***In situ* Raman spectroscopic analysis of the coking resistance mechanism on**

SrZr_{0.95}Y_{0.05}O_{3-x} surface for solid oxide fuel cell anodes

Tsuyoshi Nagasawa ^{a, c, *}, Dongchang Chen ^b, Samson Yuxiu Lai ^b, Meilin Liu ^{b, **},

Katsunori Hanamura ^a

^a Department of Mechanical and Control Engineering, Tokyo Institute of Technology,

2-12-1, O-okayama, Meguro-ku, Tokyo 152-8550, Japan.

^b School of Materials Science and Engineering, Center for Innovative Fuel Cell and

Battery Technologies, Georgia Institute of Technology, 771 Ferst Drive, Atlanta,

Georgia 30332-0245, USA.

^c Research Fellow of Japan Society for the Promotion of Science.

* Corresponding author. Tel./Fax: +81 3 5734 3706

** Corresponding author. Tel.: +1 404 894 6114, Fax: +1 404 894 9140

E-mail address: nagasawa.t.ab@m.titech.ac.jp (T. Nagasawa),

meilin.liu@mse.gatech.edu (M. Liu)

Abstract

While the coking resistance of Ni/yttria-stabilized zirconia (YSZ) anodes in solid oxide fuel cells (SOFCs) toward hydrocarbon fuel can be improved by adding $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-x}$ (SZY) as a proton conductor, the exact mechanism is still unclear. In this study, the surface chemistry of SZY is investigated using *in situ* Raman spectroscopy to clarify the coking resistance mechanism. Upon exposure to dry propane at 500 °C, the intensity of the Raman peaks corresponding to $-\text{CO}_3$ species decreases with time, suggesting that the surface-located $-\text{CO}_3$ groups are consumed through a reaction with deposited carbon or dry reforming of propane, which reduces the tendency of coking. These consumed $-\text{CO}_3$ groups can then be regenerated through a reaction between water vapor and deposited carbon. The presence of adsorbed water on SZY, which facilitates a carbon removal reaction and the steam reforming of propane, is confirmed by thermogravimetric analysis (TGA). The reactivity of the $-\text{CO}_3$ groups and the adsorbed water on SZY thus contribute to removing deposited carbon, resulting in the improved coking resistance of Ni/YSZ-SZY anode.

Keywords: Solid oxide fuel cells, Hydrocarbon fuel, Anode, $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-x}$, Coking resistance mechanism, *In situ* Raman spectroscopy

1. Introduction

Solid oxide fuel cells (SOFCs) have recently attracted much attention due to their high conversion efficiency of a wide variety of chemical fuels to electricity. However, performance degradation due to carbon deposition (coking) on Ni-based anodes still remains as a technical challenge [1]. Mainly, two strategies have been investigated to suppress coking on Ni-based anodes. One is the addition of other gases such as steam, CO₂, or O₂ to the hydrocarbon fuel [2-5]. By adding those gases, the O/C ratio in the fuel increases, resulting in the situation where carbon deposition can be avoided thermodynamically [1]. However, the addition of other gases requires extra energy, resulting in a reduction of total energy efficiency. The second strategy is the introduction of an anode catalyst layer (e.g., Ru-CeO₂ [6, 7] or Cu_{1.3}Mn_{1.7}O₄ [8]) or the incorporation of a metal or oxide, such as Au [9, 10], Cu [11-14], Sn [15-18], CeO₂ [19, 20], Y₂O₃- or Sm-doped CeO₂ [21-24], CaO [25], or BaO[26], respectively. These anode catalyst layers or Ni-based anodes modified by metal or oxide incorporation can promote hydrocarbon reforming or removal of deposited carbon, resulting in the enhancement of coking resistance while maintaining high energy efficiency.

Recently, some research has shown that adding perovskite proton conductors, such

as $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_{3-x}$ (SZY) or $\text{BaCe}_{0.8}\text{Y}_{0.2}\text{O}_{3-x}$ (BCY) to Ni/yttria-stabilized zirconia (YSZ) or Ni/gadolinium-doped ceria (GDC) cermet anodes is an effective way to improve anode electrochemical properties in hydrogen and hydrocarbon fuel [27-33]. Among them, SZY showed coking resistance toward hydrocarbon fuel [31-33], suppressed performance degradation of a SZY-Ni/YSZ anode in dry methane [31], and decreased the amount of deposited carbon [32], although the mechanism is still unclear. Therefore, it is important to understand the coking resistance mechanism of SZY for the systematic rational design of anodes with enhanced electrochemical performance in hydrocarbon fuel.

Raman spectroscopy is a powerful tool to probe the surface chemistry because of its high sensitivity to both bulk phases and reaction intermediates on the electrode surface. In addition, Raman spectra can be feasibly collected under realistic operating conditions (*in situ*) due to its operability at ambient pressure and through optical windows. By using *in situ* Raman spectroscopy, the dynamics of surface reactions on SOFC electrodes can be detected [34-40]. For example, carbon deposition and removal on a Ni-based anode was investigated under SOFC operating conditions [37]. The early stages of carbon deposition on Ni-based anodes as well as the oxygen vacancy behavior on oxide surfaces can also be detected by *in situ* surface enhanced Raman spectroscopy

(SERS) [40]. The dynamics of reaction intermediates on Ba-containing oxide catalysts such as BaO [26], yttrium-doped BaZrO₃ (BZY) [41], and BaZr_{0.1}Ce_{0.7}Y_{0.1}Yb_{0.1}O_{3-x} (BZCYYb) [42], all of which show strong coking resistance when added into Ni-based anodes, were also investigated by *in situ* Raman spectroscopy [43]. These studies showed that –OH and –CO₃ groups on the surface of Ba-containing oxides contribute to removing deposited carbon. In this study, the interaction between the SZY surface and various gas species (N₂, CO₂, H₂O, and C₃H₈) at high temperature (500 °C) was investigated by *in situ* Raman spectroscopy to evaluate the coking resistance mechanism of SZY.

2. Experimental

SrZr_{0.95}Y_{0.05}O_{3-x} (SZY) powder was fabricated by Kojundo Chemical Laboratory Co., Ltd. The average particle diameter of the SZY powder is about 0.8 μm. The SZY powder was first characterized by X-ray diffraction and Raman spectroscopy. For *in situ* Raman spectroscopy, the SZY powder was pressed to a dense pellet. The experimental setup for the *in situ* Raman spectroscopy is described in previous work [43]. The Raman spectra were collected at both room temperature and 500 °C. The changes of the –CO₃ (1060 cm⁻¹), –OH (3580 cm⁻¹), and carbon (1350 and 1580 cm⁻¹) bands with time were

investigated. The flow rate of each gas (N_2 , CO_2 , and C_3H_8) was controlled by mass flow controllers, and the total flow rate of the gas mixture was fixed to 100 mL/min. H_2O was introduced by flowing the gas through a water bubbler at room temperature. The introduced volume of H_2O in gases by bubbling is about 3%.

In addition to *in situ* Raman spectroscopy, the adsorption of water vapor by SZY was also studied by thermogravimetric analysis (TGA). Before the TGA test, SZY powder was heated at 1000 °C for 4 h and exposed to dry 4% H_2 -96% Ar to remove adsorbed water and other possible adsorbates on the surface.

3. Results and discussion

3.1 XRD and Raman spectra of SZY powder

Fig. 1(a) and (b) show the XRD and Raman spectrum of SZY powder used in this study, respectively. From Fig. 1(a), its crystalline structure is consistent with un-doped SrZrO_3 [44] and there are no additional peaks, proving that the SZY powder is a pure perovskite phase. In Fig. 1(b), the narrow peak around 1060 cm^{-1} ($-\text{CO}_3$) and the broad peak around 3580 cm^{-1} ($-\text{OH}$) were observed [43], indicating that the SZY powder has a strong tendency to adsorb CO_2 and H_2O from atmosphere. Peaks in the region of $< 1000 \text{ cm}^{-1}$ are attributed to pristine SZY Raman modes.

Fig. 1 (a) XRD and (b) Raman spectra of the SZY powder.

3.2 In situ Raman spectroscopy at room temperature

At room temperature, the flowing gas for *in situ* Raman experiment was changed as follows: dry 50% CO₂-50% N₂ for 1 h → wet (3% H₂O) N₂ for 1 h → dry N₂ for 1 h.

Fig. 2 shows the Raman spectroscopic evolution of the (a) -CO₃ and (b) -OH bands.

The signal intensities of the $-\text{CO}_3$ and $-\text{OH}$ bands are almost the same across all gas conditions, indicating that adsorbed CO_2 or H_2O on SZY surface is stable and the dynamics of the surface reaction are mostly unchanged at room temperature.

Fig. 2 *In situ* Raman spectra of (a) $-\text{CO}_3$ and (b) $-\text{OH}$ bands obtained of the SZY at room temperature after being exposed to dry 50% CO_2 -50% N_2 , wet 100% N_2 , and dry 100% N_2 for 1 hour.

3.3 In situ Raman spectroscopy at 500 °C

In order to evaluate the dynamics of surface chemical reactions at SOFC operating temperature, *in situ* Raman experiment was performed at 500 °C. As a typical procedure, the flowing gas was changed as follows: dry N_2 for 45 min $\rightarrow$ wet (3% H_2O) N_2 for 45 min $\rightarrow$ dry 50% CO_2 -50% N_2 for 45 min $\rightarrow$ dry 50% C_3H_8 -50% N_2 for 50 min $\rightarrow$ wet

(3% H₂O) N₂ for 45 min. Fig. 3 shows the Raman spectroscopic evolution acquired during this process. As seen in Fig. 3(a), the signal intensity of the –CO₃ band remains almost unchanged until the beginning of the dry C₃H₈ period. This means that the adsorbed CO₂ on the SZY surface is stable at 500 °C. However, the –OH peak could not be detected at 500 °C as shown in Fig. 3(b), contrary to the observation at room temperature (Fig. 2(b)). Generally, the amount of adsorbed H₂O at high temperature decreases compared to that at room temperature because the desorption rate of adsorbed H₂O increases with increasing temperature [26]. As a result, the amount of –OH stably adsorbed on the SZY surface decreased significantly, and Raman spectroscopy could not detect its signal at 500 °C.

The water vapor adsorption of SZY was also studied by TGA as shown in Fig. 4. As a reference, the water vapor adsorption of YSZ powder was also investigated. Fig. 4 shows the weight change (%) of SZY and YSZ powders with time at 500 °C. At t = 0 min, the flowing gas was switched from dry 4% H₂-96% Ar to wet 4% H₂-96% Ar. Consequently, the weight of the SZY powder increased steeply, and reached a steady state after 10 min. In the case of the YSZ powder, however, there was no significant weight change after wet gas was introduced. This results shows that the water vapor adsorption of SZY is higher than that of YSZ at 500 °C.

Fig. 3 *In situ* Raman spectra of (a) $-\text{CO}_3$ and (b) $-\text{OH}$ bands obtained from SZY at 500 °C after being exposed to dry 100% N_2 , wet 100% N_2 , and dry 50% CO_2 -50% N_2 for 45min. The spectra measured immediately after being exposed to dry 50% C_3H_8 -50% N_2 are also shown.

Fig. 4 Thermogravimetric analysis for the SZY and YSZ powders in dry 4% and wet 4% H_2 -96% Ar at 500 °C. At $t = 0$ min, the gas condition was changed from dry to wet.

On the basis of understanding the strong tendency of CO₂ and water absorption for SZY surface, *in situ* Raman experiments using hydrocarbon fuel were performed to directly evaluate the coking mechanism at SOFC operating temperature. Fig. 5 shows the Raman spectroscopic evolution of the (a) carbon and (b) –CO₃ bands. At t = 0 min, the flowing gas was switched from dry 50% CO₂-50% N₂ to dry 50% C₃H₈-50% N₂. In Fig. 5(a), it is shown that the signal intensities of the carbon D and G bands increased gradually with exposure time, indicating the continuous increase of coking. On the other hand, the signal intensity of the –CO₃ band decreased with time as shown in Fig. 5(b). To evaluate the effect of H₂O, after exposing the sample to propane, water vapor was introduced to the flowing gas as shown in Fig. 6. In Fig. 6(a), the signal intensities of carbon D and G bands decreased gradually with exposure of wet N₂, indicating that the deposited carbon on the SZY surface was continuously removed. On the other hand, in Fig. 6(b), it was observed that the signal intensity of the –CO₃ band increased with time, and finally recovered to same level as shown in Fig. 3(a), before propane was introduced.

Fig. 5 *In situ* Raman spectra of (a) carbon and (b) $-\text{CO}_3$ bands obtained from SZY at 500 °C during being exposed to dry 50% C_3H_8 -50% N_2 . At $t = 0$ min, the gas condition was switched from dry 50% CO_2 -50% N_2 to dry 50% C_3H_8 -50% N_2 .

Fig. 6 *In situ* Raman spectra of (a) carbon and (b) $-\text{CO}_3$ bands obtained from SZY at 500 °C during being exposed to wet 100% N_2 . At $t = 50$ min, the gas condition was switched from dry 50% C_3H_8 -50% N_2 to wet 100% N_2 .

3.4 Coking resistance mechanism of SZY

Based on the above results, the dynamics of surface chemical species and the coking resistance mechanism of SZY are discussed. The mechanisms of coking and carbon removal are proposed as the surface-bound chemical reactions described as follows. First, as shown in Fig. 5(a), carbon accumulated on the SZY after propane was introduced, indicating that propane decomposition occurs as follows:

Simultaneously, $-\text{CO}_3$ groups on the SZY were consumed as shown in Fig. 5(b). From this behavior, the following reaction can be proposed as a carbon removal reaction on the SZY:

Here, $-\text{O}_{\text{s}}$ represents an oxygen atom on the SZY surface. The deposited carbon reacts with adsorbed CO_2 , and CO is produced. The reactivity of $-\text{CO}_3$ groups with deposited carbon may provide coking resistance toward hydrocarbon fuels. Second, adsorbed water also plays an important role for carbon removal. When SZY is exposed to a wet atmosphere at high temperature, H_2O is adsorbed on the surface as shown in Fig. 4.

According to Fig. 6(a), the deposited carbon was removed after the SZY was exposed to

wet atmosphere. Therefore, we propose that the adsorbed water can contribute to carbon removal reaction as follows.

Finally, the $-CO_3$ groups consumed by reacting with propane can be recovered in the wet atmosphere as shown in Fig. 6(b) as follows:

The spectroscopic evidence implies that the $-CO_3$ groups can potentially be used for carbon removal repeatedly, which can contribute to long-term coking resistance toward hydrocarbon fuels. Interestingly, the coking resistance mechanism of SZY is different from that of Ni-based anode modified by other metal [9-18] or CeO_2 -based oxide [19-24]. The suppression of carbon deposition on Au-, Cu-, or Sn-modified anodes is attributed to the lower catalytic activity for hydrocarbon decomposition or weakened adsorption energy of C on Ni [1, 45-47]. In anodes modified by CeO_2 -based oxides, the coking resistance originates from a carbon removal or hydrocarbon reforming reaction with oxide ions in ceria [21, 23, 48, 49]. On the other hand, the present work on SZY and the previous *in situ* Raman study related to BaO, BZY, and BZCYYb [43] indicate that in the case of alkaline-earth metal-containing oxides, the reactivity of water and $-CO_3$ groups on the surface provide strong coking resistance.

Another reported characterization of SZY is correlated with our proposed mechanism. Jin et al. investigated the distribution of deposited carbon on the cross-section of a Ni/YSZ anode by SEM-EDX after power generation in dry methane fuel [32]. This study concluded that the amount of deposited carbon near the surface was larger than that near the electrolyte interface. At the area near the electrolyte, which is called the electrochemically active area or thickness [50], the amount of oxide ions supplied from the electrolyte was enough for methane oxidation or carbon removal, however, the supply of oxide ions was not enough at the surface (non-active area). As a result, carbon deposits easily around the non-active area. To target the region prone to coking, Jin et al. infiltrated SZY into the non-active area of a Ni/YSZ anode, resulting in strong suppression of coking [32].

Fig. 7 shows a schematic of the proposed coking resistance mechanism for a Ni/YSZ anode infiltrated with SZY. At the electrochemically active area, methane is oxidized by oxide ions from the electrolyte, and H_2O and CO_2 are produced. In the non-active area, mainly methane decomposition occurs and carbon is deposited. However, the deposited carbon can be removed through the reaction with adsorbed water and $-\text{CO}_3$ on the SZY surface. Finally, the consumed $\text{H}_2\text{O}_{\text{ad}}$ and $-\text{CO}_3$ on SZY are regenerated from electrochemically produced H_2O and/or CO_2 . The repeatability of the

above process can thus remove deposited carbon continuously, resulting in the coking resistance of the Ni/YSZ-SZY anode toward dry methane fuel.

Fig. 7 Schematic of proposed coking resistance mechanism at Ni/YSZ anode infiltrated with SZY operated in dry methane fuel. At the electrochemically active area, methane is oxidized by oxide ions from the electrolyte, and H_2O and CO_2 are produced. In the non-active area, the carbon deposited through methane decomposition is removed through the reaction with adsorbed water and $-\text{CO}_3$ on the SZY surface. The consumed $\text{H}_2\text{O}_{\text{ad}}$ and $-\text{CO}_3$ on SZY are regenerated from electrochemically produced H_2O and/or CO_2 .

Conclusion

The surface chemistry on SZY was investigated by using *in situ* Raman spectroscopy to clarify the coking resistance mechanism of SZY. From the results, we propose that $-\text{CO}_3$ groups on the SZY surface oxidize the deposited carbon into carbon monoxide. The $-\text{CO}_3$ groups, once depleted, can then be regenerated through a reaction between water vapor at a low concentration and deposited carbon around the electrochemically non-active area where there is an insufficient supply of oxide ions. In the non-active area, water vapor is also proposed to oxidize deposited carbon into carbon monoxide. Each of these reactions is based on tracking characteristic Raman modes *in situ* as different gas environments are introduced at 500 °C. The reversibility and repeatability of these reactions explain the long-term coking resistance observed when SZY is infiltrated into a Ni-YSZ anode and the results are correlated with literature on SZY and other catalysts that depend on water vapor and surface $-\text{CO}_3$ species for coking resistance. The affinity for water adsorption on SZY relative to YSZ

was further quantified with TGA. As shown in this study, *in situ* Raman spectroscopy was vital in providing direct evidence of the surface chemical species and their dynamics to strongly support insight into the coking behavior of hydrocarbon-fueled SOFC anodes.

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