

PAPER

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Identification and understanding of activation procedures critical for nickel-based anodes in anion-exchange membrane fuel cells

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Anion-exchange membrane fuel cells (AEMFCs) hold promise as high-performance devices free of platinum group metals. A major bottleneck to achieve this goal is the moderate performance of nickel-based anodes. Metallic nickel is critical for hydrogen binding, which is essential for the electrocatalysis of the hydrogen oxidation reaction (HOR), but is prone to passivation. Here, we show that for representative mainstream Ni-based catalysts, their spontaneous passivation in ambient air blocks the HOR, necessitating activation protocols. In a three-electrode rotating-disk electrode setup, activation is readily accomplished by lowering the electrode potential. In an AEMFC, galvanostatic and chemical activation strategies are explored, revealing the strong influence of O₂ crossover from the cathode, which can repassivate Ni. Chemical activation involving an initial H₂/N₂ feed at the anode/cathode proved to be the most practical, enabling a high open-circuit voltage, power density and stability in subsequent H₂/O₂ and H₂/air AEMFC measurements. A chemically activated Ni@NC anode paired with a Pt/C cathode achieved an outstanding AEMFC peak power density of 1.2 W cm⁻² using H₂/O₂ as feed and an unprecedented peak power density of 0.5 W cm⁻² using H₂/air (ambient) as feed.

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Broader context

Sustainable and cost-effective fuel cells are essential for deploying hydrogen technologies. Anion-exchange membrane fuel cells (AEMFCs) have strong potential to meet these objectives using catalysts comprising earth-abundant metals. Nanostructured nickel catalysts have demonstrated high hydrogen oxidation reaction (HOR) activity. However, low AEMFC peak power densities have hitherto been attained by nickel-based anodes. Although the propensity of metallic nickel to oxidize and its negative effect on HOR activity have been recognized, implications for the integration of nickel-based anodes in AEMFCs have not yet been thoroughly studied. This work demonstrates that the surfaces of the three mainstream nickel-based HOR catalysts considered in this study are initially passivated, fully blocking the HOR, both in aqueous alkaline electrolyte and in the AEMFC. An appropriate activation procedure is therefore required, which

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depends on the thickness of the nickel oxide layer. Moreover, in the AEMFC, O₂ crossover through the AEM was shown to be sufficient to define an oxidizing environment for passivated nickel. Chemical activation involving an initial H₂/N₂ feed at the anode/cathode in the AEMFC proved most practical, enabling high power density and stability in subsequent H₂/O₂ and H₂/air AEMFC measurements. The importance and understanding of the activation procedure for nickel-based anodes along with the identification of O₂ crossover as an important and nickel-specific parameter provide guidance for the integration of Ni-based HOR catalysts in AEMFC stacks.

Introduction

Proton-exchange membrane fuel cells are suitable for mobility and transportation applications¹ but necessitate the use of Pt-based catalysts for both the oxygen reduction reaction (ORR) and hydrogen oxidation reaction (HOR), hampering their large-scale deployment.^{2,3} Anion-exchange membrane fuel cells (AEMFCs) facilitate the introduction of platinum-group-metal-free (PGM-free) catalysts,⁴ and peak power densities of 1.8–2.0 W cm^{−2} have been achieved with PGM-free cathodes (paired with PGM anodes).^{5–7} Comparatively, lower peak power densities of 0.7–0.8 W cm^{−2} have been achieved with PGM-free anodes (paired with PGM cathodes).^{8,9} Due to the balanced hydrogen binding energy of metallic nickel (Ni), PGM-free HOR catalysts for alkaline media typically involve Ni.¹⁰ Nonetheless, metallic Ni readily passivates upon exposure to molecular oxygen,^{11,12} blocking the HOR. In a three-electrode setup, the reference electrode allows the application of a low electrochemical potential, which activates the Ni-based layers.¹³ However, such an activation approach is challenging for AEMFCs that lack a reference electrode. Surprisingly, neither the need for activation nor the applied protocol has been mentioned in any studies on AEMFCs comprising Ni-based anodes since 2013, including very recent works,^{8,9} with the exception of a study in 2026 by Abruña and co-workers.¹⁴ In contrast, the activation issue was clearly stated in two early works in 2008 and 2013.^{15,16} Li *et al.* recently addressed the passivation issue by protecting an Ni-based catalyst from oxidation at every step, including synthesis, storage, anode preparation and AEMFC assembly.¹⁴ Overall, the activation protocols necessary for Ni-based anodes in AEMFCs remain under-investigated and insufficiently reported, preventing the reproducible and optimized implementation of various Ni-based catalysts.

Here, considering three mainstream HOR Ni-based catalysts, it is established that an activation procedure is required for them, both in a rotating-disk electrode (RDE) setup and in an AEMFC, without which no activity is observed. In the AEMFC, Ni-electrode activation can be achieved either electrochemically by imposing a reduction current or chemically under open-circuit conditions by feeding H₂ at the anode and N₂ at the cathode. The step number or duration needed for activation varies with the thickness of the native Ni-oxide layer of each catalyst. We also reveal the competition between the reducing conditions needed to activate Ni and O₂ diffusion across the anion exchange membrane (AEM). Once activated, Ni-based anodes achieve high performance and operate stably in the AEMFC. This understanding will help reproducibly implement Ni-based catalysts in AEMFCs and design strategies that mitigate Ni passivation before or during fuel cell operation.

Results and discussion

Physico-chemical characterization of the materials

Three catalysts were synthesized, which are representative of three mainstream Ni-core@carbon-shell, Ni nitride, and NiMo-alloy sub-classes of Ni-based catalysts (see Methods), and they were labelled Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. The Ni@NC particles are not supported on carbon, Ni₃N particles are supported on a commercial micro-mesoporous carbon black support (Vulcan carbon, VC), while NiMo particles are supported on an in-house mesoporous N-doped carbon (MPNC) (see Methods). These catalysts with various Ni nanostructures, chemistries and pore size distributions of the carbon supports were chosen to illustrate and investigate the general activation issue of Ni-based catalysts with respect to the HOR. X-ray diffraction (XRD) identifies metallic fcc Ni in Ni@NC and NiMo/MPNC, and the Ni₃N (111) peak at 44.4° in Ni₃N/VC (Fig. 1a). The average sizes of the Ni crystallites are 15.8, 3.3, and 13.2 nm for Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively, as derived from Scherrer's equation applied to the (111) peak. However, the other diffraction peaks of Ni₃N hcp are not observed in the diffractogram of Ni₃N/VC, possibly due to the high disorder and/or small crystallite size. In contrast, a broad and weak signal is observed at 37.0°, which may be assigned to NiO (111). The broad peak at *ca.* 44° assigned mainly to Ni₃N (111) (expected at 44.4°) may, however, also comprise a contribution from NiO (200), expected at 43.0°. Overall, the XRD pattern of Ni₃N/VC suggests the coexistence of the Ni₃N and NiO phases. The catalysts were also characterised using Ni K-edge X-ray absorption spectroscopy. The X-ray absorption near-edge structure (XANES) and Fourier-transformed (FT) extended X-ray absorption fine structure (EXAFS) spectra of Ni@NC and NiMo/MPNC closely resemble those of a reference metallic Ni foil (Fig. S1) although the more intense white line and lower pre-edge intensity (*e.g.* at 8335 eV) in the XANES spectrum of NiMo/MPNC *vs.* Ni@NC reveal the minor presence of oxidized Ni in NiMo/MPNC. The XANES spectrum of Ni₃N/VC exhibits a substantial white-line and low pre-edge intensity, more closely resembling the XANES of NiO (Fig. S1a). Moreover, the FT-EXAFS spectrum is in line with the coexistence of Ni₃N and NiO. The peak at 2.30 Å can be attributed to the Ni–Ni back-scattering signal from the Ni₃N structure, while the peaks at *ca.* 1.5 and *ca.* 2.6 Å can be attributed to the Ni–O and Ni–Ni signals, respectively, from the NiO structure.¹⁷ X-ray photoelectron spectroscopy (XPS) reveals that Ni(II) species co-exist with zerovalent Ni, most notably in NiMo/MPNC and Ni₃N/VC, which are attributed to spontaneous passivation in ambient air (Fig. 1b). The Ni²⁺_a and Ni²⁺_b components correspond to the main peaks of the NiO and Ni(OH)₂ species, respectively.¹⁸

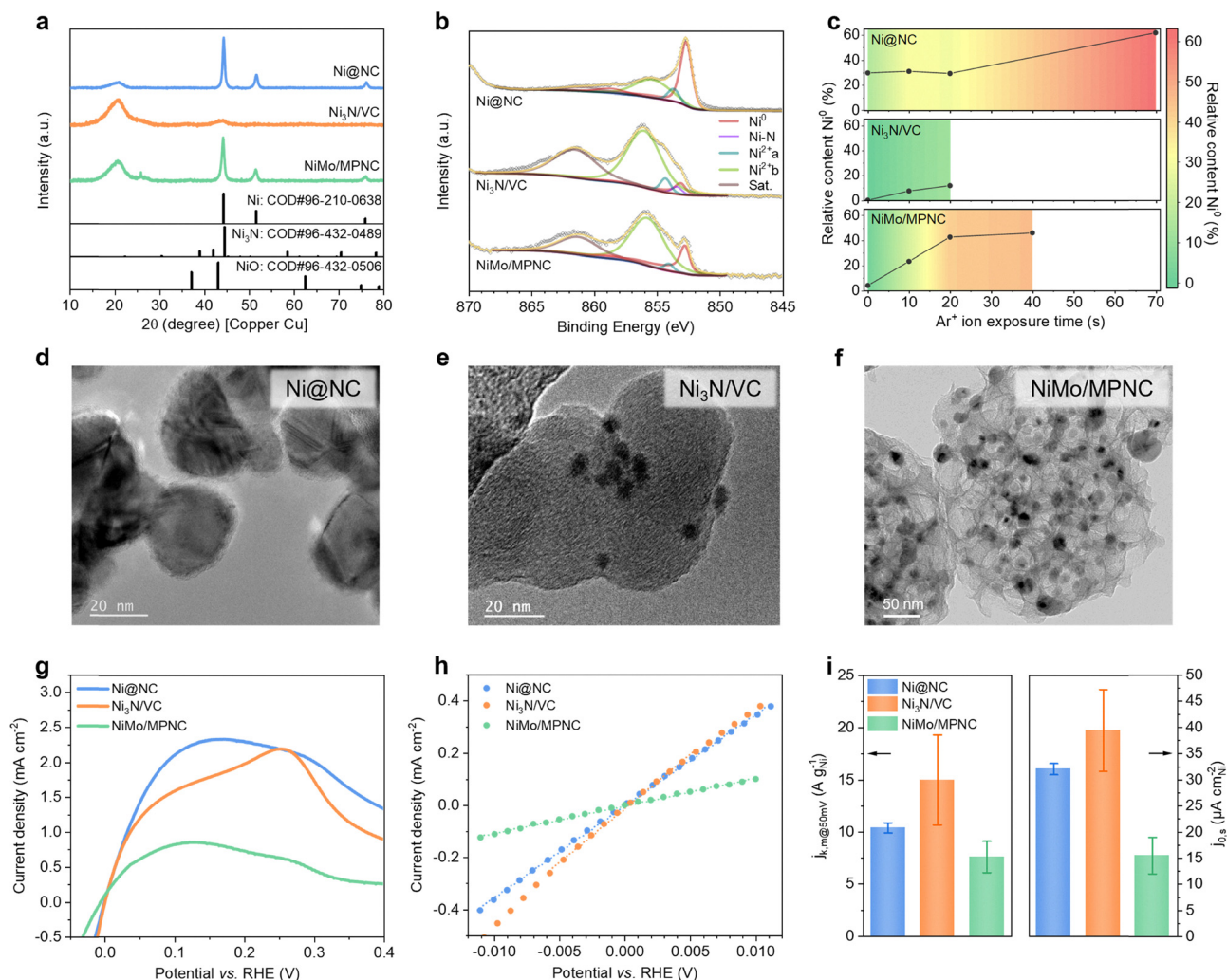


Fig. 1 Structural and electrochemical characterization of Ni@NC, Ni₃N/VC and NiMo/MPNC. (a) XRD patterns; (b) Ni_{2p} narrow scan XPS spectra; (c) depth-resolved XPS analysis of the Ni 2p_{3/2} spectra showing the evolution of Ni species as a function of Ar⁺ sputtering time; (d and e) HRTEM micrographs of Ni@NC and Ni₃N/VC, respectively; (f) STEM micrograph of NiMo/MPNC; (g) RDE HOR polarization curves measured in a positive-going scan in H₂-saturated 0.1 M KOH at 1600 rpm; (h) micropolarization region used to assess the exchange current density, with the linear fit represented as a dotted line; and (i) HOR kinetic current density at 50 mV vs. RHE normalized by Ni loading, $j_{k,m@50mV}$, and exchange current density normalized by the Ni ECSA, $j_{0,s}$. RDE measurements (g–i) were performed at room temperature at a scan rate of 5 mV s^{−1} and a catalyst loading of 0.3 mg_{catalyst} cm^{−2}, and the reported data were measured in the 6th cycle (Fig. S11), after 20 activation cycles over a broader potential range and with fast scan (see Methods). The polarization curves (g and h) are corrected for the iR-drop. The error bar in (i) represents the standard deviation upon repeats from three catalytic layers of the same catalyst's ink. For XRD patterns (a), diffraction peaks of NiMo/MPNC are negatively shifted by 0.12–0.15° vs. Ni@NC, evidencing an NiMo alloy. For XPS spectra (b), Ni²⁺_a can be attributed predominantly to NiO, and Ni²⁺_b predominantly to Ni(OH)₂ contribution. For XPS depth-profiling measurements (c), Ni 2p_{3/2} spectra were recorded before and after exposure to an Ar⁺ ion beam. The total sputtering time was tuned for each catalyst as a function of the measured Ni particle size.

The elemental composition of Ni and N species were quantified using XPS (Fig. S2 and Tables S1–S6). The proportions of zerovalent Ni to total Ni in the as-synthesized catalysts are 45.6, 6.2, and 17.7% for Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively (Table S5). XPS depth-profiling measurements of each catalyst demonstrate the preferential surface location of Ni (hydr)oxides (Fig. S3–S5). For each catalyst, the relative amount of Ni⁰ increases with the sputtering time (proportional to the probed depth) (Fig. 1c). Moreover, the detailed analysis of the Ni²⁺ components supports the previously proposed Ni/NiO/Ni(OH)₂ bilayer-oxide structure (Fig. S6 and Note S1).¹⁹

The average size and standard deviation of the Ni particles are 28.1 ± 5.0 , 5.8 ± 1.0 , and 15.8 ± 3.3 nm for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively, as determined from HRTEM micrographs (Fig. 1d–f and Fig. S7–S10). For Ni@NC, a nanometric carbon shell surrounding the Ni particles is observed, demonstrating the core@shell structure (Fig. 1d and Fig. S7).

Electrochemical activity

The HOR activity was evaluated in H₂-saturated 0.1 M KOH using a three-electrode RDE setup, keeping the total catalyst loading at 0.3 mg_{catalyst} cm^{−2}. Due to the different Ni contents

(Table S7), the Ni loadings were 231, 112, and 84 $\mu\text{g}_{\text{Ni}} \text{cm}^{-2}$ for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. The catalytic layers were first activated by 20 cycles of cyclic voltammetry (CV) from -0.050 to 0.300 V vs. RHE at 50 mV s^{-1} , followed by CVs at 5 mV s^{-1} for HOR activity assessment. The lower apparent HOR activity of NiMo/MPNC (Fig. 1g and h) is primarily attributed to its lower Ni loading. For all the catalysts, the current density never reaches the expected diffusion-limited value of 3.3 mA cm^{-2} (Note S2) and starts decreasing above a certain potential assigned to excessive passivation. The peak/shoulder at *ca.* 0.250 V vs. RHE observed for all catalysts (with different amplitudes) is consistent with the reversible oxidation of metallic Ni into $\alpha\text{-Ni(OH)}_2^{20}$ (Fig. S11). The mass activity was quantified using $j_{k,m@50\text{mV}}$, the kinetic current density at 0.050 V vs. RHE normalized by the Ni mass (Note S2). This potential was selected in accordance with the literature. The values of $j_{k,m@50\text{mV}}$ are 10.4 ± 0.5 , 15.0 ± 4.3 , and $7.6 \pm 1.8 \text{ A g}_{\text{Ni}}^{-1}$ for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively (Fig. 1i and Table S8), in line with the literature.^{21,22} The HOR mass activity was also quantified at 0.02 V vs. RHE ($j_{k,m@20\text{mV}}$) following the same method. The values of $j_{k,m@20\text{mV}}$ are 3.5 ± 0.1 , 6.5 ± 1.6 , and $3.6 \pm 0.7 \text{ A g}_{\text{Ni}}^{-1}$ for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. Ni₃N/VC is the most active HOR catalyst at both potentials. The slight relative activity changes of Ni@NC and NiMo/MPNC may be attributed to their different

sensitivities to passivation as a function of potential. The intrinsic specific activity was additionally quantified using $j_{0,s}$, the exchange current density normalized by the Ni electrochemical surface area (ECSA) (Note S3). The values of $j_{0,s}$ are 32.1 ± 1.1 , 39.5 ± 7.8 , and $15.6 \pm 3.5 \mu\text{A cm}_{\text{Ni}}^{-2}$ for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively, following the same order as the mass activity at 0.05 V vs. RHE (Fig. 1i and Table S8) or at 0.02 V vs. RHE. These values are also in line with the literature.^{21,22}

Evidence for the need for an activation step in the AEMFC and RDE

Although there was seemingly no issue with testing the Ni materials for HOR activity in RDE, these materials implemented at the anode of an AEMFC (paired with a Pt/C cathode) resulted in a low open-circuit voltage (OCV, $\text{OCV} = \text{OCP}_{\text{cathode}} - \text{OCP}_{\text{anode}}$) of *ca.* 0.2 V after 15 min of H₂/O₂ feed at 60°C (Fig. 2a). The cell itself worked properly, as the PtRu/C anode and Pt/C cathode assembly quickly reached an OCV of 1.030 V (Fig. 2a). It can be inferred that $\text{OCP}_{\text{cathode}}$ is *ca.* 1.030 V vs. RHE, implying that $\text{OCP}_{\text{anode}}$ of the Ni-based anodes is 0.830 – 0.900 V vs. RHE. Similarly, high OCP values of 0.720 – 0.890 V vs. RHE were measured for the Ni layers before any activation at room temperature in H₂-saturated 0.1 M KOH in RDE (Fig. 2b). This is consistent with the presence of a passivated Ni surface

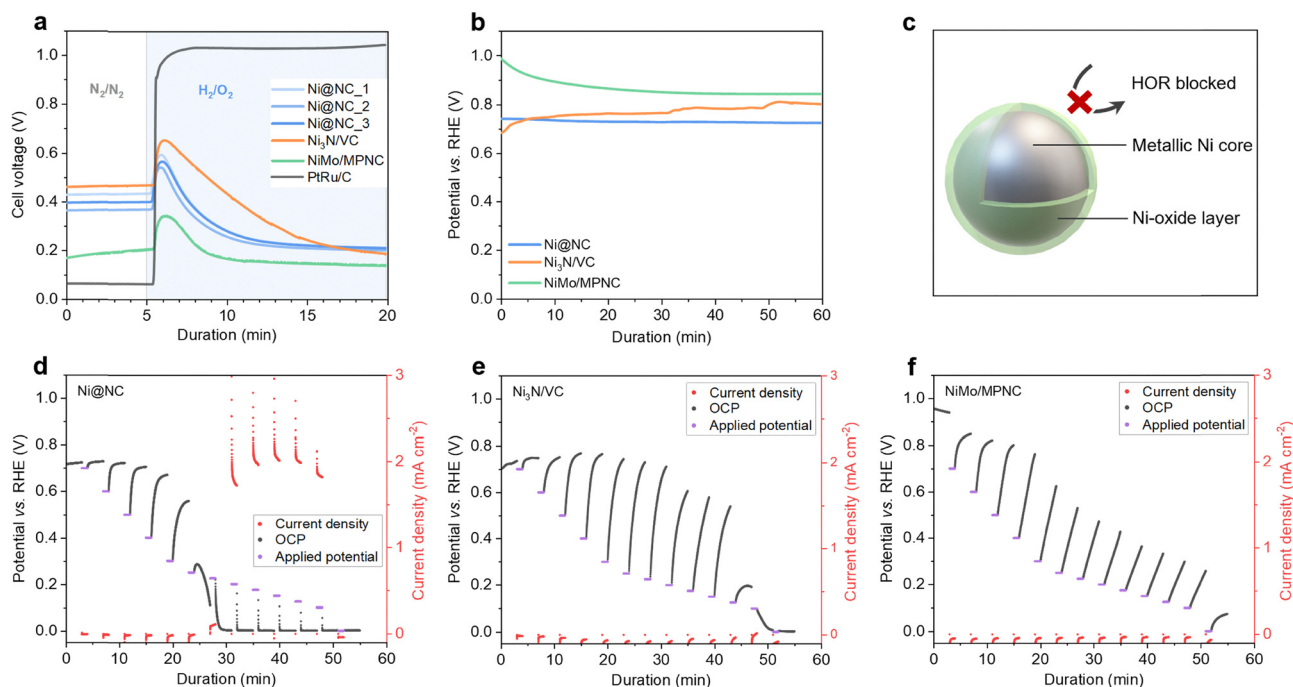


Fig. 2 Activation issues of Ni-based catalysts in AEMFC and RDE setups and identification of a potentiostatic activation protocol for the RDE setup. (a) OCV of single-cell AEMFC comprising a Pt/C cathode paired either with a PtRu/C or an Ni-based anode, (b) OCP of the Ni-layers in RDE measured in 0.1 M KOH saturated with H₂ (solid curves), (c) scheme of the passivating Ni (hydr)oxide layer on the surface of metallic Ni nanoparticles, and (d–f) sequence of consecutive potential steps (purple dots)/OCP measurements (black dots) of 1 min/3 min, each applied to reduce the Ni surface and the response in current density (red dots) for Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively. The sequence was measured at RT in a H₂-saturated 0.1 M KOH electrolyte with the working electrode rotating at 1600 rpm . The potential was lowered in steps of -100 mV down to 0.3 V vs. RHE, then at 50 mV steps to 0.25 V vs. RHE, and finally at 25 mV steps to 0 V vs. RHE. The total catalyst loading is $0.3 \text{ mg}_{\text{catalyst}} \text{cm}^{-2}$. For (a), AEMFC OCV measurements were performed at 60°C cell temperature with gases humidified at 60°C , flow rates of 0.3 L min^{-1} and a back pressure of 100 kPa . The cathode is Pt/C ($0.2 \text{ mg}_{\text{Pt}} \text{cm}^{-2}$); the anode loadings were 6.8 , 6.4 and $4.4 \text{ mg}_{\text{catalyst}} \text{cm}^{-2}$ for Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively. The AEM is Versogen PiperION™ ($20 \mu\text{m}$ thick). For (d–f) the data are corrected for the iR -drop.

that initially blocked the HOR (Fig. 2c). This explains why 20 fast CVs from -0.050 to 0.300 V vs. RHE were applied before the HOR activity measurement in the RDE setup.

Potentiostatic activation in RDE

To investigate in more detail the activation process in 0.1 M KOH, the electrochemical potential of the Ni layers decreased stepwise from the initial high OCP down to 0.0 V vs. RHE while rotating the electrode. Each potential step lasted for 1 min (purple stairs in Fig. 2d–f), followed by 3 min of OCP to gain insights into the changes in the surface state (black curves in Fig. 2d–f). The current density measured during each potential step served as a marker of the HOR activity (red curves in Fig. 2d–f). For Ni@NC, the OCP spontaneously returns to high values after each of the first five potential steps (Fig. 2d), and the current density during these steps remains close to zero, indicating an insignificant HOR current. The activation starts at 0.225 V vs. RHE and seems complete during the next step at 0.200 V vs. RHE, as evidenced by the high positive current density. For Ni₃N/VC, the activation is complete during the potential step at 0.100 V vs. RHE, as demonstrated by the OCP reaching 0.0 V vs. RHE after this step. Last, NiMo/MPNC starts activating only during the potential step at 0.0 V vs. RHE. After this step, the OCP value reaches 0.070 V vs. RHE, suggesting that another potential step is needed for complete activation.

In summary, Ni layers need an activation procedure in RDE, which can be achieved by a controlled electrochemical potential. In AEMFC, however, such activation is challenging due to the usual lack of a reference electrode.

Galvanostatic activation in the AEMFC

As an alternative to potentiostatic activation, an Ni electrode can be activated by applying a reduction current, provided that the current mainly corresponds to Ni (hydr)oxide reduction. Importantly, the counter-electrode is forced to create an oxidation current, and its potential increases. AEMFC measurements in this subsection and in the next one were therefore performed with stainless steel flow-field plates in order to avoid carbon corrosion. The galvanostatic activation procedure consisted of alternating galvanostatic control and OCV measurements of 1 min each, starting with a low current of 1 mA, and incrementing it by 1 mA after each OCV measurement. The stepped increase in current aimed to gain a detailed understanding of the activation phenomenon. Because the AEMFC was continuously fed with H₂ at the Ni electrode and O₂ at the Pt/C-electrode, the OCV measurements allow for the assessment of the Ni-electrode activation. For the Ni@NC anode, the initial cell OCV is *ca.* 0.2 V (Fig. 3a). The OCV returns to this value after each of the first nine galvanostatic steps and then gradually increases to 0.440 V during the next four galvanostatic/OCV steps. After the

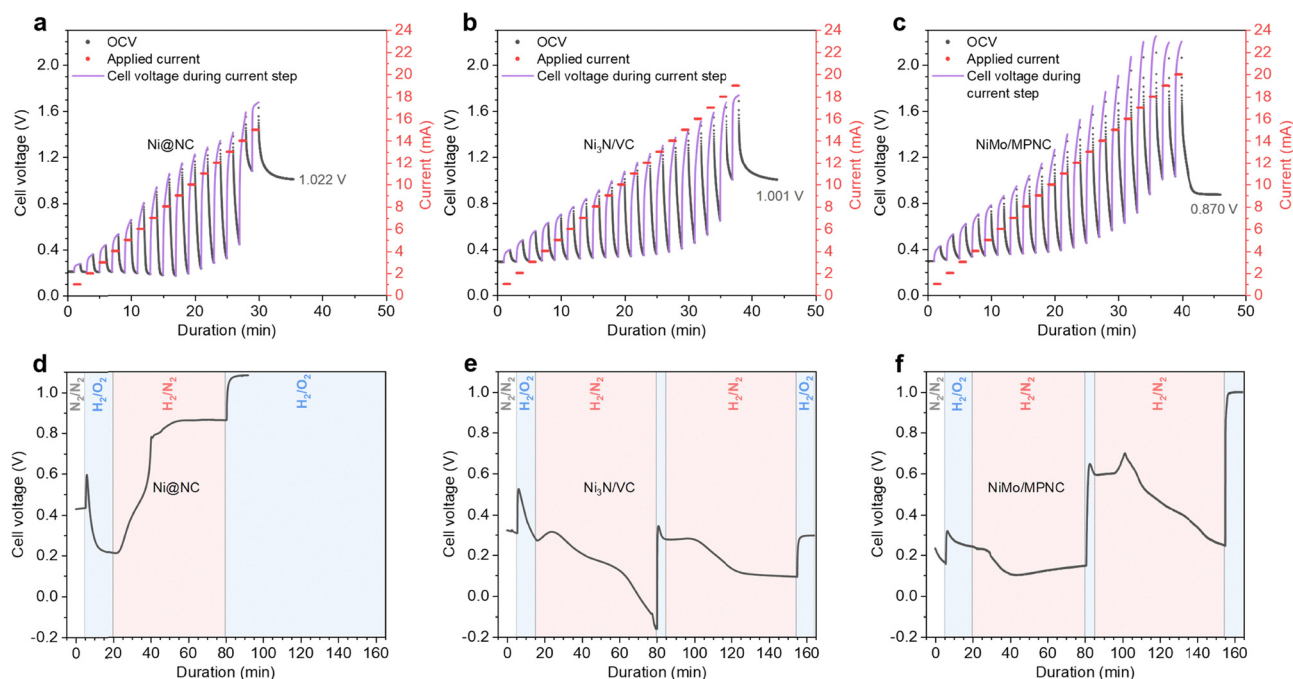


Fig. 3 Galvanostatic or chemical activation of Ni-based anodes in the AEMFC. (a–c) Sequence of galvanostatic step (red)/OCV measurement (black) of 1 min/ 1 min and the cell voltage (purple) measured during the galvanostatic holds with a Pt/C electrode paired with an electrode based on Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively. Humidified H₂ and O₂ gases are fed at the Ni and Pt/C electrodes, respectively. The positive sign of the applied current corresponds to electro-oxidation at Pt/C and electro-reduction at the Ni electrode. (d–f) OCV measurements of the AEMFC comprising a Pt/C cathode paired with an Ni@NC, Ni₃N/VC or NiMo/MPNC anode, respectively. The Ni-based anode is continuously fed with pure H₂, while the Pt/C cathode feed is alternated between O₂ (blue regions) and N₂ (red regions). AEMFC measurements were performed at a cell temperature of 60 °C with gases humidified at 60 °C, flow rates of 0.300 L min^{−1} and a backpressure of 100 kPa. The cathode was Pt/C (0.2 mg_{Pt} cm^{−2}), the AEM was Versogen PiperION™ (20 μm thickness), and the anode loadings were 6.8 , 6.4 , and 4.4 mg_{catalyst} cm^{−2} for Ni@NC, Ni₃N/VC and NiMo/MPNC, respectively. For (a–c), the data are not corrected for the iR-drop. The electrode geometric area was 4.84 cm².

14th step, the OCV suddenly increases to 1.080 V, revealing Ni-based anode activation. With the same procedure, Ni₃N/VC and NiMo/MPNC show delayed activation relative to Ni@NC (Fig. 3b and c), in line with their more oxidized state (Fig. 1b and c). After this activation protocol, a polarization curve could be acquired, as shown in Fig. S13a, for Ni@NC.

Variants of the galvanostatic activation procedure were investigated on Ni@NC, including one in which the 1 min/1 min galvanostatic/OCV protocol was repeated, but with a fixed current of 7 mA. With this variant, Ni@NC remains HOR-inactive even after 37 galvanostatic steps (Fig. S14). The corresponding cumulative reducing charge (15.5 C) is much higher than that needed to activate Ni@NC, as depicted in Fig. 3a (6.3 C), revealing that passing a given reducing charge through a given Ni electrode is not a sufficient condition for activation. This charge must also be selectively used to reduce native Ni (hydr)oxides. In AEMFC, the small O₂ diffusion flux across the membrane can directly (ORR current) or indirectly (Ni repassivation) increase the electric charge required for Ni activation. The activation, therefore, becomes difficult (or impossible) if the applied current is equal to or lower than the O₂ crossover current. Studies on gas permeability through polymeric membranes have hitherto typically focused on H₂,^{23,24} while some studies have reported both H₂ and O₂ permeabilities across different AEMs.^{25,26} Additional drawbacks of galvanostatic activation include the need for a potentiostat to force the AEMFC to operate in reverse mode and the high polarization of the oxygen electrode, which can be damaged upon repeated start-stop. A chemical reduction approach was therefore investigated.

Chemical activation in the AEMFC

Although the mentioned Ni-based catalysts did not activate upon immersion in the H₂-saturated KOH electrolyte at room-temperature under open circuit (Fig. 2b), we hypothesized that the higher temperature and increased H₂ concentration in the AEMFC may facilitate chemical activation. The first experiments conducted in an AEMFC with Ni-based anodes showed low OCV after 15 min of H₂/O₂ feeds at 60 °C (Fig. 2a). However, galvanostatic activation in the AEMFC suggests that Ni surface reduction may be competing with re-passivation due to O₂ crossover. This is also supported by OCV measurements at 60 °C on a cell featuring an Ni@NC-electrode on one side and a PtRu/C-electrode on the other side, both being fed with H₂. The OCV quickly reaches 0.0 V (Fig. S15), suggesting that both electrodes reach 0.0 V *vs.* RHE. This implies that Ni@NC can be chemically activated by H₂ at 60 °C when O₂ is completely absent. A chemical activation procedure was thus designed that involves humidified H₂ and N₂ feeds at 60 °C for 1 h to the anode and cathode, respectively.

For Ni@NC paired with a Pt/C cathode, the strong rise in OCV after 20 min suggests that Ni@NC is activated (Fig. 3d). This is confirmed after switching to H₂/O₂ feed, with the OCV reaching 1.1 V. Once activated, Ni@NC does not re-oxidize *via* O₂ crossover, as supported by the high OCV measured for >60 h under H₂/O₂ feed (Fig. S16). We hypothesize that fast ORR at 0 V *vs.* RHE on activated Ni@NC can scavenge O₂ molecules that

diffuse through the AEM sufficiently fast to avoid Ni passivation. The polarization curve recorded after chemical activation features a slightly higher performance than after galvanostatic activation (Fig. S13a and b). For Ni₃N/VC and NiMo/MPNC anodes, after 1 h of H₂/N₂ feed, the OCV under H₂/O₂ feed remains low (Fig. 3e and f), reflecting their more challenging activation. An additional 1 h of H₂/N₂ feed activates NiMo/MPNC but not Ni₃N/VC (Fig. 3e and f). From these observations and the XPS-depth profiling analysis, a correlation emerges between the difficulty in chemically activating an Ni-based anode and the thickness of the native Ni oxide layer in the Ni catalyst (Fig. 1c and Fig. S6).

Understanding activation in the AEMFC with a reference electrode

To gain fundamental insights, an RHE reference electrode was designed for the AEMFC, adapted from ref. 27. The practical design of this reference electrode is described in the Methods and Supp. Info (see Methods: 'Three-electrode AEMFC design and experiments' and Fig. S17). The working principle is that a Pt/C nanostructured catalyst in contact with an OH⁻ conducting ionomer and exposed to H₂ equilibrates at an electrochemical potential of 0.0 V *vs.* RHE when no current flows through the reference electrode. In practice, the designed reference electrode is in contact with the ionomeric phase of the membrane-electrode-assembly but has no electronic contact with the anode and cathode. Chemical activation of the Ni@NC anode (paired with a Pt/C cathode) was performed as previously. The OCV (OCP_{cathode} – OCP_{anode}) under consecutive N₂/N₂, H₂/O₂, H₂/N₂, and H₂/O₂ feeds (Fig. 4a, top) behaves similarly to the corresponding two-electrode AEMFC (Fig. 3d). The time dependences of OCP_{cathode} and OCP_{anode} *vs.* RHE are shown in Fig. 4a, bottom panel. Note that the reference electrode becomes an RHE only after the introduction of H₂. OCP_{anode} equilibrates at *ca.* 0.8 V *vs.* RHE after 5 min of H₂/O₂ feed, with a slight increase over time. This confirms that O₂ crossover through the AEM is sufficient to maintain and even strengthen the passivation layer. This is further supported by the fact that a fresh Ni@NC anode (non-activated) does not activate after 1 h of H₂/N₂ feed if the duration of the initial H₂/O₂ feed is increased from 15 min to 1 h (Fig. S18). Thus, a low percentage of O₂ in H₂ at the anode resulting from crossover can further oxidize a metallic Ni particle if the latter is initially already passivated. This is in line with a report showing that only 8 nTorr of O₂ blocks hydrogen adsorption on polycrystalline Ni.²⁸ Upon switching from H₂/O₂ to H₂/N₂ feed, OCP_{anode} immediately starts decreasing, reaching 0.0 V *vs.* RHE after less than 10 min (Fig. 4a). Upon switching back to H₂/O₂ after 1 h, OCP_{anode} remains stable at 0.0 V *vs.* RHE. The performance under H₂/O₂ of this chemically activated AEMFC is shown in Fig. 4b, with disentangled cathode and anode polarization curves. The Ni@NC anode reaches 0.2–0.3 V *vs.* RHE in the high current-density region; these potentials can induce re-oxidation, possibly explaining the stronger hysteresis at the anode upon reversal of the scan direction.

Investigation of Ni@NC activation using *in situ* techniques

To demonstrate that activation relates to a change in surface chemistry, Ni@NC was first studied using environmental XPS

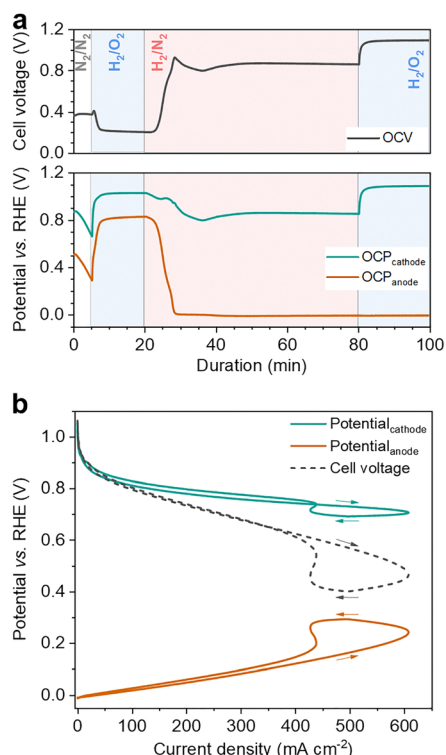


Fig. 4 Tracking anode potential during and after chemical activation with a three-electrode AEMFC. (a) Cell voltage, anode and cathode potentials against time during chemical activation, while the cell is at open circuit. (b) Cell, anode and cathode polarization curves measured on the same assembly after chemical activation. AEMFC measurements were performed at 60 °C cell temperature with gases humidified at 60 °C, flow rates of 0.300 L min^{-1} and a back pressure of 100 kPa. The cathode, AEM and anode were Pt/C (0.2 $\text{mg}_{\text{Pt}} \text{cm}^{-2}$), Versogen PiperION™ (20 μm thickness) and Ni@NC (6.6 $\text{mg}_{\text{catalyst}} \text{cm}^{-2}$), respectively. The data are not corrected for the iR-drop.

(see Methods). The Ni 2p_{3/2} spectra measured before and after exposure of the Ni@NC powder to pure H₂ (1 atm) for 1 h at

60 °C evidence a significant increase in the metallic Ni contribution (852.8 eV) and a decrease in the contribution from the Ni²⁺_a and Ni²⁺_b components, corresponding to the main peak of NiO and Ni(OH)₂, respectively (Fig. 5a). This demonstrates the partial reduction of the native Ni oxide layer of Ni@NC after a reduction step mimicking the AEMFC chemical activation protocol.

Surface changes may also affect Ni fcc crystallinity. It has been reported for Pt-based nanocatalysts that H or O adsorption at low and high electrochemical potentials, respectively, leads to a reversible increase in the metallic Pt fcc lattice constant through a so-called breathing mechanism.^{29,30} *Operando* wide-angle X-ray scattering (WAXS) measurements were therefore conducted in 0.1 M KOH using an Ni@NC layer in a three-electrode flow-cell (see Methods and Fig. S19). In this case, the conditions mimic the potentiostatic activation applied in RDE. WAXS patterns were collected during the CV of Ni@NC from which the lattice constant and scale factor of Ni fcc were extracted with Rietveld refinement (see Methods and Fig. S20). Below 0.100 V vs. RHE, reversible expansion of the lattice is observed (Fig. 5b). This can be attributed to both H adsorption on the Ni surface and/or H absorption in Ni when forming an Ni hydride.³¹ In fact, as observed previously on Pd electrodes,²⁹ WAXS does not allow distinguishing H adsorption from H absorption processes at low H insertion content, as the first stage of the formation of a metal hydride does not produce a phase transition but only results in a mild lattice expansion of the metallic phase. The intensity of the Ni fcc phase does not decrease significantly, also supporting the absence of a phase transition toward Ni hydrides. Such a transition, in fact, would be expected only at more negative potentials and/or after longer polarization times.³¹ This interpretation is further supported by the absence of characteristic diffraction peaks associated with Ni hydrides in the XRD pattern. Above 0.100 V vs. RHE, the lattice also undergoes expansion, which is likely associated with the metal-oxide phase transition toward Ni (hydr)oxides.

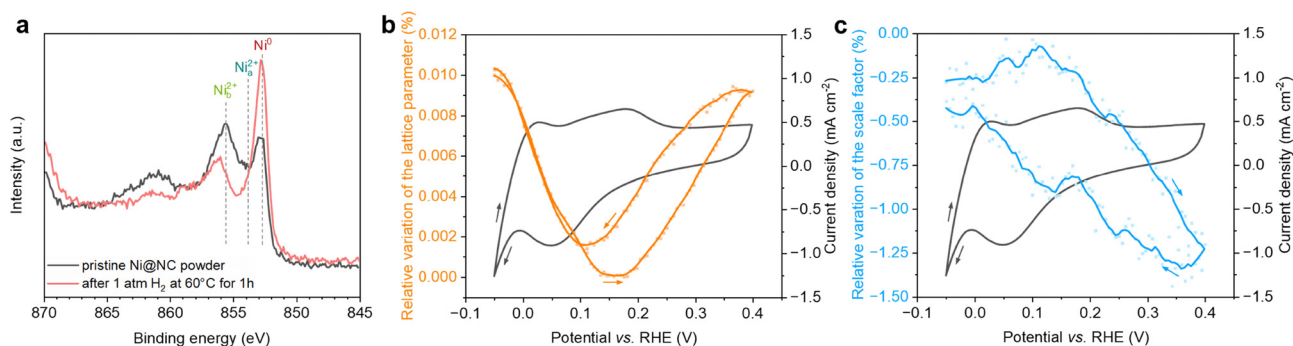


Fig. 5 *In situ* studies of Ni@NC surface changes. (a) E-XPS Ni 2p_{3/2} spectra of Ni@NC powder in its pristine state and after reduction in 1 atm H₂ at 60 °C for 1 h. (b) *In situ* WAXS measurements of the lattice parameter of the metallic Ni fcc phase during a CV measured in a H₂-saturated 0.1 M KOH electrolyte, showing potential-dependent lattice breathing. (c) *In situ* WAXS measurements of the scale factor of the metallic Ni fcc phase during the same CV. The CV is corrected for iR-drop. The WAXS patterns were collected with a temporal resolution of 1 s. The y-axis depicted in (b) represents the relative difference between the lattice parameter measured at a given potential and its minimum value measured during the CV (measured at ca. 0.17 V vs. RHE in the positive-going scan). The lattice parameter varies maximum by 0.01%, i.e. by ca. 40 fm. This still largely exceeds the standard deviation of ± 4 fm associated with the fits. The y-axis in (c) represents the relative difference between the scale factor measured at a given potential and its maximum value measured during the CV (measured at ca. 0.12 V vs. RHE in the positive-going scan).

Note that the highly amorphous phase of Ni oxide could not be detected in the WAXS patterns and that the expansion of the lattice is observed on the remaining metal phase, in great similarity with previous observations on Pt.³² A significant hysteresis with reversed scan direction is observed in the high-potential region but not observed in the low-potential region. This can be explained by the fast and slow kinetics of the corresponding processes. The reduction in Ni oxides during the negative scan partially overlaps with the onset of H-adsorption/absorption, suggesting a possible role of hydrogen in the complete reduction of the oxides.

These conclusions are supported by the scale-factor variation, which reflects the quantity of Ni and/or $\text{NiH}_{x-\alpha}$ fcc unit cells contributing to the diffraction pattern (Fig. 5c). Above 0.150 V *vs.* RHE, the scale factor decreases due to surface oxidation. During the negative scan, it increases back close to its initial value, confirming that the Ni@NC microstructure is not irreversibly modified after polarization to 0.400 V *vs.* RHE. Overall, these characterizations shed some light on the complex mechanisms behind (electro)chemical Ni oxidation-reduction. The fundamental relationship with HOR blocking or activation requires more studies. The passivation of metallic Ni might suppress HOR kinetics through coupled mechanisms. Beyond acting as a simple physical barrier to H_2 adsorption on metallic Ni, the oxidized Ni surface may bind OH species too

strongly, preventing the reversible OH_{ad} exchange necessary for the HOR.³³

Performance-focused AEMFC investigation

Following the identification and understanding of activation protocols, various cell components and operating conditions were modified to improve performance. We first optimized the duration of the pyrolysis applied to synthesize the Ni@NC catalyst (see Methods). The preparation of the Ni@NC and Pt/C electrodes was also improved by tuning the ionomer/carbon ratio in the catalytic ink and increasing the catalyst loadings (see Methods). Graphite flow field plates and a different AEM were also used. After chemical activation at 80 °C, the cell reached an OCV of 1.030 V. Polarization curves were then acquired under different operating conditions (Fig. 6a), including at cell temperatures above 100 °C, which was recently reported by Dekel's group³⁴ to offer key advantages, especially for CO_2 management.³⁵ The peak power densities achieved at 80, 95, and 110 °C with H_2/O_2 feed are 822, 993, and 1187 mW cm^{-2} , respectively. To the best of our knowledge, 1187 mW cm^{-2} is *ca.* 50% higher than the highest $\text{H}_2\text{-O}_2$ AEMFC peak power density using an Ni-based anode reported until 2025⁸ and is only surpassed by a 2026 study from Abruna's group.¹⁴ In that work, an AEMFC with an Ni-based anode and a Pt-based cathode reached *ca.* 1450 mW cm^{-2} at 80 °C.

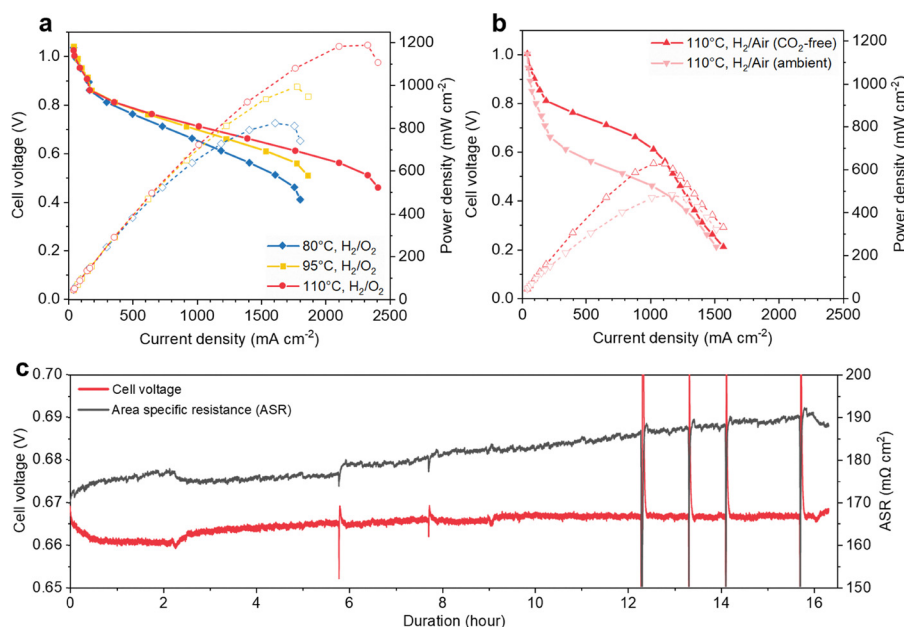


Fig. 6 AEMFC performance obtained with improved Ni@NC anode preparation and after chemical activation. Chemical activation was performed at 80 °C cell temperature with 96% humidified gases, flow rates of 0.500 L min^{-1} and a backpressure of 100 kPa at the anode and cathode. (a) AEMFC polarization and power density curves recorded at 80, 95 and 110 °C cell temperature with H_2 and O_2 flow rates of 1.0 L min^{-1} and anode/cathode backpressures of 250/250 kPa. The RH at the anode inlet was 90%, 91%, and 90% at 80, 95, and 110 °C, respectively, while the RH at the cathode inlet was 96% for all tests. The cathode was Pt/C (0.5 $\text{mg}_{\text{Pt}} \text{ cm}^{-2}$), the AEM was AT-1, and the anode was Ni@NC (Ni@NC loading of 8.1 mg cm^{-2} , corresponding to a Ni loading of 5.66 mg cm^{-2}). The flow-field plates were made of graphite. (b) AEMFC polarization curves recorded at a cell temperature of 110 °C with H_2 feed at the anode and a feed of $\text{CO}_2\text{-free}$ air or ambient air at the cathode at a flow rate of 1.0 L min^{-1} , under otherwise identical operating conditions. (c) Cell voltage and area-specific resistance measured during an initial stability test performed at a constant current density of 200 mA cm^{-2} . The cell temperature was 110 °C, the flow rates of H_2 and ambient air were 0.200 L min^{-1} and the anode/cathode backpressures were 250/250 kPa. The data are not corrected for the iR-drop.

The AEMFC was further evaluated at 110 °C using CO₂-free air or ambient air as the cathode feed, delivering peak power densities of 626 or 480 mW cm⁻², respectively (Fig. 6b). This constitutes the highest peak power density reported to date under such conditions, *ca.* 10% and 40% higher than previously reported for an AEMFC comprising an Ni-based anode coupled with a Pt/C cathode fed with synthetic air (CO₂-free)⁹ or ambient air containing 400 ppm CO₂,³⁴ respectively. Moreover, the AEMFC exhibited promising initial stability over 16 h of operation at 110 °C and at a constant current density of 200 mA cm⁻² with H₂/ambient-air feed (Fig. 6c). The area specific resistance (ASR) increased only slightly from *ca.* 170 to 190 mΩ cm² during the stability test likely due to mild carbonation. The cell voltage remained mostly constant, possibly decreasing by a few mV between 6 and 16 h of operation, which can be explained by the simultaneous 20 mΩ cm² increase in ASR during that period. Thus, one can conclude that the Ni-based anode was fully stable or insignificantly modified during the stability test.

Discussion on the implementation of the chemical activation of Ni-based anodes in AEMFC stacks

The present work demonstrates that specific start-up procedures need to be developed for AEMFCs comprising Ni-based anodes. Although flowing H₂/N₂ at anode/cathode at 60 °C was shown to activate Ni@NC anodes after *ca.* 15 min, this chemical activation procedure needs to be adapted for practical and economic implementation in AEMFC stacks. The main operational drawbacks are the typical non-availability of pure N₂ (especially in the context of transportation applications), the waste of a significant amount of H₂ (if the chemical activation needs to be repeated for every start-stop, as expected), the predicted need to heat the cell to complete the activation, and the significant duration needed for activation. From our observations, the chemical activation of Ni-based anodes requires the simultaneous presence of H₂, absence or very low partial pressure of O₂, and a certain temperature. Regarding the latter, assisted and non-assisted cold-start procedures of proton exchange membrane fuel cells (PEMFCs) have been studied and developed, which may partially be transferable to AEMFCs.^{36,37} To minimize the heat necessary to activate Ni-based anodes (which would likely stem from the electric energy of a battery or supercapacitor during AEMFC start-up) and to minimize the activation duration, heating strategies could be designed to target the Ni-based anodes and avoid heating the entire stack. Regarding the use of N₂ to remove O₂ on the cathode side during the chemical activation procedure, feeding H₂ on both sides would result in the same reductive effect on the anode side, thereby avoiding the need for pure N₂. Lastly, in order to minimize the amount of H₂ necessary to activate the Ni-based anodes, O₂ sensors designed to quantify or detect low amounts of O₂ diluted in H₂ may provide real-time information about the O₂ partial pressure. This would allow for informed decision-making regarding when the H₂ flow can be stopped (at an O₂ partial pressure below a certain threshold) while securing chemical activation of the Ni-based anodes at a given

temperature. The implementation of such a control process requires extensive studies on the combined effects of temperature and gas phase composition (in particular, ternary mixes of H₂-N₂-O₂ to simulate the crossover of ambient air through the AEM) on their reductive or oxidative effects on various Ni-based anodes. Materials development can also be envisaged that generally facilitates Ni-based anode chemical activation, including AEMs with low oxygen permeability and Ni-based catalysts with more facile activation behaviour. In addition to start-up procedures, shutdown procedures need to be developed in order to avoid the excessive oxidation of Ni-based anodes during shutdown. It is particularly important to avoid the simultaneous combination of a high temperature and high O₂ partial pressure on the Ni-based anode side. Feeding H₂ to both the anode and cathode sides during shutdown while cooling the cell and monitoring the decrease in the O₂ partial pressure with specific sensors may be used to decide when the conditions are safe to stop the H₂ flow. This may be combined and accelerated with the electrochemical removal of O₂ present on the cathode side by short-circuiting each single cell.

Conclusions

The need for an activation protocol was demonstrated for three mainstream HOR Ni-based catalysts. Their OCP was initially ≥ 0.7 V *vs.* RHE in H₂-rich environments in both aqueous alkaline electrolyte and AEMFC, reflecting the presence of a passivation layer that blocks the HOR. Experiments in the RDE and AEMFC indicated that partial reduction in the passivation layer is a prerequisite for allowing the HOR. In a three-electrode RDE setup, this is easily achieved by applying a low electrochemical potential. In the AEMFC, galvanostatic and chemical activation approaches were explored. Chemical activation, achieved by initially feeding humidified H₂ to the anode and N₂ to the cathode, proved more practical. Whatever the activation procedure, we demonstrated the strong influence of O₂ crossing over the AEM, which can re-passivate the nickel surface. Thus, while thin AEMs are advantageous for low ohmic drop and improved water management, our results highlight the need to also consider O₂ permeability. Overall, the findings reveal the criticality of activation procedures for Ni-based anodes, which are essential for achieving high AEMFC performance.

Methods

Materials

Nickel(II) acetate tetrahydrate (Ni(OAc)₂·4H₂O, 98%, Sigma-Aldrich), trimesic acid (H₃BTC, 95%, Sigma-Aldrich), oleylamine (OAm, Sigma-Aldrich), oleic acid (OA, technical grade, 90%, Sigma-Aldrich), nickel(II) acetylacetonate (Ni(Acac)₂, 95%, Sigma-Aldrich), borane triethylamine complex (97%, Sigma-Aldrich), nickel(II) nitrate hexahydrate (Ni(NO₃)₂·6H₂O, 99.999% trace metal basis, Sigma-Aldrich), ammonium heptamolybdate tetra hydrate ((NH₄)₆Mo₇O₂₄·4H₂O, >99%, Carl Roth), ethanol 96° (RE Pure,

Carlo Erba), ethanol absolute anhydrous (RE pure, Carlo Erba), isopropanol (2-Propanol, for HPLC, 99.9%, Sigma-Aldrich), potassium hydroxide (KOH, ACS Reagent, $\geq 85\%$, pellets, Sigma-Aldrich), Vulcan[®]-XC72R (Cabot), Nafion[™] dispersion (1100 EW, 5 wt%, low aliphatic alcohol, 15%–20% water, Sigma-Aldrich), ultrapure water (Veolia Purelab Chorus, 18.2 M Ω cm⁻¹), ultrasonic cleaner bath (VWR USC-TH), pure nitrogen (N₂, 4.5, ≥ 99.995 , Linde), hydrogen/nitrogen gas mixture (H₂/N₂, 5:95 v/v, ultrapure, Linde) and pure ammonia (NH₃, 99.997%, Air Liquide) gas bottles were used for pyrolysis, and pure hydrogen for RDE measurements was provided from a generator (Claind Brezza HyGen 600, $\geq 99.9995\%$). For AEMFC measurements aimed at identifying and understanding activation protocols, pure hydrogen (H₂, 5.0, $\geq 99.999\%$, Linde), pure oxygen (O₂, 5.0, $\geq 99.999\%$, Linde), pure nitrogen (N₂, 5.0, $\geq 99.999\%$, Linde), Pt/C-1 (Pt 40 wt% on Vulcan Carbon, SKU:3151725, Fuel Cell Store), ETFE poly-VBC TMA-grafted powder anion exchange ionomer, and an AEM (Versogen Piper-ION[™], 20 μ m, Self-Supporting, Fuel Cell Store) were used. For performance-focused AEMFC measurements, H₂, O₂, and N₂ ($\geq 99.999\%$, Maxima); CO₂-free air (O₂/N₂, 21:79 v/v, Maxima); ambient air (O₂/N₂, 21:79 v/v + 400 ppm CO₂, Maxima); Pt/C-2 (HiSPEC 4000, 40 wt% Pt on carbon black, Thermo Scientific, USA), TMA-functionalized Fumion[®] anion exchange ionomer; and AT-1 AEM (Hephas Energy Co., China) were used.

Synthesis of the Ni-based catalysts

Ni@NC. Ni@NC was synthesized in two steps. First, the Ni₃(BTC)₂ metal–organic-framework (MOF) was synthesized by ball milling using an adapted reported method.³⁸ A mass of 1.000 g of H₃BTC, 1.832 g of Ni(OAc)₂·4H₂O (corresponding to a molar ratio of BTC/Ni of 2/3) and 38.5 g of 5 mm diameter ZrO₂ balls (96 units) are introduced into a grinding bowl (Fritsch, 45 mL, ZrO₂) and pre-mixed at 200 rpm for 2 min in a planetary mill (Fritsch, Pulverisette 7, premium line). Then, 1 mL of ultrapure water is added, and 2 × 15 min milling is performed at 600 rpm (reversed rotation direction, without pause). The solid product is extracted with anhydrous ethanol and centrifuged for 15 min at 4000 rpm (Eppendorf 5804, Rotor A-4-44). The supernatant is then extracted and replaced with fresh anhydrous ethanol. This washing step was carried out three times. The supernatant-free product is then placed in a 25 mL glass vial and dried overnight in an air-ventilated oven at 70 °C. The obtained MOF powder is stored in a vacuum cabinet.

The second step consists of temperature-controlled pyrolysis of the MOF following an adapted reported method.³⁹ A mass of 0.550 g of Ni₃(BTC)₂ MOF is placed in a quartz crucible (10 × 150 × 10 mm³) and introduced in the center of a quartz tube of 25.4 mm diameter. The tube is connected to gas flow lines, sealed and placed in a tubular split-hinge oven (Thermcraft). The quartz tube is first purged with pure N₂ at *ca.* 1 L min⁻¹ for 5 min, then the gas is switched to H₂/N₂ (5:95, v/v) at 400 mL min⁻¹ and the oven is heated to 175 °C at a ramp of 10 °C min⁻¹. The purge (N₂) gas flow is monitored using a rotameter (Sho-Rate, 1355 VD2 Buna, tube: R2-15-D, float: stainless steel, Brooks), H₂/N₂ gas mixture reactant gas flow is

monitored using a multi-gas mass flowmeter (DPC17S-VOL6-BB5, Aalborg), and the pure NH₃ reactant gas flow is monitored using a mass flowmeter (GFC17S, Aalborg). When the temperature reaches 175 °C, a flow of 100 mL min⁻¹ of pure NH₃ is introduced in addition to the H₂/N₂ (5:95, v/v) flow at 400 mL min⁻¹ and the oven is further heated to 390 °C at a ramp rate of 10 °C min⁻¹. The gas composition during that step is thus H₂/NH₃/N₂ (4:20:76, v/v/v). The temperature is maintained at 390 °C for 1 h (or 1.5 h for the Ni@NC catalyst used for cell testing with improved electrode preparation). After this, the tube is immediately removed from the split-hinge oven, and the tube is purged with N₂ (*ca.* 1 L min⁻¹ flow rate) and allowed to cool down for 30 min. Before removing the catalyst from the tube and exposing it to ambient air, the inlet and outlet gas tubes (4 mm diameter) are disconnected and the two ends of the quartz tube are covered with a perforated aluminum foil to allow air to slowly enter the tube and mix with N₂ overnight, resulting in the passivation of the catalyst powder. This step is of critical importance because unpassivated Ni@NC is a pyrophoric material and direct exposure to air leads to irreversible and full oxidation of the catalyst.

Ni₃N/VC. Ni₃N/VC was synthesized in two steps. First, an NiO/VC precursor is synthesized using a reported method.⁴⁰ A mass of 80 mg Vulcan XC-72R powder is placed in a two-neck flask containing a solution of 30 mL oleylamine (OAm) and 0.64 mL oleic acid (OA) and sonicated for 20 minutes to obtain a dispersion. 513.8 mg (2 mmol) of Ni(Acac)₂ is added to this solution under magnetic stirring. The solution is heated to 110 °C in an oil bath under a continuous primary vacuum to remove oxygen and water. Once the temperature reaches 110 °C, the heating is stopped, and the system is filled with nitrogen through a rubber septum. The solution is naturally cooled down in the oil bath to 90 °C, and 2 mL of OAm containing 0.5 g (643.5 μ L) of triethylamine borane complex (previously dissolved) is added. The solution is maintained at 90 °C for 1 h under magnetic stirring. The solution is then removed from the oil bath to cool to room temperature, and 40 mL of ethanol is added. After washing three times with a large amount of ethanol and centrifuging at 8500 rpm for 5 min, Ni/VC is obtained. It is subsequently converted into NiO/VC by heating it overnight at 70 °C in an air-ventilated oven.

The second step involves temperature-controlled pyrolysis of NiO/VC. A mass of 285 mg of NiO/VC is placed in a quartz crucible (10 × 150 × 10 mm³) and introduced in the center of a quartz tube (25.4 mm diameter). The tube is connected to gas flow lines, sealed and placed in a tubular split-hinge oven (Thermcraft). The quartz tube is first purged with NH₃ at 400 mL min⁻¹ for 5 min and heated to 350 °C at a ramp of 10 °C min⁻¹ under a flow rate of 150 mL min⁻¹ of pure NH₃. The purge gas flow is monitored using a rotameter (Sho-Rate, 1355 VD2 Buna, tube: R2-15-D, float: stainless steel, Brooks), and the flow rate of pure NH₃ is monitored using a mass flowmeter (GFC17S, Aalborg). The quartz tube and sample were maintained at 350 °C for 3 h under NH₃ flow. After this, the tube was immediately removed from the split-hinge oven to allow cooling to room temperature under NH₃ flow for 30 min

and then purged with N₂ for 5 min. Before removing the catalyst from the tube and exposing it to ambient air, the inlet and outlet gas tubes (4 mm diameter) were disconnected, and the two ends of the tube were covered with a perforated aluminium foil to allow air to slowly enter the tube and mix with N₂, resulting in the passivation of the catalyst powder.

NiMo/MPNC. The mesoporous N-doped carbon (MPNC) support with a pore size of 60 nm and a particle size of 350 nm was synthesized as reported previously.⁴¹ The subsequent deposition of NiMo nanoparticles is performed in a two-step loading of the MPNC carbon support, followed by a thermal reduction. In detail, MPNC-60-1000 (500 mg) is added to a solution of (NH₄)₆Mo₇O₂₄·4H₂O (77.22 mg) in H₂O (3 mL), followed by the slow removal of the solvent using a rotary evaporator (40 °C bath temperature). Subsequently, the MPNC/(NH₄)₆Mo₇O₂₄ composite is ground using an agate mortar and added to a solution of Ni(NO₃)₂·6H₂O (1079.86 mg) dissolved in isopropanol (9 mL). As before, the solvent is removed using a rotary evaporator. The composite is then placed in a crucible inside a tubular oven (tube diameter 6 cm, Carbolite furnace) and reduced at 550 °C for 1 h using a heating ramp of 10 °C min⁻¹ and 5% H₂/Ar with a gas flow of 300 mL min⁻¹. After cooling to room temperature, both tube connectors are removed, and air is allowed to enter over 2 h into the tube to slowly passivate the catalyst surface.

Material characterisations

X-ray diffraction (XRD). The catalyst powders were analyzed using a Philips X'Pert PRO MPD Reflection-Transmission Spinner (PANalytical) diffractometer operating at 45 kV and 20 mA using Cu-K α X-ray radiation ($\lambda = 1.5406$ Å) in Bragg-Brentano mode (2θ angle from 5° to 80°, step of 0.033 s, total time 20 min). HighScore Plus software (PANalytical) was used to remove the background and identify the phases that match the diffraction peaks (COD database). The average crystallite size of Ni phases was estimated with Scherrer's equation applied to the main diffraction peak of each Ni phase identified ($D = 0.90\lambda/B \cdot \cos \theta$), where D is the crystallite size (nm), λ is the X-ray wavelength (0.154 nm), B is the full width at half maximum (FWHM) of the diffraction peak, and θ is the peak position in radian.

X-ray absorption spectroscopy. Ni K-edge X-ray absorption spectra were collected in transmission mode at room temperature at the SAMBA beamline (Synchrotron SOLEIL). The beamline is equipped with a sagittally focusing Si 220 monochromator and two Pd-coated mirrors that are used to remove X-ray harmonics. The catalysts were pelletized as disks of 10 mm diameter with 1 mm thickness using cellulose powder as a binder. The data were normalized to the incident photon flux, and the beam energy was calibrated with reference Ni foils, aligning the maximum of the first derivative of the absorption spectra with the theoretical edge energy (8333 eV). The software Fastosh⁴² was used to treat and extract the data.

Inductively coupled plasma mass spectrometry (ICP-MS). The bulk Ni content of the Ni-based catalysts was assessed using a PerkinElmer NexION 2000 ICP-MS instrument and

quantified by calibration curves comprising ICP-MS standard aqueous solutions (Carl Roth GmbH & Co.) of Ni²⁺ covering Ni concentrations of 0, 5, 10, 20 and 50 $\mu\text{g}_{\text{Ni}} \text{L}^{-1}$ in 2% HNO₃. All Ni-based catalysts were digested in HNO₃ (Suprapur[®] 68%, Analpure) and ultrapure water, totaling 2% HNO₃. Quantification of the Ni content was carried out on the ⁶⁰Ni and ⁵⁹Ni isotopes, with similar values confirming the absence of interference and matrix effects under these experimental conditions.

Ex situ X-ray photoelectron spectroscopy (XPS). The *ex situ* XPS characterization was performed using the Thermo Electron ESCALAB 250 instrument. The excitation source was the monochromatic Al K α line (1486.6 eV). The surface analyzed has a diameter of 500 μm . The binding energy was calibrated relative to the energy of the C-C component of C 1s set at 284.8 eV. The charge was compensated for by a low-energy electron beam (-2 eV). The deconvolution of the narrow scan spectra of Ni 2p_{3/2} and N 1s was realized using the Avantage software (Thermo Fisher Scientific). The Ni 2p_{3/2} spectra were analyzed based on a model described by Beisinger *et al.*¹⁸

Ex situ X-ray photoelectron spectroscopy (XPS) depth profiling. The Thermo Fisher Scientific NEXSA G2 XPS instrument was used to perform X-ray photoelectron spectroscopy depth profiling analysis with an Al-K α monochromatic source and a 400 μm X-ray spot size. Elemental scans were acquired at a pass energy of 50 eV with a step size of 0.1 eV. Binding energies were calibrated by fixing the adventitious C 1s peak at 284.8 eV as an internal reference. For depth profiling, a nominal sputter rate of 0.2 nm s⁻¹ was used to estimate the depth based on instrument calibration using a reference silicon wafer under identical conditions (2 keV Ar⁺, 2 mm $\times$ 2 mm area). Thus, the estimated depth (nm) is given by $\text{depth} = t_{\text{sputter}}/5$, where t_{sputter} is the sputter time in seconds. Elemental compositions (at%) were obtained using CasaXPS relative sensitivity factors (RSFs), and the area of the peaks was integrated after background subtraction.

Environmental X-ray photoelectron spectroscopy (E-XPS). The E-XPS was measured using an EnviroESCA device (SPECS). A monochromated Al K α source (1484.71 eV) generated X-rays. A hemispherical photoelectron analyzer, Phoibos 160 NAP 1D-DLD (SPECS), was used to measure the energy of the outgoing photoelectrons with a pass energy of 20 eV, a measurement step of 0.1 eV, and a dwell time of 0.3 s per point. The Ni 2p_{3/2}, Ni 3p, C 1s, O 1s, and VB spectra were recorded. The effective analysis area (300 μm in diameter) is defined by both the X-ray beam size and the entrance aperture (300 μm) of the differentially pumped analyzer. The Ni 2p_{3/2} spectra were analyzed using CasaXPS based on a model described by Biesinger *et al.*¹⁸

All E-XPS spectra were measured under vacuum conditions (10⁻⁶ mbar) at room temperature (RT). After the initial XPS scan, the sample was lowered into a load-lock chamber, a valve between the analyzer chamber and the load-lock was closed, and the load-lock was filled with 1 bar of H₂ before heating the sample to 60 °C. After 1 h at 60 °C, the sample was cooled in H₂ to approximately 35 °C, H₂ was pumped down, and the sample was transferred back into the analysis chamber for subsequent XPS measurements at RT.

In situ wide-angle X-ray scattering (WAXS) measurements and data analysis. A SP-300 potentiostat (BioLogic) and custom-made three-electrode electrochemical flow cells were used. The electrolyte (0.1 M KOH, reagent grade, 90%, Sigma-Aldrich) was prepared prior to each measurement, saturated with H₂ by bubbling, and the electrolyte flow through the cell was maintained at 20 mL min⁻¹ using a peristaltic pump. The counter-electrode was a Pt wire placed close to the electrolyte outlet (downstream of the working electrode) to avoid any electro-deposition of Pt on the working electrode from Pt cations that might originate from the counter-electrode. It must be noted, however, that under such experimental conditions (H₂-saturated electrolyte), the Pt counter electrode only electrocatalyses the HOR and/or HER with small overpotentials, thus preventing any Pt dissolution. The reference electrode was a commercial leakless miniature Ag/AgCl electrode (ET072, eDAQ). The working electrode consisted of a thin film of the Ni@NC catalyst on a glassy carbon substrate. The catalyst layer was prepared from an ink with the same formulation used for the RDE measurements. An 8 μ L aliquot of the ink was drop-cast on the glassy carbon substrate under rotation (400 rpm) and dried under rotation with the help of a heat gun until a uniform film was obtained, targeting a metal loading of 0.300 mg cm⁻². After an electrochemical activation procedure consisting of 20 CV cycles from -0.050 V to 0.050 V *vs.* RHE at a scan rate of 50 mV s⁻¹, the electrode potential was cycled between -0.050 V and 0.400 V *vs.* RHE at 5 mV s⁻¹, and WAXS measurements were recorded simultaneously. Synchrotron WAXS measurements were performed at the ID31 beamline of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. The high energy X-ray beam (75 keV) was focused on the catalyst layer through the cell in a grazing incidence configuration, and the scattered signal (1 s temporal resolution) was collected using a Dectris Pilatus 3X CdTe 2M hybrid photocounting area detector. The energy, detector distance and tilts were calibrated using a standard CeO₂ powder, and the 2D diffraction patterns were reduced to the presented 1D curves using the pyFAI software package.⁴³ Rietveld refinement of the WAXS patterns was performed to extract lattice parameters and scale factor using the Fm3m structure of Ni and the Fullprof software. The instrumental resolution function was determined by the refinement of a CeO₂ standard sample. Thomson-Cox-Hastings profile function was adopted. The contribution of water and glassy carbon was subtracted from the overall scattered signal to isolate the contribution from Ni. The background of the patterns was described by an interpolated set of points with refinable intensities. A typical WAXS pattern and corresponding fit are shown in Fig. S20.

High-resolution transmission electron microscopy (HR-TEM). The Ni@NC and Ni₃N/VC catalyst powders were dispersed in pure isopropanol and ultrasonicated for 10 minutes. 10 μ L of the suspension was deposited onto a clean Cu-Lacey carbon grid. Ni@NC and Ni₃N/VC were analyzed using a JEOL 2010 transmission electron microscope operated at 200 kV with a LaB6 filament of 0.19 nm point-to-point resolution. The NiMo/MPNC catalyst powder was dispersed in a mixture of ultrapure H₂O/pure ethanol

(95 : 5, v/v) and ultrasonicated for 10 minutes. 1 μ L of the suspension was deposited onto a Cu-Lacey carbon grid, and the excess liquid was removed from the backside of the grid using a Kimtech wipe and dried at 60 °C for 5 min. This procedure was repeated twice. The NiMo/MPNC sample was analyzed using a Talos F200X G2 electron microscope (Thermo Fisher) operated at an acceleration voltage of 200 kV with a high-brightness X-FEG.

Electrochemical characterisation with the RDE setup

The catalytic ink was prepared by dispersing 4.0 mg of catalyst powder for 30 min in 0.182 mL isopropanol, 0.358 mL ultrapure water, and 4.7 μ L Nafion solution (5 wt%) using an ice-cooled ultrasonication bath. The electrochemical measurements were conducted using an SP-300 potentiostat (BioLogic) and monitored using EC-Lab software (BioLogic). The experimental setup consisted of a 150 mL PTFE-based electrochemical cell (Laborxing, SKU: 4FDJC-150) with a three-electrode setup, utilizing a commercial RHE (Gaskatel HydroFlex) as the reference electrode, a porous carbon rod as the counter electrode (Sigma-Aldrich), a glassy carbon (GC) disk electrode tip (Pine Research, PTFE shroud, 0.196 cm²) and a RDE rotator (Pine Research). All electrochemical characterizations were acquired at a rotating speed of 1600 rpm, at room temperature, while the electrolyte was saturated with H₂ gas with continuous bubbling.

For every new measurement, the PTFE cell is filled with 150 mL of 0.1 M KOH ($\geq 85\%$). An aliquot of 8 μ L of the ink is drop-cast onto the GC tip held upwards and rotated at 500 rpm under a N₂ flow, resulting in a catalyst loading of 0.3 mg_{catalyst} cm⁻². For each catalytic layer, the electrochemical characterisation protocol begins with a 1 min OCP measurement, followed by a linear scan voltammetry (LSV) starting from the previously measured OCP down to 0.050 V *vs.* RHE at 20 mV s⁻¹, immediately followed by a measurement of the high frequency resistance by electrochemical impedance spectroscopy at 0.050 V *vs.* RHE (ZIR, 10 kHz, 20 mA amplitude). All subsequently measured CVs are corrected for iR-drop with the high frequency resistance obtained with the ZIR technique (EC-Lab software, 95% compensation). The working electrode is then subjected to a conditioning treatment of 20 cycles of CV from -0.050 V to 0.300 V *vs.* RHE at 50 mV s⁻¹. HOR polarization curves are then obtained by recording seven CVs from -0.100 V to 0.400 V *vs.* RHE at 5 mV s⁻¹ in H₂-saturated electrolyte. The sixth cycle in the positive-going scan direction was selected for analysis. The entire protocol is applied to three casts of the same catalytic ink in order to obtain the mean and standard deviation (Table S8). The sixth cycle of HOR polarization curves is then analyzed to quantify the HOR activity in two ways: first, by estimating the mass activity at 0.050 V *vs.* RHE (Note S2 and Table S8), and second, by assessing the exchange current density of the HOR/HER in the linear micropolarization domain and normalizing it by the ECSA (Note S3 and Table S8). The ECSA curves (Fig. S12) were obtained by recording twenty CVs from -0.100 V to 0.400 V *vs.* RHE at 20 mV s⁻¹ in a N₂-saturated electrolyte. The twentieth cycle in the negative-going scan direction was selected for the determination of the integration area used in Note S3.

For RDE measurements designed to determine the potential at which an Ni-based catalytic layer becomes activated for HOR (section “Potentiostatic activation in RDE”), the potentiostatic control was conducted in H₂-saturated electrolyte without any conditioning of the catalytic layer. The electrochemical protocol alternated 180 s of OCP measurement and 60 s of potentiostatic control. The applied potentials were in chronological order as follows: 0.700, 0.600, 0.500, 0.400, 0.300, 0.250, 0.225, 0.200, 0.175, 0.150, 0.125, 0.100 and 0.000 V vs. RHE. For these experiments, the data were not corrected for the iR-drop.

Electrochemical characterisation in the AEMFC for the identification and understanding of activation protocols

Ni-based anode preparation. The method was adapted from a previously reported procedure.⁴⁴ Gas diffusion electrodes (GDEs) for Ni-based catalysts were prepared by spray deposition using a hand spray gun (Iwata Eclipse HP-CS). The AEI used was ETFE poly-VBC TMA-grafted powder (IEC = 1.87).⁴⁵ The anode preparation starts with the ink preparation using a 100 mm diameter agate mortar and pestle. The AEI is first ground for 10 min to break any aggregates, and the catalytic powder is added and ground together with the AEI for 5 min. For the Ni@NC and Ni₃N/VC catalysts, an amount of Vulcan XC-72R carbon black is added that corresponds to 25 wt% of the catalyst mass, and the two powders are ground together for an additional 5 min. Next, 2.5 mL of ultrapure water is added, and the slurry is ground for 5 min. The mixture becomes homogeneous and sticky. Then, 5 mL of isopropanol is slowly added under continuous grinding. After 2 min, the slurry starts to be transferred to a 25 mL glass vial. Finally, 17.5 mL of isopropanol is added to complete the transfer of the slurry from the mortar to the glass vial. The slurry is dispersed for 1 h in an ice-cooled ultrasonic bath prior to hand-spray. The targeted loading for all the anodes (Ni@NC, Ni₃N/VC, and NiMo/MPNC) was 7.0 mg_{catalyst} cm⁻², and the amounts of catalytic powder used to prepare the inks were 250, 215, and 250 mg for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. The ionomer-to-carbon (I/C) ratio was 0.41 for the GDE ink of all Ni-based anodes, which was calculated from the weight ratio of carbon in the catalyst and the carbon added. The amounts of AEI used were 56, 68, and 66 mg for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. The anode GDEs are then prepared by hand-spray deposition of the anode ink onto 25 cm² gas diffusion layers (GDLs) (TGP-H-060 with 5 wt% PTFE wet proofing) using a hot plate at 70 °C. Last, the prepared anode GDEs are cut into four 4.84 cm² anodes, suitable for the fuel cell hardware. The resulting catalyst loadings were 6.8, 6.4, and 4.4 mg_{catalyst} cm⁻² for Ni@NC, Ni₃N/VC, and NiMo/MPNC, respectively. The strongest deviation from the targeted anode loading was observed for NiMo/MPNC and is possibly explained by the higher ‘volatility’ of the ink during spraying due to the higher relative amount of carbon in this catalyst. Using the same protocol, additional GDEs were prepared using Ni@NC for three-electrode AEMFC experiments, with a loading of 6.6 mg_{catalyst} cm⁻².

Pt/C cathode preparation. The method was adapted from a previously reported procedure.⁴⁴ GDEs for Pt/C catalysts were

prepared by spray deposition using a hand spray gun (Iwata Eclipse HP-CS). The AEI used was ETFE poly-VBC TMA-grafted powder (IEC = 1.87).⁴⁵ The cathode preparation starts with the ink preparation using a 100 mm diameter agate mortar and pestle. 6.15 mg of the AEI is first ground for 10 min to break any aggregates, and 25 mg of Pt/C-1 is then added and ground together with the AEI for 5 min. Next, 1 mL of ultrapure water is added, and the slurry is ground for 5 min. The mixture becomes homogeneous and sticky. Then, 2 mL of isopropanol is slowly added under continuous grinding. After 2 min, the slurry starts to be transferred to a 25 mL glass vial. Finally, 7 mL of isopropanol is added to complete the transfer of the slurry from the mortar to the glass vial. The slurry is dispersed for 1 h in an ice-cooled ultrasonic bath prior to hand-spray. The ionomer-to-carbon (I/C) ratio is 0.41. The cathode GDEs are obtained by hand-spray deposition of the cathode ink onto 25 cm² gas diffusion layers (GDLs) (TGP-H-060 with 5 wt% PTFE wet proofing) using a hot plate at 70 °C. Last, the prepared cathode GDEs are cut into four 4.84 cm² cathodes suitable for the fuel cell hardware. The AEI : C : Pt ratio was 0.625 : 1.5 : 1. The estimated catalyst loading of the cathode GDEs was 0.2 mg_{Pt} cm⁻².

Cell assembly and AEMFC connection to the test station. The AEM was a 20 µm-thick commercial AEM (Versogen PiperION™, 20 µm, Self-Supporting, Fuel Cell Store). The AEMFC was controlled by an 850 Fuel Cell Test System (Scribner), and the electrochemical measurements were controlled and recorded using an SP-150 potentiostat (BioLogic) associated with a VMP3B-20 booster (20A/20V, BioLogic) and monitored using the EC-Lab software (BioLogic). Stainless steel flow-field plates were chosen instead of graphite for the investigation of the galvanostatic and chemical activation. This choice was made to avoid carbon corrosion of the flow field plates during the galvanostatic activation protocol applied to activate Ni-based anodes.

The AEM is ion-exchanged to the OH⁻ form by immersion in a N₂-bubbled 1.0 M KOH aqueous solution for at least 24 h prior to mounting the cell. On the day of the experiment, humidifier tanks are first pre-heated at 60 °C. The AEM and GDEs are then soaked in N₂-bubbled 1.0 M KOH for 60 min while exchanging the N₂-bubbled 1.0 M KOH aqueous solution with fresh solution every 20 min. After this, the AEM is rinsed in ultrapure water, and excess KOH is removed from the GDEs with a small piece of tissue. Finally, all cell components are mounted in the fuel cell hardware using stainless steel flow field plates (EquiLABrium) with a 5 cm² active-geometric-area serpentine flow field and PTFE gaskets (Goodfellow). The thickness of PTFE gaskets is chosen so as to reach a compression rate of the GDEs between 20% and 25% for each cell assembly. Last, the cell is connected to the test station, wrapped with a thermal isolator, and the inlet gas lines are wrapped with heated cuffs (Scribner). The AEMFC is then heated to 60 °C under a N₂ flow rate of 0.300 L min⁻¹ (fully humidified at 60 °C) on each side, and the cell temperature is allowed to stabilize for 1 h.

Cell conditioning. Prior to any activation of the Ni anodes, AEMFC conditioning is performed. The OCV under N₂/N₂ flows

is recorded for 5 min as a baseline. Then, the N_2/N_2 flows are switched to fully humidified H_2 and O_2 gases (0.300 L min^{-1}) at the anode and cathode, respectively, while 100 kPa of backpressure is applied. The AEMFC OCV under H_2/O_2 flows is then recorded for 15 min. For all the tested Ni-based anodes, the OCV is stabilized at values close to 0.2 V. Subsequently, a galvanostatic or chemical activation protocol is applied to the cell in order to activate the Ni-based anode.

Galvanostatic activation. Galvanostatic activation was conducted under fully humidified H_2/O_2 flows (0.300 L min^{-1} and 100 kPa backpressure) by alternating 60 s of OCV measurement and 60 s of galvanostatic control. The first applied current was 1 mA (reduction current for the Ni electrode), and the absolute value of the reduction current applied in each subsequent galvanostatic step was incremented by +1 mA. The sign of the current corresponds to a reduction at the Ni electrode and oxidation at the Pt/C electrode. The galvanostatic activation was stopped when the OCV reached a value above 0.9 V at the end of the 60 s OCV step or when the cell voltage reached a threshold value. In the figures, the applied current (rather than the current density) was reported during the galvanostatic steps to facilitate the interpretation of the results (e.g. the 14th galvanostatic step corresponds to a current of 14 mA, which can be easily identified).

Chemical activation. Chemical activation was conducted by switching from humidified H_2 and O_2 flows at the Ni and Pt electrodes, respectively, to fully humidified H_2 and N_2 flows (0.300 L min^{-1} and 100 kPa backpressure). The cell was maintained under OCV (no current) for 1 h. After 1 h, the flow configuration was switched back to humidified H_2 and O_2 flows at the Ni and Pt electrodes to assess the OCV values, respectively. If the OCV was still low ($\leq 0.9\text{ V}$, as observed for Ni_3N/VC and $NiMo/MPNC$ anodes), the operation was repeated.

Acquisition of polarization curves. After galvanostatic or chemical activation leading to AEMFC OCV $\geq 0.9\text{ V}$ with fully humidified H_2 and O_2 flows, polarization curves were recorded to assess the cell performance and obtained by scanning the cell voltage between OCV and 0.400 V at a scan rate of 5 mV s^{-1} . Polarization curves were conducted at a cell temperature of $60\text{ }^\circ\text{C}$ with the anode and cathode humidifiers heated at $60\text{ }^\circ\text{C}$. H_2 and O_2 flow rates were fixed at 0.300 L min^{-1} . The current density was reported and obtained by dividing the values of current by the geometric active area (4.84 cm^2).

Three-electrode AEMFC design and experiments. A three-electrode assembly was mounted using an $Ni@NC$ anode and Pt/C cathode according to a procedure similar to that used for two-electrodes, as described above in this Methods section, with an additional edge-type reference electrode on the anode side, which can work as an RHE when exposed to H_2 . The cell assembly design was adapted from a recently reported method.²⁷ Two graphite plates with 25 cm^2 active-area serpentine flow fields were mounted in the fuel cell hardware to provide H_2 to the anode GDE and the RHE on one side, and to provide O_2 to the cathode GDE on the other side (Fig. S17).

The RHE consists of a $1\text{ cm} \times 10\text{ cm}$ copper foil ($17\text{ }\mu\text{m}$ -thick, Goodfellow) covered on both sides with a $1\text{ cm} \times 2\text{ cm}$ hand-sprayed Pt/C layer (*ca.* $0.5\text{ mg}_{Pt}\text{ cm}^{-2}$) (Fig. S17a) using the same Pt/C cathode ink formulation as that used for preparing the cathode GDEs in the Methods section (Electrochemical characterisation in AEMFC for the identification and understanding of activation protocols). Two gaskets are used at the anode side: gasket 1 is in contact with the anode flow-field plate and has 8 small pinholes (0.5 mm diameter) to allow fast H_2 access to the RHE while preventing electric contact between the RHE and the anode plate. Gasket 2 is installed between gasket 1 and the AEM, comprises a bigger hole (1 cm diameter) aligned with the small pin-holes of gasket 1, and acts as an H_2 reservoir for the active part of the RHE. The small pin-holes and the bigger hole are both positioned *ca.* 0.3 cm away from the edge of the 5 cm^2 anode GDE. The part of the copper foil coated with Pt/C is then positioned to cover *ca.* half of the gasket's holes (Fig. S17b). This configuration prevents electric contact between the RHE and the anode flow-field plate while allowing for fast H_2 supply to the Pt/C coating of the RHE.

The experimental protocol for the AEMFC operation was then the same for the three-electrode and two-electrode cell assemblies, as described above in the Methods (Electrochemical characterisation in AEMFC for the identification and understanding of activation protocols). In particular, one still controlled the cell voltage for the acquisition of polarization curves with the three-electrode assembly, and not cathode *vs.* RHE or anode *vs.* RHE potential.

Performance-focused AEMFC electrochemical characterization

$Ni@NC$ anode preparation. First, the duration of pyrolysis for the synthesis of $Ni@NC$ was optimised. The duration leading to maximum activity was found to be 1.5 h (instead of 1 h used for the $Ni@NC$ used in all other parts of the present work) according to RDE measurements. Similar to the methodology used to prepare Ni-based anodes for identifying and understanding activation protocols (Methods section entitled "Electrochemical characterisation in AEMFC for the identification and understanding of activation protocols"), the spray deposition of ink on a GDE was applied to prepare improved anode GDEs using a hand-held spray gun (Iwata Eclipse HP-TH, Japan). The anode ink was prepared in an agate mortar. First, 26.5 mg of TMA-functionalized Fumion[®] AEI was ground for 10 min to disrupt any AEI aggregates. Subsequently, 53 mg of $Ni@NC$ was added and co-ground with the AEI for 5 min, followed by the addition of 53 mg of Vulcan XC-72R and further grinding for 5 min. Next, 4 mL of ultrapure water was added, and the mixture was ground for an additional 5 min until a homogeneous viscous slurry was obtained. Then, 16 mL of isopropanol was added slowly under continuous grinding, and the resulting slurry was transferred to a 50 mL centrifuge tube. The slurry was ultrasonically dispersed for 1 h in an ice-cooled bath prior to spraying. Anode GDEs were fabricated by hand-spray deposition of the anode ink onto 4.41 cm^2 GDLs (TGP-H-060, 5 wt% PTFE wet proofing) placed on a hot plate maintained at $90\text{ }^\circ\text{C}$. The resulting electrodes were cut into 1 cm^2

anodes. The estimated total catalyst loading was $8.1 \text{ mg}_{\text{catalyst}} \text{ cm}^{-2}$ (resulting in a Ni loading of $5.7 \text{ mg}_{\text{Ni}} \text{ cm}^{-2}$).

Pt/C cathode preparation. Pt/C-based cathodes were prepared in a manner analogous to the above-described anode GDE, using an ink containing 262.5 mg of Pt/C-2 and 66 mg of TMA-functionalized Fumion[®] AEI, which was spray-deposited onto 25 cm^2 GDLs (TGP-H-060, 5 wt% PTFE wet proofing). The resulting electrodes were cut into 1 cm^2 anodes. The total Pt loading was $0.5 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$.

Assembly and cell testing. The procedure for AEMFC testing was analogous to the one described in the Methods (section entitled “Electrochemical characterisation in AEMFC for the identification and understanding of activation protocols”). Besides the above-described differences in electrode preparation, the cell tests with improved electrode preparation also featured the use of a different AEM (AT-1, Hephass Energy Co., China) and the use of graphite-based flow field plates. The testing procedure generally followed the one described in a previous report.⁴⁶ A $2.5 \times 2.5 \text{ cm}^2$ AEM piece was soaked in 1.0 M KOH aqueous solution at 80°C overnight, with the solution exchanged after approximately 2, 18, and 20 h. The $1 \times 1 \text{ cm}^2$ electrodes were soaked in a 1.0 M KOH aqueous solution at room temperature for 1 h, with the solution refreshed every 20 min. Finally, all cell components were mounted in the fuel cell hardware (Scribner) using graphite plates with a 5 cm^2 serpentine flow field area and PTFE gaskets (FuelCell Store) with a $1 \times 1 \text{ cm}^2$ cutout. The thickness of the PTFE gaskets was chosen to achieve a compression rate of approximately 30% for each GDE. Subsequently, the cell was compressed with a torque of 4.5 N m, connected to the Scribner 850e Fuel Cell Test System and wrapped with silicon pads for thermal insulation, while the inlet gas lines were wrapped with heated cuffs (Scribner). The AEMFC was heated to 80°C under a N_2 flow of 0.5 L min^{-1} at 96% RH without applying backpressure and was allowed to stabilize for 1 h. Subsequently, the chemical activation protocol, as described in the Methods section “Electrochemical characterisation in AEMFC for the identification and understanding of activation protocols”, was applied at 80°C , after which the cell was fed with H_2 and O_2 at a flow rate of 1 L min^{-1} and a backpressure of 250 kPa. The electrochemical measurements were controlled and recorded using the Scribner 850e test station. For break-in after chemical activation, the cell voltage decreased stepwise from OCV to 0.5 V in 0.1 V decrements, with each step held for approximately 20 min. Subsequently, polarization curves were recorded starting from the OCV at a scan rate of 10 mV s^{-1} , with cell temperatures of 80, 95, and 110°C . The RH was adjusted to maximize the peak power density at each temperature. At 110°C , the cathode feed was additionally switched to CO_2 -free air and ambient air (400 ppm CO_2) at a flow rate of 1 L min^{-1} and a backpressure of 250 kPa. Following this, an initial stability test was conducted at a constant current density of 200 mA cm^{-2} . The cell temperature was maintained at 110°C , with H_2 and ambient air supplied at a flow rate of 0.200 L min^{-1} and anode/cathode backpressures of 250/250 kPa.

Author contributions

S.A., N.B., E.P., R.C., F.J. conceived the ideas; S.A., F.J. wrote and edited the manuscript; S.A., E.P., N.B., E.G., P.E. contributed to material syntheses; S.A. conducted the RDE measurements; S.A., E.P., N.B., E.G., F.L., M.D. performed the AEMFC measurements for the identification and understanding of activation protocols; M.E., A.G., R.C., J.D. carried out WAXS characterization; M.R., T.H. performed the E-XPS characterization; L.D., S.H. characterized the catalysts with electron microscopies; L.C., X.C. performed the depth-profiling XPS characterization; M.S.Z., A.A.B. carried out the performance-focused investigation of the AEMFC; R.C., L.D., F.M., A.E., A.A.F., D.R.D., F.J. revised the manuscript and coordinated the project; and F.J. directed the research. All co-authors participated in the discussion and commented on the manuscript.

Conflicts of interest

The authors have no conflicts to declare.

Data availability

Data are available upon reasonable request to the authors.

Supplementary information (SI): supplementary notes, figures and tables on the electrochemical and structural characterisation of Ni-based catalysts, supplementary figures on the activation in AEMFC and the design of the AEMFC reference electrode. See DOI: <https://doi.org/10.1039/d6ee03112a>.

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