Enhanced methane steam reforming activity and electrochemical performance of Ni_{0.9}Fe_{0.1}-supported solid oxide fuel cells with infiltrated Ni-TiO\textsubscript{2} particles

Kai Li, Lichao Jia, Xin Wang, Jian Pu, Bo Chi & Jian Li

Ni_{0.9}Fe_{0.1} alloy-supported solid oxide fuel cells with NiTiO\textsubscript{3} (NTO) infiltrated into the cell support from 0 to 4 wt.% are prepared and investigated for CH\textsubscript{4} steam reforming activity and electrochemical performance. The infiltrated NiTiO\textsubscript{3} is reduced to TiO\textsubscript{2}-supported Ni particles in H\textsubscript{2} at 650 °C. The reforming activity of the Ni_{0.9}Fe_{0.1}-support is increased by the presence of the TiO\textsubscript{2}-supported Ni particles; 3 wt.% is the optimal value of the added NTO, corresponding to the highest reforming activity, resistance to carbon deposition and electrochemical performance of the cell. Fueled wet CH\textsubscript{4} at 100 mL min\textsuperscript{-1}, the cell with 3 wt.% of NTO demonstrates a peak power density of 1.20 W cm\textsuperscript{-2} and a high limiting current density of 2.83 A cm\textsuperscript{-2} at 650 °C. It performs steadily for 96 h at 0.4 A cm\textsuperscript{-2} without the presence of deposited carbon in the Ni_{0.9}Fe_{0.1}-support and functional anode. Five polarization processes are identified by deconvoluting and data-fitting the electrochemical impedance spectra of the cells under the testing conditions; and the addition of TiO\textsubscript{2}-supported Ni particles into the Ni_{0.9}Fe_{0.1}-support reduces the polarization resistance of the processes ascribed to CH\textsubscript{4} steam reforming and gas diffusion in the Ni_{0.9}Fe_{0.1}-support and functional anode.

On-cell methane (CH\textsubscript{4}) reforming in Ni-based anodes is an attractive option for directly using CH\textsubscript{4}-based fuels for solid oxide fuel cells (SOFCs) with high fuel efficiency and simplified system design. CH\textsubscript{4} steam reforming is a catalytic process for commercial production of H\textsubscript{2} or syngas at a H\textsubscript{2}:CO molar ratio of 3:1 according to the endothermic reaction of

\[
\text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \quad \Delta H^0 = 206.1 \text{kJ/mol} \tag{1}
\]

Excessive addition of H\textsubscript{2}O will further converts CO to CO\textsubscript{2} by the slightly exothermic water gas shift (WGS) reaction.

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad \Delta H^0 = -41.2 \text{kJ/mol} \tag{2}
\]

If these reactions are taking place in the anode of an SOFC, H\textsubscript{2} is consumed via electrochemical oxidation to generate electrical power, forming by-product of H\textsubscript{2}O. Such in-situ formed H\textsubscript{2}O is simultaneously used for CH\textsubscript{4} steam reforming, which reduces the amount of externally added H\textsubscript{2}O to improve the electrical efficiency of the SOFC system.

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However, for on-cell CH4 reforming in Ni-based anodes, coking is frequently observed in the anode when steam/carbon (H2O/CH4) ratio is low, since Ni catalyzes CH4 decomposition that produces deposited carbon in the form of filament or particle via either CH4 cracking or the Boudouard reactions as follow

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2 \text{(CH}_4\text{ cracking)} \]  

\[ 2\text{CO} \rightarrow \text{CO}_2 + \text{C} \text{(Boudouard reaction)} \]

The soot-like carbon particles are distributed on the surface of Ni particles, occupying the active sites for electrochemical reaction and the pores for fuel gas transport; and the carbon filaments formed by carbon diffusion into/precipitation out the Ni particles disintegrate the Ni-cermet anode by lifting out the Ni particles from the anode (dusting).

It has been demonstrated that infiltration of oxides, such as rare-earth doped CeO2, BaO, and CaO-MgO, into the Ni-based anode is an effective way to enhance its coking resistance by suppressing carbon formation and promoting steam-carbon reactions. Although TiO2 has not been investigated in SOFCs, it was used as a support in catalysts for steam reforming of hydrocarbons (methanol, ethanol, and glycerol), CO2 reforming of CH4, and CO oxidation; and high coking resistance was demonstrated in CH4 and ethanol reforming. Stimulated by these investigations, TiO2 was evaluated in direct-CH4 SOFCs for the enhancement of CH4 on-cell reforming in the present study.

Compared with electrolyte- and electrode-supported SOFCs, metal-supported SOFCs have some advantages in the aspects of electrical/thermal conductivity and mechanical ductility; consequently, the temperature distribution in and tolerance to thermal cycle of the cell are improved. In our previous study, Ni-Fe alloy-supported SOFCs were investigated with the purpose of using wet (3 vol.% H2O) CH4 as the fuel, and high performance (0.6 V at 0.4 A cm-2 and 650 °C for 50 h) was achieved. However, the Ni0.9Fe0.1-support used was not fully resistant to carbon deposition, and carbon lumps were formed in its large pores. In order to develop metal-supported direct-hydrocarbon SOFCs, Ni0.9Fe0.1-supported SOFCs were prepared with NiTiO3 infiltrated into the Ni0.9Fe0.1-support. It was expected that NiTiO3 would be reduced into TiO2-supported Ni particles in H2 to enhance CH4 reforming activity and resistance to carbon deposition of the Ni0.9Fe0.1-supported cells.

Results

Materials and cell characterization. Figure 1a–c show the XRD patterns of the as-synthesized and reduced NTO and co-fired powder mixture of NiO, Fe2O3 and NTO. The as-synthesized NTO demonstrated a perovskite structure of NiTiO3 (JCPDF# 76-0334), and the reduced product was a mixture of TiO2 (JCPDF# 21-1276) and Ni (JCPDF# 04-0850). Figure 1d shows EDS mappings of Ni, Ti and O for TiO2-supported Ni particles.
and the porous cell support (~1 mm). The thickness of the BSCF-LSM cathode was averagely 15 μm. Figure 3 respectively present the microstructure of the sintered and reduced cell supports with various amounts of infiltrated NTO from 1 to 4 wt.% of the weight of the half cell (NiO-Fe2O3 anode-support | NiO-GDC anode | GDC electrolyte).

Reforming activity of infiltrated Ni0.9Fe0.1-supports. CH4 reforming in the Ni0.9Fe0.1-support is a chemical process that in situ produces H2, which is electrochemically oxidized on the functional Ni-GDC anode to generate electrical power with byproduct of steam via the reaction of

\[ \text{H}_2 + \text{O}^2- \rightarrow \text{H}_2\text{O} + 2e^- \]

Thus the reforming activity of the Ni0.9Fe0.1-support is of critical importance for the performance of the cell with on-cell CH4 reforming. Figure 4 shows the CH4 conversion rate and reforming product distribution at 650 °C in the Ni0.9Fe0.1-supports loaded with different amounts of TiO2-supported Ni particles. The initial values of CH4 conversion rate were approximately 50%, 55%, 58%, 61% and 60% for the Ni0.9Fe0.1-supports loaded with 0%, 1%, 2%, 3% and 4 wt.% of NTO (designated as 0NTO, 1NTO, 2NTO, 3NTO and 4NTO), respectively. This indicates that the addition of TiO2-supported Ni particles in the Ni0.9Fe0.1-support promoted its reforming activity with a limit of 3 wt.% NTO, more than which the conversion rate decreased, possibly due to the over-cover of the reforming active sites on the surface of the Ni0.9Fe0.1 scaffold by TiO2 and increased surface area of the small Ni particles for carbon deposition. The CH4 conversion rate of 0NTO, 1NTO, 2NTO and 4NTO decreased obviously with time after approximately 12 h, only which of 3NTO remained relatively stable during the testing period of 24 h. The main reforming products were H2, CO and CO2 (Fig. 4b–d), and their concentrations varied accordingly with the testing time.

Cell performance. The cells with NTO-infiltrated Ni0.9Fe0.1-supports were evaluated at 650 °C with wet CH4 (3 vol.% H2O) as the fuel; Fig. 5 shows their initial I-V-P curves. The open circuit voltage (OCV) of all the cells was around 0.78 V, due to the partial electronic conduction of GDC electrolyte. The maximum power densities increased from 0.99 to 1.20 W cm⁻² as the NTO loading was increased from 0 to 3 wt.%. Further increasing NTO loading to 4 wt%, it decreased to 1.17 W cm⁻². Figure 6 shows the initial impedance spectra of the cells under a current density of 0.4 A cm⁻² (Fig. 6a), from which the ohmic (Rτ) and polarization (RP) resistances were determined, and the corresponding distributions of relaxation time (DRT, Fig. 6b). The value of Rτ of each cell was similar, around 0.063 Ω cm⁻², and that of RP varied in an opposite direction to the cell voltage and power density. This tendency of cell performance change with the amount of loaded NTO in the Ni0.9Fe0.1-support is consistent with that of the activity for CH4 steam reforming shown above, which suggests that cell performance improvement is due to the increased reforming activity of the Ni0.9Fe0.1-support and the consequent increase in the amount of H2 available for the anode reaction.

The DRT G(τ) was associated with the impedance Z(w) by the following expression:

\[
Z(w) = Z'(\infty) + \int_0^\infty \frac{G(\tau)}{1 + jw\tau} d\tau
\]

Where G(τ) is defined as the DRT of impedance Z, τ is relaxation time, Z'(∞) is the limitation of the real part of Z as angular frequency w approaches infinity. Consequently, impedance could be represented as series connection of infinite number of parallel polarization resistor G(τ)dτ and a capacitor τ/G(τ)dτ. For a more detailed description of DRT method and application were referred.

After the initial evaluation, all the cells were further tested at 650 °C and a constant current density of 0.4 A cm⁻² for up to 96 h; the results are shown in Fig. 7. The improvement on cell performance durability is in consistence with that on CH4 steam reforming activity. The cells with 0NTO, 1NTO, 2NTO and 4NTO Ni0.9Fe0.1-supports performed 67, 78, 90 and 96 h before the sudden drop of the cell voltage; and the cell with 3NTO Ni0.9Fe0.1-support outperformed the others, degrading linearly at a slow rate of 0.5 mV h⁻¹ during the testing period. Post-test examination confirmed that the sudden voltage drop at the end of the test was caused by cell
disintegration due to dusting of the Ni$_{0.9}$Fe$_{0.1}$-support. The linear voltage decrease, at nearly the same rate for all the cells, may represent the intrinsic cell degradation that needs further understanding for mechanism, whereas the non-linear voltage decrease is attributed to carbon deposition in the Ni$_{0.9}$Fe$_{0.1}$-support and functional anode.

Figure 3. Fractured cross-sectional microstructure of (a) sintered and (b) reduced Ni$_{0.9}$Fe$_{0.1}$-supports with various amounts of infiltrated NTO.
Since the deposited carbon remained in the cell, its amount can be quantified from the temperature-programmed oxidation (TPO) profile of the post-test cells, as shown in Fig. 8. The area of CO$_2$ peak, an indication of the amount of CO$_2$ formed from deposited carbon, were $7.89 \times 10^{-8}$, $6.93 \times 10^{-8}$, $2.61 \times 10^{-8}$ and $3.15 \times 10^{-8}$ for the cells with 1NTO, 2NTO, 3NTO and 4NTO Ni$_{0.9}$Fe$_{0.1}$-supports, respectively. These values support the explanation of the durability testing results and indicate that the cell with 3NTO anode-support is the most resistant to carbon deposition among the cells investigated.

**Discussion**

According to previous studies$^{19,27}$, the effectiveness of TiO$_2$ on improving reforming activity can be attributed to its enhanced capability of H$_2$O adsorption and consequently the coking resistance. It is the H$_2$O adsorbed on the catalyst that increases the reforming activity$^{29}$, and the prevalent presence of subsurface defects of TiO$_2$ in reduced atmosphere, such as oxygen vacancies and Ti interstitials, enhances H$_2$O adsorption due to surface relaxation and...
charge localization. On-cell methane reforming, constant adsorption of H₂O in anode will shift the equilibrium reaction of Eqs (1) and (2) in a forward direction. Therefore, H₂ and CO₂ concentration increases whereas CO concentration decrease with increase in the amount of H₂O. The increase in H₂ concentration and the decrease in CO concentration subsequently prevent possible carbon formation by shifting Boudard reaction (Eq. 3) and decomposition of CH₄ (Eq. 4) in a backward direction. In addition, the excess H₂ reacts with oxygen ion from electrolyte to product electrical power and steam, which enhances the water-gas shift reaction and retards CH₄ decomposition. In addition to the contribution of H₂O adsorption on TiO₂, the TiO₂-supported Ni particles on the surface of Ni₀.₉Fe₀.₁ scaffold are also considered to increase the reforming activity, due to its known tendency to form a strong metal-support interaction (SMSI) between TiO₂ support and Ni metal and widely used catalyst of CH₄ and ethanol steam reforming¹⁶,²⁸.

Based on the DRT shown in Fig. 6b and the results reported in a previous investigation²⁵, five polarization processes were identified for individual cells, which are two high-frequency processes ascribed to the gas diffusion
and charge transfer/ionic transport within the functional anode (P_{3A} and P_{4A}), one high-frequency process associated with oxygen surface exchange and bulk diffusion within the BSCF-LSM cathode (P_{2C}), one low-frequency process related to mass transport in the Ni_{0.9}Fe_{0.1}-support (P_{1A}) and one low-frequency process attributed to CH\textsubscript{4} reforming in the Ni_{0.9}Fe_{0.1}-support (P_{Ref}). The contribution of each process to the total polarization resistance was obtained by data fitting the impedance spectra (Fig. 6a) using the complex nonlinear least-squares method and an equivalent circuit (inset in Fig. 6a) consisting of an ohmic resistor $R_O$, two RQ elements for P_{2A} and P_{3A}, a Gerischer element (G) for P_{2C}, a generalized finite length Warburg element (W) for P_{1A} and another RQ element for P_{Ref}. The change of the polarization resistance for each process, $R_{1A}$, $R_{2A}$, $R_{3A}$, $R_{2C}$ and $R_{Ref}$, with the amount of loaded NTO is demonstrated in Fig. 6c. $R_{3A}$ and $R_{2C}$ remained almost unaffected by NTO infiltration, since the cathode was identical for all the cells, and the electrochemical reaction in the functional Ni-GDC anodes was the same reaction of H\textsubscript{2} oxidation\cite{25} regardless of the amount of NTO loaded in the Ni_{0.9}Fe_{0.1}-support. The resistance of diffusion of reformate in the Ni_{0.9}Fe_{0.1}-support and Ni-GDC functional anode, $R_{1A}$ and $R_{2A}$, decreased with increasing NTO amount till 3 wt.% and then increased at 4 wt.%, which reflects the amount change of H\textsubscript{2} in the reformate. It is expected that higher concentration of H\textsubscript{2} in the reformate lead to lower diffusion resistance in porous cell support and functional anode due to the high diffusivity of H\textsubscript{2}. $R_{Ref}$ is assigned to CH\textsubscript{4} steam reforming process; its change with the amount of loaded NTO in the Ni_{0.9}Fe_{0.1}-support is consistent with that of the reforming activity. According to the data-fitting results and discussions, it may be concluded that the cell performance improvement with NTO infiltration in the Ni_{0.9}Fe_{0.1}-support is attributed to the improved CH\textsubscript{4} reforming activity and the decreased potential of carbon deposition; consequently the polarization resistances related to CH\textsubscript{4} reforming and reformate transport processes are decreased.

NTO infiltration into Ni_{0.9}Fe_{0.1}-supports was investigated with the purpose of enhancing CH\textsubscript{4} steam reforming activity, carbon deposition resistance and cell performance. Based on the obtained results and discussion, the following conclusions are drawn.

1. The activity of the Ni_{0.9}Fe_{0.1}-support for CH\textsubscript{4} steam reforming is enhanced by infiltrated NTO, which is reduced into TiO\textsubscript{2}-supported Ni (0) particles in H\textsubscript{2}. The TiO\textsubscript{2} improves the resistance to carbon deposition by adsorbing H\textsubscript{2}O, while the supported small Ni particles promote CH\textsubscript{4} decomposition.

2. 3 wt.% of the weight of the half cell (anode-support | functional anode | electrolyte) is the optimal value for the amount of NTO infiltrated into the Ni_{0.9}Fe_{0.1}-support. Increased CH\textsubscript{4} reforming activity lead to the improvement of cell performance, durability and resistance to carbon deposition.

3. The overall cell polarization resistance is contributed by five polarization processes associated with CH\textsubscript{4} reforming (P_{Ref}), mass transport in anode-support (P_{1A}), gas diffusion in functional anode (P_{3A}), charge transfer within functional anode (P_{2A}), and oxygen surface exchange and bulk diffusion within cathode (P_{2C}). The addition of NTO into the Ni_{0.9}Fe_{0.1}-support reduces the polarization resistance of P_{Ref}, $P_{1A}$ and $P_{2A}$.

### Methods

#### Cell fabrication.

Ni_{0.9}Fe_{0.1}-supported cells were fabricated by tape casting-screen printing-sintering process. NiO (Haite Advanced Materials) and Fe\textsubscript{2}O\textsubscript{3} (Sinopharm) powders were mixed at a Ni:Fe molar ratio of 9:1 and ball-milled for 24 h in xylene/ethanol solvent with fish oil (Richard E. Mistler, Inc.) as the dispersant, corn starch as the pore former, poly vinyl butyral (Solutia Inc.) as the binder and butyl benzyl phthalate and poly alkylene glycol (Solutia Inc.) as the plasticizer. The prepared slurry was cast into a tape with a dry thickness of ~1.2 mm, which was then die-cut into discs (25 mm in diameter) as the cell support, on which NiO (Inco)-GDC (10 mol.% Gd-doped CeO\textsubscript{2}, NIMTE, CAS) functional anode and GDC electrolyte were screen printed in sequence, followed by sintering at 1450 °C in air for 5 h. La_{0.8}Sr_{0.2}MnO_{1.9} coated Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3} (LSM-BSCF) cathode\cite{29} was then screen-printed on the sintered GDC electrolyte and sintered in air at 1050 °C for 2 h.

To introduce TiO\textsubscript{2}-supported Ni particles onto the stem of NiO-Fe\textsubscript{2}O\textsubscript{3} scaffold (~40% porosity\cite{30}), an aqueous solution containing Ti and Ni ions at the stoichiometric concentration of NiTiO\textsubscript{3} (NTO) was prepared as follow. Tetrabutyl titanate (C_{4}H_{10}TiO, Sinopharm) was dissolved in a dilute nitric acid aqueous solution under
stirring, and then stoichiometric amount of Ni nitrate (Ni(NO₃)₂·6H₂O, Sinopharm) was added prior to the addition of citric acid (CA) and ethylenediamine tetraacetic acid (EDTA) as the chelants. The molar ratio of metal ions:CA:EDTA in the solution was 1:1.5:1.5. Ammonia solution was used to adjust the pH value of the solution to approximately 7. Such prepared solution was infiltrated into the pores of the sintered NiO-Fe₂O₃ scaffold and calcined in air at 1000 °C for 2 h to form crystallized NTO nano particles. This infiltration process was repeated to achieve the desired amounts of loaded NTO in the scaffold. The crystal structure of NTO and its chemical reaction with NiO and Fe₂O₃ were determined by X-ray diffraction (XRD, X'Pert) using a NiO-Fe₂O₃-NTO powder mixture co-fired in air at 1000 °C for 2 h. The NTO powder was obtained by calcining the dried solution in air at 1000 °C for 2 h, and its reduced form (650 °C in H₂ for 2 h) was characterized by XRD for phase identification and examined by using a scanning electron microscope (SEM, FEI sirion 200).

**Steam reforming activity evaluation.** To evaluate the catalytic activity of the infiltrated Ni₀.₉Fe₀.₁-support for CH₄ steam reforming, the NiO-Fe₂O₃ support sintered at 1450 °C in air for 5 h was sealed in a ceramic housing using a Cerambond™ sealant (Aremco Product, Inc.) and reduced at 650 °C in H₂ for 2 h. Then a mixture of 10% CH₄, 10% H₂O and 80% He. CH₄ gas was fed into the porous support at a constant rate of 100 ml min⁻¹. The steam content in the mixture was controlled by flowing dry CH₄ and He gases through a saturator containing distilled water at 50 °C according to the following equation

\[
\log [P(H_2O)] = \frac{-2961}{T_{bubbler}} - 5.13 \log (T_{bubbler}) + 21.133
\]  

(7)  

Compositional analysis of the effluent gas from the reactor was conducted with an on-line Pfeiffer Vacuum Mass Spectrometer. The steam reforming was performed at temperatures between 500 and 700 °C, and the CH₄ conversion rate (X(%) ) was estimated using the following equation.

\[
x(\%) = \frac{[CO] + [CO_2]}{[CO] + [CO_2] + [CH_4]}
\]  

(8)  

**Cell testing and characterization.** The cell performance wasevaluated at 650 °C with wet (3 mol.% H₂O) CH₄ as the fuel and ambient air as the oxidant at a flow rate of 100 ml min⁻¹. Using a power supply of Solartron 1480A in 4-probe mode, the current density (i)–voltage (V)–power density (P) polarization curves were obtained at a frequency range from 100 KHz to 0.01 Hz and an AC signal amplitude of 10 mV. The microstructure of the cell was examined by using a SEM. The resistance to carbon deposition of (the amount of deposited carbon in the Ni₀.₉Fe₀.₁-supported cell was characterized by temperature-programmed-oxidation (TPO) method at a flow rate of 20 ml min⁻¹ of pure oxygen.

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Author Contributions
K.L., L.J. and X.W. conducted the experiments and prepared the manuscript; J.P. and J.L. provided suggestions to the experiments; B.C. initiated the study, discussed the results and revised the manuscript.

Additional Information
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