



Synergistically enhanced anode performance of $\text{PrBaMn}_2\text{O}_{5+\delta}$ for proton ceramic fuel cells via nickel doping and exsolution

Xingyu Duan¹, Fuzhong Wu^{1,*}, Jie Tang¹, Wei Wang^{2,3,4}, Yongwang Zhao^{2,3,*}, Jialu Qu^{2,3}, Xinyi Dai¹, Zhihua Zhao⁵, Li Wang⁵, Sining Yun^{6,*}, Shengli An^{2,3,*}

Keywords:

In situ exsolution, lattice structure modulation, methane steam reforming, electrochemical performance, fuel electrode, proton ceramic cells

Citation: Duan, X.; Wu, F.; Tang, J.; Wang, W.; Zhao, Y.; Qu, J.; Dai, X.; Zhao, Z.; Wang, L.; Yun, S.; An, S. Synergistically enhanced anode performance of $\text{PrBaMn}_2\text{O}_{5+\delta}$ for proton ceramic fuel cells via nickel doping and exsolution. *Energy Mater.* 2026, 6, 600009. <https://dx.doi.org/10.20517/energymater.2025.158>

Received: 23 Sep 2025

First Decision: 26 Nov 2025

Revised: 9 Dec 2025

Accepted: 30 Dec 2025

Published: 21 Jan 2026

Academic Editor:

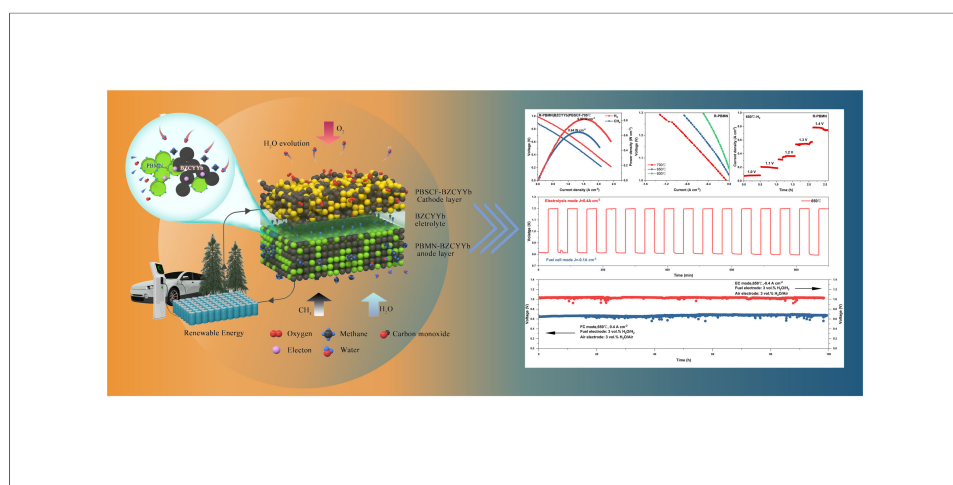
Yuping Wu

Copy Editor:

Fangling Lan

Production Editor:

Fangling Lan



Abstract

Proton ceramic fuel cells (PCFCs) are considered highly efficient energy conversion devices, yet their performance is strongly governed by the catalytic activity and stability of anode materials. Although $\text{PrBaMn}_2\text{O}_{5+\delta}$ (R-PBM) has demonstrated intrinsic tolerance to hydrocarbon fuels, its electrochemical activity at intermediate and low temperatures remains insufficient for practical reversible PCFCs (r-PCFCs) applications. Therefore, a Ni-doped R-PBM anode material, $\text{PrBaMn}_{1.95}\text{Ni}_{0.05}\text{O}_{5+\delta}$ (R-PBMN), was studied in this work. The *in situ* exsolution of Ni nanoparticles after partial Ni substitution for Mn sites significantly improved the anode activity. The exsolved Ni nanoparticles effectively lower the activation energy for C-H bond cleavage, thereby enhancing methane activation and decomposition. Meanwhile, the R-PBMN lattice provides intrinsic hydrophilicity and high proton mobility, which enable cooperative $\text{CH}_4/\text{H}_2\text{O}$ activation and facilitate the formation of CH_3OH^* intermediates that suppress carbon deposition. As a result, R-PBMN exhibits substantially enhanced electrochemical performance. At 650 °C, R-PBMN demonstrated substantially lower polarization resistance than R-PBM: $0.56 \Omega \text{ cm}^2$ in H_2 and $3.38 \Omega \text{ cm}^2$ in

¹Guizhou Provincial University Key Laboratory of High-Performance Battery Materials, College of Materials and Metallurgy, Guizhou University, Guiyang 550025, Guizhou, China.

²Key Laboratory of Green Extraction & Efficient Utilization of Light Rare-Earth Resources (Inner Mongolia University of Science and Technology), Ministry of Education, Baotou 014010, Inner Mongolia, China.

³Inner Mongolia Key Laboratory of Advanced Ceramic Materials and Devices, School of Rare Earth Industry, Inner Mongolia University of Science and Technology, Baotou 014010, Inner Mongolia, China.

⁴Baotou Light Industry Vocational Technical College, Baotou 014035, Inner Mongolia, China.

⁵State Key Laboratory of Baiyunobo Rare Earth Resource Researches and Comprehensive Utilization, Baotou 014010, Inner Mongolia, China.

^eSchool of Materials Science and Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, China.

***Correspondence to:** Dr. Fuzhong Wu, Guizhou Provincial University Key Laboratory of High-Performance Battery Materials, College of Materials and Metallurgy, Guizhou University, Guiyang 550025, Guizhou, China. E-mail: gutwfz@163.com; Dr. Yongwang Zhao, Key Laboratory of Green Extraction & Efficient Utilization of Light Rare-Earth Resources (Inner Mongolia University of Science and Technology), Ministry of Education, Baotou 014010, Inner Mongolia, China. E-mail: yongwangzhao@163.com; Dr. Shengli An, Key Laboratory of Green Extraction & Efficient Utilization of Light Rare-Earth Resources (Inner Mongolia University of Science and Technology), Ministry of Education, Baotou 014010, Inner Mongolia, China. E-mail: san@imust.edu.cn; Dr. Sining Yun, School of Materials Science and Engineering, Xi'an University of Architecture and Technology, Xi'an 710055, Shaanxi, China. E-mail: yunsining@xauat.edu.cn

CH₄, representing a 90% and 55% reduction, respectively, while retaining a high impedance stability for 120 h in methane-steam atmosphere. At 700 °C, the peak power density of R-PBMN in H₂ and CH₄ reached 0.82 and 0.64 W cm⁻², respectively, a 15.5% and 18.5% increase compared to R-PBM. Furthermore, the R-PBMN anode retained the intrinsic coking resistance of the Pr_{0.5}Ba_{0.5}MnO_{3-δ} (PBM) framework, ensuring stable operation for 100 h in a 50% H₂O/CH₄ atmosphere. This work highlights a cooperative design strategy that transforms PBM from a hydrocarbon-tolerant but low-activity oxide into a high-performance PCFC anode with balanced activity and durability.

INTRODUCTION

Proton ceramic fuel cells (PCFCs) offer the advantage of efficient energy conversion at lower operating temperatures (< 650 °C) compared to conventional solid oxide fuel cells (SOFCs)^[1,2]. Additionally, PCFCs exhibit remarkable fuel flexibility^[3-6], allowing the direct utilization of hydrocarbons such as methane (CH₄) instead of pure hydrogen, thereby significantly broadening their application potential^[7].

However, several critical challenges must be overcome before PCFCs can be widely commercialized. The conventional Ni/electrolyte composite anode, commonly referred to as Ni cermet, exhibits high catalytic activity for fuel oxidation but suffers from deactivation due to carbon deposition arising from the incomplete oxidation of hydrocarbons in practical fuels^[8]. Coke formation blocks the active sites of Ni, thereby reducing its catalytic activity and long-term stability^[9]. Moreover, redox-induced volume changes and Ni particle coarsening during long-term operation further compromise the energy efficiency and durability of Ni-based ceramic anodes in PCFCs^[10].

To address these challenges, extensive research efforts have been devoted to the development of novel anode materials and composite anode architectures for PCFCs^[11,12]. For instance, Hu *et al.* developed a Ru@Ru-Sr₂Fe_{1.5}Mo_{0.5}O_{6-δ} (SFM)/Ru-Gd_{0.1}Ce_{0.9}O_{2-δ} (GDC) anode^[10]. This nano-heterostructure exhibited outstanding electrochemical performance, achieving peak power densities of 1.03 and 0.63 W cm⁻² at 800 °C under humidified H₂ and CH₄ atmospheres, respectively. Moreover, it maintained stable performance for over 200 h in humidified CH₄, indicating strong resistance to carbon deposition^[10]. Separately, Liu *et al.* engineered a novel samarium (Sm)-doped CeO₂-supported Ni-Ru (SCNR) catalyst for steam methane reforming (SMR)^[13]. The optimized configuration achieved a peak power density of 0.733 W cm⁻² at 650 °C, representing a 55% enhancement over conventional CH₄ systems (0.473 W cm⁻²)^[13]. In another study, Liu *et al.* synthesized a high-performance nanocomposite catalyst consisting of Ni nanoparticles supported on Sm-doped CeO₂ (SDC) for use as an efficient internal SMR catalyst^[14]. This catalyst exhibited excellent electrochemical performance, achieving a peak power density of over 0.35 W cm⁻² at 600 °C - a threefold improvement relative to conventional CH₄-fueled metal-supported catalysts^[14]. These representative catalysts highlight promising directions for the development of PCFC anodes and underscore the need to design electrodes with high catalytic activity and strong coking resistance at low temperatures.

Double perovskite-structured materials provide highly tunable crystal structures and abundant active sites, rendering them promising candidates for anode materials in SOFCs. Among these, $\text{PrBaMn}_2\text{O}_{5+\delta}$ (PBM) has been extensively studied as an anode material in SOFCs because of its excellent electrochemical properties, redox stability, and methane tolerance. In particular, layered PBM-based anodes have shown great promise in methane dry reforming and sulfur-tolerant operation, as demonstrated in previous studies by Bahout *et al.*^[15], Song *et al.*^[16] and Guo *et al.*^[8]. However, these studies have predominantly focused on conventional oxygen-ion-conducting SOFCs, which typically operate at high temperatures (800–1,000 °C) with oxide-ion electrolytes such as yttria-stabilized zirconia (YSZ) or GDC. In contrast, protonic ceramic fuel cells (PCFCs), or proton-conducting SOFCs, employ proton-conducting perovskite electrolytes (e.g., BaCeO_3 - or BaZrO_3 -based solid solutions) and can achieve efficient operation at intermediate temperatures (400–700 °C). In PCFCs, protons are the primary ionic charge carriers and water is formed mainly at the cathode side, which avoids fuel dilution at the anode and enables higher theoretical efficiency and improved fuel utilization compared with oxygen-ion-conducting SOFCs. Significant progress has been made in developing proton-conducting electrolytes and electrodes for hydrogen-fueled PCFCs; however, systematic studies of anode materials for direct hydrocarbon or internal steam reforming operation in PCFCs remain relatively limited. In this context, a comprehensive understanding of how B-site Ni doping and exsolved Ni nanoparticles interact with the oxygen-vacancy-rich R-PBM backbone under realistic CH_4 /steam reforming conditions in PCFCs (600–700 °C) is still lacking. In particular, the correlations between Ni exsolution, oxygen-defect chemistry, surface hydrophilicity, and the electrode kinetics of CH_4 electro-oxidation at intermediate temperatures have not been clearly established for R-PBM-based anodes.

Despite their outstanding structural stability and intrinsic coking resistance, R-PBM-based perovskites suffer from insufficient electrochemical activity at intermediate and low temperatures, limiting their practical application in PCFCs. To address this challenge, we designed a Ni-modified derivative, R-PBMN, by minimally substituting Ni at the Mn sites of R-PBM, followed by *in situ* exsolution of Ni nanoparticles under reducing conditions. This cooperative strategy integrates the catalytic advantages of exsolved Ni with the lattice-driven hydrophilicity and oxygen mobility of R-PBM, thereby enhancing methane activation while retaining the intrinsic resistance to carbon deposition. Without Ni exsolution, the anode retains good carbon tolerance but exhibits much lower electrochemical activity, and without the $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{MnO}_{3-\delta}$ (PBM) host, the Ni nanoparticles would rapidly coke and deactivate, making their synergy essential for superior performance. Benefiting from this synergy, R-PBMN demonstrates significantly improved electrochemical performance and durability compared with pristine R-PBM, achieving peak power densities of 0.82 W cm^{-2} in H_2 and 0.64 W cm^{-2} in CH_4 at 700 °C, along with stable operation in methane-steam atmospheres. These findings provide a concrete materials-design guideline for developing Ni-exsolving, PBM-based fuel electrodes that bridge the gap between highly active but coking-prone Ni cermets and intrinsically coking-tolerant but less active PBM electrodes, thus offering a technically important route toward robust CH_4 -fueled PCFCs.

EXPERIMENTAL

Synthesis of powders

PBM and $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{Mn}_{0.975}\text{Ni}_{0.025}\text{O}_{3-\delta}$ (PBMN) powders were prepared using a sol-gel method. $\text{Pr}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (all Aladdin, > 98%) were dissolved in deionized water with ethylenediaminetetraacetic acid (EDTA) and citric acid as dual complexing agents (molar ratio of total metal ions: EDTA: citric acid = 1:1:2). The solution pH was adjusted to 7.0 ± 0.1 using $\text{NH}_3 \cdot \text{H}_2\text{O}$ (25%) and heated at 90 °C under stirring (300 rpm) for 12 h to form a viscous gel. The gel was dried at 300 °C for 5 h and calcined in air at 950 °C for 10 h to obtain crystalline PBM and PBMN powders. The layered perovskite oxides R-PBM and R-PBMN were obtained by thermal reduction in H_2 at 800 °C for 1 h (heating rate: $3 \text{ }^\circ\text{C min}^{-1}$).

Cell preparation

The $\text{BaZr}_{0.1}\text{Ce}_{0.7}\text{Y}_{0.1}\text{Yb}_{0.1}\text{O}_{3-\delta}$ (BZCYYb) electrolyte powder was prepared via a solid-state reaction. Stoichiometric amounts of BaCO_3 ($\geq 99.5\%$), ZrO_2 ($\geq 99.9\%$), CeO_2 ($\geq 99.9\%$), Y_2O_3 ($\geq 99.9\%$), and Yb_2O_3 ($\geq 99.9\%$) were ball-milled in anhydrous ethanol (400 rpm, 4 h) with zirconia media, followed by calcination in air at $1,450^\circ\text{C}$ for 5 h (5°C min^{-1}). The obtained BZCYYb electrolyte powder was uniaxially pressed into pellets (~ 15 mm diameter, ~ 1 mm thickness) at 200 MPa for symmetrical cell fabrication. The anode ink was prepared by mixing the anode material, ethyl cellulose binder, and terpineol solvent (1:0.06:0.94 by weight) using a three-roll mill, screen-printed onto both sides of the BZCYYb electrolyte pellets ($\sim 10\text{ }\mu\text{m}$ per layer), and sintered in air at 950°C for 2 h to form porous symmetrical electrodes ($\sim 30\text{ }\mu\text{m}$).

A single anode-supported cell was fabricated with an R-PBMN-BZCYYb (60:40 wt.%) substrate containing 10 wt.% nanographite, pressed at 100 MPa. A $\sim 10\text{ }\mu\text{m}$ anode functional layer (prepared from the same R-PBMN-BZCYYb composite as the anode support, with a R-PBMN:BZCYYb weight ratio of 6:4, but without pore former) and a $\sim 20\text{ }\mu\text{m}$ BZCYYb electrolyte layer were sequentially deposited by spin-coating (4,000 rpm, 40 s per layer). The multilayer structure was co-sintered at $1,450^\circ\text{C}$ for 5 h (2°C min^{-1}) to obtain a dense electrolyte. Finally, a $\text{PrBa}_{0.5}\text{Sr}_{0.5}\text{Co}_{1.5}\text{Fe}_{0.5}\text{O}_{5+\delta}$ (PBSCF) cathode was screen-printed and fired at 950°C for 2 h to form a porous cathode ($\sim 30\text{ }\mu\text{m}$ thickness).

Characterization and electrochemical tests

The crystalline phases of R-PBM and R-PBMN powders were analyzed by X-ray diffraction (XRD, MiniFlex 600, Rigaku, Japan, $\text{Cu K}\alpha$, $\lambda = 1.5406\text{ }\text{\AA}$) over a 2θ range of 20 – 80° (step size: 0.02° , 2 s per step). Rietveld refinement was performed using the General Structure Analysis System (GSAS) with EXPGUI, a graphical user interface for GSAS. High-Angle Annular Dark-Field Scanning Transmission Electron Microscopy (HAADF-STEM) and energy dispersive spectroscopy (EDS) were performed on an aberration-corrected 300 kV microscope (JEM-ARM300F, JEOL Ltd., Japan). The crystal structures of PBM, PBMN, R-PBM, and R-PBMN were investigated by high-resolution transmission electron microscopy (HRTEM) using a JEM-F200 transmission electron microscope (JEOL Ltd., Japan). X-ray photoelectron spectroscopy (XPS) measurements were performed using a K-Alpha X-ray photoelectron spectrometer (Thermo Fisher Scientific, USA). Electrical conductivity relaxation (ECR) measurements were performed using the four-probe direct current (DC) method with a Keithley 2100 digital multimeter (Keithley Instruments, USA). Thermogravimetric analysis (TGA) was carried out using a Q5000 IR (TA Instruments, USA) from room temperature to $1,000^\circ\text{C}$ at a heating rate of 2°C min^{-1} for two cycles. Cell morphologies were examined by scanning electron microscopy (SEM; EVO-18, Carl Zeiss, Germany). Electrochemical impedance spectroscopy (EIS) was performed on symmetrical and single cells using a Solartron 1260/1287 system (Solartron Analytical, UK) over the frequency range of 0.1 Hz – 1 MHz with an amplitude of 10 mV . Raman spectra were collected using a Bruker Senterra (Bruker, Germany), and Semi-in-situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) was conducted using a Bruker TENSOR II Fourier transform infrared (FTIR) spectrometer (Bruker, Germany). Distribution of relaxation times (DRT) analysis was conducted using DRTtools, a MATLAB-based tool utilizing Tikhonov regularization, to resolve the characteristic timescales of the underlying electrochemical processes^[17,18]. Symmetrical cells were tested in humidified H_2 or CH_4 (500 – 700°C), while single cells were fed with humidified H_2 ($\sim 3\%$ H_2O , 50 mL min^{-1}) at the anode and air at the cathode. The gas atmospheres, compositions, and flow rates used for different measurements are summarized in [Supplementary Table 1](#).

The methane adsorption/desorption capacity and hydrogen reduction behavior of R-PBM and R-PBMN were further evaluated by CH_4 -temperature programmed desorption (TPD), H_2 -temperature programmed reduction (TPR), and electron paramagnetic resonance (EPR) spectra were recorded using an EMXplus EPR spectrometer (Bruker, Germany). SMR activity was evaluated in a fixed-bed quartz reactor at 1 atm. Catalysts

were reduced in 20% H₂/Ar (50 sccm) at 600 °C for 30 min, then heated to 700 °C under an inert atmosphere. Methane (10 sccm) was introduced through a temperature-controlled bubbler to maintain a steam-to-carbon (S/C) ratio of 1:2. Effluent gases were analyzed online by micro gas chromatography (μGC) equipped with a thermal conductivity detector (TCD). The system was stabilized ≥ 30 min before measurement, and methane conversion (X_{CH_4}) was calculated as:

$$X_{CH_4}(\%) = \frac{F_{CH_4,in} - F_{CH_4,out}}{F_{CH_4,in}} \times 100\% \quad (1)$$

where $F_{CH_4,in}$ and $F_{CH_4,out}$ represent the inlet and outlet methane flow rates, respectively.

RESULTS AND DISCUSSION

Crystal structure and microstructure characterizations

The XRD patterns of PBMN powder, calcined in air at 950 °C for 10 h and subsequently reduced in H₂ at 800 °C for varying durations, are presented in Figure 1A. XRD analysis revealed that the as-prepared PBMN sample consisted of a mixed phase, including a cubic perovskite structure (*Pm-3m*, PBMN with disordered A-site cations) and a tetragonal perovskite structure (*P4/mmm*, R-PBMN with layered A-site ordering) [Supplementary Figure 1]. Reduction in H₂ at 800 °C induced pronounced phase evolution. After 10 min, the BaMnO₃ phase disappeared, while new phases of Ni, MnO, and PrO₂ emerged. Concurrently, the XRD peaks shifted to lower angles, indicating an expansion of the unit cell volume in the reduced phase. This expansion was attributed to Mn reduction and the generation of oxygen vacancies. After 1 h of reduction, the material predominantly transformed into an A-site cation-ordered double perovskite, R-PBM, with a layered [BaO]-[MnO₂]-[PrO_x]-[MnO₂]-[BaO] configuration. Only trace amounts of Ni and MnO remained detectable. Both materials crystallized in a tetragonal (*P4/mmm*) double perovskite structure. Notably, the XRD peak at 32.5° for R-PBMN shifted to a lower angle compared with R-PBM, indicating further expansion of the unit cell. This lattice expansion is primarily ascribed to the substitution of Mn³⁺ (0.58 Å, low spin) by the larger Ni²⁺ cation (0.69 Å).

Rietveld refinements of the XRD data for R-PBM and R-PBMN were carried out, and the results are shown in Figure 1B and C, respectively. The refined lattice parameters of R-PBM and R-PBMN are presented in Supplementary Table 2. These results demonstrate that Ni doping reduces the lattice parameters along the *a*- and *b*-axes while slightly increasing the *c*-axis. This anisotropic lattice modification, induced by Ni substitution, may facilitate proton transport along the *b*-axis by increasing the O-O spacing, thereby lowering the migration barrier.

To investigate the crystal structures of as-prepared PBMN and reduced R-PBMN, HRTEM was conducted along the [100] zone axis [Figure 1D and E]. Both images exhibit clear and continuous lattice fringes, confirming the high crystallinity of the perovskite framework at the atomic scale. The interplanar spacings of 3.17 Å for PBMN and 2.75 Å for R-PBMN correspond to the (102) planes, with the slight contraction in R-PBMN consistent with lattice reduction and the exsolution of Ni nanoparticles under reducing conditions. Additional transmission electron microscopy (TEM) images of R-PBM are provided in Supplementary Figure 2, while Supplementary Figure 3 further illustrates the morphological evolution before and after reduction. The as-prepared PBMN shows smooth, compact grains with no visible particles, while reduced R-PBMN displays numerous Ni nanoparticles exsolved from the perovskite lattice. These nanoparticles are mainly uniformly dispersed but also form localized clusters due to partial coarsening. STEM-EDS elemental mapping [Figure 1F] revealed a homogeneous distribution of Pr, Ba, Mn, and O,

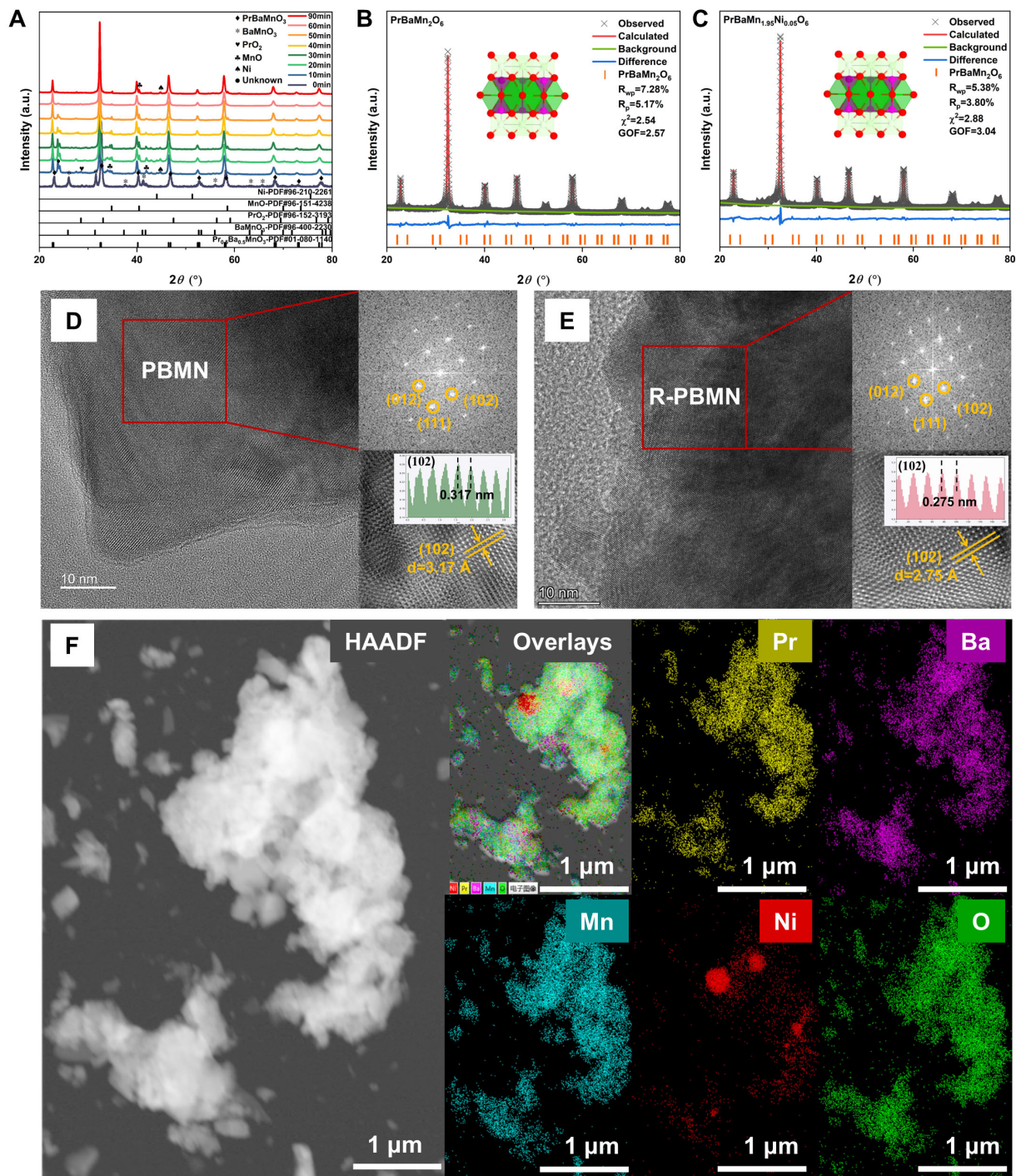


Figure 1. (A) XRD patterns of PBMN and R-PBMN samples after reduction in H_2 at 800 °C for 0–90 min, showing phase evolution. Rietveld refinement profiles of (B) R-PBM and (C) R-PBMN, demonstrating good agreement between experimental and calculated patterns; HRTEM images and corresponding FFT patterns of (D) PBMN grain and (E) R-PBMN grain (zone axis [100]); (F) STEM-EDS elemental mappings of Pr, Ba, Mn, Ni and O in an R-PBMN grain.

whereas Ni was locally enriched on the surface as *in situ* exsolved metal nanoparticles (50–200 nm, mainly as agglomerated clusters; individual particles are a few nanometers; see [Supplementary Figure 3B](#)). Although exsolved nanoparticles are initially well-dispersed, prolonged reduction or strong reducing atmospheres promote particle coarsening. A stable, synergistic interface between the exsolved Ni nanoparticles and the

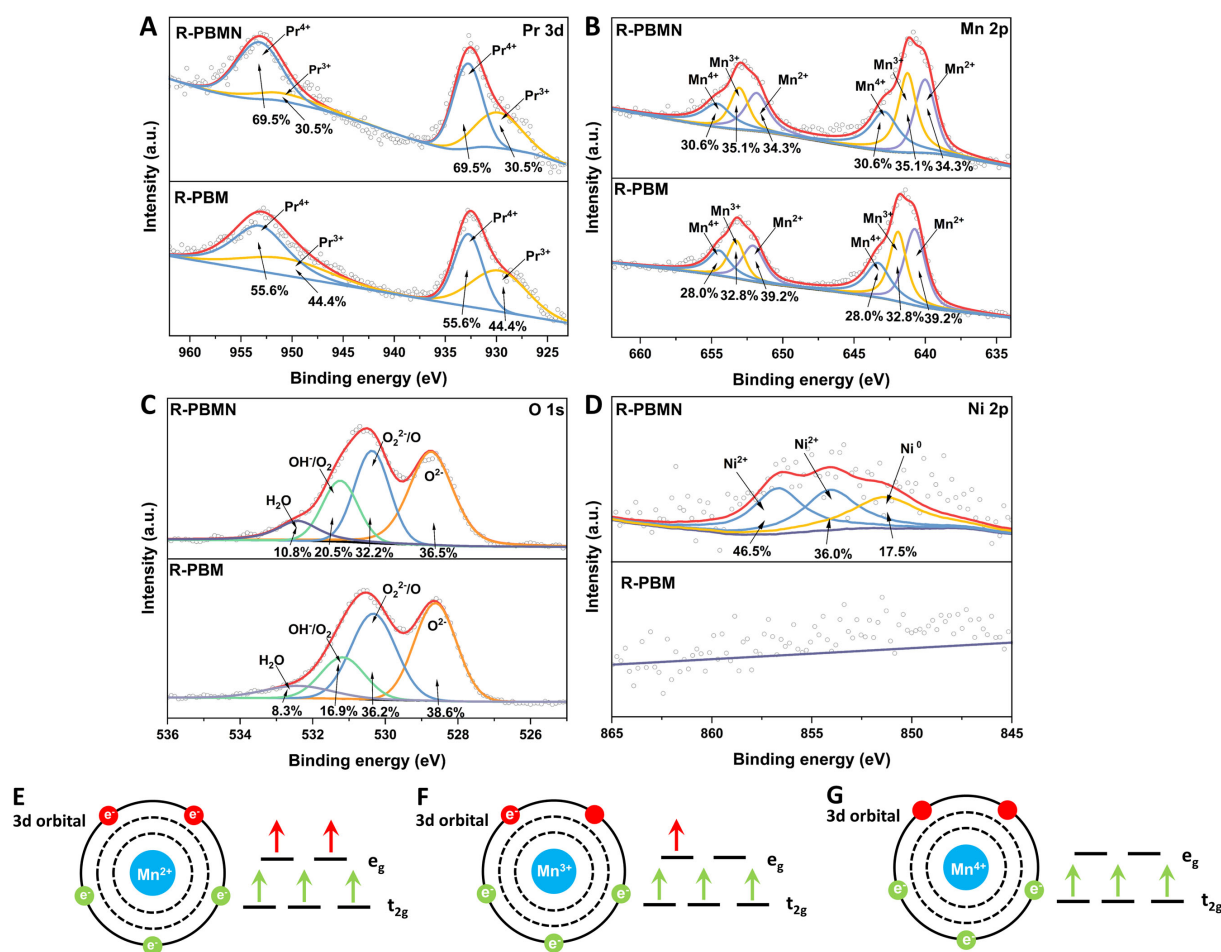


Figure 2. XPS spectra of R-PBM and R-PBMN: (A) Pr 3d; (B) Mn 2p; (C) O 1s; (D) Ni 2p (for R-PBMN only, no Ni signal detected in R-PBM). Schemes illustrate the degeneracy of (E) Mn^{2+} ; (F) Mn^{3+} ; (G) Mn^{4+} 3d orbitals.

perovskite host was established, which itself functions as an active and carbon-resistant anode rather than merely an inert scaffold. This integrated interface provides highly active catalytic sites for methane activation and facilitates coupled $\text{CH}_4/\text{H}_2\text{O}$ reactions, thereby enhancing electrochemical performance and effectively suppressing carbon deposition.

The valence state of elements

To elucidate the influence of Ni doping on the mixed-valence metal ions in double perovskite (R-PBM), XPS was conducted to examine the valence states of Pr, Mn, Ni, and O in both pristine R-PBM and R-PBMN [Figure 2]. The Pr 3d spectra [Figure 2A] exhibited two distinct peaks at 929.4 eV (Pr^{3+} , $3d_{5/2}$)/949.5 eV (Pr^{3+} , $3d_{3/2}$) and 933.4 eV (Pr^{4+} , $3d_{5/2}$)/953.9 eV (Pr^{4+} , $3d_{3/2}$). Upon Ni doping, the Pr^{4+} content increased markedly from 55.6% (R-PBM) to 69.5% (R-PBMN), corresponding to an $\sim 20\%$ relative increase. This result suggests that Ni incorporation promoted the oxidation of Pr^{3+} to Pr^{4+} , likely through charge compensation or ligand-hole formation.

The Mn 2p spectra [Figure 2B] revealed three oxidation states: 640.6 eV (Mn^{2+} , $2p_{3/2}$)/652.8 eV (Mn^{2+} , $2p_{1/2}$), 641.8 eV (Mn^{3+} , $2p_{3/2}$)/653.7 eV (Mn^{3+} , $2p_{1/2}$), and 642.9 eV (Mn^{4+} , $2p_{3/2}$)/654.9 eV (Mn^{4+} , $2p_{1/2}$). Ni doping increased the Mn^{4+} content from 28.0% to 30.6% (+8.5% relative) and the Mn^{3+} content increased from 32.8% to 35.1% (+6.6% relative). These results indicate that Ni doping not only substantially elevated the average oxidation state of Pr but also moderately increased that of Mn, likely due to electron transfer from Mn to Ni

or local structural distortion.

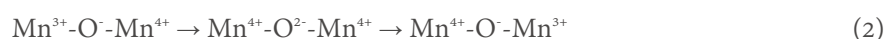
In an octahedral crystal field, the 3d orbitals of transition-metal cations (e.g., Mn) are split into lower-energy t_{2g} (d_{xy} , d_{yz} , and d_{xz}) and higher-energy e_g (d_{z^2} and $d_{x^2-y^2}$) orbitals. The e_g orbitals participate in σ -bonding with adsorbates, and their occupancy critically affects catalytic activity^[19-21]. As illustrated in Figure 2E-G, the electronic configurations of Mn^{2+} , Mn^{3+} and Mn^{4+} are $(t_{2g})^3(e_g)^2$, $(t_{2g})^3(e_g)^1$, and $(t_{2g})^3(e_g)^0$, respectively. The decrease in e_g occupancy (from Mn^{2+} to Mn^{4+}) enhances the ability of the material to form stronger σ -bonds with reactive intermediates, thereby improving its catalytic performance in gas-phase reactions.

The O 1s XPS spectra of R-PBM and R-PBMN were deconvoluted into four components [Figure 2C], corresponding to lattice oxygen (O^{2-}), highly oxidized oxygen species (O_2^{2-}/O^-), adsorbed oxygen (OH^-/O_2), and surface-adsorbed H_2O . R-PBMN exhibited a significantly larger OH^- contribution than R-PBM, suggesting a higher concentration of oxygen vacancies and enhanced proton uptake capacity. The increased surface-adsorbed H_2O in R-PBMN further indicates enhanced water adsorption capability. The enhanced hydrophilicity of the anode not only improves its resistance to carbon deposition but also positively influences its electrochemical performance. A higher water uptake capacity facilitates the adsorption and activation of H_2O molecules, which promotes steam reforming and carbon-water gasification reactions ($C+H_2O \rightarrow CO+H_2$, $C+2H_2O \rightarrow CO_2+2H_2$). Increased water adsorption facilitates proton generation and transport, expands the effective triple-phase boundary, and accelerates surface redox kinetics.

The Ni 2p spectrum of R-PBMN [Figure 2D] revealed the coexistence of Ni^{2+} (82.5%) and Ni^0 (17.5%), indicating predominant incorporation of Ni^{2+} into the bulk lattice with surface precipitation of metallic Ni. No Ni signal was observed in undoped R-PBM.

Electrical conductivity, oxygen surface exchange, and bulk diffusion

The electrical conductivity of R-PBM and R-PBMN was measured as a function of temperature in 5% H_2 /Ar and CH_4 atmospheres [Figure 3A and B]. R-PBM exhibited p-type semiconducting behavior in the range of 300–800 °C. At 800 °C, the conductivities of R-PBM and R-PBMN were 1.38 and 2.29 S cm^{-1} , respectively, in 5% H_2 /Ar, and 0.98 and 1.88 S cm^{-1} , respectively, in CH_4 . In H_2 , the stronger reducing environment facilitates the reduction of Mn^{4+} to Mn^{3+} , which enhances small-polaron hopping and thereby increases the electronic conductivity. In contrast, in CH_4 , the relatively weaker reducing power suppresses the extent of Mn reduction, leading to comparatively lower conductivity. These results demonstrate that Ni doping markedly enhanced conductivity under both atmospheres. The improvement was attributed to enhanced overlap between O 2p and Mn 3d orbitals in the perovskite lattice, which facilitated charge transfer through the Mn-O-Mn network. The conduction mechanism followed a small-polaron hopping process, as given in:



Ni doping increased the average Mn valence state, broadened electron-transfer pathways, and improved both electronic/ionic conductivity and catalytic activity. The linear Arrhenius behavior further confirmed small-polaron hopping as the dominant conduction mechanism^[22]. Notably, R-PBMN exhibits lower activation energy than R-PBM in both atmospheres [Figure 3C and D], indicating that Ni doping reduces conduction energy barriers and enhances charge transfer efficiency.

The oxygen surface-exchange coefficient (K_{ex}) and bulk diffusion coefficient (D_{chem}) were determined by ECR [Figure 3E and F]. R-PBMN showed significantly shorter relaxation times than R-PBM, indicating superior catalytic activity for H_2 and CH_4 oxidation. Further analysis of the calculated D_{chem} and K_{ex} values revealed

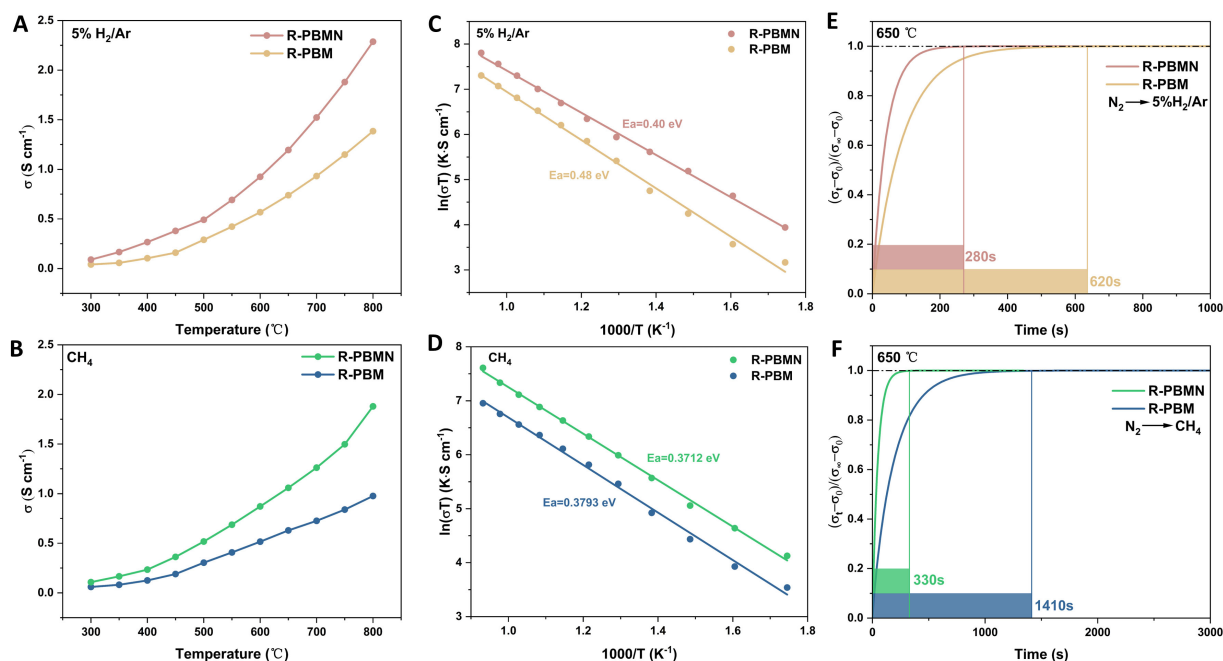


Figure 3. Electrical conductivity of R-PBM and R-PBMN as a function of temperature in (A) 5 %H₂/Ar and (B) CH₄ atmospheres. Arrhenius plots of electrical conductivity for R-PBM and R-PBMN in (C) 5 %H₂/Ar and (D) CH₄ atmosphere. Normalized conductivity relaxation profiles for R-PBM and R-PBMN during gas switching from (E) N₂ to 5 %H₂/Ar and (F) N₂ to CH₄.

that, at 650 °C in 5% H₂/Ar, R-PBMN exhibited higher D_{chem} ($8.87 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and K_{ex} ($7.36 \times 10^{-4} \text{ cm s}^{-1}$) compared with R-PBM ($D_{chem} = 8.22 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $K_{ex} = 3.29 \times 10^{-4} \text{ cm s}^{-1}$). Similarly, in CH₄ at 650 °C, R-PBMN exhibited higher D_{chem} ($1.83 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$) and K_{ex} ($6.23 \times 10^{-4} \text{ cm s}^{-1}$) than R-PBM ($D_{chem} = 1.09 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$, $K_{ex} = 2.14 \times 10^{-4} \text{ cm s}^{-1}$). These results confirm that R-PBMN exhibited faster oxygen surface exchange and bulk diffusion kinetics, further underscoring its enhanced catalytic performance in energy-conversion applications.

Electrochemical performance and electrode reaction kinetics

The electrode kinetics of the anodes were investigated at 650 °C by measuring the polarization resistance (R_p) of symmetrical cells (R-PBM|BZCYYb|R-PBM and R-PBMN|BZCYYb|R-PBMN) under varying partial pressures of H₂ and CH₄. EIS revealed that R-PBMN had a significantly higher catalytic activity than R-PBM in both H₂ and CH₄ atmospheres. At 650 °C, R-PBMN exhibited substantially lower R_p : 0.56 Ω cm² in H₂ (vs. 5.50 Ω cm² for R-PBM) and 3.38 Ω cm² in CH₄ (vs. 7.49 Ω cm² for R-PBM). The superior performance of R-PBMN originates from three synergistic effects: (1) Electronic structure modulation: Ni doping increases the Mn valence state. In an octahedral crystal field, Mn 3d orbitals split into lower-energy t_{2g} and higher-energy e_g orbitals. The e_g orbitals participate in σ -bonding with adsorbates, where reduced electron occupancy enhances catalytic activity^[23,24]. As shown in Figure 2E–G, the electronic configurations are Mn²⁺: (t_{2g})³(e_g)², Mn³⁺: (t_{2g})³(e_g)¹ and Mn⁴⁺: (t_{2g})³(e_g)⁰. Decreasing e_g occupancy correlates with stronger catalytic activity for H₂ and CH₄ oxidation; (2) Oxygen vacancy formation: The increased Pr⁴⁺ content promoted oxygen vacancy generation during reduction, creating additional active sites for fuel adsorption and oxidation; (3) Ni catalytic properties: Surface-precipitated metallic Ni (17.5%) exhibited high catalytic activity due to its partially filled 3d orbitals, low electronegativity (1.91), and relatively low first-ionization energy. These properties facilitated oxidative addition reactions critical for fuel reforming. This multifunctional enhancement accounts for the superior electrochemical performance of R-PBMN under both reducing atmospheres.

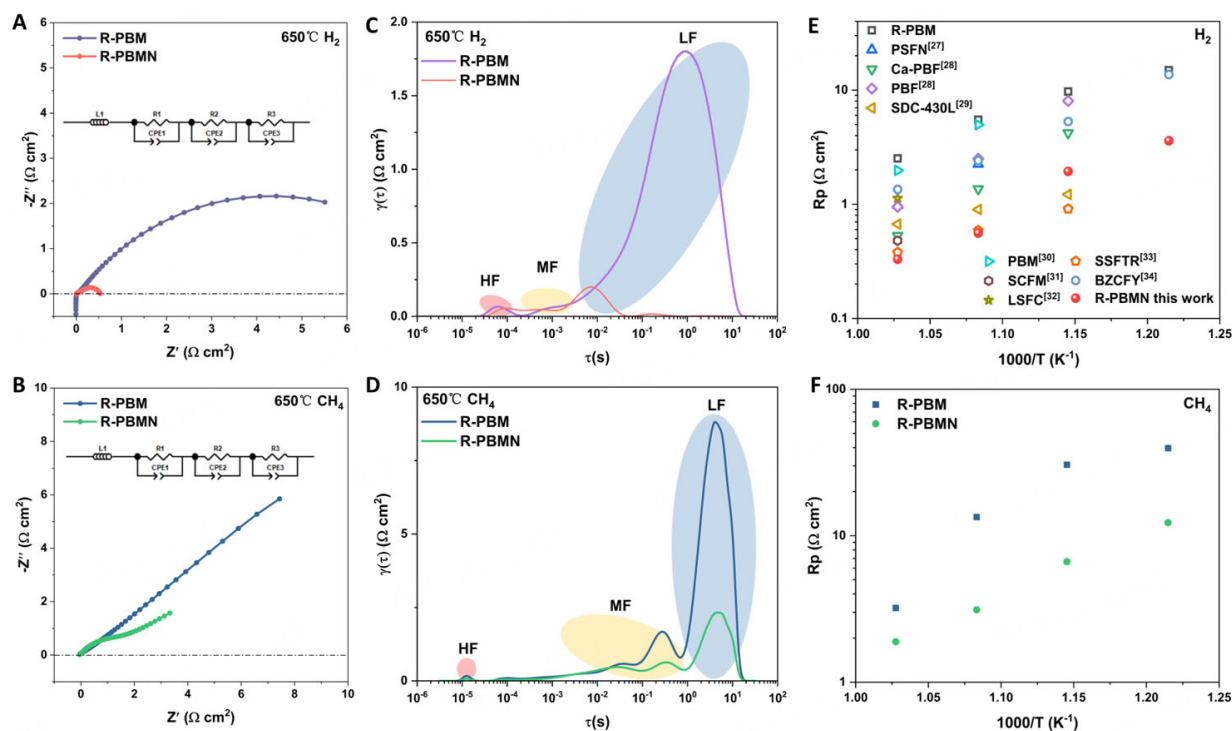


Figure 4. Electrochemical impedance spectra of symmetrical cells (R-PBM|BZCYYb|R-PBM and R-PBMN|BZCYYb|R-PBMN) measured at 650 °C in (A) H₂ and (B) CH₄ atmospheres. Distribution of relaxation times (DRT) analysis for (C) H₂ and (D) CH₄ at 650 °C. Temperature-dependent polarization resistance (R_p) in (E) H₂ with other materials reported recently [27–34] and (F) CH₄ from 550–700 °C.

To further elucidate this performance enhancement, DRT was applied to deconvolute the impedance spectra and identify rate-limiting steps. Based on the frequency range, the overall reaction was deconvoluted into three electrochemical steps. The low-frequency (LF) region, associated with gas adsorption, dissociation, and surface diffusion, was identified as the dominant rate-limiting step. The medium-frequency (MF) region represents gas diffusion and surface exchange at the electrode-electrolyte interface, while the high-frequency (HF) region corresponds to charge transfer involving ionic species at the electrode-electrolyte three-phase boundary (TPB) [25,26]. The corresponding EIS and DRT results are shown in Figure 4A–D. The area under each peak was used to quantify the resistance of the corresponding process. Analysis showed that the LF peaks exhibited the highest intensity and largest area in both atmospheres, confirming that gas adsorption/dissociation is the rate-limiting process. Critically, R-PBMN showed significantly reduced LF peak intensities and smaller areas compared with R-PBM, indicating enhanced gas adsorption-dissociation kinetics. The improvement was most pronounced in CH₄ atmosphere, suggesting enhanced C–H bond activation capability. This kinetic enhancement may be attributed to the increased oxygen vacancy concentration induced by Ni²⁺ doping, the *in situ*-formed Ni nanoparticles that provide additional active sites. In addition, optimization of the electronic structure - specifically, Mn *e_g* orbital occupancy - enhances adsorbate interactions. The combined effects account for lower R_p and superior fuel adsorption-dissociation performance of R-PBMN under both reducing atmospheres compared to R-PBM and other materials reported in the literature [Figure 4C and D]. Overall, the improved anode kinetics of R-PBMN can be attributed to the synergistic effects of Ni substitution and *in situ* exsolved Ni nanoparticles, which promote fuel adsorption/dissociation and facilitate charge transfer, thereby reducing R_p . Figure 4E benchmarks R_p in H₂ against representative anode materials reported in the literature, whereas Figure 4F shows the R_p measured in CH₄.

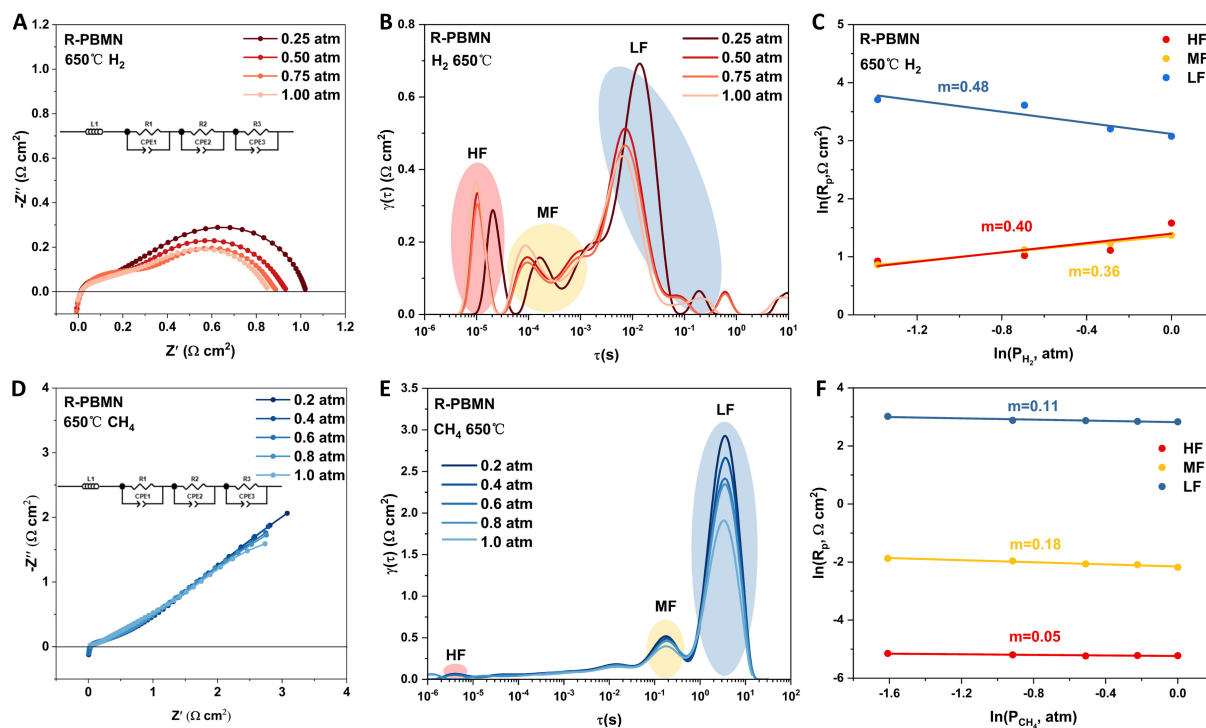


Figure 5. Electrochemical impedance spectroscopy of R-PBMN anode measured at 650 °C under varying partial pressures of (A) H_2 and (D) CH_4 . Corresponding distribution of relaxation times (DRT) analysis for (B) H_2 and (E) CH_4 atmosphere. Polarization resistance (R_p) dependence on (C) H_2 and (F) CH_4 partial pressures.

Electrode kinetics and reaction mechanism analysis

The electrode kinetics of the anodes were investigated at 650 °C by measuring the R_p of symmetrical cells (R-PBM|BZCYYb|R-PBM and R-PBMN|BZCYYb|R-PBMN) under varying partial pressures of H_2 and CH_4 . The power-law relationships $R_p = k(P_{H_2})^{-m}$ and $R_p = k(P_{CH_4})^{-m}$ were applied to determine the reaction order m . Here, R_p is the polarization resistance, k is a proportionality constant, P_{H_2} and P_{CH_4} are the partial pressures of H_2 and CH_4 , respectively^[35,36]. The obtained m correlates with specific electrochemical reaction steps [Figure 5A–F]. Remarkably, R-PBMN exhibited significantly lower R_p values even at reduced partial pressures, demonstrating superior catalytic performance. DRT analysis was employed to deconvolute the impedance spectra and identify the underlying reaction processes. To provide quantitative parameters for each relaxation contribution, the impedance spectra were additionally fitted using the equivalent circuit [Figure 5A and D], and the corresponding constant phase element (CPE) parameters (Q , n), together with the derived effective capacitances (C_{eff}), are summarized in Supplementary Table 3. The characteristic time constants estimated from $\tau_i \approx R_{iCeff,i}$ are in good agreement with the DRT peak positions within the same order of magnitude, thereby supporting the assignments of the HF/MF/LF processes. In H_2 , the LF region ($m = 0.48$) was associated with gas diffusion limitations; the MF region ($m = 0.36$) was attributed to hydrogen surface-exchange reactions; and the HF region ($m = 0.40$) corresponded to ionic charge transfer at the TPB. Conversely, in CH_4 , the LF response ($m = 0.11$) was dominated by methane transport limitations and slow carbon-related reactions, while the MF region ($m = 0.18$) reflected intermediate surface reactions, and the HF region ($m = 0.05$) was associated with charge-transfer across the electrode-electrolyte interface and proton conduction. The distinct reaction orders revealed fundamentally different rate-limiting mechanisms in H_2 and CH_4 environments. The strong dependence of R_p on gas partial pressure in the LF region confirmed that gas adsorption/dissociation governed the overall reaction kinetics. These results clearly demonstrated electrocatalytic activity of R-PBMN, which can be attributed to optimized surface chemistry and improved charge-transfer properties.

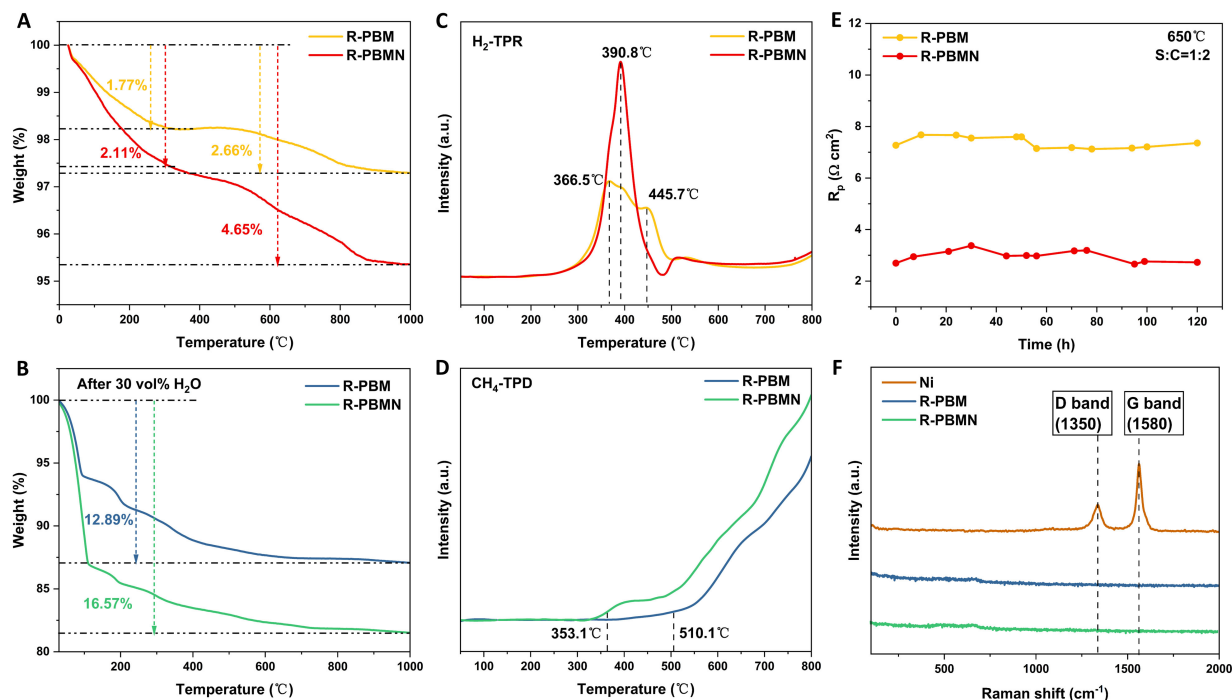


Figure 6. (A) Thermogravimetric analysis (TGA) of R-PBM and R-PBMN from room temperature to 1,000 °C. (B) TGA profiles after treatment in wet air (30 vol% H₂O) at 650 °C for 3 h. (C) CH₄-temperature programmed desorption (TPD) profiles. (D) H₂-temperature programmed reduction (TPR) profiles. (E) Area-specific resistance (R_p) stability of symmetrical cells with R-PBM and R-PBMN electrodes at 650 °C in steam methane reforming (S/C = 1:2) for 120 h. (F) Raman spectra of R-PBM, R-PBMN, and reference Ni catalyst after steam methane reforming (S/C = 1:2) at 650 °C for 24 h.

The water absorption capability of electrode materials plays a critical role in the reaction kinetics of SMR. TGA was conducted to evaluate this property [Figure 6A and B]. The comparative weight-loss profiles of R-PBM and R-PBMN revealed significant differences in hydration behavior. Oxygen-vacancy characterization [Figure 6A] showed that both materials gradually lost weight with increasing temperature. A distinct plateau at ~300 °C indicated lattice oxygen release, and R-PBMN exhibited greater total weight loss, confirming a higher oxygen-vacancy concentration. Water absorption analysis [Figure 6B] after pretreatment (600 °C, 3 h, 30 vol% H₂O) showed rapid weight loss between 30 and 100 °C, attributed to desorption of surface-adsorbed water^[37]. This was followed by progressive weight loss from 100 to 400 °C, associated with the release of lattice-incorporated water via the transformation $2\text{OH}^\bullet \rightarrow \text{H}_2\text{O}_{(\text{g})} + \text{V}_{\text{O}}^\bullet + \text{O}_{\text{O}}^\times$. Here, OH[•] denotes a lattice hydroxyl group, H₂O (g) is water vapor, $\text{V}_{\text{O}}^\bullet$ represents an oxygen vacancy, and $\text{O}_{\text{O}}^\times$ is a lattice oxygen site^[38]. Significantly, R-PBMN exhibited a 1.8-fold higher total water uptake than R-PBM. This enhanced hydration capability strengthens the synergistic mechanism of our anode: exsolved Ni nanoparticles catalyze methane activation, while the PBM host- enriched in oxygen vacancies and water adsorption sites- supplies abundant hydroxyl species to remove surface carbon and prevent coking. Without Ni exsolution, the anode retains good carbon tolerance but lower catalytic activity in methane, and without the water-adsorption property of the PBM host, the Ni particles would rapidly coke and deactivate.

CH₄-TPD, H₂-TPR, and EPR were used to further evaluate the methane adsorption/desorption capacity and hydrogen reduction behavior of R-PBM and R-PBMN. As shown in Figure 6C, H₂-TPR results revealed the critical influence of Ni on reducibility. R-PBM exhibited two distinct reduction peaks near 400 °C, corresponding to the phase transition from single to double perovskite. In contrast, R-PBMN displayed a more intense low-temperature peak (~400 °C), attributable to both the perovskite phase transition and

metallic Ni precipitation^[39]. CH₄-TPD analysis [Figure 6D] indicated significantly lower CH₄ adsorption onset for R-PBMN (~360 °C) compared with R-PBM (~510 °C), demonstrating that Ni doping facilitates low-temperature CH₄ adsorption for SMR. The larger peak area for R-PBMN further confirmed enhanced CH₄ catalytic activity. EPR analysis detected signals of unpaired electrons in both materials, with R-PBMN showing higher intensity. Calculated free-radical concentrations (R-PBM: 3.112×10^{15} spins g⁻¹; R-PBMN: 3.582×10^{15} spins g⁻¹) correlated with oxygen-vacancy concentrations, confirming that R-PBMN had a higher defect density and stronger catalytic activity under reducing atmosphere.

Figure 6E illustrates the evolution of area-specific resistance (ASR, R_p) in symmetrical cells with R-PBM and R-PBMN electrodes during 120 h of operation at 650 °C under a steam-to-methane ratio of S/C = 1:2. Both materials maintained stable ASR, demonstrating excellent short-term stability and high coking tolerance under SMR conditions. To evaluate structural stability post-operation, Raman spectroscopy was conducted on catalysts exposed to S/C = 1:2 for 24 h [Figure 6F]. The characteristic D-band (~1,350 cm⁻¹) and G-band (~1,580 cm⁻¹) of graphitic carbon served as critical indicators of carbon deposition^[40,41]. While a reference Ni catalyst exhibited prominent D- and G-bands, confirming carbon deposition, neither R-PBM nor R-PBMN showed detectable coke-related bands, demonstrating exceptional resistance to carbon formation.

To systematically evaluate the catalytic performance of the newly developed SMR catalyst, comprehensive activity tests were performed in a packed-bed reactor (PBR) system under a S/C ratio of 1:2. As shown in Figure 7A, the R-PBMN catalyst exhibited superior catalytic activity, achieving the highest CH₄ conversion efficiency over 550–700 °C. At 700 °C, R-PBMN achieved 33.2% CH₄ conversion, a 56.1% increase compared with R-PBM. This performance advantage persisted at lower temperatures, with R-PBMN reaching 15.9% conversion at 550 °C compared with 7.3% for R-PBM [Figure 7B]. These results confirmed that Ni doping significantly enhanced CH₄ conversion and SMR activity.

To elucidate the SMR mechanism, Semi-in-situ DRIFTS analysis was employed to probe surface adsorbates under operando conditions [Figure 7C–F]. Steady-state spectra for R-PBMN [Figure 7C] and R-PBM [Figure 7D] between 100–700 °C revealed distinct bands in two primary regions: 4,000–2,500 cm⁻¹ (hydroxyl groups, -OH) and 2,500–500 cm⁻¹ (gaseous CO₂: 2,380–2,260 cm⁻¹; gaseous CO: 2,183–2,108 cm⁻¹; adsorbed CHO*: ~1,725 cm⁻¹; adsorbed CH_xOH*: ~1,420 cm⁻¹)^[13,42–44]. The exceptional carbon-deposition tolerance of R-PBMN suggested a self-carbon-cleaning process on the electrode surface proceeding via three key intermediates: (1) CO formation ($C^* + O^* \rightarrow CO^*$), (2) CH_xO formation ($CH_x^* + O^* \rightarrow CH_xO^*$), and (3) CH_xOH formation ($CH_x^* + OH^* \rightarrow CH_xOH^*$)^[7,10]. Characteristic peaks for these intermediates (CO*: ~2,050 cm⁻¹; CH_xO*: ~1,725 cm⁻¹; CH_xOH*: ~1,420 cm⁻¹) were observed for both catalysts [Figure 7C and D]. Notably, CH_xOH* intensity increased with temperature [Figure 7E and F], confirming its role as a critical self-carbon-cleaning intermediate. R-PBMN exhibited stronger CH_xOH* formation than R-PBM, which promoted CO generation and enhanced coking resistance. This process coincided with hydroxyl formation (3,750–3,550 cm⁻¹), with R-PBMN showing higher OH* intensity. Crucially, Ni doping accelerated C–O bond formation. While R-PBM generates C–O* at 600 °C, R-PBMN forms C–O* at 500 °C. This finding indicated that Ni incorporation facilitated CO production through carbon self-cleaning pathways, thereby significantly improving coking tolerance (schematized in Figure 7G and H). Thus, R-PBMN underwent a self-carbon-cleaning process driven by the evolution of hydroxyl species into CH_xOH*, thereby demonstrating superior anti-coking performance.

Figure 8A compares the morphological evolution of NiO and R-PBMN anodes under a S/C ratio of 1:2. The NiO anode darkened within 10 min, indicating the onset of carbon deposition accompanied by surface cracking, and was fully deactivated after 30 min due to severe coking. Conversely, the R-PBMN anode maintained structural integrity without detectable degradation throughout the test. Raman analysis

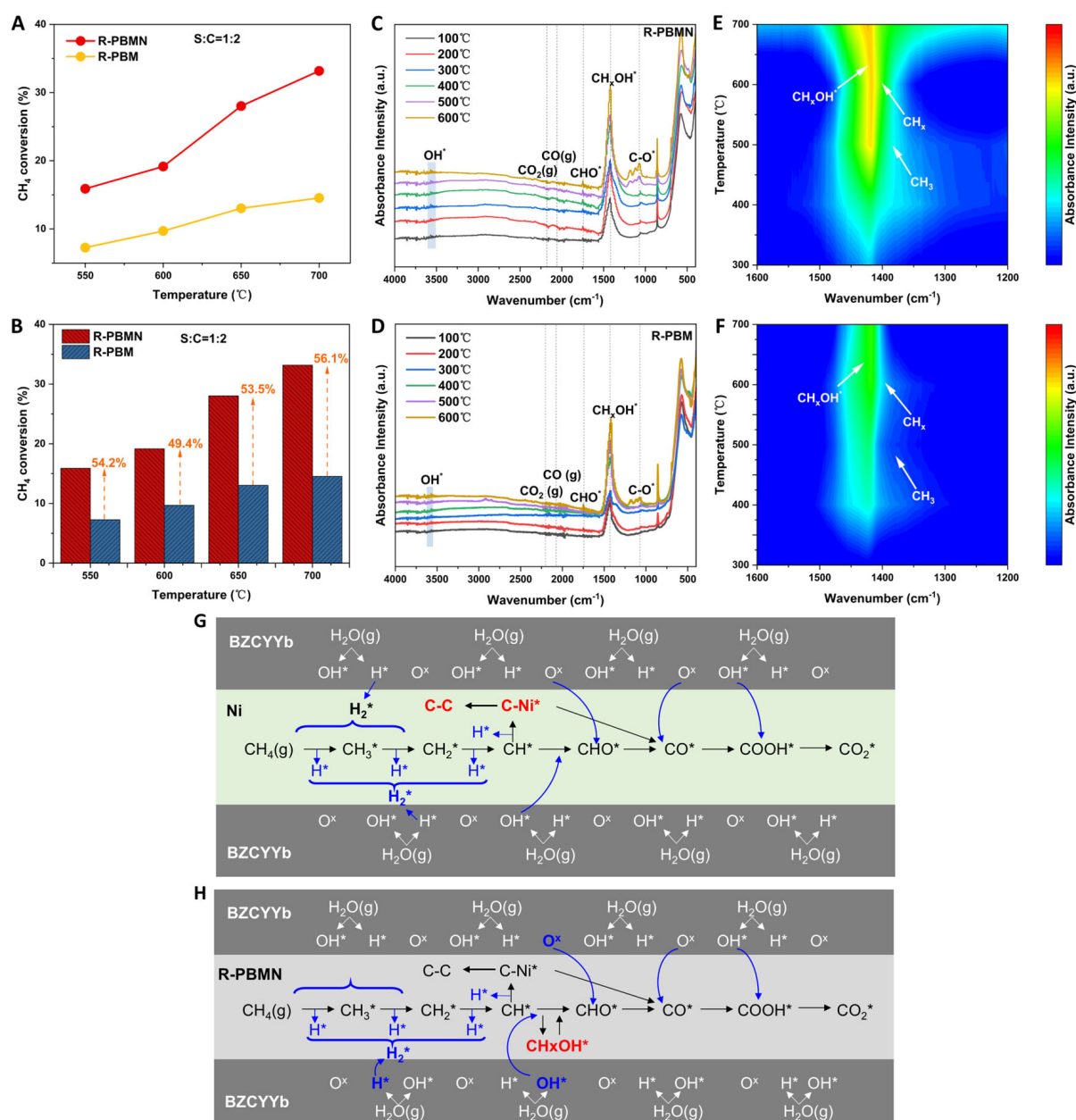


Figure 7. (A and B) CH₄ conversion of R-PBM and R-PBMN in PBRs at S/C = 1:2. Semi-in-situ DRIFTs spectra for (C and E) R-PBMN and (D and F) R-PBM under steam methane reforming conditions (S/C = 1:2, 100–700 °C) probing intermediate species. (G and H) Proposed reaction pathways for steam methane reforming on (G) Ni and (H) R-PBMN derived from Semi-in-situ DRIFTS analysis.

[Figure 8B] confirmed progressive carbon accumulation on NiO, evidenced by the D-band ($\sim 1350\text{ cm}^{-1}$) and G-band ($\sim 1580\text{ cm}^{-1}$). The continuously increasing D-band indicated the formation of disordered carbon, whereas the stabilized G-band suggested limited graphitic ordering^[45,46]. Remarkably, R-PBMN exhibited no detectable carbon-related signals even after 300 min [Figure 8C], demonstrating exceptional resistance to coking. Figure 8D schematizes the functionality of R-PBMN during methane steam reforming: H₂-induced surface reconstruction enabled the *in situ* precipitation of Ni nanoparticles, whereas enhanced hydrophilicity promoted water activation. This synergistic design ensured robust SMR operation through intrinsic carbon-cleaning mechanisms.

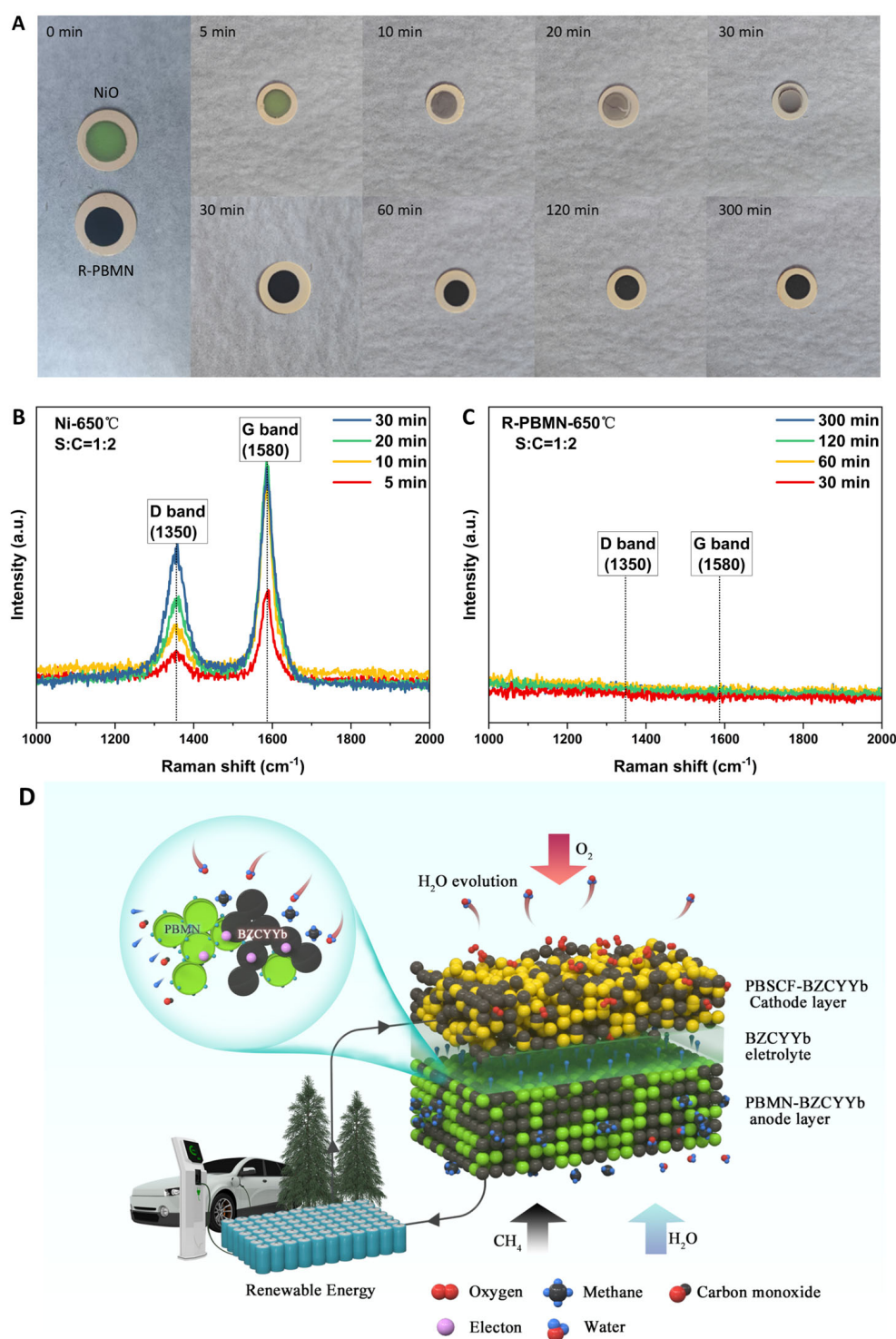


Figure 8. (A) Morphology evolution of NiO and R-PBMN fuel electrodes under steam methane reforming conditions ($S/C = 1:2$) at various exposure times. Raman spectra of (B) NiO and (C) R-PBMN fuel electrodes after $S/C = 1:2$ treatment for increasing durations. (D) Schematic diagram of steam methane reforming with R-PBMN as fuel electrode.

Electrochemical activity of r-PCFCs

Laboratory-scale single cells with the configuration R-PBMN-BZCYYb|BZCYYb|PBSCF-BZCYYb were fabricated to evaluate the electrochemical performance of the R-PBMN anode. Figure 9A shows the current density-voltage (I-V) and power density (I-P) curves in fuel cell (FC) mode using H₂ and CH₄ as fuels at

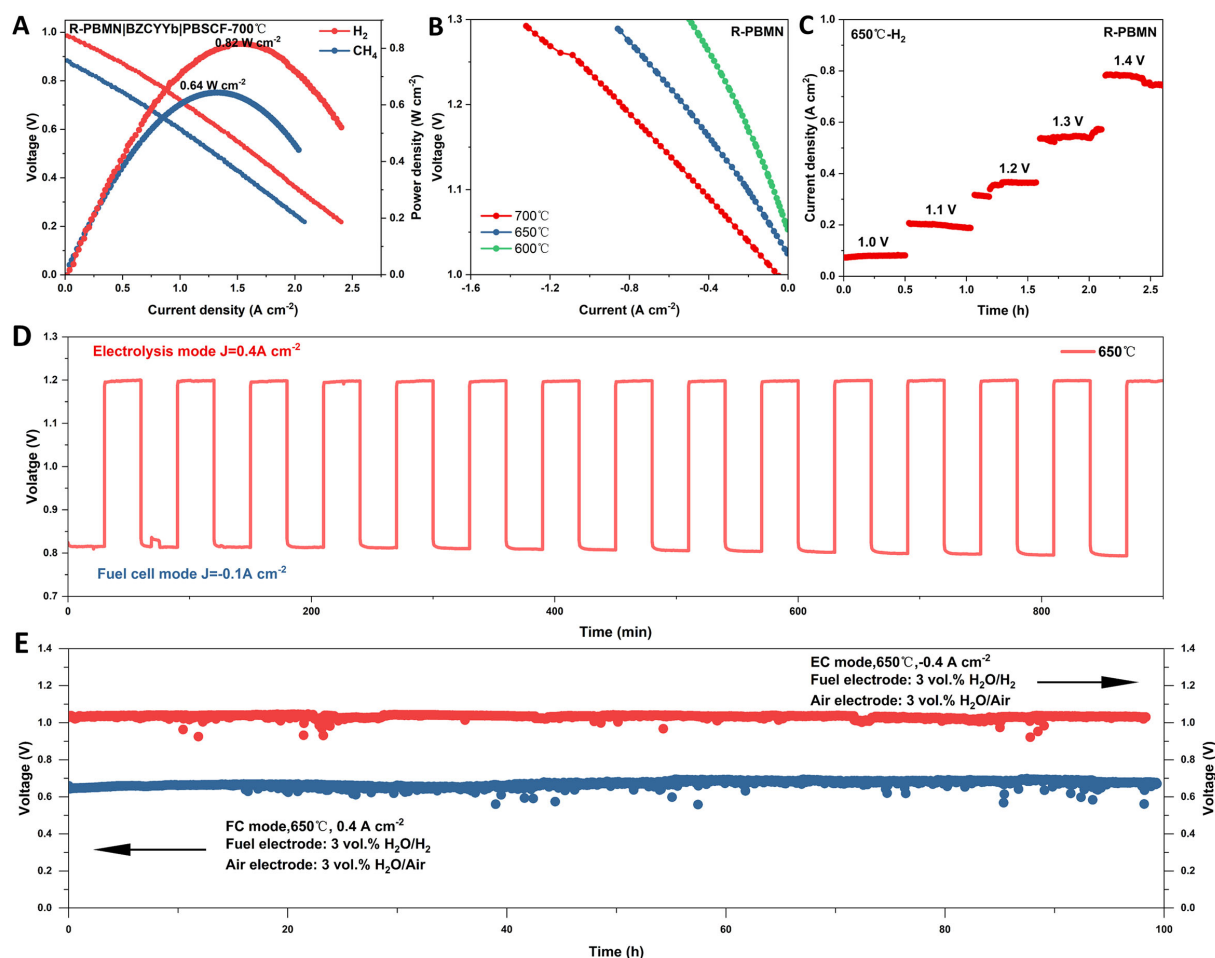


Figure 9. (A) I-V and I-P curves in fuel cell (FC) mode at 700 °C with humidified H₂ (3 vol.% H₂O) or CH₄ fuel. (B) I-V curves in electrolysis cell (EC) mode with humidified H₂ fuel (3 vol.% H₂O). Both for R-PBMN-BZCYYb|BZCYYb|PBSCF-BZCYYb cells. (C) Short-stability under stepped voltages. (D) Reversible cycling operation at 650 °C (current densities of 0.4–0.1 A cm⁻²). (E) Long-term operational stability at ±0.4 A cm⁻² in FC/EC modes.

700 °C. The improved catalytic activity of R-PBMN was demonstrated by its peak power density of 0.82 W cm⁻² in H₂ and 0.64 W cm⁻² in CH₄ at 700 °C. These values represent increases of 15.5% and 18.5% in H₂ and CH₄, respectively, compared to R-PBM's peak power densities of 0.71 and 0.54 W cm⁻². The power density and impedance of R-PBMN at 600–700 °C under H₂ and CH₄ fuels are shown in [Supplementary Figures 4 and 5](#). Interestingly, the electrolyte resistance, as shown in [Supplementary Figure 6](#), was observed to be higher when CH₄ was used compared to H₂, which can be attributed to the differences in the electrochemical reactions involved. H₂ undergoes a simpler oxidation reaction with fewer intermediate products, leading to a more stable interface with the electrolyte, thus resulting in lower electrolyte resistance. In contrast, CH₄ oxidation involves multiple reforming reactions, including the formation of CO and CO₂, which introduces additional intermediates and a more complex reaction environment at the electrode-electrolyte interface, thereby increasing the electrolyte resistance. The open circuit voltage (OCV) observed in [Supplementary Figure 6](#) was also lower for CH₄ than for H₂, consistent with the literature^[7]. The H₂ oxidation reaction is more straightforward, yielding a higher OCV due to its high efficiency and fewer reaction steps. In contrast, CH₄ requires a more complex reforming process, leading to a lower OCV due to the multiple electrochemical steps and intermediate products involved in the reaction.

In electrolysis cell (EC) mode [[Figure 9B](#)], current densities of -1.30, -0.86, and -0.50 A cm⁻² at 1.3 V were

achieved at 700, 650, and 600 °C, respectively. Short-term stability tests under stepped-voltage conditions [Figure 9C] confirmed the cell's robustness. Excellent cyclic stability was observed over 15 reversible FC/EC cycles lasting 15 h at 650 °C [Figure 9D]. The power density and current density of R-PBM under FC and EC modes were shown in Supplementary Figure 6. Long-term operation [Figure 9E] further demonstrated the stability and durability of the cell. These results indicated that the single cell with the R-PBMN anode exhibited remarkable stability. Under a current density of 0.4 A cm⁻², the cell remained stable in FC mode for 100 h. The rate of performance degradation was calculated as 0.02% per hour, based on the change in power density over the cycling period. Similarly, in EC mode, the maintained stability for 100 h at a current density of -0.4 A cm⁻², with a power density degradation rate of only 0.02% per hour over the 100-h cycling period. Additionally, high-resolution SEM (HR-SEM) images revealed no significant interfacial delamination between R-PBMN and BZCYYb after 100 h of single-cell testing, demonstrating the structural stability of the cell under operating conditions [Supplementary Figure 7]. The exceptional operational stability of the cell underscored the promising potential of R-PBMN as an anode material for reversible PCFCs (r-PCFCs).

CONCLUSIONS

In summary, a high-performance anode material, R-PBMN, was successfully developed through partial Ni substitution at Mn sites followed by *in situ* exsolution of Ni nanoparticles. This cooperative design strategy effectively enhanced the electrochemical activity of the parent R-PBM perovskite material, particularly at intermediate and low temperatures where its intrinsic performance is insufficient for PCFC applications. The exsolved Ni nanoparticles lowered the activation barrier for C-H bond cleavage, accelerating methane activation and electrochemical oxidation, while the R-PBM lattice provided inherent hydrophilicity and oxygen mobility that facilitated CH₄/H₂O co-activation and intermediate formation. As a result, R-PBMN exhibited significantly improved power densities, achieving 0.82 W cm⁻² in H₂ and 0.64 W cm⁻² in CH₄ at 700 °C, along with long-term operational stability. Importantly, this performance enhancement was achieved without compromising the intrinsic coking resistance of the PBM framework. Future work could explore the effect of other dopants, such as Ni, Co, or Fe, on the electrochemical performance and stability of R-PBMN anodes. Overall, this work demonstrates an effective pathway to transform PBM from a hydrocarbon-tolerant but low-activity oxide into a high-performance PCFC anode that combines superior electrochemical activity with durable stability.

DECLARATIONS

Author's contributions

Writing - original draft, visualization, investigation and data curation: Duan, X.

Investigation, and data curation: Tang, J.; Qu J.; Dai X.; Zhao Z.; Wang L.

Validation and investigation: Wang, W.

Writing - review & editing, project administration, funding acquisition, conceptualization: Zhao Y.; Yun S.; An S.; Wu F.

Availability of data and materials

Data supporting the results of this study are available from the corresponding author upon request.

Financial support and sponsorship

This work was supported by the National Natural Science Foundation of China (U24A2099, 52264046, 51974167); the Natural Science Research Project of the Guizhou Provincial Department of Education ([2022]041); the Guizhou High-Level and Innovative Talents Projects ([2022]009-1); the Guizhou Provincial Major Scientific and Technological Program ([2024]021, [2024]017); the Guizhou Science and Technology Planning Project (CXTD[2025]018); the First-Class Discipline Research Special Project of Inner Mongolia (YLXKZX-NKD-002); the Fundamental Scientific Research Funds for Universities Directly under Inner Mongolia (201-04060822030, 2023QNJS028); and the Natural Science Foundation of Inner Mongolia (2023QN05038).

Conflicts of interest

Dr. Yun S. is Associate Editor of the journal *Energy Materials*. Dr. Yun S. was not involved in any steps of the editorial process, notably including reviewers' selection, manuscript handling, or decision-making, while the other authors have declared that they have no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Copyright

© The Author(s) 2026.

Supplementary Materials

[Supplementary Materials](#)

REFERENCES

- Xie, M.; Cai, C.; Duan, X.; Xue, K.; Yang, H.; An, S. Review on Fe-based double perovskite cathode materials for solid oxide fuel cells. *Energy Mater.* **2024**, 4, 400007. DOI
- He, F.; Liu, S.; Wu, T.; et al. Catalytic self-assembled air electrode for highly active and durable reversible protonic ceramic electrochemical cells. *Adv. Funct. Mater.* **2022**, 32, 2206756. DOI
- Bian, W.; Wu, W.; Gao, Y.; et al. Regulation of cathode mass and charge transfer by structural 3D engineering for protonic ceramic fuel cell at 400 °C (Adv. Funct. Mater. 33/2021). *Adv. Funct. Mater.* **2021**, 31, 2170244. DOI
- Duan, C.; Kee, R. J.; Zhu, H.; et al. Highly durable, coking and sulfur tolerant, fuel-flexible protonic ceramic fuel cells. *Nature* **2018**, 557, 217-22. DOI
- He, F.; Hou, M.; Liu, D.; et al. Phase segregation of a composite air electrode unlocks the high performance of reversible protonic ceramic electrochemical cells. *Energy Environ. Sci.* **2024**, 17, 3898-907. DOI
- Bian, W.; Wu, W.; Wang, B.; et al. Revitalizing interface in protonic ceramic cells by acid etch. *Nature* **2022**, 604, 479-85. DOI
- Hong, K.; Choi, M.; Bae, Y.; et al. Direct methane protonic ceramic fuel cells with self-assembled Ni-Rh bimetallic catalyst. *Nat. Commun.* **2023**, 14, 7485. DOI PubMed PMC
- Sengodan, S.; Choi, S.; Jun, A.; et al. Layered oxygen-deficient double perovskite as an efficient and stable anode for direct hydrocarbon solid oxide fuel cells. *Nat. Mater.* **2015**, 14, 205-9. DOI
- Wang, W.; Su, C.; Wu, Y.; Ran, R.; Shao, Z. Progress in solid oxide fuel cells with nickel-based anodes operating on methane and related fuels. *Chem. Rev.* **2013**, 113, 8104-51. DOI
- Hu, F.; Chen, K.; Ling, Y.; et al. Smart dual-exsolved self-assembled anode enables efficient and robust methane-fueled solid oxide fuel cells. *Adv. Sci.* **2024**, 11, e2306845. DOI PubMed PMC
- Yan, J.; Chen, H.; Li, Y. W.; Li, S.; Shao, Z. Bifunctional electrocatalysts $\text{Pr}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.1}\text{Fe}_{0.9-x}\text{Ni}_x\text{O}_{3-\delta}$ ($x = 0.1, 0.2$) for the HOR and ORR of a symmetric solid oxide fuel cell. *J. Mater. Chem. A* **2023**, 11, 21839-45. DOI
- Song, L.; Chen, D.; Pan, J.; et al. B-site super-excess design $\text{Sr}_2\text{V}_{0.4}\text{Fe}_{0.9}\text{Mo}_{0.7}\text{O}_{6-\delta}\text{-Ni}_{0.4}$ as a Highly active and redox-stable solid oxide fuel cell anode. *ACS Appl. Mater. Interfaces* **2023**, 15, 48296-303. DOI
- Liu, F.; Deng, H.; Wang, Z.; et al. Synergistic effects of in-situ exsolved Ni-Ru bimetallic catalyst on high-performance and durable direct-methane solid oxide fuel cells. *J. Am. Chem. Soc.* **2024**, 146, 4704-15. DOI
- Liu, F.; Diercks, D.; Hussain, A. M.; et al. Nanocomposite catalyst for high-performance and durable intermediate-temperature methane-fueled metal-supported solid oxide fuel cells. *ACS Appl. Mater. Interfaces* **2022**, 14, 53840-9. DOI
- Bahout, M.; Managutti, P. B.; Dorcet, V.; Le, Gal. La. Salle. A.; Paofai, S.; Hansen, T. C. *In situ* exsolution of Ni particles on the $\text{PrBaMn}_2\text{O}_5$ SOFC electrode material monitored by high temperature neutron powder diffraction under hydrogen. *J. Mater. Chem. A* **2020**, 8, 3590-7. DOI
- Song, Y.; Kim, H.; Jang, J.; et al. Pt_3Ni alloy nanoparticle electro-catalysts with unique core-shell structure on oxygen-deficient layered perovskite for solid oxide cells. *Adv. Energy Mater.* **2023**, 13, 2302384. DOI
- Wang, Z.; Wang, Y.; Py, B.; et al. DRTtools: freely accessible distribution of relaxation times analysis for electrochemical impedance spectroscopy. *ACS Electrochem.* **2025**, 1, 2680-9. DOI

18. Wan, T.; Saccoccio, M.; Chen, C.; Ciucci, F. Influence of the discretization methods on the distribution of relaxation times deconvolution: implementing radial basis functions with DRTtools. *Electrochim. Acta*. **2015**, *184*, 483–99. DOI
19. Yin, Y.; Dai, H.; Yu, S.; Bi, L.; Traversa, E. Tailoring cobalt-free $\text{La}_{0.5}\text{Sr}_{0.5}\text{FeO}_{3-\delta}$ cathode with a nonmetal cation-doping strategy for high-performance proton-conducting solid oxide fuel cells. *SusMat* **2022**, *2*, 607–16. DOI
20. Guo, Y.; Wang, S.; Li, R.; et al. In situ exsolved CoFe alloy nanoparticles for stable anodic methane reforming in solid oxide electrolysis cells. *Joule* **2024**, *8*, 2016–32. DOI
21. Yao, S.; Wang, S.; Liu, Y.; et al. High flux and stability of cationic intercalation in transition-metal oxides: unleashing the potential of Mn t_{2g} orbital via enhanced π -donation. *J. Am. Chem. Soc.* **2023**, *145*, 26699–710. DOI
22. Li, W.; Guan, B.; Yang, T.; et al. Layer-structured triple-conducting electrocatalyst for water-splitting in protonic ceramic electrolysis cells: Conductivities vs. activity. *J. Power. Sources*. **2021**, *495*, 229764. DOI
23. Wang, N.; Tang, C.; Du, L.; et al. Advanced cathode materials for protonic ceramic fuel cells: recent progress and future perspectives (Adv. Energy Mater. 34/2022). *Adv. Energy Mater.* **2022**, *12*, 2270145. DOI
24. Ding, H.; Wu, W.; Jiang, C.; et al. Self-sustainable protonic ceramic electrochemical cells using a triple conducting electrode for hydrogen and power production. *Nat. Commun.* **2020**, *11*, 1907. DOI PubMed PMC
25. Zhou, C.; Wang, X.; Liu, D.; et al. New strategy for boosting cathodic performance of protonic ceramic fuel cells through incorporating a superior hydronation second phase. *Energy. Environ. Mater.* **2024**, *7*, e12660. DOI
26. Shao, S.; Li, X.; Cai, Y.; et al. Interfacial metal ion self-rearrangement: a new strategy for endowing hybrid cathode with enhanced performance for protonic ceramic fuel cells. *Chem. Eng. J.* **2023**, *460*, 141698. DOI
27. Yao, X.; Cheng, Q.; Bai, X.; et al. Enlarging the three-phase boundary to raise CO_2/CH_4 conversions on exsolved Ni-Fe alloy perovskite catalysts by minimal Rh doping. *ACS. Catal.* **2024**, *14*, 5639–53. DOI
28. Bang, S.; Kim, J. G.; Wen, Y.; Lee, J.; Lee, W. Equalized oxygen partial pressure for carbon coking-free dry reforming of methane in intermediate temperature solid oxide fuel cells. *Chem. Eng. J.* **2025**, *514*, 163163. DOI
29. Liu, Y.; Luo, J.; Li, C.; et al. $\text{BaCe}_{0.8}\text{Fe}_{0.1}\text{Ni}_{0.1}\text{O}_{3-\delta}$ -impregnated Ni-GDC by phase-inversion as an anode of solid oxide fuel cells with on-cell dry methane reforming. *J. Adv. Ceram.* **2024**, *13*, 834–41. DOI
30. Wang, H.; Cui, G.; Lu, H.; et al. Facilitating the dry reforming of methane with interfacial synergistic catalysis in an Ir@CeO_{2-x} catalyst. *Nat. Commun.* **2024**, *15*, 3765. DOI PubMed PMC
31. Zhang, X.; Zhang, Z.; Wang, Q.; et al. Enhanced photothermal methane dry reforming through electronic interactions between nickel and yttrium. *Nanoscale. Horiz.* **2025**, *10*, 905–14. DOI
32. Li, Y.; Yao, L.; Li, J.; et al. GaN nanowire-supported NiO for low-temperature and durable dry reforming of methane toward syngas. *Appl. Catal. B. Environ. Energy*. **2025**, *366*, 125051. DOI
33. Chen, J.; Liu, Y.; Chen, Z.; et al. Highly efficient transformation of tar model compounds into hydrogen by a Ni-Co alloy nanocatalyst during tar steam reforming. *Environ. Sci. Technol.* **2024**, *58*, 3540–51. DOI
34. Han, F.; Wang, Z.; Zhang, S.; Li, C.; Barnett, S. A. Highly efficient perovskite-based fuel electrodes for solid oxide electrochemical cells via in-situ nanoparticle exsolution and electron conduction enhancement. *Appl. Catal. B. Environ. Energy*. **2025**, *361*, 124676. DOI
35. Wang, S.; Ye, X.; Zhou, Y. All symmetrical metal supported solid oxide fuel cells. *J. Inorg. Mater.* **2016**, *31*, 769. DOI
36. Gu, Y.; Zhang, Y.; Zheng, Y.; Chen, H.; Ge, L.; Guo, L. $\text{PrBaMn}_2\text{O}_{5+\delta}$ with praseodymium oxide nano-catalyst as electrode for symmetrical solid oxide fuel cells. *Appl. Catal. B. Environ.* **2019**, *257*, 117868. DOI
37. Wang, S.; Zheng, H.; Wu, Y.; et al. Characterization of $\text{Pr}_{0.5}\text{A}_{0.5}\text{Fe}_{0.9}\text{W}_{0.1}\text{O}_{3-\delta}$ (A = Ca, Sr and Ba) as symmetric electrodes for solid oxide fuel cells. *Sustain. Energy. Fuels*. **2022**, *6*, 4741–8. DOI
38. Li, X.; Li, R.; Tian, Y.; et al. Tuning $\text{Pr}_{0.5}\text{Ba}_{0.5}\text{FeO}_{3-\delta}$ cathode to enhanced stability and activity via Ca-doping for symmetrical solid oxide fuel cells. *Int. J. Hydrogen. Energy*. **2024**, *60*, 650–6. DOI
39. Zhang, W.; Meng, J.; Zhang, X.; Zhang, L.; Liu, X.; Meng, J. Co-incorporating enhancement on oxygen vacancy formation energy and electrochemical property of $\text{Sr}_2\text{Co}_{1+x}\text{Mo}_{1-x}\text{O}_{6-\delta}$ cathode for intermediate-temperature solid oxide fuel cell. *Solid. State. Ion.* **2018**, *316*, 20–8. DOI
40. Zhou, J.; Shin, T.; Ni, C.; et al. In situ growth of nanoparticles in layered perovskite $\text{La}_{0.8}\text{Sr}_{1.2}\text{Fe}_{0.9}\text{Co}_{0.1}\text{O}_{4-\delta}$ as an active and stable electrode for symmetrical solid oxide fuel cells. *Chem. Mater.* **2016**, *28*, 2981–93. DOI
41. 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*, 23168–79. DOI
42. Yu, Y.; Yu, L.; Shao, K.; et al. $\text{BaZr}_{0.1}\text{Co}_{0.4}\text{Fe}_{0.4}\text{Y}_{0.1}\text{O}_{3-\delta}$ -SDC composite as quasi-symmetrical electrode for proton conducting solid oxide fuel cells. *Ceram. Int.* **2020**, *46*, 11811–8. DOI

43. Escudero, M.; Aguadero, A.; Alonso, J.; Daza, L. A kinetic study of oxygen reduction reaction on La_2NiO_4 cathodes by means of impedance spectroscopy. *J. Electroanal. Chem.* **2007**, *611*, 107-16. DOI
44. Liu, X.; Huang, L.; Xi, X.; et al. Regulating the d-p orbital hybridization in $\text{BaCo}_{0.4}\text{Fe}_{0.4}\text{Zr}_{0.1}\text{Y}_{0.1}\text{O}_{3-\delta}$ via Cu doping for high-performance solid oxide fuel cells cathode. *Chem. Eng. J.* **2025**, *513*, 162958. DOI
45. Cao, X.; Ke, L.; Zhao, K.; Yan, X.; Wu, X.; Yan, N. Surface decomposition of doped $\text{PrBaMn}_2\text{O}_{5+\delta}$ induced by in situ nanoparticle exsolution: quantitative characterization and catalytic effect in methane dry reforming reaction. *Chem. Mater.* **2022**, *34*, 10484-94. DOI
46. Li, J.; Zhou, X.; Wu, C.; et al. Self-stabilized hybrid cathode for solid oxide fuel cell: a-site deficient perovskite coating as solid solution for strontium diffusion. *Chem. Eng. J.* **2022**, *438*, 135446. DOI

Disclaimer/Publisher's Note: All statements, opinions, and data contained in this publication are solely those of the individual author(s) and contributor(s) and do not necessarily reflect those of OAE and/or the editor(s). OAE and/or the editor(s) disclaim any responsibility for harm to persons or property resulting from the use of any ideas, methods, instructions, or products mentioned in the content.



© The Author(s) 2026. Open Access This article is licensed under a Creative Commons Attribution 4.0 International License (<https://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, sharing, adaptation, distribution and reproduction in any medium or format, for any purpose, even commercially, as long as you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.