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**ZnO-promoted surface diffusion on NiO-Ce_0.8Sm_0.2O_{1.9} anode for solid oxide fuel cell**

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**Abstract**

Ni_{1-x}Zn_xO-Ce_{0.8}Sm_{0.2}O_{1.9} is studied as an anode material for solid oxide fuel cells with hydrogen and methanol as fuels. After reduction, Zn is incorporated into the lattice of Ni when x is less than 0.5, while NiZn alloy accompanied with ZnO is formed when x reaches 0.8. The electrochemical oxidation process of H_2 on the anode is investigated with a symmetric cell under various H_2 partial pressures. The addition of Zn increases the electron cloud density of Ni and thus weakens the adsorbing strength of H on Ni, accelerating the surface diffusion of H species, which is the rate determining step when the content of Zn is lower than 0.5. ZnO in the reduced Ni_{0.2}Zn_{0.8}O-Ce_{0.8}Sm_{0.2}O_{1.9} anode facilitates H spillover, resulting in the variation of the rate determining step and the highest activity of the anode. The cell with Ni_{0.2}Zn_{0.8}O-Ce_{0.8}Sm_{0.2}O_{1.9} anode shows
the highest performance with both H₂ and methanol fuels at 700 °C. ZnO also improves coking resistance of NiO-Ce₀.₈Sm₀.₂O₁.₉ anode.

Keywords: Anode; Solid oxide fuel cell; ZnO; Surface diffusion; Methanol fuel
1. Introduction

Nickel-based cermet materials, such as Ni-yttrium stabilized zirconia, are the most mature anode materials for solid oxide fuel cells (SOFCs) [1-3]. Ni serves as a good electronic conductor and exhibits promising catalytic activity with hydrogen as fuel. However, hydrogen is not an ideal fuel for practical application in a large scale at this stage due to its high cost of production and severe safety risk. Using hydrocarbons such as methane and methanol, which are much cheaper and more stable, instead of hydrogen as fuels will drives the widespread use of SOFCs. On the other hand, it leads to sluggish anode kinetics and carbon deposition at anode. An additional external or internal reforming process converts hydrocarbon fuels into hydrogen before they reach the anode functional layer, bringing about high and stable performance of single cells [4, 5]. However, the endothermic reforming processes with introduction of a great amount of water increase complexity of heat management and reduce energy efficiency of the whole system significantly [6, 7].

Direct electro-oxidation of hydrocarbons at anode of SOFCs has drawn great attention in recent years [8, 9], and the bottleneck is anode materials with high catalytic activity and stability. The anode materials recently developed such as Cu-based cermet and perovskite oxides show high coking resistance but insufficient activity with hydrocarbon fuels [10-12]. Consequently, until now, modification of Ni-based materials has been one of the main strategies for design of anode. Adding other metals forming alloys with Ni is an effective way to optimize electron structure of Ni and thus to improve activity and selectivity of electrochemical oxidation of hydrocarbons. Noble
metals such as Ru and Pd were used in early works, which upgraded the performance of Ni-based anode with CH₄ as fuel [13, 14]. Based on experimental and theoretical calculation results, Schwank and co-workers [15-17] demonstrated that Sn depressed the formation of C-C bonds on Ni and improved the stability of the anode in CH₄ atmosphere. Yoon and Manthiram [18] added W in Ni-Ce₁₋ₓGdₓO₂₋₀.₅ₓ anode, which formed hydrogen tungsten bronze (HₓWO₃) in a humid atmosphere, providing hydroxyl groups to remove carbon on Ni surface. The addition of BaO also facilitated the adsorption of water and accelerated the oxidation of carbon on Ni [19].

Methanol is a renewable fuel that can be produced through biomass fermentation. With a high volumetric energy density, methanol is an ideal fuel for mobile power supply. Our previous works demonstrated that transition metals such as Co and Mo improved the coking resistance of Ni-based anodes with methanol as fuel [20, 21]. ZnO is an excellent promoter in Cu-based catalysts for methanol synthesis, which weakens the bonds between intermediates and the catalyst [22]. Zn can form alloys with Ni, Pd and Pt, and influence the crystal facet and electronic structure of the active sites, resulting in the modification of activity and selectivity of the catalysts for methanol steam reforming, hydrogenation of acetylene and selective hydrogenolysis of glycerol [23-26]. A few of previous works reported the performance improvement of Ni-based anode with the addition of Zn using H₂ as fuel [27, 28]. However, that improvement was mainly attributed to the increase of electronic conductivity of the anode, while the effect of Zn/ZnO on catalytic activity was not well recognized. In this work, Ni₁₋ₓZnxO is mixed with Ce₀.₈Sm₀.₂O₁.₉ (SDC) powder as an anode material for SOFCs. The effects
of Zn on crystal and electronic structure of Ni are investigated. The influence of Zn/ZnO on electrochemical oxidation of H₂ is systematically studied. The activity and coking resistance of the anode with methanol as fuel are also examined.

2. Experimental

2.1. Material preparation

Ni₁₋ₓZnₓO (x = 0, 0.2, 0.5, 0.8, 1) powders were synthesized through a glycine-nitrate process [28, 29]. Stoichiometric Ni(NO₃)₂·6H₂O (99%, Adamas Reagent Co., Ltd.) and Zn(NO₃)₂·6H₂O (99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) were dissolved in deionized water with a total cation concentration of 2 mol L⁻¹. Then glycine (99%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) was added in the solution at a glycine/nitrate ratio of 0.5. The solution was stirred at 80 °C to form a gel, which was then rapidly heated to 350 °C and ignited. The foamy ash obtained was subsequently calcined at 800 °C in air for 4 h. SDC powder was prepared through an oxalate co-precipitation method with Ce(NO₃)₃·6H₂O (99.5%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) and Sm(NO₃)₃·6H₂O (99.9%, Shanghai Aladdin Bio-Chem Technology Co., Ltd.) as starting materials [30]. Ni₁₋ₓZnₓO and SDC at a weight ratio of 1:1 were mixed and ball milled for 24 h and then calcined at 800 °C in air for 4 h to form Ni₁₋ₓZnₓO-SDC composite anode powders. For characterization, the anode powders were reduced in H₂ at 700 °C for 2 h, noted as Ni₁₋ₓZnₓO-SDC-R. The electrolyte was composed of 70 wt% SDC and 30 wt% (Li₀.₆₇Na₀.₃₃)₂CO₃. The cathode consisted of 30 wt.% composite electrolyte and 70 wt.% lithiated NiO [31, 32].
X-ray diffraction (XRD) patterns of the anode powders were recorded at a scanning rate of 8° min\(^{-1}\) using a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-K\(\alpha\) radiation, 40 kV and 200 mA. Hydrogen temperature-programmed reduction (H\(_2\)-TPR) was carried out with Auto Chem II 2920 (Micromeritics, America) from room temperature to 800 °C at a heating rate of 10 °C min\(^{-1}\) in 10% H\(_2\)-90% Ar. The morphology of reduced Ni\(_{0.2}\)Zn\(_{0.8}\)O-SDC powder was studied with a field emission transmission electron microscope (TEM, Tecnai G2 F20, FEI, Netherlands). X-ray photoelectron spectroscopy (XPS) was performed using a ESCALAB 250Xi (Thermo Fisher Scientific, America) with Al-K\(\alpha\) radiation to study the surface property of reduced anode powders.

Carbon deposition on the reduced anode powder was performed in a tubular quartz reactor fed with gasified anhydrous methanol (150 ml min\(^{-1}\), STP) for 4 h at 700 °C. After the sample cooled down in N\(_2\) atmosphere to room temperature, the amount of carbon was measured with a Perkin Elmer Diamond Thermogravimetric analyzer (TGA) from 300 to 900 °C at a heating rate of 10 °C min\(^{-1}\) in air.

2.3. Fuel cell test

Electrolyte-supported single cells and symmetric cells were fabricated with a screen-printing technique. The composite electrolyte powder was pressed into a pellet with a thickness of 650 μm, and then sintered at 700 °C in air for 1 h. The anode and cathode powders were made into slurries with a binder (V006, Heraeus Ltd.), respectively. As for single cells, the cathode slurry was screen-printed on one side of the electrolyte pellet and sintered at 700 °C in air for 30 min. Then the anode slurry was
printed on the other side of the pellet, followed by sintering at 700 °C in air for 30 min. The effective area of the electrodes was 0.64 cm². The surface of the anode and the cross-sectional morphology of the single cell were observed with a Hitachi S-4800 scanning electron microscope (SEM). Ag paste was used as current collector. Hydrogen and gasified anhydrous methanol were used as fuels, and oxygen is used as oxidant. The flow rate of all of the gases were 100 ml min⁻¹ (STP). Before the test, the anode was reduced in H₂ at 700 °C for 2 h. Then the current-voltage (I-V) and current-power (I-P) curves of the single cell were measured with an electrochemical workstation (VersaSTAT 3, Ametek) from 700 to 550 °C. The electrochemical impedance spectrum (EIS) of the single cell was also recorded with the workstation.

As for symmetric cells, the anode slurry was screen-printed on both sides of the electrolyte pellet, and then sintered at 700 °C in air for 30 min. After the coating of Ag paste and the reduction of both electrodes, EIS of the symmetric cell was recorded at 700 °C under various hydrogen partial pressures (P₁₂) using N₂ as the balance gas at both sides.

3. Results and discussion

3.1. Characterization

The characteristic peaks of NiO (JCPDS#73-1519) and SDC (JCPDS#75-0158) are observed in the XRD patterns of NiO-SDC powder before reduction without any other impure peaks (Fig. 1a), proving the chemical stability between SDC and NiO. The left-shift of the NiO peaks in Ni₀.₈Zn₀.₂O-SDC (Fig. 1b) indicates the incorporation of Zn²⁺ into the lattice of NiO since the effective ionic radius of Ni²⁺ (VI coordinated,
0.69 nm) is smaller than that of Zn\textsuperscript{2+} (VI coordinated, 0.74 nm) [33]. No characteristic peak of ZnO is observed in Ni\textsubscript{0.8}Zn\textsubscript{0.2}-SDC. The increase of Zn amount (Ni\textsubscript{0.5}Zn\textsubscript{0.5}-SDC) leads to no further left-shift of the NiO peaks but the appearance of peaks corresponding to ZnO phase (JCPDS#36-1451). The peaks of ZnO in Ni\textsubscript{0.5}Zn\textsubscript{0.5}-SDC and Ni\textsubscript{0.2}Zn\textsubscript{0.8}-SDC shift right compared with those of ZnO-SDC (Fig. 1c), implying the doping of Ni\textsuperscript{2+} into ZnO lattice. Pure ZnO and SDC peaks are observed in the XRD result of ZnO-SDC powder.

The NiO phase in NiO-SDC forms metallic Ni (JCPDS#04-0850) with a cubic structure after reduction (Fig. 1d). The peaks of Ni shift left with the increase of Zn amount until x reaches 0.5. The further rise of Zn amount (Ni\textsubscript{0.2}Zn\textsubscript{0.8}-SDC-R) leads to the disappearance of the peaks of Ni and the formation of new tetragonal NiZn alloy phase (JCPDS#06-0672) accompanied with ZnO. The XRD pattern of ZnO-SDC shows no obvious change after reduction.
Two $\text{H}_2$ consumption peaks are shown in the $\text{H}_2$-TPR curve of NiO-SDC (Fig. S1). The peak with a high intensity at 381 °C corresponds to the reduction of bulk NiO, and the other wide peak between 450 °C and 600 °C with a low intensity is attributed to the reduction of NiO with a strong interaction with the SDC phase [34, 35]. The reduction temperature rises with the increase of Zn content because ZnO is less reducible. No $\text{H}_2$ consumption peak is observed in the $\text{H}_2$-TPR result of ZnO-SDC, demonstrating that pure ZnO cannot be reduced below 800 °C, which is in accordance with the XRD result (Fig. 1d). However, ZnO can be reduced when it is mixed with other metals such as Pd and Ni, and alloys such as PdZn and NiZn are usually formed [26, 28, 36]. In this study, Ni facilitates the dissociated adsorption of $\text{H}_2$, resulting in the almost complete
reduction of ZnO in Ni$_{0.8}$Zn$_{0.2}$O-SDC and Ni$_{0.5}$Zn$_{0.5}$O-SDC, and the partial reduction of ZnO in Ni$_{0.2}$Zn$_{0.8}$O-SDC by hydrogen spillover (Fig. 1d).

The TEM image of Ni$_{0.2}$Zn$_{0.8}$O-SDC-R powder is shown in Fig. 2. The sizes of most of the particles are in the range of 40-200 nm. NiZn alloy particles with a (1 1 0) crystal plane and an interplanar spacing of 0.19 nm contact closely with ZnO, which shows a (1 0 0) crystal plane with an interplanar spacing of 0.28 nm.
The Ni 2p$_{3/2}$ excitation in the XPS results of the reduced anode powders are illustrated in Fig. 3. The peaks at about 855 eV are ascribed to Ni$^{2+}$, which are probably due to the re-oxidation of surface Ni after reduction [37-39], and the peaks at 852-853 eV correspond to metallic Ni$^0$. A decrease in the binding energy of Ni$^0$ peak is observed with the increase of Zn content. The electrons in the fulfilled 3d orbital of Zn (3d$^{10}$) can transfer to the unfulfilled 3d orbital of Ni (3d$^8$), resulting in the increase of the electron cloud density of Ni.
Fig. 3. XPS spectra of Ni 2p\textsubscript{3/2} of various anode powders after reduction.

Fig. 4 shows the TGA curves of the reduced anode powders after carbon deposition. The curves start at 300 °C to eliminate the adsorbed water. The weight loss of the anode powders between 450 and 700 °C is generally attributed to the gasification of carbon deposits. NiO-SDC-R shows the greatest weight loss of more than 40%, indicating that NiO-SDC-R suffers from the most serious carbon deposition. The weight loss decreases with the increase of Zn content in the anode powder, and no obvious loss of weight is observed in the curve of ZnO-SDC-R, demonstrating that Zn improves the coking resistance of the anode. It should be mentioned that a slight increase of weight is observed in the curves of some anodes in 400-550 °C, which is due to the reoxidation
of Ni and Zn. However, it is difficult to distinguish the reoxidation of the metals from the oxidation of carbon since those two processes are partly overlapped.

![TGA curves of the anode powders after carbon deposition.](image)

**Fig. 4.** TGA curves of the anode powders after carbon deposition.

3.2. Fuel cell test

The agglomeration of particles is observed on the surface of Ni$_{0.2}$Zn$_{0.8}$O-SDC anode layer before reduction (Fig. S2a). After reduction in H$_2$, a large amount of pores less than 1 μm in size are formed in the sponge-like anode (Fig. S2b). The thickness of the porous anode layer is about 20 μm (Fig. S2c), which adheres tightly to the electrolyte layer.
The open circuit voltages (OCVs) of the single cells with anodes containing Ni are around 1.05 V at 700 °C using H₂ as fuel (Fig. 5). The $P_{\text{max}}$ of the cell with NiO-SDC anode reaches 506 mW cm$^{-2}$. The addition of Zn in the anode (Ni$_{0.8}$Zn$_{0.2}$O-SDC) results in an increase of the $P_{\text{max}}$ to 610 mW cm$^{-2}$. However, a further rise of the Zn content to 0.5 leads to a drop of the $P_{\text{max}}$ to 430 mW cm$^{-2}$. Nevertheless, the $P_{\text{max}}$ rises again significantly to 720 mW cm$^{-2}$ when the content of Zn reaches 0.8. The single cell with ZnO-SDC anode exhibits the lowest OCV of 0.92 V and $P_{\text{max}}$ of 135 mW cm$^{-2}$ due to the low catalytic activity of ZnO.
Fig. 6. (a) Nyquist plots and (b) Bode plots of the symmetric cells with H₂ as fuel at 700 °C; (c) Bode plots of the symmetric cell with NiO-SDC anode at 700 °C under various $P_{H2}$.

The electrochemical properties of the anodes with H₂ fuel are studied based on the EIS results of the symmetric cells (Fig. 6a). The intercepts of the Nyquist plots on the real axis correspond to the ohmic resistances of the cells, which are almost the same for all of the cells. In contrast, the anode polarization resistances ($R_p$) represented by the arcs are in an order of ZnO-SDC > Ni$_{0.5}$Zn$_{0.5}$O-SDC > NiO-SDC > Ni$_{0.8}$Zn$_{0.2}$O-SDC > Ni$_{0.2}$Zn$_{0.8}$O-SDC, opposite to the order of the cell performance shown in Fig. 5. Unfortunately, the Nyquist plot is the superposition of a series of processes in the anode. In order to specify the effect of Zn on the anode reaction, Bode plots of the symmetric
cells are presented in Fig. 6b. Though it is difficult to decouple the curves with a high accuracy, we can divide the plots roughly into two parts, i.e., a high frequency (HF, $10^4$-$10^1$ Hz) region and a low frequency (LF, $10^1$-$10^{-2}$ Hz) region. With the addition of Zn in the anode, a slight variation is observed in the HF region, while the main change of $R_p$ happens in the LF region. Fig. 6c shows the influence of $P_{H_2}$ on the $R_p$ of NiO-SDC anode. The decrease of $P_{H_2}$ results in a negligible change of $R_p$ in HF and a remarkable increase of $R_p$ in LF, indicating that the HF region mainly includes the processes not affected by $P_{H_2}$, while most of the $P_{H_2}$-controlled processes are in the LF region.

Generally, the electrochemical oxidation of H$_2$ on the surface of cermet anodes can be briefly divided into a series of anode processes starting from the dissociative adsorption of H$_2$ on the surface of the anode (step 1), which happens preferentially on Ni of a Ni-based cermet anode, forming adsorbed H atoms. Then the H adsorbed is transferred to the reaction site, i.e., three-phase boundary (TPB), through surface diffusion or spillover (step 2). Meanwhile, oxygen ions are transferred from electrolyte to TPB via oxygen vacancies in the anode (step 3). Subsequently, the charge-transfer reaction (step 4) happens at the TPB region, followed by the desorption of H$_2$O formed and electron conduction.

\begin{align}
    \text{H}_2(g) & \leftrightarrow 2\text{H}_{\text{ad}} \\
    \text{H}_{\text{ad}} & \leftrightarrow \text{H}_{\text{TPB}} \\
    \text{O}_{\text{O,bulk}}^\bullet + \text{V}_{\text{O,TPB}}^\bullet & \leftrightarrow \text{O}_{\text{O,TPB}}^\bullet + \text{V}_{\text{O,bulk}}^\bullet \\
    2\text{H}_{\text{TPB}} + \text{O}_{\text{O,TPB}}^\bullet & \leftrightarrow \text{V}_{\text{O,TPB}}^- + \text{H}_2\text{O}_{\text{TPB}} + 2\text{e}^- 
\end{align}

The overall $R_p$ is inversely proportional to $P_{H_2}$ ($R_p \sim P_{H_2}^{-1}$) if step 1 is the rate-
determining step (RDS). In contrast, if step 2 is the RDS and step 1 reaches an equilibrium state correspondingly, $R_p$ versus $P_{H2}$ should exhibit a power law relationship with a power exponent of -0.5 ($R_p \sim P_{H2}^{-0.5}$). No obvious dependence of $R_p$ on $P_{H2}$ will be observed if step 3 or 4 is the RDS. Fig. 7a shows the Nyquist plots of the symmetric cells at 700 °C under various $P_{H2}$. With the decrease of $P_{H2}$, the $R_p$ of NiO-SDC, Ni$_{0.8}$Zn$_{0.2}$O-SDC and Ni$_{0.5}$Zn$_{0.5}$O-SDC increase remarkably, while that of Ni$_{0.2}$Zn$_{0.8}$O-SDC changes negligibly. The slopes of log$R_p$-log $P_{H2}$ curves of NiO-SDC, Ni$_{0.8}$Zn$_{0.2}$O-SDC and Ni$_{0.5}$Zn$_{0.5}$O-SDC anodes are between -0.47 and -0.60 (Fig. 7b), indicating that the surface diffusion of adsorbed H is the RDS. The heats of H$_2$ chemisorption and experimental results have demonstrated that the adsorption of H$_2$ on Zn is weaker than that on Ni [40-42]. Meanwhile, the desorption temperature of H$_2$ on the anode power decreases with the increase of the content of Zn (Fig. S3 and Table S1), which also proves that the addition of Zn in NiO-SDC weakens the adsorbing strength of H. Zn increases the electron cloud density of Ni (Fig. 3), resulting in the weakened adsorbing strength of H, and thus accelerates the surface diffusion of H, resulting in a low $R_p$ of Ni$_{0.8}$Zn$_{0.2}$O-SDC compared with that of NiO-SDC. The further addition of Zn reduces the amount of Ni active sites and lowers the catalytic activity of Ni$_{0.5}$Zn$_{0.5}$O-SDC consequently. When the content of Zn reaches 0.8, the double logarithmic curve of $R_p$ versus $P_{H2}$ exhibits a slope of -0.10, implying that oxygen ionic conduction or charge-transfer reaction becomes the RDS instead of surface diffusion of H. A noticeable amount of ZnO exists in the Ni$_{0.2}$Zn$_{0.8}$O-SDC anode after reduction (Fig. 1b), which is widely recognized as a promoter accelerating the spillover of H.
Therefore, surface diffusion of H on Ni$_{0.2}$Zn$_{0.8}$O-SDC anode is significantly improved, bringing about the lowest $R_p$. As shown in Fig. 6b, the rate of the reaction on Ni$_{0.2}$Zn$_{0.8}$O-SDC anode is mainly determined by the process responding in the LF region, indicating that the RDS is probably oxygen ionic conduction in the anode, not the charge-transfer reaction.

(a)
Fig. 7. (a) Nyquishit plots of the symmetric cells with different anodes at 700 °C under various $P_{H2}$; (b) $R_p$ of the symmetric cells versus $P_{H2}$ at 700 °C.

The OCVs of the single cells fed with methanol are above 1.0 V at 700 °C (Fig. 8a). The $P_{max}$ of the cells fed with methanol show a same order as those of the cells with H2 fuel, i.e., ZnO-SDC < Ni$_{0.5}$Zn$_{0.5}$O-SDC < NiO-SDC < Ni$_{0.8}$Zn$_{0.2}$O-SDC < Ni$_{0.2}$Zn$_{0.8}$O-SDC. ZnO in Ni$_{0.2}$Zn$_{0.8}$O-SDC could weaken the bonds between the anode and intermediates in the electrochemical oxidation of methanol, such as $^*$HCOO, $^*$H$_3$CO and $^*$COO [22], facilitating the surface diffusion and desorption of the intermediates and resulting in the highest cell performance. The $P_{max}$ of the cells with NiO-SDC, Ni$_{0.8}$Zn$_{0.2}$O-SDC, Ni$_{0.5}$Zn$_{0.5}$O-SDC and Ni$_{0.2}$Zn$_{0.8}$O-SDC anodes reach 540, 658, 495 and 834 mW cm$^{-2}$, respectively, slightly higher than those of the same cells
fed with H₂. The cell with ZnO-SDC anode shows a $P_{\text{max}}$ of 337 mW cm$^{-2}$, more than twice the $P_{\text{max}}$ of that cell with H₂ as fuel. The performance of the cells increases with the rise of temperature. The cell with Ni$_{0.2}$Zn$_{0.8}$O-SDC anode exhibits $P_{\text{max}}$ of 354, 533, 606 and 834 mW cm$^{-2}$ at 550, 600, 650 and 700 °C, respectively (Fig. 8b). No obvious change of anode microstructure is observed after the test (Fig. S2d-e).

To further confirm the positive effect of ZnO on the performance of the anode, 5 wt% ZnO was added into Ni$_{0.5}$Zn$_{0.5}$O-SDC powder through impregnation with Zn(NO$_3$)$_2$·6H$_2$O as raw material [21]. The cell with the impregnated anode exhibits $P_{\text{max}}$ of 518 and 709 mW cm$^{-2}$ at 700 °C with H₂ and methanol fuels, respectively (Fig. S4), much higher than those of the cell with the un-impregnated Ni$_{0.5}$Zn$_{0.5}$O-SDC anode. The results prove that ZnO promotes the catalytic activity of the anode.
Fig. 8. $I$-$V$ and $I$-$P$ curves of (a) single cells with various anodes at 700 °C and (b) the cell with Ni$_{0.2}$Zn$_{0.8}$O-SDC anode at different temperatures with methanol as fuel.

4. Conclusions

In this work, the activity and coking resistance of NiO-SDC anode are improved with the addition of ZnO. NiZn alloy with a cubic structure is formed after reduction when the content of Zn is less than 0.5. Ni accepts electrons from Zn, leading to an increase of electron cloud density of Ni. The rate of H$_2$ electrochemical oxidation on the anodes with Zn contents lower than 0.5 is determined by the surface diffusion of H species. Zn weakens the adsorbing strength of H species on the anode and improves the activity of the anode. When the content of Zn increases to 0.8, tetragonal NiZn alloy and ZnO phases are formed after reduction, and the anode shows the highest activity since ZnO facilitates H spillover. The cell supported by a 650-μm-thick SDC-
(Li_{0.67}Na_{0.33})_2CO_3 composite electrolyte with Ni_{0.2}Zn_{0.8}O-SDC as the anode shows the highest $P_{\text{max}}$ of 720 and 834 mW cm$^{-2}$ at 700 °C with H$_2$ and methanol as fuels, respectively. Furthermore, the coking resistance of the anode in methanol atmosphere increases with the rise of the content of Zn.

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