

Ionomer-free Nanoporous Iridium Nanosheet Electrodes with Boosted Performance and Catalyst Utilization for High-Efficiency Water Electrolyzers

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Abstract

Increasing the catalyst utilization efficiency and simplifying electrode fabrication processes are crucial to accelerate development of low-cost proton exchange membrane electrolyzer cells (PEMECs). Here, we develop a facile route to fabricate ionomer-free iridium nanosheet integrated electrodes, in which nanoporous iridium nanosheets (IrNS) with abundant exposed edges and nanopores are deposited on thin titanium liquid/gas diffusion layers (TT-LGDLs) via a low-temperature chemical synthesis strategy. Benefiting from high catalytic activity, good electrode conductivity and excellent liquid/gas transport properties, such nanoporous IrNS electrodes with low catalyst loadings require low cell voltages of 1.65 V and 1.78 V at 3000 and 6000 mA/cm², respectively. More impressively, a stable performance can be well maintained under extremely high current density tests of 5000 mA/cm², demonstrating the potential of low-loading nanoporous IrNS electrodes in solid-electrolyte based electrochemical conversion cells that require high current density operation.

Keywords: green hydrogen production, nanoporous iridium nanosheets, thin titanium liquid/gas diffusion layers, low catalyst loading, PEM water electrolysis

1. Introduction

The climate change and global decarbonization is deriving the urgent demand for clean energy conversion and storage technologies[1-6]. The proton exchange membrane electrolyzer cell (PEMECs) has emerged as a very promising energy storage technology for hydrogen production from water electrolysis when integrated with solar, wind and other renewable energy sources[2, 3, 7-9]. Compared with conventional water electrolyzer systems, PEMECs have many unique advantages, including high efficiency, quick startup, compact design, low maintenance cost, and close-to-zero emissions. The membrane electrode assembly (MEA) is very important to the overall cell performance and cost of the PEMEC. To achieve high efficiency and long durability of a PEMEC, high loadings of platinum-group metals ($2\sim3.0\text{ mg}_{\text{Ir}}/\text{cm}^2$) are generally required for the oxygen evolution reaction (OER) [5, 10-13].

Currently, the catalyst-coated membrane (CCM) and catalyst-coated porous transport layer as gas diffusion electrode (GDE) are two main electrode designs in PEMECs. Nafion ionomers are commonly applied in anode and cathode catalyst layers (CLs) for both CCM and GDE designs. The main roles of Nafion ionomer in CLs are as follows: 1) serving as proton conductors to facilitate proton transport from PEM to the catalyst surface and to extend the electrode/electrolyte reaction zone; 2) functioning as the binder to physically stabilize the catalysts on the PEM surface. For the CCM design, Bernt *et al.* studied the impact of ionomer content in anode CLs on cell performances and reported that 11.6 wt% Nafion ionomer in $\text{IrO}_2/\text{TiO}_2$ anode CLs showed the best cell performance among the tested anodes with an ionomer content from 2.2 to 28 wt% [14]. Kulkarni *et al.* fabricated ionomer-containing CCMs and GDEs, and compared their cell performances at different catalyst loadings [15]. They found that the ionomer in CLs hinders the catalyst utilization efficiency to some extent in both cases.

Recent studies have demonstrated advantages of ionomer-free electrode designs over conventional ionomer-containing electrodes, including improvement of catalyst utilization efficiency, energy efficiency enhancement, stability and remarkably simplified electrode fabrication steps [16-22]. For example, Sapountzi *et al.* fabricated CCMs with ionomer-free IrO_x and Pt catalyst layers at anode and cathode via a spark ablation process [16]. Such ionomer-free CCMs with low catalyst loadings (0.8 mg_{Ir}/cm², 0.5 mg_{Pt}/cm²) demonstrated significantly improved cell performance compared to conventional ionomer-containing CCMs (2 mg_{IrRuO_x}/cm² at anode, 4 mg_{Pt}/cm² at cathode). More recently, Higashi *et al.* fabricated ionomer-free IrO₂ nanostructured textile based CCMs by the combination of electrospun PVP textiles and subsequent magnetron radiofrequency (RF) sputtering of IrO₂ catalysts and hot-pressing transfer to Nafion 212 membrane [17]. The cell performances at low loading levels of 0.1~0.3 mg_{Ir}/cm² are superior to ionomer-containing electrodes with the similar loadings. However, complicated CCM fabrication process and involvement of expensive electrospinning, sputtering and hot press equipment would limit the scale-up manufacturing, especially for large-size samples. Choe *et al.* reported an ionomer-free GDE design composed of electrodeposited IrO₂ catalysts on the Ti mesh substrate (0.4 mg/cm²), and demonstrated a higher current density of 0.97 A/cm² at 1.6 V and improved stability compared to ionomer-containing IrO₂ GDE [18]. Lim *et al.* fabricated ionomer-free Pt@IrO₂ core-shell structured anodes by using sequential electrodeposition of 0.27 mg_{Pt}/cm² hemispherical Pt particles as support and 0.16 mg_{Ir}/cm² IrO₂ as catalysts on the Ti felt substrate [19]. This electrode with the total precious metal loading of 0.43 mg/cm² displayed enhanced cell performances than electrodeposited IrO₂ anode without Pt support.

To further enhance the catalyst utilization and performance of ionomer-free electrode designs, engineering nanostructures and tuning compositions of catalyst layers as well as

electrode patterns have been explored [15, 17-19, 21, 23-28]. Nevertheless, the cell performance and durability of most previously reported OER electrodes at high current densities are still far from satisfactory for real applications. Therefore, there is a continuing need to optimize the electrolyzer electrode design with minimal catalyst use, and meanwhile to further improve energy efficiency and durability in harsh acidic and oxidizing conditions.

In this study, we report a simple process to prepare ionomer-free iridium nanosheet electrodes, in which nanoporous iridium nanosheets (IrNS) with abundant exposed edges and nanopores are deposited on thin titanium liquid/gas diffusion layers (LGDLs). Different from other reported electrolyzer electrodes in the literature, the nanoporous IrNS electrode has the following unique advantages: (1) Multifunctional TT-LGDLs can minimize ohmic and mass transport losses as compared to conventional 3D porous transport layers (PTLs); (2) The ionomer-free nanoporous iridium catalyst layer can provide abundant reaction sites for electrochemical reactions and significantly reduce the reaction overpotentials or activation losses in a PEMEC. (3) The required loading of catalysts can be greatly reduced from several mg/cm^2 down to $0.3 \text{ mg}/\text{cm}^2$ or lower, thus decreasing the catalyst material cost. (4) The whole electrode fabrication and assembly are simplified compared to conventional electrodes (CCM/LGDLs) with multi-step and complicated fabrication processes. Thanks to the above-mentioned benefits, nanoporous IrNS electrodes with low catalyst loadings can deliver the current densities of $2000 \text{ mA}/\text{cm}^2$ at a low cell voltage of 1.78 V when coupled with Nafion 117 ($\sim 175 \text{ }\mu\text{m}$), showing a about 10 times higher mass specific current than that of the conventional CCM baseline. More impressively, when coupled with Nafion 212 ($\sim 50 \text{ }\mu\text{m}$), a higher current density of $6000 \text{ mA}/\text{cm}^2$ can be achieved at the low cell voltage of 1.78 V . The stable cell performances are demonstrated for both Nafion 117 and Nafion 212 cases at high current densities, indicating the

great potential for the application of nanoporous IrNS electrodes in the practical PEMECs under the high current density operation. The whole electrode design in this work can also be generalized to other solid-electrolyte based electrochemical conversion cells that require high current density operation.

2. Experimental section

2.1. Fabrication of ionomer-free IrNS integrated electrodes

TT-LGDLs with distributed circular pores were manufactured by chemical wet etching of titanium foils with the assistance of lithographically-patterned resist masks [29]. TT-LGDLs were cleaned thoroughly by sonication in acetone, ethanol and deionized (DI) water for 15 min in each step. Afterwards, oxalic acid (OA) treatment was performed to remove the native titanium oxide layer from LGDL substrates. The LGDL substrates were completely immersed into the reaction solution containing 1 mL 40 mM IrCl_3 solution (Sigma-Aldrich), 1 mL dimethylformamide (DMF) (Sigma-Aldrich), 1 mL DI water, 1 mL formic acid (Sigma-Aldrich), and 5 mg of poly(ethylene oxide)-b-polystyrene (PEO-b-PS, Polymer Source Inc). The reaction solution was heated at 80 °C for 5 h and cooled down to room temperature. Finally, the IrNS was deposited on the surface of LGDL substrates, forming the nanoporous IrNS electrode. After post-washing with acetone and ethanol for at least three times, the nanoporous IrNS electrode was annealed at 150 °C for 15 min in vacuum for sample characterizations and cell performance testing. The catalyst loadings were achieved and determined by measuring the mass difference before and after the IrNS deposition on the employed LGDL substrate. Afterwards, based on the wetted surface area of the substrate, the catalyst loading is calculated.

2.2. Materials characterization

The surface morphology and chemical composition of nanoporous IrNS electrodes were characterized by a field emission scanning electron microscope (SEM) (JSM-IT700HR), which is equipped with energy-dispersive X-ray spectroscopy (EDS). The nanostructure of IrNS catalysts was characterized by aberration-corrected scanning transmission electron microscopy (STEM) on a JEOL JEM-ARM200F “NEOARM” operated at an acceleration voltage of 80 kV. A Rigaku SmartLab X-ray diffraction (XRD) system was used to investigate the crystalline structure of the sample. The surface chemistry of samples was identified by X-ray photoelectron spectroscopy (XPS) analysis on a Thermo Scientific K-Alpha spectrometer.

2.3. Electrochemical measurements

The as-synthesized IrNS catalysts on Ti substrate as the working electrode, a graphite rod as the counter electrode and an Ag/AgCl reference electrode were employed in a three-electrode system with 0.5 M H₂SO₄ as the liquid electrolyte. The linear sweep voltammetry (LSV) data were collected by a Potentiostat (VSP/VMP3B-100, Bio-Logic) at a scan rate of 5 mV/s at room temperature.

2.4. Cell assembly and performance evaluation of the PEMEC

A carbon paper (Toray 090) (280 μm in thickness, 78% porosity) was used as the cathode LGDL. The grade 2 Ti-made bipolar plate and graphite-made bipolar plate (AXF-5Q) with parallel flow channels were used at anode and cathode, respectively. The nanoporous IrNS electrode, single-sided CCM, and carbon paper, together with the gaskets and the bipolar plates were sandwiched by two stainless steel end-plates to assemble a PEMEC. Afterwards, the PEMEC was compressed by eight evenly distributed ¼ 20 bolts, which were tightened to a torque of 40 lb-in. A schematic illustration of electrode assembly in a PEM water electrolyzer is shown in **Fig. S1**. All the cell tests were performed in a PEM electrolyzer cell with a 5 cm²

active area. A temperature of 80 °C, atmospheric pressure at both anode and cathode, and a water flow rate of 20 mL/min at anode side were used for all cell tests. The commercial cathode-only single-sided CCMs with the Pt black (1.0 mg_{Pt}/cm²) at the cathode and Nafion 117 with a thickness of 175 µm serving as the electrolyte, and the commercial two-sided CCMs with 2.0 mg_{Ir}/cm² IrO_x at the anode, 1.0 mg_{Pt}/cm² Pt black at the cathode and N117 membrane as the baseline were supplied by Nel. The Pt/C (0.14 mg_{Pt}/cm²) at cathode and Nafion 212 with a thickness of ~ 50 µm serving as the electrolyte were home-made by a direct spray coating process, based on the modified recipe in our previous publication [30]. The polarization curves were collected by a Potentiostat (VSP/VMP3B-100, Bio-Logic). The electrochemical impedance spectroscopy (EIS) plots were recorded from 10 kHz to 50 mHz at 1000 mA/cm². The high-frequency resistance (HFR) refers to the ohmic resistance value obtained at high frequencies, which is usually used to represent the total ohmic resistance of the PEM electrolyzer cell. The HFR plots were recorded under the high frequency of ~ 3 kHz by using the Staircase Galvano Electrochemical Impedance Spectroscopy (SGEIS) technique with Biologic EC-Lab software. HFR correction is conducted by using the mean HFR values and current density densities to calculate the HFR-free cell voltages according to the following equation: $V_{\text{HFR-free}} = V_{\text{cell}} - I \cdot \text{HFR}$. With the help of HFR-correction, the activation losses between the IrNS electrode and CCM baseline in the PEMECs can be directly compared.

3. Results and discussions

3.1 Morphology and crystal structure of nanoporous IrNS electrode

The schematic in **Fig. 1** illustrates the cost-effective and facile fabrication of the nanoporous IrNS integrated electrode via a low-temperature chemical synthesis approach. The microstructures (e.g., pore size, porosity, etc.) of the TT-LGDL substrate have been

systematically studied and optimized in our previous research. For instance, the TT-LGDL with the pore size of 100 μm and thickness of 25 μm exhibited over 9% energy efficiency enhancement at 2000 mA/cm^2 and enhanced mass transport properties compared to conventional 350- μm -thick Ti felt LGDLs [29]. Moreover, with the same porosity, the TT-LGDL with the pore size of 100 μm displayed smaller activation and mass transport losses than TT-LGDLs with larger pore sizes of 200 and 300 μm [20]. As a proof of concept, we selected the TT-LGDL with ~ 100 μm pore size and $\sim 40\%$ porosity as the substrate for deposition of the IrNS on TT-LGDLs in this study. The surface-treated TT-LGDL substrates were completely immersed into the reaction solution and kept at 80 $^{\circ}\text{C}$ for 5 h to obtain the nanoporous IrNS electrode, in which IrNS was deposited on the modified TT-LGDL substrates. During the synthesis process, the reducing agent of formic acid (HCOOH) undergoes decomposition and generates the carbon monoxide (CO) molecules. Previous studies have demonstrated that CO is capable of strongly binding to the specific crystal facets of diverse catalytic metals (e.g., Ir, Pd, etc.), facilitating the two-dimensional (2D) nanosheet formation [31, 32]. With the help of block polymer PEO-*b*-PS template, Ir nanocrystals nucleate and grow into 2D Ir nanosheets with numerous nanopores. In addition to the nanopore formation on the basal planes of Ir nanosheets, the secondary porous structure with large pores is also constructed among individual nanosheets during the continuous growth process.

Different nanoporous IrNS catalyst loadings can be achieved by merely adjusting the iridium precursor concentrations under the same reaction time and temperature. Based on our experimental results, the minimum concentration of the Ir chemical precursor (IrCl_3) of at least 40 mM is required for successful and relatively uniform deposition of IrNS on the LGDL substrate. The amount of iridium loss during the deposition process is about 10%. Increasing the

Ir concentration would result in the IrNS loading increase on the employed LGDL substrate without altering the nanostructures of IrNS catalysts. Conversely, when the IrCl_3 concentration is lower than 40 mM, the deposition of IrNS catalysts on the LGDL substrate becomes non-uniform. Our research work is still ongoing to better understand IrNS deposition mechanism on the LGDL substrate.

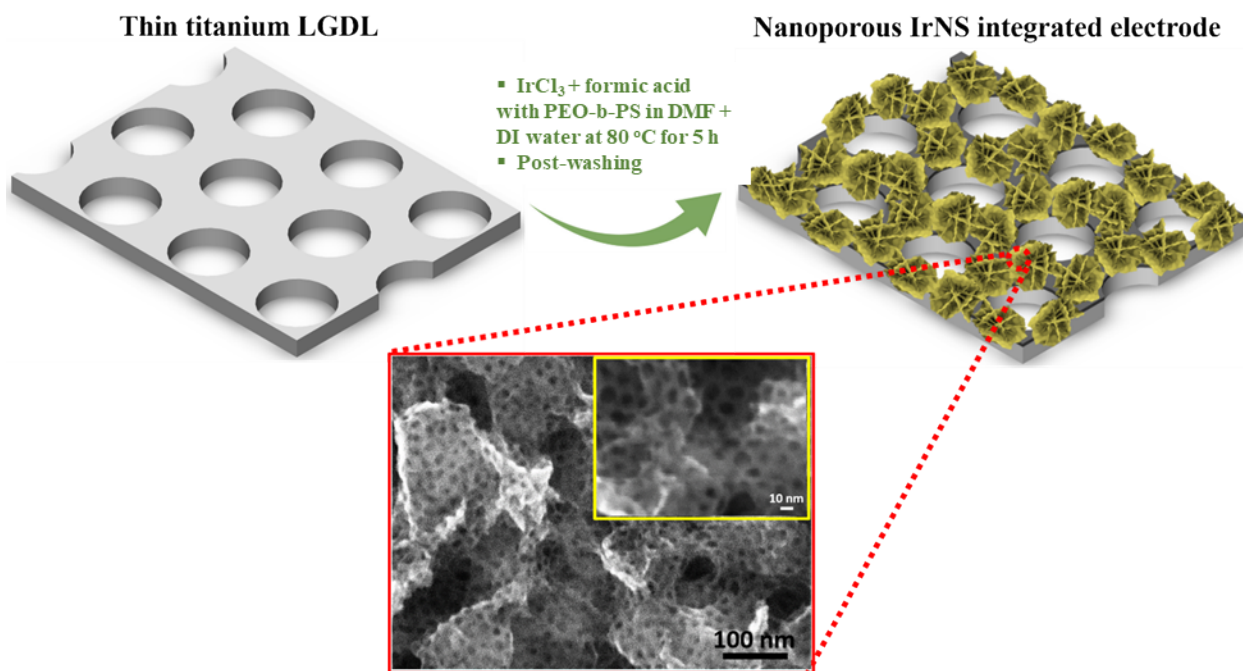


Fig. 1. Schematic illustrating the design of the nanoporous IrNS integrated electrode composed of *in-situ* deposited ultrathin nanoporous iridium nanosheets on thin titanium LGDLs via a low-temperature chemical synthesis strategy.

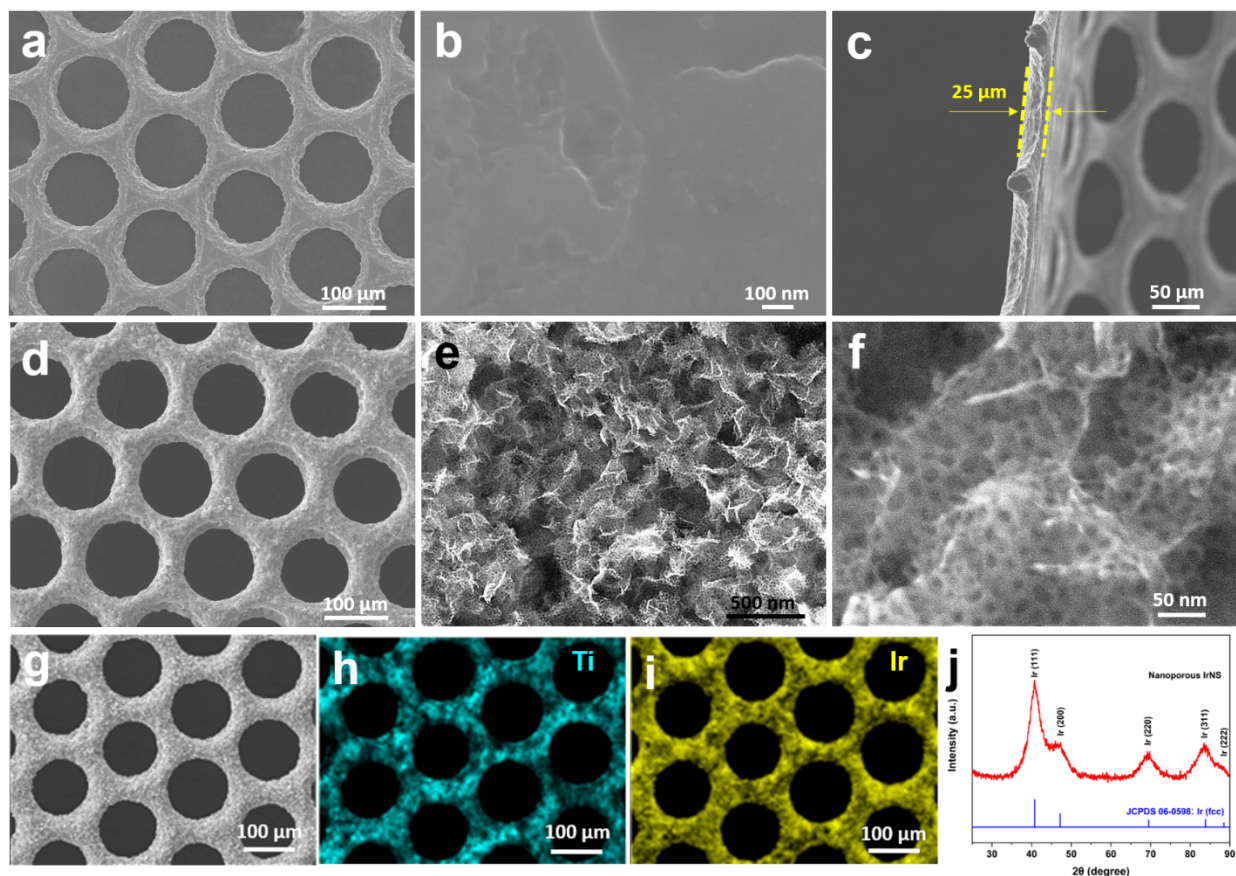


Fig. 2. Morphological and compositional characterizations. (a-b) Top-view and (c) cross-section SEM images of the employed TT-LGDL substrate. (d-f) SEM images of the nanoporous IrNS integrated electrode. (g-i) SEM-EDS elemental mapping of the electrode. (j) XRD pattern of the nanoporous IrNS catalysts.

The morphology, nanostructure and elemental composition of the nanoporous IrNS integrated electrode were first characterized by SEM and EDS techniques. As shown in **Fig. 1**, the applied TT-LGDL substrate in this study shows relative smooth surface and well-defined circular pore morphology with the average pore size of $\sim 100 \mu\text{m}$, calculated porosity of $\sim 40\%$ and $\sim 25 \mu\text{m}$ in thickness. The high-resolution SEM images in **Fig. 2d-2f** reveal that nanoporous IrNS catalysts with abundant exposed active edges were successfully deposited on a surface-treated TT-LGDL substrate with a full surface coverage and good uniformity. The SEM images

and corresponding EDS maps in **Fig. 2g-2i** and **Fig. S2** show the relatively homogenous elemental distribution of Ir across the entire nanoporous IrNS integrated electrode, further confirming the uniform surface coverage of IrNS on the TT-LGDL substrate. To study the crystal structure of as-synthesized nanoporous IrNS catalysts, the catalysts and the underlying substrate were separated by sonication and then the catalysts were collected for the XRD measurement. The XRD pattern in **Fig. 2j** indicates that as-synthesized nanoporous IrNS catalysts are polycrystalline and composed of metallic Ir with the fcc crystal structure, which matches well with the standard XRD pattern of Ir fcc (JCPDS No.: 06-0598). There are no detected secondary impurity phases or oxidized Ir phase in the sample. The metallic IrNS is expected to give rise to better conductivity of the entire catalyst layers than other iridium oxide based catalysts. More importantly, the elimination of ionomer in the catalyst layer would also greatly reduce the ohmic resistance of the electrodes in practical PEMECs, especially compared to most commonly used ionomer-mixed catalyst layers. Collectively, the above SEM, EDS and XRD characterization results demonstrate the successful fabrication of ionomer-free nanoporous IrNS integrated electrodes with desirable nanostructure, good surface coverage and uniformity as well as the dominant metallic IrNS.

3.2 Nanostructure of nanoporous IrNS catalysts

To obtain more detailed structural information, high-angle annular dark-field (HAADF)-STEM images of as-synthesized IrNS catalysts were obtained. As seen from STEM images in **Fig. 3a**, nanopores are formed within the individual nanosheets. The measured lattice fringes in **Fig. 3b** are 0.19 and 0.22 nm, corresponding to (002) and (111) planes of the metallic iridium with a fcc crystal structure. The inset in **Fig. 3b** shows the fast Fourier transform (FFT) pattern

calculated from the corresponding green box, further confirming the (111) crystal plane for the metallic iridium.

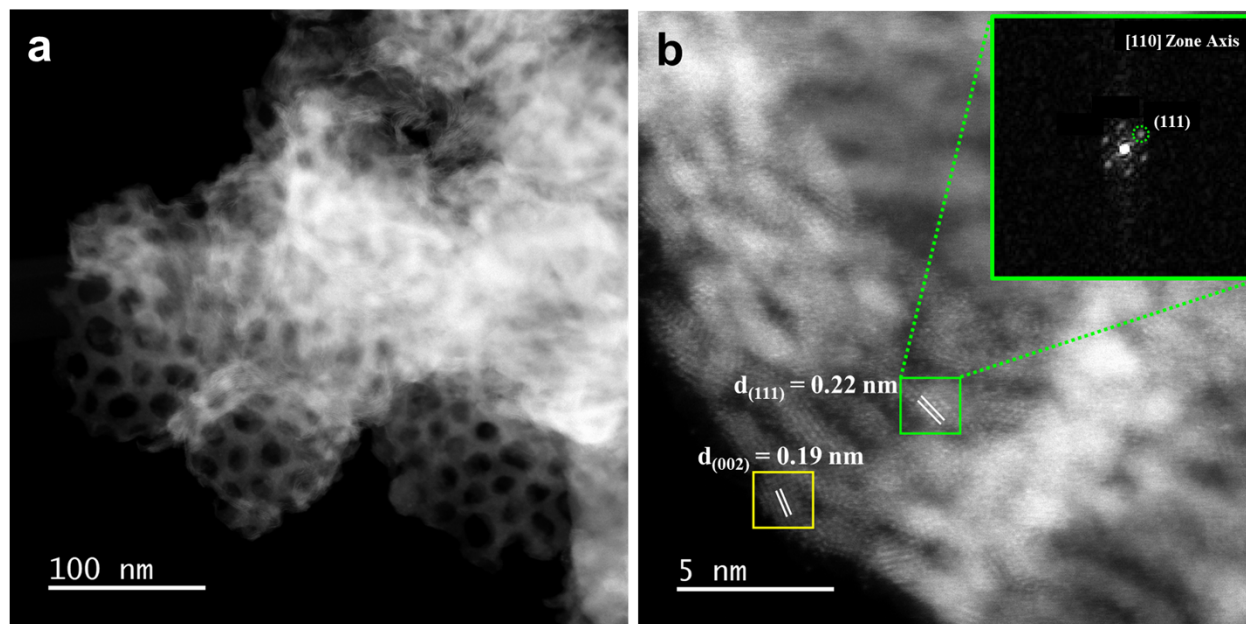


Fig. 3. (a-b) HAADF-STEM images of as-synthesized IrNS catalysts prior to cell test in PEMECs.

3.3 Full cell characterization of nanoporous IrNS in PEMECs with N117 membrane

Prior to the full cell characterization in PEMECs, the intrinsic activity of nanoporous IrNS catalysts for the OER was first evaluated in a half electrochemical cell via a three-electrode system in 0.5 M H₂SO₄ liquid electrolyte. As shown in **Fig. S3**, the nanoporous IrNS electrode displays a low overpotential of 270 mV and small Tafel slope of 53 mV/dec, outperforming benchmarking IrO₂ nanoparticles and other Ir-based OER catalysts in the literatures [40, 55]. The nanosheet structure and nanopores in the individual nanosheets can expose abundant active sites, leading to improved OER performance. When coupled with Nafion 117 (~ 175 μm), the polarization curves in **Fig. 4a** show that the nanoporous IrNS integrated electrode with a low catalyst loading of 0.28 mg_{Ir}/cm² can deliver the current densities of 1000, 2000, 3000 and 4000

mA/cm² at low cell voltages of 1.65, 1.78, 1.90 and 2.02 V, respectively. On the contrary, the conventional CCM/TT-LGDL baseline with a high loading of 2.0 mg_{Ir}/cm² requires a higher cell voltage of 1.88 V at 2000 mA/cm², which is much larger than the nanoporous IrNS electrode by 100 mV. After high-frequency resistance (HFR) correction, nanoporous IrNS electrode displays about 10 mV activation loss reduction in comparison with the high-loaded CCM/TT-LGDL baseline, indicating boosted catalyst utilization with the newly developed nanoporous IrNS electrode design. Furthermore, large ohmic loss generally occurs in PEMECs with the conventional ionomer-mixed MEA, due to the poor conductivity of the entire catalyst layers. For instance, as shown in **Fig. 4b**, the CCM/TT-LGDL baseline exhibits a high average HFR value of 143 mΩ*cm² at 80 °C. However, benefiting from the ionomer-free IrNS catalyst layer, the nanoporous IrNS electrode shows an average HFR value of as small as 101 mΩ*cm², which is about 42 mΩ*cm² smaller than the baseline, which are consistent with the EIS results in **Fig. S4**. Such large HFR reduction results in about 84 mV improvement of the overall cell performance at 2000 mA/cm². The HFR-free EIS analysis at 1000 mA/cm² in **Fig. 4c** shows that the PEMEC with nanoporous IrNS electrode has smaller activation and mass transport losses in total than the CCM/TT-LGDL baseline, as evidenced by the smaller size of semi-arch than the CCM/TT-LGDL baseline. This result implies that the ionomer-free nanoporous IrNS electrode could facilitate the electron transfer across the entire catalyst layer, superior to conventional ionomer-mixed catalyst layers in the CCM-based PEMECs.

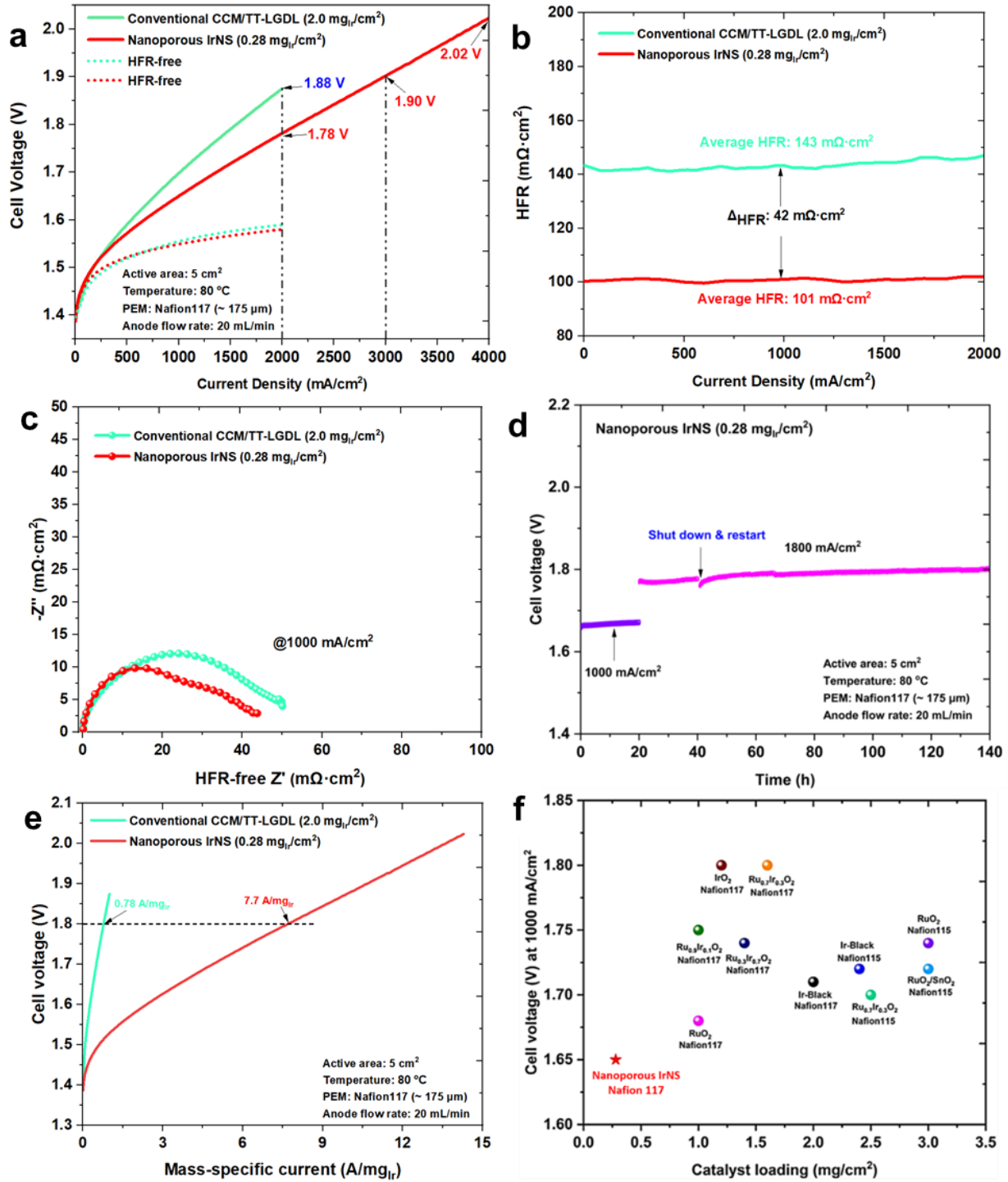


Fig. 4. (a) Polarization curves of a nanoporous IrNS integrated electrode ($0.28 \text{ mg}_{\text{Ir}}/\text{cm}^2$) coupled with Nafion 117 membrane and conventional CCM/TT-LGDL baseline in PEMECs at 80°C . (b) The high-frequency resistance (HFR) comparison between 0 and $2000 \text{ mA}/\text{cm}^2$. (c) The HFR-

free EIS plots of nanoporous IrNS ($0.28 \text{ mg}_{\text{Ir}}/\text{cm}^2$) and conventional CCM/TT-LGDL baseline at $1000 \text{ mA}/\text{cm}^2$. (d) Cell stability test at $1000 \text{ mA}/\text{cm}^2$ for initial 20 hours and subsequent test at $1800 \text{ mA}/\text{cm}^2$ for over 120 h. (e) Mass-specific current comparison. (f) Cell performance comparison of nanoporous IrNS integrated electrodes with previously reported Ir and Ru-based OER electrodes at $1000 \text{ mA}/\text{cm}^2$ in the literature.

To validate the electrode stability in PEMECs, the stability test of nanoporous IrNS electrodes under a high current density of $1800 \text{ mA}/\text{cm}^2$ was conducted. As seen from **Fig. 4d**, after the initial 20-h test at $1000 \text{ mA}/\text{cm}^2$, the cell voltage slightly increases from $\sim 1.762 \text{ V}$ to 1.802 V during the subsequent 120-h test at $1800 \text{ mA}/\text{cm}^2$, displaying a small performance degradation rate of $0.33 \text{ mV}/\text{h}$. To compare the catalyst utilization levels, the mass-specific current plots are derived by normalizing the delivered current to mass for nanoporous IrNS integrated electrode ($0.28 \text{ mg}_{\text{Ir}}/\text{cm}^2$) and conventional CCM/TT-LGDL baseline, as shown in **Fig. 4e**. By comparison, the mass-specific current of nanoporous IrNS integrated electrode is as high as $7.7 \text{ A}/\text{mg}_{\text{Ir}}$ at the cell voltage of 1.8 V , which is about 10 times higher than the CCM/TT-LGDL baseline. This mass-specific current comparison demonstrates that boosted catalyst utilization and performance can be achieved by adopting ionomer-free nanoporous IrNS integrated electrode. Moreover, by comparison with the literature in **Fig. 4f**, the cell performance of the PEMEC with nanoporous IrNS electrode in this study is superior to most previously reported noble metal-based OER electrodes in PEMECs up to date [33-42].

3.4 Full cell characterization of nanoporous IrNS in PEMECs with N212 membrane

To further explore the application of a nanoporous IrNS integrated electrode under high current densities of up to $6000 \text{ mA}/\text{cm}^2$, a thinner Nafion 212 membrane with the thickness of $\sim 50 \mu\text{m}$ was applied for the cell test. The Pt/C ($0.14 \text{ mg}_{\text{Pt}}/\text{cm}^2$) was spray coated onto the Nafion

212 membrane as cathode. As observed from the polarization curve in **Fig. 5a**, low cell voltages of 1.60, 1.65 and 1.78 V were obtained at the current densities of 2000, 3000 and 6000 mA/cm², respectively, which exceeds the U.S. Department of Energy (DOE) 2026 technical performance target (1.8 V at 3000 mA/cm²) [43]. A stable HFR of 39 mΩ*cm² was observed between 0 and 6000 mA/cm² in **Fig. S5**. After HFR-correction, the corresponding HFR-free cell voltages are as low as 1.53 and 1.57 V at 2000 and 6000 mA/cm², respectively.

Currently, various accelerated stress test (AST) protocols are still under development, and the available AST protocols in the literatures are still not able to fully correlate AST results to prediction of real-life durability in commercial PEM water electrolyzer systems. This challenge stems from the involvement of many stressors during the long-term operation conditions, such as high current density, dynamic load operation, on/off operation, temperature, water quality and differential gas pressure [44-46]. Unavoidable coupling effects between these stressors are complicated and have not been clearly understood yet. So far, stability tests of PEM water electrolyzers under constant current densities of 500~2000 mA/cm² have been widely reported in previous publications. In our work, we particularly chose 5000 mA/cm² as the main stressor to evaluate the stability of the nanoporous IrNS electrode. As seen from **Fig. 5b**, our stability AST protocol includes a nominal current density operation at 1800 mA/cm² for 90 h and a subsequent high current density operation at 5000 mA/cm² for 130 h. At both current densities, the nanoporous IrNS electrode displays stable performances. Notably, the degradation rate is only about 3.32 μV/h during the continuous 70-h test within the period of 150-220 h at 5000 mA/cm². Therefore, the developed nanoporous IrNS integrated electrode at low loadings in this work shows the potential applications for the highly efficient and robust OER under high current density operation in practical PEMECs. Except the high current density operation stressor, other

stressors such as dynamic load and differential gas pressure will be incorporated in our future studies.

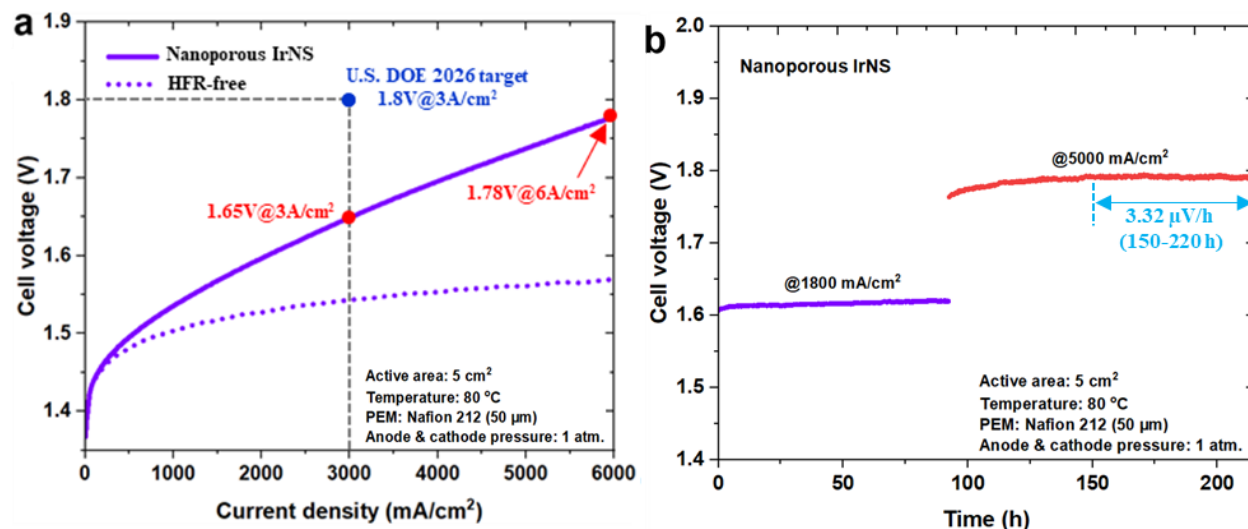


Fig. 5. (a) Polarization curves of a nanoporous IrNS integrated electrode coupled with Nafion 212 membrane under high current densities of up to 6000 mA/cm². (b) Cell stability tests at 1800 mA/cm² for 90 h and 5000 mA/cm² for 130 h.

3.5 Post-analysis of IrNS catalysts after the electrolyzer test

The morphology/nanostructure, crystal structures and chemical compositions of IrNS catalysts after the cell durability test at 5000 mA/cm² were analyzed by using STEM and XPS techniques. The STEM image in **Fig. 6a** verifies that most nanopores are remained in IrNS catalysts but the partial loss of the nanosheet morphology appears after the cell durability test. The observed changes in morphology and nanostructure are probably attributed to the following reasons. First, unavoidable iridium dissolution occurs during the stability test [47]. Second, the bubble generation and detachment processes during the OER might introduce damages to the IrNS catalysts, especially under such a high current density of 5000 mA/cm². The bubble evolution influence on the catalyst structural stability has been previously reported in the

literatures [48-52]. The STEM image at a higher magnification in **Fig. 6b** shows that the tested IrNS catalysts are composed of iridium oxide nanocrystals with the tetragonal crystal structure, as evidenced by the measured lattice fringes of 0.31 and 0.27 nm, corresponding to the (110) and (101) crystal planes of iridium oxide. The (110) crystal plane for iridium oxide is further confirmed by the diffraction spots in the FFT pattern calculated from the corresponding red box in the inset of **Fig. 6b**. Therefore, the STEM results of as-synthesized IrNS catalysts in **Fig. 3** and tested IrNS catalysts in **Fig. 6** reveal that metallic IrNS catalysts before the cell test converted to iridium oxide after the stability test at 5000 mA/cm² in a PEM electrolyzer cell.

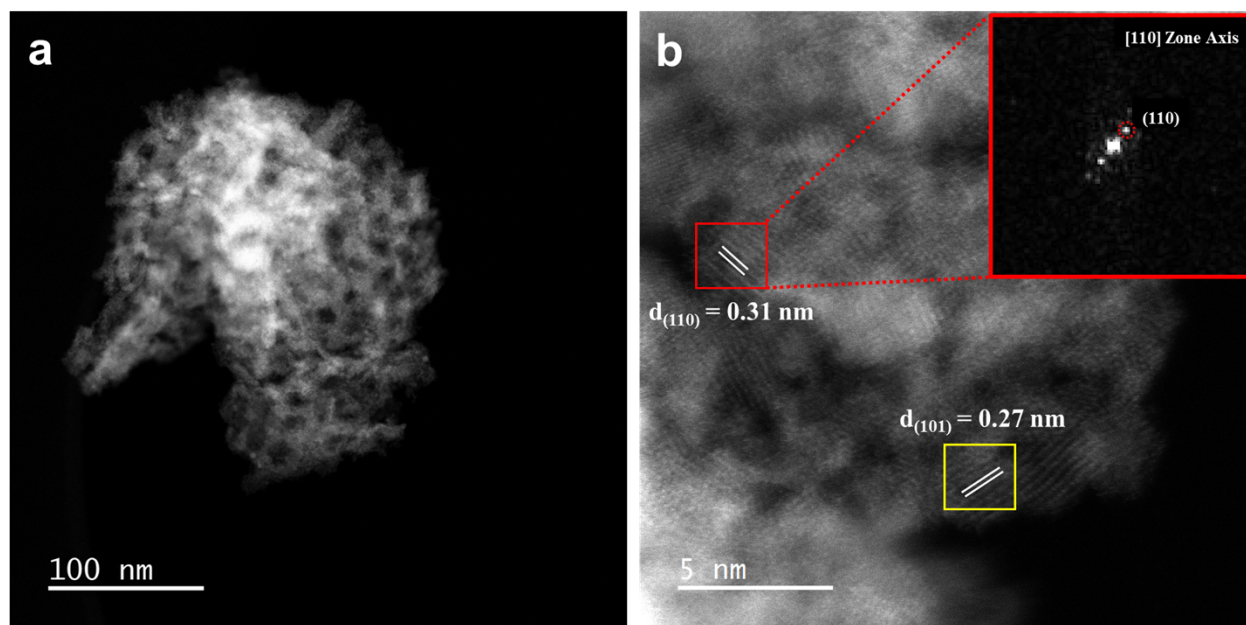


Fig. 6. (a, b) HAADF-STEM images of IrNS catalysts after the cell stability test at 5000 mA/cm².

The chemical composition of IrNS catalysts before and after the cell stability test was analyzed by using the XPS characterization. The high-resolution XPS spectra of Ir 4f are presented in **Fig. S6**. To obtain an adequate curve-fitting, both spectra need three sets of 4f_{7/2} doublets (marked as Ir-1, Ir-2 and Ir-3), which are centered at ~62, ~63 and ~65 eV, respectively.

These are tentatively assigned to Ir^{3+} , Ir^{4+} and Ir^{X+} ($X>4$). For the as-synthesized IrNS catalysts, the iridium species with a mix of Ir^{3+} , Ir^{4+} and Ir^{X+} ($X>4$) coexist on the catalyst surface, which is likely due to natural oxidation by air exposure. However, the metallic iridium is dominant in as-synthesized IrNS catalysts, as confirmed by the XRD analysis in **Fig. 2j** and STEM characterization in **Fig. 3**. This combination of metallic iridium with oxidized surface might improve the OER kinetics by providing good electronic conductivity and more active iridium species for the OER [53]. Compared to as-synthesized IrNS catalysts, it is found that the Ir $4f_{7/2}$ peak shifts towards higher binding energy after the cell stability test, which is probably attributed to the increased oxidation of catalysts during the long-term OER process. This phenomenon is consistent with previously reported studies on Ir-based OER catalysts [53-55].

4. Conclusions

In summary, we report a novel ionomer-free nanoporous iridium nanosheet electrode design, in which nanoporous iridium nanosheets with abundantly exposed edges and highly porous structures are successfully coated on TT-LGDLs by a low-temperature chemical synthesis method. The combination of high catalytic activity, good electrode electronic conductivity and excellent liquid/gas transport properties enables significantly boosted catalyst utilization and enhanced cell performance of nanoporous NS electrode. When coupled with Nafion 117 ($\sim 175\ \mu\text{m}$), nanoporous IrNS electrodes with low catalyst loadings can deliver the current densities of $2000\ \text{mA}/\text{cm}^2$ at a low cell voltage of 1.78 V, and a ~ 10 times higher mass specific current is achieved compared to the conventional CCM baseline at 1.8 V. Moreover, when coupled with Nafion 212 ($\sim 50\ \mu\text{m}$), the nanoporous IrNS electrode manifests cell voltages as low as 1.65 V and 1.78 V at 3000 and 6000 mA/cm^2 , respectively. The durability test provides additional

confirmation that nanoporous IrNS is capable of maintaining stable performances at both 1.8 and 5 A/cm² for over 200 h. Therefore, our research has revealed the beneficial effects of ionomer-free nanostructured catalysts in enhancing catalyst utilization, cell performance, and durability in PEMECs, which offers new opportunities to minimize the usage and cost of Ir-based catalysts, while accelerating the commercialization of efficient, robust and scalable PEM water electrolysis in hydrogen production.

CRedit authorship contribution statement

Zhiqiang Xie: Conceptualization, Methodology, Data curation, Writing - original draft, review & editing, Investigation, Validation. **Lei Ding:** Methodology, Investigation, Validation, Writing - review & editing. **Shule Yu:** Methodology, Investigation, Validation, Writing - review & editing. **Weitian Wang:** Investigation, Validation, Writing - review & editing. **Christopher B. Capuano:** Investigation and Validation. **Alex Keane:** Investigation and Validation. **Kathy Ayers:** Investigation, Validation, Writing - review & editing. **David A. Cullen:** Resources, Investigation, Validation, Writing - review & editing. **Harry M. Meyer:** Investigation and Validation. **Feng-Yuan Zhang:** Resources, Supervision, Project administration, Funding acquisition, Writing - review & editing.

Conflict of Interest

The authors declare no conflict of interest.

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