**The First High-Performing Commercial PGM-free Cathodes for Anion Exchange
Membrane Fuel Cells**

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Abstract

The structural and electrochemical properties are presented for the first high-performing commercial oxygen reduction catalyst that is not only platinum group metal (PGM)-free, but also does not use any critical-resource-materials (non-CRM). This Fe-N-C catalyst was specially developed for alkaline media operation and is demonstrated in the cathode of operating anion exchange membrane fuel cells (AEMFCs). With H₂/O₂ reacting gases, AEMFCs made with Fe-N-C cathodes achieved a record peak power density of 2.1 W cm⁻² (> 1 W cm⁻² on H₂/air) and operated with very good voltage durability for more than 100 h. These AEMFCs also realized an iR-corrected current density at 0.9 V of 100 mA cm⁻², well-exceeding the U.S. Department of Energy (DOE) target for PGM-free cathodes of 44 mA cm⁻². Finally, in a second configuration, Fe-N-C cathodes paired with low-loading PtRu/C anodes (0.125 mg_{Pt-Ru} cm⁻², 0.08 mg_{Pt} cm⁻²) demonstrated a specific power of 10.4 W mg_{PGM}⁻¹ (16.25 W mg_{Pt}⁻¹), exceeding the DOE 2022 AEMFC initial performance target for the first time.

1. Introduction:

To be considered as the ultimate power source for transportation systems and portable devices, low temperature polymer electrolyte fuel cells need to overcome significant cost barriers. The long-term U.S. Department of Energy (DOE) goal for the cost of a light-duty vehicle fuel cell system is \$30/kW_{net} at a production volume of 500 000 units per year^{1,2}. The current estimated cost of a proton exchange membrane fuel cell (PEMFC) system at this production volume is between \$45³ and \$51⁴ per kW_{net}. Although the estimated cost at full production volume has reduced significantly in comparison with where it was in the early 2000s, it has been plateaued in recent years⁵, which led some researchers to suggest changing the operating chemistry from acidic to alkaline to create so-called anion exchange membrane fuel cells (AEMFCs).

The performance and durability of AEMFCs have increased significantly in recent years^{6–12}, with some studies even able to achieve peak power densities of 3.5 W cm⁻²¹³ with H₂/O₂ gas feeds and more than 2000 hours of continuous operation with less than 5% voltage decay¹⁴. Where AEMFCs have a true advantage over PEMFCs is the opportunity to lower cost¹⁵ by allowing for cheaper membranes, a wider class of materials for bipolar plates and enhanced oxygen reduction reaction (ORR) kinetics^{16,17}. The latter is expected allow researchers to either significantly reduce or entirely eliminate the Pt in the cathode (one of the primary drivers for high PEMFC cost¹⁸). However, all of the above-mentioned achievements for AEMFCs have been made also using platinum group metal (PGM)-based catalysts with a high loading in both the anode and cathode^{19,20}. In fact, the total PGM loading of state-of-the-art AEMFCs typically range 1 – 1.5 mg_{PGM} cm⁻² (ca. 1 mg_{Pt} cm⁻²).

In general, there are two strategies to reduce the amount of PGM in an operating fuel cell: 1) reduce the PGM loading; or 2) develop PGM-free catalysts²¹. Both of these strategies have their own advantages and drawbacks in terms of performance and stability. Given the water management issues with modern AEMFCs^{22,23} and the fact that both the ORR and hydrogen oxidation reaction (HOR) experience notable overpotentials²⁰ it is unlikely that even the interim PGM performance milestones can be achieved by making ultra-thin catalyst layers with low-PGM loading at both electrodes. This suggests that to reduce the PGM loading in operating AEMFCs, there will need to be at least some development of PGM-free catalysts¹⁹. Unfortunately, no high performing PGM-free anode catalysts have been reported – for either PEMFCs or AEMFCs. Because the discovery, understanding and deployment of PGM-free ORR cathodes has been much easier than PGM-free anodes²⁴, the most promising configuration to achieve a low-PGM AEMFC is to deploy a high-performing PGM-free cathode with a low-loading PGM anode.

Over the past decade, a variety of PGM-free catalysts have been investigated for the ORR^{25–30}. Among non-precious metal catalysts, iron and nitrogen co-doped carbon (Fe–N–C) catalysts have been the most promising alternatives to Pt-based catalysts due to their high ORR activity^{31–33}. In fact, state-of-the art Fe–N–C catalysts often show intrinsic activities very close to Pt and half-wave potentials that exceed 0.85 V. However, the performance of AEMFCs and PEMFCs deploying such catalysts has been low compared with Pt-based cathodes in AEMFCs. This is because in addition to high catalyst activity, reaching high-performance PGM-free cathodes in AEMFCs requires mass transport to be more effectively managed, meaning that material-level structure and electrode engineering will play key roles in determining the electrode-level structure, pore size and distribution, and water management. One thing that has

hampered the performance of PGM-free cathodes in the past is the need for high catalyst loading, which leads to thick catalyst layers with inadequate transport rates for both O₂ and H₂O³⁴.

Therefore, this study has two aims. The first is to understand the influence of structure – from the nano-scale to the mesoscale – on the behavior of Fe-N-C catalysts with single-atom Fe-N_x active sites in the AEMFCs cathode. The selected catalyst for this work is a newly commercially available Fe-N-C catalyst that was specifically designed for the operation at AEMFC conditions. As discussed earlier, water is generated on the anode side of AEMFC, which will lead to the substantial drying of the cathode at high current densities. **Therefore, this Fe-N-C material was constructed with two changes from conventional materials used in PEMFCs – both intended to make the transport of liquid water more facile in the catalyst layer. The first change was to increase the average pore size. The second change was to increase the level of graphitization of the catalyst, decreasing its hydrophilicity – as shown in Figure S6 and discussed in the Supporting Information.** Importantly, this work not only reports the extremely high activity of Fe-N-C catalyst in ex-situ tests, but the catalyst is also integrated into state-of-the-art AEMFC electrode structures, enabling record performance to be achieved. The second aim is to develop and deploy ultra-low-PGM loading PtRu/C anodes and to pair them with the Fe-N-C based cathodes to create the first AEMFC that is able to meet U.S. Department of Energy performance milestones.

2. Results and Discussion

2.1. Catalyst Structure and Fe Distribution

The synthesis method for producing the Fe-N-C catalyst in this work is illustrated in Figure 1 and described in detail in the Methods section. Post-synthesis, the structure of the Fe-N-C catalyst was investigated through a series of physical characterization techniques, Figure 2.

Figure 1. Illustration of the synthesis pathway and desired structure of the Fe-N-C ORR catalyst.

Though most of the Fe in the catalyst took the form of single atoms in a Fe-N_x configuration, the X-ray diffraction (XRD) pattern in Figure 2a does show that a small amount of metallic iron was left in the catalyst after acid treatment. The non-Fe peaks in the XRD pattern were broad were a combination of the response from turbostratic carbon and some SiO₂ that remained from the template^{35,36}. The carbon-related peaks included were located at 2θ = 25° (002), 45° ((100) and (101)), and 79° (110). Raman spectroscopy (Figure 2b) of the catalyst showed the typical carbon fingerprint peaks³⁷, including a peak for the defect-induced D band at 1337 cm⁻¹ and graphitic sp² carbon (G band) at 1570 cm⁻¹ as well as the broad 2D bands around

2700 cm^{-1} . The specific surface area and pore size distribution for the catalyst was determined by BET N_2 adsorption and BJH analysis. The Fe-N-C catalyst showed a typical type-IV (Figure S4 in the Supporting Information) isotherm, suggesting that the catalyst structure was mesoporous. The catalyst possessed a large specific surface area of $550 \text{ m}^2 \text{ g}^{-1}$ and a narrow pore size distribution that consisted mainly of pores that were 5 – 30 nm (Figure 2c). The primary particle size distribution for the catalyst, determined by Dynamic Light Scattering (DLS) analysis, is shown in Figure 2d. An overwhelming majority of the catalyst particles were less than 1 μm in size, with an average particle diameter of 0.6 μm . When combined, the BET and DLS experiments suggest a catalyst particle that is highly porous, though with a modest size, and high surface area to expose a large fraction of active sites to the reaction zone. This was confirmed by high resolution microscopy, as discussed below.

Figure 2. Physico-chemical characterization of Fe-N-C: **a)** Recorded (dark blue) and deconvoluted XRD pattern showing peaks of carbon, SiO₂, and the different Fe-based components; **b)** Raman spectrum of carbon structure; **c)** Adsorption/desorption pore size distribution of the catalyst; and **d)** Particle size distribution by DLS.

Figure 3a shows an SEM image of the catalyst surface structure, which confirms the BET and DLS results above. First, a typical particle had an average diameter of ca. 1 micron. Also, the throughout the catalyst, pores ranging in diameter from 5 to 40 nm were observed throughout. Such large pores are desirable for fuel cell operation as they provide high accessibility features to the active centers and play an important role in mass transfer because large pores are less likely to be blocked by liquid water. Figure 3b shows a 2D TEM image of the catalyst primary particle. Since the electron beam passes through the sample and reaches the detector, this image is able to provide a “see-through” visual confirmation of the pore structure throughout the catalyst.

Figure 3. Morphology and elemental distribution of Fe-N-C: **a)** FESEM image of the Fe-N-C catalyst pore structure; **b)** TEM image of Fe-N-C; **c)** Z-contrast STEM image; **d)** SEM elemental distribution maps of **e)** oxygen, **f)** silicon, **g)** nitrogen, **h)** iron, and **i)** carbon.

The z-contrast dark-field STEM images of the Fe-N-C catalyst were also collected to further understand the atomic distribution throughout the catalyst, with a particular interest in determining how many of the Fe atoms in the catalyst existed as single atoms in the Fe-N-C vs. agglomerated Fe particles. Here, because Fe is the heaviest element, it will show up as the brightest element in the z-contrast STEM images. Figure 3c shows a representative catalyst particle on the hollow carbon STEM substrate, showing that Fe was well-dispersed over the entire catalyst. There was no evidence of agglomerated Fe particles at this scale. EDS mapping (Figures 3d, 3e, 3f, 3g, 3h, and 3i) also suggests that the catalyst composition is homogenous. Importantly, both N and Fe are clearly evenly dispersed throughout the catalyst.

To further probe the Fe distribution throughout the catalyst, atomically resolved STEM images are shown in Figure 4. A few Fe nanoparticles were found in each catalyst particle (Figure 4a-b), though very few large agglomerated particles were present. In fact, of over 100 particles imaged, only three large Fe nanoparticles greater than 10 nm were observed. What this means is that an overwhelming majority of the Fe in the catalyst was present as single atoms, which is supported by the STEM image in Figure 4c, which was taken near the edge of a single pore. The STEM images also support that the Fe single-atoms were present both on the primary surface, but also on the catalyst surface within the pores, which explains why some of the single atoms in Figure 3c appear blurry. To help the eye to more clearly see the single atom sites, a selection of Fe atoms is circled in Figure 4d. The later findings suggests that the density of Fe-N_x sites still can be increased, providing a guidance to the future research on PGM-free catalysts.

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163 **Figure 4.** Atomically resolved STEM images of the Fe-N-C catalyst: **a)** exemplar small hemispherical nanoparticle
164 with single atoms around it, **b)** Single Fe atoms on a sample area of the 3D N-C support, **c)** atomically dispersed
165 single Fe atoms on the edge of the Fe-N-C catalyst pore, and **d)** circled single atoms in focus on the edge of a pore.

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167 2.2. Ex-situ Electrochemical Behavior

168 The activity and selectivity towards ORR of the Fe-N-C catalyst in O₂-saturated 0.10 M
169 KOH is shown in Figure 5. During cyclic voltammetry (CV), the catalyst exhibited a well-
170 defined ORR reduction peak between 0.8 V and 0.9 V vs. RHE. To better understand the ORR
171 kinetics and mechanism, the Fe-N-C catalyst was deposited onto a glassy carbon rotating ring

disk electrode (RRDE) and linear sweep voltammetry (10 mV s^{-1}) was done at several rotation rates between 400 – 2500 rpm (Figure 5b), to calculate the H_2O_2 yield and average number of electrons transferred (n). The half-wave potential for the catalyst in this work was 0.846 V, which is one of the highest values reported^{34,38,39} for a Fe-N-C catalyst, which is only 20 mV more negative than commercial 40 wt% Pt/C (0.866 V, for a RDE with $20 \mu\text{g cm}^{-2}$ loading, Figure 5b), indicating excellent ORR activity in alkaline media. The peroxide yield at the ring and the calculated n value (details in the Methods section) are shown in Figure 3c. The average value for n was 3.967 over the entire potential window; however, between 0.6 V- 1 V (where the cathode actually would operate in an AEMFC) the n value was 3.99 (Figure 5d). In this potential range the $\text{H}_2\text{O}_2\%$ is less than 1 which is very good for a PGM-free catalyst. The high activity of this Fe-N-catalyst, in addition to its high surface area and open structure, make it an ideal replacement for PGM material in the AEMFC cathode.

Figure 5. a) Cyclic voltammograms for Fe-N-C in O₂-saturated aqueous KOH (0.10 M) electrolyte at a scan rate of 20 mV s⁻¹ at room temperature; **b)** ORR linear sweep polarization curves for Fe-N-C in O₂-saturated aqueous KOH (0.10 M) electrolyte at various rotation rates (10 mV s⁻¹); **c)** Number of electrons (n) transferred per O₂ molecule and hydrogen peroxide yield on the Fe-N-C catalyst as a function of potential. **d)** Number of electrons (n) transferred per O₂ molecule and hydrogen peroxide yield on the Fe-N-C catalyst as a function of potential between 0.6 V -1 V.

2.3. Integration into Operating AEMFCs and Performance

Figure 6a shows polarization curves for an AEMFC with a Fe-N-C cathode (1 mg cm⁻²) and PtRu/C (0.6 mg cm⁻²) anode. The AEM used in all tests was a high-density polyethylene (HDPE) with benzyltrimethylammonium cationic head groups⁹. To achieve high-performing, long-life, PGM-free AEMFCs, there are operational conditions concerns that must be addressed beyond catalytic limitations, such as water management²⁰. This is shown in Figure 6a. **For operation at low temperature and full humidity (anode/cathode/cell temperatures of 60 °C/60 °C/60 °C) the cell performance is low because of high water accumulation at the anode. One effective strategy to enhance AEMFC performance is to adjust the relative humidity (via the dew points) of the inlet gases during cell operation⁴⁰ and to increase the cell temperature.** Reducing the dewpoints below full saturation allows for convective evaporation of water into the anode flow-field, reducing the amount of water in the anode ionomer as well as the amount of ionomer swelling⁴¹. In Figure 6a with a constant cell temperature of 70°C, the peak power density increased from 1.4 W cm⁻² to 1.6 W cm⁻² when the anode/cathode dewpoints were reduced from 60°C/64°C to 60°C/72°C. When the cell temperature was increased to 80°C and optimum anode/cathode gas dew points of 70°C/75°C were used (red line in Figure 6a), the peak power density was further increased to 1.9 W cm⁻². Finally, in AEMFCs backpressurization reduces water evaporation in the electrode by increasing its boiling point. Though this can be problematic for the anode side¹¹, increased liquid water in the AEMFC cathode can actually improve cell performance by reducing Ohmic resistance and providing increased concentration of reactive water. In this cell, applying backpressure to the anode led to a decrease in the cell

performance while applying backpressure to the cathode always led to an increase in cell performance. This is shown in Figure 6a where 200 kPa backpressure was applied under the previous optimum dew points at 80°C (blue line). The result was an extremely high peak power density of 2.05 W cm⁻² and a current density at 0.4 V of 7.4 A cm⁻².

There are some very important observations to note here. First, as shown in Figure 7, the peak power density and maximum current density are new literature records for polymer membrane fuel cells using a PGM-free cathode, especially taking into account that Fe-N-C loading was ~4x lower compared to the previously reported performances^{20,28,29,34,42–48}. This is true not only when this data is compared to previous AEMFCs (Figures 7a-b) but this is also true when compared to the best-reported PEMFCs in the literature as well (Figures 7c-d). The performance of top-performing AEMFCs with a PGM-free cathode are also summarized in Table S1 in the Supporting Information.

Next, an identical cell to the one discussed in Figure 6a was exposed to a short-term 150 h durability test operating at 600 mA cm⁻². This is important as Fe-N-C catalysts in PEMFCs have shown particularly poor durability due to radical attack and oxidative instability^{41,50–52}. The results of the durability test are shown in Figure 6b. For this cell, the reacting gas flow rates were both 0.3 L min⁻¹, and no backpressure was applied. The initial anode/cathode reacting gas dew points were 74°C/78°C, though the dew points were slightly adjusted (± 0.5 °C) during the test to maintain adequate humidification. To match the high beginning-of-life performance, this AEMFC setup also showed outstanding durability compared to previous literature. The voltage decay rate was only 0.46 mV h⁻¹ and the HFR only increased by around 1 mΩ during the experiment. This is the first time that an AEMFC containing a nonprecious cathode was reported to operate over 100 h with the cell voltage remaining above 0.6 V (0.68V

– 0.611V). The best result for an AEMFC with a PGM-free cathode in the literature is a 100 h H₂/air(CO₂-free) cell with the operated voltage decaying at a rate of 1 mV h⁻¹⁴⁴. The best PEMFC durability in the literature over 100 h operation at 600 mA cm⁻² was a degradation rate of 0.2 mV h⁻¹, but with a lower cell voltage (0.55V – 0.5V) during the durability test⁵³.

Then, to evaluate the feasibility of the Fe-N-C cathodes for more practical applications, cells were also tested with simulated air (CO₂-free) as the oxidant (Figure 6c). Positively, the Fe-N-C cathode supported a mass transport limited current density of 3.4 A cm⁻² and achieved a peak power density of just over 1 W cm⁻². Compared to prior reported results for PGM-free H₂/air(CO₂-free) AEMFCs in the literature (Figure S3 in the Supporting Information)^{28,44}, the Fe-N-C catalyst in this work showed greatly enhanced performance. Both values were the highest values reported in the literature to date. Additional tests to show the advancement of these materials, and PGM-free AEMFC cathodes in general, towards realistic operation were also done, with a specific goal of satisfying important U.S. Department of Energy targets. The first test in this regard was informed by the polarization curve for the best-performing cell in Figure 6a, where the apparent current density at 0.9 V was approximately 125 mA/cm². This appeared to satisfy the DOE target for PGM-free cathodes of 44 mA/cm². However, the condition in that experiment was not identical to the DOE protocol, and the experiment was transient (10 mV/s scan rate). Therefore, an experiment was run with a 0.6 mg_{Pt} cm⁻² anode and 1.0 mg_{Fe-N-C} cm⁻² cathode at steady state at the DOE-defined protocols: 0.9 V (iR free), cell temperature 80°C, and 100 kPa backpressure to both sides of the cell. The result is shown in Figure 6e, where the steady-state current density at 0.9 V (iR-free) was 100 mA/cm², which is more than twice the DOE target. It is also noteworthy that this value is quite close to an identical cell that had a high loading Pt/C cathode electrode (Figure S2 in the Supporting

Information), where a current density at 0.9 V (iR-free) of 131 mA cm⁻² and a peak power density of 2.6 W cm⁻² were achieved, though the operating conditions were slightly different.

Figure 6. a) Current-voltage (solid) and current-power density (dash) curves for a H₂/O₂ AEMFC: cathode with 1 mg cm⁻² of Fe-N-C, anode with 0.6 mg cm⁻² of PtRu, and 1 L min⁻¹ gas flows (anode/cathode/cell temperatures and pressurization state given in the legend); b) voltage vs. time recorded at a constant current density of 600 mA cm⁻² with the same catalyst loadings and unpressurized 0.3 L min⁻¹ H₂-O₂ flows. (cell temperature of 80 °C with the anode/cathode temperatures of 74/78°C); c) H₂/air (CO₂-free) fuel cell performance data: cathode with 1 mg cm⁻² of Fe-N-C, anode with 0.6 mg cm⁻² of PtRu with 0.15 MPa backpressurization of the 1 L min⁻¹ gas flows (temperatures given in the legend); d) LowPGM fuel cell performance data: cathode with 1 mg cm⁻² of Fe-N-C, anode with 0.125 mg cm⁻² of PtRu with 0.1 MPa backpressurization of the 1 L min⁻¹ gas flows (temperatures given in the legend); e) Results for a constant potential hold of 0.9 V (iR-corrected) to determine the kinetic current of the cell with an anode consisting of 0.6 mg cm⁻² of PtRu, cathode with 1.0 mg cm⁻² of Fe-N-C and 100 kPa backpressurization on both anode and cathode of the 1 L min⁻¹ gas flows (75/77/80°C Anode/Cathode/cell

temperature) **f**) Fuel cell durability data with a very low PGM loading anode of 0.125 mg cm^{-2} of PtRu: cathode with 1 mg cm^{-2} of Fe-N-C and 0.1 MPa backpressurization of the 1 L min^{-1} gas flows ($68/72/80^\circ\text{C}$ temperature settings). The AEM used was a HDPE-based radiation-grafted benzyltrimethylammonium type (ion-exchange capacity $\text{IEC} = 2.4 \text{ mmol g}^{-1}$)⁹, while the ETFE-based benzyltrimethylammonium-type radiation-grafted ionomer powders ($\text{IEC} = 1.24 \pm 0.06 \text{ mmol g}^{-1}$) were 20% by solid mass of the catalyst layers.

Figure 7. Comparison of the single-cell AEMFC performances between this work and state-of-the-art literature PGM-free cathode fuel cell work: **a**), **b**) i-V and i-power density AEMFC curves $\text{H}_2\text{-O}_2$ comparing this work to the following prior reported PGM-free cathodes: Fe_{0.5}-NH₃²⁰, CF-VC²⁸, CoMn₂O₄/C²⁹, MnCo₂O₄/C²⁹, FeCoPc/C⁴³, N-

C-CO_x⁴⁴, Mn₂O₃/Fe_{0.5}-NH₃³⁴; **c**), **d**) i-V and i-power density curves on H₂-O₂ between this AEMFC work and and prior reported PEMFC PGM-free cathodes: Fe-N-C with dense active sites⁴⁵, Fe-MOF⁴², Fe-N-C-Phen-PANI⁴⁶, FeNC_NCeO_x⁴⁷, and Fe₂-Z8-C⁴⁸; **e**) Comparison of specific peak power (W PGM⁻¹ loading) on H₂-O₂ between different AEMFCs⁴⁹, both state of the art PGM-types and those employing PGM-free electrocatalysts.

Finally, cells were assembled with the specific goal of meeting the U.S. DOE 2022 milestone for AEMFCs: beginning of life operating voltage of 0.65 V at 1 A cm⁻² operating on H₂/O₂ reacting gases with a total PGM loading less than 0.2 mg cm⁻²⁵⁵. To do this, a Fe-N-C cathode was paired with an anode with a very low loading of PtRu/C. The total PGM loading of the AEMFC tested here was 0.125 mg_{PtRu} cm⁻² (0.08 mg_{Pt} cm⁻²). The value of 0.125 mg_{PGM} cm⁻² was chosen to show that these cells could meet both early AEMFC and mature PEMFC targets^{56,57}. These very low PGM loading cells were able to support a high peak power density of 1.3 W cm⁻² under H₂/O₂ reacting gases (Figure 6d), yielding a remarkable specific power output of 16 W mg⁻¹_{Pt}, the highest of any AEMFC reported to date (Figure 7). Under steady-state operation at 1 A cm⁻², the low loading cell was able to achieve a stable operating voltage of 0.66V (Figure 6f), which not only presents the first time that any AEMFC has met the 2022 performance milestone but it was able to do so with 62% of the “allowed” PGM loading for AEMFCs and exactly the allowable target for PEMFCs (the DOE 2020 PGM target for PEMFCs is 0.125mg_{PGM} cm⁻²^{56,57}). The promising results in Figure 6 clearly demonstrate that ultra-low-loading PGM AEMFCs are coming closer to a reality. By meeting the 2022 DOE milestone, and showing that PGM-free AEMFC cathodes can clearly surpass the long-difficult DOE target of 44 mA/cm², this moves the field forward towards the eventual goal: completely PGM-free AEMFCs with high performance and long life.

3. Conclusions

In this study, a commercial Fe-N-C-based PGM-free non-CRM catalyst has been tested that, for the first time, yields the ability to replace PGM-based catalysts in AEMFC cathodes without a severe loss in performance. RDE measurements showed that the Fe-N-C catalyst had high activity, with a half-wave potential of 0.846V and full 4-electron reduction of oxygen across the potential range of utilization (0.5 – 0.85 V vs. RHE). When integrated into a H₂/O₂ AEMFCs, the cathodes made with this Fe-N-C electrocatalyst is the first to date to achieve a peak power density of $> 2 \text{ W cm}^{-2}$ (with mass-transport controlled current density of $> 7 \text{ A cm}^{-2}$). The catalyst also showed excellent in-situ kinetics. Specifically, at 0.9 V (iR-free) a current density of 100 mA cm^{-2} was achieved, exceeding the U.S. Department of Energy target for PGM-free cathodes of 44 mA cm^{-2} . Also, it was notable that this non-CRM catalyst was also able to operate stably over an initial 100 h durability test. With a CO₂-free air fed to the cathode, the Fe-N-C AEMFC is also the first to achieve a milestone 1 W cm^{-2} (mass-transport controlled current density of 3.6 A cm^{-2}). In a second configuration, the Fe-N-C cathode was paired with a low-loading PtRu/C anode electrode to create AEMFCs with a total PGM loading of only $0.125 \text{ mg}_{\text{PtRu}} \text{ cm}^{-2}$ ($0.08 \text{ mg}_{\text{Pt}} \text{ cm}^{-2}$), which achieved a peak power output of $10.4 \text{ W mg}_{\text{PGM}}^{-1}$ ($16.3 \text{ W mg}_{\text{Pt}}^{-1}$) and is the world-first to exceeded the U.S. Department of Energy 2022 milestone for AEMFC initial performance.

4. Methods

4.1. Catalyst Synthesis and Characterization

The Fe-N-C catalyst used in this work is commercially available from Pajarito Powder LLC (PMF11904). It is manufactured using the VariPore™ method, which was modified for this material to use Pipemidic acid (PA) instead of other common materials such as

aminoantipyrine (AAPyr). There two main reasons for selection of PA. The first is related to higher nitrogen content because the ratio between C-N_x, as well as amount of carbon atoms, helps to drive the formation of Fe-N-C catalysts with a higher density of Fe-N_x centers. The more carbon you have, the higher the number of positions in the graphene sheets that are available for the insertion of active sites. PA has more than 20% higher of carbon in the structure compared to AAPyr). The second, and main, reason that PA was used is that the amino groups in AAPyr are easily oxidized (even at room temperature) by iron nitrate and do not participate in formation of Fe-N_x active sites.

Related to the synthesis procedure, in short, the transition metal precursor (iron nitrate, 80g) was mechanically mixed with PA (150g) and a medium surface area fumed silica (Cabot Cab-O-sil® LM-150, 50g). The homogeneous powder was dried and then pyrolyzed in an inert environment (Ultra High Purity, UHP, N₂) at 95 °C for 90 min. After heat treatment, silica was removed by 25wt% HF, followed by washing with DI water until a neutral pH was achieved. The obtained powder was thermally dried at 85 °C. To remove as many metallic Fe particles as possible, the catalysts were acid treated with nitric acid and then exposed to a final high temperature treatment in UHP nitrogen atmosphere at 1000 °C for 45min.

4.2. Electron Microscopy

A ZEISS Gemini 500, 0.02 – 30 kV Ultraplus Thermal FESEM equipped with Inlens secondary electron detector and EDS (energy dispersive x-ray spectroscopy) detector was used to evaluate the catalyst pore structure and elemental distribution. The SEM images were collected with a 5 kV electron beam, while the EDS mapping was carried out with a 20 kV electron beam. A Hitachi HT7800 RuliTEM, 20-120 kV TEM equipped with a standard lens

for unsurpassed high contrast and resolution of 0.204 nm (Off-axis, 100 kV) was used to capture bright-field images of the catalyst. The catalyst was deposited onto a holly carbon-coated TEM copper grid. TEM images were captured with a 100 kV electron beam.

An imaging JEOL 2100F 200 kV scanning transmission electron microscope (STEM) equipped with a CEOS Cs corrector on the illumination system was used to characterize the catalyst via Z-contrast imaging. High angle annular dark-field (HAADF) STEM images were captured with a Fischione Model 3000 HAADF detector with a camera length such that the detector spanned 50 - 250 mrad. The scanning acquisition was synchronized to 60 Hz AC electrical power to minimize 60 Hz noise in the images, and a pixel dwell time of 15.7 μ s was chosen. The catalyst was suspended in IPA and dispersed using ultrasonic vibration for 1 min. Then, a droplet of the suspension was placed on the holly carbon-coated (mesh 200, SPI Inc.) TEM copper grid using a platinum ring. A filter paper underneath the TEM grid absorbed the liquid that passed through the carbon-coated TEM grid, and small particles were deposited on the carbon mesh. The sample was cleaned using an electron beam shower under vacuum for 15 min to clean the surface of chemical residue.

4.3. Electrochemical Measurements - (RRDE)

All electrochemical measurements were performed on a thin-film rotating ring disk electrode (RRDE) in a customized three-electrode cell (Adams & Chittenden Scientific Glass) using a platinum mesh as the counter electrode and a double junction Ag/AgCl reference electrode (Pine Research Instrumentation, 4 M aqueous KCl internal solution). Cyclic voltammograms and ORR polarization curves were recorded using an Autolab PGSTA302N potentiostat. The working electrodes using Fe-N-C catalyst were prepared on a glassy carbon

disk electrode The working electrode was a rotating ring-disk electrode (E6R2 Fixed-Disk RRDE Tips PEEK ,Pine Research Instrumentation) with a Pt ring (geometric surface area: disk: 0.237 cm²) and a glassy carbon disk (geometric surface area: disk: 0.235 cm²). by dropping 8.5 µL of a catalyst ink with the following composition onto the electrode: 5 mg of PGM-free catalyst, 744 µL of IPA, 92 µL of DI water, and 54 µL of 5 wt% Nafion ionomer dispersion (DuPont). The pH of the ink was adjusted to 10 by adding aqueous 0.1 M KOH. For Pt/C (Alfa Aesar HiSPEC 4000, Pt nominally 40 wt%, supported on Vulcan XC-72R carbon) working electrodes, 4.2 µL of a catalyst ink with the following composition was deposited onto the electrode: 2.5 mg catalyst, 744 µL IPA, 92 µL DI water and 54 µL 5wt% Nafion ionomer dispersion (DuPont). All of the films were dried on a leveled, inverted rotator at 700 rpm at room temperature. Prior to thin-film deposition, the glassy carbon electrodes were polished with a 0.05 µm alumina suspension and carefully washed with 18.2 MΩ cm Millipore ultrapure water (UPW) and dried in air for 20 min. The Fe-N-C catalyst loading on the glassy carbon was 200 µg cm⁻² and the Pt loading was 20 µg cm⁻². The three-electrode cell was washed using the UPW and aqueous 0.1 M KOH (10 times and 5 times before use, respectively).

The disk electrode was rotated at 1600 rpm with scan rate of 10 mV/s in potential range of 0.2 V- 1.05 V vs RHE. The ring electrode potential was set to 1.1 V vs. RHE. The hydrogen peroxide yield (%H₂O₂) and electron transfer number (*n*) were calculated by the following Equation 1 and Equation 2, respectively⁵⁸.

$$H_2O_2\% = 200 \times \frac{i_r}{i_d + \frac{i_r}{N_c}} \quad (1)$$

$$n = 4 \times \frac{i_d}{i_d + \frac{i_r}{N_c}} \quad (2)$$

Where: *n* is the number of electrons transferred per reacting oxygen, *i_d* is the disk current, *i_r* is the ring current, and *N_C* is the collection efficiency of the RRDE (38%)

4.4. GDE Fabrication and AEMFC Testing

To prepare anode and cathode GDEs, inks were prepared from a combination of the catalyst powder, ionomer powder, and solvent^{7,40}. For all the experiments, the cathode catalyst was the Fe-N-C described above, except for one control experiment where the cathode catalyst was a commercial Pt/C (Alfa Aesar HiSPEC 4000, Pt nominally 40 wt%, supported on Vulcan XC-72R carbon). The anode catalyst was PtRu/C (Alfa Aesar HiSPEC 10000, Pt nominally 40wt%, and Ru, nominally 20wt%, supported on Vulcan XC-72R carbon).

Ink preparation began by grinding an ETFE-based radiation-grafted benzyltrimethylammonium-type powder anionomer (AEI IEC = 1.24 ± 0.06 mmol g⁻¹)⁵⁹ in a well-cleaned mortar and pestle for 10 min to reduce the number of large agglomerated particles. Next, the catalyst and 1 mL of UPW was added to the mortar and ground for an additional 10 min until a visually homogeneous slurry was formed. The AEI powder mass comprised 20wt% of the total solid mass of all of the catalyst layers (CLs) in this paper. After the slurry was homogenized, 1.5 mL of IPA was added into the mortar, followed by another 5 min of grinding. A final 5 mL of IPA was added to the mortar, and the final ink mixture was transferred to a PTFE- lined vial and sonicated for 1 h in an ice bath to make an ink. The ink was sprayed onto the gas diffusion layer (GDL, Toray TGP-H-60, 5 wt% PTFE wet proofing) using an air-assisted sprayer (Iwata) to fabricate the GDEs. The target loading for the cathode GDEs was 1 mg_{Fe-N-C} cm⁻². The standard target loading for the anode GDEs was 0.6 mg_{PtRu} cm⁻². It should also be noted that additional carbon and were PTFE (8 wt %) was added to the anode catalyst layers per our typical procedure¹⁴ to obtain a AEI:C:Pt ratio of 0.417:1.5:1.

To remove impurities and ion exchange the quaternary ammonium groups, the anode GDE, cathode GDE, and anion exchange membrane (AEM) were hydrated in DI water for 20 min and then soaked three times in aqueous 1.0 M KOH. The AEMs used in this study were radiation-grafted high-density polyethylene (HDPE) type with covalently-bound benzyltrimethylammonium (BTMA) cationic head-groups (20 μm when hydrated, IEC = 2.4 mmol g^{-1}).⁶⁰ Cells were assembled in-cell without prior hot pressing in 5 cm^2 active area Scribner hardware with single channel serpentine flow fields. The average thickness of anode and cathode was measured to be 216 and 270 μm , respectively. Thus, 152 and 203 μm Teflon gaskets were used on anode and cathode, respectively, to maintain a pinch around 25%. The AEMFCs were controlled by a Scribner 850e fuel cell test station. After a break-in procedure, the relative humidity (RH) of both the cathode and anode were adjusted to optimize the cell performance at the operating cell temperature (either 65 or 80°C). The gases used in this study were ultra-high purity (UHP) H_2 , UHP O_2 and simulated CO_2 -free air (a mix of UHP N_2 and O_2) from Airgas.

4.5. Low PGM AEMFC electrodes fabrication.

The low Pt loading anode Gas diffusion electrode (GDE) was fabricated by introducing a microporous layer (MPL) onto the Toray GDL (TGP-H-060 5 wt% wet proofed) with a subsequent catalyst layer deposition. In this fabrication technique, two types of inks were prepared separately and sprayed onto the GDL. Firstly, the ink for MPL was prepared by mixing AEI with carbon (Vulcan XC-72R)(AEI:C ratio of 0.417:1 wt) and PTFE (8 wt%). The AEI was soaked in DI water for 30 min before the Vulcan and PTFE were added. The

ingredients were mixed to form uniform slurry. IPA was used as solvent and was added to the slurry to make a dilute mixture which was then transferred to a vial and sonicated for 1 h to make uniform ink. The same procedure was applied to make the catalyst ink where, AEI, PtRu-based electrocatalyst, additional Vulcan and (AEI:C:Pt ratio of 0.417:1.5:1 wt) PTFE (8 wt%) were used.. The MPL was built by spraying the first ink on the GDL and then the catalyst layer was built by spraying second ink onto the MPL. The PGM loading was calculated by mass difference before and after spraying.

Data Availability

The data that supports the plots within this paper and other findings of this study are available from the corresponding author upon reasonable request.

Code Availability

The code that supports the data processing within this paper and other findings of this study are available from the corresponding author upon reasonable request.

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References:

1. U.S. Department of Energy. Fuel Cell Technologies Program Multi-Year Research, Development, and Demonstration Plan. *Energy Efficiency and Renewable Energy* 3.4–1 <https://www.energy.gov/eere/fuelcells/downloads/fuel-cell-technologies-office-multi-year-research-development-and-22>.
2. U.S. Department of Energy. Fuel Cell Technical Team Roadmap. *Energy Efficiency and Renewable Energy* 1–26 (2013).
3. James, B. D. & Spisak, A. B. Mass production cost estimation of direct H₂ PEM fuel cell systems for transportation applications: 2012 update. *Rep. by Strateg. Anal. Inc., under Award Number DEEE0005236 US Dep. Energy* **18**, (2012).
4. James, B. 2018 Cost Projections of PEM Fuel Cell Systems for Automobiles and Medium-Duty Vehicles. *Energy Efficiency and Renewable Energy* 1–44 https://www.energy.gov/sites/prod/files/2018/04/f51/fcto_webinarslides_2018_costs_pe_m_fc_autos_trucks_042518.pdf (2018).
5. Satyapal, S. *2017 Annual Progress Report: DOE Hydrogen and Fuel Cells Program*. <https://www.osti.gov/servlets/purl/1460682> (2018).
6. Wang, Y., Wang, G., Li, G., Huang, B., Pan, J., Liu, Q., Han, J., Xiao, L., Lu, J. & Zhuang, L. Pt–Ru catalyzed hydrogen oxidation in alkaline media: oxophilic effect or electronic effect? *Energy Environ. Sci.* **8**, 177–181 (2015).
7. Omasta, T. J., Park, A. M., LaManna, J. M., Zhang, Y., Peng, X., Wang, L., Jacobson, D. L., Varcoe, J. R., Hussey, D. S., Pivovar, B. S. & Mustain, W. E. Beyond catalysis and

membranes: visualizing and solving the challenge of electrode water accumulation and flooding in AEMFCs. *Energy Environ. Sci.* **11**, 551–558 (2018).

8. Huang, G., Mandal, M., Peng, X., Yang-Neyerlin, A. C., Pivovar, B. S., Mustain, W. E. & Kohl, P. A. Composite Poly(norbornene) Anion Conducting Membranes for Achieving Durability, Water Management and High Power (3.4 W/cm²) in Hydrogen/Oxygen Alkaline Fuel Cells. *J. Electrochem. Soc.* **166**, F637–F644 (2019).

9. Wang, L., Peng, X., Mustain, W. E. & Varcoe, J. R. Radiation-grafted anion-exchange membranes: the switch from low-to high-density polyethylene leads to remarkably enhanced fuel cell performance. *Energy Environ. Sci.* **12**, 1575–1579 (2019).

10. Maurya, S., Noh, S., Matanovic, I., Park, E. J., Villarrubia, C. N., Martinez, U., Han, J., Bae, C. & Kim, Y. S. Rational design of polyaromatic ionomers for alkaline membrane fuel cells with > 1 W cm⁻² power density. *Energy Environ. Sci.* **11**, 3283–3291 (2018).

11. Wang, T., Shi, L., Wang, J., Zhao, Y., Setzler, B. P., Rojas-Carbonell, S. & Yan, Y. High-Performance Hydroxide Exchange Membrane Fuel Cells through Optimization of Relative Humidity, Backpressure and Catalyst Selection. *J. Electrochem. Soc.* **166**, F3305–F3310 (2019).

12. Li, Q., Peng, H., Wang, Y., Xiao, L., Lu, J. & Zhuang, L. The Comparability of Pt to Pt-Ru in Catalyzing the Hydrogen Oxidation Reaction for Alkaline Polymer Electrolyte Fuel Cells Operated at 80 °C. *Angew. Chemie Int. Ed.* **58**, 1442–1446 (2019).

13. Mandal, M., Huang, G., Hassan, N. U., Peng, X., Gu, T., Brooks-Starks, A. H., Bahar, B., Mustain, W. E. & Kohl, P. A. The Importance of Water Transport in High Conductivity and High-Power Alkaline Fuel Cells. *J. Electrochem. Soc.* **167**, (2020).

- 509 14. Ul Hassan, N., Mandal, M., Huang, G., Firouzjaie, H. A., Kohl, P. A. & Mustain, W. E.
510 Achieving High-Performance and 2000 h Stability in Anion Exchange Membrane Fuel
511 Cells by Manipulating Ionomer Properties and Electrode Optimization. *Adv. Energy*
512 *Mater.* **n/a**, 2001986 (2020).
- 513 15. Setzler, B. P., Zhuang, Z., Wittkopf, J. A. & Yan, Y. Activity targets for nanostructured
514 platinum-group-metal-free catalysts in hydroxide exchange membrane fuel cells. *Nat.*
515 *Nanotechnol.* **11**, 1020 (2016).
- 516 16. Greeley, J., Stephens, I. E. L., Bondarenko, A. S., Johansson, T. P., Hansen, H. A.,
517 Jaramillo, T. F., Rossmeisl, J., Chorkendorff, I. & Nørskov, J. K. Alloys of platinum and
518 early transition metals as oxygen reduction electrocatalysts. *Nat. Chem.* **1**, 552–556
519 (2009).
- 520 17. Sheng, W., Gasteiger, H. A. & Shao-Horn, Y. Hydrogen oxidation and evolution reaction
521 kinetics on platinum: acid vs alkaline electrolytes. *J. Electrochem. Soc.* **157**, B1529–
522 B1536 (2010).
- 523 18. Miller, H. A. & Vizza, F. Electrocatalysts and Mechanisms of Hydrogen Oxidation in
524 Alkaline Media for Anion Exchange Membrane Fuel Cells BT - Anion Exchange
525 Membrane Fuel Cells: Principles, Materials and Systems. in (eds. An, L. & Zhao, T. S.)
526 79–103 (Springer International Publishing, 2018). doi:10.1007/978-3-319-71371-7_3.
- 527 19. Omasta, T. J., Zhang, Y., Park, A. M., Peng, X., Pivovar, B., Varcoe, J. R. & Mustain,
528 W. E. Strategies for reducing the PGM loading in high power AEMFC anodes. *J.*
529 *Electrochem. Soc.* **165**, F710–F717 (2018).
- 530 20. Firouzjaie, H. A. & Mustain, W. E. Catalytic Advantages, Challenges, and Priorities in

- 531 Alkaline Membrane Fuel Cells. *ACS Catal.* **10**, 225–234 (2020).
- 532 21. Yang, X., Zhang, G., Du, L., Zhang, J., Chiang, F.-K., Wen, Y., Wang, X., Wu, Y., Chen,
533 N. & Sun, S. PGM-Free Fe/N/C and Ultralow Loading Pt/C Hybrid Cathode Catalysts
534 with Enhanced Stability and Activity in PEM Fuel Cells. *ACS Appl. Mater. Interfaces* **12**,
535 13739–13749 (2020).
- 536 22. Mustain, W. E. Understanding how high-performance anion exchange membrane fuel
537 cells were achieved: Component, interfacial, and cell-level factors. *Curr. Opin.*
538 *Electrochem.* (2018).
- 539 23. Mustain, W. E., Chatenet, M., Page, M. & Kim, Y. S. Durability challenges of anion
540 exchange membrane fuel cells. *Energy Environ. Sci.* (2020) doi:10.1039/D0EE01133A.
- 541 24. Davydova, E. S., Mukerjee, S., Jaouen, F. & Dekel, D. R. Electrocatalysts for Hydrogen
542 Oxidation Reaction in Alkaline Electrolytes. *ACS Catal.* **8**, 6665–6690 (2018).
- 543 25. Jiang, L., Hsu, A., Chu, D. & Chen, R. Oxygen Reduction Reaction on Carbon Supported
544 Pt and Pd in Alkaline Solutions. *J. Electrochem. Soc.* **156**, B370 (2009).
- 545 26. Analysis and Optimization of Transport Losses in Hydroxide Exchange Membrane Fuel
546 Cells. *ECS Meet. Abstr.* (2019) doi:10.1149/ma2019-02/36/1693.
- 547 27. Kabir, S., Lemire, K., Artyushkova, K., Roy, A., Odgaard, M., Schlueter, D.,
548 Oshchepkov, A., Bonnefont, A., Savinova, E. & Sabarirajan, D. C. Platinum group
549 metal-free NiMo hydrogen oxidation catalysts: high performance and durability in
550 alkaline exchange membrane fuel cells. *J. Mater. Chem. A* **5**, 24433–24443 (2017).
- 551 28. Peng, X., Kashyap, V., Ng, B., Kurungot, S., Wang, L., Varcoe, R. J. & Mustain, E. W.

- 552 High-Performing PGM-Free AEMFC Cathodes from Carbon-Supported Cobalt Ferrite
553 Nanoparticles. *Catalysts* vol. 9 (2019).
- 554 29. Yang, Y., Peng, H., Xiong, Y., Li, Q., Lu, J., Xiao, L., DiSalvo, F. J., Zhuang, L. &
555 Abruña, H. D. High-Loading Composition-Tolerant Co–Mn Spinel Oxides with
556 Performance beyond 1 W/cm² in Alkaline Polymer Electrolyte Fuel Cells. *ACS Energy*
557 *Lett.* **4**, 1251–1257 (2019).
- 558 30. Hossen, M. M., Artyushkova, K., Atanassov, P. & Serov, A. Synthesis and
559 characterization of high performing Fe-N-C catalyst for oxygen reduction reaction (ORR)
560 in Alkaline Exchange Membrane Fuel Cells. *J. Power Sources* **375**, 214–221 (2018).
- 561 31. Woo, J., Yang, S. Y., Sa, Y. J., Choi, W.-Y., Lee, M.-H., Lee, H.-W., Shin, T. J., Kim,
562 T.-Y. & Joo, S. H. Promoting Oxygen Reduction Reaction Activity of Fe–N/C
563 Electrocatalysts by Silica-Coating-Mediated Synthesis for Anion-Exchange Membrane
564 Fuel Cells. *Chem. Mater.* **30**, 6684–6701 (2018).
- 565 32. Hu, H.-S., Liu, R.-J., Si, S., Kong, D.-S. & Feng, Y.-Y. Iron and nitrogen codoped carbon
566 catalyst with excellent stability and methanol tolerance for oxygen reduction reaction.
567 *Int. J. Energy Res.* **43**, 7107–7119 (2019).
- 568 33. Gokhale, R., Chen, Y., Serov, A., Artyushkova, K. & Atanassov, P. Direct synthesis of
569 platinum group metal-free Fe-N-C catalyst for oxygen reduction reaction in alkaline
570 media. *Electrochem. commun.* **72**, 140–143 (2016).
- 571 34. Santori, P. G., Speck, F. D., Cherevko, S., Firouzjaie, H. A., Peng, X., Mustain, W. E. &
572 Jaouen, F. High Performance FeNC and Mn-oxide/FeNC Layers for AEMFC Cathodes.
573 *J. Electrochem. Soc.* **167**, 134505 (2020).

- 574 35. Li, Z., Li, G., Jiang, L., Li, J., Sun, G., Xia, C. & Li, F. Ionic Liquids as Precursors for
575 Efficient Mesoporous Iron-Nitrogen-Doped Oxygen Reduction Electrocatalysts. *Angew.
576 Chemie Int. Ed.* **54**, 1494–1498 (2015).
- 577 36. Li, Z. Q., Lu, C. J., Xia, Z. P., Zhou, Y. & Luo, Z. X-ray diffraction patterns of graphite
578 and turbostratic carbon. *Carbon N. Y.* **45**, 1686–1695 (2007).
- 579 37. Xu, X., Shi, C., Li, Q., Chen, R. & Chen, T. Fe–N-Doped carbon foam nanosheets with
580 embedded Fe₂O₃ nanoparticles for highly efficient oxygen reduction in both alkaline and
581 acidic media. *RSC Adv.* **7**, 14382–14388 (2017).
- 582 38. Yan, Z., Dai, C., Zhang, M., Lv, X., Zhao, X. & Xie, J. Nitrogen doped porous carbon
583 with iron promotion for oxygen reduction reaction in alkaline and acidic media. *Int. J.
584 Hydrogen Energy* **44**, 4090–4101 (2019).
- 585 39. Huo, L., Liu, B., Zhang, G., Si, R., Liu, J. & Zhang, J. 2D Layered non-precious metal
586 mesoporous electrocatalysts for enhanced oxygen reduction reaction. *J. Mater. Chem. A*
587 **5**, 4868–4878 (2017).
- 588 40. Omasta, T. J., Wang, L., Peng, X., Lewis, C. A., Varcoe, J. R. & Mustain, W. E.
589 Importance of balancing membrane and electrode water in anion exchange membrane
590 fuel cells. *J. Power Sources* **375**, 205–213 (2018).
- 591 41. Peng, X., Kulkarni, D., Huang, Y., Omasta, T. J., Ng, B., Zheng, Y., Wang, L., LaManna,
592 J. M., Hussey, D. S., Varcoe, J. R., Zenyuk, I. V & Mustain, W. E. Using operando
593 techniques to understand and design high performance and stable alkaline membrane fuel
594 cells. *Nat. Commun.* **11**, 3561 (2020).

- 595 42. Uddin, A., Dunsmore, L., Zhang, H., Hu, L., Wu, G. & Litster, S. High Power Density
596 Platinum Group Metal-free Cathodes for Polymer Electrolyte Fuel Cells. *ACS Appl.*
597 *Mater. Interfaces* **12**, 2216–2224 (2020).
- 598 43. Wang, L., Bellini, M., Miller, H. A. & Varcoe, J. R. A high conductivity ultrathin anion-
599 exchange membrane with 500+ h alkali stability for use in alkaline membrane fuel cells
600 that can achieve 2 W cm⁻² at 80 °C. *J. Mater. Chem. A* **6**, 15404–15412 (2018).
- 601 44. Peng, X., Omasta, T. J., Magliocca, E., Wang, L., Varcoe, J. R. & Mustain, W. E.
602 Nitrogen-doped Carbon–CoOx Nanohybrids: A Precious Metal Free Cathode that
603 Exceeds 1.0 W cm⁻² Peak Power and 100 h Life in Anion-Exchange Membrane Fuel
604 Cells. *Angew. Chemie Int. Ed.* **58**, 1046–1051 (2019).
- 605 45. Wan, X., Liu, X., Li, Y., Yu, R., Zheng, L., Yan, W., Wang, H., Xu, M. & Shui, J. Fe–N–
606 C electrocatalyst with dense active sites and efficient mass transport for high-
607 performance proton exchange membrane fuel cells. *Nat. Catal.* **2**, 259–268 (2019).
- 608 46. Fu, X., Zamani, P., Choi, J.-Y., Hassan, F. M., Jiang, G., Higgins, D. C., Zhang, Y.,
609 Hoque, M. A. & Chen, Z. In Situ Polymer Graphenization Ingrained with Nanoporosity
610 in a Nitrogenous Electrocatalyst Boosting the Performance of Polymer-Electrolyte-
611 Membrane Fuel Cells. *Adv. Mater.* **29**, 1604456 (2017).
- 612 47. Shao, Y. Highly Active and Durable PGM-free ORR Electrocatalysts through the
613 Synergy of Active Sites. *Pacific Northwest Natl. Lab.* (2018).
- 614 48. Liu, Q., Liu, X., Zheng, L. & Shui, J. The Solid-Phase Synthesis of an Fe–N–C
615 Electrocatalyst for High-Power Proton-Exchange Membrane Fuel Cells. *Angew. Chemie*
616 *Int. Ed.* **57**, 1204–1208 (2018).

- 617 49. Tatus-Portnoy, Z., Kitayev, A., Vineesh, T. V., Tal-Gutelmacher, E., Page, M. & Zitoun,
618 D. A low-loading Ru-rich anode catalyst for high-power anion exchange membrane fuel
619 cells. *Chem. Commun.* **56**, 5669–5672 (2020).
- 620 50. Dekel, D. R. Review of cell performance in anion exchange membrane fuel cells. *J.*
621 *Power Sources* **375**, 158–169 (2018).
- 622 51. Cheng, J., He, G. & Zhang, F. A mini-review on anion exchange membranes for fuel cell
623 applications: Stability issue and addressing strategies. *Int. J. Hydrogen Energy* **40**, 7348–
624 7360 (2015).
- 625 52. Ramaswamy, N. & Mukerjee, S. Alkaline Anion-Exchange Membrane Fuel Cells:
626 Challenges in Electrocatalysis and Interfacial Charge Transfer. *Chem. Rev.* **119**, 11945–
627 11979 (2019).
- 628 53. Wang, J., Huang, Z., Liu, W., Chang, C., Tang, H., Li, Z., Chen, W., Jia, C., Yao, T.,
629 Wei, S., Wu, Y. & Li, Y. Design of N-Coordinated Dual-Metal Sites: A Stable and
630 Active Pt-Free Catalyst for Acidic Oxygen Reduction Reaction. *J. Am. Chem. Soc.* **139**,
631 17281–17284 (2017).
- 632 54. Banham, D., Kishimoto, T., Zhou, Y., Sato, T., Bai, K., Ozaki, J., Imashiro, Y. & Ye, S.
633 Critical advancements in achieving high power and stable nonprecious metal catalyst–
634 based MEAs for real-world proton exchange membrane fuel cell applications. *Sci. Adv.* **4**,
635 eaar7180 (2018).
- 636 55. Thompson, S. T., Peterson, D., Ho, D. & Papageorgopoulos, D. Perspective—The Next
637 Decade of AEMFCs: Near-Term Targets to Accelerate Applied R&D. *J. Electrochem.*
638 *Soc.* **167**, 84514 (2020).

56. OFFICE, H. A. F. C. T. No Title. *DOE Technical Targets for Polymer Electrolyte Membrane Fuel Cell Components* <https://www.energy.gov/eere/fuelcells/doe-technical-targets-polymer-electrolyte-membrane-fuel-cell-components>.
57. OFFICE, H. A. F. C. T. Fuel Cells. 15–20 (2016).
58. Zhou, R., Zheng, Y., Jaroniec, M. & Qiao, S.-Z. Determination of the Electron Transfer Number for the Oxygen Reduction Reaction: From Theory to Experiment. *ACS Catal.* **6**, 4720–4728 (2016).
59. Poynton, S. D., Slade, R. C. T., Omasta, T. J., Mustain, W. E., Escudero-Cid, R., Ocón, P. & Varcoe, J. R. Preparation of radiation-grafted powders for use as anion exchange ionomers in alkaline polymer electrolyte fuel cells. *J. Mater. Chem. A* **2**, 5124–5130 (2014).
60. Wang, L., Brink, J. J., Liu, Y., Herring, A. M., Ponce-González, J., Whelligan, D. K. & Varcoe, J. R. Non-fluorinated pre-irradiation-grafted (peroxidated) LDPE-based anion-exchange membranes with high performance and stability. *Energy Environ. Sci.* **10**, 2154–2167 (2017).