Robust Ruddlesden-Popper phase $\text{Sr}_3\text{Fe}_{1.3}\text{Mo}_{0.5}\text{Ni}_{0.2}\text{O}_{7-\delta}$ decorated with in-situ exsolved Ni nanoparticles as an efficient anode for hydrocarbon fueled solid oxide fuel cells

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Abstract
A highly efficient Ruddlesden-Popper structure anode material with a formula of $\text{Sr}_3\text{Fe}_{1.3}\text{Mo}_{0.5}\text{Ni}_{0.2}\text{O}_{7-\delta}$ (RP-SFMN) has been developed for hydrocarbon fueled solid oxide fuel cells (HF-SOFC) application. It is demonstrated that a nanostructured RP-SFMN anode decorated with in-situ exsolved Ni nanoparticles (Ni@RP-SFMN) has been successfully prepared by annealing the anode in reducing atmosphere similar to the operating conditions. The phase compositions, valence states, morphologies, and electrocatalytic activities of RP-SFMN material have been characterized in detail. In addition, the in-situ exsolution mechanism of the metallic Ni phase from the parent oxide is clearly explained by using density function theory calculation. The peak output power density at 800°C is significantly enhanced from 0.163 to 0.409 W/cm$^2$ while the electrode polarization resistance is effectively lowered from 0.96 to 0.30 Ω cm$^2$ by the substitution of B-site Fe by Ni, which is attributed to the improved electrocatalytic activities induced by the in-situ exsolved Ni nanocatalysts. Moreover, the single cell with RP-SFMN anode exhibits good stability in 3% H$_2$O humidified H$_2$ and syngas for 110 and 60 h at 800°C, respectively. Our findings indicate that RP-SFMN is a greatly promising anode candidate of HF-SOFCs due to its good electrochemical performance and stability during the operation.

KEYWORDS
density function theory, in-situ exsolution, nanostructured anode, Ruddlesden-Popper oxide, solid oxide fuel cells
1 | INTRODUCTION

Solid oxide fuel cells (SOFC), which can directly convert the chemical energy stored in fuels, such as hydrocarbons into electrical energy, by an electrochemical redox reaction without any intermediate steps, is a promising energy conversion device due to its advantages of low energy consumption, high efficiency, cleanliness, flexibility in using fuel, and no noble metal catalysts, etc.\(^1\)\(^-\)\(^7\) Therefore, it has been considered to occupy an important key position in the future energy system.\(^8\)\(^,\)\(^9\)

Currently, extensive efforts have been focused on the development of novel alternative anode materials because the-state-of-art Ni-based anodes suffer from poor long-term stability, severe carbon coking, and sulfur poisoning when fueled with hydrocarbon fuel. Perovskite type (ABO\(_3\)) mixed ionic-electronic conducting oxides, such as La\(_{0.75}\)Sr\(_{0.25}\)Cr\(_{0.5}\)Mn\(_{0.5}\)O\(_3\), Y-doped SrTiO\(_3\), Sr\(_2\)MgMoO\(_6\)-\(δ\), and Sr\(_2\)Fe\(_{1.5}\)Mo\(_{0.5}\)O\(_{6-δ}\), have attracted much attention due to their excellent long-term stability and resistance to carbon deposition and sulfur poisoning.\(^10\)\(^-\)\(^14\) However, their electrocatalytic activity and electrochemical performance are inferior compared with traditional Ni-based anodes. In this context, a series of novel alternative anode materials have been explored to balance the electrocatalytic activity and long-term stability. The introduction of metallic nanoparticles with superior electrocatalytic activity, such as Ni, Co, and Ru, to form metallic nanoparticles-decorated oxide anode, is an effective strategy to improve the anode electrocatalytic activity and cell electrochemical performance.\(^15\)\(^-\)\(^18\)

In recent years, physical deposition, solution infiltration/ion impregnation, and in-situ exsolution methods have been developed to realize the introduction of high-performance nanoelectrocatalysts.\(^19\)\(^-\)\(^24\) For example, as one of the most studied perovskite-type oxides, Ni-doping Sr\(_2\)Fe\(_{2-x}\)Mo\(_x\)O\(_6-δ\) (SFMN), has been proven to be transformed to Ni-Fe alloy nanoparticles structured SFMN (Ni-Fe@SFMN) anode in the working conditions through the in-situ exsolution process.\(^25\)\(^-\)\(^27\) For a nanostructured anode prepared via the in-situ exsolution method, the active metallic catalysts are first incorporated into the lattice of the parent oxides during the powder synthesis process in an oxidizing atmosphere, and then released from parent oxides to form metallic or alloy nanoparticles with good electrocatalytic activity on the surface of the parent oxides in the reducing atmosphere or working condition. Compared to the conventional methods, including the physical deposition method, solution infiltration/ion impregnation method, the nanoparticles in-situ exsolved from the parent oxides are strongly anchored into the parent oxides, resulting in improved long-term stability. In addition, the anode microstructure can be more easily and precisely controlled by manipulating the working conditions and parent phase composition, and the in-situ exsolved metallic nanoparticles are well-dispersed on the surface of the parent oxides. Based on the above-mentioned advantages, the in-situ exsolution technique is more and more attractive for the preparation of nanostructured anodes with desired electrochemical performance and stability.\(^28\)\(^-\)\(^33\)

Recently, the Ruddlesden–Popper (RP) type oxides with general formula A\(_{n+1}\)B\(_n\)O\(_{3n+1}\) or AO(ABO\(_3\))\(_n\), where A and B are rare earth or alkaline earth ion and transition metal ion, respectively, while n is the layers of perovskites ABO\(_3\) between rock salt AO layers along the crystallographic c direction, have been extensively explored as alternative cathode materials for SOFCs due to their good electrocatalytic activity toward oxygen reduction reaction, long-term stability, and chemical stability, owing to their more significant amount of oxygen vacancies or considerable interstitial oxygen accommodations than perovskite-type materials.\(^12\)\(^,\)\(^28\)\(^-\)\(^34\)\(^-\)\(^39\) Nevertheless, these RP-type oxides, especially RP-type oxides decorated with in-situ grown metallic nanoparticles, have been seldomly chosen as alternative anode materials for SOFCs.

In this work, two RP type oxides Sr\(_2\)Fe\(_{1.5}\)Mo\(_{0.5}\)O\(_7-δ\) (RP-SFM) and Sr\(_3\)Fe\(_{1.3}\)Mo\(_{0.5}\)Ni\(_{0.2}\)O\(_7-δ\) (RP-SFMN), which are consisted of two layers of ABO\(_3\) (SrFe\(_{0.75}\)Mo\(_{0.25}\)O\(_3\) or SrFe\(_{0.65}\)Ni\(_{0.1}\)Mo\(_{0.25}\)O\(_3\)) and one layer of AO (SrO), were prepared as the anode materials by using the citric acid and glycine assisted combustion method. The phase compositions of these materials were recorded by using X-ray diffraction (XRD), while the valance states of each element, including Sr, Fe, Mo, Ni, O, and C, were analyzed by an X-ray photoelectron spectroscopy (XPS). Their morphological evolution was then evaluated by using a scanning electron microscopy (SEM) and a high-resolution transmission electron microscope (HRTEM). Additionally, their phase evolution, as well as their catalytic activity, was determined through energy-dispersive X-ray spectroscopy (EDS), HRTEM, thermogravimetric analysis (TGA), and hydrogen temperature-programmed reduction (H\(_2\)-TPR). Meanwhile, the density function theory (DFT) calculation was used to explain the phase transformation process during the operation. Moreover, the electrochemical properties of these two anodes, including the current density-cell voltage-power density (i-V-p) and the electrochemical impedance spectra (EIS), were studied to demonstrate the evolution of electrocatalytic activity. Finally, the long-term stability and redox stability of RP-SFMN were tested.
2 | RESULTS AND DISCUSSION

2.1 | Phase composition

Figure 1A shows the XRD patterns of RP-SFM and RP-SFMN powders before and after reducing in the H₂ atmosphere. Both of the RP-SFM and RP-SFMN pristine powders have exhibited a typical RP structure (PDF Card No. 96-152-8688). No other phase has been detected in the RP-SFMN powders, indicating that Fe sites in the lattice have been successfully substituted with Ni ions by doping. After reducing the powders at 800°C for 10 h in the H₂ atmosphere, the reduced powders have also maintained the RP structure. However, the magnified XRD patterns of 2θ from 31 to 33° in Figure 1B show that the diffraction peaks have slightly shifted toward a lower angle direction, similar to the results in the literature. It can be explained by the fact that the substitution of Fe³⁺ with Ni²⁺ has triggered off the lattice expansion, as the ionic radius of Ni²⁺ (0.72 Å) is between Fe²⁺ (0.76 Å) and Fe³⁺ (0.64 Å). Moreover, an additional diffraction peak at the 2θ of 43.317°, assigned to metallic Ni (PDF Card No. 96-901-3035), has also been detected for the reduced RP-SFMN powders in Figure 1C. No similar signal is detected for the reduced RP-SFM powders, indicating that Ni ions are easier to be reduced compared to Fe ions, and Ni doping can facilitate the exsolution of B-site metal elements.

Moreover, XPS analysis was also carried out to determine the Ni doping effect on the elemental compositions and valence states. Note that the C Is peak is collected and set as the reference and baseline. As shown in Figure 1D, characteristic peaks of Sr, Fe, Mo, and O elements can be clearly observed for all these four powders. However, Ni signal can only be collected in RP-SFMN powders (Figure 1E), confirming that Ni element has been effectively doped into Fe site. On the contrast, no obvious change for Fe signal has been detected for these four powders ever after reduction and Ni doping (Figure 1F).
Meanwhile, to better understand the evolution of Ni and Fe elements before and after reduction, the Ni 2p and Fe 2p binding energy regions of RP-SFMN powders before and after reduction have been analyzed and presented in Figure 1G-J. Three typical peaks with the XPS binding energies centered at 854.8, 856.2, and 860.9 eV for Ni\(^{2+}\) 2p (Figure 1G) have been detected for pristine RP-SFMN powders, while a mixed valence state is observed for Fe element, which is presented by the Fe\(^{3+}\) peaks located at 709.3 and 723.0 eV as well as Fe\(^{3+}\) peaks centered at 710.1, 711.6, 713.1, 718.3, and 724.2 eV (Figure 1I, J and Supporting information Figure S1).\(^{27,16,43}\) However, after reduction in pure H\(_2\) and 800°C for 10 h, one additionally peak centered at 852.3 eV for Ni\(^0\) has been evidently observed (Figure 1H), indicating the exsolution of Ni element from parent RP-SFMN phase to form metallic Ni phase during the reduction process.\(^{45}\) On the other hand, no visible peak at the binding energy of about 706.4 eV, which is assigned to metallic Fe phase (Fe\(^0\)), can be fitted for both reduced RP-SFM and RP-SFMN powders (Figure 1J and Supporting information Figure S1), demonstrating the excellent phase stability of B-site Fe element in a broad range of oxygen partial pressure up to 800°C.\(^{27,16,44}\) These results are also highly consistent with the clearly detected secondary metallic Ni phase but not Ni-Fe alloy phase in the XRD patterns (Figure 1A-C). In addition, a mixture of Mo\(^{5+}\) and Mo\(^{6+}\) is observed for both these RP oxides (Supporting information Figures S2-3), and the calculated average valence state of Mo element is decreased from +5.85 for pristine RP-SFM material to +5.66 for pristine RP-SFMN material, implying that Ni doping can facilitate the formation of oxygen vacancy because of the charge compensation, which is strongly associated with the in-situ exsolution property of B-site elements.\(^{22–24}\)

### 2.2 Morphology

To further reveal the morphology details of the RP-SFMN powders and determine the phase composition of the in-situ exsolved metallic phase, SEM and HRTEM-EDS images were collected and presented in Figure 2. Different from the clean surface of the pristine RP-SFMN bar sample (Figure 2A), a large number of spherical nanoparticles with a diameter of 32.5 ± 6.1 nm are released from and uniformly distributed on the reduced RP-SFMN substrates (Figure 2B). At the same time, the HRTEM images in Figure 2C-D show that the nanoparticles have been in-situ exsolved from parent RP-SFMN powders and uniformly decorated on the surface of the parent grains after the reduction treatment. The magnified HRTEM images of Figure 2D marked in the yellow square show two typical diffraction fringes with lattice distances of 0.278 and 0.208 nm, respectively, corresponding well to the spacing of the (110) plane for the RP-SFMN powders (PDF Card No. 96-152-8688) and (200) plane for the metallic Ni nanoparticles (PDF Card No. 96-901-3035), as determined by XRD results shown in Figure 1A-C. Almost half of the exsolved particles are beneath the parent oxide surface (Figure 2E), indicating strong interaction and high lattice mismatch. The HAADF image of the reduced RP-SFMN powders (Figure 2F) shows that a significant number of nanoparticles are uniformly exsolved from the parent matrix, whose EDS elemental distribution mapping images (Figure 2G-K) also confirm the aggregation of Ni nanoparticles. The results concluded that Ni nanoparticles structured RP-SFMN (Ni@RP-SFMN) material have been successfully fabricated by the in-situ exsolution technique.

The compatibility of these two RP oxides with La\(_{0.8}\)Sr\(_{0.2}\)Ga\(_{0.8}\)Mg\(_{0.2}\)O\(_3\)-δ (LSGM) and Ce\(_{0.8}\)Sm\(_{0.2}\)O\(_{1.9}\) (SDC) is examined before using them as the SOFC anodes by mixing RP oxides with LSGM or SDC with a weight ratio of 1:1 and then heat treating at 1050°C for 2 h. The XRD patterns of LSGM, SDC, RP-SFM, RP-SFMN, and their mixed powders (Supporting information Figure S4) show no additional diffraction peaks belonging to a foreign substance, demonstrating that RP-SFM and RP-SFMNi materials are both compatible with the LSGM and SDC electrolyte.

### 2.3 In-situ exsolution mechanism

TGA measurements and H\(_2\)-TPR characterization were performed to disclose the in-situ exsolution mechanism of metallic phase from parent RP oxides. Figure 3A shows the weight loss of pristine RP-SFM and RP-SFMN materials exposed to a 3%H\(_2\)-97%N\(_2\) atmosphere in the temperature range of 100–800°C. The first stage (Stage I) at 100–300°C for both the samples is mainly related to the evaporation of water adsorbed on the powders. The weight loss in the temperature range of 300–800°C is related to the release of lattice oxygen from the RP oxides.\(^{45,46}\) For RP-SFM material, the curve has slowly dropped with a mass weight ratio of 1.62% from 300 to 700°C (Stage II), and then decreased dramatically with a weight ratio of 1.22% in the last 50°C (Stage III). However, for the RP-SFMN material, an additional flat stage in little weight loss appears between 500 and 700°C, which corresponds to a large oxygen capacity. Moreover, the last stage starts about 35°C earlier compared to the RP-SFM powders, resulting from the facilitation of the in-situ reduced Ni nanoparticles. The catalytic activity, as well as the reduction property, are also evaluated by the H\(_2\)-TPR in the 10%H\(_2\)-90%Ar atmosphere from
100 to 800°C (Figure 3B). Three typical peaks are detected, which correspond to three physicochemical processes. The first peak appears near 200–300°C, which agrees well with the Stage I of TGA curves, is attributed to the evaporation of adsorbed water. The second positive peak located at 300–600°C, corresponding to Stage II in TGA curves, may be associated with the gradual reduction of Fe$^{3+}$ and Mo$^{6+}$ to lower valence states, such as Fe$^{3+}$, Mo$^{6+}$, and AMoVI$\text{O}_4$ to Fe$^{2+}$, Mo$^{5+}$, and AMoIVO$_3$, respectively. The third peak is overlapped between 600 and 800°C, which can be attributed to the formation of intermediate species or further reduction of Fe and Mo species such as Ni$^{2+}$ to Ni$^0$. The latter two peaks of RP-SFMN material start earlier than the RP-SFM material, again confirming that Ni doping can facilitate the in-situ exsolution. As a result, the RP-SFMN material has a more favorable capacity toward reduction and enhanced catalytic activity.

To better address how the in-situ exsolution phenomenon occurs in the RP-SFMN material and to more
clearly explain why only Ni element can exsolve from the parent oxides, DFT calculations were used to calculate the oxygen vacancies formation energy. The optimized most stable structures of RP-SFM and RP-SFMN are shown in Figure 4. To understand the Ni effect on the bulk oxygen vacancy formation, the bulk oxygen vacancy formation energies of RP-SFM and RP-SFMN materials were compared. Based on the detailed study, considering all possible oxygen vacancy locations, it was found that the most stable oxygen vacancies in RP-SFM and RP-SFMN were located between the Mo and Fe, and Mo and Ni atoms, respectively. The calculated corresponding oxygen vacancy formation energies were 2.47 and 1.87 eV, respectively, indicating that the Ni doping facilitated to release the bulk oxygen leaving the oxygen vacancies, improving the ability of Ni exsolution from the bulk.
2.4 Electrochemical performance

Electrolyte-supported single cells with the configuration of RP-SFM(RP-SFMN)-SDC/LSGM/La0.6Sr0.4Co0.2Fe0.8O3–Ce0.9Gd0.1O1.95 (LSCF-GDC) are fabricated for power generation. As shown in Supporting information Figures S5 and S6 that ∼400 μm-thick LSGM electrolyte is well connected to ∼20 μm-thick RP-SFMN-SDC (or RP-SFM-SDC) anode and ∼50 μm-thick LSCF-GDC cathode. According to the $i$–$V$–$p$ curves (Figure 5A), both the RP-SFM and RP-SFMN single cells present an open-circuit voltage (OCV) up to 1.0 V at 800°C when exposing the anode and the cathode to 40 mL/min flowing 3%H2O humidified H2 and static ambient air, respectively. The value is consistent with theoretical Nernst potential, indicating that the cells are well sealed with no gas leakage. At 800°C, the RP-SFM single cell has generated a peak power density ($p_{\text{max}}$) of 0.163 W/cm2, which remarkably increases to 0.409 W/cm2 for the RP-SFMN cell. EIS are also collected under OCV conditions to evaluate the electrode polarization resistance ($R_p$), which is recognized by the intercept between two intersections at the x-axis. As shown in Figure 5B, the RP-SFM single cell has an $R_p$ of 0.96 Qcm², which decreases to 0.30 Qcm² for the RP-SFMN one. These results demonstrate that Ni doping can effectively improve cell performance, and RP-SFMN is a promising alternative anode for SOFC.

It is well-known that the overall electrode reaction process consists of several subelectrode reaction processes, and the rate-limiting substep responsible for the electrode reaction process can be effectively separated and identified by using the distribution of relaxation times (DRT) technique.26,49–52 To better understand the effect of Ni doping on electrochemical performance, EIS has been further analyzed in detail and shown in Figure 5C by using the DRT technique. Each spectrum can be divided into four peaks named P1, P2, P3, and P4, indicating that the whole electrode reaction is possibly related by four substeps. According to the results in the literature, P1 and P2 located in the low frequency of 0.1–32 Hz are possibly associated with gas conversion including gas adsorption, dissociation, and ionization substeps. P3 and P4 in the frequency range of 32–4000 Hz could be assigned to the electrochemical substeps, involving oxygen ion ($O^{2-}$) bulk diffusion to three-phase boundaries (TPBs), charge transfer, and surface diffusion.26,51 The polarization resistance, shown as the peak area, indicates that it has been remarkably reduced for the RP-SFMN because the in-situ exsolved Ni nanoparticle can serve as an efficient electrocatalyst for the hydrogen oxidation reaction ($H_2 + O^{2-} = H_2O + 2e^-$). Therefore, the enhanced electrode performance can be attributed to the in-situ exsolved Ni nanoparticle from RP-SFMN parent oxides (Supporting information Figure S6B).

Moreover, the electrochemical performance of RP-SFMN anode at different operating temperatures is also studied. As shown in Figure 6A, $p_{\text{max}}$ value is obtained to be 0.131, 0.243, 0.409, and 0.603 W/cm² at 700, 750, 800, and 850°C, respectively. In addition, the corresponding $R_p$ values, as well as the ohmic resistance ($R_{\text{ohmic}}$) and total resistance ($R_{\text{total}}$) at OCV and 0.8 V conditions, are also recorded by collecting the EIS at different operating temperatures and applied voltages, which are all summarized in Figure 6B and C. It can be seen from Figure 6B that $R_{\text{ohmic}}$, described by the high-frequency intersection at $x$-
FIGURE 6 (A) The i–V–p curves, (B) the Nyquist plots of the EIS, and (C) the DRT analysis results of (B) for the single cell with RP-SFMN-SDC anode measured at 700–850 °C with feeding 40 mL/min 3%H₂O humidified H₂ to the anode and exposing the cathode to ambient air. (D) The evolution of $p_{\text{max}}$, $R_{\text{total}}$ operated at OCV and 0.8 V, and (E) current density operated under a constant cell voltage of 0.8 V as a function of elapsed time for the RP-SFMN-SDC single cell measured at 800 °C by exposing the anode and the cathode to 40 mL/min flowing 3%H₂O humidified H₂ and static ambient air, respectively.

axis, is measured to be 0.485, 0.346, 0.270, and 0.223 Ωcm² at 700, 750, 800, and 850 °C, respectively, while the corresponding $R_p$ value is calculated to be 1.357, 0.522, 0.298, and 0.196 Ωcm², respectively. The decrease of $R_{\text{ohmic}}$ is ascribed to the increased oxygen ion conductivity of the LSGM electrolyte material at higher working temperature, while the lowered $R_p$ can be attributed to the increased oxygen ion conductivity and enhanced electrocatalytic activity of the electrodes.

Meanwhile, these EIS measured at 700–850 °C are also further analyzed by using DRT technique. As shown in Figure 6C that four typical peaks in the entire frequency range, named as P1–P4, can be clearly distinguished for all the DRT analysis results of these EIS, and the heights for the peaks are all gradually decreased with increasing the operating temperature, indicating that not only the low-frequency gas conversion process in the electrodes but also high-frequency electrode surface and bulk diffusion process have been effectively accelerated by raising the working temperature. These results are highly associated with the increased oxygen ion conductivity and enhanced electrocatalytic activity of the electrodes. Additionally, the evolution of $p_{\text{max}}$ and $R_{\text{total}}$ operated at OCV and 0.8 V conditions over the elapsed time is also recorded for the single cell with RP-SFMN-SDC anode, and the results are shown in Figure 6D. It is found that the $R_{\text{total}}$ values at OCV and 0.8 V are both gradually lowered from the initial values of 0.59 and 0.76 Ω cm² to 0.57 and 0.63 Ω cm² after exposing the anode to 3%H₂O humidified H₂ for 60 h, and then these two values are almost stable with a fluctuation lower than 0.05 Ω cm² in the following 50-h operation, indicating that three stages, simplified as “activation-stabilization-degradation,” can be clearly observed during the durability testing. The activation in the initial stage
FIGURE 7 (A) The i–V–p curves, (B) the Nyquist plots of the EIS, and (c) the DRT analysis results of (B) for the single cell with RP-SFMN-SDC anode measured at 700–850°C with feeding 30 mL/min 3%H₂O humidified syngas to the anode and exposing the cathode to ambient air, and (D) current density operated under a constant cell voltage of 0.7 V as a function of elapsed time for the RP-SFMN-SDC single cell measured at 800°C by exposing the anode and the cathode to 30 mL/min flowing 3%H₂O humidified syngas and static ambient air, respectively.

is possibly attributed to the gradually in-situ exsolved Ni nanocatalysts from the parent oxide, while the degradation after long-term isothermal operation is probably ascribed to the decreased TPBs caused by the coalescence of in-situ exsolved Ni nanoparticles. Note that in view of the fact that $R_{\text{ohmic}}$ almost does not change during the test, the evolution of $R_p$ can be obtained from the evolution of $R_{\text{total}}$. At the same time, $p_{\text{max}}$ is continuously increased from 0.369 to 0.476 W/cm² in the initial 60 h, and then drops slightly to 0.445 W/cm², which is consistent with the evolution of $R_{\text{total}}$ and $R_p$ during the 110-h operation. Figure 6E presents the time dependence of the current density, which is performed on a single cell at 800°C with a constant cell voltage of 0.8 V. It is also found that no obvious degradation of current density is observed during the 110-h operation, which is also consistent with the stable $p_{\text{max}}$ and $R_{\text{total}}$ shown in Figure 6D. These results indicate the excellent stability of the single cell and RP-SFMN anode during the operation.

Finally, the electrochemical performance of RP-SFMN single cell toward 3%H₂O humidified syngas (mixture of H₂ and CO, 67%H₂–33%CO) is also investigated, as shown from the i–V–p curves in Figure 7A, the $p_{\text{max}}$ value has decreased from 0.409 to 0.213 W/cm² at 800°C after switching the fuel from H₂ to syngas, since the anode has a lower electrochemical activity toward CO oxidation.56–58 However, as summarized in Supporting information Table S1 that the $p_{\text{max}}$ of RP-SFMN single cell achieved in the syngas fuel is still much higher than that of Ni-based anodes and some ceramic anodes such as Sr₂TiMoO₆−δ and Laₐ₀.₇₅Sr₀.₂₅Cr₀.₅Mn₀.₅O₃−δ, (NiO-La₀.₅Sr₁.₅MnO₄+δ-H₂O: 0.061 W/cm², Sr₂TiMoO₆−δ: 0.164 W/cm², La₀.₇₅Sr₀.₂₅Cr₀.₅Mn₀.₅O₃−δ: 0.119 W/cm²).56,59–61 while comparable to that of other ceramic anodes, such as 0.270 W/cm² for La₀.₆₅Sr₀.₃Ce₀.₀₅Cr₀.₅Fe₀.₅O₃−δ and 0.240 W/cm² for La₀.₇₅Sr₀.₂₅Cr₀.₅Fe₀.₅O₃−δ–SDC composite anode.62,63

Polarization resistance of the single cell operated in the 3%H₂O humidified H₂ and syngas is also investigated according to the EIS. As shown in Figure 7B, the ohmic resistance, $R_{\text{ohmic}}$, recognized as the first intersection of the Nyquist plot with the x-axis, remains stable. However, the total resistance, $R_{\text{total}}$, recognized as the second
intersection of the Nyquist plot with the x-axis, has remarkably increased from 0.54 to 0.76 Ωcm² after switching the fuel to syngas, agreeing well with the reduced $p_{\text{max}}$ in Figure 7A. The EIS is further analyzed using the DRT method to disclose the difference in electrochemical performance between the two kinds of fuel. The high-frequency peak (P4) is almost the same. However, the low-frequency peaks (P1–P3) are remarkably increased, indicating a declined gas conversion rate of syngas fuel due to a lower electrocatalytic activity toward CO (Figure 7C).

The short-term stability of the single cell with the RP-SFMN anode running on syngas is shown in Figure 7D. During the initial 21-h potentiostatic test at 0.7 V, the current density has decreased by 54% from 0.312 to 0.144 A/cm². However, considering the excellent redox stability of RP oxide, the single cell is regenerated by treating the anode in the air at 800°C for 12 h and then reducing it again in the 3%H₂O humidified H₂ atmosphere for 6 h. After the regeneration operation, the current density has completely recovered up to 0.200 A/cm² and maintained stably in the following 16 h, indicating a prolonged service time of RP-SFMN anode. The microstructure of the post-test RP-SFMN anode is also examined (Supporting information Figure S6), where no carbon has been formed due to the strong interaction between isolated Ni nanoparticles and the parent substrate.

2.5 | Optimization mechanism

The optimization mechanism of the RP-SFMN-SDC anode precipitated by Ni nanoparticles can be schematically explained in Figure 8. As can be seen in Figure 8A, the single cell studied in this work is composed of dense LSGM electrolyte and electrodes covered on both sides including RP-SFMN-SDC anode and LSCF-GDC cathode. During SOFC operation, oxygen ion ($O^{2-}$) reaches the anode from the cathode through the electrolyte, while electron ($e^-$) arrives at the cathode from the anode through the external circuit. However, after reduction treatment by exposing the anode to the hydrocarbon fuel, Ni alloy particles were evenly precipitated on the surface of the RP-SFMN matrix (Figure 8B). As shown in Figure 8C, two paths for fuel (syngas or H₂) oxidation, marked as Path 1 and Path 2, can be observed. For Path 1, a fuel oxidation reaction occurs on the bare RP oxide with relatively lower electrocatalytic activity, resulting in higher activation energy. In the contrast, as schematically shown in Path 2, the fuel oxidation reaction can be significantly accelerated and the activation energy can be effectively lowered by the in-situ exsolved Ni nanoparticles with greatly enhanced electrocatalytic activity toward fuel oxidation.

3 | CONCLUSIONS

In summary, a promising anode material candidate, the in-situ exsolved Ni nanoparticles decorated RP-SFMN, has been successfully prepared by annealing in flowing humidified H₂. The phase composition, morphology, and valence states are characterized to verify the exsolution of Ni nanoparticles from the parent oxide. The in-situ exsolved Ni nanoparticles, serving as electrocatalytical active sites for the HOR, could significantly improve catalytic activity for hydrocarbon fuel oxidation, thus, leading to significantly decreased $R_p$ value from 0.96 to 0.30 Ωcm² at 800°C. In addition, the $p_{\text{max}}$ values of 0.476 and 0.213 W/cm² are achieved for the single cell fueled with humidified H₂ and syngas, respectively. Moreover, the electrochemical performance of the single cell stays stable when exposing the anode to humidified H₂ and syngas. These excellent features illustrate that RP-SFMN can be a promising candidate as an anode of SOFCs, and the results obtained in this work can also guide the development of other nanostructured ceramic electrodes for energy conversion and storage devices applications.

4 | MATERIALS AND METHODS

4.1 | Synthesis of powders

RP-SFM and RP-SFMN powders were synthesized by the citric acid- and glycine-assisted combustion method. A stoichiometric amount of (NH₄)₆Mo₇O₄•4H₂O, citric acid, Sr(NO₃)₂, Fe(NO₃)₃•9H₂O, Ni(NO₃)₂•6H₂O, and glycine were dissolved in the deionized water and stirred at 70–80°C for 3 h to form a homogeneous solution. The molar ratio of citric acid/glycine:metal ion was 1.5:1.1. The solution was then transferred to an evaporator and heated at 70–80°C for 3 h to form a homogeneous solution. The molar ratio of citric acid/glycine:metal ion was 1.5:1.1. The solution was then transferred to an evaporator and heated at 250°C. After high-temperature evaporation, the solution has been converted into sol, gel, and xerogel, which spontaneously ignited to produce RP-SFM (RP-SFMN) precursor powders. Finally, RP-SFM (RP-SFMN) powders with a RP structure were subjected to a heat treatment at 1050°C for 5 h in air. The reduced RP-SFMN powders were obtained by reduction at 800°C for 10 h in a pure hydrogen atmosphere. SDC powders, LSGM powders, and LSCF–GDC cathode ink were all purchased from FuelCellMaterials Inc.

4.2 | Fabrication of single cells

Electrolyte-supported single cells with a configuration of RP-SFM-SDC(RP-SFMN-SDC)/LSGM/LSCF–GDC were prepared to evaluate the electrochemical performance.
Dense LSGM electrolyte with a thickness of ∼400 μm was obtained by pressing commercial LSGM powders into pellets and then sintering at 1400°C for 5 h. The RP-SFM and RP-SFMN anode slurry was prepared by mixing the electrode powders with α-terpineol in a weight ratio of 1:1.3. The as-prepared anode ink was screen-printed on one side of the LSGM pellet, while LSCF–GDC commercial cathode ink was screen-printed on the other side. The single cells were then dried under an infrared lamp and calcined at 1050°C for 2 h. Gold(Au) paste was printed on both sides of the electrodes and calcined at 800°C to serve as the current collector. The effective cell area was 0.2 cm².

4.3 Characterization

Phase compositions of the pristine powders and reduced powders were examined by XRD (Xpert Pro) with Cu Kα radiation, while XPS (ESCALAB250Xi) was used to determine valence states. SEM (MIRA 3, Tescan) and HRTEM (Japan, Talos F200x) were applied to observe the microstructure of the cells as well as the anodes. The element distributions and lattice structure of the powders were determined via HRTEM and EDS (Aztex, Oxford Instrument). TGA of these two pristine powders was carried out at a heating rate of 10°C/min in a 3%H2–97%N2 atmosphere in the temperature range of 100–800°C by using a thermogravimetric analyzer (HTC-01, Henven) to determine the weight loss regime, while H2-TPR (VDSorb-91i, VODO) measurement was performed under a flow of 5% H2/N2 in 20 sccm using a linear heating rate of 10°C/min from 100°C temperature up to 800°C.

The home-made setup used for electrochemical performance measurements can be schematically displayed by Supporting information Figure S7. After sealed to the alumina tube by conducting paste and ceramic adhesive and dried under an infrared lamp, the single cells were fastened in a furnace. A 3% H2O humidified hydrogen or syngas was fed to the anode side with a precisely controllable flow.
rate monitored by a digital mass flowmeter (APEX, Alicat Scientific Inc.), while the cathode was exposed to the ambient air. The electrochemical workstation (Vera STAT3, Princeton Applied Research) was used to evaluate the cell electrochemical performance, including the EIS, the i–V–p curves, and the current density evolution under the constant potential condition. EIS under OCV and 0.8 V conditions at 700–850°C were recorded in the frequency range of 10⁴ to 10⁻² Hz with an amplitude of 30 mV when the anode was fed with 3%H₂O humidified H₂ or syngas (67%H₂–33%CO), while the cathode was exposed to ambient air. Meanwhile, the i–V curves of the cells were collected in the voltage range from OCV to 0.2 V with a sweeping rate of 0.03 V/s. In addition, the durability of the RP-SFM anode was performed under the potentiostatic mode.

### 4.4 DFT calculations

Spin-polarized DFT calculations were performed using VASP and the exchange-correlation interaction was described by PBE functional. The Kohn–Sham equations were solved using a plane-wave basis set with a kinetic energy cutoff of 700 eV. A (3×6×1) k-point mesh was used to sample the Brillouin zone. The DFT + U calculations were applied for the Fe and Ni d-orbitals with a U value of 4.0 and 6.4 eV, respectively, while the U correction for Mo d-orbital was not considered based on the literature. The bulk RP-SFM and RP-SFMN were modeled on the basis of the bulk Sr₃Fe₂O₇ with a space group of I4/mmm and a (2×2) unit cell (Sr₁₂Fe₅O₂₈), as shown in Supporting information Figure S8.

With proper Mo and Ni doping, RP-SFM and RP-SFMN were respectively constructed as Sr₁₂Fe₆Mo₂O₂₈ and Sr₁₂Fe₅Mo₂NiO₂₈, where the B-site metal ratios were similar to that in the experimentally synthesized samples. To model Sr₁₂Fe₆Mo₂O₂₈, two Fe atoms of Sr₁₂Fe₈O₂₈ were substituted by two Mo atoms, and various possible doping positions were considered to get the most stable structure. On the basis of this most stable structure, another Fe atom of Sr₁₂Fe₆Mo₂O₂₈ was substituted by Ni atom to model Sr₁₂Fe₅Mo₂NiO₂₈, and similarly, the most stable structure was determined by considering various possible Ni doping positions. During the optimization, all atoms were allowed to relax until the energy difference and force were less than 10⁻⁶ eV and 0.02 eV Å⁻¹, respectively. The oxygen vacancy formation energy was calculated as:

\[
E_{\text{form}}(V_O) = E_{\text{defect}} - E_{\text{host}} + 1/2E_{O_2},
\]

where \(E_{\text{defect}}, E_{\text{host}},\) and \(E_{O_2}\) are the total energies of the RP oxides with one oxygen vacancy, the RP oxides, and the gas-phase oxygen molecule, respectively.

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### CONFLICT OF INTEREST

The authors declare no conflict of interest.

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