A Ce/Ru co-doped SrFeO_{3-δ} Perovskite for a Coke-resistant Anode of a Symmetrical Solid Oxide Fuel Cell (SSOFC)

Bangxin Li,[†] Shuai He,[‡] Jibiao Li,^{§,||} Xiangling Yue,[‡] John T.S. Irvine,^{†,‡} Deti Xie,^{†,⊥} Jiupai Ni,^{*,†,⊥} and Chengsheng Ni^{*,†,⊥}

[†] College of Resources and Environment, Southwest University, Chongqing 400716, China

^{*t*} School of Chemistry, University of St Andrews, Fife, KY16 9ST Scotland, UK

[§] Center for Materials and Energy (CME) and Chongqing Key Laboratory of Extraordinary Bond Engineering and Advanced Materials Technology (EBEAM), Yangtze Normal University, Chongqing 408100, China

// Institute for Clean Energy and Advanced Materials, Southwest University, Chongqing 400715, China

 $^{\perp}$ National Base of International S&T Collaboration on Water Environmental Monitoring and Simulation in Three Gorges Reservoir Region, Chongqing 400716 China

Corresponding author: C.Ni.: nichengsheg@swu.edu.cn; J.Ni.: nijiupai@swu.edu.cn.

KEYWORDS: ceria, propane, coke resistance, metal exsolution, oxide anode, carbonaceous fuel, catalysis, solid oxide fuel cell (SOFC).

Abstract

Employment of identical oxides for the cathode and anode in a symmetrical solid oxide fuel cell (SSOFC) is beneficial for decreasing the fabrication costs of a robust cell. Ce doping on the A-site in SrFeO₃ increased the structural stability in a reducing atmosphere, but ceria was found to exsolve from the perovskite during the cooling process in the air if the doping level reached 20 at. %. The additional doping of 5 at. % Ru in Sr_{0.8}Ce_{0.2}FeO₃ on the Fe site could prevent the ceria segregation in air and induce the surface decomposition under fuel conditions for the formation of nanoscale SrO, CeO₂ and Ru⁰. The SSOFC with Ce/Ru co-doped SrFeO₃ on a Sr- and Mg-doped LaGaO₃ (LSGM) electrolyte showed a small R_p value (0.12 Ω cm²) when H₂ and the ambient air were used as fuel and oxidant, respectively. The peak power densities of 846 mW cm⁻² and 310 mW cm⁻² were achieved at 800 °C using H₂ and C₃H₈ as fuel, respectively. The excellent coke resistance of the anode could be related to the simultaneous *in situ* exsolution of CeO₂, SrO and Ru⁰ nanoparticles.

Introduction

Solid oxide fuel cells (SOFCs) have been considered as one of the most promising energygeneration devices for direct conversion of the chemical energy in fuel into electricity^{1, 2}. Conventional SOFCs employed different materials for the anode and cathode to accommodate their distinct working environment and electrochemical roles ³. However, the recent advances in SOFCs showed that some oxides could be used simultaneously as both cathodes and anodes to obtain symmetrical solid oxide fuel cells (SSOFCs) ^{4, 5}. SSOFCs have attracted a lot of interest because they notably simplified the device assembly as it is processed in just one thermal step to reduce costs ⁶. In the meantime, the exploration of oxide anodes that suppress the coking as in conventional Ni(O)-based anode under the commonly available carbonaceous fuels would reduce the cost of the overhaul in the current infrastructure for H₂ transport and thus accelerate the commercialization of the fuel cell technology ⁷⁻⁹.

Perovskite-type oxides with the nominal formula ABO_3 (A = large cations such as rare-earth or alkaline-earth elements, B = smaller cations of transition elements) ^{10, 11} are popular choices of electrode materials for SSOFC due to their special framework of $<BO_6>$ octahedra and the structural

stability under reducing or oxidizing atmosphere. Besides the pioneering work on $La_{0.75}Sr_{0.25}Cr_{0.5}Mn_{0.5}O_3$ (LSCM) ¹² or other manganite ¹³, ferrite perovskites has been investigated as the oxide electrodes of SSOFCs in more recent work ^{6, 14}.

While the doping of reducible elements for the metal exsolution during the reduction period has been proven to be beneficial for the electrochemical activity and resistance towards coking in stable perovskite oxides, such as titanates and chromites ^{10, 15-19}, as for the ferrites perovskite, the doping of different redox stable cations such as Ti⁴⁺, Nb⁵⁺, Zr⁴⁺, Mo⁶⁺ and W⁶⁺ on the B site has been used to increase the stability of perovskite under fuel conditions ^{4, 20, 21}. The simultaneous doping of redox-stable and reducible cations on the B site of perovskite has been used to engineer the controllable exsolution of metal particles while maintaining the phase stability in a reducing atmosphere ²².

Besides the exsolution or infiltration of metal particles, the incorporation of Ce or alkalineearth elements on the surface of an electrode could also be crucial in improving the electrocatalysis for the oxidation of carbon-related species ^{23, 24}. Fluorite-type ceria as an important catalyst for water gas shift reaction has been infiltrated into the oxide anode to improve the ionic conduction and conversion of carbonaceous fuel ^{25, 26}, because it displays the catalytic activity for the combustion of carbon ^{27, 28} and its composite with metal was found to be more effective in decreasing carbon deposition than metal alone ²⁹. Although Ce doping on the A site ³⁰ has been demonstrated to increase the stability and performance of SmFeO₃ ^{31, 32}, the report on the *in situ* exsolution of ceria nanoparticles from A site of the perovskite electrode for an SOFC has not been reported. Unlike the exsolution of B-site metals where the nucleation of metals are the driving force ³³, the reduction of Ce⁴⁺ to Ce³⁺ increases the ionic radius, r_i , for better residence on the A-site and stability of the perovskite³⁴, so the exsolution of ceria from a perovskite under a reducing condition could be very difficult. Apart from ceria, the addition of BaO to the Ni/YSZ surface has been demonstrated to increase the performance and stability under a C₃H₈ fuel as the BaO absorbs water to react with C on Ni⁰ to produce CO and H species ²³.

In this study, we present a novel doping strategy for $SrFeO_3$ by replacing partially the Sr^{2+} on the A site with Ce^{4+} and the Fe^{4+} on the B site with Ru^{4+} to increase the structural stability under fuel

conditions and the ambient air, respectively. The doping strategy increased the electronic conductivity under 5% H₂-Ar and the catalysis for H₂ oxidation. A H₂-fueled SSOFC based on Ce_{0.2}Sr_{0.8}Fe_{0.95}Ru_{0.05}O_{3-δ} and a La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-δ} (LSGM) electrolyte of 0.32 mm in thickness showed a small polarization resistance, R_p , around 0.12 Ω cm². The peak power densities were around 846 mW cm⁻² and 310 mW cm⁻² at 800 °C under pure H₂ and propane as fuel, respectively. The simultaneous *in situ* exsolution of ceria, Ru⁰ and SrO increased the coke resistance under a C₃H₈ fuel comparing with the one with ceria only. In the meantime, no clear carbon deposition was found after the operation under propane for 10 hours. This work provides significant insights into the design of superficial metal/oxide exsolution at an intermediate temperature on a stable perovskite-type ferrite anode.

Experimental section

Materials synthesis

Ce_xSr_{1-x}FeO₃, Ce_xSr_{1-x}FeO₃ is noted as SF, Ce15SF and Ce20SF when x=0, 0.15 and 0.20, respectively, and those with an additional 5 at. % Ru on Fe site are noted with an "R" as a suffix. Stoichiometric amounts of Ce(NO₃)₃·9H₂O (99.9% Macklin, China), SrCO₃ (99.9% Macklin, China), Fe(NO₃)₃·9H₂O (99.9% Aladdin, China) and (N₂O₅)₂Ru (99.9% in solution, UIVChem, China) were dissolved in the deionized water for the perovskite compositions of SF, Ce15SF, Ce20SF and Ce20SFR. Citric acid (1:1 in a molar ratio to the total metal cations) was added to the above solution as a complexing agent. The solution was heated and stirred continuously until forming a viscous gel which was then calcined at 600 °C for 5 hours. The resulting powder was calcined subsequently at 1250 °C for 5 hours in air to yield the final perovskites.

 $La_{0.8}Sr_{0.2}Ga_{0.8}Mg_{0.2}O_{3-\delta}$ (LSGM) powder for the electrolyte was prepared by the solid-state reaction method. Firstly, stoichiometric amounts of La_2O_3 (99.9% Macklin, China), SrCO₃ (99.9% Macklin, China), MgO (99.9% Macklin, China), Ga₂O₃ (99.9% Macklin, China) were ball milled in ethanol for 0.5 hour and the admixture was calcined subsequently at 800 °C for 5 hours in air. The pre-calcined powder was ball milled for another 0.5 hour and then pressed into a pellet under a pressure of 10 MPa. Dense LSGM electrolyte pellets were prepared by a calcination at 1480 °C for 5 hours. The LSGM pellets were polished to around 320 μ m in thickness using sandpapers.

Characterization

X-ray diffraction (XRD) patterns of the prepared samples were acquired using a laboratory diffractometer ($K_{\alpha 1}$ =1.5406 Å, Persee XD-3, China) in the 2 θ range from 10° to 100° at a step size of 0.02°. Powdered SF, Ce15SF, Ce20SF and Ce20SFR were reduced for 5 hours in Ar-5% H₂ at 800 °C followed by postmortem XRD analysis to study phase stability. Thermogravimetric (TG) analysis data in Ar-5% H₂ were recorded on TG209 F3 tarsus (NETZSCH, Germany): Samples were initially heated up to 800 °C (5 °C minute⁻¹) then kept at this temperature for 5 hours. For conductivity measurement, pellets were cut into a rectangular bar of 5 mm × 3 mm × 15 mm and four Ag wires were attached as probes. The conductivity was measured using a high-accuracy multimeter (Keithley 2100, USA) using a standard DC four-probe method in flowing air and Ar-5% H₂. A P(O₂) sensor based on a zirconia tube was used to determine the oxygen partial pressure near the sample. To obtain further insights on the relationship of conductivity at various oxygen partial pressure. First, samples were initially held the temperature at 800 °C under Ar for 20 minutes for removing any traces of oxygen and then they were kept at this temperature for 5 hours under Ar-5% H₂. X-ray photoelectron spectroscopy (XPS) was obtained on a Thermo ESCALAB 250Xi spectrophotometer using 150W Al K_{α} radiation. Scanning electron microscopy (SEM) and high angle annular dark field scanning transmission electron microscope (HAADF-STEM) for Ce20SF and Ce20SFR powders or transmitting electron microscopy (TEM) for Ce20SFR electrode were performed on a Thermo Scientific Scios Dual Beam system.

Cell fabrication and fuel cell testing

To fabricate symmetric cells for fuel cell testing, the hand-ground Ce20SF and Ce20SFR powders were ground in a zirconia jar with beads (2 mm in diameter) at a high speed of 600 revolutions per minute (rpm) for 1 hour. D_{50} of the ground powders was around 2 μ m from particle size analysis (Microtrac S3500, USA). They were then mixed with an equal weight of vehicle containing polyvinyl butyral in terpineol to obtain a viscous slurry. The obtained slurry was painted

on both sides of an LSGM electrolyte pellets to make the symmetric cells after a sintering at 1100 °C for 2 hours in ambient air. Ag paste containing 20 wt. % starch powder was applied on both sides of the cell for the current collection. Noble metals, such as Ag and Pt, could pose influence on the performance on the electrode³⁵, but Ag paste was chosen because it less active in catalyzing the activation of C-H bonds in hydrocarbon than Pt or the oxidation of H₂ on oxide anode³⁶. Button cells were then mounted on top of the Al₂O₃ tube using a ceramic bond and the tube furnace was used to heat the cell assembly to the desired temperature for fuel cell measurements. Hydrogen and propane were fed into the anode side at a low rate of 20 ml minute⁻¹ while the cathode was exposed to the static ambient air. A prior reduction in humidified H₂ for more than 10 hours was placed before the electrochemical measurements to achieve the equilibration of silver paste and exsolution of metal/oxide particles.

The electrochemical measurements, including current-voltage (I-V) and current-power (I-P), and the electrochemical impedance spectroscopy (EIS) were carried out on a Zennium Pro electrochemical workstation at 700-800 °C. The sine wave for EIS measurement was in an amplitude of 10 mV from 1 MHz to 0.1 Hz. The EIS data were fitted *via* the Zman software.

Density functional theory calculations

DFT calculations were performed by using the QUANTUM ESPRESSO package. Electron-ion interactions were modeled by the use of the projector augmented wave (PAW) method. Electron exchange and correlation effects were represented by the Perdew-Burke-Ernzerhof form (PBE) with the van de Waals correction. Spin polarization was taken into consideration throughout all the calculations. Kohn-Sham orbitals were expanded in a plane wave basis set with a cutoff energy of 49 Ry and 599 Ry for the charge density cutoff. The Brillouin zone integration was performed by the Gaussian special point technique, with a smearing parameter of 0.02 Ry and *k*-point meshes of $4 \times 4 \times 1$.

The bulk SrFeO₃ was represented by a cubic unit cell (11.56 Å \times 11.56 Å \times 11.56 Å) which contains 135 atoms in a (3 \times 3 \times 3) supercell. The periodic boundary conditions were applied to the model structure in geometry optimization. The Ce doped SrFeO₃ materials were modeled by replacing one Sr atom with one Ce atom at the center of the unit cell of CeSr₈Fe₉O₂₇, because the Ce doping at the inner site gives a total energy of 0.89 eV lower than the one with Ce doping at the surface, confirming the stability of the doped Ce atoms in the inner sites. The Ce doped SrFeO₃ (100) was modelled by tetrahedral unit cell (11.56 Å × 11.56 Å × 37.39 Å) with a sufficient vacuum thickness. A propane molecule was placed on the Ce doped SrFeO₃ (100) to simulate the propane adsorption. In addition to different molecular orientations, all high-symmetry sites were considered to obtain a global stable structure. To conduct a comparative investigation, the propane molecule on CeO₂ (100), SrO (100), and Ru (001) was also calculated. The CeO₂ (100), SrO (100), and Ru (001) surfaces were modelled by unit cells of (10.82 Å × 10.82 Å × 29.2 Å), (10.2 Å × 10.2 Å × 27.56 Å), and (8.11 Å × 9.37 Å × 24.4 Å) respectively. Structure optimizations of the propane adsorption were performed with the upper several layers were fully relaxed until the Hellmann-Feynman forces were lower than 0.001 Ry/a.u. A calculation was considered converged when the energy change per atom was less than 10⁻⁵ Ry and the mean displacement less than 0.001 Å. The convergence threshold for SCF calculations was set to 10⁻⁵ Ry. The force convergence threshold for geometry optimizations was set to 0.02 eV Å⁻¹.

The charge density differences (CDD) of the global minimum structure of propane adsorbed on Ce doped SrFeO₃ (100) were represented in three cutting planes by subtracting the densities of the bare slab and the C₃H₈ molecule from the adsorbed slab: $\delta_{n(r)} = n_{ads}(r) - n_{bare}(r) - n_{mol}(r)$. Likewise, the CDD plots of Ce doped bulk SrFeO₃ were also obtained in two cutting planes by subtracting the densities of the bulk SrFeO₃ without the Ce atom from those with Ce doped SrFeO₃: $\delta_{n(r)} = n_{bulk}(r) - n_{de-bulk}(r) - n_{Ce}(r)$.

Result and discussions

Doping of Ce⁴⁺ in ferrite perovskite oxide could be a viable way to enhance redox properties and catalytic properties for steam reforming, likely *via* the Ce⁴⁺/Ce³⁺ redox couple ³⁷. XRDs of SF, Ce15SF and Ce20SFR (Figure 1(a)) showed that the monophasic perovskite could be obtained in the ambient air while a low-intensity peak in Ce20SF was shown at about 28.5° for CeO₂. Deganello et al. also found that Ce15SF is a single phase while Sr_{0.75}Ce_{0.25}FeO₃ showed a CeO₂ segregation ³⁴. The synthesis of monophasic CeFeO₃ required a low-temperature calcination in a reducing atmosphere and the valence state was found to be Ce^{3+} and Fe^{3+} rather than Ce^{4+} and Fe^{2+} , ³⁸ so the incorporation of large amount of Ce^{4+} in the perovskite would destabilize the perovskite structure. The CeO_2 in Ce20SF was found to arise from the cooling process in air as the quenched Ce20SF (Ce20SF-Q) showed a monophasic perovskite from XRD (Figure 1(b)).



Figure 1. (a) XRD patterns of SF, Ce15SF, Ce20SF and Ce20SFR in air. (b) XRD of Ce20SF under normal cooling and quenching (Ce20SF-Q). (c) Structure and CDD of Ce doped bulk SrFeO₃ where Ce

lies in the body center. Sr, Fe and O atoms are in blue, gray and red, respectively, in the crystal structure. CDD in the cutting plane "A" and "B" was presented in the structure of (c), respectively. (d) XRD patterns of SF, Ce15SF, Ce20SF and Ce20SFR after reduction in Ar-5% H₂ at 800 °C (SF-R, Ce15SF-R, Ce20SF-R and Ce20SFR-R). The peak for Ru⁰, CeO₂ and SrCO₃ in the reduced Ce20SFR is highlighted in (e) using the logarithmic counts of intensity.

The formation of an oxide-ion vacancy can induce a lattice contraction primarily due to electrostatic interactions, but it can also cause lattice expansion mainly as a result of the collateral steric change in the cation radius.³⁹ The orthorhombic unit cell of SF calcined at 1250 °C (pseudocubic volume 58.48 Å³, Table 1) was larger than the cubic one calcined at 900 °C (SF-900, 57.31 Å³, see Figure S1 for XRDs), which could be related to the reduction of Fe⁴⁺ to Fe³⁺ as a result of oxygen deficiency since the loss of oxygen generally causes the expansion of unit cell of SF (Figure S2). The larger unit-cell parameter of Ce15SF than SF could be related to the increase in Fe³⁺/Fe⁴⁺ ratio in the former since the ionic radii of Ce⁴⁺ is much smaller than that of Sr²⁺. Moreover, the pseudocubic cell volume of the single perovskite Ce20SF-Q (59.00 Å³) showed much larger than Ce15SF (58.88 Å³) or Ce20SF (58.86Å³), which is in an indication of even higher oxygen non-stoichiometry. Previous doping of Ce⁴⁺ in SrFeO₃ also induced the increase of the lattice parameter if Ce content is less than 15 at. % ⁴⁰. A similar expansion in unit cell was observed in the Ce doping in SrMnO₃, where the release of oxygen was stipulated to be the explanation ⁴¹. The shrinkage of unit cells at ceria level higher than 15 at. % could be related to the exsolution of ceria causing the A-site deficiency or the increase of the smaller Ce⁴⁺ cation.

Sample	a (Å)	b (Å)	с (Å)	Crystal lattice	Volume (ų)	Volume/4 (ų)
SF-900 ^a	3.8554(2)			Cubic	57.31(1)	-
SF	5.4762(3)	5.4948 (4)	7.7731(4)	Orthorhombic	233.90(3)	58.48

Table 1. Unit cell parameters of the samples in air.

Ce15SF	5.4869(1)	5.5091(1)	7.7911(2)	Orthorhombic	235.51(1)	58.88
Ce20SF	5.4856 (2)	5.5094(2)	7.7904(4)	Orthorhombic	235.45(1)	58.86
Ce20SFR	5.4689(1)	5.4921(2)	7.7692(2)	Orthorhombic	233.36(1)	58.34
Ce20SF-Q	5.4932(1)	5.5118(1)	7.7948(2)	Orthorhombic	236.01(1)	59.00

a: SF-900 indicates SF calcined at 900 °C, while the rest calcined at 1250 °C.

Because LaFeO₃ and SrFeO₃ are intermiscible and the r_i of Ce³⁺ (1.34 pm) and La³⁺ (1.36 pm) are similar, the low dissolution limit (15 at. %) of Ce⁴⁺ (1.14 pm) on the Sr²⁺ site could be related to the local charge imbalance and smaller size of Ce⁴⁺ causing the local strain or under-bonding in the lattice. The Ce doping in SrFeO₃ gives rise to (Figure 1(c)) significant electronic rearrangement around the Ce atom to which the oxygen atoms in the nearest neighbors are suffered from more pronounced density enhancement which is actually carried by the interactions of the eg orbitals with the O 2p orbitals. By contrast, the t_g orbitals exhibit apparent density depletion, indicating the onset of strong Pauli repulsion exerted by the Sr atoms in the next neighbors. It is a bit surprising that the Fe atoms show obvious density depletion in one of e_g orbitals but accumulation in two t_g orbitals as a result of the electronic alignment in the Fe-O-Fe chains. The shorter Ce-O bond (2.5472 Å) than Sr-O bond (2.5778 Å) in the optimized crystal structure of Ce-doped SF indicated that Ce4+ could be stable under a coordination lower than 12 as Sr²⁺ in SrFeO₃, which is in accord with the single perovskite phase of the quenched sample (Ce20SF-Q) where the coordination number is reduced by the losing of oxygen. The exsolution of ceria in Ce20SF could be related to the production of Ce⁴⁺ and the re-absorption of oxygen that increases the Ce⁴⁺ coordination during the cooling: i.e. the incorporation of smaller Ce⁴⁺ cation on the A site (causing a decrease in tolerance factor) together with the increase in the coordination number of Ce⁴⁺ at low temperature will induce extra strain on the perovskite structure.

The effect of Ce⁴⁺ substitution for the Sr²⁺ on the stability under reducing conditions (Figure 1 (d)) was examined using XRD after reduction in Ar-5% H_2 at 800 °C for 5 hours. While SF was found to be unstable and partially transformed to brownmillerite, Ce15SF maintained its perovskite phase.

The relative intensity of CeO₂ peak to the main peak of perovskite for Ce20SF-R (Figure 1(d)), 4.27%, decreased slightly from that for Ce20SF, 7.47%, indicating the reduction is beneficial for the incorporation of Ce^{3+/4+} into the perovskite lattice. The Ce20SFR also maintained the main perovskite phase but showed minor peaks for CeO₂, SrCO₃ and Ru⁰ in Figure 1 (e). The morphology (Figure S3) before and after reduction in Ar-5% H₂ indicates that isles on the scale of 200 nm were presented on the surface of Ce20SFR after reduction. According to the XRD analysis, these large isles could be related to the bulky SrCO₃, Ru⁰ and ceria.

The variation of oxygen non-stoichiometry and oxidation state of iron were determined from the mass losses under the Ar-5% H_2 (Figure 2) indicates that the sample lose weight in the range from 1.78% to 3.07% during the heating to 800 °C and the following isothermal period. Ceria doping in the perovskite (Ce15SF and Ce20SF) lowers the weight loss than SF, while the Ru doping in Ce15SF and Ce20SF increases weight loss than the undoped counterparts as a result of production of Ru⁰.



Figure 2. Thermogravimetric analysis of SF, Ce15SF, Ce20SF and Ce20SFR under Ar-5% H_2 atmosphere. The red lines are for the mass change while the green ones are the dTG during the

heating.

If one assumes that the oxygen stoichiometry in the perovskite does not change during the Ce⁴⁺ doping on Sr²⁺ site, CeO₂ doping on the Sr site accompanied by the reduction of Fe cation. The defect chemistry in Kröger–Vink notation could be:

$$CeO_2 + 2 Fe_{Fe}^x + Sr_{Sr}^x = SrO + Ce_{Sr}^{\bullet\bullet} + 1/2 O_2 + 2 Fe_{Fe}'$$
 (1)

During the reduction period, oxygen will be released from the lattice to react with hydrogen followed by the creation of oxide-ion vacancies:

$$Fe_{Fe}^{x} + O_{x}^{x} = 1/2 O_{2} + Fe_{Fe}^{'} + 1/2 V_{0}^{\bullet \bullet}$$
 (2)

According to Equation 1 and 2, the donor doping of Ce^{4+} on Sr^{2+} site will decrease the valence state of Fe in the oxygenated sample, so it would be reasonable to obtain less weight loss during the reduction process. The reduction could also cause the reduction of Ce^{4+} to Ce^{3+} for more weight loss, but the effect could be minor as the oxygen non-stoichiometry of CeO_2 could be 0.01 in a reducing atmosphere at 800 °C.⁴²

The weight loss for SF started from 350 °C and the corresponding derivative of TG (dTG) peaked at 650 °C, but the dTG peak for Ce15SF and Ce20SF is located at 480 and 500 °C, respectively, indicating that Ce-doping decreased the reduction temperature. CeO₂-doping in LaFeO₃ lowered the weight loss temperature under H₂, which is attributed to <FeO₆> octahedra distortion ⁴³. Similarly, the distortion of <FeO₆> in Ce doped SrFeO₃ implied from the bond length variation in DFT calculation could also be the reason for the lower dTG peak.

The simultaneous Ce⁴⁺ and Ru⁴⁺ doping in Ce20SFR or Ce15SFR showed a dTG peak at 320 °C apart from the one at 537 °C. The comparison between samples with and without Ru doping indicates that the weight loss at 320 °C could be related to the reduction of Ru⁴⁺ cation to Ru^{3+.44} On the other hand, Ru⁴⁺ doping increased the isothermal weight loss at 800 °C and this could be related to the exsolution of Ru⁰ or ceria as the cation ordering and reorganization are slow diffusion-limiting weight-loss process.

The electronic conductivities, σ , of SF, Ce15SF, Ce15SFR, Ce20SF and Ce20SFR was recorded during the cooling process after the 5 hours' reduction in Ar-5% H₂ (Figure 3(a)). The σ of Ce20SFR (0.94 S cm⁻¹), close to that of Ce20SF (0.78 S cm⁻¹) was higher than Ce15SF and SF (0.23 S cm⁻¹) at 800 °C under a P(O₂) of 10⁻¹⁹ atm. The reported σ of SF in Ar-5% H₂ at 800 °C varied in the range from 0.03 to 1.58 S cm^{-1 15, 45, 46}, depending on the oxygen partial pressure. Doping on the B site in SF with high valence transition metals such as Mo⁶⁺ and Zr⁴⁺ may stabilize the cubic polymorph and increase conductivity in a reducing atmosphere ^{4, 20}, and we found that doping in Sr²⁺ site with Ce⁴⁺ was also able to increase the conductivity after reduction. The activation energy, E_{a} , of σ for Ce20SFR and Ce20SF (0.7 eV) was consistent through the investigated temperature range (800-560 °C), while SF showed a decreased E_a during the cooling process. The typical relation between σ and P(O₂) for Ce20SFR at 800 °C (Figure 3(b)) showed that the conductivity of Ce20SFR in air was 12.3 S cm⁻¹ at 800 °C, but it maintained a relatively high conductivity in a reducing atmosphere. The conductivity is a *p*-type in the region of higher oxygen partial pressure and *n*-type under reducing condition. ^{4, 41} The slope for the plot of $Lg(\sigma/Scm^{-1})$ and $P(O_2)$ was found to be -0.14 and 0.19 in the low and high oxygen partial pressure region, respectively. The slope at low oxygen partial pressure is close to -1/6 following the defect equilibrium of $[V_0^{\bullet\bullet}] \approx 1/2n$, while the one at high oxygen partial pressure (close to 1/4) could be explained by $[V_0^{\bullet\bullet}] \approx 1/2 [Fe/Fe']$.⁴⁷ The decrease of σ at P(O₂) lower than 10⁻¹⁹ atm. could be related to the partial decomposition of the material.



Figure 3. (a) Temperature dependence of electronic conductivity of SF, Ce15SF, Ce15SFR Ce20SF, Ce20SFR samples after 5 hours' reduction under Ar-5% H₂ flow during the cooling time. (b)

Conductivity of Ce20SFR as a function of $P(O_2)$ during the isothermal period of 800 °C. The rectangle in (b) indicates the dropping of conductivity under prolonged aging in Ar-5% H₂.

The electron core level XPS spectra of the as-prepared and reduced Ce20SF and Ce20SFR were obtained to study the chemical composition and valance states of the elements. The C 1s spectrum (figure 4(a)) of Ce20SF and the reduced one (Ce20SF-R) consists of peak C-C (284.5 eV), C-O (286.6 eV) and C=O (288 eV) ⁴⁸, but it also includes the peak Sr 3p_{1/2} (279.0 eV) at a higher binding energy, which is in agreement with the XRD result where traces of SrCO₃ was identified in these samples. For the Ce20SFR and the reduced one (Ce20SFR-R), the peak of the Ru $3d_{5/2}$ (281.0 eV) and Ru $3d_{3/2}$ (284.2 eV) are overlapping with between the peak for Sr 3p_{1/2} and C 1s. The simulated peak for Ru moved to the lower binding energy for Ru⁰ after reduction in Ar-5% H₂. The Ce 3d spectrum (Figure 4(b)) is anything but a simple one and can be fitted into multiple splits as a result of the complex spectrum splits of ceria species containing asymmetrical peaks and the overlapping between Ce³⁺ and Ce⁴⁺. However, the characteristic peak at 916.2 eV could be related to the presence of Ce⁴⁺ while the low energy one at 880.9 eV could be related to the presence of Ce^{3+, 49} The comparison between the Ce 3d spectra indicates that Ce³⁺ actually became more obvious after reduction in either Ce20SF or Ce20SFR. The Fe 2p spectra (figure 4(c)) represented by the Fe²⁺, Fe³⁺ and Fe⁴⁺ peak at binding energy of 709.48 eV, 710.48 eV and 712.68 eV, respectively ⁵⁰. After the reduction, the high Fe²⁺ content facilitates the charge carrier transport along with Fe³⁺-O-Fe²⁺ bonds, which is consistent with the *n*-type electronic conductivity at $P(O_2)$ lower than 10^{-16} atm. The O 1s XPS spectrum (Figure 4(d)) for Ce20SF, Ce20SF-R and Ce20SFR showed two splits at 529.5 eV and 531.5 eV, which are attributed to the lattice oxygen (marked as M-O) and oxygen vacancies or carboxyl groups, respectively ⁵¹. In Ce20SFR-R, the O 1s split with very high binding energy at 534.5 eV could be related to the absorbed C=O species on the surface of Ru^{0 52}.

14



Figure 4. X-ray photoemission spectroscopy of Ce20SF, Ce20SFR samples before and after 5 hours' reduction (with "-R" as suffix) in Ar-5% H₂ atmosphere in terms of (a) C 1s, (b) Ce 3d, (c) Fe 2p and (d) O 1s. The triangle and diamond mark in (b) indicate the characteristic peaks for Ce⁴⁺ at 916.2 eV and Ce³⁺ at 880.9 eV, respectively.

The EIS of the symmetrical cell in ambient air (Figure S4) was used to study the electrocatalysis for the oxygen reduction reaction. The intersections at the high and low frequency of the spectrum represents the ohmic resistance and area-specific resistance (ASR), respectively, and the width of the impedance arcs provides the values of the polarization resistance, R_p . The EIS indicated that the ceria-containing Ce20SF showed a smaller R_p than Ce20SFR as cathode of an SOFC: 0.08 versus 0.10 Ω cm² at 800 °C. The presence of ceria could be the reason for the low R_p for oxygen reduction reaction as reported in ceria and NiO co-doped SrFeO₃ perovskite ⁵³. The Nyquist plots and IV curves for SSFOC based on the Ce20SF and Ce20SFR under the H₂-fuel and static air oxidant were presented in Figure 5. The R_p of the Ce20SF cell in H₂ from EIS (Figure 5(a)) was 0.51 Ω cm², while that of Ce20SFR (Figure 5(b)) was 0.12 Ω cm² at 800 °C. Though Pt is known to increase the cell performance at 800 °C by assisting the oxidation of H₂ on an oxide anode³⁶, the cell performance is even higher with Ag paste than the one with Pt paste (Figure S5). This could be explained by (1) Pt paste needs optimum prior calcination to obtain good contact with the electrode and (2) the catalysis of our oxide electrode for H₂ oxidation is good enough to overtaken the effect of Pt.



Figure 5. The EIS of (a) Ce20SF/LSGM/Ce20SF and (b) Ce20SFR/LSGM/Ce20SFR using H₂ as fuel and air as oxidant. The IV and I-P curves of (c) Ce20SF/LSGM/Ce20SF and (d) Ce20SFR/LSGM/Ce20SFR at various temperatures. The straight-line plots (solid signals) correspond to the voltages (left y axis) and the curved plots (open signals) correspond to the power densities (right y axis). The thickness of the LSGM electrolyte is around 320 μ m in thickness.

The comparison of the R_p between the cell in ambient air and fuel cell mode indicates that the

 R_p of the anodes were 0.43 and 0.02 Ω cm² for Ce20SF and Ce20SFR, respectively. The high performance of the anode for Ce20SFR cell could be related to the presence of Ru⁰ as a highly efficient catalyst for H₂ oxidation⁵⁰ since CeO₂ was present in both oxides. Actually, with CeO₂, Ru⁰ and SrO exsolution, Ce20SFR became a quasi-SSOFC, but the main phase is identical in the cathode and anode. The Ce20SF cell shows a peak power density of 482 mW cm⁻² at 800 °C (Figure 5(c)), whereas the cell of Ce20SFR exhibits a peak power density of 846 mW cm⁻² at 800 °C due to the exsolution of Ru⁰ which enhances greatly the performance (Figure 5(d)). The performance of the Ce20SFR |LSGM | Ce20SFR cell showed higher performance than the other reported SSOFC using H₂ fuel at 800 °C (Table S1). Moreover, the exsolution of Ru⁰ on the oxide surface avoided the downward curvature as in the IV curve in Ce20SF at a voltage lower than 0.85 V. The comparison of the present work with the representative ferrite-based SSOFC in literature was listed in Table S1, and one can be found that the cell performance of Ce20SFR under H₂ fuel is higher than ferrite perovskite with or without metal exsolution ^{21, 54-63}.

The morphology of the Ce20SFR-based anode after test under humidified H₂ was evaluated using SEM (Figure 6(a-c)) and HAADF-STEM (Figure 6(d)). According to the SEM images, the crosssectional microstructures of the symmetric cells clearly showed that both the cathode and anode are well anchored on the electrolyte and the thickness of the LSGM electrolyte and the Ce20SFR anode are about 320 µm and 60 µm, respectively. The high-resolution SEM image (Figure 6(c)) indicates the oxide under humidified H₂ shows a matt surface with small spherical particles of 10 nm in diameter. The HAADF-STEM image with EDX mapping (Figure 6(d-k)) proves that Ce20SFR anode after 5 hours' testing under H₂ shows clear Ru segregation, but the Ce20SF has quite homogeneous elements distribution (Figure S6). According to the XRD analysis, the exsolved particles could be Ru⁰ that are evenly dispersed throughout the entire particle, but the elemental segregation of Sr and Ce is not very clear at this magnification. The superimposed image of Ce/Ru and Sr/Ru showed that Ru turns to be on the surface of the other two elements.

17



Figure 6. (a) SEM images of Ce20SFR/LSGM/Ce20SFR cross-sectional microstructure after test in H₂ at 800 °C. (b, c) SEM enlarged image of the Ce20SFR anode after test in H₂ at 800 °C. (d) HAADF-STEM image for individual Ce20SFR particles reduced by H₂ for 5 hours and the corresponding EDS mappings of the main elements are presented in (e) to (k).

The high-resolution TEM image (Figure 7) of Ce20SFR confirmed that Ru⁰ was on the scale of 10 nm but the size of ceria was only 5 nm. The fine particle size explains the indistinguishable CeO₂ oxides at lower magnification is in the SEM of Ce20SF. SrO oxides remain in the interior of the particles though SrCO₃ as shown in XRD. The conversion between SrO and the bulky SrCO₃ could cause the microstructure variation and this explains the large isles of 200 nm on the surface of Ce20SFR pellets are more subjected to the absorption of CO₂ from the ambient air. The Ru⁰, CeO₂ and SrO are in good contact with each other as they are from the direct superficial decomposition of the parent perovskite. As the crystal of the parent perovskite is defective, we cannot confirm the formation of R-P type layered perovskite as on the conventional B-site exsolution would cause the enrichment of A site ^{10, 64}. The exsolution of Ru⁰ from the lattice would cause the under-coordinated

bonding of Ce^{4+} cation as in Ce20SF and induce the segregation of CeO₂ particles as in Ce20SF. The formation of adjacent CeO₂/SrO oxide also explains the ultra-small Ru⁰ particles as they constrain the grain growth. The absence of SrCeO₃ perovskite could be related to its thermodynamic instability is in high steam environment, i.e. it can decompose easily into to CeO₂ and SrO.⁶⁵



Figure 7. High resolution TEM image of Ce20SFR electrodes after test in H_2 fuel at 800°C for 5 hours.

At 800 °C, the maximum power density of the SSOFC with Ce20SFR was 310 mW cm⁻² under propane conditions, much higher than the one with Ce20SF (190 mW cm⁻²) from the IV curves in Figure 8(a). This power output is higher than most of the reported SSOFCs using carbonaceous fuels at 800 °C (Table S1). The cell (Figure 8(b)) with Ce20SFR at a constant voltage of 0.45 V showed a slight variation in output current density and the current density reached 0.28 A cm⁻² at 0.75 V after 22 hours. The current density of the SSOFC with Ce20SF at 0.75 V started from 0.16 A cm⁻², decreased rapidly to 0.11 A cm⁻² and gradually increased to 0.17 A cm⁻² after 20 hours' aging. The increase of the current density of the cell with Ce20SF could be related to the deposition of carbon (Figure 8(c)) that increased the conductivity of the electrode ^{66, 67} and reduced the ohmic resistance or increased the area of effective electrode since silver covers only the core area of the electrode. The porous YSZ containing a small amount of ceria was found to induce the deposition of polyaromatics under nbutane at 700 °C which increased mainly the conductivity (i.e. R_s) without affecting the R_p ⁶⁷. The deposition of polyaromatics explained the agglomerates larger than 20 µm on the surface of Ce20SF, indicating that ceria alone is insufficient to suppress the formation of carbonaceous species. The gaps between the grain of Ce20SF could be filled with coke deposition as the carbonaceous materials were found to deposit on the triple phase boundaries (Figure 8(c)) ⁶⁸. The surface of Ce20SFR (Figure 8(d)) maintained a nanoscale structure and distinguishable carbon species was not found.



Figure 8. (a) The I-V and I-P curves for cells of Ce20SF/LSGM/Ce20SF and

Ce20SFR/LSGM/Ce20SFR in C₃H₈ at 800 °C. (b) Current density variation of the Ce20SF cell (bottom) and Ce20SFR cell (up) under different voltages. SEM of (c) Ce20SF and (d) Ce20SFR anode after the durability test under C₃H₈ at 800 °C.

The adsorption of propane onto the electrode surface as the initial step is critically important to the reaction hereafter. As dry propane is used as fuel, the absorption energy (ΔE) was calculated for the molecule on the surfaces of Ce-doped SF, Ru⁰, CeO₂ and SrO (Figure 9(a-d)). CeO₂ showed the highest affinity to propane molecules, though ΔE is dependent on the molecular orientations and bonding sites (Figure S7). Specifically, the $-\Delta E$ decreases in the sequence of CeO₂ > Ru⁰ > Srterminated CeSr₈Fe₉O₂₇ \approx SrO. As CeO₂ was presented in both Ce20SF and Ce20SFR, the absorption of propane should be similar at OCV and this is consistent with the similarity in IV curves in the range above 0.90 V as the oxidation of fuel is minimal.

The calculated activation energies (*E*_a) of the C-H bond dissociation for the propane molecule on the four surfaces in the Figure 9 are 7.2, 4.8, 3.8, and 2.7 eV for SrO, CeSr₈Fe₉O₂₇, CeO₂ and Ru⁰, respectively. Together with the endothermic characteristic of the dehydronation of the propane, the highest E_a value SrO surface provides a chemical basis on which the anode is capable of exhibiting the coke-resistant property. Thus, the phases of SrO, CeO₂ and Ru⁰ in the anode may play different roles in achieving the high-performance of coke-resistance. Ru⁰ may act as the active phase while SrO accounts for the origin of the coke-resistance. Moreover, SrO in Ce20SFR lattice is beneficial to the transport of CO₂ from CeO², Ru⁰ or perovskite to produce SrCO₃ to increase the cok-resistant of the electrode similar to CaO in La_{0.6}Ca_{0.4}Fe_{0.8}Ni_{0.2}O_{3.6} electrode⁶⁹.



Figure 9. Optimized structures of one propane molecule on (a) Ce-doped SrFeO₃ (100), (b) CeO₂ (100), (c) SrO (100) and (d) Ru (001). The adsorption energies after the pre-screening for lowest values are given in the side views and the adsorption energy (Δ E) was provided in the respective image. Sr, Ce, Fe, Ru, O, C and H are in blue, purple, gray, pale purple, red, yellow and white, respectively. (e, f, g) Charge density differences (CDD) of the global minimum structure of propane adsorbed on Ce doped SrFeO₃ (100). (f) and (g) presents the CDD on the cutting plane "f" and "g" shown in (e), respectively. Atoms other than Sr were omitted in the image (e-g).

The interaction between the absorbed propane molecule and oxide substrate was further studied via the CDD before and after adsorption. In the cutting plane of the carbon backbone (Figure 9(e)), the interactions of the propane molecule with the substrate surface, e.g. Sr-terminated SF, result in clear 2sp electron accumulation in the interior region of the adsorption, with observable

electron depletion in the upper half of the Sr p orbital, suggesting the presence of the ionic component of the C-Sr bonds. This feature can be more clearly observed in the cutting plane through the Sr atom (Figure 9(f)). The exterior side of the molecule, however, is suffered from apparent electron depletion, which gives rise to the polarized molecule interacted with the surface and the establishment of a strong electric field across the molecule. Moreover, we can observe that the C-H bonds pointing away from the surface (Figure 9(f)) are strongly polarized toward the carbon atom. Similar polarization occurs in the C-H bonds pointing to the surface (Figure 9(g)), where the H-O bonds exhibit a reversed polarization balancing the electric field established in the molecule. In a word, all C-H bonds experience simultaneous bond polarization with enhanced ionic characters. Therefore, the electrostatic component would play a vital role in the molecule-surface interactions, in addition to the covalent and ionic channels, for the activation of C-H bonds.

The rearrangement of electron density in the absorbed propane may also ease the production of radicals through the activation of C-H bounds for the coke production as shown in the microscopy of Ce20SF after test. With the progressive oxidation of the adsorbed propane by the oxide ion from the cathode at lower voltage (<0.9 V), the production of C- and H-species may be subjected to change the reaction as a result of water molecule production. According to previous research, the carbon deposition on a Ni-based anode under dry hydrocarbon fuel at 800 °C could be ascribed to the direct pyrolysis since the carbon monoxide disproportionation would be suppressed ^{28, 70}, but the deposition of oxides of alkaline earth was found to be beneficial to water-mediated oxidation of hydrocarbon ^{23, 71}. The anti-coking behavior was found to be governed by the water affinity on the alkaline metal oxides adjacent to the metal particles ⁷² in a SOFC anode. In addition, the addition of Ru⁰ in the Ni-YSZ electrode was found to enhance the electrochemical and thermochemical reaction for better coke resistance under a carbonaceous fuel ^{73, 74} and the decrease in the coverage of –CO on the surface induced by Ru⁰ deposition could be the reason⁷⁵.

Conclusions

Ce doping and Ce/Ru co-doping have been performed on SrFeO₃, aiming to construct an efficient electrode for SSOFC with simultaneous surface exsolution of metal and oxides. It is found that the doping of 20 at. % Ce on Sr the site in SrFeO₃ (Ce20SF) could produce a single perovskite at

23

1250 °C, but ceria can segregate from the lattice of perovskite during the cooling process. The codoping of 5 at. % Ru⁴⁺ on the Fe site could stabilize the perovskite structure and lessen the formation of fluorite-type ceria during the cooling. The Ce doping increases the stability of the perovskite in a reducing atmosphere and the Ce/Ru co-doping induces the surface decomposition for the formation of nanoscale SrO, ceria and Ru⁰. At 800 °C, Ce20SFR-based SSOFC with an LSGM electrolyte of 320 µm in thickness presented small R_p values (0.12 Ω cm²) and excellent peak power densities not only in H₂ fuel (846 mW cm⁻²) but also in C₃H₈ (330 mW cm⁻²). The exsolution of Ru⁰ was important to the H₂ oxidation though the superficial CeO₂ was important to the absorption of propane molecules, while simultaneous superficial exsolution of SrO was found to be important for the coke resistance under carbonaceous fuel.

Supporting Information

Pseudocubic cell volumes and XRD of SF in Figure S1 and S2; SEM and EIS plot of Ce20SF and Ce20SFR in Figure S3, S4 and S5; HAADF-STEM image and the site of propane adsorbed on Ce20SF in Figure S6 and S7; electrochemical performance of SSOFC with ferrite electrode in Table S1.

Acknowledgements

This work is supported by the NSFC (grant No. 51702264; 41371275) and National Key Research and Development Program of China (grant No. 2018FYD0200701) and research funding for central universities (XDJK2020B066). B.L. acknowledges the Chongqing Graduate Scientific Research Innovation Project (grant No. CYS20114). C.N. also thanks to the award of Chongqing Bayu Young Scholar from Chongqing Teaching Committee.

References

1. Minh, N. Q., CERAMIC FUEL-CELLS. J. Am. Ceram. Soc. 1993, 76 (3), 563-588.

2. Ni, C. S.; Vohs, J.; Gorte, R. J.; Irvine, J. T. S., Fabrication and characterisation of a large-area solid oxide fuel cell based on dual tape cast YSZ electrode skeleton supported YSZ electrolyte with vanadate and ferrite perovskite- impregnated anode and cathode. *J. Mater. Chem. A* **2014**, *2*, 19150-19155.

3. EG&G Technical Services, I. *Fuel Cell Handbook (Seventh edition)* West Virgina, 2004.

4. dos Santos-Gómez, L.; Compana, J. M.; Bruque, S.; Losilla, E. R.; Marrero-López, D., Symmetric electrodes for solid oxide fuel cells based on Zr-doped SrFeO_{3-δ}. *J. Power Sources* **2015**,

24

279, 419-427.

5. Ruiz-Morales, J. C.; Marrero-Lopez, D.; Canales-Vazquez, J.; Irvine, J. T. S., Symmetric and reversible solid oxide fuel cells. *RSC Advances* **2011**, *1* (8), 1403-1414.

6. Su, C.; Wang, W.; Liu, M. L.; Tade, M. O.; Shao, Z. P., Progress and Prospects in Symmetrical Solid Oxide Fuel Cells with Two Identical Electrodes. *Adv. Energy Mater.* **2015**, *5* (14), 1500188.

7. Atkinson, A.; Barnett, S.; Gorte, R. J.; Irvine, J. T. S.; McEvoy, A. J.; Mogensen, M.; Singhal, S. C.; Vohs, J., Advanced anodes for high-temperature fuel cells. *Nat. Mater.* **2004**, *3* (1), 17-27.

8. Boldrin, P.; Brandon, N. P., Progress and outlook for solid oxide fuel cells for transportation applications. *Nature Catalysis* **2019**, *2* (7), 571-577.

9. Yan, N.; Pandey, J.; Zeng, Y.; Amirkhiz, B. S.; Hua, B.; Geels, N. J.; Luo, J.-L.; Rothenberg, G., Developing a Thermal- and Coking-Resistant Cobalt–Tungsten Bimetallic Anode Catalyst for Solid Oxide Fuel Cells. *ACS Catalysis* **2016**, *6* (7), 4630-4634.

10. Ni, C.; Zeng, Q.; He, D.; Peng, L.; Xie, D.; Irvine, J. T. S.; Duan, S.; Ni, J., A B-site doped perovskite ferrate as an efficient anode of a solid oxide fuel cell with in situ metal exsolution. *J. Mater. Chem. A* **2019**, *7*, 26944-26953.

Konysheva, E. Y.; Xu, X.; Irvine, J. T. S., On the existence of A-site deficiency in perovskites and its relation to the electrochemical performance. *Adv. Mater. (Weinheim, Ger.)* 2012, *24* (4), 528-532.
 Bastidas, D. M.; Tao, S.; Irvine, J. T. S., A symmetrical solid oxide fuel cell demonstrating redox stable perovskite electrodes. *J. Mater. Chem.* 2006, *16* (17), 1603-1605.

13. Zheng, Y.; Zhang, C.; Ran, R.; Cai, R.; Shao, Z.; Farrusseng, D., A new symmetric solidoxide fuel cell with La0.8Sr0.2Sc0.2Mn0.8O3-δ perovskite oxide as both the anode and cathode. *Acta Mater.* **2009**, *57* (4), 1165-1175.

14. Zhou, J.; Shin, T.-H.; Ni, C.; Chen, G.; Wu, K.; Cheng, Y.; Irvine, J. T. S., In situ Growth of Nanoparticles in Layered Perovskite La_{0.8}Sr_{1.2}Fe_{0.9}Co_{0.1}O_{4-δ} as an Active and Stable Electrode for Symmetrical Solid Oxide Fuel Cells. *Chem. Mater.* **2016**, *28* (9), 2981-2993.

15. Fernández-Ropero, A. J.; Porras-Vázquez, J. M.; Cabeza, A.; Slater, P. R.; Marrero-López, D.; Losilla, E. R., High valence transition metal doped strontium ferrites for electrode materials in symmetrical SOFCs. *J. Power Sources* **2014**, *249*, 405-413.

16. Vecino-Mantilla, J. S.; Gauthier-Maradei, P.; Huvé, M.; Serra, J.; Roussel, P.; Gauthier, G., Nickel exsolution - driven phase transformation from an n = 2 to an n= 1 Ruddlesden-Popper manganite for methane steam reforming reaction in SOFC conditions. *ChemCatChem* **2019**, *11*, 4631-4641.

17. Neagu, D.; Oh, T.-S.; Miller, D. N.; Ménard, H.; Bukhari, S. M.; Gamble, S. R.; Gorte, R. J.; Vohs, J. M.; Irvine, J. T. S., Nano-socketed nickel particles with enhanced coking resistance grown in situ by redox exsolution. *Nat. Commun.* **2015**, *6*, 8120.

18. Neagu, D.; Tsekouras, G.; Miller, D. N.; Ménard, H.; Irvine, J. T. S., In situ growth of nanoparticles through control of non-stoichiometry. *Nature Chem.* **2013**, *5*, 916.

19. Neagu, D.; Kyriakou, V.; Roiban, I.-L.; Aouine, M.; Tang, C.; Caravaca, A.; Kousi, K.; Schreur-Piet, I.; Metcalfe, I. S.; Vernoux, P.; van de Sanden, M. C. M.; Tsampas, M. N., In Situ Observation of Nanoparticle Exsolution from Perovskite Oxides: From Atomic Scale Mechanistic Insight to Nanostructure Tailoring. *ACS Nano* **2019**, *13* (11), 12996-13005.

20. Meng, X.; Liu, X.; Han, D.; Wu, H.; Li, J.; Zhan, Z., Symmetrical solid oxide fuel cells with

impregnated SrFe_{0.75}Mo_{0.25}O_{3-δ} electrodes. J. Power Sources **2014**, 252, 58-63.

21. Liu, Q.; Dong, X.; Xiao, G.; Zhao, F.; Chen, F., A novel electrode material for symmetrical SOFCs. *Adv. Mater. (Weinheim, Ger.)* **2010**, *22* (48), 5478-5482.

22. Zhu, T.; Troiani, H. E.; Mogni, L. V.; Han, M.; Barnett, S. A., Ni-Substituted Sr(Ti,Fe)O3 SOFC Anodes: Achieving High Performance via Metal Alloy Nanoparticle Exsolution. *Joule* **2018**, *2* (3), 478-496.

23. Yang, L.; Choi, Y.; Qin, W.; Chen, H.; Blinn, K.; Liu, M.; Liu, P.; Bai, J.; Tyson, T. A.; Liu, M., Promotion of water-mediated carbon removal by nanostructured barium oxide/nickel interfaces in solid oxide fuel cells. *Nat. Commun.* **2011**, *2*, 357.

24. Ye, L.; Pan, C.; Zhang, M.; Li, C.; Chen, F.; Gan, L.; Xie, K., Highly Efficient CO2 Electrolysis on Cathodes with Exsolved Alkaline Earth Oxide Nanostructures. *ACS Appl. Mater. Interfaces* **2017**, *9* (30), 25350-25357.

25. Cargnello, M.; Jaén, J. J. D.; Garrido, J. C. H.; Bakhmutsky, K.; Montini, T.; Gámez, J. J. C.; Gorte, R. J.; Fornasiero, P., Exceptional Activity for Methane Combustion over Modular Pd@CeO2 Subunits on Functionalized Al2O3. *Science* **2012**, *337* (6095), 713-717.

26. Lu, L.; Ni, C.; Cassidy, M.; Irvine, J. T. S., Demonstration of high performance in a perovskite oxide supported solid oxide fuel cell based on La and Ca co-doped SrTiO₃. *J. Mater. Chem. A* **2016**, *4*, 11708-11718.

27. Sun, Y.-F.; Zhou, X.-W.; Zeng, Y.; Amirkhiz, B. S.; Wang, M.-N.; Zhang, L.-Z.; Hua, B.; Li, J.; Li, J.-H.; Luo, J.-L., An ingenious Ni/Ce co-doped titanate based perovskite as a coking-tolerant anode material for direct hydrocarbon solid oxide fuel cells. *J. Mater. Chem. A* **2015**, *3* (45), 22830-22838.

28. Murray, E. P.; Tsai, T.; Barnett, S. A., A direct-methane fuel cell with a ceria-based anode. *Nature* **1999**, *400* (6745), 649-651.

29. Kim, J.-S.; Nair, V. V.; Vohs, J. M.; Gorte, R. J., A study of the methane tolerance of LSCM–YSZ composite anodes with Pt, Ni, Pd and ceria catalysts. *Scr. Mater.* **2011**, *65* (2), 90-95.

30. Chueh, W. C.; Hao, Y.; Jung, W.; Haile, S. M., High electrochemical activity of the oxide phase in model ceria-Pt and ceria-Ni composite anodes. *Nature Materials* **2011**, *11*, 155-161.

31. Fan, W. W.; Sun, Z.; Wang, J. K.; Zhou, J.; Wu, K.; Cheng, Y. H., A new family of Ce-doped SmFeO3 perovskite for application in symmetrical solid oxide fuel cells. *Journal of Power Sources* **2016**, *312*, 223-233.

32. Fan, W.; Sun, Z.; Zhou, J.; Wu, K.; Cheng, Y., Characterization of Sr/Ru co-doped ferrite based perovskite as a symmetrical electrode material for solid oxide fuel cells. *J. Power Sources* **2017**, *348*, 94-106.

33. Irvine, J. T. S.; Neagu, D.; Verbraeken, M. C.; Chatzichristodoulou, C.; Graves, C.; Mogensen, M. B., Evolution of the electrochemical interface in high-temperature fuel cells and electrolysers. *Nature Energy* **2016**, *1*, 15014.

34. Deganello, F.; Liotta, L. F.; Longo, A.; Casaletto, M. P.; Scopelliti, M., Cerium effect on the phase structure, phase stability and redox properties of Ce-doped strontium ferrates. *J. Solid State Chem.* **2006**, *179* (11), 3406-3419.

35. Simner, S. P.; Anderson, M. D.; Pederson, L. R.; Stevenson, J. W., Performance variability of La(Sr)FeO3 SOFC cathode with Pt, Ag, and Au current collectors. *J. Electrochem. Soc.* **2005**, *152* (9), A1851-A1859.

36. Kim, G.; Lee, S.; Shin, J. Y.; Corre, G.; Irvine, J. T. S.; Vohs, J. M.; Gorte, R. J., Investigation of the Structural and Catalytic Requirements for High-Performance SOFC Anodes Formed by Infiltration of LSCM. *Electrochem. Solid-State Lett.* **2009**, *12* (3), B48-B52.

37. Rath, M. K.; Lee, K.-T., Superior electrochemical performance of non-precious Co-Ni-Mo alloy catalyst-impregnated Sr₂FeMoO_{6- δ} as an electrode material for symmetric solid oxide fuel cells. *Electrochim. Acta* **2016**, *212*, 678-685.

38. Robbins, M.; Wertheim, G. K.; Menth, A.; Sherwood, R. C., Preparation and properties of polycrystalline cerium orthoferrite (CeFeO3). *J. Phys. Chem. Solids* **1969**, *30* (7), 1823-1825.

39. Marrocchelli, D.; Bishop, S. R.; Tuller, H. L.; Yildiz, B., Understanding Chemical Expansion in Non-Stoichiometric Oxides: Ceria and Zirconia Case Studies. *Adv. Funct. Mater.* **2012**, *22* (9), 1958-1965.

40. Trofimenko, N. E.; Ullmann, H., Oxygen stoichiometry and mixed ionic-electronic conductivity of Sr_{1-a}Ce_aFe_{1-b}Co_bO_{3-x} perovskite-type oxides. *Journal of the European Ceramic Society* **2000**, *20* (9), 1241-1250.

41. Lay, E.; Dessemond, L.; Gauthier, G. H., Synthesis and Characterization of CexSr1xCr0.5Mn0.5O3-δ Perovskites as Anode Materials for Solid Oxide Fuel Cells (SOFC). *Electrochim. Acta* **2016**, *216*, 420-428.

42. Mogensen, M.; Sammes, N. M.; Tompsett, G. A., Physical, chemical and electrochemical properties of pure and doped ceria. *Solid State Ionics* **2000**, *129* (1–4), 63-94.

43. Zhang, X.; Pei, C.; Chang, X.; Chen, S.; Gong, J. J. J. o. t. A. C. S., FeO6 Octahedral Distortion Activates Lattice Oxygen in Perovskite Ferrite for Methane Partial Oxidation Coupled with CO2-Splitting. **2020**, *142* (26), 11540-11549.

44. Li, S. S.; Gong, D. D.; Tang, H. G.; Ma, Z.; Liu, Z. T.; Liu, Y., Preparation of bimetallic Ni@Ru nanoparticles supported on SiO₂ and their catalytic performance for CO methanation. *Chem. Eng. J. (Lausanne)* **2018**, *334*, 2167-2178.

45. Zhu, C.; Hou, S.; Hou, L.; Xie, K., Perovskite SrFeO3–δ decorated with Ni nanoparticles for high temperature carbon dioxide electrolysis. *Int. J. Hydrogen Energy* **2018**, *43* (36), 17040-17047.
46. Patrakeev, M. V.; Leonidov, I. A.; Kozhevnikov, V. L.; Kharton, V. V., Ion–electron transport in strontium ferrites: relationships with structural features and stability. *Solid State Sci.* **2004**, *6* (9), 907-913.

47. Tuller, H. L.; Bishop, S. R., Point Defects in Oxides: Tailoring Materials Through Defect Engineering. *Annu. Rev. Mater. Res.* **2011**, *41* (1), 369-398.

48. Ni, C.; Carolan, D.; Rocks, C.; Hui, J.; Fang, Z.; Padmanaban, D. B.; Ni, J.; Xie, D.; Maguire, P.; Irvine, J. T. S.; Mariotti, D., Microplasma-assisted electrochemical synthesis of Co_3O_4 nanoparticles in absolute ethanol for energy applications. *Green Chem.* **2018**, *20* (9), 2101-2109.

49. Connor, P. A.; Yue, X.; Savaniu, C. D.; Price, R.; Triantafyllou, G.; Cassidy, M.; Kerherve, G.; Payne, D. J.; Maher, R. C.; Cohen, L. F.; Tomov, R. I.; Glowacki, B. A.; Kumar, R. V.; Irvine, J. T. S., Tailoring SOFC Electrode Microstructures for Improved Performance. *Adv. Energy Mater.* **2018**, *8* (23), 1800120.

50. Fan, W.; Sun, Z.; Bai, Y.; Wu, K.; Cheng, Y., Highly Stable and Efficient Perovskite Ferrite Electrode for Symmetrical Solid Oxide Fuel Cells. *ACS Appl. Mater. Interfaces* **2019**, *11* (26), 23168-23179.

51. Zeng, Q.; Liu, X.; Xie, D.; Ni, J.; Ni, C., A strontium-free and iron-based oxygen electrode for

solid-oxide electrochemical cells (SOCs). Int. J. Hydrogen Energy 2019, 44 (29), 15387-15399.

52. Rodriguez, J., Metal-metal bonding on surfaces: electronic and chemical properties of Ag on Ru(001). *Surf. Sci.* **1993**, *296* (2), 149-163.

53. Song, Y.; Chen, Y.; Xu, M.; Wang, W.; Zhang, Y.; Yang, G.; Ran, R.; Zhou, W.; Shao, Z., A Cobalt-Free Multi-Phase Nanocomposite as Near-Ideal Cathode of Intermediate-Temperature Solid Oxide Fuel Cells Developed by Smart Self-Assembly. *Adv. Mater. (Weinheim, Ger.)* **2020**, *32* (8), 1906979.

54. Lu, C.; Niu, B.; Yu, S.; Yi, W.; Luo, S.; Xu, B.; Ji, Y., Efficient and stable symmetrical electrode La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.7}Mo_{0.1}O_{3-δ} for direct hydrocarbon solid oxide fuel cells. *Electrochimica Acta* **2019**, *323*, 134857.

55. Gou, M.; Ren, R.; Sun, W.; Xu, C.; Meng, X.; Wang, Z.; Qiao, J.; Sun, K., Nb-doped Sr2Fe1.5Mo0.5O6-δ electrode with enhanced stability and electrochemical performance for symmetrical solid oxide fuel cells. *Ceram. Int.* **2019**, *45* (12), 15696-15704.

56. Niu, B.; Jin, F.; Zhang, L.; Shen, P.; He, T., Performance of double perovskite symmetrical electrode materials $Sr_2TiFe_{1-x}Mo_xO_{6-\delta}$ (x = 0.1, 0.2) for solid oxide fuel cells. *Electrochimica Acta* **2018**, *263*, 217-227.

57. Xie, Z.; Zhao, H.; Chen, T.; Zhou, X.; Du, Z., Synthesis and electrical properties of Al-doped Sr₂MgMoO_{6-δ} as an anode material for solid oxide fuel cells. *Int. J. Hydrogen Energy* **2011**, *36* (12), 7257-7264.

58. Lai, B.-K.; Kerman, K.; Ramanathan, S., Nanostructured La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃/Y_{0.08}Zr_{0.92}O_{1.96}/La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O₃ (LSCF/YSZ/LSCF) symmetric thin film solid oxide fuel cells. *J. Power Sources* **2011**, *196* (4), 1826-1832.

59. Ben Mya, O.; dos Santos-Gomez, L.; Porras-Vazquez, J. M.; Omari, M.; Ramos-Barrado, J. R.; Marrero-Lopez, D., La_{1-x}Sr_xFe0.7Ni_{0.3}O_{3-δ} as both cathode and anode materials for Solid Oxide Fuel Cells. *Int. J. Hydrogen Energy* **2017**, *42* (36), 23160-23169.

60. Bian, L.; Duan, C.; Wang, L.; O'Hayre, R.; Cheng, J.; Chou, K.-C., Ce-doped La0.7Sr0.3Fe0.9Ni0.1O3– δ as symmetrical electrodes for high performance direct hydrocarbon solid oxide fuel cells. *J. Mater. Chem. A* **2017**, *5* (29), 15253-15259.

61. Niu, B.; Jin, F.; Feng, T.; Zhang, L.; Zhang, Y.; He, T., A-site deficient (La_{0.6}Sr_{0.4})(_{1-x)}Co_{0.2}Fe_{0.6}Nb_{0.2}O₃₋₈ symmetrical electrode materials for solid oxide fuel cells. *Electrochim. Acta* **2018**, *270*, 174-182.

62. Bian, L.; Duan, C.; Wang, L.; Zhu, L.; O'Hayre, R.; Chou, K.-C., Electrochemical performance and stability of La_{0.5}Sr_{0.5}Fe_{0.9}Nb_{0.1}O_{3-δ} symmetric electrode for solid oxide fuel cells. *Journal of Power Sources* **2018**, *399*, 398-405.

63. Chen, M.; Paulson, S.; Thangadurai, V.; Birss, V., Sr-rich chromium ferrites as symmetrical solid oxide fuel cell electrodes. *J. Power Sources* **2013**, *236*, 68-79.

64. Du, Z.; Zhao, H.; Yi, S.; Xia, Q.; Gong, Y.; Zhang, Y.; Cheng, X.; Li, Y.; Gu, L.; Świerczek, K., High-performance anode material $Sr_2FeMo_{0.65}Ni_{0.35}O_{6-\delta}$ with in situ exsolved nanoparticle catalyst. *ACS Nano* **2016**, *10* (9), 8660-8669.

65. Cordfunke, E. H. P.; Booij, A. S.; Huntelaar, M. E., The thermochemical properties of BaCeO₃(s) and SrCeO₃(s) fromT=(5 to 1500) K. *The Journal of Chemical Thermodynamics* 1998, *30* (4), 437-447.
66. McIntosh, S.; He, H.; Lee, S.-I.; Costa-Nunes, O.; Krishnan, V. V.; Vohs, J. M.; Gorte, R. J., An Examination of Carbonaceous Deposits in Direct-Utilization SOFC Anodes. *J. Electrochem. Soc.*

2004, *151* (4), A604-A608.

67. Shin, T. H.; Ida, S.; Ishihara, T., Doped CeO₂–LaFeO₃ Composite Oxide as an Active Anode for Direct Hydrocarbon-Type Solid Oxide Fuel Cells. *J. Am. Chem. Soc.* **2011**, *133* (48), 19399-19407.

68. Liu, W.; Sang, J.; Wang, Y.; Chang, X.; Lu, L.; Wang, J.; Zhou, X.; Zhai, Q.; Guan, W.; Singhal, S. C., Durability of direct-internally reformed simulated coke oven gas in an anode-supported planar solid oxide fuel cell based on double-sided cathodes. *J. Power Sources* **2020**, *465*, 228284.

69. Tian, Y.; Zhang, L.; Liu, Y.; Jia, L.; Yang, J.; Chi, B.; Pu, J.; Li, J., Self-recovering robust electrode for highly efficient CO2 electrolysis in symmetrical solid oxide electrolysis cells. *Journal of Materials Chemistry A* **2019**, *7* (11), 6395-6400.

70. Trembly, J. P.; Marquez, A. I.; Ohrn, T. R., Effects of coal syngas and H₂S on the performance of solid oxide fuel cells: Single-cell tests. *J. Power Sources* **2006**, *158* (1), p.263-273.

71. Xie, Y.; Shi, N.; Hu, X. Y.; Liu, M. Q.; Yang, Y.; Huan, D. M.; Pan, Y.; Peng, R. R.; Xia, C. R., Novel in-situ MgO nano-layer decorated carbon-tolerant anode for solid oxide fuel cells. *Int. J. Hydrogen Energy* **2020**, *45* (20), 11791-11801.

72. Han, Z. Y.; Yang, Y. R.; Kong, D. X., Surface-scale affinity and adsorption selectivity of alkaline earth metal oxides to H2O and CO2: Insight into SOFC anode modification. *Appl. Surf. Sci.* **2020**, *503*, 9.

73. Thieu, C.-A.; Yang, S.; Ji, H.-I.; Kim, H.; Yoon, K. J.; Lee, J.-H.; Son, J.-W., Effect of secondary metal catalysts on butane internal steam reforming operation of thin-film solid oxide fuel cells at 500–600 °C. *Appl. Catal. B* **2020**, *263*, 118349.

74. Kim, H. S.; Jeon, Y.; Kim, J. H.; Jang, G. Y.; Yoon, S. P.; Yun, J. W., Characteristics of Sr_{1-x}Y_xTi_{1-y}Ru_yO_{3+/- δ} and Ru-impregnated Sr_{1-x}Y_xTiO_{3+/- δ} perovskite catalysts as SOFC anode for methane dry reforming. *Appl. Surf. Sci.* **2020**, *510*, 9.

75. Jeong, H. J.; Kim, J. W.; Bae, K.; Jung, H.; Shim, J. H., Platinum–Ruthenium Heterogeneous Catalytic Anodes Prepared by Atomic Layer Deposition for Use in Direct Methanol Solid Oxide Fuel Cells. *ACS Catal.* **2015**, *5* (3), 1914-1921.