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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

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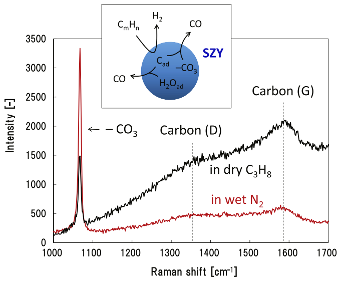
HIGHLIGHTS

- Coking resistance mechanism of $SrZr_{0.95}Y_{0.05}O_{3-x}$ (SZY) was studied for SOFC anode.
- Dynamics of adsorbates on SZY surface was investigated by *in situ* Raman spectroscopy.
- Interaction between carbon and $-CO_3$ on SZY was observed in C_3H_8 and wet atmosphere.
- $-CO_3$ group and adsorbed H_2O on SZY surface contribute to carbon removal reaction.

GRAPHICAL ABSTRACT



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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 $SrZr_{0.95}Y_{0.05}O_{3-x}$ (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 $-CO_3$ species decreases with time, suggesting that the surface-located $-CO_3$ groups are consumed through a reaction with deposited carbon or dry reforming of propane, which reduces the tendency of coking. These consumed $-CO_3$ 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 $-CO_3$ groups and the adsorbed water on SZY thus contribute to removing deposited carbon, resulting in the improved coking resistance of Ni/YSZ-SZY anode.

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

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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, CO_2, or O_2 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–CeO_2 [6,7] or $Cu_{1.3}Mn_{1.7}O_4$ [8]) or the incorporation of a metal or oxide, such as Au [9,10], Cu [11–14], Sn [15–18], CeO_2 [19,20], Y_2O_3- or Sm-doped CeO_2 [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 $SrZr_{0.95}Y_{0.05}O_{3-x}$ (SZY) or $BaCe_{0.8}Y_{0.2}O_{3-x}$ (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 $BaZrO_3$ (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 –CO_3 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 (N_2, CO_2, H_2O, and C_3H_8) 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 –CO_3 (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} (–CO_3) and the broad peak around 3580 cm^{-1} (–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 cm^{-1} are attributed to pristine SZY Raman modes.

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% CO_2-50% N_2 for 1 h → wet (3% H_2O) N_2 for 1 h → dry N_2 for 1 h. Fig. 2 shows the Raman spectroscopic evolution of the (a) –CO_3 and (b) –OH bands. The signal intensities of the –CO_3 and –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.

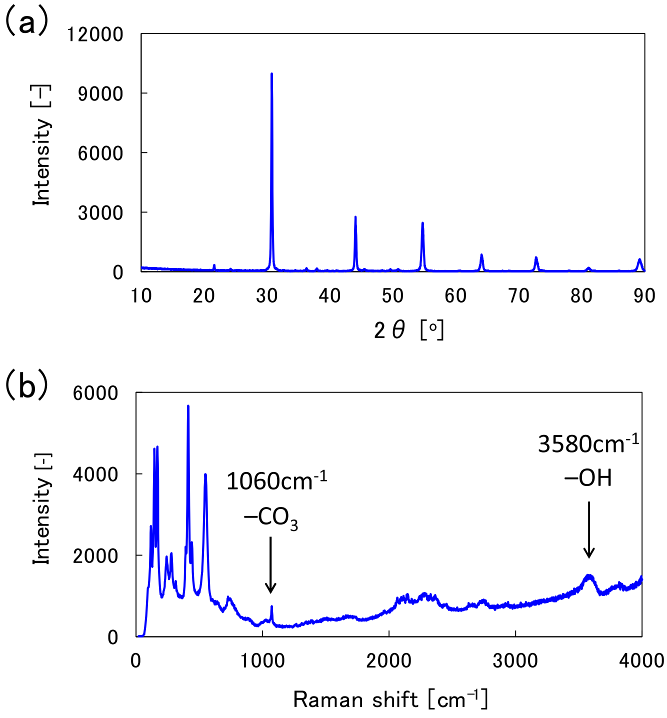

Fig. 1. (a) XRD and (b) Raman spectra of the SZY powder.