activity and stability of the anode because the $\Delta H^0_{M\text{-}N}$ of Cr is relatively high (-410 kJ mol^{-1}), which will bring about a high catalytic activity for dissociative NH_3 adsorption as well as stable nitrides formation at the anode in NH_3 reforming reaction. The Cr-modified Ni/SDC anodes were prepared by the impregnation of $CrCl_3$ solution into the pre-sintered Ni/SDC cermets, and their catalytic activity for NH_3 oxidation was investigated in a wide temperature range of 773 to 1173 K. We also performed durability tests of a Cr-modified Ni/SDC anode under the open-circuit conditions in NH_3 atmosphere at 873 K to investigate the effect of Cr addition on the stability of the anode cermets.