

Enhanced performance and stability of ammonia-fueled SOFCs enabled by an *in situ* catalytic microreactor constructed within anode channels

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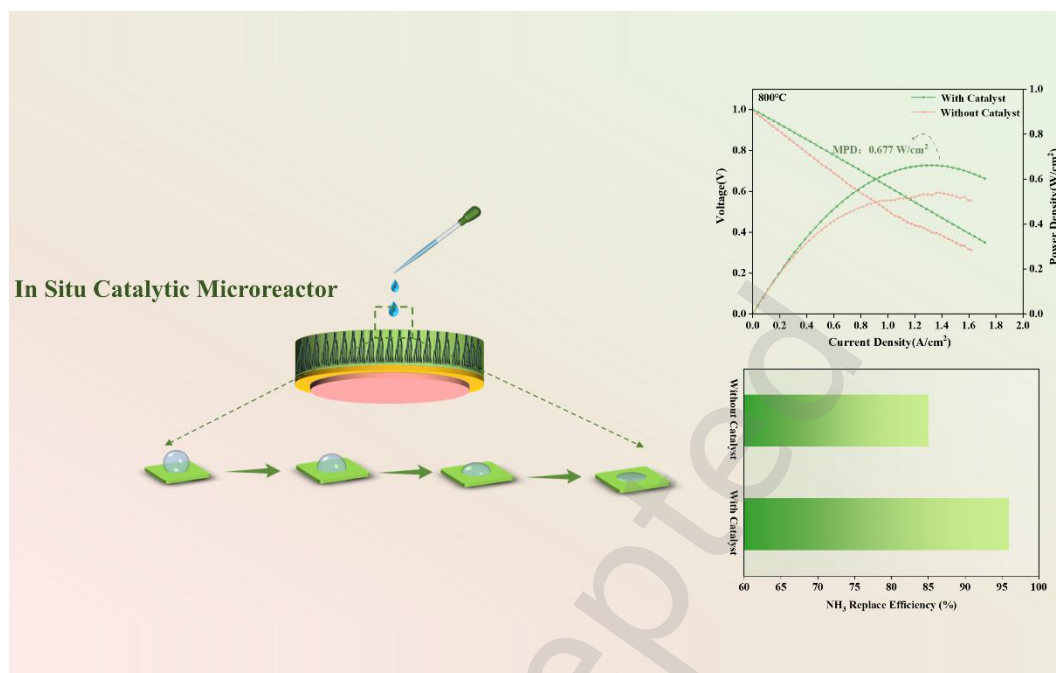
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Graphical abstract



An in situ catalytic microreactor was constructed by introducing nanofiber catalysts into the interconnected channels of a dendritic porous SOFC anode. The channel-distributed nanofiber catalysts enhanced NH₃ cracking and its coupling with downstream electrochemical utilization, resulting in increased peak power density and prolonged stable operation.

Research Article

Enhanced performance and stability of ammonia-fueled SOFCs enabled by an *in situ* catalytic microreactor constructed within anode channels

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Abstract

Ammonia, as a zero-carbon fuel with high hydrogen storage density and easy storage and transportation, holds significant promise for direct utilization in solid oxide fuel cells (SOFCs). However, under ammonia-fueled conditions, SOFCs are readily constrained by anode-side steam generation, deterioration of the local reaction environment, and insufficient coordination between reaction and mass transport, which consequently lowers ammonia utilization efficiency and operational stability. To address these issues, this study proposes a synergistic optimization strategy that integrates a

dendritic porous anode structure with intrachannel Pd–GDC nanofiber catalysts. Through the analysis of electrochemical responses and NH_3 replacement efficiency under different ammonia concentrations, an optimal fuel condition was identified. On this basis, a dendritic porous NiO–GDC anode support with interconnected channels was fabricated by the phase inversion method, and Pd–GDC nanofiber catalysts were introduced into the anode channels by vacuum-assisted infiltration, thereby forming an in situ catalytic microreactor within the anode to enhance ammonia cracking, improve the local reaction environment, and promote the subsequent electrochemical conversion of cracking products. Under 800 °C and 66.7% NH_3 , the peak power density increased by 25.4%, the NH_3 replacement efficiency rose from 84% to 96%, and the stable operating time was extended from 91 to 172 h. These results demonstrate that this strategy can simultaneously improve the output performance, ammonia utilization efficiency, and long-term operational stability of ammonia-fueled SOFCs, thereby providing a new approach for the efficient design of ammonia-fueled SOFCs.

Keywords

ammonia-fueled SOFCs; dendritic porous anode; Pd–GDC nanofiber catalyst; ammonia utilization; stability enhancement

1. Introduction

Against the backdrop of the accelerating global transition toward low-carbon and sustainable energy systems, the development of efficient, clean, and easily transportable

energy carriers has become a major research focus. Ammonia (NH_3), owing to its carbon-free nature, high hydrogen storage density, mild liquefaction conditions, and relatively mature storage and transportation infrastructure, is widely regarded as a highly promising hydrogen carrier and zero-carbon fuel ^[1-3]. Compared with high-purity hydrogen, ammonia offers greater practical feasibility for large-scale storage, transportation, and long-distance distribution. Moreover, because ammonia decomposition primarily produces hydrogen and nitrogen, it exhibits distinct advantages in carbon-emission-constrained energy utilization scenarios. Solid oxide fuel cells (SOFCs), as high-temperature electrochemical energy conversion devices, possess broad fuel flexibility and high energy conversion efficiency, making them particularly suitable for the direct utilization of fuels such as ammonia that can undergo in situ cracking under elevated-temperature conditions. Therefore, the development of ammonia-fueled SOFC systems is expected not only to expand the efficient utilization of non-carbon-based fuels in SOFCs, but also to provide important support for future ammonia-based power generation and energy storage technologies ^[4-6].

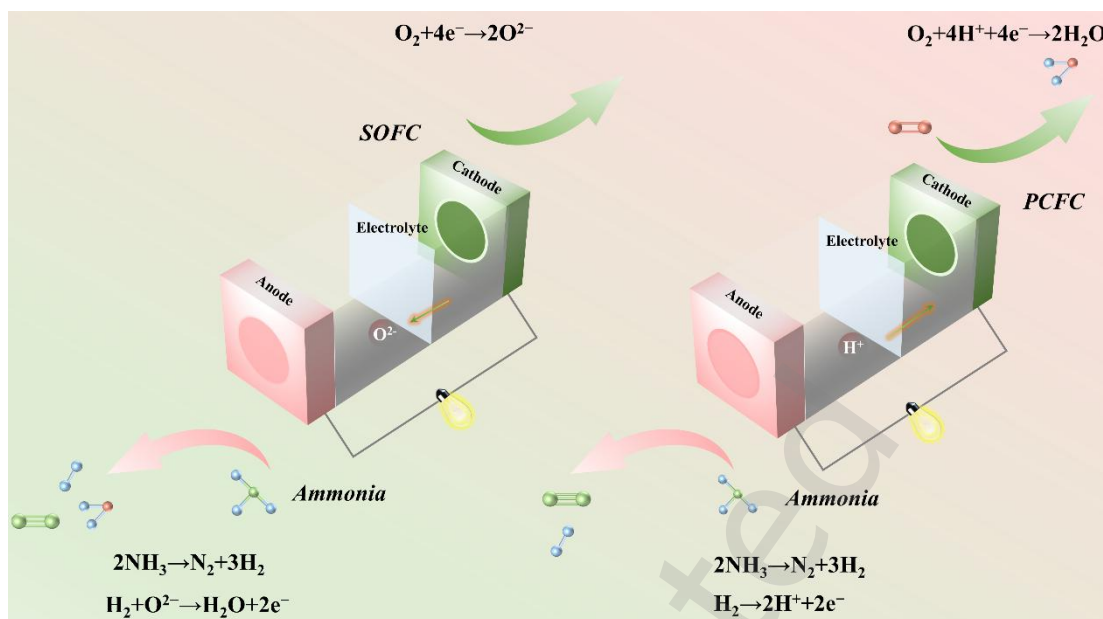


Fig. 1. Schematic illustration of the operation of SOFCs and PCFCs under ammonia-fueled conditions.

Despite this promise, ammonia utilization in SOFCs is not a single-step process, but rather a multistage reaction network governed by the coupling of catalytic and electrochemical processes, as shown in **Fig. 1**. In typical oxygen-ion-conducting SOFCs, NH₃ is first catalytically cracked at the anode to generate H₂ and N₂, after which the produced H₂ is electrochemically oxidized by O²⁻ ions transported from the cathode through the electrolyte. As a result, ammonia utilization in SOFCs fundamentally involves the coupling of NH₃ cracking, gas diffusion, oxygen-ion transport, and interfacial electrochemical reactions at the anode, and the overall cell performance is strongly dependent on the degree of coordination among these subprocesses [7, 8]. Of particular importance, the H₂O generated at the anode during electrochemical oxidation alters the local gas composition, dilutes the fuel stream, and increases the local steam partial pressure, thereby suppressing NH₃ cracking and further affecting subsequent fuel

conversion and electrochemical reaction processes. In contrast, proton-conducting fuel cells (PCFCs) employ H^+ as the charge carrier, and water is produced at the air electrode rather than at the fuel electrode, thereby avoiding direct dilution of the anode fuel stream by product water. This distinction endows PCFCs with an inherent advantage in ammonia utilization. However, the selection of a practical fuel-cell platform also depends on technological maturity, manufacturing feasibility, cost, and system compatibility. SOFCs benefit from relatively mature material systems, fabrication processes, and stack-integration technologies, which provide a strong foundation for large-scale manufacturing and practical system development. Their relatively high operating temperatures are also favorable for NH_3 -cracking kinetics and facilitate the integration of ammonia conversion with conventional Ni-based anodes and internal catalytic strategies. In comparison, further advances are still needed for PCFCs in large-scale fabrication, electrolyte densification, long-term durability, and stack-level validation. Accordingly, compared with PCFCs, the efficient utilization of ammonia in SOFCs is more susceptible to the constraints imposed by anode-side steam generation, local atmosphere evolution, and mismatches in reaction–transport coupling, thereby placing more stringent requirements on the regulation of anode microstructure, reaction-zone distribution, and local reaction environments [9, 10].

However, the structural design of current ammonia-fueled SOFC anodes still struggles to simultaneously satisfy the multiple requirements of rapid gas transport, sufficient NH_3 cracking, and efficient utilization of electrochemically active reaction

zones. Previous studies have demonstrated that electrode microstructure, pore connectivity, and local reaction environments can significantly affect mass transport efficiency, the effective reaction-zone thickness, and concentration polarization behavior in solid oxide cells. For ammonia-fueled systems, this insufficient coordination among structure, transport, and reaction is particularly pronounced. In relatively thick anodes or architectures with tortuous transport pathways, significant concentration gradients of NH_3 , H_2 , N_2 , and H_2O can readily develop along the electrode thickness direction. These concentration gradients can cause nonuniform local fuel supply, underutilization of reaction zones, and increased concentration polarization. Furthermore, local atmosphere fluctuations, steam accumulation, and uneven reaction distribution may induce performance degradation during long-term operation. This degradation further constrains the stable output of ammonia-fueled SOFCs. These observations indicate that, in addition to the intrinsic catalytic activity of the anode material, the internal structural characteristics of the anode, mass transport behavior, and local reaction environment are also key factors governing the performance and durability of ammonia-fueled SOFCs [11-13].

To improve the output performance and operational stability of ammonia-fueled SOFCs, extensive efforts have been devoted to the optimization of anode materials, catalytic activity, and electrode architecture. Among the various candidates, Ni-based cermet anodes remain the most widely used anode system because of their good electrical conductivity, relatively high ammonia cracking activity, and well-established

technological foundation. On this basis, the introduction of active species such as Ru and Fe, or the construction of synergistic metal/oxide interfaces, has been shown to further enhance ammonia decomposition, reduce polarization losses, and improve long-term stability [7, 14, 15]. In addition to intrinsic anode-material modification, catalytic enhancement has also been pursued through catalyst-infiltration-based functionalization, the coating of NH₃-cracking catalyst layers on the fuel-electrode surface for NH₃ precracking, and the incorporation of additional catalytic components within anode-support regions, including catalyst particles, locally deposited catalytic domains, or porous catalytic inserts [16-18]. Collectively, these studies demonstrate that catalytic functionality can be introduced at different locations and in different configurations to promote NH₃ conversion and improve the electrochemical performance of ammonia-fueled SOFCs.

For a built-in catalyst integrated within a Ni-containing SOFC anode, catalyst selection should not rely only on intrinsic NH₃-cracking activity, but should also consider long-term structural stability, compatibility with the anode support, tolerance to the water-containing anode atmosphere, and noble-metal utilization. In this study, Pd-GDC was selected as the intrachannel catalyst system because the GDC matrix is compositionally compatible with the NiO-GDC dendritic anode support, which is favorable for anchoring the Pd-containing catalytic phase within the interconnected pore channels and avoiding the introduction of a chemically mismatched foreign support phase. In addition, CeO₂-based supports can interact strongly with Pd species, helping

to stabilize dispersed Pd and mitigate catalyst agglomeration or restructuring under steam-containing reaction conditions ^[19]. Therefore, Pd–GDC was employed as a balanced intrachannel catalyst–support system that considers NH₃-cracking functionality, anode compatibility, steam tolerance, structural stability, and low noble-metal loading.

Meanwhile, increasing attention has been paid to the role of electrode microstructure in ammonia conversion behavior. It has been reported that pore characteristics, transport pathways, and the spatial distribution of reaction interfaces can strongly influence local reaction environments, gas transport efficiency, and the effective utilization of reaction zones, thereby affecting both device performance and long-term stability. Beyond the individual effects of catalytic composition and electrode morphology, the spatial arrangement of catalytic functionality relative to the internal gas-transport network is also important for coordinating NH₃ cracking, transport of the cracking products, and their subsequent electrochemical utilization. Although recent studies have begun to address electrode structural evolution and its cross-scale effects in ammonia-fueled SOFCs, integrating catalytic functionality with interconnected internal transport pathways provides a complementary structural route for regulating the local reaction environment and strengthening reaction–transport coordination ^[6, 11, 20].

Based on the above background and the unresolved challenges, this work focuses on the key bottlenecks associated with the complex anode-side reaction environment and the insufficient coordination between mass transport and reaction processes in

ammonia-fueled SOFCs. Specifically, a phase-inversion-derived dendritic porous NiO–GDC anode support with interconnected gas-transport channels was constructed, and preformed Pd–GDC nanofibers were introduced into these channels by vacuum-assisted infiltration. This design integrates catalytic functionality with the internal transport network, enabling the dendritic support to serve simultaneously as a mechanical framework, gas-transport medium, and channel-distributed catalytic environment. Such spatial integration is intended to facilitate NH_3 cracking, transport of the cracking products, and their subsequent electrochemical consumption within the same anode network. Through this synergistic structural and catalytic design, the dendritic anode is expected to provide a structural basis for integrating catalytic NH_3 conversion with internal gas transport, thereby improving the overall ammonia-utilization performance of SOFCs. This study therefore provides a new design strategy for achieving efficient and stable operation of ammonia-fueled SOFCs.

2. Materials and methods

2.1 Cell preparation

The SOFC single cell employed in this study consists of a dendritic porous NiO–GDC anode support, a YSZ electrolyte layer, a GDC barrier layer, and a PBSCF–GDC composite cathode layer. Among these components, the dendritic porous NiO–GDC layer serves as the anode support, providing the main structural framework of the cell as well as fuel transport pathways. The YSZ layer acts as a dense electrolyte responsible

for oxygen-ion conduction. The GDC layer is introduced between the electrolyte and the cathode as a barrier layer to improve interfacial compatibility and suppress unfavorable interfacial reactions. The PBSCF–GDC composite layer functions as the cathode to facilitate the oxygen reduction reaction.

For comparison, a previously developed PCFC single-cell system was also introduced in this study. The PCFC single cell consists of a porous NiO–BZCYYb anode support, a BZCYYb electrolyte layer, and a PBSCF–BZCYYb composite cathode layer. Among these components, the porous NiO–BZCYYb layer serves as the anode support, providing the main structural framework of the cell and fuel transport pathways. The BZCYYb layer acts as a dense electrolyte responsible for proton conduction. The PBSCF–BZCYYb composite layer functions as the cathode to facilitate the oxygen reduction reaction and provide active sites for water formation. The detailed fabrication procedures for the full cell have been reported in our previous work ^[21] and are therefore not repeated here.

The 60 wt% NiO–GDC anode support was fabricated using the mesh-assisted phase inversion method previously reported by our group ^[22-25]. Briefly, NiO and GDC powders were dispersed in a PES–NMP solution to form a slurry, which was then subjected to casting, phase inversion, and subsequent calcination to obtain a dendritic porous anode support. The resulting support was first pre-sintered in air at 1050 °C for 2 h and subsequently used for the deposition of the electrolyte layer.

The YSZ electrolyte layer and the GDC barrier layer were sequentially deposited

onto the surface of the pre-sintered anode support by dip coating. First, commercial YSZ powder (YSZ-U1, Fuel Cell Materials) and GDC powder were separately dispersed in anhydrous ethanol, with polyvinylpyrrolidone (PVP, Mw = 40,000) added as a dispersant and stabilizer. The resulting suspensions were then ball-milled at 300 rpm for 24 h to obtain homogeneous and stable coating slurries. Subsequently, the pre-sintered anode support was sequentially immersed in the YSZ electrolyte slurry and the GDC barrier-layer slurry. The dip-coating time for each step was controlled to ensure uniform deposition of the corresponding functional layer on the support surface. After each dip-coating step, the sample was dried at room temperature. After the two-layer structure had been completed, the sample was calcined in air at 1400 °C for 8 h to obtain a dense YSZ electrolyte layer and GDC barrier layer.

PBSCF powder was synthesized by the sol-gel method ^[26]. The as-prepared PBSCF powder was then mixed with GDC at a mass ratio of 7:3, followed by the addition of an appropriate amount of PVP and anhydrous ethanol to prepare a homogeneous cathode slurry through roll milling. The resulting slurry was deposited onto the electrolyte surface by spray coating and subsequently sintered in air at 1050 °C for 2 h to form the PBSCF-GDC composite cathode layer. The fabricated SOFC single cell had a button-cell configuration with an effective active area of 0.5 cm².

2.2 Preparation and loading of catalyst

The Pd-based catalyst used in this study was a Pd-GDC nanofiber catalyst. The

catalyst was prepared by electrospinning followed by high-temperature calcination [27]. Specifically, palladium nitrate, cerium nitrate, and gadolinium nitrate were dissolved in a mixed solvent of deionized water and anhydrous ethanol (mass ratio = 1:7) according to a designed Pd content of 6 wt% in the Pd–GDC nanofiber catalyst, thereby forming a homogeneous precursor solution. Polyvinylpyrrolidone (PVP, $M_w = 1,300,000$) was then added to the solution at 5 wt% of the total solution mass, followed by continuous stirring until complete dissolution to obtain a uniform and stable spinning solution. Electrospinning was carried out using a commercial electrospinning apparatus (Ucalery ET-2535H, Beijing, China). The distance between the needle tip and the metal mesh collector was set at 240 mm, the applied voltage was 15 kV, and the feed rate was 0.025 mL min⁻¹. The electrospinning process was performed at room temperature under a relative humidity of approximately 60% to ensure the stability of the fiber morphology. The obtained precursor fibers were subsequently calcined at a heating rate of 2 °C min⁻¹ to produce the Pd–GDC nanofiber catalyst. GDC was selected as the composite component because its material composition and structural characteristics are better matched with those of the NiO–GDC anode support, which is beneficial for the uniform distribution of the catalyst within the anode pores and for interfacial synergistic interactions.

The prepared Pd–GDC nanofiber catalyst was introduced into the dendritic porous anode by vacuum-assisted infiltration. Prior to infiltration, the Pd–GDC nanofibers were dispersed in ethanol to form a catalyst suspension with a concentration of 2 mg mL⁻¹.

The suspension was introduced into the anode side under a vacuum pressure of -0.08 MPa for 10 min, followed by drying at $90\text{ }^{\circ}\text{C}$ to remove the solvent. The infiltration–drying process was repeated until the target mass increase was reached. The total catalyst loading was determined from the mass difference of the cell before and after infiltration and was normalized by the geometric electrode area. The final Pd–GDC nanofiber catalyst loading was 0.8 mg cm^{-2} .

2.3 Characterization and test of SOFCs

During cell testing, the cell was sealed inside a custom-fabricated ceramic tube. The ceramic tube was designed according to the cell dimensions and sealed using high-temperature ceramic adhesive (Fuel Cell Materials, USA) to prevent gas leakage. Prior to sealing, the surface of the ceramic tube was polished and cleaned to ensure good adhesion of the ceramic adhesive. The adhesive was uniformly applied at the interface between the cell and the ceramic tube. After assembly, the sealed region was heated using a hot air gun (approximately $300\text{ }^{\circ}\text{C}$) to promote adhesive curing. Upon curing, the sealing quality was inspected, and additional adhesive was applied if necessary to improve gas tightness. This sealing procedure enabled effective separation of the anode and cathode atmospheres and ensured gas environment stability during electrochemical testing.

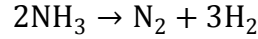
The pore structure and morphology of the anode support were examined using a scanning electron microscope (SEM, Phenom Pro X, Netherlands). The phase

composition of the materials was characterized by X-ray diffraction (XRD, D8 Advance, Bruker, Germany) using a Cu K α radiation source ($\lambda = 1.5406 \text{ \AA}$), with a scanning range of 10° – 80° and a step size of 2° . The electrochemical performance of the solid oxide fuel cells was evaluated using an electrochemical workstation (Gamry Reference 3000). Current–voltage (I–V) curves were obtained under steady-state conditions using a linear sweep method over a voltage range of 0–1.0 V at a scan rate of 1 mV s^{-1} . Electrochemical impedance spectroscopy (EIS) was conducted over a frequency range of 0.01 Hz to 100 kHz with a sinusoidal excitation amplitude of 5 mV. The impedance spectra were fitted using ZView software, and the equivalent circuit employed for fitting is shown in **Fig. S1**. In this circuit, R_0 corresponds to the high-frequency intercept and mainly represents the ohmic resistance of the cell, including contributions from electrolyte ionic conduction, current collection, and interfacial contact. The $R_1||CPE_1$ element is mainly associated with electrode interfacial processes in the higher- to intermediate-frequency range, such as charge transfer, interfacial ion transport, and reactant adsorption/activation, whereas the $R_2||CPE_2$ element mainly reflects lower-frequency processes related to gas transport and concentration polarization. The DRT spectra were extracted from the EIS data using the DRTtools package implemented in MATLAB, based on the Bayesian regularization algorithm. A fixed regularization parameter of $\lambda = 1 \times 10^{-3}$ was consistently applied to all spectra. To ensure linear system response and measurement reproducibility, different excitation amplitudes were applied during the EIS tests for comparative verification.

During ammonia-fueled cell operation, the fuel-electrode outlet was directly connected to an online gas chromatograph (GC-2014, Shimadzu, Japan) for operando analysis of the anode outlet gas. After the cell reached a stable electrochemical operating state under the selected testing condition, the anode outlet stream was continuously delivered to the GC sampling line. The outlet gas was periodically introduced into the GC at fixed 12 min intervals, with Ar used as the carrier gas. This online configuration enabled time-resolved monitoring of the evolution of H_2 , N_2 , residual NH_3 , and other possible gaseous components under actual cell operating conditions. The concentration of each gas component was quantitatively determined from the corresponding chromatographic peak areas using calibration curves established with standard gas mixtures. The outlet gas compositions reported in this study were expressed on a dry basis. The concentrations of H_2 , N_2 , and residual NH_3 were normalized to the sum of these major detected dry-gas components. Water vapor was excluded because the outlet-gas composition was reported on a dry basis. Trace nitrogen-containing gaseous species, including NO and N_2O , had a combined concentration below 0.1 vol.% and were therefore not included in the normalization.

For the evaluation of NH_3 replacement efficiency, the total inlet flow rate of the NH_3 – N_2 feed was fixed at 100 SCCM in this study. The baseline H_2 -fueled measurements were conducted using theoretical fully cracked NH_3 -equivalent gas mixtures, rather than using only the corresponding H_2 concentration at a fixed total flow rate. For each NH_3 -fuel condition, the composition of the H_2 reference gas was

determined according to the stoichiometry of complete NH_3 decomposition:



Specifically, for an NH_3 feed flow rate of F_{NH_3} , the corresponding H_2 reference mixture contained $1.5F_{\text{NH}_3}$ of H_2 and $0.5F_{\text{NH}_3}$ of product-equivalent N_2 . N_2 was used as the diluent gas in this study, and the original N_2 diluent flow in each NH_3 feed condition was retained unchanged in the corresponding H_2 reference mixture. The total N_2 content in the H_2 reference mixture consisted of the original diluent N_2 and the product-equivalent N_2 generated from complete NH_3 decomposition. The total inlet flow rate of the H_2 reference mixture was adjusted according to the theoretical total molar flow after complete NH_3 decomposition, rather than being maintained at the original NH_3 -feed flow rate. The H_2 reference measurements were performed at the same operating temperature and using the same electrochemical testing protocol as the corresponding NH_3 -fueled measurements.

To quantitatively analyze the temperature dependence of cell resistance, the Arrhenius equation was applied to both ohmic resistance R_{ohm} and polarization resistance R_{p} :

$$R = R_0 \exp \left(\frac{E_a}{k_B T} \right)$$

where R is the resistance ($\Omega \cdot \text{cm}^2$), R_0 is the pre-exponential factor ($\Omega \cdot \text{cm}^2$), E_a is the apparent activation energy (eV), k_B is the Boltzmann constant ($8.617 \times 10^{-5} \text{ eV} \cdot \text{K}^{-1}$), and T is the absolute temperature (K). By plotting $\ln(R)$ as a function of $1/T$, the apparent activation energy E_a was obtained from the slope of the linear fit ^[28].

Detailed methodologies for quantifying the pore structure and gas-transport parameters of the dendritic porous support, including pore-size analysis, tortuosity estimation, N₂ permeation measurement, and NH₃ effective diffusion-coefficient calculation, are provided in Section S1 of the Supporting Information, whereas the NH₃ conversion calculation based on calibrated online GC data and nitrogen balance is described in Section S2. The MIP characterization procedure used to evaluate the anode pore structure, including the determination of cumulative mercury intrusion volume, differential pore-size distribution, normalized pore-volume contributions, and porosity, is provided in Section S3.

3. Results and discussion

3.1 Comparison of Ammonia Utilization Characteristics between SOFCs and PCFCs

Based on the above analysis of ammonia utilization characteristics in SOFCs and PCFCs, the electrochemical performances of the two cell types under ammonia-fueled conditions were first compared to further clarify their differences in ammonia adaptability and to derive implications for subsequent structural optimization. From a mechanistic perspective, PCFCs use H⁺ as the charge carrier, and H₂O is mainly generated at the cathode side, which can, to some extent, avoid the adverse effects of steam accumulation at the anode on ammonia decomposition equilibrium, fuel concentration, and the local reaction environment. Therefore, PCFCs are generally more

favorable for the efficient electrochemical utilization of ammonia. In contrast, SOFCs generate H_2O at the anode side and are thus more susceptible to the limitations imposed by steam dilution, local atmosphere evolution, and mismatches in reaction–mass transport coupling. These considerations suggest that the transition from O^{2-} -conducting SOFCs to H^+ -conducting PCFCs represents one of the important pathways for improving ammonia utilization efficiency. However, the selection of a practical cell platform is not determined only by electrochemical advantages under a specific fuel condition, but also by technological maturity, manufacturing feasibility, cost-related factors, and system compatibility. From this perspective, O^{2-} -conducting SOFCs remain a practically important platform for ammonia-fueled power generation. SOFCs have well-established material systems, fabrication routes, stack-development experience, and system-integration foundations. Many SOFC components, such as Ni-based anodes, fluorite- or zirconia-based electrolytes, and perovskite air electrodes, have been extensively investigated and integrated into practical stack architectures. These factors are closely related to manufacturing reliability, scale-up feasibility, cost control, and compatibility with existing SOFC balance-of-plant designs. In contrast, although PCFCs are highly promising, further development is still needed in terms of large-scale fabrication, electrolyte densification, compatibility between electrodes and electrolytes, long-term durability, and stack-level validation. Given the different optimal operating temperature windows of the two cell systems, the SOFC and PCFC were evaluated within their respective representative temperature ranges to ensure a meaningful

comparison of ammonia-fueled electrochemical behavior under practically relevant conditions. To further verify the above analysis, **Fig. 2** shows a systematic comparison of the electrochemical behaviors of PCFCs and SOFCs under ammonia-fueled conditions in terms of overall output performance, impedance response, and kinetic characteristics.

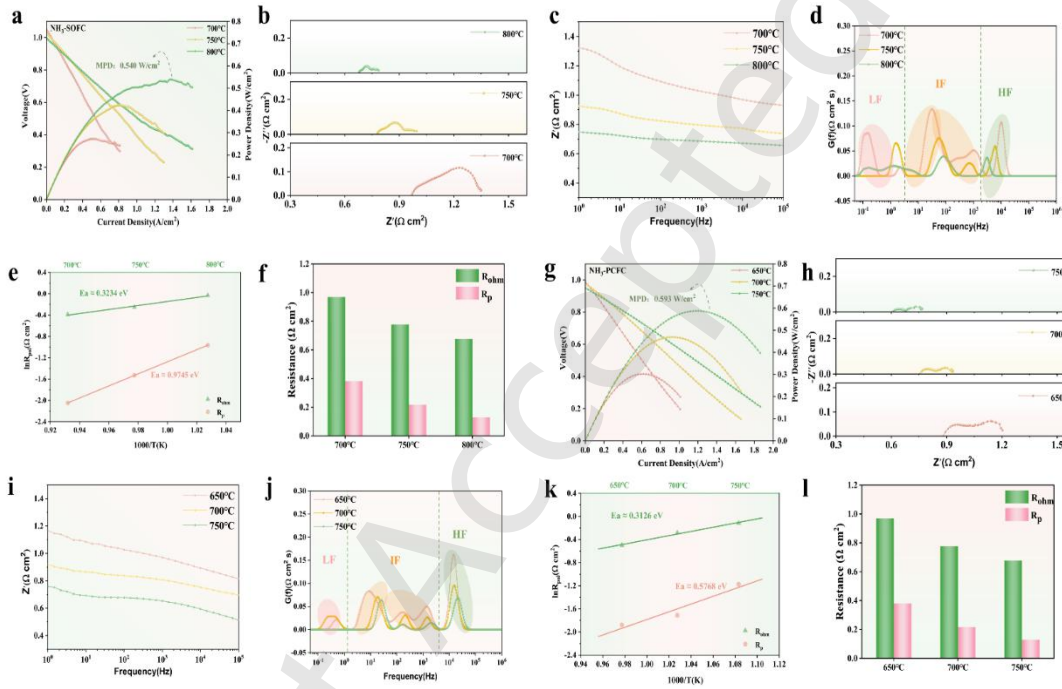


Fig. 2. Electrochemical performance characterization of the SOFC under 66.7% NH_3 fuel at 700–800 °C: (a) I–V and power density curves; (b) EIS spectra; (c) Bode plots; (d) DRT fitting results; (e) Arrhenius plots; (f) bar-chart comparison of ohmic resistance and polarization resistance. Electrochemical performance characterization of the PCFC under 66.7% NH_3 fuel at 650–750 °C: (g) I–V and power density curves; (h) EIS spectra; (i) Bode plots; (j) DRT fitting results; (k) Arrhenius plots; (l) bar-chart comparison of ohmic resistance and polarization resistance.

As shown in **Figs. 2a and 2g**, both the SOFC and PCFC were able to achieve stable power generation under ammonia-fueled conditions, and the output performance of both cells gradually improved with increasing temperature, indicating that elevated temperature effectively promotes ammonia cracking and the associated electrochemical

reaction processes. However, a clear difference in performance was observed between the two cell types. For the SOFC, the peak power density continuously increased with temperature over the range of 700–800 °C and reached 0.540 W cm⁻² at 800 °C. In contrast, the PCFC also exhibited favorable output performance within the lower temperature range of 650–750 °C, achieving a peak power density of 0.593 W cm⁻² at 750 °C. In other words, the PCFC delivered a higher maximum power output than the SOFC despite operating at a lower temperature, indicating that it provides more favorable reaction conditions and higher fuel utilization efficiency during ammonia conversion. By comparison, although the SOFC was operated at a higher temperature, its output performance remained slightly lower than that of the PCFC, suggesting that ammonia utilization in the SOFC is subject to more pronounced system-level limitations.

This difference is reflected more clearly in the impedance results. As shown in **Figs. 2b and 2h**, the radii of the impedance arcs for both the SOFC and PCFC gradually decreased with increasing temperature, indicating that elevated temperature promotes both ionic transport and electrode reaction kinetics in the two cell types. However, within the corresponding test temperature ranges, the total impedance of the SOFC at all three temperature points was significantly higher than that of the PCFC, and both its ohmic resistance and polarization resistance were also greater. These results indicate that, compared with the PCFC, the SOFC suffers from both higher conduction resistance and more severe polarization losses under ammonia-fueled conditions. Specifically, the larger ohmic resistance suggests a higher resistance associated with the

electrolyte and related charge-transport processes, whereas the larger polarization resistance indicates more pronounced kinetic limitations in the electrode reactions, particularly in the anode-side processes related to ammonia cracking, hydrogen generation and diffusion, and the subsequent electrochemical oxidation steps.

As indicated by the Bode plots and DRT results shown in **Figs. 2c, d, i, and j**, both cell types exhibit multiple characteristic response peaks over different frequency ranges, indicating the presence of several coupled processes under ammonia-fueled conditions, including interfacial charge transfer, surface reactions, and gas transport. Furthermore, the DRT spectra deconvolute the total polarization resistance into impedance contributions associated with different relaxation times. Specifically, the high-frequency region is mainly associated with ionic transport and rapid interfacial charge-transfer processes. The intermediate-frequency region is primarily related to ammonia cracking, surface adsorption and dissociation, and subsequent hydrogen-related electrochemical reactions. The low-frequency region mainly reflects gas diffusion and concentration polarization within the porous electrodes [29-31]. With increasing temperature, the characteristic peaks of both the SOFC and PCFC generally decrease in intensity, indicating gradual reductions in the corresponding impedance contributions and improvements in both electrode reaction kinetics and mass transport processes. Overall, the SOFC exhibits stronger characteristic peak intensities, particularly in the intermediate- and low-frequency regions, suggesting that its performance is more strongly limited by surface-reaction- and gas-transport-related processes. In contrast, the

PCFC shows overall weaker peak responses, indicating a more coordinated local reaction environment and relatively lower coupling resistance among the individual processes. Combined with the impedance results, it can be further inferred that the higher polarization loss in the SOFC is not governed by a single process, but is jointly associated with anode-side steam generation, local fuel dilution, and insufficient coordination between reaction and mass transport.

The Arrhenius plots and resistance bar charts further corroborate the above conclusions. As shown in **Figs. 2e, f, k, and l**, both the ohmic resistance and polarization resistance of the SOFC and PCFC exhibit clear thermally activated behavior and decrease markedly with increasing temperature. Linear fitting results show that the activation energies of the ohmic resistance and polarization resistance for the SOFC are 0.3234 and 0.9745 eV, respectively, whereas those for the PCFC are 0.3126 and 0.5768 eV, respectively. It can be seen that the activation energies for ohmic resistance are very similar in the two cell types, indicating that their intrinsic conduction processes exhibit comparable temperature dependence. In contrast, the activation energy for polarization resistance in the SOFC is significantly higher than that in the PCFC, suggesting that the electrode reactions in the SOFC involve a higher energy barrier and are therefore more sensitive to temperature variation. This indicates that, although increasing temperature can more effectively promote interfacial reactions and local mass transport processes in the SOFC, ammonia utilization in this system remains subject to stronger kinetic limitations. The resistance bar charts in **Figs. 2f and 2l**

further demonstrate that, over the entire temperature range investigated, both the ohmic resistance and polarization resistance of the SOFC are higher than those of the PCFC, and the polarization resistance accounts for a larger proportion of the total impedance, especially at lower temperatures. These results suggest that the performance improvement of ammonia-fueled SOFCs is mainly limited by electrode reaction and mass-transport-related processes, whereas the PCFC exhibits lower polarization losses and a more favorable reaction environment.

To minimize the influence of the different temperature windows, the electrochemical responses of the SOFC and PCFC were further compared at the common temperatures of 700 and 750 °C. At both temperature points, the PCFC exhibited higher peak power density than the SOFC under the same 66.7% NH₃ fuel condition. Meanwhile, the corresponding ohmic and polarization resistances of the PCFC remained lower than those of the SOFC, and its DRT profiles showed relatively weaker intermediate- and low-frequency responses. These temperature-matched results indicate that the differences in output performance and polarization behavior between the two cell systems are maintained under identical thermal conditions. By contrast, the full temperature-range measurements were retained to characterize, within each cell system, the temperature-dependent evolution of power output, ohmic and polarization resistances, and frequency-resolved electrochemical responses.

Taken together, the results in **Figs. 2a–l** indicate that both SOFCs and PCFCs are capable of directly utilizing ammonia for electrochemical power generation, and that

increasing temperature effectively improves their output performance and kinetic behavior. However, compared with the SOFC, the PCFC exhibits superior output performance, lower total impedance, and weaker intermediate- and low-frequency polarization responses within a lower operating temperature range, indicating a more favorable reaction environment and higher ammonia utilization efficiency. From an experimental perspective, these results further confirm that the transition from O^{2-} -conducting SOFCs to H^{+} -conducting PCFCs represents an important pathway for improving ammonia utilization efficiency. At the same time, this comparison further reveals the key factors limiting SOFC performance, namely anode-side steam generation, local atmosphere evolution, and insufficient coordination between reaction and mass transport. Therefore, while retaining the advantages of SOFCs, such as high-temperature adaptability and mature material systems, improving the local reaction environment and ammonia utilization efficiency through the synergistic design of anode structure and catalysis represents a practically meaningful optimization strategy.

It is worth noting that, while the above comparison provides a useful reference for assessing the ammonia-fueled electrochemical behavior of the two cell types, the results should be interpreted in the context of their respective cell systems. In addition to the different charge carriers and water-generation locations, variations in electrolyte materials, electrode compositions and microstructures, cell configurations, and representative operating-temperature windows may also influence the measured power density and impedance response. Accordingly, the comparison in this section focuses on

the characteristic trends and possible mechanistic implications associated with ammonia operation. Nevertheless, the consistent trends observed in the temperature-matched and frequency-resolved analyses identify the coordination between anode reactions and mass transport as a key target for improving the ammonia utilization performance of SOFCs.

3.2 Screening of the Optimal NH₃ Concentration and Analysis of NH₃ Replacement Efficiency

To clarify the influence of ammonia feeding conditions on the output behavior of SOFCs and to establish a unified testing basis for the subsequent evaluation of structurally optimized cells, the electrochemical responses of the cell under different ammonia concentrations were first systematically compared. As shown in **Fig. 3a**, NH₃ can decompose into H₂ and N₂ at elevated temperatures. This reaction is a typical endothermic process accompanied by an increase in system entropy; therefore, its Gibbs free energy gradually decreases with increasing temperature, making ammonia decomposition thermodynamically more favorable [32]. This thermodynamic tendency provides the basis for the in situ conversion of ammonia fuel in SOFCs. Based on the stoichiometric relationship of ammonia decomposition, equivalent H₂ concentration conditions corresponding to different NH₃ concentrations were further selected for performance comparison. Specifically, 20%, 40%, 66.7%, and 80% NH₃ correspond to 25%, 43%, 60%, and 66.7% H₂, respectively.

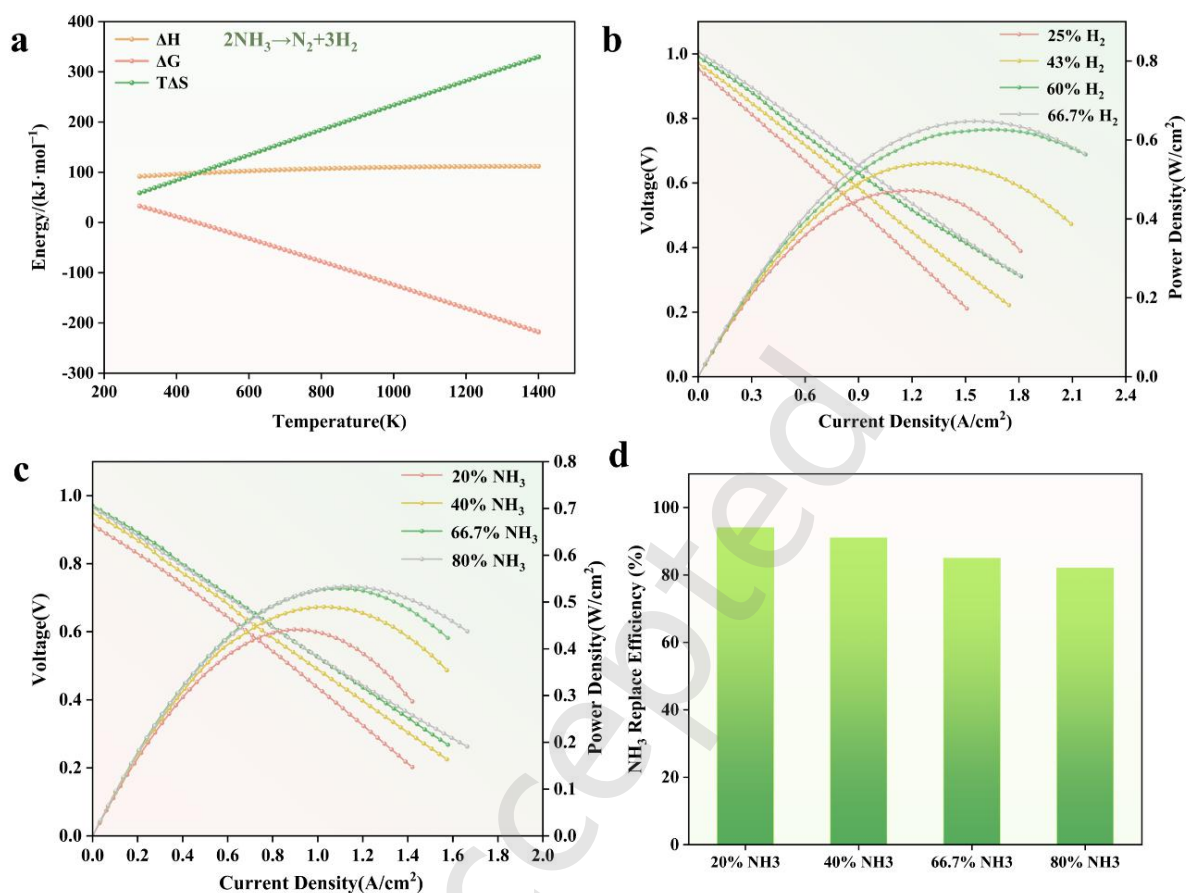


Fig. 3. (a) Thermodynamic schematic of the NH_3 decomposition reaction; (b) I–V and power density curves of the cell under different H_2 concentrations; (c) I–V and power density curves of the cell under the corresponding NH_3 concentrations; (d) NH_3 replacement efficiency at different NH_3 fuel concentrations.

As shown in **Figs. 3b and 3c**, at 800 °C, the I–V and power density curves of the SOFC generally shift upward with increasing NH_3 concentration, indicating that a higher ammonia concentration increases the supply of available fuel and thereby enhances cell output performance. This suggests that, within a certain range, a higher NH_3 partial pressure is beneficial for promoting ammonia cracking at the anode as well as the subsequent electrochemical conversion processes. However, when the NH_3 concentration was further increased from 66.7% to 80%, the improvement in peak power density became very limited, indicating that further increasing the ammonia

concentration did not lead to a significant performance gain. In other words, at relatively high NH_3 concentrations, the cell output gradually approached a plateau region, and the marginal contribution of simply increasing the ammonia concentration to performance improvement was markedly weakened.

To further evaluate the extent to which ammonia can replace hydrogen under different NH_3 concentration conditions, the NH_3 replacement efficiency was introduced as an additional evaluation metric. This metric incorporates the concept of the “corresponding hydrogen concentration,” which refers to the hydrogen concentration generated after the complete decomposition of NH_3 . For example, when the NH_3 concentration in the fuel gas is 20%, complete decomposition corresponds to an H_2 concentration of 25%. A higher NH_3 replacement efficiency indicates that the electrochemical output performance under NH_3 fuel more closely approaches that obtained under the corresponding H_2 fuel. An NH_3 replacement efficiency of 100% means that the output performance of the cell under NH_3 fuel is equivalent to that obtained under the corresponding H_2 fuel produced by complete NH_3 decomposition. The NH_3 replacement efficiency was calculated according to the following equation:

$$\text{NH}_3 \text{ replacement efficiency} = \frac{MPD_{\text{NH}_3}}{MPD_{\text{H}_2}}$$

Where MPD denotes the maximum power density, and H_2 represents the fuel at the corresponding hydrogen concentration.

The calculated results shown in **Fig. 3d** indicate that the NH_3 replacement efficiency exhibits a gradual overall decline with increasing NH_3 concentration.

Specifically, the NH_3 replacement efficiency reaches 94.5% at 20% NH_3 , decreases to approximately 85% at 66.7% NH_3 , and further declines to about 81% at 80% NH_3 . These results indicate that, although increasing the NH_3 concentration can enhance the absolute output performance of the cell to some extent, its equivalent substitution capability for hydrogen is not improved accordingly, but instead decreases. This behavior may be attributed to the reduced coordination among ammonia cracking, hydrogen transport, and the subsequent electrochemical oxidation processes at the anode as the NH_3 partial pressure continues to increase, causing the additional ammonia fuel to be converted into effective electrochemical output with lower efficiency.

Taken together, the results in **Fig. 3** indicate that, under 66.7% NH_3 , the cell achieves relatively high output performance while still maintaining an acceptable NH_3 replacement efficiency. By contrast, when the NH_3 concentration is further increased to 80%, the performance gain becomes rather limited, whereas the NH_3 replacement efficiency decreases more noticeably. Therefore, considering the overall balance between output performance and NH_3 replacement efficiency, 66.7% NH_3 was ultimately selected as the standard fuel condition for the subsequent structural optimization and performance evaluation of the SOFC.

3.3 Cell Architecture and Interfacial Morphology Analysis

The performance comparison between SOFCs and PCFCs in Sections 3.1 and 3.2, together with the analysis of electrochemical responses under different ammonia

concentrations, indicates that the output behavior of ammonia-fueled cells is determined not only by the intrinsic reaction system itself, but also by the local reaction environment and mass transport conditions within the electrodes. Based on this understanding, the present study further analyzes the overall cell architecture and the interfacial morphologies of the functional layers from the perspective of microstructural construction. It is worth noting that the SOFC and PCFC single cells discussed in Sections 3.1 and 3.2 both employed anode supports fabricated by the phase inversion method, thereby forming porous support structures with biomimetic dendritic characteristics. This method enables the construction of directionally interconnected mass-transport channels and a continuous skeletal network within the support, thus providing a favorable structural foundation for gas transport, reaction-zone distribution, and the subsequent fabrication of functional layers.

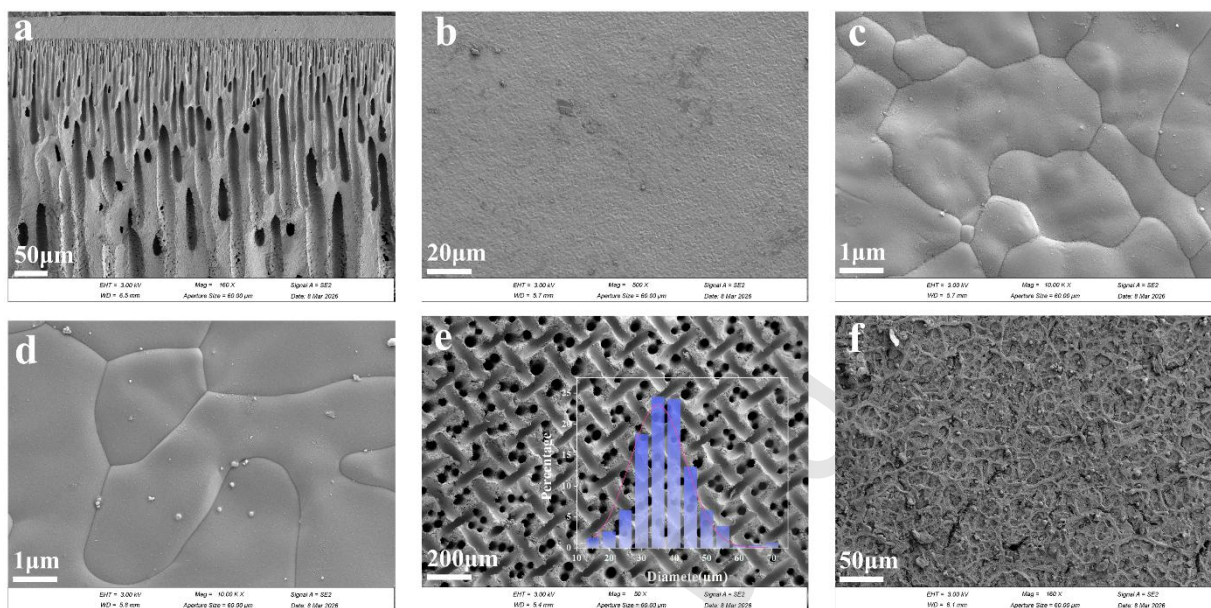


Fig. 4. (a) Cross-sectional SEM image of the overall single-cell structure; (b–d) interfacial morphology of the electrolyte region and corresponding enlarged views; (e) surface morphology and pore-size distribution of the dendritic porous anode support; (f) interfacial morphology of the cathode region.

As shown in **Fig. 4a**, the overall cross-sectional morphology of the single cell clearly reveals a typical biomimetic dendritic anode support structure. It can be observed that a dendritic porous network, composed of large pore channels and branched skeletal frameworks, is formed within the anode. This structure extends upward from the bottom of the support and exhibits a clear boundary with the dense functional layers above. Mercury intrusion porosimetry measurements show that the porosity of the anode support reaches 61.22%, indicating a highly open pore structure and strong potential for gas transport. On the one hand, this biomimetic dendritic architecture provides relatively well-interconnected fast pathways for fuel transport, thereby reducing diffusion resistance. On the other hand, the continuous branched skeleton helps maintain the structural integrity and mechanical stability of the support,

thus balancing mass transport performance and mechanical support. For ammonia-fueled cells, such a porous structure is expected to promote the distribution and diffusion of NH_3 and its cracking products within the anode, while alleviating the adverse effects caused by local steam accumulation and concentration gradients.

As shown in **Fig. 4b**, the interfacial morphology in the electrolyte region can be clearly observed at a larger scale. The electrolyte layer is continuous and smooth, with no obvious cracks, delamination, or through-thickness defects, indicating good interfacial integrity of the fabricated cell. This suggests that the biomimetic dendritic porous anode support constructed by the phase inversion method provides a stable structural foundation for subsequent electrolyte deposition and high-temperature sintering, thereby facilitating the formation of an intact and dense electrolyte interfacial structure. **Figs. 4c and 4d** further present enlarged views of this region. From the local morphology, it can be more clearly seen that a continuous and tightly bonded interface is formed between the electrolyte layer and the adjacent functional layers, without noticeable pores or interfacial separation. Meanwhile, the electrolyte layer remains dense and uniform, indicating that it can effectively prevent gas crossover and ensure stable ionic conduction.

As shown in **Fig. 4e**, the porous anode surface layer exhibits a pronounced porous network structure. The pore architecture is well developed, and the pore channels are interconnected, indicating high openness and favorable mass transport capability. The pore-size distribution extracted from the SEM image further reveals the hierarchical

porous feature of the dendritic anode support, with primary pore channels mainly distributed in the range of 30–60 μm . The estimated through-plane tortuosity factor is 2.25, while the intrinsic N_2 permeability determined at room temperature is $6.8 \times 10^{-13} \text{ m}^2 \text{ s}^{-1}$. The effective diffusion coefficient of NH_3 at 800 $^\circ\text{C}$ is calculated to be $5.6 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}$. These quantitative parameters indicate that the dendritic support provides continuous gas-transport pathways favorable for NH_3 delivery and the removal of cracking and electrochemical reaction products. In addition, such a porous surface can provide more accessible loading sites and interfacial contact areas for the subsequent introduction of catalysts.

Fig. 4f shows the interfacial morphology of the fabricated cathode region. It can be seen that the cathode layer is relatively uniformly attached to the electrolyte surface and forms a comparatively intact interfacial bonding state, indicating that the spray-coating and subsequent sintering processes can effectively construct a cathode layer with a uniform structure and good adhesion. Taken together, the results in **Fig. 4** demonstrate that the biomimetic dendritic porous anode support fabricated by the phase inversion method can provide favorable gas transport pathways and a suitable structural foundation for interface construction while maintaining overall structural integrity. Meanwhile, the dense electrolyte layer and the well-bonded cathode layer further ensure the structural integrity of the cell and the coordination among the functional layers.

3.4 Intrachannel Loading of Nanofiber Catalysts and Its Effect on the Ammonia Utilization Performance of SOFCs

After identifying that SOFC performance during ammonia utilization is mainly limited by the complex anode-side reaction environment and insufficient coordination between reaction and mass transport, a Pd–GDC nanofiber catalyst was further introduced into the dendritic porous anode channels by vacuum-assisted infiltration to enhance ammonia cracking and optimize the distribution of local reaction zones. This intrachannel catalytic configuration establishes a channel-distributed catalytic environment along the interconnected gas-transport pathways of the dendritic support, providing a structural basis for integrating catalytic NH_3 conversion with internal gas transport. The selection of Pd as the catalytic component was informed by previous literature [33], which reported that Pd-based built-in catalysts exhibit favorable activity toward ammonia decomposition and can improve the electrochemical performance of ammonia-fueled SOFCs. To balance catalytic activity with practical catalyst utilization, Pd was incorporated into a GDC-based nanofiber catalyst with controlled Pd content and total catalyst loading. The Pd–GDC catalyst was located in the reducing fuel-electrode environment, with a maximum operating temperature of 800 °C. The GDC-containing oxide framework can help disperse and anchor the Pd-containing catalytic phase through metal–support interactions, which is consistent with previous reports showing that CeO_2 -based supports can regulate the chemical state and thermal stability of Pd species [34]. The catalyst used in this study was a 6% Pd–GDC nanofiber catalyst, whose morphology is shown in **Fig. S2**. The surface chemical state of Pd in the as-prepared Pd–GDC nanofiber catalyst was further analyzed by Pd 3d XPS, as shown in **Fig. S3**. The fitted peaks at 335.20 and 340.46 eV are assigned to Pd^0 , whereas those at 337.55 and 342.81 eV correspond to Pd^{2+} . These results indicate the coexistence of metallic and oxidized Pd species in the catalyst. Metallic Pd can provide active surface sites for NH_3 dissociation, whereas the Pd^{2+} component is associated with Pd–O bonding and interactions between Pd and the GDC framework. In this catalyst, Pd serves as the primary active component, providing effective catalytic sites for NH_3 decomposition and the subsequent hydrogen-related electrochemical reactions, thereby promoting ammonia cracking and enhancing anode reaction kinetics. The GDC-containing oxide framework also maintains good compositional and structural compatibility with the NiO–GDC anode support, which is beneficial for the stable loading and distribution of the catalyst within the anode channels.

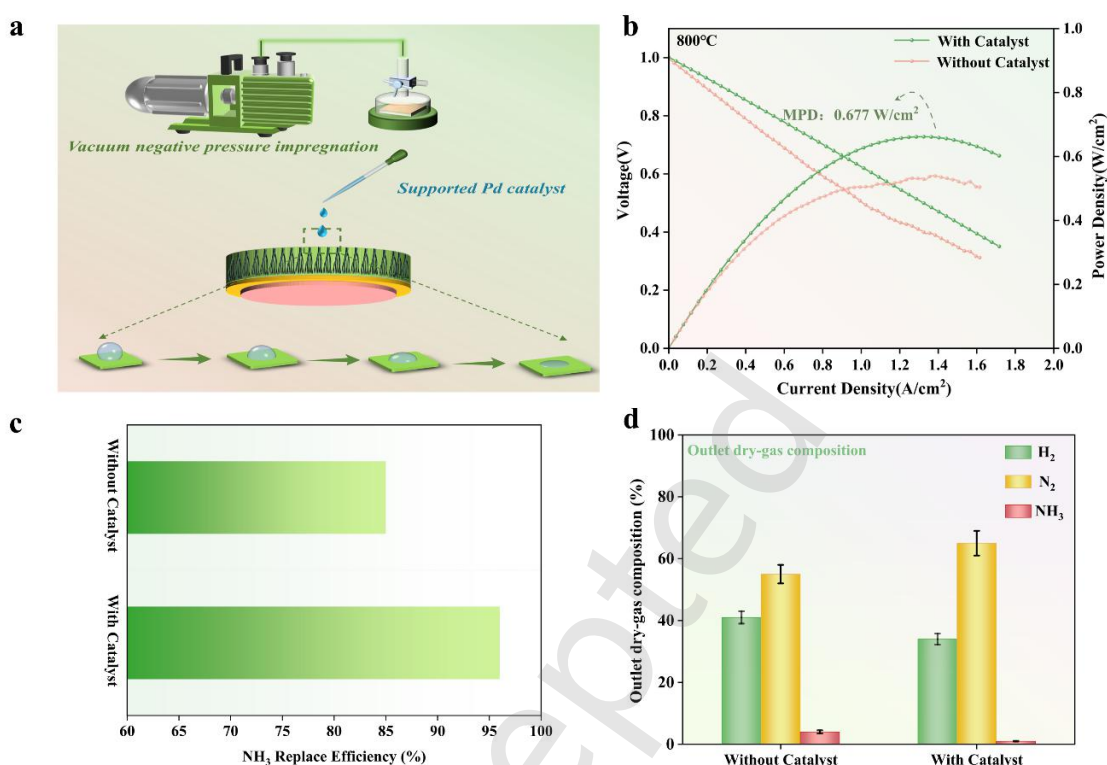


Fig. 5. (a) Schematic illustration of nanocatalyst loading within the cell channels; (b) comparison of the I–V and power density curves of cells with and without catalyst loading at 800 °C; (c) comparison of NH₃ replacement efficiency between cells with and without catalyst loading; (d) GC analysis results of the anode outlet dry-gas for cells with and without catalyst loading.

As shown in **Fig. 5a**, the Pd–GDC nanofiber catalyst was introduced into the interior of the dendritic porous anode by vacuum-assisted infiltration. Under vacuum conditions, the catalyst slurry can penetrate more effectively into the deeper regions of the anode channels and attach to the internal skeletal surfaces, rather than remaining only in the outer surface region. This method helps extend the distribution of catalytic active sites from the conventional external surface to the interior of the pore channels, allowing ammonia fuel to come into sufficient contact with the catalyst along its

diffusion pathway. As a result, in situ cracking can be enhanced, and the spatial coupling among ammonia cracking, hydrogen transport, and the subsequent electrochemical conversion processes can be improved. For the dendritic porous anode, this intrachannel loading strategy enables fuller utilization of its interconnected channels and highly open porous structure, thereby creating more favorable conditions for establishing an improved local reaction environment.

Fig. 5b shows the I–V and power density curves before and after catalyst loading under 800 °C and 66.7% NH₃. After the introduction of the Pd–GDC nanofiber catalyst, the peak power density of the single cell increased from 0.540 to 0.677 W cm⁻², corresponding to an enhancement of 25.4%. This improvement in peak power density is consistent with enhanced NH₃ conversion and improved overall electrochemical performance after catalyst loading.

To identify the electrochemical processes affected by catalyst loading, the EIS spectra and corresponding DRT profiles were quantitatively compared under identical ammonia-fueled operating conditions, as shown in **Fig. S4**. As shown in **Fig. S4a**, the high-frequency intercept remains nearly unchanged at approximately 0.675 Ω cm² after Pd–GDC loading, indicating that the ohmic resistance is essentially unaffected. In contrast, the polarization resistance decreases from approximately 0.128 to 0.073 Ω cm², corresponding to a reduction of about 43.0%. The corresponding DRT results in **Fig. S4b** further reveal that the impedance responses in the low- and middle-frequency regions are reduced after catalyst loading. Among them, the decrease in the middle-

frequency region is particularly pronounced, indicating an improvement in the processes associated with NH_3 adsorption and subsequent hydrogen-related anode reactions. Meanwhile, the reduced low-frequency response is consistent with mitigated gas-diffusion and concentration-polarization losses within the porous anode. By comparison, the relatively smaller variation in the high-frequency response suggests that the faster interfacial charge-transfer and ion-transport-related processes are less affected by catalyst loading. These results indicate that the intrachannel Pd-GDC catalyst mainly reduces the polarization losses associated with NH_3 conversion and gas-transport-related processes, which is consistent with the improved electrochemical performance shown in **Fig. 5b**.

To determine whether the intrachannel catalyst loading adversely affected the anode pore structure, MIP measurements were performed before and after Pd-GDC nanofiber catalyst loading, as shown in **Fig. S5**. The cumulative mercury intrusion volume decreased only slightly from 0.225 mL g^{-1} before catalyst loading to 0.210 mL g^{-1} after loading. Correspondingly, the MIP-derived porosity decreased from 56.57% to 55.77%, representing a reduction of only 0.80 percentage points. As shown in **Fig. S5b**, pores in the 30–60 μm range remained the dominant pore-size interval, accounting for approximately 58% and 57% of the total pore volume before and after catalyst loading, respectively. Only limited variations were observed in the other pore-size ranges. Moreover, the differential mercury intrusion curves in **Fig. S5c** largely overlap, and no pronounced shift of the main pore-size distribution toward smaller pores was observed

after catalyst loading. These results demonstrate that the introduction of Pd–GDC nanofibers caused only minor changes in the accessible pore volume and pore-size distribution, while the principal dendritic gas-transport channels were largely preserved. Therefore, at the catalyst loading employed in this study, the adverse effect of catalyst infiltration on anode mass transport was limited, and no evident blockage of the main pore channels occurred.

In addition, **Table S1** compares the peak power densities of ammonia-fueled SOFCs and PCFCs reported in recent literature. The results show that, although differences exist among previous studies in terms of cell configuration, operating temperature, and fuel conditions, the system constructed in this work still exhibits relatively high output performance under ammonia-fueled conditions. This comparison further confirms the effectiveness of the synergistic integration of a dendritic porous anode and intrachannel Pd–GDC nanofiber catalysts in enhancing the performance of ammonia-fueled SOFCs.

To further evaluate the improvement in ammonia utilization efficiency after catalyst introduction, **Fig. 5c** compares the NH_3 replacement efficiency before and after catalyst loading. The results show that the NH_3 replacement efficiency increased from 84% to 96%, indicating that, under the same fuel conditions, the Pd–GDC nanofiber catalyst significantly enhanced the ability of ammonia fuel to substitute for the equivalent hydrogen fuel. This suggests that the catalyst not only improved the absolute output performance of the cell, but also increased the efficiency with which ammonia

fuel was converted into effective electrochemical output. Combined with the aforementioned improvement in power density, it can be concluded that the overall ammonia utilization capability of the SOFC was markedly enhanced after the intrachannel introduction of the Pd–GDC nanofiber catalyst.

Fig. 5d further shows the changes in outlet dry-gas composition measured by GC. After the introduction of the catalyst, the H₂ content in the outlet gas decreased from 41% to 34%, the N₂ content increased from 55% to 65%, and the residual NH₃ content decreased markedly from 4% to 1%. Among these changes, the pronounced decrease in residual NH₃ concentration and the increased N₂ fraction provide direct operando evidence for enhanced overall NH₃ conversion after catalyst loading. The NH₃ conversion was further calculated. As shown in **Fig. S6**, the calculated NH₃ conversion increased from 91.5% to 97.8% after Pd–GDC loading, providing quantitative evidence for enhanced NH₃ conversion. Notably, the cracking-derived H₂ did not accumulate in the outlet gas; instead, the outlet H₂ fraction decreased after catalyst loading. When considered together with the increased peak power density and NH₃ replacement efficiency, this trend suggests that a greater proportion of the cracking-derived H₂ was utilized in the subsequent electrochemical process before reaching the anode outlet. Collectively, the operando GC and electrochemical results support that the intrachannel Pd–GDC catalyst promotes NH₃ cracking and improves the matching between catalytic conversion and downstream electrochemical utilization.

Taken together, the results in **Fig. 5** indicate that introducing the Pd–GDC

nanofiber catalyst into the channels of the dendritic porous anode by vacuum-assisted infiltration can significantly improve both the electrochemical output performance and ammonia utilization efficiency of the SOFC under ammonia-fueled conditions. On the one hand, the intrachannel catalyst loading enhances ammonia cracking and reduces the residual NH_3 content in the outlet gas. On the other hand, it also promotes the timely electrochemical consumption of the cracking product H_2 , thereby improving the conversion efficiency of ammonia fuel into effective electrical output. On the other hand, the operando outlet-gas results are consistent with changes in the downstream utilization behavior of the cracking products. These results demonstrate that the intrachannel catalyst-loading strategy based on a dendritic porous anode structure is an effective approach for enhancing both the performance and ammonia utilization efficiency of ammonia-fueled SOFCs.

3.5 Stability of the Cell under Ammonia-Fueled Conditions

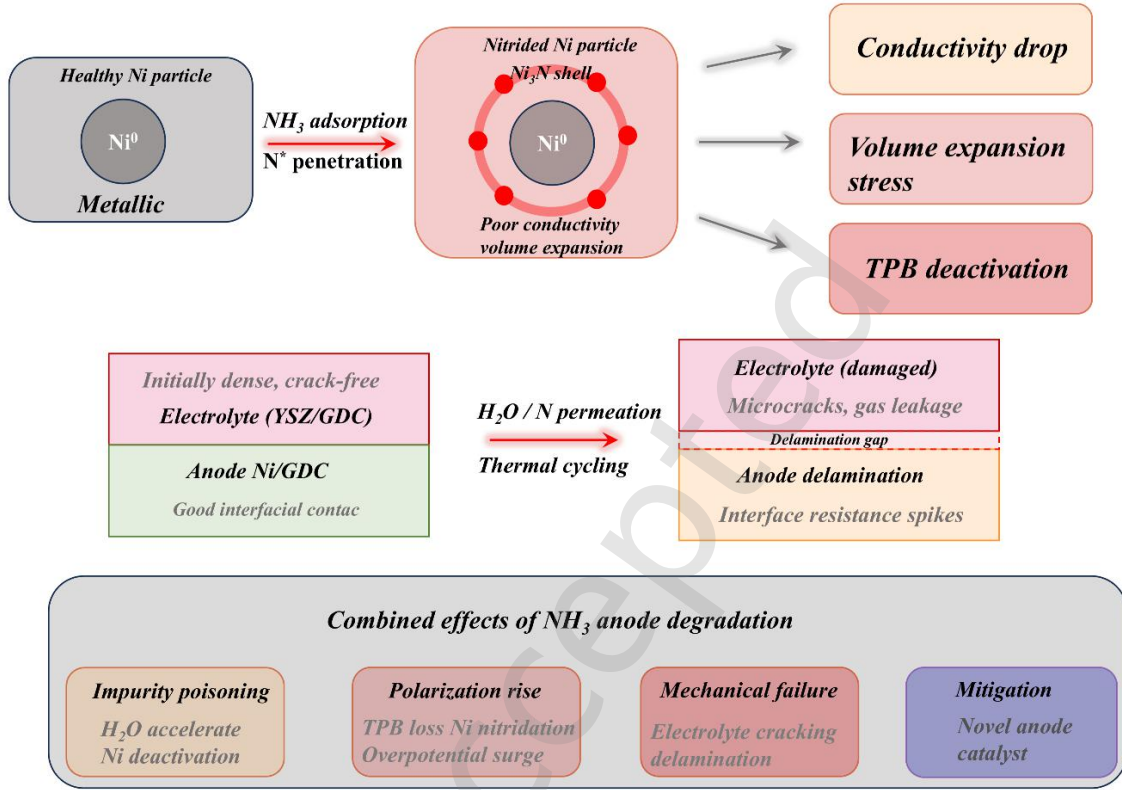


Fig. 6. Schematic illustration of the anode degradation and failure mechanisms of SOFCs under ammonia-fueled conditions. NH_3 -induced Ni nitridation, decreased conductivity, volume expansion, TPB deactivation, interfacial delamination, electrolyte microcracking, and gas leakage jointly contribute to cell performance decay and structural failure.

Although SOFCs are capable of directly utilizing ammonia as a fuel, their long-term stable operation still faces significant challenges, as shown in **Fig. 6**. This is mainly because ammonia utilization at the anode is not a single-step process, but rather involves multiple consecutive stages, including ammonia cracking, hydrogen transport, and subsequent electrochemical utilization. When stable matching among these

processes cannot be maintained, the local reaction environment at the anode becomes prone to continuous fluctuations, which in turn leads to performance degradation. This issue becomes particularly pronounced at higher current densities, where the dynamic balance among the ammonia cracking rate, hydrogen consumption rate, and water generation behavior at the anode is more easily disrupted. As a result, problems such as insufficient local fuel supply, aggravated steam accumulation, and enlarged concentration gradients may arise, ultimately causing voltage fluctuations, increased impedance, and further deterioration of cell performance [35-37].

In addition, the stability issues of SOFCs under ammonia-fueled conditions are also closely associated with the structural evolution of the anode material. Previous studies have shown that, under prolonged NH_3 atmospheres, Ni-based anodes may undergo nitridation-related changes and form nitrogen-containing phases such as Ni_3N , thereby leading to anode deactivation, interfacial degradation, and microstructural deterioration. Meanwhile, if the ammonia cracking capability within the anode is insufficient, residual NH_3 will further increase the polarization resistance and amplify the nonuniformity of the local reaction environment, thereby accelerating structural damage and performance degradation. Therefore, enhancing ammonia cracking efficiency through catalytic reinforcement, reducing the concentration of residual NH_3 , and stabilizing the local reaction environment at the anode are key to achieving the long-term stable operation of ammonia-fueled SOFCs [38, 39].

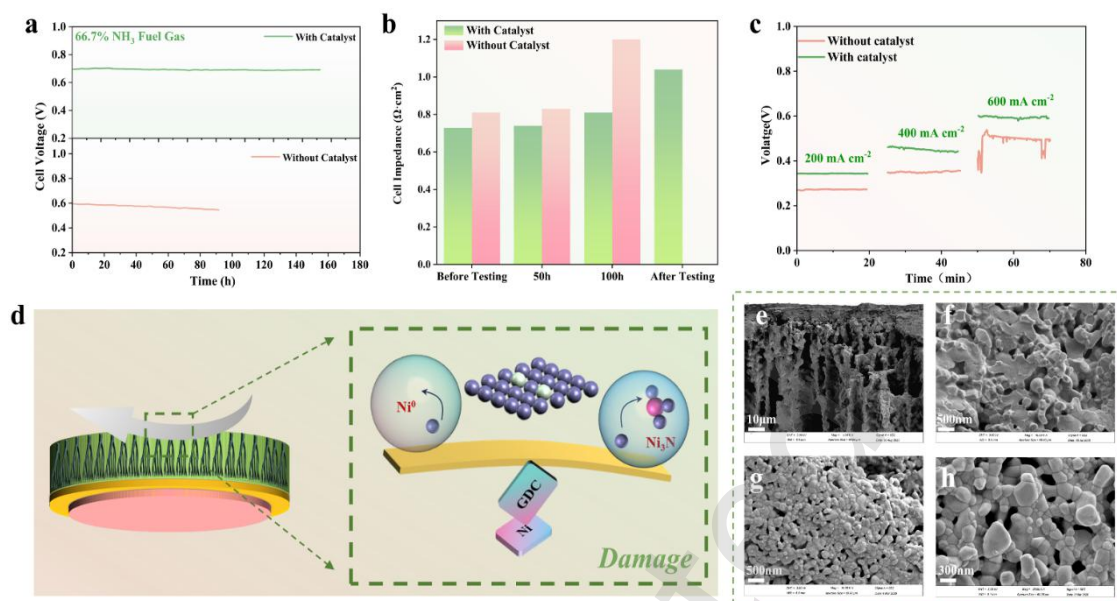


Fig. 7. (a) Stability test results of SOFCs with and without catalyst loading at a current density of 0.8 A cm^{-2} under 800°C and $66.7\% \text{ NH}_3$ fuel; (b) bar-chart comparison of cell resistance evolution during the stability test; (c) results of the variable-current stability test at current densities of 200 , 400 , and 600 mA cm^{-2} ; (d) schematic illustration of Ni_3N formation at the anode and the resulting structural degradation; (e) anode–electrolyte interfacial morphology of the failed cell; (f) enlarged view of the anode region of the cell after testing; (g, h) enlarged views of the anode–electrolyte interface of the failed cell after testing.

Based on the above analysis of the stability challenges associated with ammonia-fueled SOFCs, stability tests were further conducted to evaluate the effect of introducing Pd–GDC nanofiber catalysts into the anode channels on the long-term operating behavior of the cell, and the results are shown in **Fig. 7**. As shown in **Fig. 7a**, under a constant current density of 0.8 A cm^{-2} , the cell without catalyst loading exhibited more pronounced voltage decay within 91 h . In contrast, after loading the Pd–

GDC catalyst, the stable operating time was extended to 172 h, accompanied by a markedly reduced decay rate and smoother voltage fluctuations. Specifically, the voltage degradation rate of the cell without catalyst loading was 0.44 mV h^{-1} , whereas that of the catalyst-loaded cell was markedly reduced to 0.08 mV h^{-1} . These results indicate that the intrachannel introduction of the Pd–GDC nanofiber catalyst enables more effective coordination between ammonia cracking at the anode and the subsequent electrochemical reactions, thereby mitigating the adverse impact of local reaction-environment fluctuations on long-term operational stability. **Fig. 7b** further compares the impedance evolution at different stages during the stability test. It can be seen that the impedance increase of the cell without catalyst loading was much more pronounced before the test and after 50 and 100 h of operation, whereas the catalyst-loaded cell exhibited a much smaller increase in impedance. This suggests that the introduction of the catalyst effectively suppresses the accumulation of polarization losses caused by the deterioration of interfacial reactions and local mass-transport limitations during operation.

To further quantitatively evaluate the differences in the anode pore structure after long-term operation, MIP measurements were performed on the catalyst-loaded and unloaded anode samples. As shown in **Fig. S7a**, after the stability test, the cumulative mercury intrusion volume was 0.202 mL g^{-1} for the catalyst-loaded anode and 0.185 mL g^{-1} for the unloaded anode, indicating that the catalyst-loaded sample retained a larger accessible pore volume. The normalized pore-volume contributions shown in **Fig. S7b**

further reveal that pores in the 30–60 μm range accounted for 57% of the total pore volume in the catalyst-loaded anode, compared with 44% in the unloaded anode. In contrast, the contribution of pores in the 10–30 μm range was approximately 14% in the catalyst-loaded sample but increased to 31% in the unloaded sample. The differential mercury intrusion curves in **Fig. S7c** also show a more pronounced shift toward smaller pore sizes for the unloaded anode. These results indicate that the unloaded anode underwent more pronounced pore-channel contraction and redistribution toward smaller pore sizes, whereas the Pd–GDC-loaded sample better preserved the main dendritic pore channels.

In addition, the state of the intrachannel catalyst after prolonged operation was assessed by post-mortem SEM and Pd 3d XPS analyses, as shown in **Fig. S8**. The SEM image in **Fig. S8a** shows that the catalyst retained an elongated and interconnected nanofibrous framework after the stability test. Although the fiber surfaces became somewhat rougher and more granular, the main fibrous skeleton remained continuous, without obvious framework collapse or large-scale agglomeration. The Pd 3d XPS spectrum in **Fig. S8b** contains components attributable to Pd^0 and Pd^{2+} , indicating no evident change in the chemical states of the Pd species after prolonged operation.

As shown in **Fig. 7c**, under stepwise varying current densities of 200, 400, and 600 mA cm^{-2} , the catalyst-loaded cell exhibits a markedly more stable voltage response than the cell without catalyst loading, further indicating that the Pd–GDC catalyst helps improve the reaction adaptability and operational stability of the anode under different

load conditions. To further understand the mechanism underlying the stability improvement, **Fig. 7d** shows a schematic illustration of the effect of Ni_3N on anode stability, indicating that prolonged exposure to ammonia may induce nitridation-related evolution of the Ni-based component, thereby adversely affecting anode activity and structural stability. To provide direct evidence for this nitridation-related evolution, the phase composition and surface chemical states of the anode before and after the NH_3 -fueled stability test were further examined by XRD and XPS, as shown in **Fig. S9**. Compared with the cell sample before NH_3 stability testing, the failed cell after testing exhibited additional diffraction peaks at 38.9° , 42.1° , 58.7° , and 70.3° , which can be assigned to the (110), (002), (112), and (300) planes of Ni_3N , respectively. These additional reflections indicate the formation of a nickel nitride phase during prolonged operation under the NH_3 -containing atmosphere. The XPS results further support the XRD phase assignment. As shown in **Fig. S9b**, the N 1s spectrum collected after the NH_3 -fueled stability test exhibited a distinct low-binding-energy component at 397.3 eV, which is associated with Ni–N bonding. In contrast, no discernible N 1s signal was detected for the control sample tested without ammonia fuel, as shown in the inset. In addition, the post-test Ni 2p spectrum in **Fig. S9c** contained Ni–N-related components at 853.5 and 870.5 eV, corresponding to the Ni $2p_{3/2}$ and Ni $2p_{1/2}$ regions, respectively. Compared with the reference Ni 2p spectrum shown in **Fig. S9d**, these features confirm that the chemical state of Ni changed after prolonged operation under ammonia-fueled conditions.

The SEM results of the failed cells shown in **Figs. 7e–h** further support this interpretation: the cell without stable operation exhibits obvious structural damage after failure, indicating that the long-term degradation under ammonia-fueled conditions is manifested not only in electrochemical performance decay, but also in the continuous deterioration of the electrode microstructure. Overall, the introduction of the Pd–GDC catalyst not only improves ammonia cracking and electrochemical conversion efficiency, but also stabilizes the local reaction environment at the anode to some extent, retards impedance growth, and suppresses structural damage, thereby significantly enhancing the operational stability of the SOFC under ammonia-fueled conditions.

4. Conclusions

This study demonstrates that the performance limitations of ammonia-fueled SOFCs fundamentally originate from insufficient coordination among ammonia cracking, hydrogen transport, and subsequent electrochemical conversion under the complex reaction environment at the anode. In contrast, PCFCs exhibit superior output performance and lower impedance at lower operating temperatures, indicating that the transition from O^{2-} -conducting SOFCs to H^{+} -conducting PCFCs represents an important pathway for improving ammonia utilization efficiency. Meanwhile, within the SOFC system itself, the intrinsic disadvantages can also be effectively alleviated through the synergistic optimization of anode structure and catalysis. The dendritic porous NiO–GDC anode support constructed in this work possesses high porosity and clearly

interconnected pore channels, thereby providing a favorable structural basis for gas transport and local reaction-environment regulation. After further introducing Pd-GDC nanofiber catalysts into the anode channels by vacuum-assisted infiltration, the peak power density of the cell under 800 °C and 66.7% NH₃ increased from 0.540 to 0.677 W cm⁻², corresponding to an enhancement of 25.4%. The NH₃ replacement efficiency increased from 84% to 96%, and the stable operating time was extended from 91 to 172 h. Analyses of outlet gas composition, impedance evolution, and post-failure morphology further demonstrate that this strategy can significantly promote ammonia cracking, enhance the effective utilization of cracking products, and mitigate the deterioration of the local anode environment and structural degradation. These results indicate that this strategy can simultaneously strengthen ammonia cracking, improve the local reaction environment, and enhance long-term operational stability, thereby providing a new approach for the efficient design of ammonia-fueled SOFCs.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Authors' Contributions:

Haochen Dang: Conceptualization, Methodology, Investigation, Data curation, Formal analysis, Software, Visualization, Writing – original draft, Project administration. **Zhenyu Zhang:** Investigation, Software, Visualization, Writing – original draft. **Fujun Zhang:** Investigation, Data curation, Formal analysis, Software, Visualization. **Tao Cui:** Investigation, Visualization, Resources. Project administration.

Data Availability

Data will be made available on request.

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Enhanced performance and stability of ammonia-fueled SOFCs enabled by an *in situ* catalytic microreactor constructed within anode channels

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Section S1. Quantification of pore-structure and gas-transport parameters

The pore-size distribution of the dendritic porous anode support was obtained from representative cross-sectional SEM images. SEM images collected from different regions along the support thickness were binarized and analyzed using ImageJ software. The pore sizes were directly measured from the identified pore features, while pores intersecting the image boundary were excluded from the statistical analysis. The resulting pore-size distribution is presented in **Fig. 4e**.

The apparent through-plane geometric tortuosity of the dendritic porous support was estimated from the binarized cross-sectional SEM images. Continuous pore pathways connecting the gas-side surface and electrolyte-side region were identified by skeletonization analysis. The average effective pore-path length, l_{eff} , was determined from these connected pathways. The tortuosity factor, τ , was calculated as:

$$\tau = \left(\frac{l_{\text{eff}}}{L} \right)^2$$

where L is the thickness of the porous support. This parameter was used to describe the relative elongation of the through-plane gas-transport pathways within the dendritic structure.

The intrinsic gas permeability of the dendritic porous support was determined by room-temperature N_2 permeation. A support specimen prepared under the same fabrication and sintering conditions as the cell-support layer was mounted in a gas-tight permeation fixture, with the effective permeation area defined by the sealing aperture. Dry N_2 was supplied to one side of the specimen, while the opposite side was maintained at atmospheric pressure. The upstream pressure was varied stepwise, and the N_2 flow rate was recorded after reaching a steady state at each pressure difference. Prior to measurement, the gas-tightness of the testing fixture was verified to minimize possible edge leakage.

The superficial gas velocity, u , was calculated as:

$$u = \frac{Q}{A}$$

where Q is the volumetric flow rate at the test condition and A is the effective permeation area. In the low-flow regime, the pressure drop followed Darcy's law:

$$\frac{\Delta P}{L} = \frac{\mu}{k} u$$

where ΔP is the pressure difference across the specimen, L is the support thickness, μ is the dynamic viscosity of N_2 at the test temperature, and k is the intrinsic permeability. The intrinsic permeability was obtained from the slope of the linear fitting between $\Delta P/L$ and u .

The effective diffusion coefficient of NH_3 within the dendritic porous support was calculated at 800 °C using the Bosanquet relation:

$$D_{\text{eff},i} = \frac{\varepsilon}{\tau} \left(\frac{1}{D_{i,m}} + \frac{1}{D_{K,i}} \right)^{-1}$$

where $D_{\text{eff},i}$ is the effective diffusion coefficient of gas species i , ε is the porosity of the porous support, τ is the tortuosity factor, $D_{i,m}$ is the molecular diffusion coefficient of species i in the corresponding gas mixture, and $D_{K,i}$ is the Knudsen diffusion coefficient.

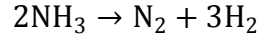
The Knudsen diffusion coefficient was calculated as:

$$D_{K,i} = \frac{2r_p}{3} \left(\frac{8RT}{\pi M_i} \right)^{1/2}$$

where r_p is the representative pore radius determined from the SEM-derived pore-size distribution, R is the universal gas constant, T is the absolute temperature, and M_i is the molar mass of gas species i . The molecular diffusion coefficient of NH_3 in the NH_3 – N_2 mixture was calculated at 800 °C and ambient pressure.

Sections S2 Calculation of NH₃ conversion

NH₃ conversion was calculated from the calibrated outlet-gas composition measured by online GC, based on a nitrogen-balance analysis of the ammonia decomposition reaction:



In the calculation, the nitrogen-containing species at the outlet were assumed to consist predominantly of N₂ and residual NH₃. The contributions of possible trace NO_x, N₂O, and other undetected nitrogen-containing species were considered negligible relative to these two major components. Accordingly, NH₃ conversion was calculated as [1,2]:

$$X_{\text{NH}_3} = \frac{2y_{\text{N}_2, \text{out}} - y_{\text{NH}_3, \text{out}}}{2y_{\text{N}_2, \text{out}} + y_{\text{NH}_3, \text{out}}} \times 100\%$$

where X_{NH_3} is the NH₃ conversion, and $y_{\text{N}_2, \text{out}}$ and $y_{\text{NH}_3, \text{out}}$ are the calibrated outlet molar fractions of N₂ and residual NH₃, respectively, as determined by online GC.

Sections S3 Mercury intrusion porosimetry characterization

Mercury intrusion porosimetry (MIP) was employed to characterize the pore structure of the anodes investigated in this study. Approximately 2–3 g of each sample was loaded into a penetrometer and vacuum-degassed before measurement to remove air and moisture from the accessible pore channels. The MIP measurements were performed using an automated mercury intrusion porosimeter (AutoPore V 9620, Micromeritics, USA).

During the measurement, mercury was progressively intruded into the accessible pores of the sample under increasing pressure. The corresponding pore-throat diameter was calculated according to the Washburn equation:

$$D = - \frac{4\gamma \cos \theta}{P}$$

where D is the pore-throat diameter, γ is the surface tension of mercury, θ is the contact angle between mercury and the solid surface, and P is the applied pressure. A mercury surface tension of 0.485 N m^{-1} and a contact angle of 130° were used for the calculation.

The cumulative mercury intrusion volume, differential intrusion-volume distribution, and MIP-derived porosity were obtained from the intrusion data. The differential pore-size distribution was expressed as $dV/d\log D$, where V is the cumulative mercury intrusion volume and D is the pore-throat diameter.

To compare the relative pore-volume contributions among different samples, the intrusion volume within the pore-diameter range of $0.1\text{--}100 \text{ }\mu\text{m}$ was normalized to the total intrusion volume within this range. The pore-throat sizes were divided into five intervals: $0.1\text{--}1$, $1\text{--}10$, $10\text{--}30$, $30\text{--}60$, and $60\text{--}100 \text{ }\mu\text{m}$. Intrusion signals corresponding to pore diameters larger than $100 \text{ }\mu\text{m}$ were excluded from the normalized analysis because they may be influenced by interparticle voids, surface defects, or gaps generated during sample loading. Signals below $0.1 \text{ }\mu\text{m}$ were also excluded to ensure consistency in the comparison of the pore-size distributions.

Anode samples were measured using the same experimental parameters and data-processing procedure. The cumulative intrusion curves, normalized pore-volume contributions, differential pore-size distributions, and porosity values were used to evaluate the changes in accessible pore volume, pore-throat distribution, and preservation of the dendritic pore channels after long-term stability testing.

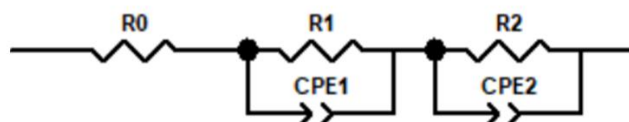


Fig. S1. Equivalent circuit model

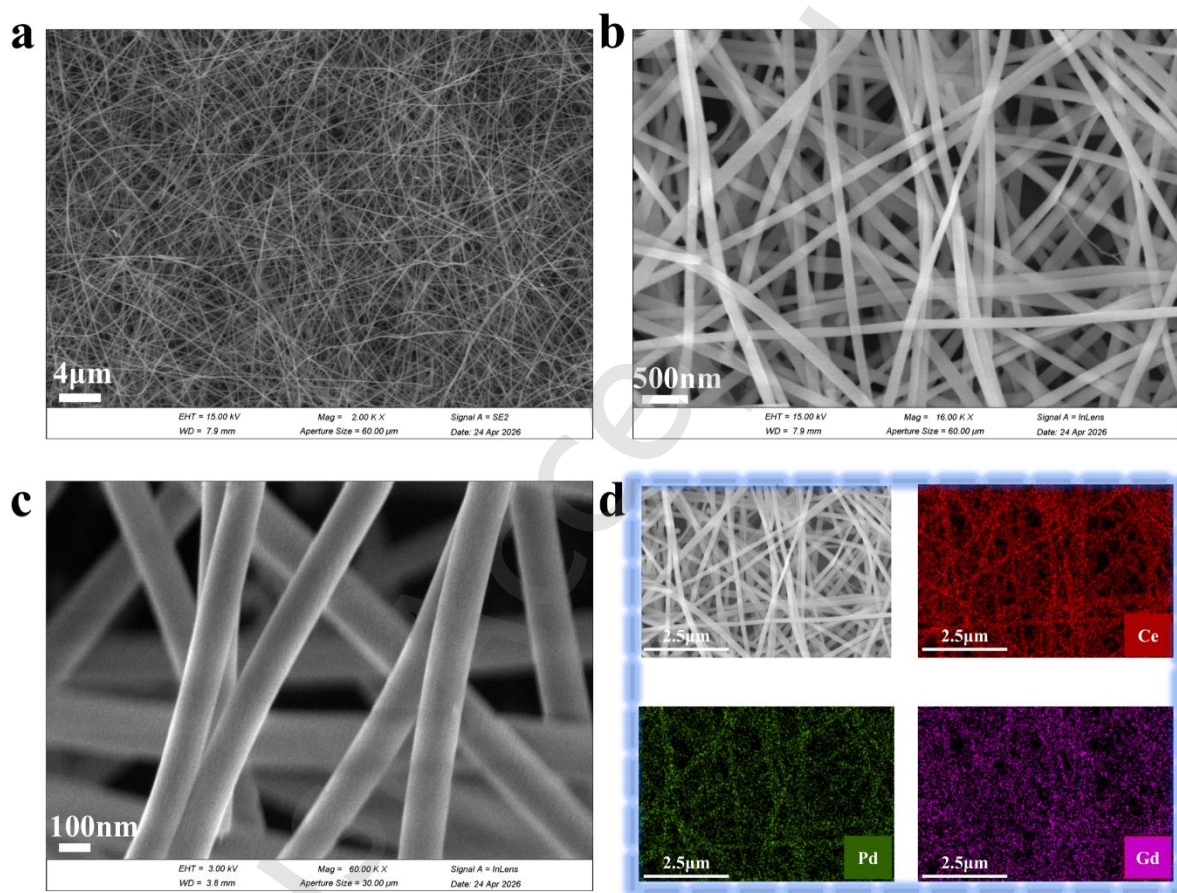


Fig. S2. Surface morphology of the Pd-GDC nanofiber catalyst and corresponding enlarged views.

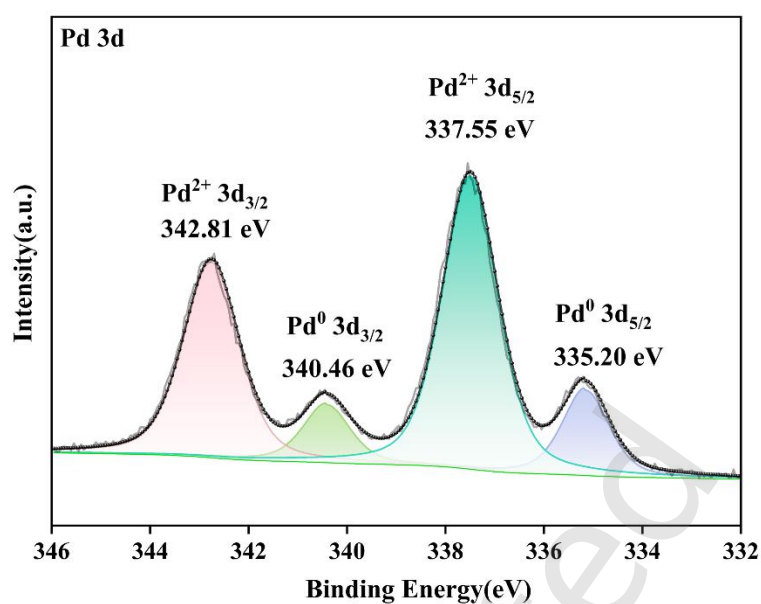


Fig. S3. Pd 3d XPS spectrum and peak-fitting results of the as-prepared Pd-GDC nanofiber catalyst.

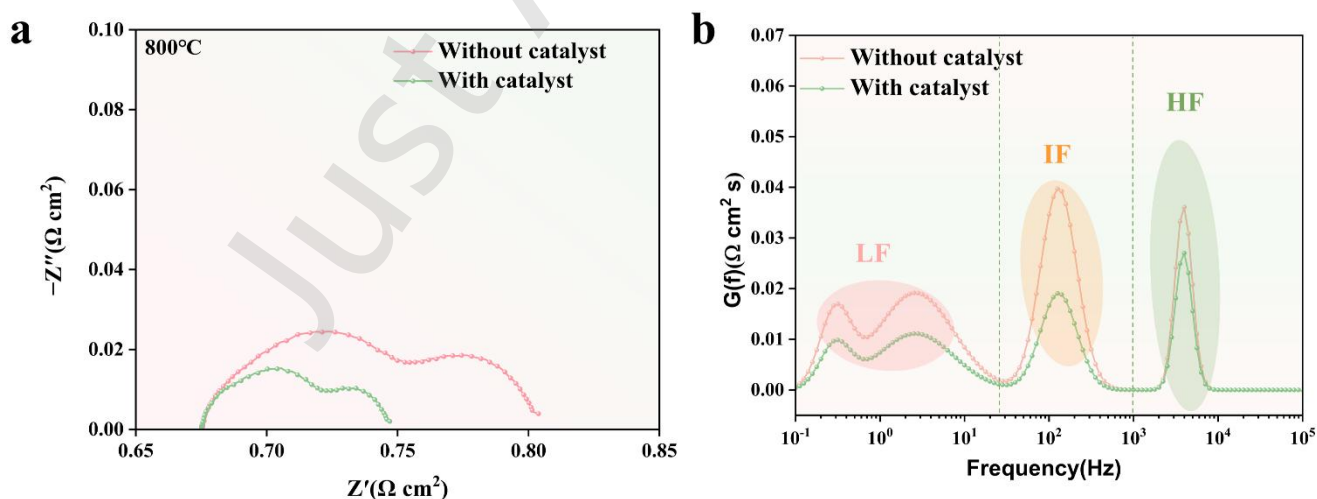


Fig. S4. Comparison of (a) EIS spectra and (b) corresponding DRT profiles of SOFCs with and without Pd-GDC catalyst loading at 800 °C under NH_3 fuel.

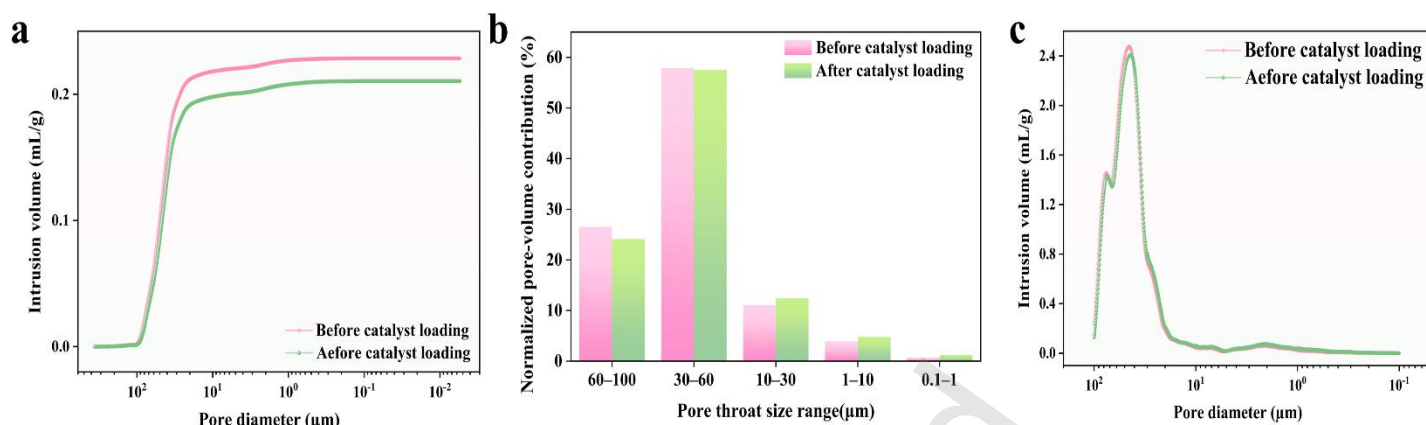


Fig. S5. MIP characterization of the dendritic anode before and after Pd-GDC nanofiber catalyst loading. (a) Cumulative mercury intrusion volume as a function of pore diameter; (b) normalized pore-volume contributions within different pore-throat size ranges; and (c) differential mercury intrusion-volume distributions.

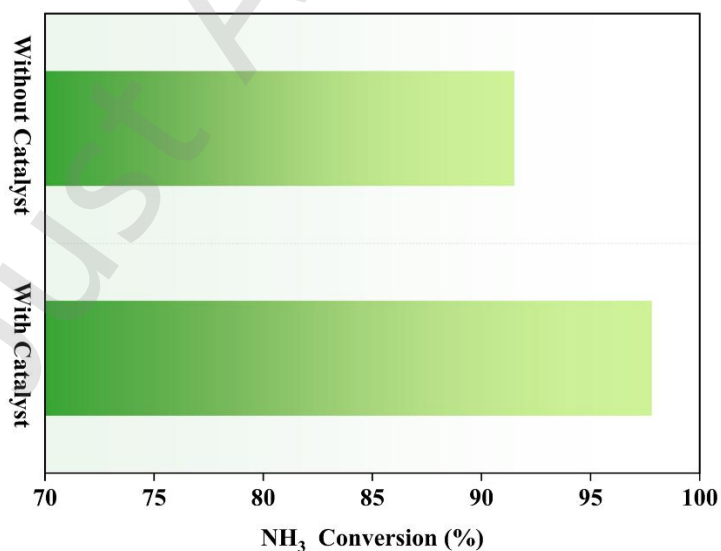


Fig. S6. Comparison of NH₃ conversion for cells with and without Pd-GDC catalyst loading.

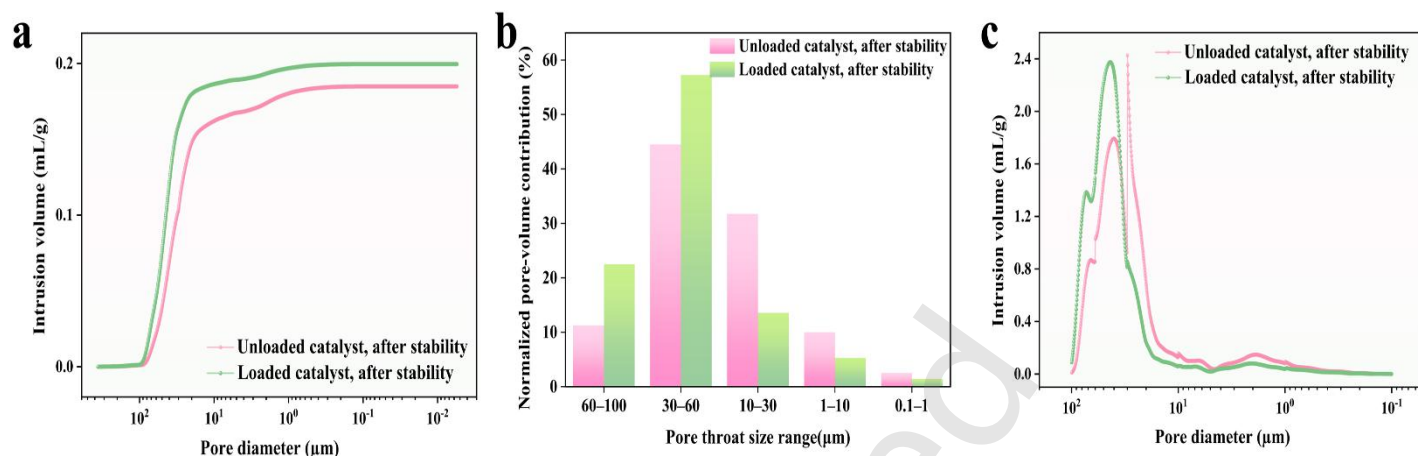


Fig. S7. MIP characterization of the catalyst-loaded and unloaded anodes after long-term stability testing. (a) Cumulative mercury intrusion volume as a function of pore diameter; (b) normalized pore-volume contributions within different pore-throat size ranges; and (c) differential mercury intrusion-volume distributions.

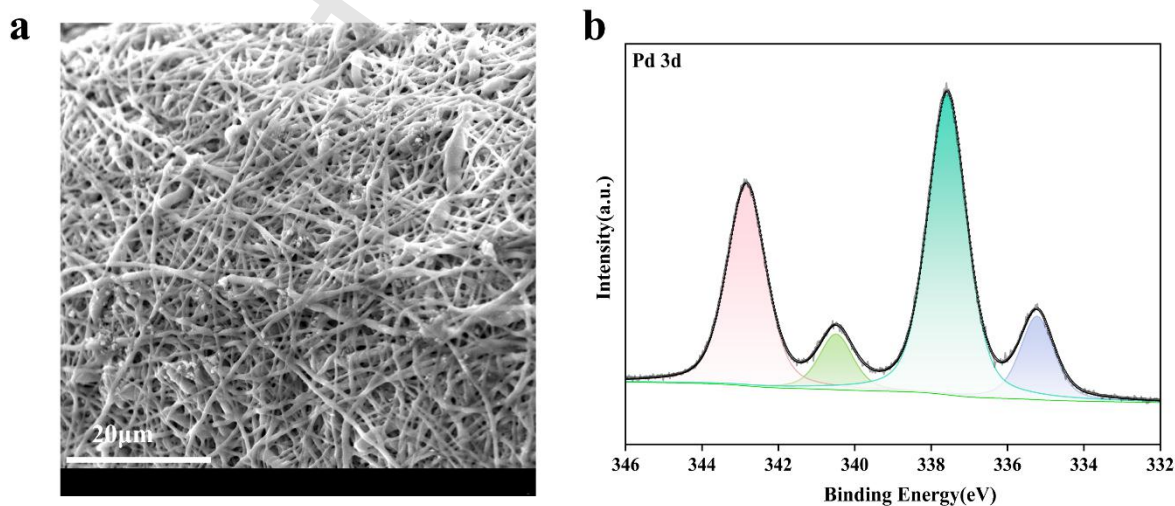


Fig. S8. Post-mortem characterization of the Pd–GDC nanofiber catalyst after the NH_3 -fueled stability test: (a) SEM morphology and (b) Pd 3d XPS spectrum with peak deconvolution.

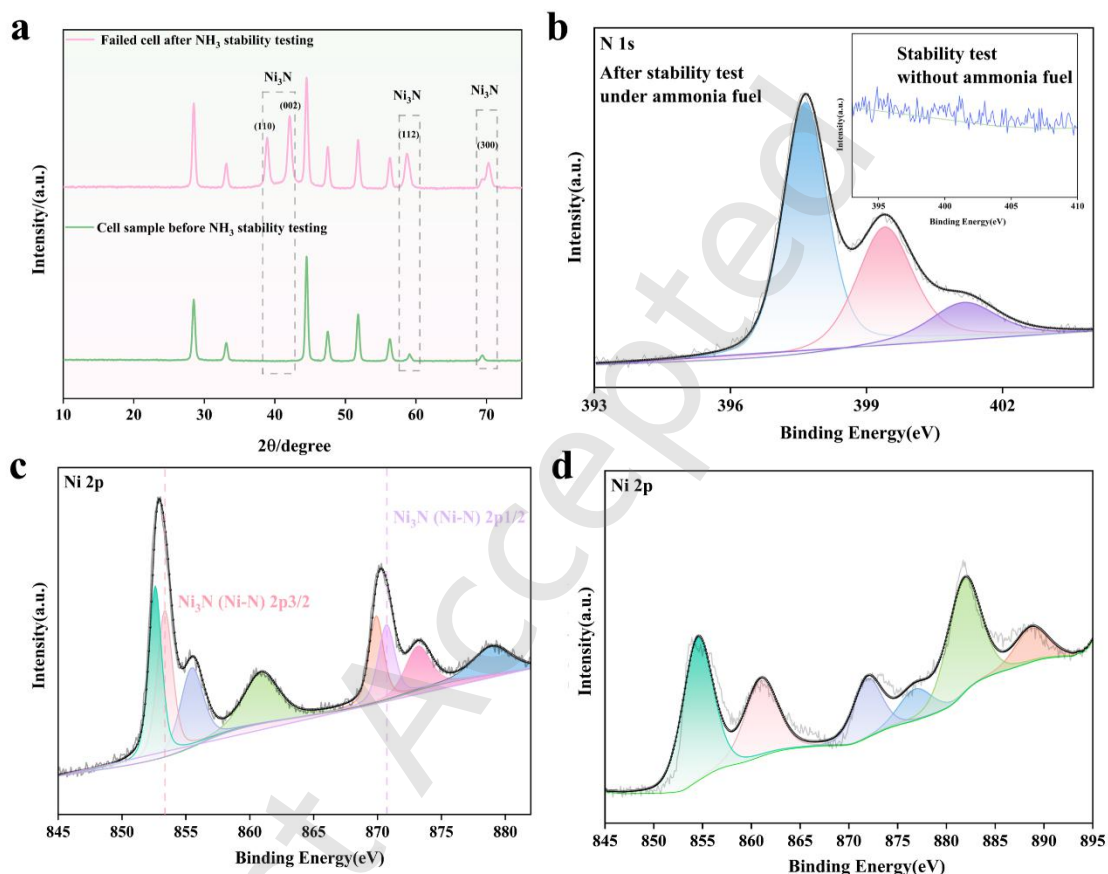


Fig. S9. Phase and chemical-state characterization of the Ni-based anode before and after NH_3 -fueled stability testing: (a) XRD patterns; (b) N 1s XPS spectrum after NH_3 -fueled stability testing, with the inset showing the control tested without ammonia fuel; (c) Ni 2p XPS spectrum after NH_3 -fueled stability testing; and (d) Ni 2p XPS spectrum before NH_3 stability testing.

Table 1. Recent studies on ammonia-fueled SOFCs and PCFCs: comparison of operating temperature and maximum power density

Cell configuration	Fuel conditions	t (°C)	MPD (mW cm ⁻²)	Refs
LSFN-SDCi /Ni-SDC/ SDC	NH ₃	800	487	[3]
SFNMx-GDC GDC LSF C-GDC	NH ₃	800	516	[4]
NiO-3YSZ NiO-3YSZ-BZCYYb NiO-BZCYYb BZCYYb	NH ₃	700	320	[5]
Ni-BZCYYb (Fe) Ni-BZCYYb BZCYYb LSCF	NH ₃	700	585	[6]
Ni-BZCYYb Ni-BZCYYb BZCYYb LSCF	NH ₃	700	490	[7]
Ni-BZCYYb BZCYYb (Pd) BSCF	NH ₃	700	379	[8]
\	NH ₃	800	300	[9]
\	NH ₃	800	200	[9]
PBSCF-BZCYYb/BZC YYb/ /Ni-BZCYYb	NH ₃	750	593	This work
PBSCF-GDC/GDC/YS Z/GDC/Ni-GDC	NH ₃	800	540	This work
PBSCF-GDC/GDC/YS Z/GDC/Ni-GDC (With Pd Catalyst)	NH ₃	800	677	This work

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