Direct-methane Solid Oxide Fuel Cells with Hierarchically Porous Ni-based Anode Deposited with Nano Catalyst Layer

Yu Chen^{a,⊥}, Yanxiang Zhang^{a,b,⊥}, Ye Lin^{a,⊥}, Zhibin Yang^c, Dong Su^d, Minfang Han^{*c} and Fanglin

Chen^{*a}

^a Department of Mechanical Engineering, University of South Carolina, Columbia, SC
29208, USA.

^b School of Materials Science and Engineering, Harbin Institute of Technology, Harbin 15
0001, P.R. China

^c School of Chemical & Environment Engineering, China University of Mining &
Technology, Beijing, 100083, China. E-mail: hanminfang@sina.com (M. Han).

^d Centre for Functional Nanomaterials, Brookhaven National Laboratory, Upton, NY
11973, USA

⊥ These authors contribute equally to this work.

* Author to whom correspondence should be addressed:

Tel: +1 803 777 4875; fax: +1 803 777 0106. E-mail address: chenfa@cec.sc.edu (F.

Chen); hanminfang@sina.com (M. Han).

Abstract

Current development of solid oxide fuel cells (SOFCs) is impeded by direct utilization of hydrocarbon fuels since SOFC anodes suffer from coking readily. We present an innovative design for enhancing the coking resistance of the conventional SOFC anode. A thin nano samaria doped ceria (SDC) catalyst layer has been deposited efficiently via infiltration on the wall surface of the Ni-yttria-stabilized zirconia (Ni-YSZ) anode internal gas diffusion channel (5-200 μm in size) fabricated from freeze-drying tape-casting and vacuum-free infiltration. The efficiency for catalyst infiltration has been significantly improved by using hierarchically porous anode structure with open and straight channels. Single cells with nano SDC layer show very stable cell performance and a peak power density of 0.65 Wcm^{-2} at 800°C using methane as fuel. High resolution transmission electron microscopy (HRTEM) analysis indicates for the first time that SDC layer can effectively prevent the formation or growth of nickel carbide (onset of coking), accounting for the excellent performance and structural stability of the Ni-based cermet anode.

Keywords: Coking resistance; Heterogeneous catalyst; Solid oxide fuel cells; Freeze-drying tape-casting; Nano nickel carbide

1. Introduction

One of the biggest challenges for hydrogen industry is that, at the present time, an estimated 96% of H_2 is produced by reforming methane or other hydrocarbons and at least 20 % of the fuel value of the hydrocarbons is lost during this process[1]. Therefore, direct utilization of hydrocarbons is of great significance and has attracted considerable interests recently [2-4]. Solid oxide fuel cells (SOFCs) in principle can operate on fuels ranging from H_2 to hydrocarbons. However, direct operation of hydrocarbon fuels in SOFCs often leads to rapid coking of the state-of-the-art nickel-based anode, resulting in significant performance drop and failure of SOFCs[5, 6]. Carbon adsorbs strongly on Ni surface and thus blocks the active site for electrochemical reactions[6], resulting in rapid performance degradation. The use of external steam reforming or partial oxidation of hydrocarbon fuel is an option, but that will lead to reduced system efficiency and additional cost and complexity of the SOFC system[7, 8]. **Internal reforming is an attractive option offering significant cost reduction, higher efficiency and faster load response of a SOFC system. However, it can lead to some issues such as carbon deposition in the anode chamber and larger temperature gradients in the stack caused by strong cooling effect of the fast reforming reaction[9, 10].** Another strategy is to develop new anode materials such as perovskite oxides with improved coking resistance[6, 11]. Although these new materials are promising, the catalytic activity towards hydrocarbon fuel and electrical conductivity under anodic atmosphere are still much lower than those of the conventional Ni-based anodes.

Ni-based anodes are still the best choice for SOFCs in terms of low cost, high electrical conductivity, excellent catalytic activities, good manufacturability and chemical

compatibility. Consequently, it will be scientifically significant and commercially valuable if Ni-based anodes can be modified to possess coking resistance. Infiltration/impregnation of catalyst, such as rare-earth doped ceria oxide[12-16], $\text{SrZr}_{0.95}\text{Y}_{0.05}\text{O}_3$ [17], yttrium-doped barium zirconate (BZY)[18], BaO[19, 20] or BaCO_3 [4] on the surface of anode particles has been proven to be an effective way to enhance the coking resistance of anode. The infiltrated oxide particles can substantially suppress the amount of carbon formation by promoting the reactions between either steam or oxygen ion and carbon species. Although considerable improvement in cell performance has been reported, no excellent operational stability has been achieved up to now[21], which may be attributed to the inhomogenous/inefficient deposition of catalyst in the sponge-like electrode[22]. Infiltration/impregnation of catalyst solution by capillary force can be a concern for sponge-like anode-supported SOFCs[22]. Limited catalyst has been reported in the area adjacent to electrode/electrolyte interface[23]. Zhan and Barnett have demonstrated that Ru-CeO₂ can be used as an anode catalyst reforming layer when deposited on the outer surface of Ni-yttria-stabilized zirconia (Ni-YSZ) anode and reform hydrocarbons to syngas to prevent coking[24]. Therefore, the direct exposure of Ni-YSZ anode to hydrocarbon fuels has been avoided. The cell showed stable power output when operating on iso-octane-air-CO₂ mixture as fuel but had a drawback of gas diffusion through catalyst layer to the Ni-based anode. To avoid the gas diffusion issue, Sun et al have achieved enhanced cell performance through microstructure improvement using mesoporous flower-like Ru-CeO₂ as catalyst layer to Ni based anode[25]. However, the high loading of Ru makes it less economically attractive. Recently, Suzuki et al have applied pure CeO₂ as the catalyst reforming layer on the Ni-based anode surface for low

temperature SOFCs operated on methane-H₂O mixture as fuel[26]. The cell peak power density with reforming layer was more than 10 times higher than that without the reforming layer, confirming that the catalyst layer enhanced the catalytic activity of the steam reforming of methane. However, limitations of introducing this reforming layer are obvious. The poor thermal-mechanical compatibility between catalyst layer and anode layer often caused delamination during thermal cycling, making it less practically feasible[21]. Further, it is challenging to collect current in the anode due to the poor electrical conductivity of the CeO₂ catalyst layer.

We report a novel design for enhancing the coking resistance of SOFC anode. A thin nano Sm-doped ceria (Sm_{0.2}Ce_{0.8}O_{1.9}, SDC) catalyst layer has been deposited through infiltration onto the inner wall surface of Ni-based anode with straight open pores/channels (5-200 μm in size) fabricated using freeze-drying tape-casting[27-29]. The nano-sized SDC layer can also function as catalyst reforming layer which was embedded in the anode, rather than deposited on the outer surface. Such a novel combination provides much more freedom to select high performance catalysts even with poor thermal compatibility with the Ni-based anode or with limited electrical conductivity. The continuously graded macro pores/channels with porosity of around 50 vol % and tortuosity factor of ~2[30-32], are not only beneficial for gas delivery in the electrodes but also for facile solution penetration during infiltration. Ceria solution will first soak in the gas diffusion channel and nano ceria particles can finally be formed on the surface of the Ni-based channel wall upon drying and combustion. Cells with Ni-YSZ anode deposited with nano SDC layer show excellent cell power output and stability when using methane as fuel. The subsequent high resolution transmission electron

microscopy (HRTEM) study indicates that nano SDC catalyst layer effectively prevents the formation or growth of nickel carbide (onset of coking), thus inhibiting the subsequent coking growth. The novel anode design we demonstrated in this study can enlarge the selection of catalyst materials for high performance electrochemical devices for various applications.

2. Experimental

2.1 Fabrication of substrates and single cells.

NiO (Sigma-Aldrich, USA), LSM (Fuel Cell Materials, USA) and YSZ (TZ-8YS, Tosoh Company, Japan) powders were purchased in this study. Aqueous based NiO-YSZ (mass ratio of 6:4) slurry was prepared with an ammonium polyacrylate dispersant (Darvan C-N, R.T. Vanderbilt Co., Inc., USA), a thickener (Vanzan, R.T. Vanderbilt Co., Inc., USA), and an acrylic latex emulsion binder system (Duramax HA-12, Rohm & Haas, USA). Solid loading of 25 vol%, freezing bed temperature of -70 °C, and Mylar-tape pulling rate of 48 mm min⁻¹ were adopted in this work. The details about NiO-YSZ substrates fabrication can be found in our previous publication[31]. The NiO-YSZ substrate pellets were first pre-sintered at a constant heating rate of 1 °C min⁻¹ to 600 °C and then at 2 °C min⁻¹ to 1100 °C. YSZ electrolyte film was then prepared on the pre-sintered NiO-YSZ substrate by a combination of air-brushing and drop-coating method. The NiO-YSZ substrate with electrolyte layer was then co-sintered at 1350 °C for 5 h. A 0.5 M aqueous solution of Ce(NO₃)₃·6H₂O (Alfa Aesar, USA) and Sm(NO₃)₂·6H₂O (Alfa Aesar, USA) mixed with glycine (mole ratio of glycine to cation is 1.5) was dropped on the surface of the NiO-YSZ substrate through infiltration, followed by drying in a oven at 80 °C for 12 h and firing at 800 °C for 2 h. The loading of SDC on the NiO-

YSZ substrate was determined by weight difference before and after each infiltration/heat-treatment cycle. For X-ray microscope scanning, the NiO-YSZ(anode)|YSZ with and without SDC catalyst layer were reduced at 800 °C for 12 h under 3 vol% humidified H₂. The LSM-YSZ composite cathode with an active area of 0.33 cm² was prepared on the YSZ surface by screen-printing and then sintered at 1100 °C for 2 h.

2.2 Characterization.

The microstructure of Ni-YSZ(anode)|YSZ(electrolyte) half cells with and without SDC catalyst layer were characterized using 3D X-ray microscope (MicroXCT-400, Xradia). The cells with and without nano SDC layer were characterized with scanning electron microscope (SEM, Zeiss Ultra plus FESEM). High resolution transmission electron microscopy (HRTEM) image of SDC-deposited anode after stability measurement using methane was acquired using a JEOL 2100F TEM equipped with a Schottky field-emission gun (FEG) with Cs=1.0 mm operated at 200 kV. Raman spectra were obtained with a Nomadic Raman Microscope (Bayspec Inc). The 785 nm line of a diode laser was used as the exciting radiation. The current density-voltage curves as well as the impedance spectra (under open circuit voltage over a frequency range of 1 MHz to 0.1 Hz) of the cells were measured with a four probe method using a multi-channel Versa STAT (Princeton Applied Research) at the operating temperatures ranging from 700 °C to 800 °C. During cell measurement, hydrogen or methane (with 3 vol% H₂O) was used as fuel while cathode side was exposed to ambient air. Gas flow rate was controlled at 40 sccm by a precision volume flow controller (APEX, Alicat Scientific). The cell

polarization resistance (R_p) was determined from the difference between the low and high frequency intercepts of the impedance spectra with real axis in the Nyquist plot.

3 Results and discussion

The microstructure of half cell Ni-YSZ|YSZ with nano SDC catalyst layer on the internal gas diffusion channel, denoted as Ni-YSZ(SDC)|YSZ, is quantitatively analyzed using 3D X-ray microscope combining with an in-house Matlab code. 3D X-ray microscope allows nondestructive virtual sectioning of the electrodes to reveal internal 3D morphology, advantageous to characterize the porous anode **by** the sectioning **or** 3D microstructure reconstructing using the conventional focused ion beam/scanning electron microscopy (FIB/SEM) method[33, 34]. 3D X-ray microscope can provide a much larger **field** of view than any 2D methods such as SEM and TEM. The spatial resolution of X-ray Computed Tomography (XCT) in this work is set as 4.53 μm to reconstruct the entire Ni-YSZ(SDC)|YSZ microstructure of its thickness dimension ($\sim 744 \mu\text{m}$). **Figure 1** (a) and (b) display the 3D X-ray microscopy image and cross-section view for half cell Ni-YSZ(SDC)|YSZ. **Figure 1** (c) shows the reconstructed 3D microstructure image for a domain with a size of 400 μm *400 μm *650 μm . The morphology is similar to that for the anode without SDC layer (Figure S1(a)). **Figure 1** (d) shows the porosity distribution of the Ni-YSZ(SDC)|YSZ in the thickness direction, also similar to that of blank anode (Ni-YSZ without SDC catalyst layer) (Figure S1(b)). The tortuosity factor of pores in the thickness direction is calculated to be 1.47, similar to that for blank anode (~ 1.3) but much smaller than that for the conventional sponge-like anode (e.g., 3~10) [35]. The details about calculations of porosity and tortuosity can be found in our previous report[28]. **The similar porosity distribution and tortuosity factor indicate that the SDC**

layer has no adverse impact on gas diffusion since gas diffusion resistance is determined by the tortuosity factor and porosity under the operating conditions (see Supplementary Materials)[36]. **Figure 1** (e) shows the distribution of a general field (e.g. fuel concentration) within the porous channels of the anode substrate, when the field is conducted along the thickness direction. As can be seen, the potential is smoothly evolved from the bottom side to the top side, indicating a low tortuosity for gas diffusion. The less tortuous anode substrates could create favorable conditions for the enhanced heat and mass transfer and are of special interest in heterogeneous catalytic process determined by heat or mass transfer. The fluent gas delivery and reaction would alleviate the issues such as temperature gradients and the load response behavior during methane reforming process.

Figure 2 show the SEM images for the cell with the anode deposited with nano SDC catalyst layer. The cell has a thick Ni-YSZ gas transport layer with straight open pores/channels, a thin dense electrolyte and thin porous LSM-YSZ cathode layer, as shown in **Figure 2** (a) and (b). After two infiltration cycles, ~4 wt% SDC layer has been deposited on the channel wall, which normally can only be obtainable after 7 infiltration cycles for the sponge-like electrode[37]. Compared with the anode without SDC layer (Figure S2), the anode particles in the layer adjacent to electrolyte (functional layer, Figure 2 (c, d)) have been effectively covered by nano SDC layer, which is very challenging for the conventional sponge-like electrodes due to high capillary force[23]. The thin SDC catalyst layer covers and protects anode functional layer, providing an ion-conducting network thus enlarging triple phase boundary (TPB) length[38].

The blank cells (without SDC catalyst) can maintain their structure well and show a maximum power density (P_{max}) of 0.045 Wcm^{-2} (Figure 3 (a), with an OCV of 0.84 V, Figure S3(a)), while the cells with the nano SDC layer show a P_{max} of 0.65 Wcm^{-2} (with an OCV of 1.05 V, Figure S3(b)), more than one order of magnitude improvement when operated with methane as fuel and ambient air as oxidant. These OCV values are lower than the calculated theoretical ($\sim 1.23 \text{ V}$ assuming that the product is H_2O and CO_2) and reported ($\sim 1.22 \text{ V}$)[39] ones when operated with methane at 800°C .

Normally, on porous Ni cermet with the conventional sponge-like microstructure, coking formation can lead to fracture of the Ni cermet anode in several minutes under open circuit condition[40, 41], and make the cell inactive, due to the formation of nickel carbide (Ni_3C) [42]. The cells without SDC layer in this study still maintain integrity after operating under open circuit voltage conditions for 12 h (Figure S3 (a)), indicating that the stress induced by coking, nickel carbide or temperature gradient might be released through the novel columnar anode structure. The OCV for cell with nano SDC catalyst layer can be kept at around 1.05 V for 28 h at 800°C (Figure S3 (b)), indicating that the anode displays good catalytic activity toward CH_4 and the nano SDC layer can protect the anode from deactivating under open circuit conditions. There have been a few reports of OCV curves for SOFCs without and with SDC catalyst layer of the conventional Ni cermet anode since high current are normally required to avoid coking or failure of the Ni-based anode[39]. Liu et al have reported an OCV value of 1.17 V at 800°C for Ni-YSZ anode[41]. However, their OCV was obtained by immediately measuring the V - I curve after operating the cell at a constant voltage load of 0.6 V. However, there was severe coking to cause the cell to crack after 10 min at 800°C when their cell was under

OCV condition, behaving similarly to the dry-pressed cells we tested, indicating that the novel columnar anode structure and/or nanoscale SDC layer can significantly enhance the coking resistance of the conventional Ni cermet anode.

Such a substantial performance improvement we present here can be attributed to the excellent catalytic activity of the SDC towards methane reforming[26], which can be further confirmed by the electrochemical impedance spectroscopy measurement (Figure 3 (b)). The interfacial polarization resistance for the cells has been greatly decreased from $\sim 2 \Omega \text{ cm}^2$ to $\sim 0.35 \Omega \text{ cm}^2$ when the anode was deposited with the nano SDC catalyst. The polarization resistance of $\sim 0.35 \Omega \text{ cm}^2$ was estimated by extrapolation using Kramers-Kronig relations[43] (Figure S3 (c)). The SDC covered on the wall surface of the anode, especially in the functional area will increase the anode TPB length, thus enhancing the electrode activity[44], manifested by the much higher (increased by $\sim 81 \%$) cell power output when using H_2 as fuel for the cells with SDC layer compared with those without SDC layer (Figure S4).

The cell performance over methane fuel is comparable with those reported for cells with different types of coking resistant anode. Qiao et al have reported a cell with impregnated $\text{CeO}_2\text{-Ni/YSZ}$ anode, YSZ electrolyte and LSM cathode, which delivered a peak power density of 0.48 W cm^{-2} at 800°C when using methane as fuel[45]. Liu et al reported a cell with configuration of $(\text{Ni}_{0.75}\text{Fe}_{0.25}\text{-5 \%MgO})/\text{YSZ}$ anode, YSZ electrolyte and LSM/YSZ cathode, showing a maximum power density of 0.648 Wcm^{-2} at 800°C when using methane as fuel (interfacial polarization resistance was not provided)[46]. Kim et al have examined the use of Cu-Ni alloys as anode for direct methane SOFC. The anode with Cu (80 wt%)-Ni (20 wt%)-ceria cermet showed a peak power density of 0.33 Wcm^{-2} at 800°C

°C when using methane as fuel[47]. The interfacial polarization resistance for such cell is higher than $0.6 \Omega \text{ cm}^2$. The cell performance can also be comparable to those reported for cells with Ni-based anode but with Ru containing catalyst layer[24, 48]. For example, Zhan et al applied Ru-CeO₂ as catalyst on Ni-YSZ anode to reform C₈H₁₈-air-CO₂ mixture using YSZ as electrolyte and LSM-YSZ as cathode. The P_{max} at 770 °C could be as high as 0.60 W cm^{-2} [24]. Wang et al have prepared 3 % Ru-Al₂O₃ catalyst layer on the surface of Ni-YSZ anode and the cell using YSZ as electrolyte and LSM-YSZ as cathode delivered a cell output of $\sim 0.7 \text{ W cm}^{-2}$ at 800 °C when using methane and H₂O mixture (volume ratio of 2:1) as fuel[48]. However, as mentioned by Zhan et al[24], the catalyst layer in those studies was expected to increase gas diffusion resistance and Ru is expensive, preventing further commercialization[24]. In comparison, the open channel in this study avoids gas diffusion issues and allows using Ru-free catalyst that can be cost-effectively deposited on the internal gas diffusion channel surface of the anode.

Figure 3 (c) shows the stability measurement for the cell with the SDC catalyst layer when operated with 3 vol% H₂O humidified methane under a constant current density of 0.33 A cm^{-2} at 800 °C for about 400 h. The cell shows much higher power output and better stability compared with the cell without the SDC catalyst layer in which the cell output power decreased rapidly to 0 under similar testing conditions (Figure S5). It has been reported that SDC nanoparticles on Ni-based composite not only decrease methane decomposition temperature but also increase methane conversion ratio[49], indicating that the deposited SDC layers are also catalytically active for direct oxidation of methane. In addition, SDC coating layer has high oxygen storage capacity (OSC) and can potentially suppress coking at the anode by supplying more oxygen ions[5]. After

switching the fuel from H₂ to methane, the Ni-YSZ anode is vulnerable to coking, which will cover the active site for electrochemical reactions, resulting in dramatic performance degradation. SDC can release/provide O²⁻ and also function as a diffusion barrier to reduce the diffusion rate of steam or CO₂ out of local Ni-YSZ anode and increase local ratio of O/C, enhancing the coking removal[24]. After coking was removed partially, the active site will become available again for further electrochemical reaction, thus enhancing the cell performance.

Figure 4 shows the high resolution transmission electron microscopy (HRTEM) results for the Ni-YSZ anode without the SDC catalyst layer after operation with CH₄. Comparing the obtained selected area electron diffraction (SAED) data (Figure 4 (a)) with the Inorganic Crystal Structure Database (ICSD), the presence of three phases of Ni₃C (#17005), YSZ (#75316) and Ni (#41508) can be clearly identified. The formation of nickel carbide (Ni_xC_y) phases can be further confirmed since the measured lattice spacing groups are mostly similar to those from the Ni₃C rather than YSZ or Ni. Figure 4 (c-f) indicate that the Ni_xC_y phases are mostly found in the range of 10~35 nm. The actual Ni/C ratio in the Ni_xC_y phases may be smaller than 3/1 as their d-spacing is larger than Ni₃C. The formation of such phases will introduce a severe expansion strain, which **originates** from the very large lattice volume changing from 41.06 Å³ for Ni to 231.95 Å³ for Ni₃C (Figure S6), accounting for the quick crack/decay (in less than half an hour) for the Ni cermet with traditional microstructure during the SOFC operation in CH₄, which has been often reported by others[42, 47].

Figure 5 shows SEM (a) for the Ni-YSZ anode with SDC catalyst layer and HRTEM (b) for the anode after stability test using CH₄ as fuel for ~400 h. Coking can be hardly

observable from the SEM image (Figure 5 (a)) compared with the anode without the SDC layer (Figure S7), consistent with EDX and Raman results (Figure S8, S9), indicating the impressive coking resistance of the Ni-YSZ anode with the nano SDC layer upon operating in CH₄. Large grains (A, B, and C) and nano particles (D, only 2-5 nm in size) in Figure 5 (b) have been identified as Ni and nickel carbide (Ni_xC_y), respectively based on the Fast Fourier Transform (FFT) images and the corresponding d-spacing values. However, for the anode without the SDC layer, the Ni_xC_y particles are much larger, in the order of 10-35 nm in size (shown in Figure 4). The nickel carbide has been reported to cause reconstruction of Ni particles and govern the growth of filament[42, 50]. In the steady-state coking growth period, carbon atoms produced by surface reaction diffuse rapidly through the surface carbide to form the filamentous carbon[51, 52], which will finally cause the crack of the anode. The carbon nucleation has been reported to occur via three distinct stages: the precipitation of carbon from the carbide nanoparticle bulk, the formation of a surface/subsurface carbide species and the formation of a nascent carbon[53]. The prevention of carbide formation has also been shown effective to minimize coking[54]. Smaller nickel carbides would impede the diffusion/growth of filamentous carbon. Consequently, for SOFCs, it is crucial to control the initial formation of nickel carbide[52]. The much smaller carbide in the anode with the SDC layer could be attributed to the protection from nano SDC catalyst layer. Nano SDC catalyst may first contact with methane and function as the active site towards methane reforming (Figure S10) since SDC has been reported to be the active site towards CH₄ oxidation/reforming[55]. SDC can release/provide O²⁻ and also function as a diffusion barrier to reduce the diffusion rate of steam or CO₂ out of local Ni-YSZ anode and

increase local ratio of O/C, enhancing the selectivity of internal reforming reactions toward H₂ and CO[24]. The significant difference in nickel carbide size for the anodes with and without nano SDC layer demonstrates that the formation of nickel carbide or subsequent filamentous carbon has been inhibited effectively by the high catalytic activity of SDC.

4. Conclusions

In summary, we present an innovative design to enhance coking resistance of conventional nickel-based SOFC anode. A nano SDC catalyst layer can be easily and uniformly deposited onto the surface of the porous Ni-YSZ internal gas diffusion channel. Nano SDC catalyst effectively minimizes nickel carbide formation, thus significantly inhibiting coking growth. This novel anode design can broaden catalyst choice by infiltrating appropriate catalyst on anode internal diffusion channel surface, potentially capable of directly utilizing any type of hydrocarbon fuels in SOFCs.

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Figure captions:

Figure 1 (a) 3D X-ray microscopy image (with a dimension of 3.20mm*3.80mm*0.74 mm); (b) cross-sectional image; (c) reconstructed 3D microstructure, The blue/blank regions represent solid/pore phase; (d) porosity distribution of the porous Ni-YSZ(SDC)|YSZ; (e) Visualization of a general field within the porous channels of the Ni-YSZ(SDC)|YSZ, when the field is conducted along the thickness direction. Colors from red to blue proportionally represent the field potential from high to low.

Figure 2 (a,b) SEM images of the cell and (c, d) SDC-covered anode adjacent to the electrolyte.

Figure 3 *I-V* and *I-P* curves (a), electrochemical impedance spectroscopy of cells with anode deposited with (red) and without (black) SDC catalyst layer (b) and stability measurement of cell with SDC catalyst layer when using H₂ or methane as fuel (c).

Figure 4 (a) The SAED patterns for the blank Ni-YSZ anode (without SDC layer) after treatment with CH₄ (Inset is the Bright Field (BF) image of the area selected for the SAED); (b) BF image of the anode aggregates (Red circled area showed small nano Ni_xC_y particles on the big YSZ particles); (c) HRTEM-image of one single crystalline Ni_xC_y particle sitting on YSZ particle and the corresponding Fast Fourier Transform (FFT) images for the selected A and B regions (Simulation of SAED using Ni₃C and YSZ were also shown for comparison); (d) and (e) HRTEM-images of other Ni_xC_y particles with different sizes sitting on the YSZ particle in different area; (f) HR-image for one single Ni_xC_y particle dropped from the YSZ particle.

Figure 5 SEM (a) for the Ni-YSZ anode with SDC catalyst layer and HRTEM (b) for Ni particles from the anode after operating in CH₄ for 400 h (FFT images and corresponding d-spacing in different area were also shown)

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Graphical abstract