

RESEARCH ARTICLE OPEN ACCESS

Test Procedures for the Evaluation of the Performance and Stability of Direct Ammonia Fuel Cells

Mehmet Turan Görüryilmaz^{1,2}  | Erno Kemppainen¹  | Iris Dorbandt^{1,2} | Karuppsamy Dharmaraj^{1,2}  | Thorsten Schultz^{3,4}  | Sam Davis⁵  | Zhaoxia Zhou⁵ | Norbert Koch^{3,6} | Michelle P. Browne² | Rutger Schlatmann¹ | Sonya Calnan^{1,5}

¹Institute Competence Centre Photovoltaics Berlin, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany | ²Helmholtz Young Investigator Group Electrocatalysis: Synthesis to Devices, Helmholtz-Zentrum Berlin für Materialien und Energie GmbH, Berlin, Germany | ³Joint Research Group Hybride Material Systems, Berlin, Germany | ⁴Institut für Physik & CSMB, Humboldt-Universität zu Berlin, Berlin, Germany | ⁵Wolfson School of Mechanical, Electrical and Manufacturing Engineering, Loughborough University, Loughborough, Leicestershire, England | ⁶Institut für Physik & IRIS Adlershof, Humboldt-Universität zu Berlin, Berlin, Germany

Correspondence: Mehmet Turan Görüryilmaz (mehmet.goerueryilmaz@helmholtz-berlin.de) | Sonya Calnan (s.calnan@lboro.ac.uk)

Received: 4 December 2025 | **Revised:** 15 May 2026 | **Accepted:** 23 June 2026

Keywords: ammonia crossover | dynamic current degradation | electrochemical testing protocol | electrochemistry | fuel cells

ABSTRACT

The first comprehensive electrochemical test protocol for probing both steady-state and transient operations of low-temperature direct ammonia fuel cells (DAFCs) is introduced. It combines galvanostatic holds, cyclic staircase loads mimicking start-up/shut-down, long dynamic current loading representative of automotive application, and extended open-circuit periods. A hydrogen reference electrode at the anode inlet enables three-electrode operation, so anode and cathode overpotentials, impedance spectra, and polarization curves can be recorded simultaneously and de-convoluted in real time. DAFCs (25 cm²) with ultralow catalyst loading (0.3 mg_{Pt}/cm²) electrodeposited on nickel foam were operated on 1.0 M NH₃ + 1.0 M KOH at 60°C. Durability measurements indicate that voltage decay is dominated by reversible anode deactivation driven by fuel depletion; full recovery upon fuel replacement confirms minimal permanent catalyst damage. Impedance analysis indicates that the cathodic double-layer capacitance increases, consistent with flooding. Mass spectrometry identifies N₂ as the sole gaseous product at 0.2 V with no detectable NO_x. The protocol's ability to identify these phenomena over a single campaign provides an essential tool for future DAFC development. Together, the results establish links between operating regime, fuel utilization, and degradation pathway. They furnish a benchmark for emerging membranes, catalysts, and cell architectures to be compared.

1 | Introduction

Direct ammonia fuel cells (DAFCs) convert the chemical energy of ammonia directly into electricity without the need for pre-cracking, mostly using an alkaline electrolyte and an anion exchange membrane (AEM). This technology enables carbon-free energy conversion with water and nitrogen as byproducts. The ease of storage and transport of ammonia, its high energy density, and compatibility with renewable ammonia synthesis make DAFCs highly promising for decarbonized power systems

and transport applications [1]. Furthermore, ammonia has a much narrower explosive limit in air (15–28 vol.%) in contrast to compressed hydrogen (4–75 vol.%) and methanol (~7–36 vol.%), and a high auto-ignition temperature (650°C) that reduces flammability risk during storage and transportation [2].

In alkaline DAFCs, ammonia undergoes electrochemical oxidation at the anode, releasing electrons, water, and nitrogen. These electrons flow through the external load, while hydroxide ions (OH[−]) generated at the cathode migrate through the AEM

This is an open access article under the terms of the [Creative Commons Attribution](https://creativecommons.org/licenses/by/4.0/) License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2026 The Author(s). *Energy Technology* published by Wiley-VCH GmbH.

toward the anode. The cathode fed with oxygen, typically from air or pure O₂, consumes the electrons to complete the oxygen reduction reaction (ORR), generating water. This setup bypasses the need for hydrogen as an intermediate fuel, simplifying logistics. Ammonia is also easier to store and distribute than compressed or cryogenic hydrogen [3].

Despite its advantages, several challenges presently delay the progress toward commercialization of DAFCs. First, the power output is still much lower than that of hydrogen fuel cells primarily because the ammonia oxidation reaction requires multi-step electron transfer and N–H bond cleavage, leading to high overpotentials, resulting in sluggish ammonia oxidation reaction (AOR) kinetics. Highly active yet low catalysts are still being sought in the community. Commercial Pt/C catalysts show limited activity, and only the more costly PtIr/C improves ammonia oxidation activity; correspondingly, power density increases from 100 to 128 mW/cm² in DAFC tests at 25°C [4]. Another challenge is the ammonia crossover through the presently available membranes from the anode to the cathode. NH₃ readily diffuses across AEMs, leading to sub optimal fuel utilization, and performance degradation through ORR catalyst poisoning, and reduced cell voltage due to parasitic AOR at the cathode [5]. Polymer electrolyte instability is another issue that needs to be addressed. Alkaline AEMs are prone to degradation by failure in hot, ammonia-rich environments after extended operation. In the short term, highly concentrated ammonia solutions are highly viscous, which reduces OH[−] conductivity, increasing the Ohmic losses [6]. Like most types of fuel cells, flooding effect DAFCs, too. Flooding at the cathode can block active sites, while membrane dehydration can limit ion conductivity. Thus, water management is required for balanced water generation and removal across the cell, especially when gaseous educts are used.

The investigation of DAFC catalyst performance under practical working conditions, mainly under variable loads and transient conditions, is poorly investigated. Understanding and optimizing the performance and durability of DAFCs is still a significant challenge due to the impact of a variety of degradation processes and non-ideal working conditions. These non-ideal working conditions can promote membrane degradation, ammonia crossover, catalyst deactivation, fuel starvation, and flooding, which are all possible causes of sub-optimal performance. Compounded by changes in working regimes and inadequately optimized startup protocols, all these processes serve to worsen the DAFC behavior, resulting in irreproducible or inconsistent results. Only a few works reported durability tests under constant current discharge, typically within idealized lab settings [7, 8]. For instance, Liu et al. [8] achieved stable performance during 25 h at 95°C under 3.0 M NH₃ feed, and Li et al. [7] achieved stable performance during 50 h of constant-current operation at 100 mA/cm² and 100°C using PtIr/C and Pt/C electrodes, with degradation primarily attributed to the decline in ammonia oxidation kinetics caused by catalyst dissolution, agglomeration, and poisoning by *N and *NO_x species. The long-term consequences of real-world operation events on the DAFC performance, such as cycling, shutdown/restart, and variable loads, are scarcely studied and thus still not well known.

Another aspect of DAFC operation that is also critical is the feedstock to the anode and cathode. Aqueous NH₃ solution is favored

over gaseous due to typically higher power densities, to mitigate safety issues, to ease integration within AEM setups, and the relative ease in controlling kinetics due to finer molar concentration tuning and reduced volatility compared to gaseous NH₃, mainly in low-temperature configurations. In addition to ammonia, also the OH[−] concentration in the anode feed is essential for the DAFC performance, as the AOR needs OH[−] as a reactant and too low OH[−] concentrations can lead to significantly reduced power [9, 10].

Electrochemical impedance spectroscopy (EIS) is one of the most important diagnostic techniques to disentangle contributions to losses in DAFCs, but the interpretation is usually made difficult by overlapping processes. EIS is not always sufficient to disentangle catalyst degradation, aging of the membrane, and mechanical clamping artifacts. Conventional two-electrode setups yield only cell-level aggregate measurements, obscuring electrode-specific losses like degradation of catalyst, Ohmic losses, and mass transport limitations. Various studies have reported the use of reference electrode setups to deconvolute electrode-specific contributions from the individual electrodes to the electrochemical cell's overall performance [11–13]. Introducing a reference electrode, external, microtubular, or integrated through pseudo-reference techniques, allows separation of half-cell overpotentials and localized electrochemical studies. Kunimatsu et al. [14] showed that a microtubular hydrogen electrode delivers a stable and reproducible potential to allow accurate impedance spectroscopy under wide-ranging temperature and molarity conditions. Kuhn et al. [11] utilized pseudo-reference electrodes imbedded in the membrane-electrode assembly (MEA) to separate anode and cathode impedance spectra, elucidating kinetic and mass transfer resistances that are indistinguishable under full-cell EIS measurement. Hinds and Brightman [13] further mapped local electrode potentials in situ, exposing gradients and asymmetries that provide information on fuel distribution and water management. Gerteisen [12] used laser ablation to imbed reference electrodes into the MEA, enabling accurate isolation of the anode and cathode overpotentials during the course of normal working of the cell. More recently, Böhre et al. [15] utilized a three-electrode configuration in PEM water electrolysis to obtain activation energies for the half-cell reactions and to separate Ohmic resistances, improving the accuracy of electrochemical impedance spectroscopy. Bensmann et al. [16] highlighted the importance of proper placement and stabilizing the reference electrode to avoid measurement artifacts during under-cyclic conditions and high-current testing. Those methods are thus useful for the currently understudied field of DAFCs, where crossover of ammonia, catalyst poisoning, and dynamic loading affect each electrode inequitably. Therefore, incorporating a reference electrode into test configurations is of utmost importance to identify degradation processes, to confirm models, and to inform focused optimization of catalyst design and operating procedures.

This study is aimed at filling in the knowledge gap by exploring systematically how various load regimes, namely, constant current, open circuit voltage (OCV), and dynamic voltage or current cycling, impact the performance and degradation of DAFCs under short-term operation. This is accomplished by implementing analytical techniques to

facilitate component-level performance losses, by adapting existing hydrogen fuel cell test protocols to allow for DAFC benchmarking, and by determining performance-degradation regimes and identifying fingerprints/signatures of degradation of DAFC catalysts based on Pt.

2 | Experimental Details

2.1 | Membrane and Catalyst Coated Electrode Preparation

The commercial AEM used in this study was a reinforced Fumasep FAA-3-PK-130 membrane manufactured by FUMATECH BWT GmbH, Germany, selected for its relative stability in a warm KOH and NH₃ mixed electrolyte. Membranes were cut into small pieces of 7.5 × 7.5 cm and immersed in a 1.0 M KOH solution, which was refreshed after 4 h, and the pieces were kept submerged for at least 24 h before the performance test. In the case of longer immersion time, the solution was changed every 24 h.

For the catalyst-coated electrodes that were prepared by electro-deposition method, Ni-foam pieces (>99.99% purity, 1.6 mm thickness, ≥95% porosity, Nanografi) were cut and cleaned with ethanol for 15 min in an ultrasonic bath. After that, they were left to dry in the oven at 80°C overnight. The electrodeposition solution was prepared using 5 mM Pt as chloroplatinic acid (H₂PtCl₆, ≥99.9% trace metals basis, Sigma-Aldrich), and 0.5 M sulfuric acid (H₂SO₄, 96%, Technic France) in DI water. Before the deposition, the solution was saturated with nitrogen to remove oxygen. A potentiostat-galvanostat (PARSTAT 4000A) controlled using VersaStudio software (AMETEK, USA) was used for electrodeposition. A rectangular 5 × 7 cm piece of Ni-foam was used as the working electrode, while a platinum sheet (5 × 5 cm, PI-KEM Limited, UK, min. 99.5% purity) was used as the counter electrode. During the depositions, the 500 ml electrolyte in 700 ml beaker was stirred magnetically at 200 rpm in a two-electrode configuration (without a reference electrode). The shorter side of each Ni-foam to be coated was clamped for electrical contact, and 5.5 cm of the longer side was submerged in the electrolyte. For deposition of the anode catalyst, a constant current density of −30 mA/cm² was applied. In contrast, the cathode catalyst deposition was made with potentiostatic pulses, −1.0 V for 5 ms and 0.05 V for 10 ms. The total deposition charge was fixed for both the anode and cathode electrodes at 0.65 C/cm² based on the geometric area. Each deposition solution was used to prepare only two electrodes, with the anode electrode first prepared, followed by the cathode electrode. The nominal catalyst loading m_{Pt} [mg_{Pt}/cm²] on both electrodes was about 0.3 mg_{Pt}/cm², calculated using Equation (1).

$$m_{Pt} = \frac{M_{Pt} \times Q}{4F} \quad (1)$$

where Q [C] is the total charge during the deposition estimated by the potentiostat software, M_{Pt} is the molecular mass of Pt [195.08 g/mol] and F is the Faraday constant [96485.31 C/mol] and 4 corresponds to the oxidation number of Pt in chloroplatinic acid (+4).

2.2 | Characterization of Electrocatalyst Materials

The global crystallographic phase character of the catalyst layers was also investigated using X-ray diffraction (XRD) conducted at the X-ray Corelab at Helmholtz-Zentrum Berlin using a Bruker D8 instrument with a Cu K α beam. The diffraction patterns were acquired in the Bragg–Brentano geometry using a step size of 0.02°. The morphology and topology of the catalysts' surfaces were examined using a scanning electron microscope (SEM). Additionally, the elemental composition and surface distribution of the catalysts were determined using energy dispersive X-ray spectroscopy (EDX). Both SEM and EDX were conducted at the Correlative Microscopy and Spectroscopy (CCMS) Corelab (Helmholtz-Zentrum Berlin für Materialien und Energie, Germany) using a field emission (FE)-SEM (Crossbeam 340 by Zeiss, Germany) fitted with a Bruker XFlash EDX system. Lamella were lifted out of the Pt-coated nickel foam samples using a ThermoFisher Scios 2 Ga DualBeam focused ion beam instrument at the Loughborough Materials Characterization Center (LMCC). The lamellas were used for a detailed investigation of the electrodeposited Pt on a scanning transmission electron microscope fitted with a cold field emission gun (FEG-STEM, Thermo Fisher Scientific (TFS) Talos F200i) and operated at 200 kV accelerating voltage. A Ceta (4 × 4 k) CCD camera was used to acquire the TEM images, and the selected area electron diffraction (SAED) patterns were analyzed using TFS Velox software.

The elemental composition and chemical state at the surface of catalyst samples were analyzed by X-ray photoelectron spectroscopy using a JEOL JPS-9030 instrument with a base pressure of 2 × 10^{−9} mbar. The catalyst-coated Ni foam substrates were mounted on a sample holder via copper tape. Al-K α radiation of a non-monochromated source was used for excitation with a power of 300 W. A hemispherical analyzer with a pass energy of 50 eV for the survey spectra and 20 eV for the narrow scans was used to detect the kinetic energy of the emitted electrons under normal emission, yielding an overall energy resolution of 1.1 eV. The binding energy scale of the analyzer was calibrated using argon sputter-cleaned polycrystalline gold and copper foils, and setting the binding energies of the Au4f_{7/2} and the Cu2p_{3/2} peaks to 84.00 and 932.66 eV, respectively. For peak fitting, CasaXPS was used, employing Shirley backgrounds, asymmetric line shapes (LF(0.78,1.5,20,40)) for the metallic Pt4f peaks and symmetric line shapes (GL(30)) for the Ni3p peak [17].

2.3 | Electrochemical Characterization

After deposition of the ORR and AOR catalysts, these were dried in an oven overnight at 80°C, and a 1.0 cm wide piece was cut from the coated sample. The strip was then painted with epoxy glue (UHU PLUS Endfest 2 K-epoxy glue), only exposing an area of 1.0 × 1.0 cm at one end, to avoid the electrolyte spreading beyond the area of interest by the capillary effect. The electrochemical tests on the catalyst-coated strip electrodes were done in a 150 ml jacketed glass cell in a three-electrode (3-E) configuration following a protocol given in Supporting Information (Table S3-E). For all the tests, a graphite rod (Alfa Aesar, 6.3 mm in diameter, 99%, metal basis) was used as a counter electrode for catalyst testing with a reversible hydrogen electrode

(mini RHE, Gaskatel GmbH, Germany) serving as the reference electrode. All electrochemical tests were done using a Zahner ZENNIUM PRO potentiostat controlled by Thales software (Zahner-Elektrik GmbH & Co. KG, Germany).

For ORR tests, the working electrode was the catalyst-coated Ni-foam. The tests were carried out in a jacketed glass electrochemical cell at room temperature and at 60°C in a 1.0 M KOH solution. At the beginning of the test, the 80 ml electrolyte was saturated with nitrogen for 30 min to prevent oxygen from interfering with the electrochemical surface cleaning, activation, and blank ORR test. Next, an 80 ml fresh electrolyte that was saturated with oxygen for 30 min was used for ORR measurements. Tafel slopes were obtained with linear sweep voltammetry at a scan rate of 1 mV s⁻¹.

For AOR tests, a piece of 1.0 × 1.0 cm electrodeposited Pt (e-Pt) on Ni foam was used as the working electrode, under the constant purging of nitrogen while stirring the electrolyte at 250 rpm. The measurements were performed in 1.0 M KOH in presence and absence of 1.0 M NH₃ in a jacketed electrochemical cell at 25°C and 60°C. Tafel slopes were determined from linear scan voltammetry (LSV) data acquired at a scan rate of 2 mV s⁻¹. The protocol followed for ORR and AOR are given in Table 1, Supporting Information.

2.4 | DAFC Test Methods

The membrane electrode assembly (MEA) consisted of catalyst-coated Ni-foam electrodes sized 5 × 5 cm sandwiching a commercial AEM. The DAFC was completed by tightening the eight bolts with a torque of 2 Nm to clamp the stainless-steel endplates and the MEA together. A photograph of the cell and the in-house-made test bench is shown in Figure S1.

For all tests, the anode was fed with an electrolyte consisting of 1.0 M KOH + 1.0 M NH₃ at a flow rate of 25 ml/min while the

cathode was fed with dry, room temperature O₂ gas (Air Liquide, Alphagaz 2, 99.9995% purity) flowing at 50 ml/min. We elected to use a liquid-fed anode since ammonia solution is safer to handle than gas and because there is no need for additional membrane humidification. All measurements were done with both the cell and anolyte temperatures fixed at 60°C and with ambient pressure at both outlets.

The cell conditioning and testing procedure was developed by adjusting and combining procedures from EU Harmonized Test Protocols for PEMFC MEA Testing in Single Cell Configuration for Automotive Applications [18] and Florida Solar Energy Center's Procedures for Performing PEM Single Cell Testing [19].

The DAFCs were tested to investigate the performance (to benchmark their quality), load behavior (to study the reliability under different loading levels), and to determine short-term endurance (to study the stability after exposure to stress tests). Tables describing the sequence tests used for the DAFC tests are presented in the Supporting Information (Tables S3–S7).

2.4.1 | Description of the DAFC Test Set up

A schematic of the in-house DAFC test system is given in Figure 1.

Before starting the performance test, both the fuel electrolyte in its reservoir and the DAFC were heat soaked to reach the desired temperature, while cathode was purged with oxygen at a flow rate of 50 ml/min. Once the fuel and the cell both reached the desired temperature, the fuel electrolyte was pumped through the cell and held for 5 min to saturate the AOR catalyst sites with NH₃ and to ensure adequate hydration of the membrane. Thereafter, the cell was electrically connected to the potentiostat to start the measurements.

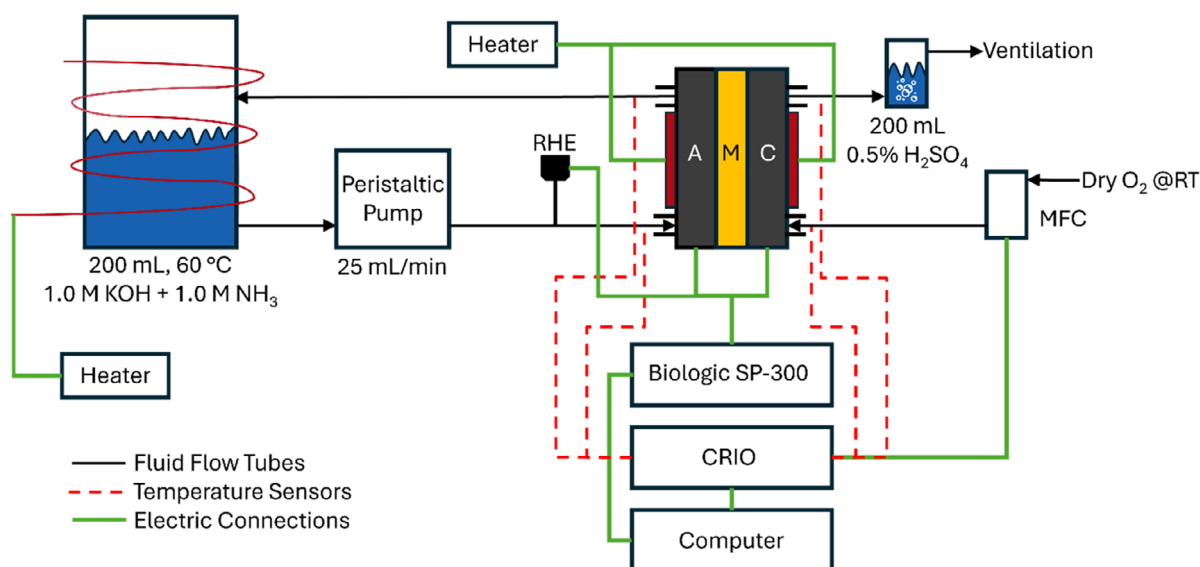


FIGURE 1 | Schematic of the test set up for DAFC measurements. CRIO, compact real-time input/output controller; MFC, mass flow controller; RHE, reversible hydrogen electrode; RT, room temperature.

membrane hydration, wetting of flow fields, and catalyst precursor transformation. The conditioning sequence and parameters were selected according to the EU Harmonized Test Protocols for PEMFC MEA Testing in Single Cell Configuration for Automotive Applications [18]. In our case, instead of 3 h of constant current, we applied 3 h of constant voltage and followed by stepped polarization. After the stepped polarization, a performance test was performed to determine the OCV, the maximum power point, and the limiting current close to 0 V, as well as the efficiency for a given set of operating parameters. This set of parameters would then be used to specify the beginning of test performance of the DAFC.

The cell conditioning (A) consisted of an open circuit (OCV-A1) hold for 5 min, followed by cyclic voltammetry (CV-A1) between 0–1.2 V for 50 cycles, chronoamperometry (CA-A1) for 3 h at 0.2 V, potentiostatic electrochemical impedance spectroscopy (PEIS-A1) at 0.2 V, and lastly, CA-A2 at 0.1 V for 10 min. The reason for choosing 0.1 V instead of 0 V is to avoid irreversible cell damage, mass transport limitations, and accelerated catalyst degradation. Another reason is that there is no useful power output below this value. The next part was to determine the beginning of test (BOT) cell performance (B), which consisted of

- LSV-B1 at 1 mV/s to determine the quality of the DAFC. If a cell fails at this point, further performance tests need not be continued.
- During a 2 min pause in testing, the final value of cell current $I_{0.1V}$ during the CA-A2 measurement at 0.1 V, was noted to be used as the maximum current of the staircase polarization curve, $I_{0.1V}$ in Step 7 (staircase polarization with constant current steps). We avoided using the true maximum current of the DAFC at $V=0$ because of safety concerns and to avoid unnecessarily accelerating the irreversible degradation of the membrane and/or catalysts due to potentially excessive joule heating.

Variable load performance (C) was tested using staircase polarization SPC-CP-C1 with constant current steps ranging from 0%–100% of I_{MAX} . This was followed by the determination of the interim End of Test parameters using

- A second LSV-D1 at 1 mV/s to analyze the short-term stability/recovery of the DAFC performance after load variation,

- A second set of PEIS-D1 measurements at 0.3, 0.2, and 0.1 V was conducted to understand how the cell's impedance and its constituents vary with increasing current load.
- And finally, GEIS-D1 measurement at a current corresponding to 0.2 V, to check the behavior under the load instead of voltage.
- The detailed testing protocol is given in Tables S3 and S4. Note that the PEIS measurements are taken at three levels determined for the LSV performance curve (i.e., the voltage close to maximum power and two equidistant levels above and below it, that are at least 100 mV away from OCV and short circuit).

The aim of the staircase polarization curve is to obtain a steady state polarization curve, whose values are not affected by the influence of the preceding load levels, and as well as hysteresis [23]. The test procedure started at open circuit voltage (OCV), and the stack voltage was decreased stepwise, with 10- and/or 15-minute-long hold for each set point until ~ 100 mV, after which the scan direction was reversed using the same reduction step and interval.

The protocol of the DAFC cell conditioning and performance tests, including the beginning of test BOT parameters determined from LSV-B1 and LSV-C1, respectively, is given in Figure 3.

Operando diagnosis of the effects of the individual cell components can be elucidated by electrochemical impedance spectroscopy (EIS), which in this study was performed in both potentiostatic (0.3, 0.2, and 0.1 V) and galvanostatic mode (using the value of cell current around 0.2 V, close to the maximum power point). In both cases, EIS was measured over a frequency range from 200 kHz to 100 mHz with a 10 mV AC amplitude.

2.4.5 | Protocol for Static and Dynamic Degradation Tests

After successful tests of the cell performance and load behavior, the DAFC's reliability under different loading conditions was tested using the same performance test procedure. For the degradation tests, consisting of a static current hold at relatively high voltage corresponding to low-load operation and a dynamic current profile corresponding to frequent load transients, were made to assess the cell's endurance to severe operating conditions. Each degradation test was followed right after a

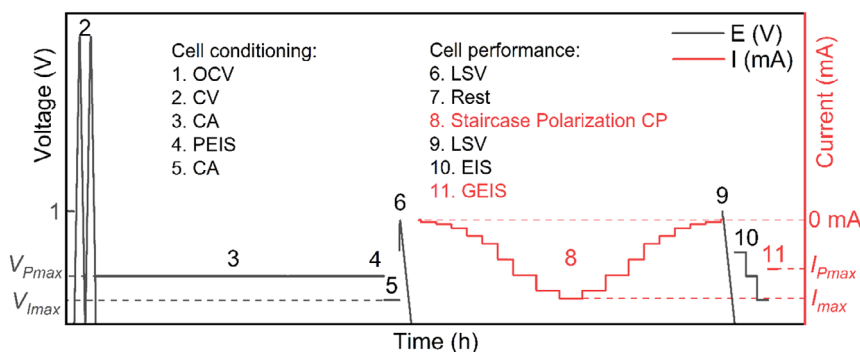


FIGURE 3 | Typical measurement protocol, black lines are applied potential (except for OCV), and the red lines are applied current.

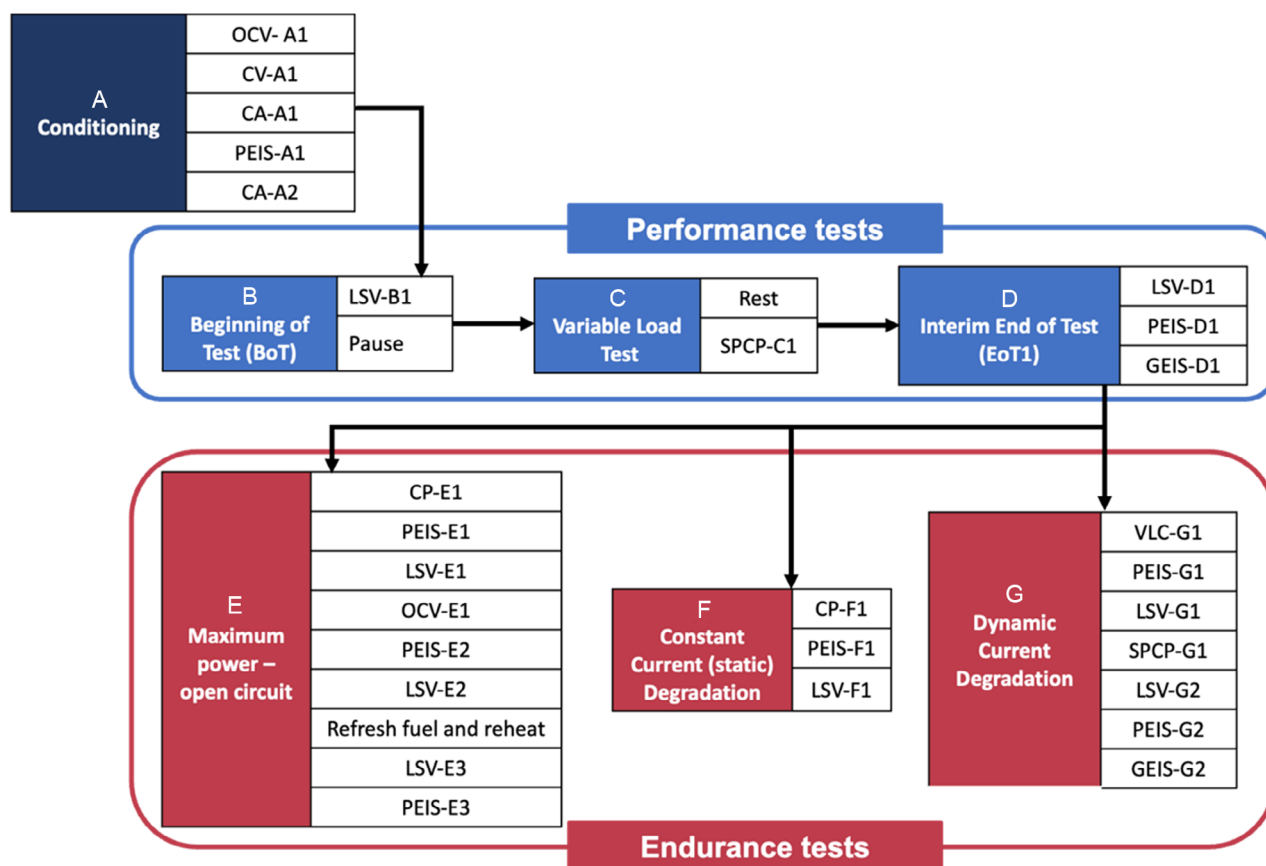


FIGURE 4 | Flow chart for test protocols. A typical test campaign starts with conditioning tests (A) followed by sequential performance tests (B) beginning of test (BoT), (C) variable load test, and (D) interim end of test, which are followed by one of three endurance tests. (E) Maximum power-open circuit test, (F) constant current/static degradation and (G) dynamic current degradation).

performance test made with a fresh MEA. A flowchart for the protocols is given in Figure 4.

For each MEA, a series of tests was run initially to mimic a possible use scenario, such as providing electricity overnight with no operation during the day, where the DAFC operates close to maximum power for several hours and is then left to rest with no load (E). For this, a current at the maximum power point was applied to the DAFC for 6.5 h (CP-E1) followed by PEIS-E1 measurements at 0.3, 0.2, and 0.1 V. Then the DAFC was left at open circuit for 9 h (OCV-E1) to determine the stable open circuit potential (OCP) at either electrode. Prolonged OCV operation is believed to decrease cell performance by reducing catalyst activity through loss of electrochemically active surface area (ECSA) [24]. Thus, a PEIS-E2 measurement at 0.2 V and a polarization curve acquired with 1 mV/s (LSV-E1) were used to compare the performance to that after the BOT state. After that, the electrical cell was disconnected from the potentiostat, and the fuel was refreshed, then heated to the desired test temperature. Meanwhile, the oxygen flow was increased to 200 ml/min to purge the cathode side of the cell to get rid of the fuel build-up caused by crossover (to be discussed later). When the refreshed fuel reached the desired temperature, the oxygen flow was reduced to 50 ml/min, electrical connections were established, and another set of LSV and PEIS tests were conducted to determine the performance of the DAFC after harsh operating conditions and to gauge the cell's ability to recover its performance.

For the static current degradation test, Table S5, a cell current corresponding to a voltage of 100 mV below OCV from the performance polarization curve (determined previously by LSV-B1), was applied to the cell for 10 h (CP-F1) right after the polarization curve sequence. This was followed by PEIS measurements (PEIS-F1) used to compare the performance to that after the BOT state.

For the dynamic current degradation test, a variable load cycle consisting of a current profile (Figure 5) mimicking a drive train was adapted from the literature [25] and applied in 10 super-cycles to the DAFC for a total duration of about 10 h. The current values were adjusted as percentages of the maximum current (Table S6). This, too, was followed by PEIS measurements

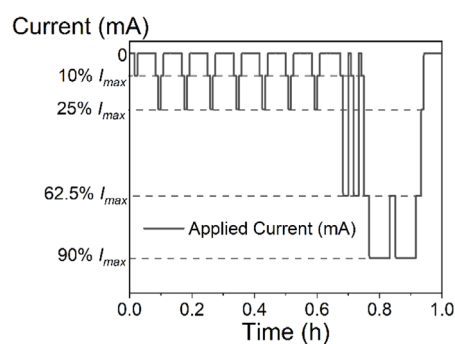


FIGURE 5 | Dynamic current load trace applied to the DAFC in endurance test 3 (G).

(PEIS-G1) and a polarization curve acquired with 1 mV/s (LSV-G1), used to compare the performance to that after the BOT state.

2.4.6 | Analysis of Cell Performance and Endurance

The quality of the DAFC's performance and endurance was measured primarily using OCV, the high frequency resistance (HFR), and the maximum power, as well as the electrical efficiency for a given set of conditions (temperature, feed rates of fuel and oxidant, electrolyte compositions). We note here that there is no consensus yet in the community for standard test conditions of DAFCs, as the field is considered nascent. However, we recognize and emphasize the importance of reporting the conditions under which the tests were performed to aid comparisons among different reports.

For practical application purposes, the effectiveness of a fuel cell is measured by electrical energy efficiency. We estimated the electrical efficiency of the fuel cell by using the ratio of the power output to the energy contained in the fuel (NH_3) using the formula in Equation (4).

$$\eta_{\text{DAFC}} = \frac{V_{\text{cell}} \times I_{\text{cell}}}{\dot{n}_{\text{NH}_3} \times \text{HHV}_{\text{NH}_3}} \quad (4)$$

where HHV_{NH_3} is the higher heating value of ammonia = 382.6 kJ/mol, V_{cell} and I_{cell} correspond to the maximum power from the polarization curve for 1.0 M KOH + 1.0 M NH_3 mixture at 60°C and $\dot{n}_{\text{NH}_3}$ is the rate of consumption of ammonia in moles given by the relation between the cell current and Faraday's constant, shown in Equation (5).

$$\dot{n}_{\text{NH}_3} = \frac{I_{\text{cell}} - I_{\text{loss}}}{6 \times F} \quad (5)$$

I_{loss} was calculated from the ammonia crossover tests at a cell voltage of 1.0 V (protocol discussed in the next sub-section) for 1.0 M KOH + 1.0 M NH_3 mixture at 60°C. At higher cell voltages, NH_3 oxidation becomes more diffusion-controlled and better reflects the maximum crossover rate. Also, it is less affected by double-layer capacitance or residual background currents.

2.5 | Results and Discussion

Direct-ammonia fuel cells (DAFCs) remain constrained by sluggish ammonia-oxidation kinetics, catalyst degradation, and

fuel crossover; therefore, a rigorous understanding of how the electrode architecture and the operating regime affect performance is essential for progress. In the following section, we present a systematic electrochemical evaluation of low-temperature DAFCs operated under stepped, constant, and dynamic loads, using a newly developed test protocol that decouples anode and cathode behaviors with an internal reference electrode. The electrodeposition methods were selected for the best electrode performance (Figure S2).

2.6 | Surface Morphology and Bulk Chemical Composition Results of the Electrocatalysts

The morphology of the Pt-coated nickel foam electrodes was investigated using scanning electron microscopy (SEM), as shown in Figure 6 and compared to that of the bare nickel foam support in Figure S3. The bare Ni foam exhibited a typical three-dimensional open-cell structure, consisting of interconnected ligaments and macropores in the range of approximately 100–500 μm wide. The ligament surfaces were relatively smooth and free of visible contaminants, consistent with effective cleaning using ethanol and ultrapure water in an ultrasonic bath.

SEM images from the electrode prepared by pulsed voltage deposition showed platinum clusters with smooth, rounded shapes, typically ranging from 300 to 600 nm in diameter. These clusters were well-defined and generally occupied a large fraction of the visible surface. Across multiple regions, the Pt appeared relatively closely spaced, with less exposed Ni surface between the clusters, suggesting substantial localized growth. The morphology was compact, and no fine-scale branching or textural roughness was observed on the particle surfaces. While some regions showed variations in particle density, the overall deposition appeared consistent at this magnification scale.

In contrast, the constant current-deposited electrode showed markedly different features. Pt deposits in this sample were composed of smaller aggregates, typically 100–300 nm in size, with more granular surface texture. However, despite the finer particle size, many regions exhibited larger visible gaps between adjacent clusters, and areas of exposed Ni surface were more frequently observed. The overall spacing between features was greater than in the pulsed voltage sample, suggesting that the deposition,

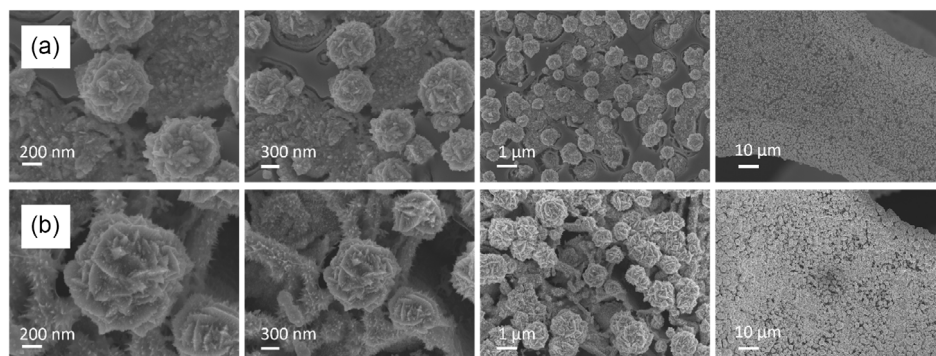


FIGURE 6 | SEM images of as-prepared Pt on Ni foam for (a) anode electrode, electrodeposited using -30 mA/cm^2 constant current, (b) cathode electrode, electrodeposited using pulsed bias between -1.0 V (5 ms) and $+0.05 \text{ V}$ (10 ms).

while more finely structured, was also more sparsely distributed at the mesoscale. The particle morphology in these regions was consistent with nucleation under hydrogen evolution conditions, leading to nodular, cauliflower-like clusters.

Taken together, these observations indicate that the two deposition protocols resulted in different spatial distributions of Pt. Pulsed voltage deposition produced larger but more closely spaced clusters, while constant current deposition yielded smaller, more isolated aggregates with relatively greater spacing between them. The visual evidence does not support the assumption that constant current deposition leads to more uniform or denser surface coverage; instead, it suggests that both methods produce distinct morphologies with different packing characteristics, despite having the same nominal overall Pt loading.

EDX was used to analyze the elemental composition and spatial distribution of platinum on Ni foam electrodes prepared by constant current and pulsed voltage electrodeposition (Figure S4). Both deposition protocols produced Pt-rich clusters, with normalized mass concentrations of 76.20% and 80.24% for the constant current and pulsed deposition samples, respectively. Nickel was also detected in both cases, indicating either incomplete surface coverage by Pt or partial electron beam penetration through the Pt layer to the underlying Ni substrate. A low but consistent oxygen signal was observed in both samples (2.76% and 2.31%, for constant current and pulsed deposition, respectively). Although the electrodeposition solutions were thoroughly de-aerated with nitrogen prior to

use, the electrolyte itself is strongly acidic and capable of chemically oxidizing both the Ni surface and freshly deposited Pt. Thus, the detected oxygen is attributed to surface oxidation driven by acidic conditions and subsequent air exposure. Elemental mapping revealed that Pt was localized on the clusters visible in SEM images. In the constant current sample, Pt coverage appeared more granular and discontinuous, with a stronger Ni signal visible around and beneath the deposits. In contrast, pulsed deposition resulted in more uniform Pt coverage with reduced Ni signal intensity, suggesting denser or more complete Pt layer formation. Oxygen was consistently co-localized with Pt-rich regions in both samples, supporting the presence of surface oxides.

The TEM analysis revealed that both the anode and cathode Pt consist of nanocrystallites (~ 6 nm grain size) with more nanotwins visible for the former (Figure 7). The SAED patterns (Figure 7b,d) of both samples are fully indexed to polycrystalline Pt ICDD PDF# 04-0802. These data confirm that both the anode and cathode Pt are polycrystalline, with the latter being slightly more amorphous. High-angle annular dark field (HAADF) images coupled with EDS (Figure S5) further confirmed the differences in the EDX elemental mapping presented above.

These findings confirm effective Pt deposition by both methods, with morphological and compositional differences likely arising from the distinct nucleation and growth dynamics imposed by the electrodeposition protocol.

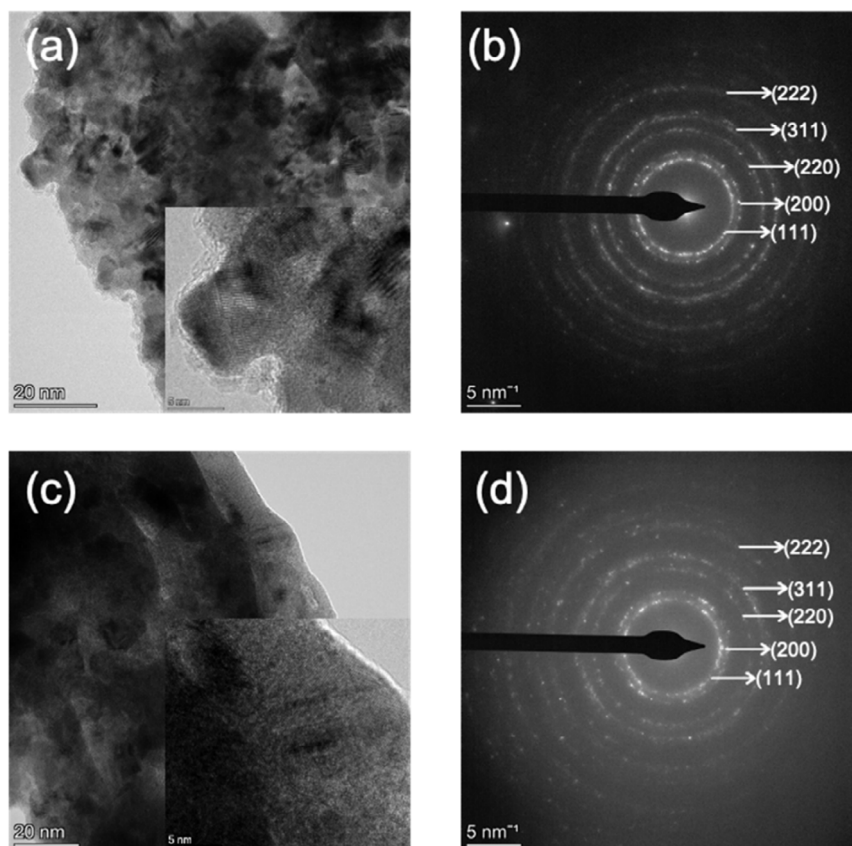


FIGURE 7 | Bright field TEM images (left) and the corresponding indexed SAED patterns (right) of as prepared Pt on Ni foam for the anode (a,b), electrodeposited using -30 mA/cm^2 constant current and the cathode (c,d), electrodeposited using pulsing over -1.0 V for 5 ms and 0.05 V for 10 ms.

2.7 | Crystalline Structure of the Electrodeposited Pt Electrocatalysts

X-ray diffraction (XRD) was conducted to characterize the crystalline phases of Pt-deposited Ni foam electrodes prepared by constant current and pulsed voltage electrodeposition (Figure 8a). Both diffraction patterns are dominated by sharp reflections at approximately 44.5°, 51.8°, and 76.4°, corresponding to the (111), (200), and (220) planes of face-centered cubic (fcc) nickel (PDF# 04-0850) from the Ni foam substrate. In addition to these intense Ni signals, reflections corresponding to fcc platinum (ICDD PDF# 04-0802) were also detected, like the SAED patterns on a microscopic scale. These include the (111), (200), (220), (311), and (222) planes of Pt at approximately 39.8°, 46.2°, 67.5°, 81.3°, and 85.7°, respectively. While these Pt peaks are visibly suppressed in the full-scale XRD plot due to the relative intensity of the Ni peaks, they become clearly observable upon zooming in on the baseline. All Pt reflections appear broad and of low relative intensity, consistent with nanocrystalline Pt deposits. A distinct, low-intensity peak was also observed at ~22.3° for bare Ni foam and the pulsed electrodeposition, which can be an impurity from the Ni foam. This feature may be attributed to surface oxidation or the formation. No significant shifts or intensity differences were observed between the constant current and pulsed deposition samples, indicating similar crystallographic properties of the deposited Pt in both cases.

2.8 | Chemical Speciation at the Surface of the Electrodeposited Pt Electrocatalysts

XPS measurements were conducted to analyze the oxidation states of the platinum electrodes and to compare the Pt loading between anode and cathode. Figure 8b shows the Pt4f core levels of both anode and cathode. The Ni3p peak appears in the same energy window with a binding energy of around 68.0 eV. For both the anode and the cathode, the Pt4f core level consists of one pair of doublets at energies of 71.0 and 74.3 eV. This is evident for metallic platinum and aligns with the asymmetric peak shapes, which result from continuous photoelectron scattering by electrons near the Fermi level [26]. No signs of any oxidation are observed for both constant current electrodeposition (anode) and pulse electrodeposition (cathode). A comparison to the intensity of the Ni3p peak suggests that the platinum loading is slightly higher on the cathode. Assuming a homogenous distribution, one obtains Pt concentrations of 16.6% for the cathode and 14.3% for the anode in comparison to nickel. However, these values should be interpreted with caution and are intended only to illustrate the relatively higher Pt loading of the cathode.

2.9 | Electrocatalytic Performance

The nickel foam electrodes were coated with platinum via pulsed electrodeposition for the cathode (ORR) and galvanostatic

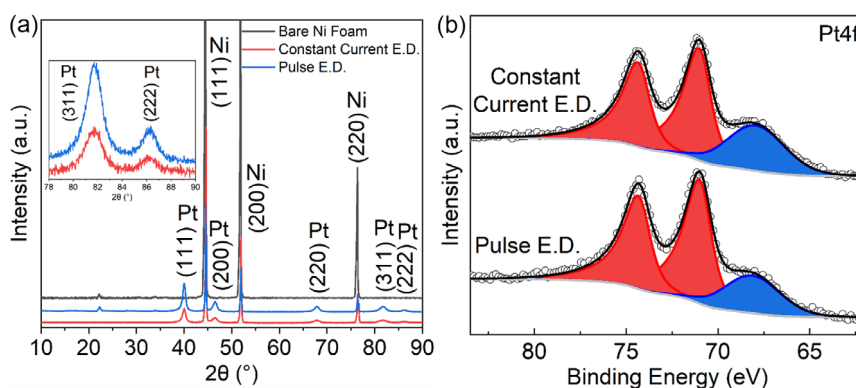


FIGURE 8 | (a) XRD, (b) XPS results of the electrodeposited electrodes.

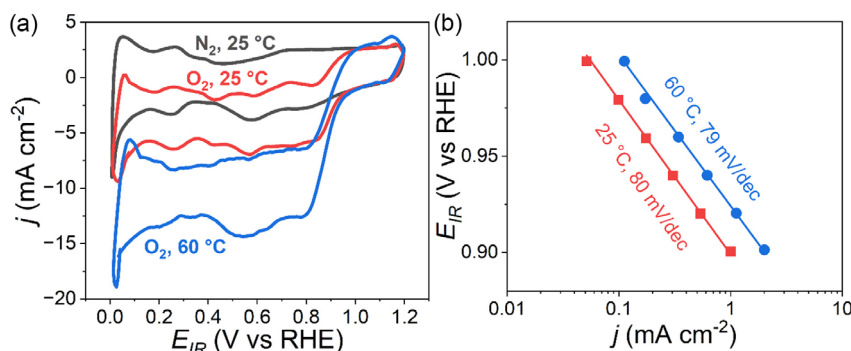


FIGURE 9 | (a) CV curves at a scan rate of 10 mV s⁻¹ of Pt electrodeposited on Ni foam, in pulsed mode in N₂ and O₂ saturated 1.0 M KOH at 25°C and in O₂ saturated electrolyte at 60°C. (b) The corresponding Tafel plots at 25°C and 60°C both in O₂ saturated 1.0 M KOH.

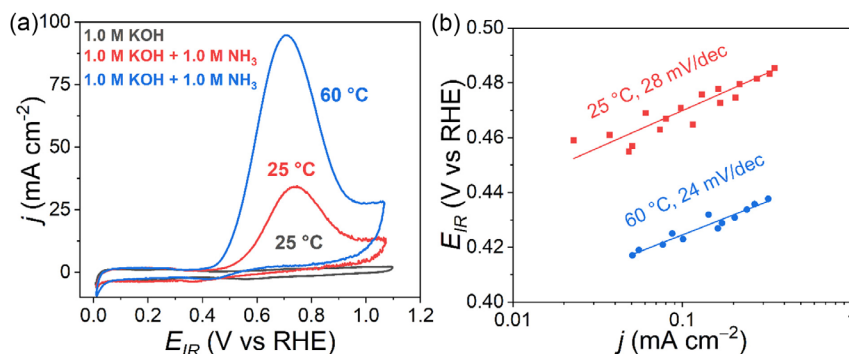


FIGURE 10 | (a) CV curves, at a scan rate of 10 mV s⁻¹, of Pt electrodeposited on Ni foam, in constant mode in N₂ and O₂ saturated 1.0 M KOH at 25 °C and in O₂ saturated electrolyte at 60 °C. (b) The corresponding Tafel plots at 25 °C and 60 °C, both in O₂ saturated 1.0 M KOH.

electrodeposition for the anode (AOR). Figure 9a shows the cyclic voltammograms (CV) of electrodeposited Pt as the cathode electrode in 1.0 M N₂ and O₂ saturated KOH. At 25 °C, the cathodic reaction starts at about 1.03 V versus RHE. After increasing the temperature to 60 °C, the onset potential of ORR shifts to 1.06 V versus RHE. The ORR current density reaches the highest current value at around 0.80 V vs RHE for both temperatures and continues as a plateau for a short while, which indicates a mass transport limitation, namely the diffusion of oxygen. Figure 9b shows the Tafel slope as 80 mV/dec at 25 °C and as 79 mV/dec at 60 °C between 0.9–1.0 V versus RHE, which is in good agreement with the literature [27–29].

Prior to the CV measurements for ammonia oxidation on the electrodeposited Pt on Ni foam, 0.05 V versus RHE was applied for 60 s to remove any adsorbates on the catalyst surface. The ammonia oxidation reaction current density with respect to the geometric area of the electrode (j_{geo}), peaked at about 0.70 V and catalyst deactivation occurred at >0.70 V due to the adsorption of intermediates (NO_x ads, N_{ads}) [30, 31]. Figure 10a shows the cyclic voltammograms of electrodeposited Pt on Ni foam in the presence and absence of 1.0 M NH₃ in 1.0 M KOH. The electrocatalyst showed an increase in anodic current density starting at 0.48 V versus RHE at 25 °C. Upon increasing the electrolyte temperature to 60 °C, the apparent onset potential of ammonia oxidation reaction decreased to 0.42 V versus RHE. Figure 10b shows the Tafel slope of 28 mV dec⁻¹, which is obtained in the potential range 0.44–0.50 V. This is close to 30 mV dec⁻¹, and thus consistent with dimerization of NH^{*} species being the rate-determining step (NH^{*} + NH^{*} → N₂H₄⁺ + *) for the ammonia oxidation reaction (Gerischer-Mauerer mechanism) on Pt catalyst [31–34].

2.10 | Electrochemical Quantification of Ammonia Crossover

Ammonia crossover through the Fumasep FAA-3-PK-130 membrane was evaluated electrochemically using linear sweep voltammetry in a full-cell setup under nitrogen flow at the cathode. The measured current, corresponding to ammonia oxidation, was used as a proxy for the extent of ammonia crossover from the anode to the cathode. At all temperatures, increasing the ammonia concentration in the anode feed led to lower measured cell currents. For example, at 70 °C and 1.0 V, the

current dropped from 116.86 mA at 0.1 M NH₃ to 86.13 mA at 1.0 M and 61.34 mA at 2.0 M. This counterintuitive drop in current, despite increased fuel availability, reflects a dominant negative effect of crossover, where excess ammonia saturates and poisons the cathode. As ammonia permeates across the membrane and accumulates at the cathode, it covers the oxygen reduction sites and produces water via AOR, thus suppressing overall reaction rates. This is consistent with reports highlighting NH₃-induced flooding and site blockage in anion-exchange membrane fuel cells [8]. The cathode experiences flooding, leading to severe mass transport limitations and deactivation of catalytic sites on the cathode side, which suppresses the observed oxidation current. Also, at fixed ammonia concentrations, the current consistently increases with temperature, confirming Arrhenius-type diffusion behavior, i.e., crossover increases exponentially with temperature due to enhanced ammonia diffusivity through the membrane. This exacerbates cathode flooding, especially at higher fuel concentrations. As a result, the decline in measured current with increasing ammonia becomes steeper at higher temperatures, reflecting the compounding effect of thermal and chemical driving forces on crossover and its impact. These results underscore that although ammonia oxidation at the cathode is used here to detect crossover, higher fuel concentrations and temperatures worsen crossover-related flooding, leading to lower apparent currents, a crucial consideration for mitigating performance loss in these types of DAFC systems. The interplay between thermal enhancement of mass transport and NH₃ flooding increases cathode degradation, as confirmed by modeling, too, in recent studies [5]. A key insight emerges when comparing both trends together: At lower temperatures (40–50 °C), the drop in current from 0.1 to 2.0 M NH₃ is moderate (~5 mA at 1 V). At higher temperatures (60–70 °C), the same increase in NH₃ leads to a much steeper drop (~27–55 mA at 1 V). This illustrates a nonlinear amplification of crossover effects with temperature, where increased diffusivity magnifies cathode flooding and mass transport resistance. The membrane's selectivity deteriorates, leading to decreased performance with increasing fuel concentration, a crucial challenge for DAFC optimization. Based on these results, we selected operation at 60 °C as a compromise between extending membrane stability, moderating NH₃ cross-over, and enhancing the electrochemical reaction kinetics. Figure 11a–d shows the crossover currents corresponding to the voltage at different temperatures. Ammonia crossover was evaluated at 1.0 V, also by subtracting the 1 M KOH current from the current values with

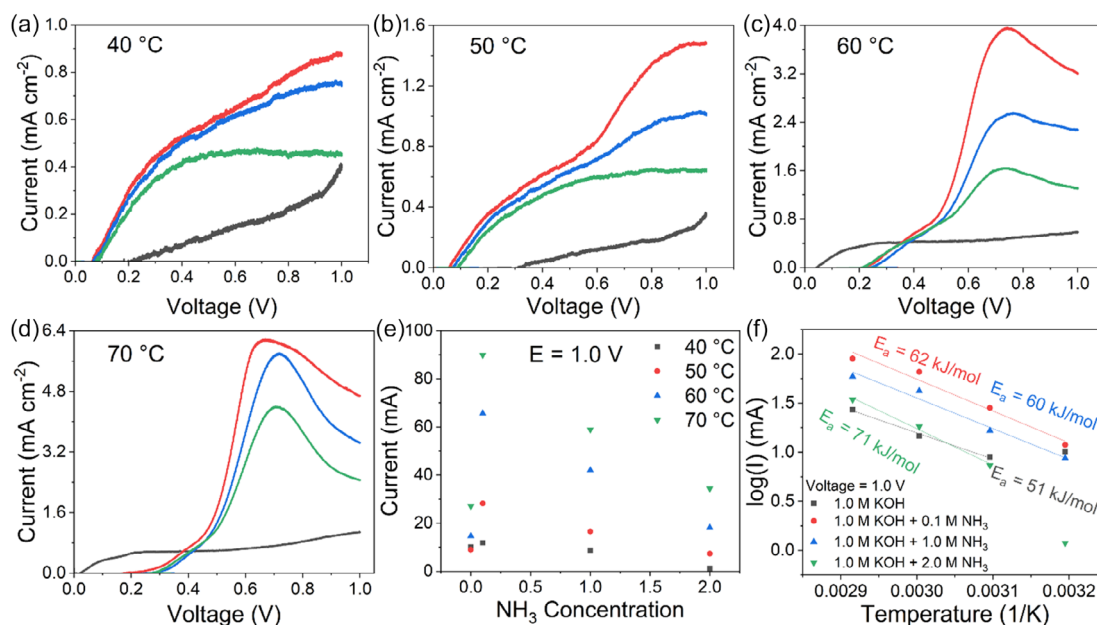


FIGURE 11 | (a–d) LSV results of ammonia crossover tests at different temperatures for different amounts of NH_3 added to the 1.0 M KOH electrolyte at the anode, (e) baseline-corrected ammonia crossover current at 1.0 V versus NH_3 concentration for 40 °C–70 °C, (f) Arrhenius plots at fixed NH_3 (0.1, 1.0, 2.0 M) and for 1.0 M KOH baseline. The DAFC was composed of a FAA-3-PK-130 (Fumasep) AEM and $\sim 0.3 \text{ mg/cm}^2$ Pt loading on 25 cm^2 nickel foam electrodes, both at the anode and cathode. The cathode was fed with 50 sccm N_2 at 1 bar and the anode with 25 mL/min of a mixture of 1.0 M KOH and varying amounts of NH_3 . Gray line: 1.0 M KOH, red line: 1.0 M KOH + 0.1 M NH_3 , blue line: 1.0 M KOH + 1 M NH_3 , green line: 1.0 M KOH + 2 M NH_3 .

NH_3 . Figure 11e,f show this subtracted current for the ammonia-containing feeds. Figure 11e shows the current behavior of the full cell at different temperatures and ammonia molarities. All the temperatures and molarities follow the same trend. Temperature increases the current across all concentrations. The crossover current peaks at 0.1 M NH_3 and then decreases with the increasing amount of ammonia. Figure 11f reveals the Arrhenius analysis results for the crossover at 51 kJ/mol (1.0 M KOH), 62 kJ/mol (0.1 M NH_3), 60 kJ/mol (1.0 M NH_3), and 71 kJ/mol (2.0 M NH_3). 0.1 M and 1.0 M NH_3 match the Arrhenius equation across the entire temperature range. For 1.0 M KOH and 2.0 M NH_3 , the 40 °C points deviate from linearity; excluding those single low temperature outliers tightens

linear fits without changing the qualitative trend (increasing E_a with NH_3 concentration beyond 1.0 M).

2.11 | DAFC Performance

The polarization curves from the beginning of test LSV-B1 and the variable load test (SPCP-C1) of a DAFC operated at 60 °C are presented in Figure 12a. The polarization curves of the individual electrodes extracted from SPCP-C1 test are presented in Figure 12b. Since the cell performance was stable with staircase polarization and LSV curves closely overlapping, the latter were used in the plots. Zero to negative (increasing

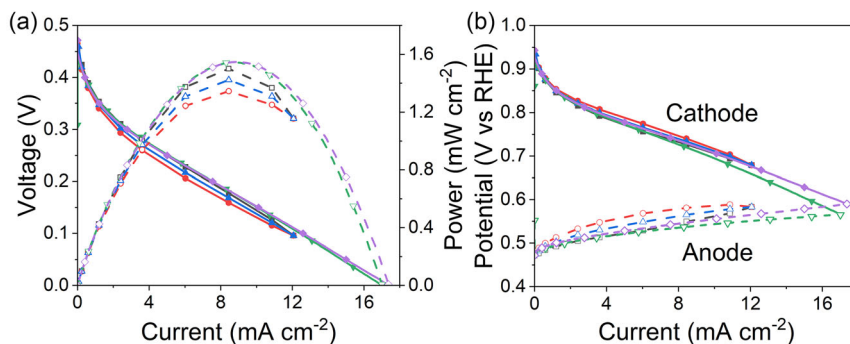


FIGURE 12 | (a) Polarization (full lines) and power (dashed lines) curves and (b) the corresponding potentials at the cathode (full lines) and anode (dashed lines). The data are derived from the beginning of test (LSV-B1: green lines with backward facing triangles), the variable load test (SPCP-C1: gray line with squares zero to negative scan, red line with circles: negative to zero scan, blue line with upright triangles: average) and the interim end of test (LSV-D1: purple line with diamonds). The DAFC comprised of a FAA-3-PK-130 (Fumasep) AEM and $\sim 0.3 \text{ mg/cm}^2$ Pt loading on 25 cm^2 nickel foam electrodes, both at the anode and cathode. The cell temperature was fixed to 60 °C. The cathode was fed with 50 sccm O_2 at 1.0 bar and the anode with 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH_3 .

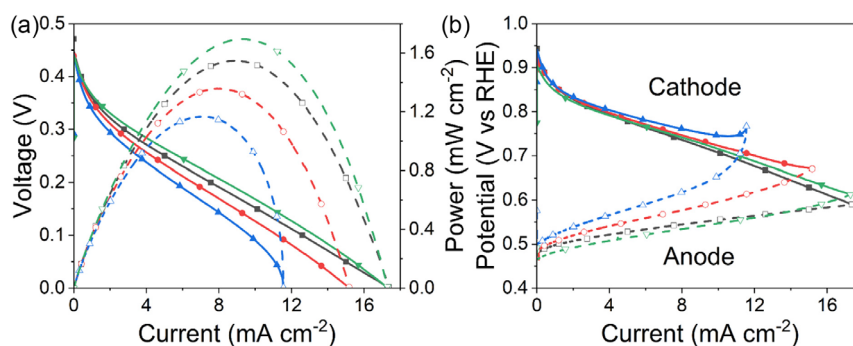


FIGURE 13 | (a) Polarization (full lines) and power (dashed lines) curves (a) and the corresponding potentials at the cathode (full lines) and anode (dashed lines), (b) for the performances after 6.5 h operation at -186 mA (LSV-E1), 9 h at open circuit (LSV-E2: blue line with upright squares) and refreshed fuel (LSV-E3: green line with inverted triangles). The curve from LSV-D1 (gray line with squares) from the EoT1 is included as a reference. The DAFC comprised of a FAA-3-PK-130 (Fumasep) AEM and ~ 0.3 mg/cm² Pt loading on 25 cm² nickel foam electrodes, both at the anode and cathode. The cell temperature was fixed to 60°C. The cathode was fed with 50 sccm O₂ at 1.0 bar and the anode with 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH₃.

current magnitude) and negative to zero (decreasing current magnitude) scan curves are shown in Figure S6, as well as evidence of the reproducibility of the method. The DAFC exhibited an initial OCV of ~ 0.48 V, consistent with reported values for Pt-based systems under similar alkaline conditions [4]. Furthermore, the cell voltage decreases rapidly with increasing current density primarily because of the poor AOR kinetics, leading to a premature limitation of the maximum current density to ~ 200 mA. A hysteresis effect is also evident, as for a given cell current, the voltage (and power) for curve representing the negative-going scan is higher than that of the positive-going scan. The hysteresis effect is especially strong in the region where Ohmic losses are expected to dominate, and is more severe in the anode curves. The staircase polarization curves (with ascending and descending branches) showed minimal hysteresis, indicating electrochemical stability under short-term cycling. However, LSV before and after staircase operation showed divergence, partially attributed to ammonia crossover, the migration of NH₃ across the membrane, and its oxidation at the cathode. This parasitic oxidation can alter cathode potentials and introduce variability in LSVs [5]. Experimental repeatability limitations further contribute to minor inconsistencies. Hysteresis in fuel cells has been attributed to membrane dehydration [35] or flooding of the cathode and/or the presence of intermediates adsorbed on the catalysts' surfaces [36]. Site poisoning, by NH₃ or its oxidation intermediates (e.g., N₂H₄, NO_x), which adsorb onto Pt catalyst sites, also hinders the electrochemical activity [37]. Platinum redox reactions have also been observed as the cause of hysteresis in methanol alkaline fuel cells [38]. Since our anode is fed with an electrolyte solution, we can exclude membrane dehydration, and considering the low activity of the AOR catalyst, the two other effects are more plausible.

The first endurance test consisted of a multistep variable load test campaign consisting of holding the cell at -186 mA (around maximum power point) for 6.5 h (CP-E1), followed by PEIS-E1 and LSV-E1, and then a 9 h hold at open circuit (OCV-E1) and a second measurement step, PEIS-E2 and LSV-E2, and lastly LSV-E3 after refreshing the fuel and reheating the DAFC to 60°C. The polarization and power curves corresponding to the variable

load test campaign (E) are presented for the full cell in Figure 13a and for the individual electrodes in Figure 13b. The voltage gradually decreases as the cell operates through 6.5 h at constant high current, mainly because of depletion of ammonia in the recirculating electrolyte and because of poisoning of the Pt anode catalyst with N^{*} and related adsorption species [39, 40]. After that, a decrease in OCV was also observed following the nine-hour hold at open circuit, caused mainly by the loss of electrochemically active area on the cathode. Gradual accumulation of ammonia at the cathode via crossover through the membrane and of water across the membrane blocks active sites for ORR at the cathode catalyst surface. The above causes of performance loss are confirmed since the cell performance significantly recovered after refreshing the fuel and drying the surface of the cathode using a dry oxygen purge (LSV-E3). The steeper decline in potential after ~ 5 h of the galvanostatic test may be caused by a local pH shift near the catalyst surface due to the consumption of hydroxide ions or an accumulation of poisonous intermediates, or an irreversible degradation of the catalyst and/or membrane. Specifically, the reaction between aqueous ammonia and oxygen may form nitrous acid, nitrite ions, and/or nitrate ions, all of which are acidic species [41]. Hydroxyl radicals associated with the oxidation of NH₃ (aq) may attack the membrane, increasing the rate of crossover NH₃, but this effect is relatively weak because the OCV and the limiting current density recovered to BOT values after refreshing the electrolyte [42, 43].

We traced the time evolution of the potentials at the individual electrodes (presented in Figure 14a) to further understand the degradation phenomena occurring during the 6.5 h at constant current. The decline of the cell current follows the increase in overpotential for the anode with time, which was mainly caused by mass transport limitations arising from the depletion of the available NH₃ in the electrolyte.

Figure 14b–d shows the PEIS results at 0.2 V for the full cell, anode, and cathode sides in different stages of testing, respectively, and allows scrutiny of the related changes observed in the DAFC's polarization behavior. After 6.5 h at constant current, the charge transfer resistance increases while it is relatively

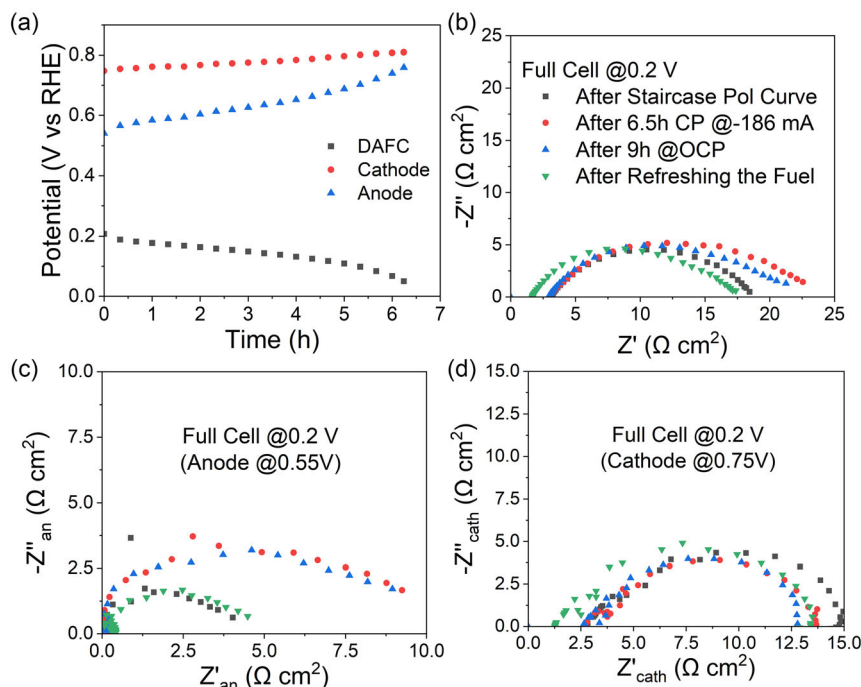


FIGURE 14 | (a) Cell voltage and electrode potential transient during 6.5 h with the cell held at -186 mA . (b) PEIS values @0.2 V of the cell, (c) the anode, and (d) the cathode. The PEIS data are derived from measurements after SPCP-C1 (PEIS-D1: black squares), CP-E1 (PEIS-E1: red circles), OCV-E1 (PEIS-E2: blue upright triangles) and refreshing the electrolyte (PEIS-E3: green inverted triangles). The DAFC comprised of a FAA-3-PK-130 (Fumasep) AEM and $\sim 0.3 \text{ mg/cm}^2$ Pt loading on 25 cm^2 nickel foam electrodes, both at the anode and cathode. The cell temperature was fixed to 60°C . The cathode was fed with 50 sccm O_2 at 1 bar and the anode with 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH_3 .

unchanged after the 9 h at open circuit. After refreshing the fuel, the high-frequency resistance (indicating AEM resistance) is reduced, and this difference can also be seen in the cathode side. However, the charge transfer is restored to its former value after staircase polarization curve, especially on the anode side, indicating that the decrease in performance was mostly due to limited concentration of ammonia at the catalyst surface by species that were removed by reducing the cathode potential. Additionally, the increase in the low-frequency resistance (LFR) of the full cell, caused by the constant current operation and the dwell at open circuit, was almost completely reversed after refreshing the fuel electrolyte. Inspection of Figure 14c reveals that the LFR variations happened on the anode indicating that a reversible process such as bubbles formed by gaseous products, such as N_2 , may have blocked the active sites on the AOR catalyst.

The corresponding Nyquist plots acquired for the full cell just before and after the staircase polarization step at 0.3, 0.2, and 0.1 V, as well as at -186 mA , are shown in Figure 15a. The Nyquist plots at 0.3, 0.2, and 0.1 V after the staircase polarization step are also presented in Figure 15 for the anode (b) and cathode (c).

The width of the arc for the full cell decreases with reducing voltage (increasing current density) from 0.3 to 0.2 V, then increases again for 0.1 V, matching the inflection points of the polarization curve near 0.3 and 0.1 V (Figure 13a). A similar trend can be seen for cathode, while the anode arc size constantly decreases with the decreasing voltage. This observation in the arc width change in EIS is consistent with what is often seen in low-temperature fuel cells, particularly PEMFCs [44, 45]. At intermediate voltages (e.g., 0.2 V) charge transfer kinetics

improve due to a higher driving force, reducing charge transfer resistance and thus shrinking the Nyquist arc. At low voltages (e.g., 0.1 V), the system enters a mass transport-limited regime, leading to increased impedance due to gas starvation or flooding, which increases the magnitude of the arc [46].

The products of the ammonia oxidation reaction (AOR) were directly monitored using an in-line JEOL mass spectrometer (MS). The DAFC was operated at 0.2 V under controlled conditions (60°C) to identify volatile gaseous products. Figure 16 shows the gas analyses of the DAFC operation at OCV and 0.2 V. At open-circuit voltage (OCV), only the carrier Ar signal was observed. Upon applying a cell voltage of 0.2 V, a distinct signal corresponding to N_2 ($m/z = 14, 28$) was detected. No evidence of N_2O , NO_2 , or other NO_x species was observed. The signal at $m/z = 16$ can be attributed to background H_2O rather than O_2 , as no primary signal at $m/z = 32$ was detected. These results demonstrate that AOR with supported Pt catalyst proceeds selectively to N_2 without the formation of NO_x intermediates. The faradaic efficiency for the NH_3 conversion to N_2 in DAFC is found to be 53%.

2.12 | Degradation Tests Using Static and Dynamic Current Load

We conducted a constant current degradation test and a current cycling degradation test for 10 h during which course the full cell voltage, and the anode and cathode potentials were continuously recorded. Figure 17a shows the voltage transient for the static current degradation test. A slight drop in the cell voltage was

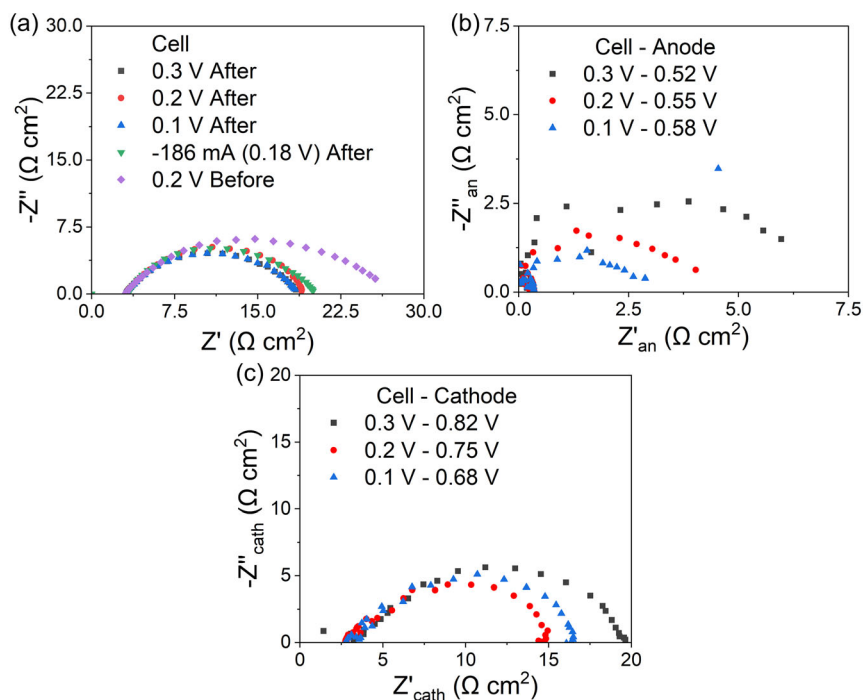


FIGURE 15 | Nyquist plots of the PEIS at various cell voltages of a DAFC with a FAA-3-PK-130 (Fumasep) and $\sim 0.3 \text{ mg/cm}^2$ Pt loading on 25 cm^2 nickel foam electrodes, taken before (only at 0.2 V) and after the staircase polarization step for the (a) full cell, (b) the anode, and (c) the cathode. (Note the different scales). The cell temperature was fixed to 60°C . Cathode flow rate: 50 sccm O_2 at 1 bar. Anode flow rate: 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH_3 . The squares, circles and upright triangles correspond to 0.3, 0.2, and 0.1 V, respectively, for PEIS-D1, the diamonds to GEIS-E1 and inverted triangles to PEIA-A1.

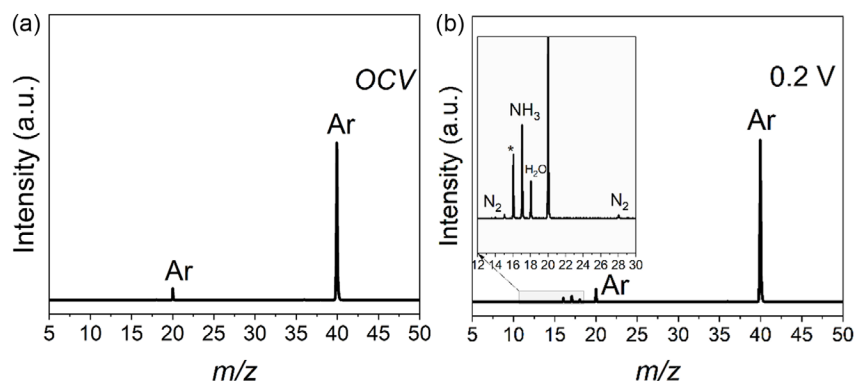


FIGURE 16 | Mass spectroscopy signal of the outlet gas of the anode of the DAFC operating at (a) open circuit voltage (OCV) and (b) 0.2 V.

observed over time, driven by the decay of anode potential. The cathode potential increased slightly in the first hour of the test and stabilized thereafter. The potential drop in the anode can be explained by the depletion of ammonia at the catalyst surface, based on the previous results of our cells, where refreshing the fuel recovered the DAFC's performance. Figure 17b shows the PEIS results of the full cell at 0.2 V before and after the static current degradation test. The charge transfer resistance increases from $618 \text{ m}\Omega$ by 17% over the course of 10 h. Figure 17c,d show the PEIS results of the anode and the cathode sides at 0.2 V, respectively. While the charge transfer resistance R_{CT} of the cathode side decreased from $480 \text{ m}\Omega$ by 4.6%, that at the anode side increased from $138 \text{ m}\Omega$ by 110%. Thus, the observed reduction in cell performance after static degradation is mainly attributed to reduced NH_3 concentration at the anode catalyst surface.

Because the change in the cathode is so small, it could be a measurement difference. Thus, there is no meaningful difference in the cathode before and after the test.

Examining the Bode plots in Figure S7 reveals that the imaginary part peaks of both electrodes in static current degradation (SCD) test are shifted to lower frequencies, but this could be simply due to the worse anode performance and the resulting lower driving force for the ORR at the cathode, as well as mass transport problems due to flooding in cathode. Assuming that the main change occurs at the anode and cathode, EIS only reflects the reduced driving force at constant voltage, the main difference in EIS between the dynamic and static tests is the larger increase in the impedance magnitude during the static tests, and the imaginary part peak is also shifted to slightly lower frequencies.

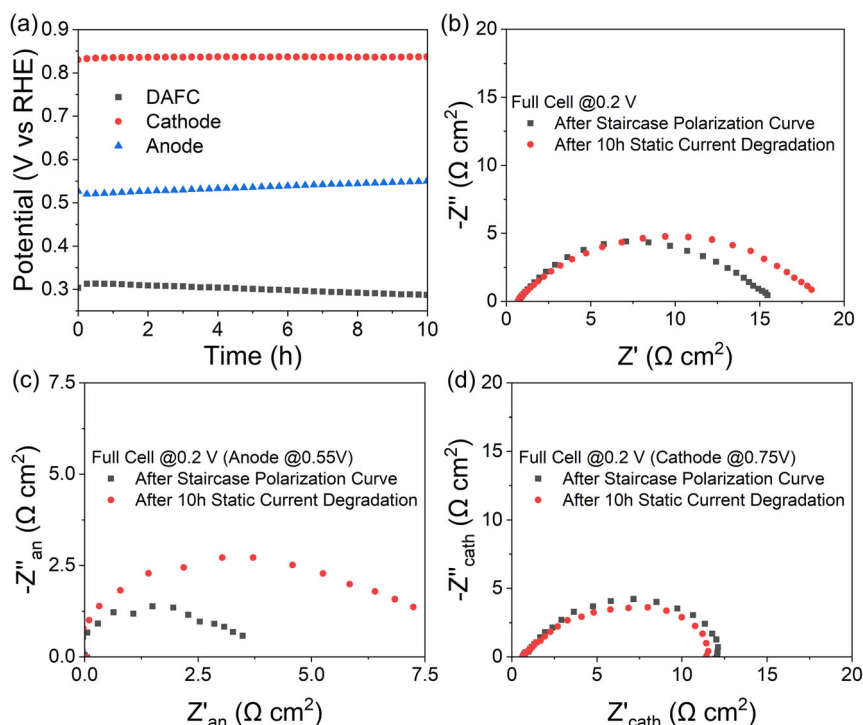


FIGURE 17 | (a) Cell voltage and electrode potential transients during the constant current degradation test (F), and PEIS results at 0.2 V before (PEIS-D1: squares) and after (PEIS-F1: circles) the static current degradation test (b) (CP-F1) for the full cell, (c) the anode, and (d) the cathode. The DAFC was composed of an AEM (FAA-3-PK-130, Fumasep) sandwiched between 25 cm² nickel foam electrodes. The nominal anode and cathode Pt loadings were both 0.3 mg/cm². Cathode flow rate: 50 sccm O₂ at 1 bar. Anode flow rate: 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH₃.

Figure 18a,b show the polarization curves before and after the dynamic stress test for the full cell and the electrodes, respectively. At the end of 10-hour cycling, the maximum cell current drops from 454 to 307 mA. A decrease in the maximum power is also observed from 37.8 to 26.3 mW, while voltage for the maximum power point shifted from 0.42 to 0.29 V (Figure 18a). The shift of the onset potential for the anode with a stable onset potential for the cathode in Figure 18b indicates that the decrease in the performance is caused by the ammonia depletion. Figure 18c,d show the voltage response during the dynamic degradation test of the full cell and the electrodes, respectively. The full cell exhibits 185.5 mV at the end of the first hour of applying the maximum current. However, this value decreases to 148.4 mV in the 10th hour of applying the maximum current, with a total decrease of 37.1 mV. At the same points, the cathode electrode exhibits 712.7 and 700.7 mV after the first and tenth hour, respectively, indicating a 12 mV decrease. Since the difference is very small, it can be a measurement error. Therefore, the cathode performance is stable, unlike the anode, whose response increases from 527.2 to 552.3 mV, indicating a 25.1 mV increase. These results support ammonia depletion as being the dominant mechanism for cell operation.

Figure 19 shows the Nyquist plots of the DAFC as well as those of the anode and cathode after different test steps in the dynamic current degradation test. Comparing the electrodes to each other, the cathode resistance is clearly higher than the anode resistance, but the changes at the anode are larger than at the cathode. Over the 10 h of the dynamic current degradation testing, the cathode resistance increases by about 120 m Ω , but this could be due to the more positive electrode potential and thus lower kinetic

overpotential and lower current density, as well as fuel build-up in the cathode. The voltage reduction is entirely due to the anode, as shown before, and matching this, the changes in anode impedance arch width are much larger than the possible change at cathode. The anode charge transfer resistance increases by about 100 m Ω .

2.13 | Estimation of DAFC Cell Efficiency

Table 1 shows the cell efficiency at different voltage values. The variation in electrical efficiency with operating current demonstrates a characteristic non-linear trend, which reflects the interplay between electrochemical kinetics, fuel utilization, and Ohmic losses and other losses during energy conversion. At higher cell voltages and lower current densities, the DAFC exhibits relatively low power output, resulting in modest efficiency despite limited ammonia consumption. As the current increases, power output rises more rapidly than the rate of ammonia consumption, leading to a peak in electrical efficiency of 42.7%, observed in this study at approximately 190 mA and 0.2 V. This region represents the optimal balance between reaction kinetics and fuel conversion, where the chemical energy of ammonia is most effectively transformed into electrical work. However, as the current continues to increase and the cell voltage drops further, efficiency declines sharply. This decrease is attributed to the disproportionate reduction in ammonia concentration at catalyst surface, as the higher current demand approaches the cell mass transport limitations, resulting in a plateau or even decline in the power output due to increased overpotentials. This behavior mirrors that of PEM fuel cells,

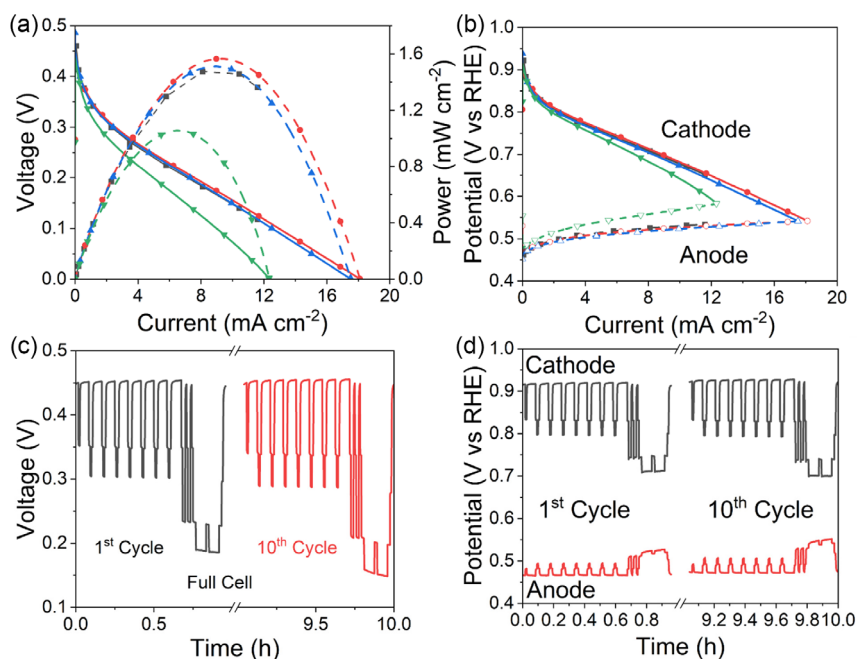


FIGURE 18 | (a) Polarization curves of the DAFC and (b) the electrodes before and after the dynamic current degradation test (red line: LSV-B1, gray line: average of SPCP-C1, blue line: LSV-D1, green line: LSV-G1 after 10 h dynamic stress test). (c) Cell voltage, and (d) electrode potential transients resulting from the dynamic current loading (VLC-G1). The DAFC was composed of an AEM (FAA-3-PK-130, Fumasep) sandwiched between 25 cm² nickel foam electrodes. The nominal anode and cathode Pt loadings were both 0.3 mg/cm². Cathode flow rate: 50 sccm O₂ at 1 bar. Anode flow rate: 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH₃.

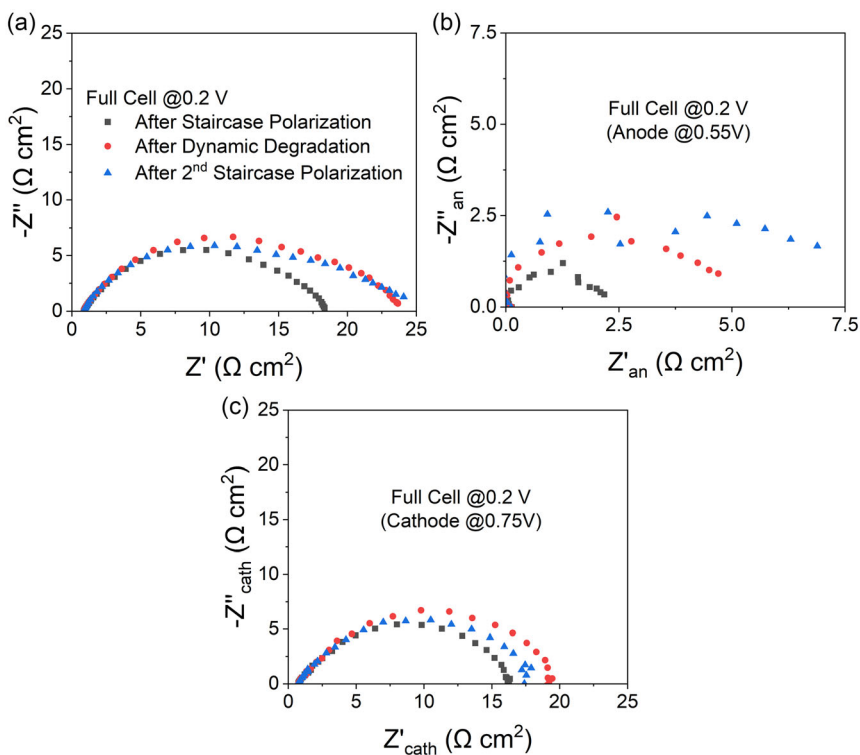


FIGURE 19 | (a) Nyquist plots of the PEIS at 0.2 V for DAFC, (b) anode, and (c) cathode, at different stages of the dynamic current degradation test (squares: PEIS-D1, circles: PEIS-G1 and triangles: PEIS-G2). DAFC with a FAA-3-PK-130 (Fumasep) and ~0.3 mg/cm² Pt loading on 25 cm² nickel foam electrodes, both at the anode and cathode. The cell temperature was fixed to 60°C. Cathode flow rate: 50 sccm O₂ at 1 bar. Anode flow rate: 25 mL/min of a mixture of 1.0 M KOH and 1.0 M NH₃.

TABLE 1 | Cell efficiency at different voltage values.

Condition	Cell voltage, mV	Current, mA	Power, mW	NH ₃ consumption, mmol/s	Efficiency, %
Max power point	173	222.0	38.4	0.286	35.6%
Moderate load	300	70.1	21.0	0.023	24.0%
Higher load, lower <i>V</i>	200	190.0	38.0	0.231	42.7%
High current, low <i>V</i>	100	316.8	31.7	0.451	18.4%

where efficiency peaks at intermediate loads due to favorable kinetics and then declines due to fuel mass transport limitations, catalyst layer flooding, or oxygen starvation at high currents [47, 48]. Additionally, higher ammonia crossover and parasitic losses at low voltages amplify the efficiency loss. These results underscore the importance of operating DAFCs within an intermediate load window to maximize fuel utilization and system efficiency. The electrical efficiencies observed in this study are in close agreement with previously reported performance metrics for AEM-based DAFCs [10, 49].

3 | Discussions

Initially, we achieved the highest power density using carbon-supported platinum catalysts; however, the operational stability was limited due to detachment of the platinum from the membrane, likely caused by ammonia-induced degradation of the Fumion ionomer. To improve stability, we transitioned to electrodeposition of catalysts directly onto nickel foam electrodes. This modification significantly improved catalyst adhesion and enabled extended testing durations, with some cells remaining operational for over 24 h. The DAFCs assembled for this study were based on a 25 cm² electrode area and employed aqueous 1.0 M NH₃ + 1.0 M KOH as the anode fuel under low-temperature conditions (60°C). Two distinct approaches for Pt electrodeposition were used, namely galvanostatic and pulsed potentiostatic deposition for the anode and cathode catalyst, respectively. The galvanostatic deposition (−30 mA/cm²) formed a finely dispersed Pt layer at the anode electrode optimized for the ammonia-oxidation reaction. In contrast, the pulsed potentiostatic deposition (−1.0 V, 5 ms/0.05 V, 10 ms) produced smoother, cluster-type structures tailored for oxygen reduction at the cathode. Our platinum catalyst loading (0.3 mg Pt/cm²) was substantially lower than those used in related studies—e.g., 2 mg PGM/cm² [50], and 0.45 mg Pt/cm² [10], the latter reporting a peak power density of 0.68 mW/cm² at 65°C. A comparison of studies is given in Table S9 [3, 8, 10, 40, 50–52].

Our tests show that the ammonia crossover from the anode through the FAA-3-PK-130 membrane to the cathode is non-trivial using commercially available AEMs. Moreover, NH₃ crossover significantly impacts DAFC performance, particularly at high NH₃ concentrations and elevated temperatures. While thermal activation boosts reaction kinetics, it also accelerates undesired NH₃ crossover, leading to cathode flooding, competition with the already sluggish ORR, and thus reduced effective current. These findings emphasize the necessity of optimizing both fuel concentration and temperature to mitigate crossover while maintaining performance. Membrane innovations or strategies

for cathode-side tolerance to ammonia mitigation are essential for DAFC advancement.

The reliability of both the performance tests and the DAFC configuration was proven for three nominally identical MEAs see Figure S6. Immediately after conditioning, the OCV was ca. 0.475 V—limited by NH₃ crossover for the polarization tests (LSV-B1 and SPCP-C1). For the voltage region just below OCV, the cathode potential is close to 0.8 V versus RHE in the region where Pt oxidizes or absorbs NO_x anions. A negative polarization scan gradually reduced adsorbed species coverage of Pt and the current increased. Since the series resistance of the cell is like that of other alkaline fuel cells, the slow kinetics dominated the performance of the DAFC over the current range investigated. The subsequent positive sweep of the staircase polarization increased adsorption of anion species on the Pt surface at the anode increasing its overpotential compared to the negative scan resulting in an overall lower cell voltage [53]. Holding the cell at a current close to the maximum value (CP-E1), polarized the cathode at a potential (ca. 0.78 V vs. RHE) just above the onset for Pt binding with anion adsorbing species. Meanwhile the anode was held above the onset potential for AOR (0.5 V vs. RHE at 60°C, Figure 10) and thus gaseous reaction products such as N₂ which has low solubility in water may accumulate at the surface of the catalyst. Another possible cause for the steeper decline in the cell voltage after ~6 h of the application of −186 mA, was a local shift pH near the anode catalyst surface by the consumption of hydroxide ions or an accumulation of poisonous intermediates. Specifically, the reaction between aqueous ammonia and oxygen may form nitrous acid, nitrite ions and/or nitrate ions, all of which are acidic species [41]. The net result of adsorption coverage at the cathode and anode as well as gas product accumulation at the anode, would lead to the gradual loss of cell voltage seen in Figure 14a. However, the EIS data taken at 0.2 V (Figure 14c,d) suggests that the gas production at the anode is the more dominant effect. The subsequent 9 h hold at open circuit maintained the cathode just above the potential onset for adsorption of anions. Moreover, the sustained crossover of NH₃ from the anode to the cathode at open circuit conditions also enhanced coverage of the catalyst with NO_x species. However, in the MS analysis we did not observe any harmful NO_x species in the anode outflow. The further gradual loss of active metallic Pt surface led to an additional loss of AOR activity at the anode when a current was allowed to flow again in the subsequent LSV test (LSV-E1). The sum of these effects manifested as the much-reduced performance after the open circuit spell. The EIS data taken at 0.2 V thereafter confirmed that the anode dominates the performance of the DAFC. The near complete recovery of the DAFC revealed by the performance test (LSV-E3) after refreshing the electrolyte supports our arguments for reversible phenomena suppressing the anode performance after prolonged operation

close to maximum power and holding at open circuit voltage. Other reports indicate that long dwell times at open circuit form radicals that may attack and damage the membrane [42, 43]. However, since the series resistance remained unchanged after tests and the DAFC performance almost completely recovered, this effect was minimal for our cell design.

Turning to the degradation tests, the 10 h current hold at -50 mA or ca. 25% of the maximum current resulted in a cathode potential well above the threshold for Pt oxidation while the anode was at a potential just above the onset potential for AOR. While the cathode potential remained relatively stable with time (Figure 17a) the anode overpotential gradually increased thus decaying the cell voltage. Additionally, a nontrivial reverse current (ca. 5 mA) also flowed across the membrane (see Figure 11) for these conditions. The subsequent EIS shows that the series resistance/HFR remained unchanged while the LFR increased, indicating that the DAFC performance was limited by the concentration of reactants. Thus, a likely reason for the reduced anode performance could be low concentration of NH_3 due to ammonia consumption.

The dynamic current, variation on the other hand, is more representative of real-world operation. The cell voltage and the electrode potentials follow the rises and dips in the applied current. However, at high currents, the cell voltage and the electrode potentials lagged the step current, even during the first cycle. We attribute this observation to the gradual coverage of the cathode by adsorbates requiring a higher overpotential to sustain the high set current level. As the cycling progressed, the cell voltage at maximum current reduced (Figure 18b), following an increase of the overpotential (Figure 18c) and increase in LFR (Figure 19a) at the anode, caused again by a drop in the local NH_3 concentration. The gradual decay of cell voltage at maximum voltage with time was likely caused by the depletion of the NH_3 content in the electrolyte by the DAFC consumption as the test progressed.

4 | Conclusions

This study presents a comprehensive performance and degradation analysis of low-temperature direct ammonia fuel cells (DAFCs) with a large electrode area (25 cm^2), using a newly developed electrochemical testing protocol. The direct ammonia fuel cells were constructed using in-house synthesized electrocatalysts and using commercially available components including a FAA-3-PK-130 (Fumasep) AEM. Specifically, the use of catalyst coated substrates led to relatively stable devices with reproducible behavior enabling multi-step sequential conditioning and tests which are necessary to understand the limitations of such devices. Electrochemical impedance spectroscopy and polarization analyses, combined with SEM, EDX, XRD and TEM characterization, revealed distinct catalyst morphologies resulting from constant current vs pulsed electrodeposition methods, influencing electrochemical performance.

We also developed and implemented a DAFC-specific electrochemical testing protocol adapted from PEMFC methodologies, incorporating constant current, open-circuit, and—for the first

time for DAFCs—dynamic current degradation tests. This protocol enabled performance benchmarking and durability assessment under realistic load profiles. The inclusion of a reference electrode allowed decoupled analysis of the anode and cathode behavior during cell operation, providing insight into the spatial origin of degradation. It was found that the cathode exhibited primarily reversible degradation, likely due to parasitic reactions involving ammonia crossover and reversible degradation from fuel starvation.

Ammonia crossover was shown to increase with both ammonia concentration and temperature, contributing to cathode flooding and decreased power output. Notably, the DAFCs demonstrated the ability to partially recover performance after refreshing the fuel, indicating that ammonia depletion and crossover are dominant contributors to short-term degradation. The electrical efficiency of the DAFC peaked at $\sim 42.7\%$ at an intermediate condition (0.2 V at 190 mA) and no harmful NO_x side products were detected in the anode outflow. The relatively low power densities observed in our work are attributable to conservative ammonia concentrations, relatively larger electrodes (25 cm^2) and moderate operational temperatures, the latter being currently unavoidable due to the lack of commercially available anion exchange membranes (AEMs) that can withstand these harsh conditions over extended periods. Nonetheless, these limitations provided valuable insight into degradation behavior and component-specific losses. In summary, this study not only identifies key performance-limiting phenomena in DAFCs, including poisoning by intermediates, membrane instability, sluggish kinetics, mass transport limitations, and catalyst detachment, but also successfully addresses the issue of catalyst adhesion through electrodeposition. The electrochemical testing protocol and degradation analysis framework developed here offers a critical foundation for future DAFC studies and paves the way for improved material and operational strategies aimed at commercial viability.

Acknowledgments

This research was mainly done under the TELEGRAM project which received funding from the European Union's Horizon 2020 Research and Innovation programme under grant agreement No. 101006941. The authors also acknowledge support from the German Federal Ministry of Research, Technology and Space in the framework of the project CatLab (03EW0015A/B). The authors acknowledge access to and use of transmission electron microscopy facilities (Talos F200i FEGSTEM) within the Loughborough Materials Characterisation Centre funded by the EPSRC grant EP/X030245/1.

Open Access funding enabled and organized by Projekt DEAL.

Funding

This study was supported by Horizon 2020 Framework Programme (101006941), CatLab (03EW0015A/B), EPSRC (EP/X030245/1).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

References

1. H. Shi, J. Tang, W. Yu, M. O. Tadé, and Z. Shao, "Advances in Power Generation from Ammonia via Electrocatalytic Oxidation in Direct Ammonia Fuel Cells," *Chemical Engineering Journal* 488 (2024): 150896.
2. W. Fu, Y. Zhou, J. Wu, K. Zhang, and X. Meng, "Flammability Limits of Ammonia in Air from 298 to 423 K at Elevated Pressures," *Energy & Fuels* 38, no. 11 (2024): 10168–10182.
3. T. Wang, Y. Zhao, B. P. Setzler, and Y. Yan, "Improving Performance and Durability of Low Temperature Direct Ammonia Fuel Cells: Effect of Backpressure and Oxygen Reduction Catalysts," *Journal of the Electrochemical Society* 168, no. 1 (2021): 014507.
4. R. Chen, S. Zheng, Y. Yao, et al., "Performance of Direct Ammonia Fuel Cell with PtIr/C, PtRu/C, and Pt/C as Anode Electrocatalysts under Mild Conditions," *International Journal of Hydrogen Energy* 46, no. 54 (2021): 27749–27757.
5. D. R. Dekel, K. Yassin, I. G. Rasin, and S. Brandon, "Modeling Direct Ammonia Anion-Exchange Membrane Fuel Cells," *Journal of Power Sources* 558 (2023): 232616.
6. Y. Liu, Z. Pan, O. C. Esan, X. Huo, X. Shi, and L. An, "Development and Performance Evaluation of a Passive Direct Ammonia Fuel Cell," *Journal of Power Sources* 570 (2023): 233057.
7. W. Li, Q. Wang, Y. Liu, et al., "Unravelling Degradation Mechanisms of Anion Exchange Membrane Direct Ammonia Fuel Cells via Distribution of Relaxation Times," *Chemical Engineering Journal* 512 (2025): 162204.
8. Y. Liu, Z. Pan, O. C. Esan, X. Xu, and L. An, "Performance Characteristics of a Direct Ammonia Fuel Cell with an Anion Exchange Membrane," *Energy & Fuels* 36, no. 21 (2022): 13203–13211.
9. R. Lan and S. Tao, "Direct Ammonia Alkaline Anion-Exchange Membrane Fuel Cells," *Electrochemical and Solid-State Letters* 13, no. 8 (2010): B83.
10. O. Siddiqui and I. Dincer, "Investigation of a New Anion Exchange Membrane-Based Direct Ammonia Fuel Cell System," *Fuel Cells* 18, no. 4 (2018): 379–388.
11. H. Kuhn, B. Andreus, A. Wokaun, and G. G. Scherer, "Electrochemical Impedance Spectroscopy Applied to Polymer Electrolyte Fuel Cells with a Pseudo Reference Electrode Arrangement," *Electrochimica Acta* 51, no. 8–9 (2006): 1622–1628.
12. D. Gerteisen, "Realising a Reference Electrode in a Polymer Electrolyte Fuel Cell by Laser Ablation," *Journal of Applied Electrochemistry* 37, no. 12 (2007): 1447–1454.
13. G. Hinds and E. Brightman, "In Situ Mapping of Electrode Potential in a PEM Fuel Cell," *Electrochemistry Communications* 17, no. 1 (2012): 26–29.
14. M. Kunimatsu, H. Qiao, and T. Okada, "Microtubular Hydrogen Electrode, a Reference Electrode for Electrochemical Analyses," *Journal of the Electrochemical Society* 152, no. 5 (2005): E161.
15. L. V. Böhre, M. Mourali, P. Trinke, et al., "Analysis of Kinetic and Ohmic Resistances in PEM Water Electrolysis through Reference Electrode Measurements," *Journal of the Electrochemical Society* 171, no. 5 (2024): 054518.
16. L. V. Böhre, B. Bensmann, and R. Hanke-Rauschenbach, "Review—Reference Electrodes in Proton Exchange Membrane Water Electrolysis: Previous Approaches, Current Application, and Perspectives," *Journal of the Electrochemical Society* 171, no. 5 (2024): 054519.
17. N. Fairley, V. Fernandez, M. Richard-Plouet, et al., "Systematic and Collaborative Approach to Problem Solving Using X-Ray Photoelectron Spectroscopy," *Applied Surface Science Advances* 5 (2021): 100112.
18. G. Tsotridis, A. Pilenga, G. Marco, and T. Malkow, "EU Harmonised Test Protocols for PEMFC MEA Testing in Single Cell Configuration for Automotive Applications," 27632 (2015).
19. FSEC's Procedures For Performing PEM Single Cell Testing: Test protocol for Cell Performance Tests, U.S. Department of Energy (2009).
20. Q. Xu, S. Z. Oener, G. Lindquist, H. Jiang, C. Li, and S. W. Boettcher, "Integrated Reference Electrodes in Anion-Exchange-Membrane Electrolyzers: Impact of Stainless-Steel Gas-Diffusion Layers and Internal Mechanical Pressure," *ACS Energy Letters* 6, no. 2 (2021): 305–312.
21. R. Zeng, R. C. T. Slade, and J. R. Varcoe, "An Experimental Study on the Reference Electrode Position in Alkaline Polymer Electrolyte Membrane Fuel Cells," *Electrochimica Acta* 56, no. 1 (2010): 607–619.
22. J. H. Ohs, U. Sauter, S. Maass, and D. Stolten, "The Effect of the Reference Electrode Position on the Measurement of Half Cell Polarization in Proton-Exchange Membrane Fuel Cells," *Journal of the Electrochemical Society* 159, no. 7 (2012): F181–F186.
23. J. Mitzel, E. Gülzow, A. Kabza, et al., "Identification of Critical Parameters for PEMFC Stack Performance Characterization and Control Strategies for Reliable and Comparable Stack Benchmarking," *International Journal of Hydrogen Energy* 41, no. 46 (2016): 21415–21426.
24. S. Kundu, M. Fowler, L. C. Simon, and R. Abouatallah, "Reversible and Irreversible Degradation in Fuel Cells during Open Circuit Voltage Durability Testing," *Journal of Power Sources* 182, no. 1 (2008): 254–258.
25. F. Wilhelm, et al., ID-FAST - Investigations on degradation mechanisms and Definition of protocols for PEM Fuel cells Accelerated Stress Testing, D4.3 – Analysis of coupling between mechanisms and definition of combined ASTs (2021), https://www.id-fast.eu/uploads/media/ID-FAST%7B%5C_%7DD4-3%7B%5C_%7DAnalysis%7B%5C_%7Dof%7B%5C_%7Dcoupling%7B%5C_%7Dbetween%7B%5C_%7Dmechanisms%7B%5C_%7Dand%7B%5C_%7Ddefinition%7B%5C_%7Dof%7B%5C_%7Dcombined%7B%5C_%7DASTs%7B%5C_%7DOK.pdf.
26. A. V. Kalinkin, M. Y. Smirnov, A. I. Nizovskii, and V. I. Bukhtiyarov, "X-Ray Photoelectron Spectra of Platinum Compounds Excited with Monochromatic AgL α Irradiation," *Journal of Electron Spectroscopy and Related Phenomena* 177, no. 1 (2010): 15–18.
27. Y. Niu, X. Teng, S. Gong, M. Xu, S. G. Sun, and Z. Chen, "Engineering Two-Phase Bifunctional Oxygen Electrocatalysts with Tunable and Synergetic Components for Flexible Zn–Air Batteries," *Nano-Micro Letters* 13 (2021): 1.
28. W. Zhou, H. Su, W. Cheng, et al., "Regulating the Scaling Relationship for High Catalytic Kinetics and Selectivity of the Oxygen Reduction Reaction," *Nature Communications* 13, no. 1 (2022): 1–10.
29. Y. Wang, Q. Wu, B. Zhang, L. Tian, K. Li, and X. Zhang, "Recent Advances in Transition Metal Carbide Electrocatalysts for Oxygen Evolution Reaction," *Catalysts* 10, no. 10 (2020): 1164.
30. A. C. A. De Voors, M. T. M. Koper, R. A. Van Santen, and J. A. R. Van Veen, "The Role of Adsorbates in the Electrochemical Oxidation of Ammonia on Noble and Transition Metal Electrodes," *Journal of Electroanalytical Chemistry* 506, no. 2 (2001): 127–137.
31. Z.-F. Li, Y. Wang, and G. G. Botte, "Revisiting the Electrochemical Oxidation of Ammonia on Carbon-Supported Metal Nanoparticle Catalysts," *Electrochimica Acta* 228 (2017): 351–360.
32. H. Gerischer and A. Mauerer, "Untersuchungen Zur Anodischen Oxidation Von Ammoniak an Platin-Elektroden," *Journal of Electroanalytical Chemistry and Interfacial Electrochemistry* 25, no. 3 (1970): 421–433.
33. V. Rosca and M. T. M. Koper, "Electrocatalytic Oxidation of Ammonia on Pt(111) and Pt(100) Surfaces," *Physical Chemistry Chemical Physics* 8, no. 21 (2006): 2513–2524.
34. J. A. Herron, P. Ferrin, and M. Mavrikakis, "Electrocatalytic Oxidation of Ammonia on Transition-Metal Surfaces: A First-Principles Study," *The Journal of Physical Chemistry C* 119, no. 26 (2015): 14692–14701.

35. D. Gerteisen, T. Heilmann, and C. Ziegler, "Modeling the Phenomena of Dehydration and Flooding of a Polymer Electrolyte Membrane Fuel Cell," *Journal of Power Sources* 187, no. 1 (2009): 165–181.
36. K. Otsuji, N. Yokota, D. A. Tryk, K. Kakinuma, K. Miyatake, and M. Uchida, "Performance Hysteresis Phenomena of Anion Exchange Membrane Fuel Cells Using an Fe–N–C Cathode Catalyst and an in-House-Developed Polymer Electrolyte," *Journal of Power Sources* 487 (2021): 229407.
37. D. K. Bora and A. Faik, "Direct Ammonia Fuel Cells for Power Generation: Recent Technological Advances and Mobility Applications," *Current Opinion in Green and Sustainable Chemistry* 48 (2024): 100944.
38. T. Haisch, F. Kubannek, L. Nikitina, et al., "The Origin of the Hysteresis in Cyclic Voltammetric Response of Alkaline Methanol Electrooxidation," *Physical Chemistry Chemical Physics* 22, no. 29 (2020): 16648–16654.
39. H. Y. Kim, J. Kim, E. Lee, et al., "Electrocatalyst Design Strategies towards High Performance Anion-Exchange Membrane-Based Direct Ammonia Fuel Cells," *Journal of Materials Chemistry A* 13, no. 9 (2025): 6176–6204.
40. S. Suzuki, H. Muroyama, T. Matsui, and K. Eguchi, "Fundamental Studies on Direct Ammonia Fuel Cell Employing Anion Exchange Membrane," *Journal of Power Sources* 208 (2012): 257–262.
41. D. K. Lee, "Mechanism and Kinetics of the Catalytic Oxidation of Aqueous Ammonia to Molecular Nitrogen," *Environmental Science & Technology* 37, no. 24 (2003): 5745–5749.
42. M. Inaba, T. Kinumoto, M. Kiriake, R. Umebayashi, A. Tasaka, and Z. Ogumi, "Gas Crossover and Membrane Degradation in Polymer Electrolyte Fuel Cells," *Electrochimica Acta* 51, no. 26 (2006): 5746–5753.
43. X. Song, C. Basheer, Y. Xia, and R. N. Zare, "Oxidation of Ammonia in Water Microdroplets Produces Nitrate and Molecular Hydrogen," *Environmental Science & Technology* 58, no. 36 (2024): 16196–16203.
44. H. Yuan, H. Dai, X. Wei, and P. Ming, "Internal Polarization Process Revelation of Electrochemical Impedance Spectroscopy of Proton Exchange Membrane Fuel Cell by an Impedance Dimension Model and Distribution of Relaxation Times," *Chemical Engineering Journal* 418 (2021): 129358.
45. L. Zhao, H. Dai, F. Pei, P. Ming, X. Wei, and J. Zhou, "A Comparative Study of Equivalent Circuit Models for Electro-Chemical Impedance Spectroscopy Analysis of Proton Exchange Membrane Fuel Cells," *Energies* 15, no. 1 (2022): 386.
46. S. Latorrata, R. Pelosato, P. G. Stampino, C. Cristiani, and G. Dotelli, "Use of Electrochemical Impedance Spectroscopy for the Evaluation of Performance of PEM Fuel Cells Based on Carbon Cloth Gas Diffusion Electrodes," *Journal of Spectroscopy* 2018 (2018): 1–13.
47. E. B., and H. R. "Mass Transport Limitations in Proton Exchange Membrane Fuel Cells and Electrolyzers," *Mass Transfer - Advanced Aspects InTech*, Jul. 07, 2011, <https://doi.org/10.5772/20349>.
48. A. Kazim, Determination of an Optimum Performance of a PEM Fuel Cell Based on Its Limiting Current Density, 2004, 159–166.
49. O. Siddiqui and I. Dincer, "Development and Performance Evaluation of a Direct Ammonia Fuel Cell Stack," *Chemical Engineering Science* 200 (2019): 285–293.
50. Y. Zhao, B. P. Setzler, J. Wang, et al., "An Efficient Direct Ammonia Fuel Cell for Affordable Carbon-Neutral Transportation," *Joule* 3, no. 10 (2019): 2472–2484.
51. M. Liu, K. Geng, Y. Huang, et al., "A High Performance Ion-Solvating Membrane-Type Direct Ammonia Fuel Cell," *Journal of Membrane Science* 692 (2024): 122222.

52. Y. Zhao, T. Wang, B. P. Setzler, R. Abbasi, J. Wang, and Y. Yan, "A High-Performance Gas-Fed Direct Ammonia Hydroxide Exchange Membrane Fuel Cell," *ACS Energy Letters* 6, no. 5 (2021): 1996–2002.

53. H. Kim, W. Yang, W. H. Lee, et al., "Operando Stability of Platinum Electrocatalysts in Ammonia Oxidation Reactions," *ACS Catalysis* 10, no. 19 (2020): 11674–11684.

Supporting Information

Additional supporting information can be found online in the Supporting Information section.