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## Perovskite-triggered dual exsolution of oxygen-deficient CeO<sub>2</sub> matrix and NiFe nanoalloys for enhanced CO<sub>2</sub> electrolysis

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Perovskite cathodes for CO<sub>2</sub> electrolysis offer excellent redox stability but suffer from limited activity. Although *in situ* exsolution of B-site cations is a powerful strategy to alleviate this issue, this process often triggers co-segregation of insulating AO<sub>x</sub> phases, which diminishes active site exposure and ionic-electronic conductivity. Here we addressed the critical issue of insulating phase segregation in conventional exsolved perovskite by developing a Ce-doping strategy in Sr<sub>1.95</sub>Ce<sub>0.05</sub>Fe<sub>1.3</sub>Ni<sub>0.2</sub>Mo<sub>0.5</sub>O<sub>6-δ</sub> (SCeFNM). This material, upon annealing in a reducing atmosphere, allowed *in situ* construction of nanoscale CeO<sub>2</sub>-NiFe/oxide heterostructures (CeO<sub>2</sub>-NiFe@SCeFNM) by co-exsolving oxygen-deficient CeO<sub>2</sub> phase and NiFe alloy nanoparticles (NPs) on the surface. The unique architecture achieved a high current density of 1.57 A cm<sup>-2</sup> at 1.5 V and 850 °C with a CO faradaic efficiency of over 96%, outperforming NiFe@SFNM and their counterparts. Combined results demonstrated that the superior activity mainly came from the synergy within the “three-in-one” heterostructure, where NiFe alloy NPs increased the electronic conductivity, and CeO<sub>2</sub> phase extended the O<sup>2-</sup> migration channels capable of enhancing CO<sub>2</sub> adsorption and activation, while the perovskite backbone ensured structural integrity. This study establishes a universal paradigm for constructing advanced catalysts for diverse applications *via* co-exsolution of metal NPs and defective oxide phases from appropriately A-site-doped perovskites.

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### Green foundation

1. High-temperature CO<sub>2</sub> electrolysis within SOECs has emerged as a transformative pathway, which enables direct conversion of CO<sub>2</sub> into CO or syngas using renewable energy. This study innovatively addresses the critical issue of an insulating SrO phase inherent in conventional exsolution processes by strategically constructing heterostructured CeO<sub>2</sub>-NiFe@SCeFNM as a SOEC cathode material, thereby advancing green chemistry and contributing to sustainable technologies.
2. We successfully achieved efficient conversion of CO<sub>2</sub> into industrially vital CO using renewable electricity in an SOEC, which delivered a high current density of 1.57 A cm<sup>-2</sup> at 850 °C and 1.5 V, together with a high CO faradaic efficiency of over 96%, therefore significantly enhancing carbon utilization efficiency.
3. Future optimization to avoid AO phase segregation of perovskites *via* lowering operating temperatures or substituting rare-earth elements at A-sites could further advance their sustainability and scalable implementation of electrocatalytic carbon-neutral technologies.

## 1. Introduction

The increasing consumption of fossil fuels has led to significant carbon dioxide (CO<sub>2</sub>) emissions, which profoundly impact global warming. An urgency to address climate change, therefore, has propelled CO<sub>2</sub> reduction technologies to the forefront of sustainable energy research, offering a dual solution for CO<sub>2</sub> utilization and renewable energy storage.<sup>1,2</sup> Among them, high-temperature CO<sub>2</sub> electrolysis within solid oxide electrolysis cells (SOECs) has emerged as a promising technology, enabling direct conversion of CO<sub>2</sub> into CO or syngas using renewable energy.<sup>3,4</sup> Despite the remarkable catalytic perform-

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ance of Ni-yttrium stabilized zirconia (Ni-YSZ) cermet as an SOEC cathode, it suffers from intrinsic redox instability, agglomeration and severe coking issues, which critically limit its further utilization at larger industrial-scale application.<sup>5–7</sup> Alternatively, perovskite oxides (e.g.,  $\text{ABO}_3$ ,  $\text{A}_2\text{BO}_4$ ) have been extensively investigated as promising catalysts for SOECs due to their mixed ionic-electronic conductivity and superior redox stability.<sup>8,9</sup> Nevertheless, a major limitation lies in their relatively inferior catalytic activity, which leads to an insufficient electrolysis performance, highlighting the imperativeness of exploring smart design strategies for perovskite oxide electrodes.

Surface engineering *via in situ* exsolution has emerged as a powerful strategy to enhance catalytic activity by enabling controlled growth of nanoscale metallic nanoparticles (NPs) on perovskite oxide surfaces.<sup>4,10–12</sup> This strategy not only achieves a uniform dispersion of catalytic NPs across porous electrode architectures, but also generates abundant oxygen vacancies at the metal–oxide interfaces, thereby creating additional electrochemically active sites that improve  $\text{CO}_2$  adsorption and activation capabilities. Furthermore, it ensures a high operational stability by mitigating active site loss caused by catalyst detachment and/or agglomeration, while maintaining structural integrity under harsh operating conditions.<sup>13</sup> Among various metal NPs (e.g., Fe, Co, Ni, and Cu), *in situ* exsolution of Fe-/Ni-based metals/alloys has been widely employed since Fe shows exceptional  $\text{CO}_2$  adsorption capacity and coking resistance, while Ni demonstrates a superior catalytic activity with the lowest activation energy barrier.<sup>12,14</sup> However, the exsolution of B-site reducible cations may induce the intergrowth of  $\text{AO}_x$  phases, which alters the functional properties of the material.<sup>11,15</sup> Previous studies have demonstrated that exsolution of B-site cations from perovskite oxides triggers SrO co-segregation on occasion—a process driving chronic electrochemical performance decay since the electronically and ionically insulating nature of surface-terminated SrO obstructs surface charge transfer and oxygen transport pathways.<sup>16,17</sup> Moreover, in cation-ordered  $\text{LnBaCo}_2\text{O}_{5+\delta}$  perovskites (Ln = lanthanide), BaO segregation is also kinetically accelerated at temperatures exceeding 400 °C, resulting in a diminished surface coverage of Co active sites on the perovskite oxide framework.<sup>18</sup>

However, it is worth noting that the exsolution of A-site oxides is not always detrimental, since precise design of A-site oxide exsolution offers unprecedented opportunities to tailor  $\text{CO}_2$  adsorption and oxygen exchange reactions, which serves as an alternative approach to enhancing SOEC performance. For instance, the exsolution of CaO and NiFe NPs from  $\text{La}_{0.6}\text{Ca}_{0.4}\text{Fe}_{0.8}\text{Ni}_{0.2}\text{O}_{3-\delta}$  doubled its specific surface area.<sup>19</sup> Likewise, Zhu *et al.* synthesized self-generated Fe/MnO<sub>x</sub> NPs by regulating A-site deficiency, and the interfacial charge redistribution of Fe/MnO<sub>x</sub> optimized  $\text{CO}_2$  dissociation pathways and promoted chemical adsorption and dissociation of  $\text{CO}_2$  molecules on the cathode surface.<sup>20</sup> Moreover, the exsolution of oxides can also increase oxygen vacancy content and boost  $\text{O}^{2-}$  migration. Previous studies have reported that Bi-doped

$\text{La}_{0.4}\text{Sr}_{0.6}\text{Co}_{0.2}\text{Fe}_{0.7}\text{Nb}_{0.1}\text{O}_{3-\delta}$  exsolved  $\text{Bi}_2\text{O}_3$  and CoFe alloy NPs, which raised the oxygen vacancy concentration by 40%,<sup>21</sup> while oxygen vacancy-enriched  $\text{PrO}_x$  NPs enhanced  $\text{O}^{2-}$  migration capability, which accelerated  $\text{O}^{2-}$  exchange and migration processes on the electrode surface.<sup>22</sup> Therefore, precise engineering of oxide-metal/oxide heterointerfaces holds the potential to enhance  $\text{CO}_2$  electrolysis activity and stability. Cerium oxide ( $\text{CeO}_2$ ), due to its exceptional oxygen storage capacity and redox cycling between  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$ , possesses a desirable level of  $\text{O}^{2-}$  conductivity, and the redox couple of  $\text{Ce}^{4+/3+}$  on the surface accelerates  $\text{O}^{2-}$  transfer between  $\text{CO}_2$  and CO. Meanwhile, NiFe alloy NPs, characterized by their high electronic conductivity and robust thermal stability, are promising candidates for  $\text{CO}_2$  dissociation and CO desorption. However, individual NiFe alloy NPs suffer from insufficient  $\text{O}^{2-}$  migration, while pure  $\text{CeO}_2$  lacks the electronic conductivity required for efficient charge transfer in  $\text{CO}_2$  electrolysis.

Recognizing this complementary potential between  $\text{CeO}_2$  and NiFe alloy NPs, herein we designed and synthesized a novel Ce-doped heterostructured catalyst by annealing  $\text{Sr}_{1.95}\text{Ce}_{0.05}\text{Fe}_{1.3}\text{Ni}_{0.2}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SCeFNM) in a reducing atmosphere to strategically construct metallic NPs with oxygen-vacancy-rich  $\text{CeO}_2$  on SCeFNM ( $\text{CeO}_2$ -NiFe@SCeFNM), realizing dual exsolution of NiFe alloy and  $\text{CeO}_2$  NPs with enhanced electronic conductivity,  $\text{O}^{2-}$  migration, and  $\text{CO}_2$  adsorption and activation. Experimental results demonstrated that a cell with a  $\text{CeO}_2$ -NiFe@SCeFNM cathode achieved a comparable current density ( $j$ ) of 1.57  $\text{A cm}^{-2}$  at 850 °C and 1.5 V for pure  $\text{CO}_2$  atmosphere, together with a high CO faradaic efficiency ( $\text{FE}_{\text{CO}}$ ) of over 96% and a stability of more than 120 hours, showcasing an exceptional catalytic activity for  $\text{CO}_2$  electrolysis. The strategic integration of dual phases through doping-induced co-precipitation offers a compelling approach to synergizing their complementary functionalities.

## 2. Experimental methods

### 2.1 Material synthesis

$\text{Sr}_2\text{Fe}_{1.3}\text{Ni}_{0.2}\text{Mo}_{0.5}\text{O}_{6-\delta}$  (SFNM), SCeFNM, and  $\text{La}_{0.4}\text{Ce}_{0.6}\text{O}_2$  (LDC) were obtained *via* a sol-gel method.<sup>23</sup> Stoichiometric amounts of  $\text{Sr}(\text{NO}_3)_2$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$  and  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  were dissolved in EDTA- $\text{NH}_3 \cdot \text{H}_2\text{O}$  combined solution under continuous heating and stirring; citric acid was then introduced into the solution. The molar ratio of EDTA: citric acid: total cation was controlled to be around 1:1.5:1. Subsequently,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  was added to adjust the pH value to around 8. The solution was stirred and heated on a hot plate at 80 °C until the formation of organic resins containing homogeneously distributed cations because of the slow evaporation of the solvent. The formed gels were heated at 300 °C for four hours to remove the organic components and the nitrates, followed by being annealed at 1100 °C for 10 hours to achieve the target powders. NiFe@SFNM and  $\text{CeO}_2$ -NiFe@SCeFNM were pre-



pared by annealing SFNM and SCeFNM powders at 850 °C for 2 hours in a 5% H<sub>2</sub>/Ar atmosphere with a flow rate of 50 mL min<sup>-1</sup> in a tubular furnace. The heating and cooling rates were both controlled at 2 °C min<sup>-1</sup>. The La<sub>0.8</sub>Sr<sub>0.2</sub>Ga<sub>0.8</sub>Mg<sub>0.2</sub>O<sub>3-δ</sub> (LSGM) electrolyte was prepared by a dry-press method, and then calcined at 1450 °C for 5 hours. The (La<sub>0.6</sub>Sr<sub>0.4</sub>)<sub>0.95</sub>Co<sub>0.2</sub>Fe<sub>0.8</sub>O<sub>3-δ</sub> (LSCF) and Ga<sub>0.2</sub>Ce<sub>0.8</sub>O<sub>2-δ</sub> (GDC) powders were used as received.

## 2.2 Material characterization

The crystalline structure of all the synthesized powders was identified by X-ray diffraction (XRD) with Rigaku Rota flex Cu K $\alpha$  radiation (40 kV, 44 mA), and the raw data were analyzed with JADE version 6.5. Microstructures were determined with a high-resolution Zeiss Sigma field emission scanning electron microscope (SEM). The low- and high-resolution transmission electron microscopy (TEM) images were acquired by using a Thermo Scientific Talos F200X STEM at an accelerating voltage of 200/300 kV. Energy-dispersive X-ray spectroscopy (EDX) combined with high-resolution TEM (HR-TEM) was applied to characterize the composition and element distribution. X-ray photoelectron spectroscopy (XPS, Kratos AXIS Ultra) was used to investigate the surface chemistry of SFNM, SCeFNM, and CeO<sub>2</sub>-NiFe@SCeFNM with adventitious carbon (C 1s) at a binding energy (BE) of 284.8 eV as the reference. Temperature-programmed desorption of CO<sub>2</sub> (CO<sub>2</sub>-TPD) was investigated with a Micromeritics chemisorption analyzer (Auto Chem II 2920) to study the CO<sub>2</sub> desorption. The CO<sub>2</sub> adsorption ability was also characterized by Fourier transform infrared (FTIR) spectroscopy (Nicolet iS50). The oxygen vacancy content was measured using an iodometric titration method under Ar atmosphere.

## 2.3 Cell fabrication and measurement

The LDC buffer layer was formed by screen-printing an  $\alpha$ -terpinol/ethyl cellulose-bound slurry onto LSGM followed by 1350 °C calcination for 2 hours. Subsequently, CeO<sub>2</sub>-NiFe@SCeFNM-GDC, NiFe@SFNM-GDC, SCeFNM-GDC, SFNM, and LSCF-GDC powders were separately mixed with a binder composed of  $\alpha$ -terpinol and ethyl cellulose ether to form their corresponding slurries. GDC was incorporated into all cathodes primarily to enhance the oxygen-ion conductivity and extend the triple-phase boundaries. The electrode slurry was screen printed on the LSGM electrolyte, followed by calcining at 1100 °C for 2 hours, to obtain a cell configuration of CeO<sub>2</sub>-NiFe@SCeFNM-GDC||LDC||LSGM||LSCF-GDC. The effective area of the electrode was 0.5 cm<sup>2</sup> and Ag paste was used as the current collector. The as-fabricated single cell was mounted on one end of an alumina support for electrochemical measurements, with the LSCF-GDC anode exposed to ambient air. Before testing, the CeO<sub>2</sub>-NiFe@SCeFNM cathode compartment was purged with 5% H<sub>2</sub>/Ar. Then, pure CO<sub>2</sub> was fed to the cathode at a flow rate of 50 mL min<sup>-1</sup> for testing. A schematic diagram of the high-temperature CO<sub>2</sub> electrolysis setup is shown in Fig. S1. The electrochemical performance of the single cell was evaluated using an EnergyLab XM electro-

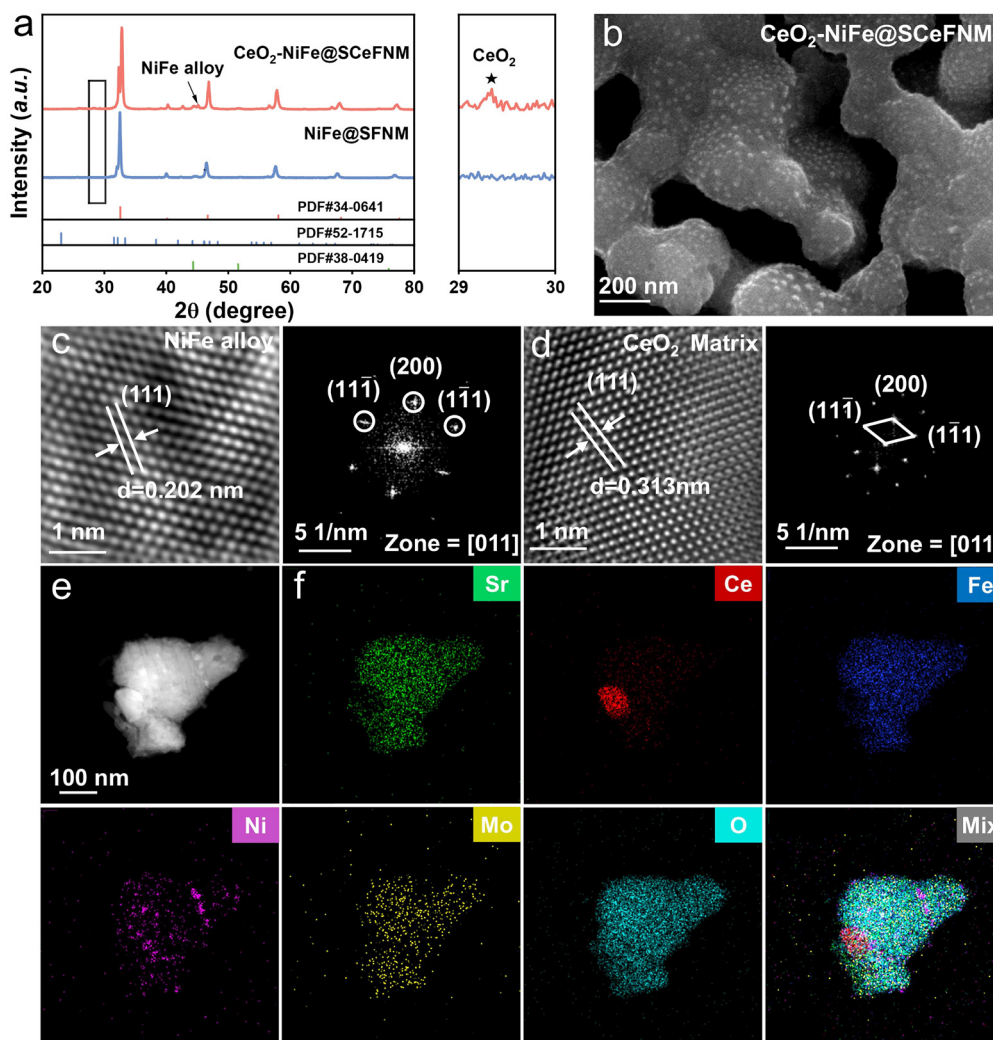
chemical workstation from OCV to 1.6 V at a scan rate of 20 mV s<sup>-1</sup>. Electrochemical impedance spectra (EIS) were acquired with an applied AC amplitude of 10 mV in the frequency range of 0.1 Hz to 1.0 MHz. The CO<sub>2</sub> and CO contents of outlet gas were determined by online gas chromatography (Agilent 8860) using a thermal conductivity detector.

## 3. Results and discussion

The pristine perovskite oxides, SFNM and SCeFNM, were synthesized using a facile sol-gel method, as reported elsewhere.<sup>24,25</sup> The XRD patterns of SFNM and SCeFNM powders after calcination at 1100 °C were detected without impure phase (Fig. S2), but slight shifts of all diffraction peaks toward higher angles were observed for SCeFNM, indicating lattice volume shrinkage due to the partial substitution of a smaller ionic radius of Ce<sup>3+</sup> (1.14 Å) to Sr<sup>2+</sup> (1.34 Å). After annealing SFNM and SCeFNM powders at 850 °C in 5% H<sub>2</sub>/Ar for 2 hours, the double perovskite oxide phase of SCeFNM was transformed into a Ruddlesden-Popper phase (Fig. 1a), together with dual exsolutions of A-site CeO<sub>2</sub> phase and B-site NiFe alloy NPs (CeO<sub>2</sub>-NiFe@SCeFNM). In contrast, only NiFe alloy NPs were *in situ* exsolved from SFNM (NiFe@SFNM), accompanied with a slight phase transformation. To gain insights into the microstructural features, SFNM, SCeFNM, NiFe@SFNM, and CeO<sub>2</sub>-NiFe@SCeFNM powders were subjected to SEM analysis. It was seen that SFNM and SCeFNM specimens showed smooth network structures (Fig. S3) whereas substantial NiFe alloy NPs appeared on the reduced SFNM and SCeFNM. Different from NiFe@SFNM, SCeFNM with Ce doping possessed a greater amount of exsolved NiFe alloy NPs, alongside a minor quantity of CeO<sub>2</sub> NPs (Fig. 1b). For further confirmation, HR-TEM was conducted, and it was found that lattice spacings of 0.202 and 0.313 nm were observed in HR-TEM images (Fig. 1c-d and S4) which corresponded to the (111) planes of CeO<sub>2</sub> and NiFe alloy, respectively. Accordingly, the high-angle annular dark-field scanning TEM (HAADF-STEM) image and EDX elemental mapping of CeO<sub>2</sub>-NiFe@SCeFNM (Fig. 1e and f) demonstrated that the perovskite oxide surface was uniformly dispersed with CeO<sub>2</sub> and abundant NiFe alloy NPs with an average size of 17.5 ± 3.2 nm, while other elements (*e.g.*, Sr, Mo, O) were homogeneously distributed within the perovskite oxide matrix. Moreover, the exsolved NPs were firmly embedded on the CeO<sub>2</sub>-NiFe@SCeFNM substrate, indicating the presence of strong oxide-metal/oxide interactions at the heterointerfaces.

Surface chemical variation of the as-synthesized perovskite oxides was characterized *via* XPS. The XPS full survey spectrum exhibited a Ce element signal in the CeO<sub>2</sub>-NiFe@SCeFNM sample, further confirming the presence of Ce<sup>4+</sup> (Fig. S5). Clearly, Fig. 2a and b showed that an increase in A-site Ce-doping led to a decrease in the intensities of Fe<sup>3+</sup> and Ni<sup>3+</sup> species instead of an increase in those of Fe<sup>2+</sup> and Ni<sup>2+</sup> species. This implied that increasing A-site Ce-doping reduced the oxidation states of Fe and Ni, and caused an enhanced





**Fig. 1** (a) XRD patterns of NiFe@SFNM and CeO<sub>2</sub>-NiFe@SCeFNM, together with an enlargement of the region at 29–30°. (b) SEM image of CeO<sub>2</sub>-NiFe@SCeFNM. HR-TEM images and corresponding FFT patterns of (c) NiFe NPs and (d) CeO<sub>2</sub> NPs. (e) HADDF-STEM image of CeO<sub>2</sub>-NiFe@SCeFNM with (f) EDX mappings of all elements.

electronegativity, which induced the formation of more oxygen vacancies in turn to maintain the charge neutrality. Notably, two additional peaks at 707 and 852 eV were observed for CeO<sub>2</sub>-NiFe@SCeFNM, which were ascribed to the presence of Fe<sup>0</sup> and Ni<sup>0</sup>. Moreover, the O 1s spectra were deconvoluted into three subpeaks, representing the lattice oxygen (O<sub>Latt</sub>), the adsorption oxygen (O<sub>Ads</sub>), and the surface carbonate/hydroxyl oxygen (CO<sub>3</sub><sup>2-</sup>/OH<sup>-</sup>) species, respectively.<sup>26</sup> Typically, the peak of O<sub>Ads</sub> represented oxygen vacancies, and it is worth noting that CeO<sub>2</sub>-NiFe@SCeFNM demonstrated a higher concentration of O<sub>Ads</sub> as compared with SFNM and SCeFNM (Fig. 2c), confirming its oxygen vacancy concentration had a considerable enhancement, which aligned well with the iodine titration results in Fig. 2d, confirming its superiority for CO<sub>2</sub> adsorption. To examine the impact of oxygen vacancies on CO<sub>2</sub>, its adsorption behaviors on SFNM, SCeFNM, and CeO<sub>2</sub>-NiFe@SCeFNM powders were explored in the tempera-

ture range of 50–850 °C using CO<sub>2</sub>-TPD. There were no desorption peaks observed at low temperatures (<300 °C) in Fig. 2e, while the peaks in the high-temperature range (>300 °C) were mainly associated with the desorption of chemisorbed CO<sub>2</sub>.<sup>27</sup> Clearly, the peak area for CeO<sub>2</sub>-NiFe@SCeFNM, benefitting from the exsolved CeO<sub>2</sub> phase with abundant oxygen vacancies, was significantly larger than those for SFNM and SCeFNM, indicative of a superior CO<sub>2</sub> adsorption capacity.<sup>28</sup> The elevated desorption temperature of 754 °C indicated an improved bonding ability between CO<sub>2</sub> molecules and perovskite oxides,<sup>16</sup> which coincided well with the working temperatures of SOECs. Furthermore, since carbonates are critical intermediate species in the CO<sub>2</sub> electrolysis process,<sup>29</sup> CO<sub>2</sub> chemisorption was further characterized by FTIR spectroscopy with samples being exposed to CO<sub>2</sub> at 800 °C for 10 hours. As shown in Fig. 2f, the CO<sub>3</sub><sup>2-</sup> absorption signals in the infrared region of ~1440 cm<sup>-1</sup> for CeO<sub>2</sub>-NiFe@SCeFNM were stronger



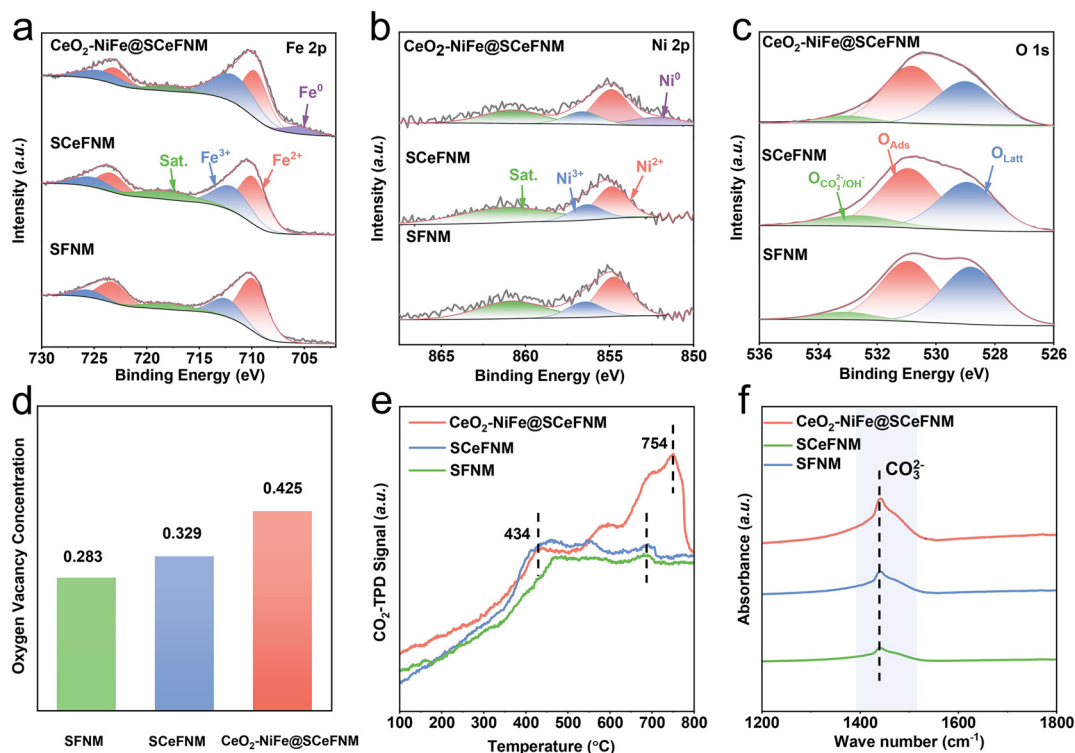


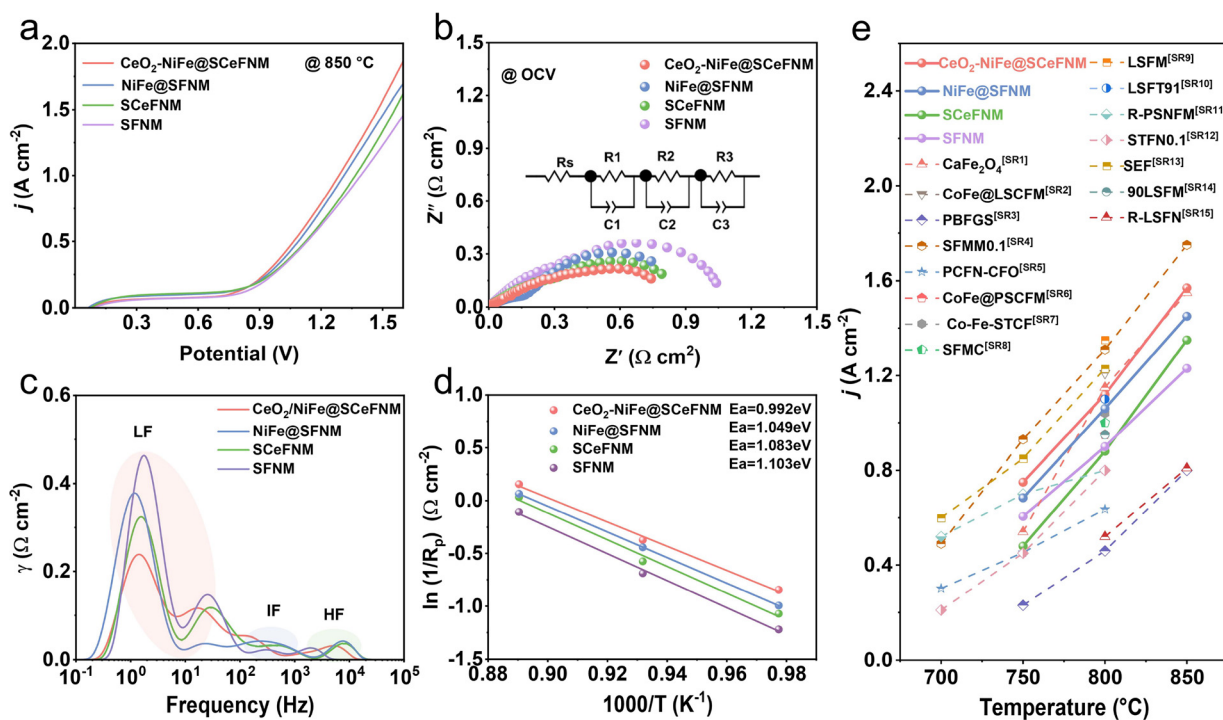
Fig. 2 (a) Fe 2p spectra, (b) Ni 2p spectra, (c) O 1s spectra, (d) oxygen vacancy concentration determined by iodometric titration, (e) CO<sub>2</sub>-TPD plots and (f) FTIR spectra of SFNM, SCeFNM, NiFe@SFNM and CeO<sub>2</sub>-NiFe@SCeFNM.

as compared to SFNM and SCeFNM, confirming that CeO<sub>2</sub>-NiFe@SCeFNM could significantly enhance CO<sub>2</sub> adsorption capacity attributed to the greater amount of oxygen vacancies.<sup>30</sup> In particular, *in situ* FTIR spectra for CeO<sub>2</sub>-NiFe@SCeFNM all presented strong CO<sub>3</sub><sup>2-</sup> signals from 750 to 850 °C (Fig. S6), demonstrating its robust CO<sub>2</sub> adsorption capability.

To unravel the impacts of exsolved CeO<sub>2</sub> phase and NiFe alloy NPs as well as their constructed oxide-metal/oxide hetero-interface on CO<sub>2</sub> electrolysis activity, SFNM, SCeFNM, NiFe@SFNM, and CeO<sub>2</sub>-NiFe@SCeFNM were fabricated as cathodes within SOECs supported by LSGM electrolyte, and were tested in pure CO<sub>2</sub> atmosphere from 750 to 850 °C. Based on the current-voltage (*I*-*V*) curves, a gradual increase in *j* was observed for all the samples with an order of SFNM < SCeFNM < NiFe@SFNM < CeO<sub>2</sub>-NiFe@SCeFNM (Fig. 3a and S7), delivering a *j* of 1.57, 1.45, 1.35 and 1.23 A cm<sup>-2</sup> at 1.5 V and 850 °C, respectively (Table S1). This implied that as compared to conventional SFNM with only NiFe alloy NPs and pristine SFNM, CeO<sub>2</sub>-NiFe@SCeFNM provided more reactive centers precisely due to the dual exsolution of precipitated CeO<sub>2</sub> and NiFe NPs, both of which synergistically facilitated the activity. Concurrently, the key reaction steps and kinetic behaviors during CO<sub>2</sub> electrolysis were investigated using EIS (Fig. S8) and the distribution of relaxation times (DRT) (Fig. S9). The Nyquist plots in Fig. 3b illustrate that the polarization resistance (*R*<sub>p</sub>) values of SFNM, SCeFNM, NiFe@SFNM, and CeO<sub>2</sub>-

NiFe@SCeFNM cathodes under open-circuit voltage (OCV) at 850 °C were 1.025, 0.885, 0.857, and 0.792 Ω cm<sup>2</sup>, respectively, in accordance with the *j* variation trend. Given that the contributions from the LSCF anode and LSGM electrolyte to the total resistance were quite close for all cells, the polarization resistance discrepancy stemmed from the different cathodes. Based on previous studies involving DRT analysis it was known that the peaks at low, intermediate, and high frequency (LF, IF, and HF) are associated with CO<sub>2</sub> adsorption and activation, migration of O<sup>2-</sup> in the electrodes, and charge/ion transfer at the electrode-electrolyte interface, respectively.<sup>13,31</sup> Apparently, the dual exsolution treatment reduced the LF region area while leaving the IF and HF regions unaffected (Fig. 3c), suggesting that the diminished LF contribution for the CeO<sub>2</sub>-NiFe@SCeFNM cathode optimized the CO<sub>2</sub> adsorption and activation kinetics. Furthermore, the *R*<sub>p</sub> value of CeO<sub>2</sub>-NiFe@SCeFNM decreased markedly with increasing applied potential (Fig. S8a and Table S2), reflecting an accelerated CO<sub>2</sub> electrolysis kinetics under high potentials. Moreover, increasing the applied potential could lower the LF region area, thus improving CO<sub>2</sub> adsorption and activation, and the ultimate CO<sub>2</sub> electrolysis activity (Fig. S9a). In contrast, raising the operating temperature lowered both the ohmic resistance (*R*<sub>o</sub>) and *R*<sub>p</sub> (Fig. S8e and Table S3), and the accordingly reduced IF and LF region areas in DRT plots revealed that the increase in temperature not only enhanced CO<sub>2</sub> adsorption and activation, but also accelerated O<sup>2-</sup> migration at the electrode (Fig. S9e).<sup>32</sup>





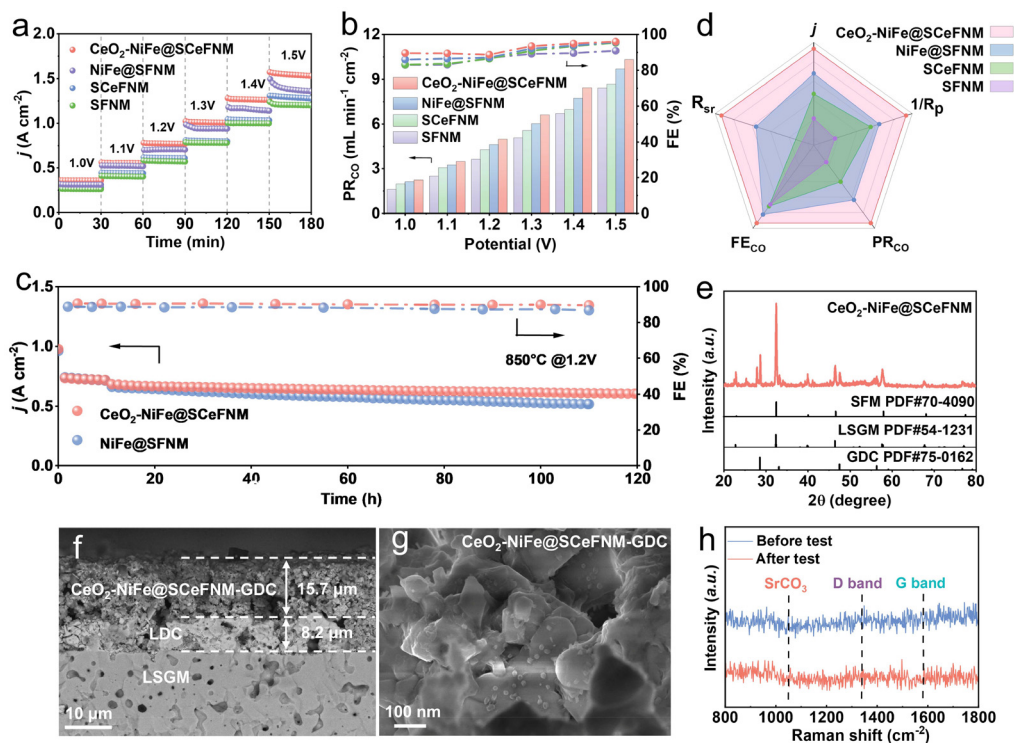
**Fig. 3** (a)  $I$ - $V$  curves, (b) Nyquist plots and (c) DRT results of SFNM, SFCeFNM, NiFe@SFNM and CeO<sub>2</sub>-NiFe@SFCeFNM at 850 °C. (d) Arrhenius plots of various cathodes from 750 to 850 °C. (e) Activity comparison of all samples in this study with previously reported state-of-the-art materials for CO<sub>2</sub> electrolysis at 1.5 V, where SR represents the reference in SI.

This was further verified by the electrochemical activation energy, an important parameter to assess the CO<sub>2</sub> electrolytic process. The Arrhenius plots in Fig. 3d show that the CeO<sub>2</sub>-NiFe@SFCeFNM cathode delivered a smaller activation energy of 0.992 eV than its counterparts, indicative of a reduced cathodic energy barrier. As a result, benefiting from the synergy of NiFe alloy NPs and CeO<sub>2</sub> phase, CeO<sub>2</sub>-NiFe@SFCeFNM achieved the optimal CO<sub>2</sub> electrolysis performance among all the control materials, and surpassed that of most of the state-of-the-art cathode materials reported to date, as shown in Fig. 3e, again confirming its superiority for CO<sub>2</sub> electrolysis in SOECs.

As crucial parameters to evaluate CO<sub>2</sub> conversion efficiency, CO production rate (PR<sub>CO</sub>) and FE<sub>CO</sub> are equally important for the development of SOECs. The potentiostatic CO<sub>2</sub> electrolysis measurements at varying applied potentials revealed that CeO<sub>2</sub>-NiFe@SFCeFNM achieved maximum  $j$  in a wide potential range from 1.0 to 1.5 V (Fig. 4a), which matched well with the  $I$ - $V$  results. Additionally, the corresponding FE<sub>CO</sub> and PR<sub>CO</sub> under different applied potentials at 850 °C were also evaluated (Fig. 4b). The single cell with the CeO<sub>2</sub>-NiFe@SFCeFNM cathode achieved a high FE<sub>CO</sub> of 96.03%, surpassing the 90.94% on SFNM and closely matching those of 95.72% on NiFe@SFNM and 95.35% on SFCeFNM in CO<sub>2</sub>-to-CO conversion, at 1.5 V and 850 °C. In addition, at 1.5 V, the PR<sub>CO</sub> of CeO<sub>2</sub>-NiFe@SFCeFNM reached 10.32 mL min<sup>-1</sup> cm<sup>-2</sup>, faster than those of 9.68, 8.68 and 8.42 mL min<sup>-1</sup> cm<sup>-2</sup> over NiFe@SFNM, SFCeFNM, and SFNM, respectively, which further

confirmed that except for  $j$ , co-exsolution of CeO<sub>2</sub> phase and NiFe alloy NPs also improved CO<sub>2</sub> conversion rate. The long-term stabilities of the cells with different cathodes were also investigated, and Fig. 4c shows  $j$  and FE<sub>CO</sub> as a function of time under a constant potential of 1.2 V at 850 °C. The CeO<sub>2</sub>-NiFe@SFCeFNM-assembled cell could maintain a good performance with a negligible  $j$  decay rate of 0.793 mA h<sup>-1</sup> during continuous operation of 120 hours, and retained a steady FE<sub>CO</sub> of 90%, superior to that of the cells with NiFe@SFNM, SFCeFNM, and SFNM. For a better holistic view, a radar map presenting  $j$  (A cm<sup>-2</sup>),  $1/R_p$  (Ω<sup>-1</sup> cm<sup>-2</sup>), PR<sub>CO</sub> (mL min<sup>-1</sup> cm<sup>-2</sup>), FE<sub>CO</sub> and stability retention rate per 100 hours ( $R_{sr} = j_{100}/j_{initial}$ )<sup>25</sup> is plotted in Fig. 4d for comparison. It illustrated clearly that dual exsolution was more beneficial for CO<sub>2</sub> electrolysis, which also highlighted the critical role of CeO<sub>2</sub> in tuning CO<sub>2</sub> electrolysis activity. In addition, no extra phase and impurity were observed in the XRD pattern post-test for the CeO<sub>2</sub>-NiFe@SFCeFNM cathode (Fig. 4e), indicating a good structural stability under harsh electrolysis conditions. Meanwhile, the cathode-electrolyte interface remained closely stacked, and no delamination was detected after long-term CO<sub>2</sub> electrolysis operation (Fig. 4f and S10a, b). Importantly, the perovskite oxide matrix still retained the uniformly anchored *in situ* exsolved NPs without severe agglomeration for the CeO<sub>2</sub>-NiFe@SFCeFNM cathode (Fig. 4g). However, there were no noticeable *in situ* exsolved NPs on the NiFe@SFNM cathode (Fig. S10c), clarifying a good structural resilience under high-temperature harsh conditions in the mixture of



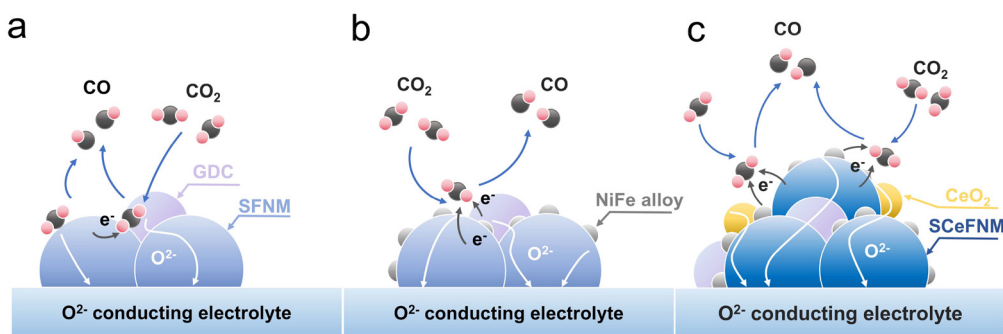


**Fig. 4** (a) The potentiostatic measurements for CO<sub>2</sub> electrolysis and (b) PR<sub>CO</sub> and corresponding FE<sub>CO</sub> under different applied potentials of all samples. (c) Long-term stability tests and the corresponding FE<sub>CO</sub> at 1.2 V and 850 °C for NiFe@SFNM and CeO<sub>2</sub>-NiFe@SCeFNM. (d) Radar map of SFNM, SCeFNM, NiFe@SFNM and CeO<sub>2</sub>-NiFe@SCeFNM. (e) XRD patterns and SEM images of (f) a cross-section of a single cell and (g) CeO<sub>2</sub>-NiFe@SCeFNM cathode as well as (h) Raman spectra of the CeO<sub>2</sub>-NiFe@SCeFNM cathodes before and after stability testing.

CO<sub>2</sub>/CO, as also confirmed by the Raman spectrum of the CeO<sub>2</sub>-NiFe@SFNM cathode after stability testing in Fig. 4h. Notably, no obvious peaks associated with SrCO<sub>3</sub> (1050 cm<sup>-1</sup>), D-band (1340 cm<sup>-1</sup>) and G-band (1580 cm<sup>-1</sup>) were observed, evidencing the good coking resistance and the strong suppression to Sr segregation of CeO<sub>2</sub>-NiFe@SCeFNM.<sup>27</sup>

To clearly elaborate the mechanism credited for the superior electrochemical activity on CeO<sub>2</sub>-NiFe@SCeFNM, a schematic illustration of the possible reaction pathways over SFNM, NiFe@SFNM and CeO<sub>2</sub>-NiFe@SCeFNM is shown in Fig. 5. It was seen that when SFNM was assembled as a cathode, its activity was limited to the slow gas-solid interface

exchange process involving CO<sub>2</sub> adsorption, activation, and O<sup>2-</sup> migration on the cathode surfaces (Fig. 5a). Nevertheless, the introduction of NiFe alloy NPs characterized by high electronic conductivity could promote charge transfer, and CO<sub>2</sub> adsorption and activation in CO<sub>2</sub> electrolysis, but individual NiFe alloy NPs suffered from insufficient O<sup>2-</sup> migration (Fig. 5b). Thus, we proposed the “three-in-one” strategy in this study by integrating both NiFe alloy NPs and defective CeO<sub>2</sub> phase *in situ* exsolved from SCeFNM (Fig. 5c), which synergistically increased the ionic-electronic conductivity and the O<sup>2-</sup> migration channels from CeO<sub>2</sub> to SCeFNM to promote CO<sub>2</sub> adsorption and activation. In addition, the intimate contact of



**Fig. 5** Schematic illustrations of possible reaction pathways for CO<sub>2</sub> electrolysis over (a) SFNM, (b) NiFe@SFNM and (c) CeO<sub>2</sub>-NiFe@SCeFNM.



SCeFNM, NiFe alloy NPs and CeO<sub>2</sub> at the nanoscale also effectively extended the triple-phase boundary length dedicated to CO<sub>2</sub> electrolysis, thus culminating in the exceptional CO<sub>2</sub> electrolysis activity.

## 4. Conclusions

In summary, we synthesized Sr<sub>1.95</sub>Ce<sub>0.05</sub>Fe<sub>1.3</sub>Ni<sub>0.2</sub>Mo<sub>0.5</sub>O<sub>6-δ</sub> (SCeFNM) using a Ce-doping strategy, and strategically constructed CeO<sub>2</sub>-NiFe/oxide heterostructures by *in situ* co-exsolving oxygen-vacancy-rich CeO<sub>2</sub> phase and NiFe alloy NPs from perovskite oxide (CeO<sub>2</sub>-NiFe@SCeFNM) to avoid the co-segregation of insulating SrO phase. It was found that CeO<sub>2</sub>-NiFe@SCeFNM cathode achieved a *j* of 1.57 A cm<sup>-2</sup> at 850 °C and 1.5 V, and a CO faradaic efficiency of 96%, outperforming NiFe@SFNM without oxygen-deficient CeO<sub>2</sub> phase, and pristine SFNM and SCeFNM. Crucially, the cathode demonstrated an exceptional operational stability over 120 hours without carbon deposition and particle agglomeration, overcoming the degradation limitations of traditional exsolution. Combined results and spectra collectively verified that the enhanced activity exhibited by CeO<sub>2</sub>-NiFe@SCeFNM was mainly derived from the three-in-one structure, where the NiFe alloy NPs on CeO<sub>2</sub>-NiFe@SCeFNM enhanced the electronic conductivity, and the CeO<sub>2</sub> phase facilitated O<sup>2-</sup> migration as well as CO<sub>2</sub> adsorption and activation, while the perovskite oxide framework ensured the structural integrity. The strong interaction between the three phases in the nanodomain creates a “win-win” effect, and results in an optimal CO<sub>2</sub> electrolysis activity, which also presents a promising approach to enhancing SOEC performances by dual exsolution of A-site metal oxides and B-site metal NPs from perovskite oxides.

## Author contributions

Biao Ouyang: conceptualization, investigation, writing – original draft preparation. Ming Yang: validation, data curation. Lin-Bo Liu: methodology. Shuo Liu: formal analysis. Yan Li: data curation. Xian-Zhu Fu: supervision. Yifei Sun: conceptualization. Subiao Liu: conceptualization, project administration, resources, supervision, writing – review and editing. Jing-Li Luo: supervision, validation.

## Conflicts of interest

There are no conflicts of interest to declare.

## Data availability

The data supporting this paper have been included as part of the supplementary information (SI). Supplementary information is available. See DOI: <https://doi.org/10.1039/d5gc04390e>.

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