A robust carbon tolerant anode for solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) have been attracting remarkable attention as one of the most promising green energy conversion devices in the recent years. However, a high susceptibility of commonly used Ni-based anodes to carbon coking is a major challenge to the successful commercialization of SOFCs. In this study, a robust anode with Ni/TiO_{2-δ} nano-network interfaces is reported, for low-cost SOFCs working at intermediate temperatures. This anode demonstrates an acceptable power density, and good stability with humidified (3% H₂O) methane. X-ray diffraction (XRD) Rietveld refinement, X-ray photoelectron spectroscopy (XPS), electron paramagnetic resonance (EPR), and high resolution transmission electron microscopy (HRTEM) images reveal that the Ni/TiO_{2-δ} network-composite anode forms from the *in-situ* reductive decomposition of NiTiO₃. Numerous Ni/TiO_{2-δ} interfaces that facilitate the water adsorption and the water-mediated carbon-removing reactions form during this decomposition process. Density functional theory calculations predict that at the Ni/TiO_{2-δ} interfaces, the dissociated OH from H₂O (adsorbed on TiO_{2-δ}) reacts with C (locating on Ni) to produce CO and H species, which are then electrochemically oxidized (combined with O²⁻) to CO₂ and H₂O at the triple-phase boundaries of the anode.

INTRODUCTION

Solid oxide fuel cells (SOFCs) have been attracting remarkable attention as one of the most promising green energy devices, which can efficiently and cost-effectively convert the chemical energy within hydrocarbons, gasified coal, etc., directly to electricity [1–3]. A major challenge to the use of conventional nickel/yttria-stabilized zirconia (Ni-YSZ) as an anode is its high susceptibility to carbon coking and its deactivation upon exposure to the common hydrocarbon fuels [4–6]. In order to address this challenge, extensive studies have been undertaken to find new carbon tolerant anode materials. For example, a number of nick-

el-free oxide materials, such as La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_{3-δ}, Sr₂Mg_{1-x}Mn_xMoO_{6-δ} (0 ≤ x ≤ 1), and doped (La, Sr)TiO₃, have been investigated as potentially coke-free anodes, although low power densities were reported at intermediate temperatures, owing to the difficulties in fabricating thin electrolytes on these porous anode supports [7–10]. Meanwhile, prior efforts to develop new anode structures have also been widely adapted. Zhan *et al.* [11] used a Ru-ceria catalyst layer with a conventional anode, allowing internal reforming of iso-octane with scarcely carbon coking on the anode. Zhu *et al.* [12] used impregnated Sm-doped ceria (SDC) coating on a Ni framework, and achieved a much improved carbon coking tolerance. Yang *et al.* [13] studied a new anode with nano-structured barium oxide/nickel (BaO/Ni) interfaces, and demonstrated its potential for high electrochemical activity and high stability in hydrocarbon fuels. However, these previous solutions still suffer from high intrinsic costs, as a result of the impregnation process, as well as from the use of noble metals and rare earth metal oxides. The high costs have retarded the actual application of such SOFCs. Therefore, the development of inexpensive anodes with low material costs, easy fabricability, and high carbon tolerance is key to the widespread application of SOFCs. Inexpensive SOFCs originating from low material and fabrication costs will be especially crucial for fuel cell-based, residential, micro-combined heat and power systems fed with natural gas [14].

TiO₂ is well known as a perfect supporter of metal catalysts, and has been widely applied to the partial oxidation of hydrocarbons, the catalytic reduction of CO₂, and other catalytic reactions. Rodriguez *et al.* [15] suggested that the high performance of Au-TiO₂ catalysts in the water-gas shift (WGS) reaction relied heavily on the direct participation of the TiO₂ oxide in the catalytic process. Wu *et al.* [16] investigated the partial oxidation of methane over a

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Ni/TiO₂ catalyst, and found that CH₄ was efficiently oxidized into CO and H₂ via a direct oxidation reaction. Tietz *et al.* [17,18] utilized a Ni/TiO₂ mixture as a composite anode in a H₂ fueled SOFC, and achieved a power output of 0.09 W cm⁻² at 750°C, discharging at 0.7 V using the YSZ electrolyte. We have previously applied Ni/TiO₂, originating from the *in-situ* reductive decomposition of NiTiO₃, as a reforming layer to the Ni-YSZ anode [19]. Significant carbon-tolerant improvements in the humidified methane and propane fuels were observed compared with the performance without the reforming layer [19]. Unfortunately, a slight carbon deposition on the Ni-YSZ anodes was detected, after 93 h test in methane, accompanied by a slight decrease in the current density, due to the thickness limitation of the reforming layer. Enhanced carbon tolerance is highly expected when the Ni/TiO₂ is directly used as the anode substrate. Another advantage to the use of Ni/TiO₂ as the SOFC anode is its low material cost compared with the SOFC anodes with rare-earth elements.

In this work, single cells using Sm_{0.2}Ce_{0.8}O_{1.9} (SDC) film electrolyte supported by anode substrate NiTiO₃ (NTO), have been evaluated as intermediate temperature solid oxide fuel cells (IT-SOFCs). Here, NTO was used to avoid anode cracking during the reduction process. A Ni/TiO_{2-δ} nano-network structure was observed after the *in-situ* reductive decomposition of NiTiO₃ in both powder form and cermet form. This nanostructured anode enabled the attainment of an inexpensive SOFC with good carbon tolerance and good performance. Furthermore, the potential processes of carbon removal at the Ni/TiO_{2-δ} interface were predicted with density functional theory (DFT) calculations.

EXPERIMENTAL

Powders of NTO were prepared through an ethylenediaminetetraacetic acid (EDTA)-citrate complexation process in distilled water. First, Ti(OCH(CH₃)₂)₄ was dissolved in a nitrate solution, which was then mixed with a nitrate solution of Ni²⁺ in a specific ratio. EDTA was dissolved in the formed solution, and then ammonium hydroxide was added to obtain a transparent solution. Citric acid was then added as a chelate, to form a precursor solution. The molar ratio of metallic cations, EDTA, and citric acid was set as 1:1.2:1.2. The precursor solution was heated and stirred on a hot plate, and then burnt into a black sponge after the evaporation. The fresh powders were calcined at 800°C for 2 h to form NTO powders. SDC and La_{0.8}Sr_{0.2}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) powders were prepared by an auto-ignition process. The proper amounts of NTO and TiO₂ powders were reduced in wet H₂, at 700°C, for 5 h. Transmission electron microscopy (TEM) and X-ray diffraction (XRD, with a scanning rate of 0.50° min⁻¹) were performed to analyze the

phase purity of the oxidized and reduced NTO powders. XRD Rietveld refinements were performed using GSAS software. X-ray photoelectron spectroscopy (XPS) was performed, using a Thermo ESCALAB 250 with monochromatized Al Kα at $h\nu = 1486.6$ eV, to analyze the surface of the oxidized and reduced NTO powders. The binding energies were calibrated to the C1s peak at 284.6 eV. Electron paramagnetic resonance (EPR) of the oxidized and reduced TiO₂ powders was recorded at 150 K, to confirm the presence of the high spin Ti³⁺ as well as oxygen deficiency, using a JES-FA200 electron spin resonance spectrometer.

Single cells with anode NTO support were fabricated by a co-pressing process. NTO powders were mixed with 20 wt.% starch, and then cold-pressed at 200 MPa, to form a substrate. Then the loose SDC powder was uniformly distributed on the anode substrate and co-pressed at 250 MPa. The resultant green pellet was sintered at 1250°C, for 5 h, to densify the SDC membrane. The thickness of the SDC electrolyte was approximately 40 μm after sintering. LSCF was mixed with SDC powders in a weight ratio of 40:60 and then applied onto the surface of the SDC electrolyte by a screen-printing technique, using 6 wt.% ethylcellulose-terpineol as an organic binder. The samples were heated at 950°C for 3 h in the air, to complete the cell fabrication procedure.

XRD patterns were obtained using a Philips X'pert PROS diffractometer, with Cu-Kα radiation, at room temperature. Single cells were tested in a home developed cell-testing system, using humidified hydrogen (~3% H₂O) or humidified methane (~3% H₂O) as fuels, and static air as an oxidant. The flow rate of fuel gas was about 40 mL min⁻¹. Fractured microstructure of the cells tested with humidified CH₄ fuel was analyzed using scanning electron microscopy (SEM), in a JEOL JSM-6700F unit.

Spin-polarized DFT calculations were carried out, using the projector augmented wave (PAW) method and a Vienna *ab initio* simulation package (VASP) [20,21]. The electronic exchange and correlation was treated with the generalized gradient approximation functional, developed by Perdew, Burke and Ernzerhof (PBE) [22]. The plane wave basis was set as 400 eV, and the convergence criteria for the electronic structure, and the geometry, were 10⁻⁴ eV, and 0.03 eV Å⁻¹, respectively. The Brillouin-zone integration, based on the Monkhorst-Pack scheme, was performed with a k point grid of 2×2×1, for the surface [23]. A vacuum spacing of 15 Å was placed in the direction perpendicular to the surface. The location and energy of the transition states were calculated with the climbing image nudged elastic band method [24]. Additionally, the TiO_{2-δ}/Ni(111) surface model was constructed by placing a small TiO_{2-δ} chain (Ti₃O₆) on the Ni(111) substrate, which was described with a 5×5 slab with three atomic layers [13,14].

Here, we adopted this anode surface model with partially coordinated Ti centers to agree with the XPS observation that many oxygen vacancies exist on the anode $\text{TiO}_{2-\delta}$ surfaces (Ti^{4+} in TiO_2 is reduced to Ti^{3+}).

RESULTS AND DISCUSSION

Figs 1a and b show the XRD Rietveld refinement results for the as-prepared NTO, and that for the reduced one in wet H_2 at 700°C for 5 h, respectively. For the NTO as-prepared oxide, the strong diffraction peaks correspond to a space group of $R\text{-}\bar{3}(148)$ with $a = b = 5.029 \text{ \AA}$, and $c = 13.786 \text{ \AA}$. However, for the reduced sample, all the strong diffraction peaks correspond to a space group of $\text{Fm-}\bar{3}\text{m}(225)$ that belongs to Ni, and a space group of $\text{P4}_2/\text{mmn}(136)$ of TiO_2 , with $a = b = 4.591 \text{ \AA}$, and $c = 2.958 \text{ \AA}$. The refinement for the oxidized and reduced NTO samples result in χ^2 , wR_p and R_p values of 8.179, 11.92%, and 8.7%, and 3.509, 8.95%, and 7.04%, respectively, indicating a close fit to the experimental data.

To confirm the presence of oxygen vacancies on the reduced NTO sample, XPS measurements were conducted on both the as-prepared and the reduced NTO sam-

ples. Figs 2a and b show the XPS signal from the oxidized NTO, corresponding to $\text{Ni}2p_3$ (Ni^{2+} , with binding energies of 855.52 and 861.52 eV), and $\text{Ti}2p_3$ (Ti^{4+} , with a binding energy of 458.45 eV) [25–27]. Surprisingly, the XPS data from the reduced NTO (Figs 2c and d) show that there is only $\text{Ti}2p_3$ (Ti^{4+} , with a binding energy of 458.51 eV), and no Ti^{3+} is detected on the sample surface [28–31]. Similarly, peaks corresponding to Ni^{2+} , in addition to the metal Ni (851.51 eV), are detected, as shown in Fig. 2c. The results reasonably suggest that the metal Ni and Ti^{3+} on the surface of the reduced Ni/ TiO_2 sample are oxidized in the air before the XPS detection [32,33]. EPR measurements were further performed, at 150 K, to determine the presence of unpaired electrons of Ti^{3+} in the oxidized and reduced TiO_2 samples, having first removed the Ni phase to avoid detection interference. As shown in Fig. 2e, the oxidized TiO_2 sample shows no EPR response, indicating the absence of the unpaired electrons. In contrast, the reduced TiO_2 sample shows a strong EPR signal at $g = 1.95$, a characteristic of paramagnetic Ti^{3+} ions [34–36], directly proving the existence of Ti^{3+} species accompanied by the formation of oxygen vacancies forming $\text{TiO}_{2-\delta}$. The presence of oxygen vacancies plays a key role in the carbon tolerance of the NTO anode in hydrocarbon fuels.

To demonstrate the potential of NTO as a practical, carbon tolerant anode, cells based on the NTO anode substrate were fabricated with SDC as the electrolyte material. Fig. 3a shows the SEM images of the single cell after testing. A dense and crack-free SDC electrolyte film, approximately $45 \mu\text{m}$ in thickness, was successfully fabricated on the reduced Ni/ $\text{TiO}_{2-\delta}$ anode support, and exhibited good adhesion to the reduced anode and the LSCF cathode. It is worth emphasizing that a special Ni/ $\text{TiO}_{2-\delta}$ nano-network-composite anode with many nanopores is achieved, originating from the *in-situ* reductive decomposition of NTO, as shown in Fig. 3b.

To further clarify the structure with anode reduction, TEM images were obtained. Fig. 4a shows that the particle morphology of the NTO sample was irregular in shape and agglomerated, with an average particle size in the range of 50–80 nm. The corresponding elemental mapping image (Fig. 4c) indicates that both Ni and Ti elements are uniformly distributed in these nanoparticles, and the interplanar distance can be clearly discerned to be 0.253 nm as shown in Fig. 4e. In contrast, the TEM image of the reduced NTO sample (Fig. 4b) shows that it consists of a Ni network, with small nanoparticles of TiO_2 decorating the network surface. The TiO_2 nanoparticles are well-dispersed on the Ni network, with an average particle size of approximately 20 nm. The corresponding elemental mapping images (Fig. 4d) reveal a clear contrast between the two segments, and indicate that the nano-network composite is

Figure 1 XRD Rietveld refinement of NTO (a) prepared by an EDTA-citrate complexation process at 800°C , and (b) after reduction in wet H_2 at 700°C . # indicates the peaks corresponding to Ni.

Figure 2 XPS of the reduced and oxidized NTO powders: binding energy of (a) Ni2p orbital of the oxidized NTO, (b) Ti2p orbital of the oxidized NTO, (c) Ni2p orbital of the reduced NTO, (d) Ti2p orbital of the reduced NTO, and (e) EPR of the oxidized and reduced TiO₂ powders, conducted at 150 K.

indeed composed of two different components. The structural analysis from the HRTEM image (Fig. 4f) further reveals that both Ni and TiO₂ are highly crystalline, and the interplanar distances are clearly discerned to be 0.204 nm and 0.345 nm, corresponding to the (111) plane of Ni, and the (101) plane of rutile TiO₂, respectively. These results are consistent with those from the XRD data.

The electrochemical performance of the cell, based on the NTO anode, is shown in Fig. 5. With humidified H₂ as the fuel, the maximum power densities of the NTO anode

based tri-layer cell, as shown in Fig. 5a, are 0.204, 0.127 and 0.065 W cm⁻², measured at 700, 650 and 600°C, respectively. As shown in Fig. 5b, with humidified CH₄ as the fuel, the maximum power densities are 0.164, 0.087 and 0.030 W cm⁻², respectively, approximately 20% lower than that with the humidified H₂ fuel. Figs 5c and d show the impedance spectra of the tri-layer cells, using humidified (3% H₂O) hydrogen, and CH₄, as fuel, respectively, at various temperatures. In these spectra, the intercepts with the real axis at low frequencies represent the total cell resistance (R_t)

Figure 3 SEM images of the cross-section of (a) the after-testing cell with the structure of NTO/SDC/LSCF-SDC, and (b) the NTO anode after reduction in hydrogen, forming the Ni/TiO₂ network-composite structure.

Figure 4 (a, b) TEM images, (c, d) TEM-EDS elemental mapping images, and (e, f) HRTEM images of the NTO particles, and the *in-situ* reductive Ni/TiO_{2-δ} nano-network composite anode.

of the cell, and the value of the intercept at high frequency is the bulk resistance (R_b). Furthermore, the difference between the two values corresponds to the polarization resistance (R_{ep}) of the two interfaces: the cathode-electro-

lyte interface, and the anode-electrolyte interface. The R_{ep} values with hydrogen as the fuel, obtained from the impedance spectra, are 0.317, 0.613, and 1.218 $\Omega \text{ cm}^2$, measured at 700, 650, and 600°C, respectively, which are lower than the values with CH₄ as the fuel.

It should be noted that the discharging performance of the cell with the NTO anode is significantly superior compared with that using traditional NiO-SDC anodes [37–39]. Additionally, the open circuit voltage (OCV) of this tri-layer cell is about 0.1 V lower than with the Ni-SDC anode. The relatively low volume fraction of Ni in the reduced NTO sample (~30 vol.%), resulting in limited triple phase boundaries and low electronic conductivities, should account for these phenomena. Fortunately, the stability of the cell with the NTO anode, in humidified methane fuel, is much better than those based on the traditional anodes, as shown in Fig. 5e. The traditional Ni-SDC anode encounters serious carbon deposition that degrades the cell performance in a few hours, and results in cracking after a 32 h test. However the cell with the NTO anode maintains stable output voltage at 0.61 V, over a 40 h test, when discharging at 100 mA cm⁻². No carbon deposition is observed in the SEM micrograph of the anode, after testing in CH₄ for 40 h, as shown in Fig. 5f. *I-V* and long term stability tests on single cells strongly suggest that the tri-layer cells based on the Ni/TiO_{2-δ} network-composite anode present good coking tolerance in wet methane fuel. These tests also indicate that better carbon tolerance can be achieved with the NTO anode than with a thin NTO reforming layer.

An understanding of the detailed mechanism for improved carbon tolerance with the Ni/TiO_{2-δ} network anode is important, in order to develop new electrode materials and to uncover the theoretical fundamentals of SOFCs. Generally, the carbon tolerance of Ni based anodes stems mainly from the depressed catalytic activity to the cracking of hydrocarbons, when forming alloys such as Ni-Cu

Figure 5 *I-V* and *I-P* curves of the tri-layer NTO/SDC/LSCF-SDC cell using the fuels, (a) humidified hydrogen, and (b) humidified methane, at different temperatures. Electrochemical impedance spectra of the tri-layer cell using (c) humidified hydrogen, and (d) humidified CH₄, at different temperatures. Durability of the tri-layer cell and the reference tri-layer NiO-SDC/SDC/LSCF-SDC cell, examined at 700°C under a discharge current of 100 mA, using (e) humidified methane as the fuel. (f) SEM picture of the NTO anode after testing in CH₄ for 40 h.

alloys, or from the enhanced steam reforming rate under large steam concentrations [40,41]. In the case of the Ni/TiO_{2-δ} anode, we believe that the key reason for the improved carbon tolerance relates to the high concentration of the surface vacancies of TiO_{2-δ} in the reduced atmosphere, which will greatly benefit water adsorption, and therefore improve the reforming rate. Many prior experimental and theoretical studies on the TiO₂/H₂O interaction indicate that water does adsorb and dissociate on the reduced TiO₂ (110) surfaces and even on the stoichiometric surfaces [42–45].

In the DFT calculation, the potential processes of carbon removal at the Ni/TiO_{2-δ} interface are predicted by the steam reforming reaction. Initially, we compared the adsorption energies of H₂O and CO on Ni and TiO_{2-δ} surfaces (Table 1), in order to determine possible adsorption sites

Table 1 Theoretical adsorption energies of CO and H₂O on Ni(111), YSZ and TiO_{2-δ}(110) surfaces

Materials	Adsorption energy (eV)	
	CO	H ₂ O
Ni(111)	−1.87	−0.25
YSZ	—	−0.26
TiO ₂ (110) ^a -perfect	−0.07	−0.75
TiO ₂ (110)-defect	−0.21	−0.74

a) p-(4×2) supercell TiO₂(110) surface slabs with 9 atomic layer thickness.

for the reactant (H₂O), and meta-product (CO), respectively. The comparison shows that H₂O is more readily adsorbed on TiO_{2-δ} surfaces than on Ni surfaces or YSZ surfaces (Table 1 shows adsorption energies of −0.25, −0.26, and −0.75 eV, for Ni, YSZ and TiO_{2-δ}, respectively), while

CO is more energetically stable on Ni surfaces than on the reduced $\text{TiO}_{2-\delta}$ surfaces (Table 1, the adsorption energy is -1.85 eV for Ni, and -0.21 eV for $\text{TiO}_{2-\delta}$). On the basis of experimental observations and the above theoretical predictions, we expect that H_2O adsorption will occur on $\text{TiO}_{2-\delta}$ anode surfaces, and then carbon will be amalgamated on Ni surfaces [46,47]. Therefore, we propose a possible mechanism for the removal of carbon near $\text{TiO}_{2-\delta}$ chains on Ni(111), as depicted in Fig. 6. The reaction pathway proposed can be described as follows: 1) H_2O is first adsorbed on those partially coordinated Ti atoms (reduced $\text{TiO}_{2-\delta}$ surfaces), which need to overcome a small barrier (transition state 1, TS1) of 0.35 eV, and release energy of 1.10 eV. This small adsorption barrier can be easily compensated by thermal fluctuation under the SOFC operating conditions. A reaction barrier (TS2) of 0.47 eV has to be overcome for the dissociation of the adsorbed H_2O into OH and H intermediates. 2) Subsequently, the dissociated OH reacts with a chemisorbed C atom on the Ni surface, to form a CHO species with a reaction barrier (TS3) of 0.63 eV. 3) Then, the CHO species dissociates to produce CO and H, via TS4 (reaction barrier of 1.00 eV), with an exothermicity of 2.32 eV. At the triple phase boundary, CO and H will be further electrochemically oxidized by O^{2-} (from the electrolyte), to form CO_2 and H_2O , respectively [14]. The overall reaction mechanisms can be summarized as follows:

Our DFT calculation clearly demonstrates that the deposited carbon at the Ni/ $\text{TiO}_{2-\delta}$ interface can be energetically-favorably removed by OH which is dissociated from H_2O and adsorbed on the $\text{TiO}_{2-\delta}$ surface.

Figure 6 Potential energy profiles for the removal of the deposited carbon species on $\text{TiO}_{2-\delta}$ /Ni(111) surface. * refers to an adsorbed species on the surface, and TS is the abbreviation for a transition state.

CONCLUSIONS

This study reports the development of a robust anode with Ni/ $\text{TiO}_{2-\delta}$ nano-network interfaces, enabling the fabrication of low-cost and intermediate temperature SOFCs, with an acceptable power density. Furthermore, good stability of the new anode, which has numerous nanostructured Ni/ $\text{TiO}_{2-\delta}$ interfaces readily facilitating water adsorption and water-mediated carbon removal reactions, is demonstrated with humidified (3% H_2O) methane. DFT calculations predict that the dissociated OH from H_2O on $\text{TiO}_{2-\delta}$ interfaces reacts with C on Ni near the Ni/ $\text{TiO}_{2-\delta}$ interfaces, to produce CO and H species, which are then electrochemically oxidized (combined with O^{2-}) to CO_2 and H_2O , at the triple-phase boundaries of the anode. This anode offers great potential for making low-cost and low-temperature SOFCs, for the efficient and low-emission conversion of readily available fuels into electricity.

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- McIntosh S, Gorte RJ. Direct hydrocarbon solid oxide fuel cells. *Chem Rev*, 2004, 104: 4845–4865
- Atkinson A, Barnett S, Gorte RJ, *et al.* Advanced anodes for high-temperature fuel cells. *Nat Mater*, 2004, 3: 17–27
- Park SD, Vohs JM, Gorte RJ. Direct oxidation of hydrocarbons in a solid-oxide fuel cell. *Nature*, 2000, 404: 265–267
- Nease J, Adams TA. Systems for peaking power with 100% CO_2 capture by integration of solid oxide fuel cells with compressed air energy storage. *J Power Source*, 2013, 228: 281–293
- Shi YX, Luo Y, Cai NS, *et al.* Experimental characterization and modeling of the electrochemical reduction of CO_2 in solid oxide electrolysis cells. *Electrochim Acta*, 2013, 88: 644–653
- la O' GJ, Ahn SJ, Crumlin E, *et al.* Catalytic activity enhancement for oxygen reduction on epitaxial perovskite thin films for solid-oxide fuel cells. *Angew Chem Int Ed*, 2010, 49: 5344–5347
- Rath MK, Choi BH, Lee KT. Properties and electrochemical performance of $\text{La}_{0.75}\text{Sr}_{0.25}\text{Cr}_{0.5}\text{Mn}_{0.5}\text{O}_{3-\delta}$ - $\text{La}_{0.2}\text{Ce}_{0.8}\text{O}_{2-\delta}$ composite anodes for solid oxide fuel cells. *J Power Source*, 2012, 213: 55–62
- Huang YH, Dass RI, Xing ZL, *et al.* Double perovskites as anode materials for solid-oxide fuel cells. *Science*, 2006, 312: 254–257
- Torabi A, Etsell TH. Electrochemical behavior of solid oxide fuel cell anodes based on infiltration of Y-doped SrTiO_3 . *J Power Source*, 2013, 225: 51–59
- Ma Q, Tietz F, Stover D. Nonstoichiometric Y-substituted SrTiO_3 materials as anodes for solid oxide fuel cells. *Solid State Ionics*, 2011, 192: 535–539
- Zhan ZL, Barnett SA. An octane-fueled solid oxide fuel cell. *Science*, 2005, 308: 844–847
- Zhu W, Xia CR, Fan J, *et al.* Ceria coated Ni as anodes for direct utilization of methane in low-temperature solid oxide fuel cells. *J Power Source*, 2006, 160: 897–902
- Yang L, Choi Y, Qin WT, *et al.* Promotion of water-mediated carbon removal by nanostructured barium oxide/nickel interfaces in solid oxide fuel cells. *Nat Commun*, 2011, 2: 357
- Alanne K, Saari A, Ugursal VI, *et al.* The financial viability of an SOFC cogeneration system in single-family dwellings. *J Power Source*, 2006, 158: 403–416
- Rodriguez JA, Ma S, Liu P, *et al.* Activity of CeO_2 and TiO_2 nanoparticles grown on Au(111) in the water-gas shift reaction. *Science*,

- 2007, 318: 1757–1760
- 16 Wu TH, Yan QG, Wan HL. Partial oxidation of methane to hydrogen and carbon monoxide over a Ni/TiO₂ catalyst. *J Mol Catal A Chem*, 2005, 226: 41–48
 - 17 Meschke F, Dias FJ, Tietz F. Porous Ni/TiO₂ substrates for planar solid oxide fuel cell applications. *J Mater Sci*, 2001, 36: 5719–5728
 - 18 Tietz F, Dias FJ, Dubiel B, *et al.* Manufacturing of NiO/NiTiO₃ porous substrates and the role of zirconia impurities during sintering. *Mater Sci Eng B*, 1999, 68: 35–41
 - 19 Wang ZQ, Wang ZB, Yang WQ, *et al.* Carbon-tolerant solid oxide fuel cells using NiTiO₃ as an anode internal reforming layer. *J Power Sources*, 2014, 255: 404–409
 - 20 Blöchl PE. Projector augmented-wave method. *Phys Rev B*, 1994, 50: 17953–17979
 - 21 Kresse G, Furthmüller J. Efficient iterative schemes for *ab initio* total-energy calculations using a plane-wave basis set. *Phys Rev B*, 1996, 54: 11169–11186
 - 22 Perdew JP, Burke K, Ernzerhof M. Generalized gradient approximation made simple. *Phys Rev Lett*, 1996, 77: 3865–3868
 - 23 Monkhorst HJ, Pack JD. Special points for brillouin-zone integrations. *Phys Rev B*, 1976, 13: 5188–5192
 - 24 Henkelman G, Uberuaga BP, Jonsson H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. *J Chem Phys*, 2000, 113: 9901–9904
 - 25 Chen D, Yang D, Wang Q, *et al.* Effects of boron doping on photocatalytic activity and microstructure of titanium dioxide nanoparticles. *Ind Eng Chem Res*, 2006, 45: 4110–4116
 - 26 Zhao W, Ma WH, Chen CC, *et al.* Efficient degradation of toxic organic pollutants with Ni₂O₃/TiO_{2-x}B_x under visible irradiation. *J Am Chem Soc*, 2004, 126: 4782–4783
 - 27 Kang M, Lee MH. Synthesis and characterization of Al-, Bi-, and Fe-incorporated mesoporous titanosilicate (MPTS) materials and their hydrophilic properties. *Appl Catal A*, 2005, 284: 215–222
 - 28 D'Addato S, Grillo V, Altieri S, *et al.* Structure and stability of nickel/nickel oxide core-shell nanoparticles. *J Phys Condens Matter*, 2011, 23: 175003
 - 29 Giovanardi C, di Bona A, Valeri S. Oxygen-dosage effect on the structure and composition of ultrathin NiO layers reactively grown on Ag(001). *Phys Rev B*, 2004, 69: 075418
 - 30 Nesbitt HW, Legrand D, Bancroft GM. Interpretation of Ni2p XPS spectra of Ni conductors and Ni insulators. *Phys Chem Miner*, 2000, 27: 357–366
 - 31 Prieto P, Nistor V, Nouneh K, *et al.* XPS study of silver, nickel and bimetallic silver-nickel nanoparticles prepared by seed-mediated growth. *Appl Surf Sci*, 2012, 258: 8807–8813
 - 32 Corneille J, He JW, Goodman DW. XPS characterization of ultra-thin MgO films on a Mo (100) surface. *Surf Sci*, 1994, 306: 269–278
 - 33 Li YX, Zhou JE, Dong DH, *et al.* Composite fuel electrode La_{0.2}Sr_{0.8}TiO_{3-δ}Ce_{0.8}Sm_{0.2}O_{2-δ} for electrolysis of CO₂ in an oxygen-ion conducting solid oxide electrolyser. *Phys Chem Chem Phys*, 2012, 14: 15547–15553
 - 34 Chong SV, Xia J, Suresh N, *et al.* Tailoring the magnetization behavior of Co-doped titanium dioxide nanobelts. *Solid State Commun*, 2008, 148: 345–349
 - 35 Soria J, Sanz J, Sobrados I, *et al.* Magnetic resonance study of the defects influence on the surface characteristics of nanosize anatase. *Catal Today*, 2007, 129: 240–246
 - 36 Glinchuk MD, Bykov IP, Slipenyuk AM, *et al.* ESR study of impurities in strontium titanate films. *Phys Solid State*, 2001, 43: 841–844
 - 37 Ling YH, Zhao L, Lin B, *et al.* Investigation of cobalt-free cathode material Sm_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-δ} for intermediate temperature solid oxide fuel cell. *Int J Hydrogen Energy*, 2010, 35: 6905–6910
 - 38 Zhao L, He BB, Zhang XZ, *et al.* Electrochemical performance of novel cobalt-free oxide Ba_{0.5}Sr_{0.5}Fe_{0.8}Cu_{0.2}O_{3-δ} for solid oxide fuel cell cathode. *J Power Source*, 2010, 195: 1859–1861
 - 39 Asamoto M, Miyake S, Sugihara K, *et al.* Improvement of Ni/SDC anode by alkaline earth metal oxide addition for direct methane-SOFC. *ECS Trans*, 2009, 25: 2155–2160
 - 40 Kim H, Lu C, Worrell WL, *et al.* Cu-Ni cermet anodes for direct oxidation of methane in solid-oxide fuel cells. *J Electrochem Soc*, 2002, 149: A247–A250
 - 41 McIntosh S, Gorte RJ. Direct hydrocarbon solid oxide fuel cells. *Chem Rev*, 2004, 104: 4845–4865
 - 42 Schaub R, Thosttrup P, Lopez N, *et al.* Oxygen vacancies as active sites for water dissociation on rutile TiO₂(110). *Phys Rev Lett*, 2001, 87: 266104
 - 43 Harris LA, Quong AA. Molecular chemisorption as the theoretically preferred pathway for water adsorption on ideal rutile TiO₂(110). *Phys Rev Lett*, 2004, 93: 086105
 - 44 Lindan PJD, Zhang CJ. Comment on “Molecular chemisorption as the theoretically preferred pathway for water adsorption on ideal rutile TiO₂(110)”. *Phys Rev Lett*, 2005, 95: 029601
 - 45 Duncan DA, Allegretti F, Woodruff DP. Water does partially dissociate on the perfect TiO₂(110) surface: a quantitative structure determination. *Phys Rev B*, 2012, 86: 045411
 - 46 Blinn KS, Abernathy H, Li XX, *et al.* Raman spectroscopic monitoring of carbon deposition on hydrocarbon-fed solid oxide fuel cell anodes. *Energy Environ Sci*, 2012, 5: 7913–7917
 - 47 Nikooyeh K, Clemmer R, Alzate-Restrepo V, *et al.* Effect of hydrogen on carbon formation on Ni/YSZ composites exposed to methane. *Appl Catal A*, 2008, 347: 106–111

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Conflict of interest The authors declare that they have no conflict of interest.

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中文摘要 固体氧化物燃料电池是一种有应用前景的绿色能源转化装置, 目前得到了广泛关注, 然而传统的Ni基金属陶瓷阳极容易因积碳而失活是固体氧化物燃料电池商业化的一个发展瓶颈. 本研究基于低成本的中温固体氧化物燃料电池, 发展了一种稳健的具有纳米网状结构的Ni-TiO_{2-δ}阳极材料, 以潮湿的甲烷为燃料展现了良好的电化学性能和长期稳定性. 结合X射线衍射、X射线光电子能谱、电子顺磁共振及高分辨透射电镜等测试结果, 揭示了NiTiO₃阳极支撑体原位还原形成了具有纳米网状结构的Ni/TiO_{2-δ}新型阳极, 可以吸附大量的水, 从而可以通过水重整过程有效地实现积碳转移. 密度泛函理论计算解释了积碳转移过程, 在阳极的三相界面处, 被TiO_{2-δ}吸附的水解离的OH与Ni吸附积碳发生电化学反应生成CO和H₂, 进而氧化成CO₂和H₂O.