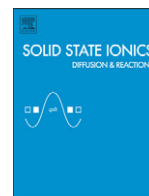




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Effect of the oxide substrate on the nickel particle properties

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ABSTRACT

Effects of the oxide substrate on the nickel (Ni) particle properties are examined by using a Ni agglomeration behavior analysis and Kelvin Force Microscope (KFM) technique. Agglomerated Ni particles are formed after annealing a Ni thin film on oxide substrates of yttria stabilized zirconia (YSZ) and gadolinia doped ceria (GDC). Nickel agglomeration is suppressed for the Ni particles on the GDC substrate compared to those particles on the YSZ substrate. Although evaluated at room temperature, the surface potential of GDC is more positive than that of YSZ, while Ni particle surface potential is about the same for both the Ni/YSZ and the Ni/GDC systems.

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1. Introduction

In recent years, micro combined heat and power (CHP) system and the distributed electricity generating system with solid oxide fuel cells (SOFCs) have been developed and commercialized. For SOFC anode, composite materials consisting of nickel and oxide ion conductor ceramics, so called cermet, are used due to their high catalytic activity for hydrogen oxidation reaction and their low material and fabrication costs. In nickel – oxide cermet anodes, the oxide component 3D-backbone imparts strength to the anode and serves as the oxide ion conducting pass, while the nickel metal network plays an important role for the catalytic activity and as the electronic conducting path.

The literature reports that cell performance and carbon deposition behavior are related to the oxide component in the anode;

1. Electrochemical reaction of Ni-base anode is enhanced by adopting oxides with a higher oxide ion conductivity [1,2].
2. Anode performance and durability for methane fuel of the Ni – ScSZ anode are “better” than the Ni – YSZ anode [3,4].

3. Carbon deposition rate follows the order: Ni – SDC > Ni – YSZ > Ni – ScSZ at 1273 K [5].

In addition, our group has also reported experimental results of the effect of the oxide substrate on the nickel surface condition as follows by using a model electrode:

4. Coverage of oxygen on the Ni surface of Ni on SDC is larger than that of Ni on YSZ [6,7].
5. Carbon deposition on the nickel surface with GDC is suppressed [8,9].
6. Nickel agglomeration behavior on the YSZ substrate is different with different additives in the YSZ substrate [10,11].

It is important to understand the difference among Ni base anodes with different oxide component for effective anode material development. In the present study, differences in surface properties of nickel particles were analyzed for yttria stabilized zirconia (YSZ) and gadolinia doped ceria (GDC) substrates. Furthermore, the effects of oxide substrates on the nickel agglomeration behavior and nickel surface potential were also examined. The effect of the oxide component on the Ni surface condition is discussed based on present results and correlation with our previous reports [6–13].

2. Experimental

Nickel agglomeration behavior was investigated using an ad-hoc developed two dimensional model systems. Nickel thin films were prepared on YSZ and GDC substrates. Commercial powders of 8YSZ (TZ-8Y, Tosoh Co., Japan) and 20GDC (AGC Seimi Chemical Co., Ltd.,

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Japan) were shaped into disks and pressed by CIP at 390 MPa. Pressed disks were sintered at 1673 K for 5 h in air. The surface of the sintered samples was mirror polished with diamond slurry.

Nickel thin film was deposited on the polished surface of substrates by the magnetron sputtering method. Thickness of nickel film was controlled to be around 60 nm by sputtering time. To obtain stable and highly reproducible microstructures, sputtered samples were annealed at 1173 K for 2 h under reducing atmosphere (1.2% H₂O–H₂ condition). It took 5 h for heating up and cooling down processes under reducing atmosphere.

Agglomerated nickel particles were statistically analyzed from images taken by scanning electron microscope (SEM, JSM-7500F, JEOL Ltd.,). Fig. 1 shows the schematic drawing of the agglomerated nickel particles on an oxide substrate. S_1 corresponds to the area of an agglomerated particle, and S_2 is the influenced area from this particle. In this case, we assumed that a nickel particle (the particle area is S_1) was gathered from S_2 area. These values were obtained by binarization of SEM images as shown in Fig. 2. Agglomeration factors were defined by the S_2/S_1 ratio. When the agglomeration factor, S_2/S_1 , becomes large, agglomeration is “enhanced”, and vice versa.

The surface potentials for both agglomerated nickel particles and oxide substrates were measured by Kelvin Force Microscope (KFM). KFM measurements in air are performed as one-pass measurements using a commercial SPM system (Nanosearch SFT-3500, Shimadzu, Kyoto, Japan) and EFM cantilevers (EFM-20, NanoWorld AG, Switzerland). The instrument enables simultaneous analysis in both topographic (AFM) and Kelvin probe (KFM) modes. In the KFM mode, DC bias was applied to the cantilever to nullify electrostatic interactions between the cantilever and the sample. Reference potential is set at the surface potential of a gold thin film also deposited on the oxide substrate and is connected to the ground by Pt wire.

3. Results and discussion

Fig. 2 summarizes backscattered electron images (BEIs) and binarized BEIs for agglomerated nickel particles on oxide substrates of YSZ and GDC. Well-isolated nickel particles were observed in the BEIs for both the Ni/YSZ and the Ni/GDC systems. In binarized BEIs, black areas and white areas correspond to the nickel particles and the oxide substrate surface, respectively. Black lines are equidistant from the edge of the neighboring Ni particles. The influenced area, S_2 , corresponds to the area enclosed by black lines; assuming that Ni diffused from those areas. Averaged values of Ni particle area, S_1 , and influenced area, S_2 , and the calculated agglomerated factor, S_1/S_2 ratio, for agglomerated nickel particles on oxide substrates of YSZ and GDC are listed in Table 1. Agglomeration factor for the Ni/GDC system is smaller than that for the Ni/YSZ system. This result indicates that Ni agglomeration is suppressed on the GDC substrate compared with the YSZ substrate.

Fig. 3 shows the scanning probe microscopy (SPM) and KFM images for agglomerated nickel particles on oxide substrates of YSZ and GDC in the same analyzed area. The surface potential for the YSZ and GDC substrates were +0.21 V and +0.67 V, respectively. The surface potential between the YSZ and the GDC is clearly different. On the other hand, the Ni surface potential value for both systems was about the same, namely, –0.09 V for the Ni/YSZ system and –0.05 V for the Ni/GDC system. These results indicate that the difference of surface potential between the nickel particle and the oxide substrate is different between the Ni/YSZ (about $\Delta = 0.3$ V) and the Ni/GDC (about $\Delta = 0.7$ V) systems.

When the wettability analysis method is adopted for solid-state agglomerated nickel particles on the solid substrates, the relationship among surface and interface energy is as follows:

$$\gamma_{\text{oxide}} = \gamma_{\text{Ni}} \cos\theta + \gamma_{\text{Ni/oxide}} \quad (1)$$

where γ_{oxide} and γ_{Ni} are the surface energy of the oxide substrate and the Ni particle, respectively, and $\gamma_{\text{Ni/oxide}}$ is the interface energy of the oxide/Ni boundary. Suppression of agglomeration for the Ni/GDC system corresponds to good wettability of the Ni metal on the GDC surface. Based on Eq. (1), we can summarize the surface and/or interface energy differences for the Ni/GDC system and the Ni/YSZ system as follows:

$$\gamma_{\text{oxide}} : \text{GDC} > \text{YSZ} \quad (2)$$

$$\gamma_{\text{Ni}} : \text{GDC} < \text{YSZ} \quad (3)$$

$$\gamma_{\text{Ni/oxide}} : \text{GDC} < \text{YSZ} \quad (4)$$

We can now assume some physical facts for all these cases:

Eq. (2): Oxide surface energy increment by reduction of Ce⁴⁺ to Ce³⁺ (or related to higher electronic conductivity of GDC)

Eq. (3): Ni surface stabilization by adsorption of molecule

Eq. (4): Enhancing the interaction related to the higher electronic conductivity of the GDC

Our group has reported experimental evidences about the difference of the Ni surface condition between Ni/zirconia and Ni/ceria systems by using different analysis techniques as follows:

- I. Raman spectroscopy [8,9]: Carbon deposition on the Ni surface with GDC substrate is suppressed after annealing under dry CH₄ condition at 873–973 K.
- II. Secondary ion mass spectrometry (SIMS) [6,7]: Oxygen is wholly detected on the Ni surface with SDC substrate, but oxygen is partly detected for that with YSZ substrate after annealing under wet CH₄ at 1073 K.

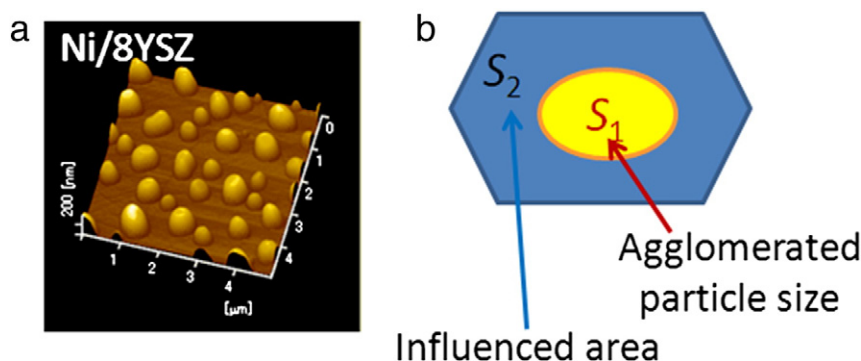


Fig. 1. (a) SPM image and (b) schematic drawing of agglomerated Ni particles on an oxide substrate.

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