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ARTICLE

A highly active Ni/Ce_{0.8}Sm_{0.2}O_{1.9} anode catalyst with a three-dimensionally ordered macroporous structure for solid oxide fuel cells

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Ni/Ce_{0.8}Sm_{0.2}O_{1.9} (SDC) with a three-dimensionally ordered macroporous (3DOM) structure is prepared with poly(methyl methacrylate) as the template and characterized using X-ray powder diffraction, scanning electron microscopy, transmission electron microscopy, H₂ temperature-programmed reduction, X-ray photoelectron spectroscopy and ultraviolet Raman spectroscopy. Lattice oxygen in 3DOM SDC shows a higher activity than that in hydrothermally-synthesized bulk SDC. 3DOM SDC also exhibits a stronger interaction with Ni compared to bulk SDC, which facilitates the release of lattice oxygen and the formation of oxygen vacancies in SDC in a reducing atmosphere. Therefore, Ni/3DOM SDC shows a much higher catalytic activity for electrochemical oxidation than Ni/bulk SDC as the anode material of solid oxide fuel cells. With Ni/3DOM SDC as the anode, a cell supported by a 500 μm-thick SDC-carbonate composite electrolyte layer exhibits maximum power densities ($P_{\max}$) of 1.28 and 1.63 W cm⁻² at 700 °C with H₂ and methanol as fuels, respectively, more than twice the $P_{\max}$ of a similar cell with Ni/bulk SDC anode. Ni/3DOM SDC anode also shows a high resistance to coking.

Introduction

Solid oxide fuel cells (SOFCs) are efficient electrochemical devices converting chemical energy of fuels into electrical power directly.¹ SOFCs are flexible in using a variety of fuels, including H₂, CO, CH₄ and other hydrocarbons.² Among them, methanol has attracted considerable attention in fuel cell industry because it is readily available, relatively pure without further removal of the impurities, and is a liquid fuel with a high volumetric energy density.^{3, 4} Conventional Ni-based cermets are the most widely used anode materials of SOFCs because Ni provides excellent electronic conductivity and catalytic activity for H₂ oxidation. Unfortunately, Ni-based anodes usually suffer from serious carbon deposition with hydrocarbon fuels, leading to rapid degradation of the cells. Meanwhile, the catalytic activity of anode materials with hydrocarbon fuels requires a significant improvement.

Several strategies have been developed to avoid carbon deposition on nickel cermet anodes. The most common approach is to add a certain amount of steam or air in hydrocarbon fuels, which suppresses carbon formation

thermodynamically,⁵ but meanwhile increases the complexity and decreases the efficiency of the process remarkably.⁶ Alloying Ni with other metals such as Cu and Sn is another effective way to improve the resistance to carbon deposition.^{7, 8} However, the catalytic activity of the anode is decreased simultaneously. The oxide phase in the anode also exhibits a significant effect on coking. A small amount of BaO or Nb₂O₅ in the Ni-based anode facilitates the adsorption of H₂O produced during discharge and the removal of carbon deposits.^{9, 10} Besides, anode supports with a high oxygen storage capacity and oxygen mobility benefit carbon removal, and thus doped ceria is usually used in the anodes of SOFCs with hydrocarbon fuels instead of yttria stabilized zirconia (YSZ).

It is well known that the performance of a catalyst is highly influenced by the texture of the support in aspects such as active surface area, pore structure and metal-support interaction. Catalysts with three-dimensionally ordered macroporous (3DOM) structures prepared through template methods have shown promising performances in many processes such as oxidation, electro-catalysis, and photocatalysis.¹¹⁻¹⁴ Guo et al.¹⁵ synthesized Pd/3DOM LaMnO₃ self-regeneration catalysts with a large surface area and a strong interaction between segregated Pd and the LaMnO₃ substrate, which exhibits an excellent catalytic activity for methane combustion. Ruiz-Morales et al.^{16, 17} prepared Ni/3DOM YSZ anodes with poly(methyl methacrylate) (PMMA) microspheres and polystyrene beads as the templates, respectively, and the performances of the cells with those anodes were higher than the cells with conventional Ni-YSZ anodes. However, those improvements were attributed only to

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the ordered pore structure, while the interaction between Ni and 3DOM YSZ supports was not studied.

Ceria with a 3DOM structure has been used extensively in oxidation reactions such as preferential CO oxidation and soot combustion in recently years.^{18, 19} In this study, $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9}$ (SDC) powder with a 3DOM structure is synthesized with PMMA as the template, and Ni is added subsequently through a wet-impregnation process. The anode shows a high activity and a promising coking resistance with methanol as the fuel. The interaction between Ni and 3DOM SDC support is investigated.

Experimental

Preparation of anode powders

3DOM SDC powders were prepared through a colloidal crystal templating method (Fig. 1). All of the chemicals (A.R. in purity) were purchased from Shanghai Aladdin Bio-Chem Technology Co., LTD and used without further purification. Well-arranged polymethyl methacrylate (PMMA) microspheres with an average diameter of 300 nm were synthesized as the template through a modified emulsifier-free emulsion polymerization technique following the procedures described elsewhere.^{20, 21} Stoichiometric $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ and $\text{Sm}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ with total amounts of 0.02, 0.04, 0.06 and 0.08 mole were dissolved in 10 mL of de-ionized water to form mixed metal nitrate aqueous solutions. Then the aqueous solutions were mixed with absolute methanol with a volume ratio of 1:1. The PMMA template was thoroughly soaked in the precursor solutions at room temperature in a vacuum oven for 1 h to ensure that all the voids of the template microspheres were permeated with the precursor. After being filtered, the obtained wet powders were dried in air at room temperature for 24 h, and then heated in N_2 at 300 °C for 3 h. Subsequently, the powders were calcined in air at 800 °C for 4 h to remove the PMMA template. The obtained SDC powders synthesized using the metal nitrate

solutions with 0.02, 0.04, 0.06 and 0.08 mole nitrates are denoted as 3DOM SDC_{0.02}, 3DOM SDC_{0.04}, 3DOM SDC_{0.06} and 3DOM SDC_{0.08}, respectively.

NiO/3DOM SDC_x powders with a theoretical Ni loading amount of 10 wt% were prepared via an incipient wetness impregnation process with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ aqueous solution. The powders after impregnation were dried in air at 80 °C overnight, and then calcined at 700 °C in air for 2 h. The obtained anode powders were reduced in H_2 at 700 °C for 2 h for characterization, which are marked as Ni/3DOM SDC_x. For comparison, SDC powder was also synthesized via a hydrothermal process.^{22, 23} Then NiO-SDC powder with the same amount of Ni loading was prepared through the same impregnation process, denoted as NiO/bulk SDC.

Characterization

The phase structures of the powders before and after reduction were identified with X-ray diffraction (XRD) using a D8 Focus diffractometer (Bruker Corp., Germany) with Cu-K α radiation at a scanning rate of 1° min⁻¹. The microstructure and morphology of the samples were observed using a scanning electron microscope (SEM, S-4800, Hitachi, Japan) and a transmission electron microscope (TEM, JEM-2100F, JEOL Inc., Japan). The N_2 sorption isotherms of the SDC powders were measured in a Micromeritics ASAP 2460 analyzer, and the specific surface areas were determined with the Brunauer-Emmett-Teller (BET) equation. Before the measurement, the samples were vacuumed and outgassed at 300 °C for 3 h.

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 surface property of the samples was analyzed with an ESCALAB 250 Xi X-ray photoelectron spectrometer (XPS, Thermo-VG Scientific, USA) using Al-K α ($h\nu = 1486.6$ eV) as the X-ray source. All spectra were

Fig. 1 Schematic of the synthesis process of NiO/3DOM SDC anode powder.

referenced to the C 1s binding energy at 284.6 eV for calibration. The Raman spectra of the reduced samples were recorded in an inVia Reflex Renishaw Raman Spectroscopy System (wave number region from 250 to 1300 cm^{-1}) with 325 nm laser as the excitation source.

In order to study the catalytic activity for carbon deposition, the anode powders were reduced in hydrogen at 700 °C for 2 h, and then treated with gasified anhydrous methanol (150 mL min^{-1} , STP) at 700 °C for 4 h. The powders after carbon deposition were observed with SEM, and the amounts of carbon deposit were measured with thermogravimetric (TGA) analysis in oxygen using a thermal analyser (NETZSCH STA449).

Cell fabrication and test

The electrolyte powder is composed of 70 wt% SDC and 30 wt% ($\text{Li}_{0.67}\text{Na}_{0.33}$) $_2\text{CO}_3$,²⁴ which is uniaxially pressed at 500 MPa into pellets with a diameter of 13 mm and a thickness of 0.50 mm, and then sintered at 700 °C in air for 2 h. The anode powder was mixed with an organic inert binder (V006, Heraeus Ltd.), and then screen-printed on both sides of the electrolyte pellets, following by calcination at 700 °C in air for 2 h to form symmetric cells. Ag paste was coated on both sides of the cells as a current collector. The active surface area of the electrodes was 0.64 cm^2 . The anode layers were reduced in H_2 at 700 °C for 2 h, and then the electrochemical impedance spectra (EIS) of the symmetric cells were measured with an electrochemical workstation (VERSASTAT 3, Ametek) at different temperatures under various H_2 partial pressures (with Ar as the balance gas) in the frequency range from 1 MHz to 0.1 Hz with an amplitude of 10 mV.

Single cells were fabricated via a similar screen-printing procedure. The cathode material consisted of 70 wt% composite electrolyte and 30 wt% lithiated NiO.²⁵ After the anode layer was reduced in H_2 at 700 °C for 2 h, the current-voltage (*I*-*V*) characteristics of the cells were measured using the electrochemical workstation with dry hydrogen and gasified anhydrous methanol (100 mL min^{-1} , STP) as the fuels and O_2 (30 mL min^{-1} , STP) as the oxidant. EIS of the cells with methanol as the fuel were also measured with the electrochemical workstation.

Results and discussion

Characterization

The template PMMA microspheres with an average diameter of about 300 nm are closely packed with a high ordering degree (Fig. 2a). A well-defined 3DOM structure of the SDC framework with interconnected macropores is obtained after the impregnation of the precursor and the removal of the PMMA template (Fig. 2b-e). The thickness of the SDC walls increases with the rise of the concentration of the precursor solution. The average wall thicknesses are about 25, 35, 40 and 60 nm in 3DOM SDC_{0.02}, 3DOM SDC_{0.04}, 3DOM SDC_{0.06} and 3DOM SDC_{0.08}, respectively. Unlike 3DOM SDC powders, the aggregation of particles with the size of 40-80 nm is observed in the bulk SDC

Fig. 2 SEM images of (a) PMMA microspheres; (b) 3DOM SDC_{0.02}; (c) 3DOM SDC_{0.04}; (d) 3DOM SDC_{0.06}; (e) 3DOM SDC_{0.08} and (f) bulk SDC powders.

powder prepared through the hydrothermal process (Fig. 2f). The specific surface areas of 3DOM SDC and bulk SDC powders are all in the range of 8-10 $\text{m}^2 \text{g}^{-1}$.

All the SDC powders prepared through the template and hydrothermal processes exhibit a face-centered cubic fluorite-structure (JCPDS #075-0158, Fig. 3a) with similar lattice parameters (Table 1), which change negligibly after reduction (Fig. 3b). Both SDC and NiO (JCPDS #0073-1523) peaks are observed in the XRD pattern of NiO-SDC (Fig. 3c), and the lattice of SDC shrinks slightly with the impregnation of NiO probably due to the partial substitution of Ce^{4+} (0.87 Å) by Ni^{2+} (0.69 Å) with a smaller radius. It has been reported that the solubility of Ni in ceria is about 4 mol%.²⁶ NiO is reduced to Ni (JCPDS #087-0712) after reduction (Fig. 2d). Meanwhile, an expansion of SDC lattice is observed, indicating the partial reduction of Ce^{4+} to Ce^{3+} (1.02 Å) with the existence of Ni. The SDC lattice in Ni/3DOM SDC is larger than that in Ni/bulk SDC, implying that Ce^{4+} in 3DOM SDC is more reducible than that in bulk SDC.

Fig. 3e shows the SEM image of NiO/3DOM SDC_{0.04}. NiO particles were highly dispersed on the surface of 3DOM SDC_{0.04}, and 3DOM structure of SDC is not changed obviously with the impregnation of NiO (Fig. 3f). The size of NiO nanoparticles is about 15 nm (Fig. 3g) and it remains almost unchanged after reduction (Fig. 3h). The (200) plane in Ni particle with a fringe spacing of 0.18 nm and the (111) plane in SDC grain with a interplanar spacing of 0.31 nm are found in the HRTEM image

Table 1 Lattice parameters of SDC in various samples before and after reduction.

Sample	Lattice parameter (nm)			
	Before reduction	After reduction	With NiO (before reduction)	With Ni (After reduction)
3DOM SDC _{0.02}	0.5434	0.5434	0.5429	0.5454
3DOM SDC _{0.04}	0.5436	0.5433	0.5429	0.5454
3DOM SDC _{0.06}	0.5432	0.5430	0.5427	0.5451
3DOM SDC _{0.08}	0.5429	0.5429	0.5421	0.5443
Bulk SDC	0.5427	0.5427	0.5418	0.5430

Fig. 3 Powder XRD patterns of (a) SDC before reduction; (b) SDC after reduction; (c) NiO/SDC before reduction and (d) Ni/SDC after reduction. (e) SEM and (f) TEM images of NiO/3DOM SDC_{0.04} powder before reduction. HRTEM images of NiO/3DOM SDC_{0.04} powder (g) before and (h) after reduction. (i) H₂-TPR profiles of various SDC and NiO/SDC samples.

of Ni/3DOM SDC_{0.04} powder (Fig. 3h), and the crossover of those two planes is observed clearly at the interface.

The H₂-TPR curves of the samples are presented in Fig. 3i. No obvious peak is observed in the result of bulk SDC. In comparison, a H₂ consumption process of 3DOM SDC_{0.04} is detected at around 560 °C, indicating that the lattice oxygen in SDC with a 3DOM structure has a higher activity, which is in good agreement with previous reports.¹⁹ Three peaks are observed in the profile of NiO/bulk SDC. The α peak at 300–350 °C is attributed to the reduction of adsorbed oxygen formed with the addition of NiO.²⁷ The β peak at 413 °C is associated with the reduction of bulk NiO and the reduction of outermost layers of Ce⁴⁺ to Ce³⁺.²⁸ The wide γ peak in the range of 470–680 °C can be assigned to the reduction of NiO with a strong

interaction with the SDC phase and the reduction of the inner Ce⁴⁺.^{20, 29} Ni promotes the dissociated adsorption of H₂, which reacts with lattice oxygen in the SDC support nearby easily. Compared with NiO/bulk SDC, the α peaks in NiO/3DOM SDC samples appear at lower temperatures, suggesting higher activities of adsorbed oxygen. The γ peaks of NiO/3DOM SDC are much weaker than that of NiO/bulk SDC, while the β peaks are considerably stronger. Meanwhile, the reduction process of 3DOM SDC_{0.04} at 560 °C is not observed in the curves of NiO/3DOM SDC. Those results demonstrate that Ni facilitates the release of lattice oxygen in 3DOM SDC, which is consistent with the XRD results, and the reducing process of Ce⁴⁺ at a lower temperature is included in the β peak. The reduction temperatures corresponding to the β peaks show an order of

Fig. 4 XPS spectra of (a) Ni 2p_{3/2}; (b) Ce 3d and (c) O 1s of the reduced samples.

NiO/3DOM SDC_{0.04} < NiO/3DOM SDC_{0.02} < NiO/3DOM SDC_{0.06} < NiO/3DOM SDC_{0.08}.

The Ni 2p_{3/2} XPS curves of the reduced anode powders can be deconvoluted into four peaks at around 852.2, 854.3, 856.7 and 860.1 eV (Fig. 4a), corresponding to metallic NiO (peak I) 30, Ni²⁺ in bulk NiO (peak II),³¹ Ni²⁺ in NiO which has strong interaction with the SDC phase (peak III),^{32, 33} and the shake-up satellite peak of Ni²⁺ in NiO (peak IV), respectively.³⁴ As shown in the XRD results, NiO is completely reduced to Ni after reduction, and Ni²⁺ observed in the XPS results is formed by the oxidation of metallic Ni on the surface when the reduced powder is exposed to air. The interaction between Ni and SDC in Ni/3DOM SDC samples are much stronger than that in Ni/bulk SDC (Table 2), which facilitates the reduction of Ce⁴⁺ in 3DOM SDC, as shown in XRD and H₂-TPR results. 3DOM SDC_{0.04} has the most Ni interacting with SDC strongly probably due to the moderate thickness of SDC walls.

The complex Ce 3d spectra (Fig. 4b) are usually deconvoluted into ten contributions. The peaks labelled as u (u, u₀, u₁, u₂ and u₃) and v (v, v₀, v₁, v₂ and v₃) are ascribed to the Ce 3d_{3/2} and Ce 3d_{5/2} spin-orbit coupling, respectively. The u-v, u₂-v₂ and u₃-v₃ doublets are contributed to Ce⁴⁺ ions, while the u₀-v₀ and u₁-v₁ peaks correspond to Ce³⁺ ions.³⁵⁻³⁷ As listed in Table 2, the content of Ce³⁺ increases with the rise of Ni interacting with SDC strongly, indicating that those Ni facilitate the

reduction of Ce⁴⁺, which is in accordance with the H₂-TPR results. With the incorporation of Ni, the Ce³⁺ content in 3DOM SDC_{0.04} increases significantly from 21.0% to 35.2%, further proving the effect of Ni on Ce⁴⁺ reduction. Fig. 4c exhibits the O 1s spectra of the samples. The peaks at around 529.0 eV are ascribed to lattice oxygen O²⁻ (O_{latt}), whereas those at around 531.3 eV are assigned to oxygen species such as O₂²⁻ or O⁻ adsorbed on surface oxygen vacancies (O_{ads}).^{38, 39} As demonstrated above, Ni accelerates the reduction of Ce⁴⁺, resulting in more O_{ads} on the surface.

The formation of oxygen vacancy in SDC is further studied with UV Raman spectroscopy. As presented in Fig. 5a and b, the characteristic band at around 460 cm⁻¹ is assigned to the typical F_{2g} Raman active mode of CeO₂ cubic fluorite structure due to the oxygen symmetric stretching mode around Ce⁴⁺ cations. The band at around 585 cm⁻¹ is related to a defect of vibration mode caused by oxygen vacancies (O_v) in SDC.^{27, 40, 41} Other weak bands at around 325 and 1170 cm⁻¹ can be attributed to the displacement of oxygen atoms from their ideal fluorite lattice position and second-order longitudinal optical mode.^{39, 42} The relative intensity ratios between O_v and F_{2g} peaks are shown in Fig. 5c, in which a higher value implies more oxygen vacancies. The addition of Ni leads to a remarkable increase of oxygen vacancies, and the oxygen vacancies in Ni/3DOM SDC samples

Table 2 The contents of Ni, Ce and O in various valence states determined by XPS peak deconvolution results.

Sample	Ni (%)			Ce (%)		O (%)	
	Ni ²⁺ interacting with SDC	Ni ²⁺ in NiO	Ni ⁰	Ce ³⁺	Ce ⁴⁺	O _{ads}	O _{latt}
Ni/3DOM SDC _{0.02}	31.7	30.6	37.7	33.4	66.6	25.0	75.0
Ni/3DOM SDC _{0.04}	37.6	22.1	40.3	35.2	64.8	26.1	73.9
Ni/3DOM SDC _{0.06}	27.1	37.7	35.2	29.1	70.9	24.3	75.7
Ni/3DOM SDC _{0.08}	26.7	44.7	28.6	28.9	71.1	23.6	76.4
Ni/bulk SDC	20.9	44.9	34.2	25.1	74.9	22.5	77.5
3DOM SDC _{0.04}	--	--	--	21.0	79.0	22.3	77.7

Fig. 5 UV Raman spectra of (a) SDC and (b) Ni/SDC samples; (c) the peak intensity ratios between O_v and F_{2g} in the Raman spectra.

are more than those in Ni/bulk SDC, which are consistent with the XPS results.

SEM micrographs of the samples after carbon deposition are shown in Fig. 6. There is a small amount of carbon filaments deposited on Ni/3DOM SDC_{0.04} which are mainly formed at the rupture of the SDC framework, whereas the Ni/bulk SDC was almost entirely enclosed by filamentous carbon. The amounts

Fig. 6 SEM images of (a) Ni/3DOM SDC_{0.04} and (b) Ni/bulk SDC powders after carbon deposition. (c) TGA curves of the various anodes after carbon deposition.

of carbon deposits on the samples are quantified with TGA. As shown in Fig. 6c, the rapid weight losses in the range of 400–650 °C is ascribed to the oxidation of the carbon deposition. The weight loss of Ni/bulk SDC is about 27%, much higher than those of Ni/3DOM SDC samples. Ni/3DOM SDC_{0.04} shows the lowest weight loss of about 8%. As discussed above, Ni/3DOM SDC_{0.04} has the highest activity of lattice oxygen in SDC (Fig. 3i) and the highest amount of O_{ads} on the surface (Fig. 4c), which are beneficial to carbon removal.

Electrochemical performance

The EIS results of the symmetric cells at 700 °C with H_2 at both sides are shown in Fig. 7a. The curves are fitted well with an equivalent circuit model ($R_0(R_1Q_1)(R_2Q_2)$). R_0 , R_1 and R_2 are resistances, while Q_1 and Q_2 represent constant phase elements. The Nyquist plots of the cells with different anodes exhibit similar intercepts on the real axis, indicating that the electrical conductivity of the anodes is almost the same. The anode polarization resistances (R_p) are represented by the arcs. The activities of the anodes show an order of Ni/3DOM SDC_{0.04} > Ni/3DOM SDC_{0.02} > Ni/3DOM SDC_{0.06} > Ni/3DOM SDC_{0.08} > Ni/bulk SDC, which is consistent with the orders of the amounts of O_{ads} on the surface. To understand the anode process better, the relationships between R_p and hydrogen partial pressure (P_{H_2}) are studied. As shown in Fig. 7b, all of the R_p increase with the decrease of P_{H_2} . R_p and P_{H_2} exhibit a power law relationship ($R_p \sim P_{H_2}^\alpha$), and the power exponents (α) are in the range between -0.37 to -0.18 (Fig. 7c). The value of α should be -1 if

Fig. 7 (a) Nyquist plots of the symmetric cells with H_2 as the fuel at 700 °C. (b) Nyquist plots of the symmetric cells with different anodes at 700 °C under various P_{H_2} . (c) R_p of the symmetric cells versus P_{H_2} at 700 °C.

Fig. 8 SEM images of a single cell with Ni/3DOM SDC_{0.04} anode before test. (a) cross-section of the cell and (b) anode surface.

the rate-determining step (RDS) in the anode process is the dissociative adsorption of H_2 , which will change to -0.5 when the surface reaction of adsorbed H is RDS, and to 0 if RDS is the transfer of oxygen ions at the anode.^{25, 43} Therefore, the electrochemical oxidation rate of H_2 at Ni/SDC anodes in this work is probably co-determined by the conduction of O^{2-} and the surface reaction of oxygen species with adsorbed H. Ni/3DOM SDC_{0.04} shows the highest α of -0.18 because it has the highest activity of oxygen species, and the anode reaction rate is mainly determined by O^{2-} diffusion.

Fig. 8a presents the cross-sectional SEM image of the single cell with Ni/3DOM SDC_{0.04} anode. The anode and cathode layers adhere tightly to the dense electrolyte layer, and the interfaces between different layers are clearly visible. The thicknesses of the anode, electrolyte and cathode layers are 70, 500 and 15 μm, respectively. The anode surface exhibits a fine and uniform microstructure with sufficient porosity (Fig. 8b), which facilitates the diffusion of gaseous reactants and products.

Fig. 9a shows the performance of the single cells with dry H_2 as the fuel at 700 °C. The open circuit voltages (OCVs) of the cells are around 1.0 V. The cell with Ni/3DOM SDC_{0.04} anode exhibits the highest maximum power density (P_{max}) of about 1.28 W cm^{-2} , much higher than that of the cell with Ni/bulk SDC anode (0.56 W cm^{-2}). When methanol is used as the fuel, the OCVs are between 1.00 and 1.05 V, and the P_{max} of the cells with Ni/3DOM SDC_{0.02}, Ni/3DOM SDC_{0.04}, Ni/3DOM SDC_{0.06}, Ni/3DOM SDC_{0.08} and Ni/bulk SDC anodes at 700 °C are 1.57, 1.63, 1.28, 1.07 and 0.73 W cm^{-2} , respectively (Fig. 9b), higher than those of the cells with hydrogen as the fuel probably due to the higher volumetric energy density of methanol, which has been also observed in previous works.^{25, 44} The cell with Ni/3DOM SDC_{0.04} anode exhibits P_{max} of 1.40, 1.22 and 0.93 W cm^{-2} when the temperature falls to 650, 600 and 550 °C, respectively (Fig. 9c). The high catalytic activity of Ni/3DOM SDC_{0.04} anode brings about those promising cell performance with methanol as the fuel in the intermediate temperature range. Fig. 9d shows the stability results of the single cells with Ni/3DOM SDC_{0.04} and Ni/bulk SDC anodes under a constant current density of 200 mA cm^{-2} at 700 °C with methanol as the fuel. The output voltage of the cell with Ni/bulk SDC anode is steady in the first 200 min, and then drops gradually probably due to the carbon deposition on the anode. In contrast, the cell

Fig. 9 *I-V* and *I-P* curves of single cells with various anodes fed with (a) dry hydrogen and (b) methanol at 700 °C. (c) *I-V* and *I-P* curves of the cell with Ni/3DOM SDC_{0.04} anode at different temperatures with methanol as the fuel. (d) Chronopotentiometry results of single cells with Ni/3DOM SDC_{0.04} and Ni/bulk SDC anodes fed with methanol at 700 °C.

with Ni/3DOM SDC_{0.04} anode shows a stable performance for more than 10 h. The high amount of O_{ads} on the surface of Ni/3DOM SDC_{0.04} anode and the high activity of lattice oxygen in SDC facilitate the electrochemical oxidation of both fuels and deposited carbon on the anode during the cell operation, which enhances the stability of the single cell.

Conclusions

In this study, 3DOM SDC powders are synthesized with PMMA template, and impregnated with 10 wt% Ni nanoparticles as anode materials for SOFCs. Ni facilitates the partial reduction of Ce⁴⁺ to Ce³⁺. Lattice oxygen in 3DOM SDC has a higher activity than that in bulk SDC synthesized hydrothermally. Furthermore, compared with bulk SDC, 3DOM SDC shows a stronger interaction with Ni, bringing about more oxygen vacancies in SDC after reduction. Therefore, the reaction between adsorbed hydrogen and surface oxygen species, which is one of the rate-determining steps in anode process, is accelerated significantly at Ni/3DOM SDC anode. $P_{\max}$ of 1.28 and 1.63 W cm⁻² are

obtained by an SDC-carbonate composite electrolyte-supported single cell with Ni/3DOM SDC_{0.04} anode at 700 °C using H₂ and methanol as the fuels, respectively, much higher than those of a similar cell with Ni/bulk SDC anode (0.56 and 0.73 W cm⁻², respectively). The high oxygen activity of Ni/3DOM SDC anode also brings about a high resistance to carbon deposition with methanol as the fuel.

Conflicts of interest

There are no conflicts to declare.

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