



## Full paper

Oxygen reduction kinetic enhancements of intermediate-temperature SOFC cathodes with novel  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}/\text{Nd}_{0.8}\text{Sr}_{1.2}\text{CoO}_{4 \pm \delta}$  heterointerfacesYun Zheng<sup>a</sup>, Yifeng Li<sup>a</sup>, Tong Wu<sup>a</sup>, Wenqiang Zhang<sup>a</sup>, Jianxin Zhu<sup>b</sup>, Zhanping Li<sup>c</sup>, Jing Chen<sup>a</sup>, Bo Yu<sup>a,\*\*</sup>, Jianchen Wang<sup>a,\*\*</sup>, Jiujun Zhang<sup>d,e,\*</sup><sup>a</sup> Institute of Nuclear and New Energy Technology (INET), Collaborative Innovation Center of Advanced Nuclear Energy Technology, Tsinghua University, Beijing 100084, PR China<sup>b</sup> Research Center for Eco-Environmental Sciences, Chinese Academy of Sciences, Beijing 100085, PR China<sup>c</sup> Department of Chemistry, Beijing Key Laboratory of Microanalytical Methods and Instrumentation, Tsinghua University, Beijing 100084, PR China<sup>d</sup> NRC Energy, Mining & Environment, National Research Council of Canada, 4250 Wesbrook Mall, Vancouver, B.C., Canada V6T 1W5<sup>e</sup> College of Sciences/Institute for Sustainable Energy, Shanghai University, Shanghai 200444, PR China

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## ABSTRACT

Solid-oxide fuel cells (SOFCs) are clean and highly efficient electrochemical energy conversion devices and in this study, novel nanolayer-structured cathodes with  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}/\text{Nd}_{0.8}\text{Sr}_{1.2}\text{CoO}_{4 \pm \delta}$  heterointerfaces for intermediate-temperature SOFCs are developed in which significantly enhanced oxygen reduction reaction (ORR) kinetics are obtained by increasing the interface layers. The electrical surface exchange coefficient ( $k^{\text{el}}$ ) of the resulting sample (NSC<sub>214/113-17L</sub>) with multilayered heterointerfaces reached  $2.917 \times 10^{-7} \text{ cm s}^{-1}$  at 10% oxygen pressure under 500 °C, and was  $10^2$ – $10^3$  times higher than those of the single-phase samples, including NSC<sub>113</sub> ( $1.335 \times 10^{-9} \text{ cm s}^{-1}$ ) and NSC<sub>214</sub> ( $1.057 \times 10^{-9} \text{ cm s}^{-1}$ ). Heterointerface characterizations were conducted using Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), Scanning Transmission Electron Microscopy (STEM), Energy Dispersive Spectrometer (EDS) and Electron Energy Loss Spectroscopy (EELS) and revealed an enrichment of Sr and a decrease in the valence state of cobalt at the interfacial regions. These two factors together induced the generation of oxygen vacancies  $\text{V}_\text{O}^\bullet$  and further facilitated ion transportation, as confirmed by density functional theory (DFT) simulations. Our findings provide a novel heterointerface with high activity and offer specific evidence to elucidate the origin of the resulting enhanced ORR kinetics.

## 1. Introduction

Solid oxide fuel cells (SOFCs) at high operating temperatures (800–1000 °C) are highly efficient, advanced electrochemical energy storage and conversion devices that are particularly attractive for the integration of renewable energies into the electric grid [1–3]. However, because of fast material degradation induced by extreme temperatures, great efforts have recently been focused on reducing operating temperatures to the intermediate range (500–700 °C) and even lower (300–500 °C) in an attempt to extend operating lifetimes and to allow for better economic feasibility [4–7]. One major issue with low-temperature operations is that the performance of the electrodes is greatly suppressed because of the slower cathode oxygen reduction reaction (ORR) kinetics as catalyzed by conventional materials (e.g.

$\text{La}_{1-x}\text{Sr}_x\text{MnO}_3$ ) [8–10]. Therefore, there is an urgent need to develop new cathode materials with high performances at lower or intermediate temperatures for SOFC applications [11,12].

Necessary properties of desirable oxygen electrode materials for IT-SOFCs include high electronic and oxide ion conductivities, better chemical and thermal compatibilities with electrolytes, and high reactivity to oxygen reduction reactions (ORR). With respect to this, Sr-doped lanthanum cobaltite cathodes ( $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$ , LSC<sub>113</sub>); possessing high oxide ion and electronic conductivities, have been extensively studied [13,14]. However, poor chemical and thermal compatibility (high thermal expansion coefficient, TEC) with conventional electrolytes (e.g. YSZ, yttria-stabilized zirconia) severely limit further applications [15]. Alternatively, studies have reported that if the La in these materials was replaced by other lanthanides Ln (Ln = Sm or Gd) with

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smaller radii, the ionicity of the Ln-O bonds and the TEC can be reduced correspondingly [15–17]. However, these replacements would also decrease conductivity because of the bending of Co-O-Co bonds and consequently decrease the bandwidth and covalency of the Co-O bonds. Therefore, to balance the need for catalytic activity and the need for thermal/chemical compatibility with conventional electrolytes (e.g. YSZ, samarium doped ceria (SDC), and gadolinia doped ceria (GDC)),  $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  appears to be a promising candidate because the ionic radius of  $\text{Nd}^{3+}$  is in the middle of the radii of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$  and  $\text{Gd}^{3+}$ , and the ionicity of the Nd-O bond is also in the middle of the corresponding Ln-O bonds [8,18,19]. Supporting information for these materials are presented in Fig. S1 and Table S1.

In order to use  $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  as an optimal ORR catalyst, the ORR kinetics need to be further studied to optimize catalyst structures. This is because the interface between different crystalline materials (heterointerfaces) can provide extraordinary local electronic or atomic structures, and subsequently produce improved properties such as significantly increased ionic conductivities [20] and electronic conductivities [21]. These two properties are closely related to ORR activity and are therefore widely investigated in supercapacitors, solar cells, lithium battery, solid oxide cells and so on. With respect to SOFCs, several recent reports have shown that the heterointerface between Perovskite (P) and Ruddlesden–Popper (R-P) phases; typically the interface between  $\text{La}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  and  $(\text{La}_{1-x}\text{Sr}_x)_2\text{CoO}_{4 \pm \delta}$ , can exhibit remarkably accelerated ORR kinetics [4,22–33] and in addition, some mechanisms were also proposed to elucidate the origin of this enhancement, including electronic structure [4,32], anisotropy [31], lattice strain [30,31] or mismatch in lattice parameter [30], and cation inter-diffusion (e.g. Sr enrichment) [27,34,35]. These studies suggest that the introduction of heterointerfaces into  $\text{Nd}_{1-x}\text{Sr}_x\text{CoO}_{3-\delta}$  is also a promising approach to achieve enhanced ORR activity.

In our previous study, porous composite materials of  $\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{NSC}_{113}$ ) and  $\text{Nd}_{0.8}\text{Sr}_{1.2}\text{CoO}_{4 \pm \delta}$  ( $\text{NSC}_{214}$ ) were prepared and evaluated as oxygen electrodes for intermediate-temperature solid oxide cells [16] and demonstrated superior electrochemical performances over single-phase materials. However, the origin of these improved performances was not clear and the assumption was that the ORR enhancement was induced by the interface between the two phases. Here, as a continuation of our previous study, novel heterostructure thin-film oxygen electrodes in the (001) direction were prepared using pulsed laser deposition (PLD) in which the electrodes consisted of  $\text{NSC}_{113}$  and  $\text{NSC}_{214}$ . Samples with multilayered heterointerfaces were also prepared to investigate the relationship between enhanced performances and areas of heterointerfaces, with the results demonstrating that the introduction of heterointerfaces can lead to a  $10^2$ – $10^3$  times increase in surface oxygen exchange kinetics, and that the increase of the number of layers (the area of triple phase boundaries of P/R/ $\text{O}_2$ ) can significantly improve ORR activity. To further understand the origin of the enhanced ORR activity at the heterointerfaces, Focused Ion Beam (FIB), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS), High-angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM), Energy Dispersive Spectrometer (EDS) and Electron Energy Loss Spectroscopy (EELS) were performed to characterize structures with high atomic-resolution as well as ion distributions and valence state changes of Co at the local heterointerfaces of  $\text{NSC}_{214}/\text{NSC}_{113}$ , with the results revealing that the enrichment of Sr and the decrease of Co valence states can lead to increased oxygen vacancy concentrations at the heterointerface, further enhancing ORR activity.

## 2. Experimental

### 2.1. Thin-film sample preparation

$\text{Nd}_{0.5}\text{Sr}_{0.5}\text{CoO}_{3-\delta}$  ( $\text{NSC}_{113}$ ),  $\text{Nd}_{0.8}\text{Sr}_{1.2}\text{CoO}_{4 \pm \delta}$  ( $\text{NSC}_{214}$ ) and hetero-

structured  $\text{NSC}_{214}/\text{NSC}_{113}$  dense thin films used in this study were prepared through pulsed laser deposition (PLD). The precursor materials (targets) were synthesized using a high temperature solid-state reaction and the reagents consisted of  $\text{Nd}_2\text{O}_3$  (99.99%),  $\text{SrCO}_3$  (99.99%) and  $\text{Co}_2\text{O}_3$  (99.99%) (all Sigma-Aldrich). For the PLD conditions, the wavelength of the KrF excimer laser was 248 nm, the pulse rate and energy were 2 Hz and 32 mJ respectively, and the oxygen pressure and growth temperature were kept at 1 Pa and 650 °C respectively. The distance between the substrate and the target was about 5 cm. After growth, the films were cooled down to room temperature at a cooling rate of 10 °C/min and the oxygen pressure was kept at 130 Pa to oxidize the films. The total thickness of the NSC ( $\text{NSC}_{113}$  and/or  $\text{NSC}_{214}$ ) layer/layers in each thin-film sample was approximately 90 nm, and the thicknesses were determined from cross sections using STEM. Five thin films include  $\text{NSC}_{113}$  (yellow, 90 nm thick);  $\text{NSC}_{214}$  (green, 90 nm thick);  $\text{NSC}_{214}/\text{NSC}_{113}$  (5 nm  $\text{NSC}_{214}$  on 85 nm  $\text{NSC}_{113}$  with one-layer heterointerface);  $\text{NSC}_{214}/\text{NSC}_{113}$ -5L (five alternate 5 nm  $\text{NSC}_{214}$  or  $\text{NSC}_{113}$  layers and a 65 nm  $\text{NSC}_{113}$  layer, possessing 5-layer heterointerfaces);  $\text{NSC}_{214}/\text{NSC}_{113}$ -17L (18 alternate 5 nm  $\text{NSC}_{113}$  or  $\text{NSC}_{214}$  layers with 17-layer heterointerfaces). Here the letter “L” is the acronym of “Layers”, and the number prior to “L” means the number of heterointerfaces (between  $\text{NSC}_{113}$  and  $\text{NSC}_{214}$  layers) in each thin film sample. The thickness of each NSC layer (5 nm) was determined by preliminary experiments and some related publications. All NSC layer/layers were grown on a YSZ (001) substrate (5 mm × 5 mm × 0.5 mm).

### 2.2. Structural characterization

High resolution X-ray diffraction (HRXRD) was performed to determine the crystal structure and phase purity of the thin films. The measurements were carried out using Cu K $\alpha$  radiation and a four-circle Rigaku diffractometer, equipped with a 2-bounce Ge (022) channel-cut monochromator and a scintillation counter.

STEM and EELS were carried out using a FEI Tian 80–300 TEM operating at 300 kV with a probe size of 0.6 Å. High angle annular dark field (HAADF) images were obtained with 90–270 mrad collection angles. The content mapping of elements (Sr and Co) was determined by matched EDS. The samples for STEM studies were prepared using a Zeiss Auriga dual beam focused ion beam (FIB) milling system. The Ga<sup>+</sup> beam acceleration and current were 30 kV and 100 pA respectively.

Atomic force microscopy (AFM) (Veeco/Asylum Research, MFP-3D-SA, USA) in tapping mode was used to observe the surface morphology of the thin films. X-ray photoelectron spectroscopy (XPS) was used to estimate surface cation compositions and binding environments. A CAE analyzer with a pass energy of 100.0 eV and an Al K $\alpha$  (1486.68 eV) X-ray source was used for XPS measurements under  $10^{-9}$  Torr pressure. Sr 3d, Nd 3d, Co 2p and O 1s photoelectron spectra were also analyzed and the quantitative analyses for all of these spectra were performed using XPS Peak 4.1 software.

### 2.3. $^{18}\text{O}$ isotope exchange

For  $^{18}\text{O}$  tracer exchange experiments, the thin films were placed inside a circular platform and heated to 500 °C (~30 °C/min). The circular platform was subsequently isolated from air and filled with 1 atm of tracer oxygen (97.1%  $^{18}\text{O}$  isotope enriched, Beijing Gaisi Chemical Gases Center, China). The tracer filling process was performed in 15 s, and after subsequent annealing for 5 min, the samples in the circular platform were cooled down (~40 °C/min) to roughly 50 °C under 1 atm  $^{18}\text{O}_2$  gas pressure and taken out for ToF-SIMS measurements.

### 2.4. ToF-SIMS depth profiling

ToF-SIMS measurements were used for depth profiling (ToF-SIMS

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