

Article

NiWO_{3-x}-Supported Pd Nanocluster Catalyst Boosts Hydrogen Oxidation Activity in Anion Exchange Membrane Fuel Cells

Tailor Peruzzolo ¹, Maria V. Pagliaro ¹, Lorenzo Poggini ^{1,2}, Marco Bellini ¹ and Hamish Andrew Miller ^{1,*}

¹ Institute of Chemistry of Organometallic Compounds (ICCOM), National Research Council (CNR), Via Madonna del Piano 10, 50019 Sesto Fiorentino, Italy; tailor.peruzzolo@iccom.cnr.it (T.P.); maria.pagliaro@iccom.cnr.it (M.V.P.); lorenzo.poggini@iccom.cnr.it (L.P.); marco.bellini@iccom.cnr.it (M.B.)

² Department of Chemistry "U. Schiff", University of Florence, Via della Lastruccia 3-13, 50019 Sesto Fiorentino, Italy

* Correspondence: hamish.miller@iccom.cnr.it

Abstract

Slow reaction kinetics of the hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER) under alkaline conditions limits the performance of anion exchange membrane fuel cells and water electrolyzers (AEMFC and AEMWE). Consequently, high loadings of PGM metal-based compounds such as Pd-CeO₂ and PtRu are required to obtain competitive performance. The amount of precious metals present can be reduced by exploiting interaction with an active support material that tunes both hydrogen desorption and hydroxyl adsorption, processes that are key descriptors of HOR activity. In this work, NiWO_{3-x}C is prepared, composed of oxygen-deficient tungsten oxide (WO_{3-x}) doped with Ni nanoparticles and mixed with conductive carbon (50:50 wt%). This material is decorated with Pd nanoparticles (6.6 wt% Pd loading). Structural analysis (XRD, XPS, and HR-TEM/STEM) confirm a hybrid morphology of Pd nanoparticles deposited on both the Ni and W portions of the support. The HOR and HER activity was studied using electrochemical tests and compared to the performance of both a Pd/C standard with equivalent Pd loading (6.9 wt%) and the NiWO_{3-x}C support. The Pd-normalized exchange current densities for the HOR (I⁰) are 18.7 A g_{Pd}⁻¹ for Pd/NiWO_{3-x}C and 3.21 A g⁻¹ for Pd/C. The enhanced HOR activity of Pd/NiWO_{3-x}C translates to high power densities in AEM fuel cell tests with this catalyst applied to the anode electrode (up to 0.9 W cm⁻²).

Keywords: hydrogen oxidation reaction; anion exchange membrane fuel cell; palladium; tungsten oxide; nickel



Academic Editors: Xiaohua Zhang and Sang-Il Choi

Received: 15 May 2026

Revised: 23 June 2026

Accepted: 21 July 2026

Published: 23 July 2026

Copyright: © 2026 by the authors.

Licensee MDPI, Basel, Switzerland.

This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Anion exchange membrane fuel cells (AEMFCs) have emerged as a promising alternative to proton exchange membrane fuel cells (PEMFCs) [1]. The alkaline nature of the membrane interface enables the use of non-platinum group metal (PGM) catalysts, as well as low-cost membranes and bipolar plates, thereby offering significant potential for cost reduction [1,2]. Despite these advantages, sluggish hydrogen oxidation reaction (HOR) kinetics in alkaline media remains a critical bottleneck, even on state-of-the-art PGM catalysts such as Pt whose intrinsic activity in alkaline electrolytes is markedly lower than in acidic environments [2–4]. Consequently, high PGM loadings required at the anode undermine the overall economic viability of AEMFC technology.

To overcome this limitation, considerable efforts have been dedicated to the development of electrocatalysts that combine high intrinsic HOR activity, long-term durability, and

reduced content of PGMs [3,4]. Among the various approaches explored, engineering the catalyst support through the addition of transition metal oxides has attracted particular attention, as it allows modulation of surface electronic properties and enhancement of interfacial reaction dynamics [5–7]. There is increasing agreement that, within the catalyst, the nature of the oxophilic site is important for the alkaline HOR, and that having an oxophilic site on the catalyst surface will speed up the reaction [8,9]. The ease of $^*\text{OH}$ adsorption on the surface is an important driver for the alkaline [6,9]. Several important examples have been reported recently. For example, the incorporation of CeO_2 into a Vulcan XC-72 carbon support enhances oxophilicity and OH adsorption properties [10,11]. This effect has been demonstrated for a number of transition metals (Pd, Pt, Ir, Rh, Ru) [12]. A nanostructured Pd- CeO_2/C catalyst employed in an AEM fuel cell produced 2 W cm^{-2} peak power density in lab testing [13]. Alternative transition-metal oxides in the + IV oxidation state (ZrO_2 , CeO_2 , SnO_2 , and RuO_2) displayed the same effect on enhancing HOR kinetics. Mixed oxides of tungsten have been exploited using interfacial engineering between Ni_4W and amorphous WO_x to enhance the HER. Ni-W and Ni-Mo compounds have also shown improved HOR activity [14,15].

In this study, we report the synthesis of a nanostructured HOR electrocatalyst consisting of nickel–tungsten oxide ($\text{NiWO}_{3-x}\text{C}$) decorated with 6.6 wt% palladium (Pd). The NiWO_{3-x} support serves as a robust, corrosion-resistant, and electronically tunable substrate that promotes favorable H and OH adsorption energetics. The Pd provides active sites for hydrogen dissociation, while its interaction with the Ni-W generates synergistic effects that enhance HOR kinetics. The morphology of the synthesized catalysts was characterized by high-resolution transmission electron microscopy (HR-TEM and STEM) and scanning electron microscopy (SEM) imaging and by X-Ray Diffraction (XRD) and XPS. Their electrocatalytic activity for the oxidation and evolution of hydrogen was evaluated by cyclic voltammetry and linear scan voltammetry. Finally, Pd/ $\text{NiWO}_{3-x}\text{C}$ was employed and tested as HOR catalyst in an AEMFC, producing close to 1 W cm^{-2} of peak power density. Durability of performance is shown for over 25 h at constant cell voltage.

2. Results and Discussion

2.1. Synthesis

NiWO_{3-x} was prepared by a hydrothermal procedure using microwave heating at $200\text{ }^\circ\text{C}$, followed by treatment at $500\text{ }^\circ\text{C}$ in flowing H_2/N_2 . This product was mixed with Ketjen-black EC-600JD carbon and Pd nanoclusters were added to give a final loading of 6.6 wt% Pd (denoted as Pd/ $\text{NiWO}_{3-x}\text{C}$). For reference, a Pd/C catalyst was prepared with a 6.9 wt% Pd loading using the same Pd deposition procedure as previously described [11,16].

2.1.1. XRD and XPS

Figure 1 compares the X-ray diffraction patterns of $\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$, W-Ni(OH)_2 , $\text{NiWO}_{3-x}\text{C}$, Pd/C, and Pd/ $\text{NiWO}_{3-x}\text{C}$. For W-Ni(OH)_2 , the diffraction peaks at 33.5° , 34.4° , and 60° correspond to the (101), (012), and (110) planes of $\alpha\text{-Ni(OH)}_2$ (JCPDS 22-0444). The broad and low-intensity diffraction peaks indicate a poorly crystalline lamellar structure, typical of $\alpha\text{-Ni(OH)}_2$, and the absence of the well-defined peaks of $\beta\text{-Ni(OH)}_2$ confirms that the sample maintains the hydrated α -phase [17,18]. After reductive thermal treatment at $500\text{ }^\circ\text{C}$ under an atmosphere of H_2/N_2 (5:95), the composition and crystal phases are also shown in Figure 1. Diffraction peaks at about 44.5° , 51.8° , and 76.4° are indexed to (111), (200), and (220), indicating the presence of metallic nickel (JCPDS No. 04-0850). The high temperature and H_2/N_2 atmosphere leads to the formation of nickel nanoparticles [19,20]. Additional broad poorly defined signals in the region $2\theta = 20\text{--}40$ can be assigned to mixed tungsten oxides (W–O), which are typically detected at lower diffraction angles ($2\theta < 40^\circ$) [21,22]. After

the addition of Pd, three peaks are assigned to Pd at $2\theta = 40.5^\circ$, 46.8° , 68.4° , corresponding to the (111), (200), (220) lattice planes. All the diffraction peaks can be well indexed to face-centered cubic (fcc) Pd according to the JCPDS card No. 05-0681 [11,23]. The XRD pattern of the Pd/C sample is also shown with corresponding peaks for Pd at $2\theta = 40^\circ$, 46.6° , and 68° . The mean Pd nanoparticle size for Pd/NiWO_{3-x}C and Pd/C was estimated from the XRD data using the Scherrer method and an internal standard (LaB6). The values obtained were 32.8 nm (Pd/C) and 13.6 nm (Pd/NiWO_{3-x}C). Such values indicate a much better dispersion of Pd over NiWO_{3-x}C compared to Pd/C. The values are corroborated by the ECSA values determined by electrochemical method which gave a value for Pd/NiWO_{3-x}C three times higher than for Pd/C. The XRD pattern of Pd/NiWO_{3-x}C also reveals a higher crystallinity for W oxide-centered reflections compared to pristine NiWO_{3-x}C. This phenomenon may account for the enhancement of diffraction signals associated with W oxide phases. The three XRD peaks at $2\theta = 31^\circ$, 36° , and 48° suggest the formation of sub-stoichiometric tungsten oxide (WO_{3-x}). The XRD signals depend strongly on the oxygen deficiency level (x). The presence of NiWO₄ in the sample Pd/NiWO_{3-x}C can be excluded as no W⁶⁺ is observed in the XPS analysis (see below) [24–26].

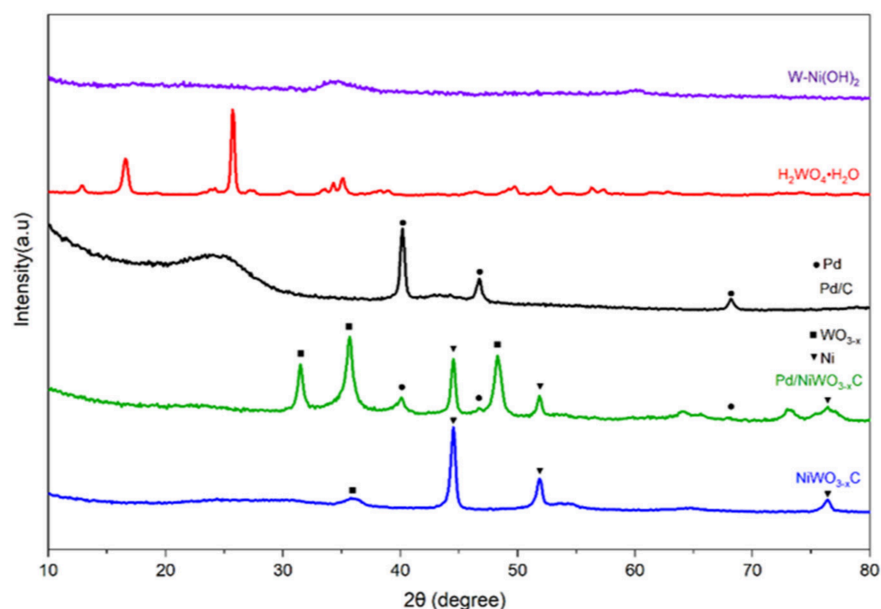


Figure 1. XRD patterns of (top to bottom) W-Ni(OH)₂, H₂WO₄·H₂O, Pd/C, Pd/NiWO_{3-x}C, and NiWO_{3-x}C.

The XPS analysis (Ni2p, W4f and Pd3d) of NiWO_{3-x}C and PdNiWO_{3-x}C is shown in Figure 2 and the composition data is shown in Table 1. Regarding Ni, the analysis of the Ni2p signals for the precursor NiWO_{3-x}C shows a nickel peak characterized by Ni²⁺, with a small portion of Ni⁰ (approximately 10%). The remaining peaks can be attributed to Nickel (II), which could be present in different forms, from NiO, to NiOOH (gamma or beta) and Ni(OH)₂ [19]. For NiWO_{3-x}C the W4f spectra is quite complex and shows the presence of W oxidation numbers (IV), (V), and (VI), in percentages of 31%, 16%, 53% respectively [27]. The Ni:W stoichiometry does not correspond to the 4 to 1 of the alloy (Ni:W) and no metallic W is observed [28,29]. After addition of Pd to the Ni-W support the XPS analysis changes significantly. The nickel peak is characterized as before by Ni²⁺, while the portion of Ni⁰ is much less (approximately 2%). The remaining peaks can be attributed to Nickel (II), which could be present in different forms, from NiO to NiOOH (gamma or beta), up to Ni(OH)₂ [29,30]. The signals for W4f show oxidation states of (IV) and (V) in percentages of 25% and 75%, respectively with no W in oxidation state (VI).

Hence, the presence of NiWO_4 can be excluded [31–33]. The ratio of Ni:W increases to 8:1, corresponding to Ni nanoparticles doped on WO_{3-x} [20,21,27]. Pd is present in both metallic and PdO forms with approximately a 1:1 ratio.

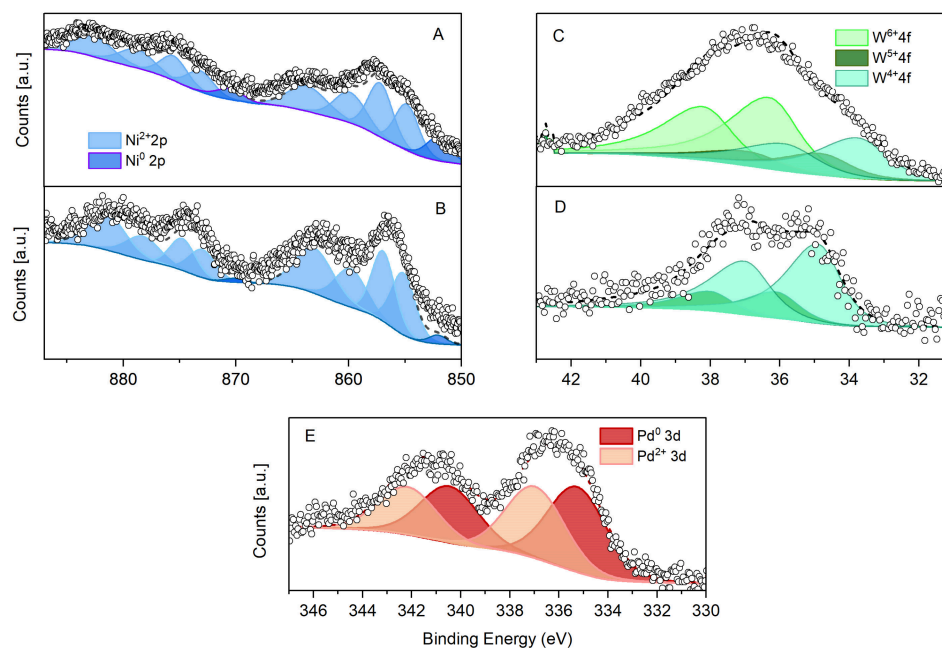


Figure 2. A comparison of the XPS for $\text{Ni}2p$; $\text{NiWO}_{3-x}\text{C}$ (A) and $\text{Pd/NiWO}_{3-x}\text{C}$ (B), $\text{W}4f$; $\text{NiWO}_{3-x}\text{C}$ (C) and $\text{Pd/NiWO}_{3-x}\text{C}$ (D), and $\text{Pd}3d$ for $\text{Pd/NiWO}_{3-x}\text{C}$ (E).

Table 1. Extrapolated XPS data in terms of surface composition and oxidation states of elements.

Catalyst	%Pd	%Ni	%W	%Pd ⁰	%Pd ²⁺	%W ⁴⁺	%W ⁵⁺	%W ⁶⁺
$\text{NiWO}_{3-x}\text{C}$	0	68.3	31.7	-	-	31	16	53
$\text{Pd/NiWO}_{3-x}\text{C}$	23.2	68.8	8.0	54.3	45.7	25	75	0

2.1.2. HR-TEM/STEM

The surface morphology of samples $\text{NiWO}_{3-x}\text{C}$ and $\text{Pd/NiWO}_{3-x}\text{C}$ was first investigated by SEM (Figure S1). The low-magnification images of both samples show typical layered agglomerated particles with interconnected nanosized grains, typical of Ni-W composite structures. The individual platelet particles undergo a reduction in size after the Pd deposition, suggesting a change in the surface composition. Structural and compositional information was also obtained by high-resolution transmission electron microscopy (HR-TEM) combined with energy-dispersive X-ray spectroscopy (EDS) and scanning transmission electron microscopy (STEM). In Figure 3, several HR-TEM images are shown of the support $\text{NiWO}_{3-x}\text{C}$, that indicate the various components of the sample. Nickel nanoparticles are dispersed over the sample (mean size 30–50 nm) identified by the lattice spacing of 0.209 nm [18,30]. The Ni NPs are supported on a W oxide material that consists of WO_{3-x} confirmed by lattice spacings of 0.185 nm, 0.240 nm, and 0.34 nm [19,34,35]. The structure of the compound can be described as Ni metallic nanoparticles supported on WO_{3-x} .

Figure 4 presents STEM images acquired using high-angle annular dark-field (HAADF) contrast, along with the corresponding energy-dispersive X-ray spectroscopy (EDX) elemental maps for Ni, W, and O respectively. The clustered WO_{3-x} particles act as support for the Ni NPs distributed over the surface. Figure 5 shows a HAADF-STEM image and corresponding EDX elemental maps of $\text{Pd/NiWO}_{3-x}\text{C}$. It can be observed that, after the deposition of Pd, the material retains the structural basis of the pre-existing support

$\text{NiWO}_{3-x}\text{C}$. A well-defined presence of palladium (Pd, yellow) is evident, distributed principally over the regions containing Ni and W, and is less evident on the carbon portions of the support. Large regions of the carbon surface, such as the upper left of the image, which are devoid of support $\text{NiWO}_{3-x}\text{C}$ contain very few Pd NPs. This clearly confirms that palladium was effectively incorporated into the Ni-W system and successfully deposited. A similar phenomenon has been observed in $\text{Pd-CeO}_2/\text{C}$ catalysts where the meliorative interaction between Pd and CeO_2 for the HOR was favored by preferential deposition of Pd on CeO_2 [10,13,23]. The enhancement in HOR was determined by the size of the Pd- CeO_2 interface in the material where a small amount of Pd was present on only carbon and hence did not contribute to the HOR activity improvement [36]. We believe an analogous situation is present, with the Pd- NiWO_{3-x} interaction contributing to improved HOR activity. Further images are shown in the SI.

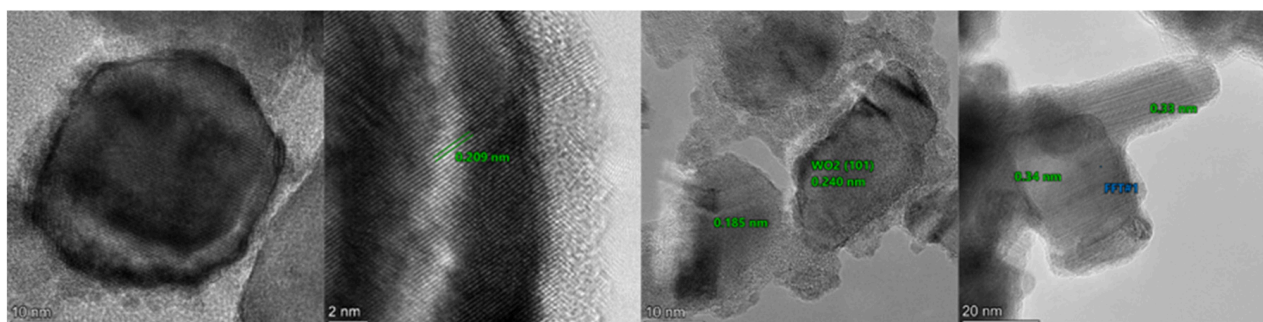


Figure 3. High-resolution transmission electron microscopy (HR-TEM) images of $\text{NiWO}_{3-x}\text{C}$.

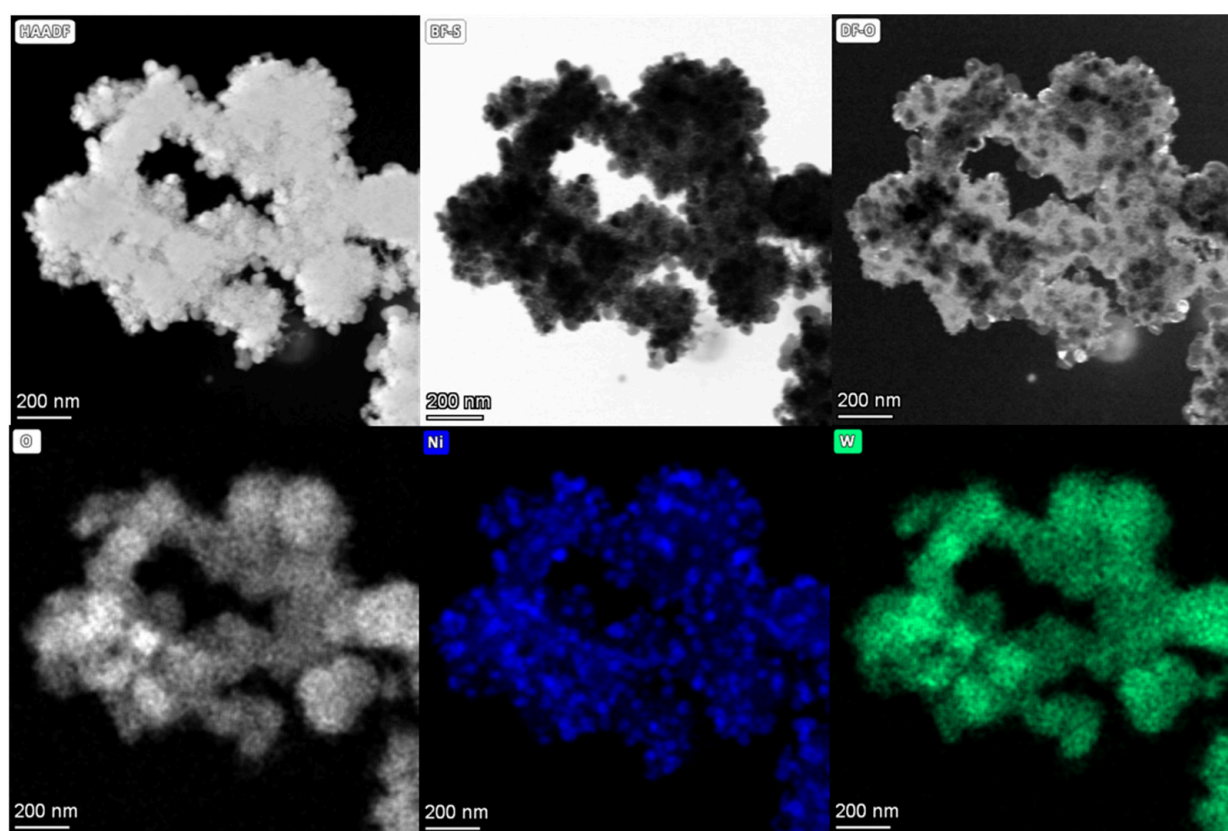


Figure 4. HAADF-STEM images (Bright field and dark field) and EDX elemental maps of $\text{NiWO}_{3-x}\text{C}$. The distribution of nickel (Ni, blue), tungsten (W, green), oxygen (O, white) is shown.

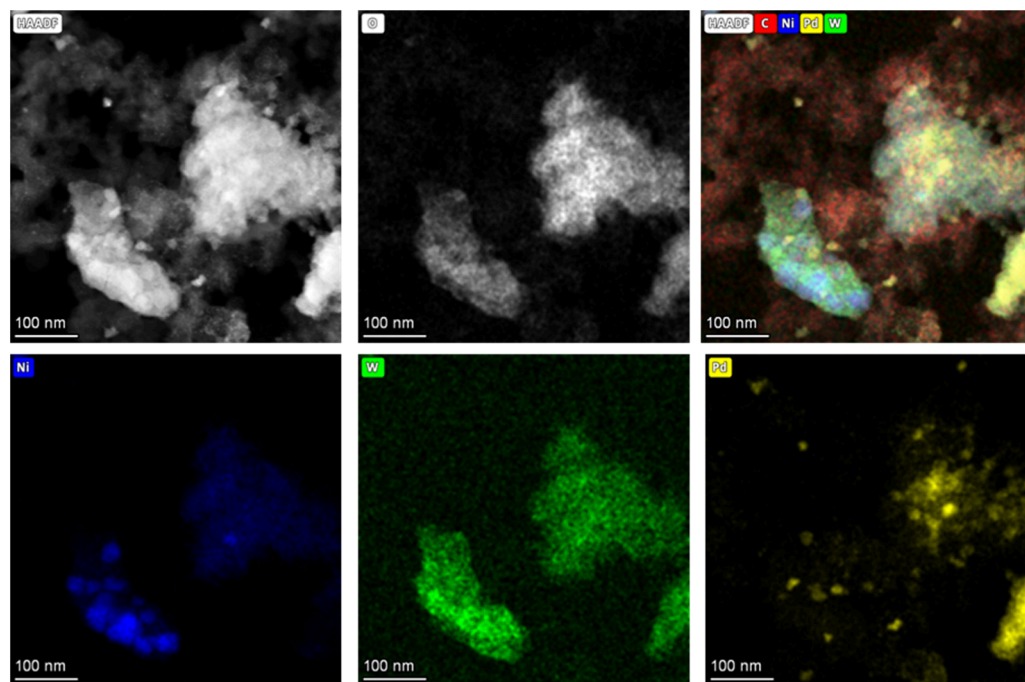


Figure 5. HAADF-STEM image and corresponding EDX elemental maps of Pd/NiWO_{3-x}C. The elemental distributions of nickel (Ni, blue), tungsten (W, green), palladium (Pd, yellow) are shown.

2.2. Electrochemical Characterization

The electrocatalytic performance for the HOR and HER was evaluated in aqueous alkaline medium (0.1 M KOH) using a three-electrode configuration, with Ag/AgCl (0.987 V vs. RHE) as the reference, a gold wire as the counter electrode, and a catalyst coated glassy carbon rotating disk electrode (RDE) as the working electrode. The catalyst ink was drop-cast onto a 0.196 cm² geometric area of glassy carbon disk and dried under ambient conditions. Linear sweep voltammetry measurements were carried out at a rotation speed of 1600 rpm, from −0.4 V to 0.5 V exploring both the HOR and HER branches, at 1 mV s^{−1}. The results of the electrochemical tests are shown in Figure 6 and important data is shown in Table 2. In Figure 6A, CVs in the range 0 to 1.4 V (RHE) of each catalyst are shown in N₂-saturated KOH 0.1 M at 20 mV s^{−1}. The CV for NiWO_{3-x}C does not exhibit any electrochemical features and shows only capacitive behavior. For Pd/NiWO_{3-x}C and Pd/C, Pd-centered processes are clearly visible. On the forward anodic scan from 0 to 1.4 V (RHE), peaks for oxidative hydrogen desorption at 0.1 V are observed, broad peaks for Pd(OH)₂ and PdO formation are also present. On the return cathodic sweep, peaks for PdO reduction and H UPD can be seen at 0.65 and 0.2 V respectively. Integration of the PdO reduction peak on the return sweep was used to estimate the electrochemical active surface area of Pd for these two catalysts (ECSA) using a well-established method described in the literature [37]. Values of 145 and 51 m² g^{−1} were obtained for Pd/NiWO_{3-x}C and Pd/C respectively. The three-times higher value obtained for the NiWO_{3-x}C support demonstrates that the interaction of Pd with NiWO_{3-x}C results in a better dispersion of Pd compared to a bare carbon support. In Figure 6B, LSV curves are shown for the region −0.4 to 0.5 V (RHE). The insert shows the HOR region (from 0 to 0.2 V). Firstly, regarding HER, Pd/NiWO_{3-x}C exhibits the highest activity and onset potential followed by the support NiWO_{3-x}C. Pd/C, by comparison, has low activity and large onset overpotential. At −0.2 V vs. RHE, the current densities were −8.22 mA·cm^{−2} for Pd/NiWO_{3-x}C, −5.00 mA·cm^{−2} for NiWO_{3-x}C, and −0.2 mA·cm^{−2} for Pd/C. Ni-W interactions are known to enhance the alkaline HER [38]. For the HOR process at 0.2 V vs. RHE, the current densities were 2.48 mA·cm^{−2} for Pd/NiWO_{3-x}C, 0.05 mA·cm^{−2} for

$\text{NiWO}_{3-x}\text{C}$, and $0.84 \text{ mA} \cdot \text{cm}^{-2}$ for Pd/C . As can be seen in Figure 6B, $\text{Pd/NiWO}_{3-x}\text{C}$ has a significantly lower onset potential for the HOR and reaches the diffusion limited current density plateau at low over potentials (0.2 V). The Tafel slopes derived from LSV data are shown in Figure 6D. The Tafel analysis presented in this work was derived from a single representative measurement for each catalyst under identical experimental conditions. The exchange current densities obtained from the Tafel analysis were 18.7 and $3.21 \text{ A g}_{\text{Pd}}^{-1}$ for $\text{Pd/NiWO}_{3-x}\text{C}$ and $\text{NiWO}_{3-x}\text{C}$ respectively, demonstrating the enhanced HOR activity of $\text{Pd/NiWO}_{3-x}\text{C}$. When calculated with respect to the ECSA, the values are 129 mA m^{-2} for $\text{Pd/NiWO}_{3-x}\text{C}$ and 63 mA m^{-2} for Pd/C . The HOR Tafel slopes for $\sim 115 \text{ mV dec}^{-1}$ indicate that a charge-transfer step involving hydrogen oxidation coupled with hydroxide adsorption (Volmer-type step) is rate-determining [39]. Electrochemical impedance spectroscopy (EIS) was recorded at 0.3 V (RHE) in the HOR region. Nyquist plots are shown in Figure 6C, the intercept at high frequency in the $Z'(\Omega)$ real axis represents the sum of the solution resistance R_s and the charge-transfer resistance R_{ct} . The values for R_{ct} calculated using equivalent circuit fitting of the data (see Figure S5 and Table S1) are 1410 ohm for $\text{Pd/NiWO}_{3-x}\text{C}$, 3929 ohm for Pd/C and $35,431 \text{ ohm}$ for $\text{NiWO}_{3-x}\text{C}$. Such values confirm the high HOR activity for $\text{Pd/NiWO}_{3-x}\text{C}$ followed by Pd/C and poor HOR activity for $\text{NiWO}_{3-x}\text{C}$. At lower frequency, the impedance plots follow typical Nyquist behavior (pseudo semi-circle) with a limiting capacitance value, which corresponds to the total capacitance of the catalyst layer, which is proportional to active surface area. The roughness factor (RF) of all catalysts was evaluated by capacitance measurements through CVs at different scan rates (from 0.01 to 0.05 V s^{-1}) in the double layer region (Figure S4, Supporting Information) [40]. The RF values obtained were 7.5 , 10.6 , and 11.8 mF cm^{-2} for $\text{NiWO}_{3-x}\text{C}$, Pd/C , and $\text{Pd/NiWO}_{3-x}\text{C}$ respectively.

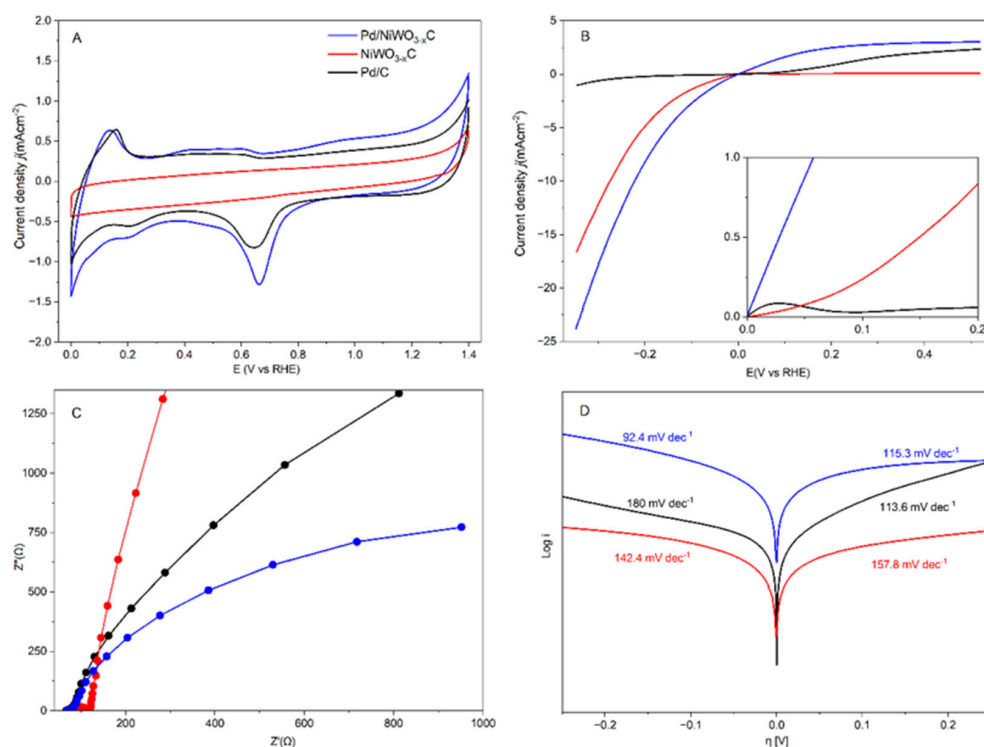


Figure 6. (A) CVs in N_2 -saturated KOH 0.1 M at 20 mV s^{-1} . (B) LSVs in H_2 -saturated KOH 0.1 M at 1 mV s^{-1} and 1600 rpm . (C) Nyquist plots in N_2 saturated 0.1 M KOH at 0.3 V RHE . (D) Tafel plots with Tafel slopes.

Table 2. Relevant electrochemical parameters for HOR and HER at room temperature on glassy carbon electrodes in H₂-saturated KOH 0.1 M at 1 mV s^{−1} and 1600 rpm.

Catalyst	Pd wt%	J _{HOR} @0.2V mA cm ^{−2}	J _{HER} @-0.2V mA cm ^{−2}	I ⁰ A g _{Pd} ^{−1}	I ⁰ mA m ^{−2}	Tafel slope (HOR/HER)	ECSA m ² g ^{−1}	J _{HER,ECSA} @0.2V A m ^{−2}	J _{HOR,ECSA} @0.2V A m ^{−2}
NiWO _{3−x} C	0	0.05	5.0	-		(158/142)	-	-	-
Pd/C	6.9	0.84	0.2	3.21	63	(114/180)	51	1.29	0.32
Pd/NiWO _{3−x} C	6.6	2.48	8.22	18.7	129	(115/92)	145	1.44	4.77

2.3. Fuel Cell Testing

The Pd/NiWO_{3−x}C catalyst powder mixed with an AEI powder, with an ion-exchange capacity (IEC) of 1.26 ± 0.06 mmol g^{−1} was applied onto Toray paper by spray coating a catalyst ink suspension. The anode electrode with a 0.43 mg_{Pd} cm^{−2} loading was pressed together with an HDPE-based radiation-grafted anion exchange membrane (thickness 29 μm, IEC 2.65 ± 0.33 mmol g^{−1}) and Pt/C cathode (Toray paper Pt loading 0.4 mg cm^{−2}) inside the fuel cell test hardware (Scribner Southern Pines, North Carolina USA). The Pt/C cathode was chosen for preliminary testing as a benchmark cathode electrode that is used generally in testing of new anode materials. The performance of the fuel cell MEA was evaluated by applying humidified H₂ and O₂ to the anode and cathode respectively. The cell was tested at a cell temperature of 60 and 80 °C. Fuel cell polarization curves were obtained using a Scribner test station (Figure 7). Important fuel cell data is shown in Table 3. The performance of the MEA with the Pd/NiWO_{3−x}C anode was compared to that of an MEA with a Pt/C-based anode and cathode (both 0.4 mg_{Pt} cm^{−2}). Both MEAs were tested by potential scans (10 mV s^{−1}) and by applying a constant cell potential of 0.5 V and monitoring the current density. In Figure 7a, the Pd/NiWO_{3−x}C cell voltage and power density curves (v. J mA cm^{−2}) are shown at cell temperatures of 60 and 80 °C. At 60 °C, a peak power density of 660 mW cm^{−2} is achieved. Increasing the cell temperature to 80 °C improves the peak power density to 900 mW cm^{−2}. At 0.6 V, the cell produces 0.6 W cm^{−2} of power density. In Figure 7b, the performance of the Pt/Pt MEA is shown by comparison. The peak power density values obtained at 60 and 80 degrees is significantly lower than for the Pd/NiWO_{3−x}C anode, reaching 330 and 680 mW cm^{−2} respectively. Interestingly, the power density obtained at 0.6 V is like the Pd/NiWO_{3−x}C cell (approx. 1 W cm^{−2}), suggesting that at high cell potentials the Pt and Pd anode catalysts perform similarly. At higher current densities, the Pd/NiWO_{3−x}C anode has significantly higher activity (1.5 A cm^{−2} 0.51 V vs. 0.45 V and at 2 A 0.45 V vs. not achievable with Pt). This trend in performance is confirmed during the tests at 0.5 V. Stable power densities of 580 and 800 mW cm^{−2} are achieved with Pd/NiWO_{3−x}C while 200 and 500 are achieved with Pt. This result is unexpected, as Pt/C is considered the state of the art for the alkaline HOR. Indeed, a comparison of LSV curves that we performed for the HOR between commercial Pt/C, Pd/NiWO_{3−x}C and Pd/C confirms that Pt/C has higher HOR activity (Figure S7). When applied to the AEM anode electrode together with the AE ionomer resin, Pd/NiWO_{3−x}C performs better than Pt/C in the mass transport-controlled region of the fuel cell curve at higher current densities. This effect may be due to the presence of the inorganic NiWO_{3−x} support for the Pd that favors ion transport within the electrode structure, removing mass transport limitations that may occur with a carbon-only supported catalyst. Further investigations are required to confirm this phenomenon. When compared to recently reported Pd-based HOR electrocatalysts applied in AEMFCs, the performance of Pd/NiWO_{3−x}C is in the region of the state of the art (Table 4).

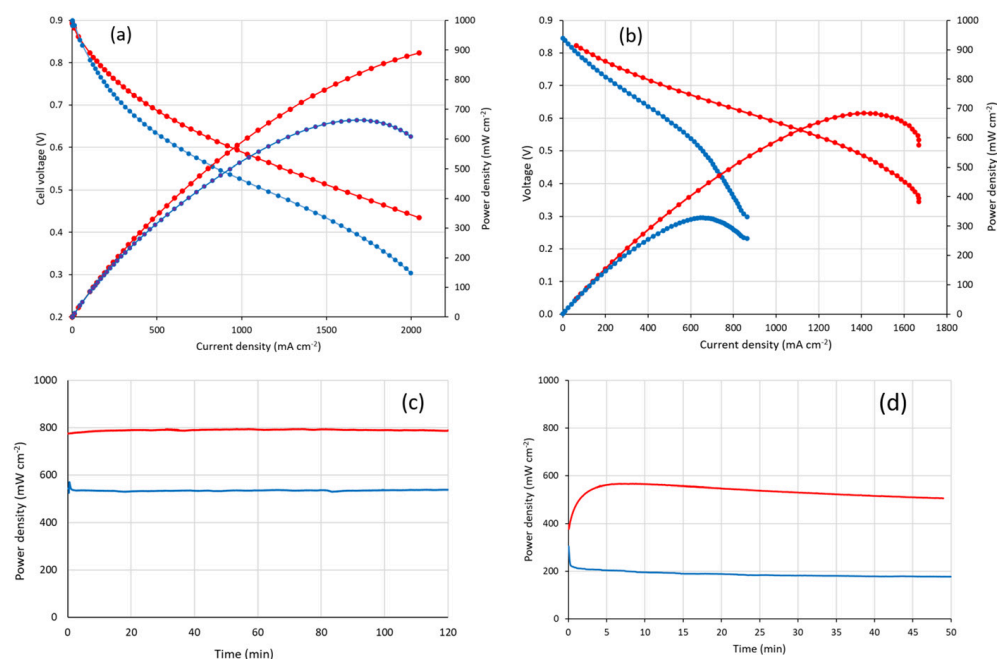


Figure 7. (a) H_2/O_2 Fuel Cell testing at T_{cell} 60 °C (blue) and 80 °C (red). The MEA was composed of Pd/NiWO_{3-x}C as anode (0.43 mg_{Pd} cm⁻²), HDPE-BTMA as anionic exchange membrane, and Pt (0.4 mg_{Pt} cm⁻²) as cathode. (b) The MEA was composed of Pt/C as anode (0.4 mg_{Pt} cm⁻²), HDPE-BTMA as anionic exchange membrane, and Pt (0.4 mg_{Pt} cm⁻²) as cathode. (c) Stability tests with Pd/NiWO_{3-x}C at a constant potential of 0.5 V T_{cell} 60 °C (blue) and 80 °C (red), with H_2/O_2 gas flow at 75 °C and 0.5 L min⁻¹. (d) Stability tests with Pt/C as anode at a constant potential of 0.5 V T_{cell} 60 °C (blue) and 80 °C (red), with H_2/O_2 gas flow at 75 °C and 0.5 L min⁻¹.

Table 3. Data performance of fuel cell testing.

MEA (Anode Catalyst)	OCV mV	Anode mg _{Pd/Pt} cm ⁻²	Cathode mg _{Pt} cm ⁻²	P _{max} mW cm ⁻²	J@P _{max} mA cm ⁻²	Operating Conditions Cell–Anode–Cathode °C H ₂ –O ₂ Flow Rate L min ⁻¹
Pd/NiWO _{3-x} C	900 900	0.43 (Pd)	0.4	660 900	1700 2050	60-55-55 1-1 80-75-75 1-1
Pt/C	850 850	0.4 (Pt)	0.4	680 330	1400 630	60-55-55 1-1 80-75-75 1-1

Table 4. Comparison of AEMFC performances using recently reported Pd-based HOR electrocatalysts. PPD (peak power density).

Anode	Loading mg cm ⁻²	Cathode	Loading mg cm ⁻²	Cell Temp °C	PPD W cm ⁻²	J(PPD) A cm ⁻²	Ref.
Pd-CeO ₂ /OLC	0.15	Pt/C	0.4	80	1	3	[41]
Pd-CeO ₂ /C	0.25	Pt/C	0.4	80	2	5	[13]
CeO _x -Pd/C	0.55	Pt/C	0.7	73	0.643	1.4	[42]
Pd _{0.33} Ir _{0.67} /N-C	0.2	Pt/C	0.3	79	0.514	1.25	[43]
Pd/NiWO _{3-x} C	0.43	Pt/C	0.4	80	0.9	2.05	This work

2.4. Determination of Catalyst Stability in Three-Electrode Cell and AEMFC

The short-term stability of Pd/NiWO_{3-x}C in AEMFC has been demonstrated over 2–3 h of fuel cell testing. To understand the stability under longer term testing, we undertook both accelerated stress testing using the three-electrode system and longer tests in

AEMFCs. Firstly, Pd/NiWO_{3-x}C and Pd/C were subjected to 3000 potential cycles between 0 to 0.9 V using the RDE system. This potential range simulates strong electrode polarization that can occur during the HOR as well as stop-start cycling. LSVs in H₂-saturated KOH 0.1 M were recorded before the stress test and after the 3000 cycles. These curves are reported in Figure 8. The difference in LSVs after the stress test indicate a significant degradation in activity for both catalysts. The value for current density at 0.1 V (RHE) drops from 1.5 to 0.75 mA cm⁻² for Pd/NiWO_{3-x}C. By comparison, with Pd/C the current density drops from 0.7 to 0.35 mA cm⁻². Such degradation in electrocatalytic activity through potential cycling is commonly associated with Pd nano-particle agglomeration and consequential loss of active surface area [44,45].

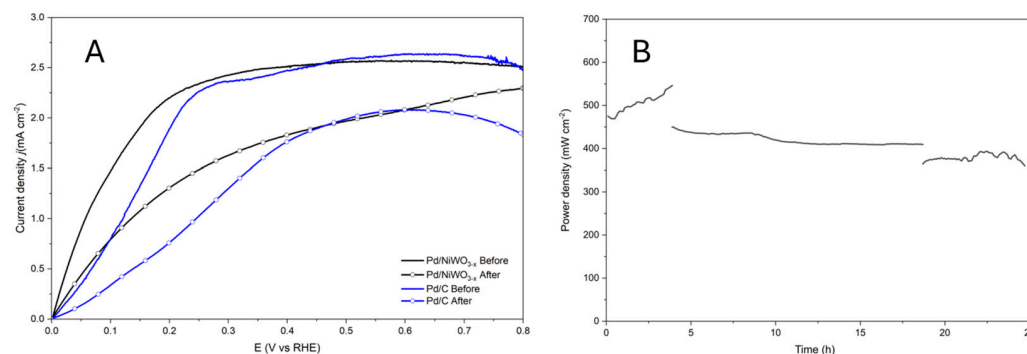


Figure 8. (A) Accelerated stress testing of Pd/C and Pd/NiWO_{3-x}C in the HOR region. LSVs in H₂-saturated KOH 0.1 M at 1 mV s⁻¹ and 1600 rpm taken before and after 3000 cycles 0 to 0.9 V (RHE); (B) 25 h stability test with Pd/NiWO_{3-x}C at a constant potential of 0.5 V T_{cell} 60 °C with H₂/O₂ gas flow at 58 °C and both gases at 0.5 L min⁻¹. The MEA was composed of Pd/NiWO_{3-x}C as anode (0.43 mg_{Pd} cm⁻²), HDPE-BTMA as anionic exchange membrane, and Pt (0.4 mg_{Pt} cm⁻²) as cathode. The break points in the curve correspond to the shutdown of the fuel cell for periods of 12 h.

To test the stability of the Pd/NiWO_{3-x}C for longer periods of operation in an AEM fuel cell, the cell was operated at constant cell potential (0.5 V) over a three-day period with occasional stop and startup operation (12 h periods of stop). The power density was recorded and is shown in Figure 8. Up to 25 h of operation were recorded. Initially, the performance increased from 470 to 550 mW cm⁻². After the first shut down, the cell ran for a further 15 h with stable operation. After the second shut-down period, the cell power density did not return to the level previously held but maintained stable operation. It is also clear that start-stop cycles cause degradation in performance. This can be due to several factors, such as physical detachment of the catalyst layer from the membrane due to heating and cooling or through the carbonation of the membrane if air enters the fuel cell from the atmosphere. This is due to CO₂ reacting with OH⁻ in the membrane to form bicarbonate HCO₃⁻ that leads to a drop in membrane conductivity.

2.5. Discussion

The active site for the HOR is Pd-centered in both materials; however, the interaction of Pd with NiWO_{3-x} is fundamental for enhancing HOR activity and this is also due to the chemical nature of NiWO_{3-x} in its oxygen-deficient form. The oxygen deficiency creates missing O atoms in the crystal lattice and reduced metal centers (e.g., W⁶⁺ → W⁵⁺ shown by XPS measurements above) which are the result of the high temperature reductive annealing process (N₂:H₂ mix at 500 °C). The missing O atoms lead to an imbalance in coordination, and the surrounding atoms become electron rich. This effect has been shown to promote water activation and overall HER kinetics. For the alkaline HOR, oxygen deficiency in NiWO_{3-x} is critical because it transforms the catalyst into a bifunctional system that helps

to tune H binding on the Pd sites and simultaneously provides strong OH adsorption sites (vacancies) on NiWO_{3-x} . These oxygen vacancies facilitate the adsorption/desorption of $^*\text{OH}$ and $^*\text{OOH}$ intermediates during the OER process [46]. Consequently, the alkaline HOR proceeds through the following mechanism. H_2 adsorption on Pd sites followed by H-H dissociation to form Pd-H. OH adsorption onto oxygen vacancy-rich NiWO_{3-x} . The final step involves the surface reaction between H and OH to form H_2O .

3. Materials and Methods

3.1. Synthesis

All chemicals were purchased from Sigma-Aldrich (Darmstadt, Germany) and used without further purification. First, the W-Ni(OH)₂ precursor was synthesized by microwave heating. Briefly, 3.03 g of nickel nitrate hexahydrate ($\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) was dissolved in 3 mL H_2O and 0.5 g of tungstic acid ($\text{H}_2\text{WO}_4 \cdot \text{H}_2\text{O}$) in 1.2 mL of $\text{NH}_3 \cdot \text{H}_2\text{O}$ and the two solutions were combined in a 25 mL microwave vessel, followed by the addition of 15 mL of ethylene glycol. After stirring for 20 min, the mixture was heated in the microwave reactor (CEM Mars 6 Synthesis, Matthews, NC, USA) at 200 °C for 6 min with continuous magnetic stirring. After cooling to room temperature, the resulting green powder was collected by centrifugation, washed with water and dried at 60 °C overnight. The powder was annealed in 5:95 H_2/N_2 atmosphere at 500 °C with a heat ramp of 5 °C min^{-1} for 1 h. The product (NiWO_{3-x}) thus obtained was collected by filtration, and subsequently physically mixed with carbon (Ketjen-black EC-600JD, Sigma-Aldrich) in a 1:1 mass ratio using a ball mill operated at 10 rpm for 30 min. A portion of the sample (0.1 g) was suspended in water (250 mL), stirred vigorously for 30 min, and sonicated for 30 min. To this mixture, a solution of K_2PdCl_4 (0.03 g) in water (15 mL) was slowly added using a peristaltic pump (1 mL min^{-1}) under vigorous stirring, followed by 2.1 mL of KOH aqueous solution (2.5 M) and then 11 mL of ethanol. The mixture was then heated at 80 °C for 60 min. The desired product Pd/ NiWO_{3-x} C was filtered, washed several times with distilled water to neutrality and finally dried at 40 °C overnight. Pd content 6.6 wt%, Ni content 7.95 wt% (ICP-OES).

3.2. Chemical–Physical Characterization

Powder X-ray diffraction (XRD) analyses were conducted at ambient temperature utilizing a PANalytical X'PERT PRO powder diffractometer (Almelo, Overijssel, Netherlands). This setup employed $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), complemented by a parabolic MPD-mirror and a PIXcel RTMS detector (also from PANalytical). The data were collected across a 2θ range of 10.0 to 80.0° with a step increment of 0.105° and a total counting duration of 428.9 s, using a silicon zero background as the sample holder. SEM, sample characterisation was performed using a TESCAN Gaia 3 FIB/SEM. The microscope hosts a 30 kV Triglav electron column and a Cobra Focused Gallium Ion Beam column (Brno, Czech Republic). SEM images of the sample surfaces were acquired using the two in-beam Secondary Electron (SE) and Back Scattered Electron (BSE) detectors, located inside the electron column. High-resolution transmission electron microscopy (HR-TEM) and scanning transmission electron microscopy (STEM) were conducted using a Talos F200X G2 TEM microscope from Thermo Scientific (Bleiswijk, The Netherlands). Utilizing its circular four-detector SuperX Energy Dispersive detector (Thermo Scientific, Bleiswijk, The Netherlands), high-resolution energy dispersive X-ray (EDX) analyses were performed. A drop of sample solution, consisting of a small amount of material dispersed in iso-propanol, was cast onto a Holey TEM copper grid, which served as the sample holder for characterization. HR-TEM images, along with High-Angle Annular Dark Field (HAADF-STEM) micrographs and corresponding EDS mapping were obtained. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) analysis was carried out with an ICP-Optical

emission dual view Perkin Elmer OPTIMA 8000 apparatus (Waltham, MA, USA). XPS analyses were carried out in a UHV chamber with a base pressure of 10^{−10} mbar and equipped with non-monochromatized Al radiation ($h\nu = 1486.6$ eV, VSW-TA1) combined with a hemispherical electron/ion energy analyzer (VSW-HA100 with a 16-channel detector, VSW Scientific Instruments Ltd., Manchester, UK). The operating power of the X-ray source was 120 W (12 kV and 10 mA), and the photoelectrons were collected normal to the sample surface, maintaining the angle between the analyzer axis and the X-ray source fixed at 54.5°. All samples were adsorbed on carbon tape, and the XPS spectra were acquired in a fixed analyzer transmission mode with a pass energy of 44.0 eV. CasaXPS software version 2.3.26PR1.0 was used to analyze the spectra and a linear or Shirley function has been used for the background correction [47]. The deconvolution of XPS spectra has been performed by applying a combination of Gaussian and Lorentzian functions (70/30 ratio) for C1s and Lorentzian Asymmetric Lineshape for and Pd3d, W4f and Ni2p. All the binding energies (B.E.) were calibrated upon fixing C1s of the carbon tape at 285.1 eV [48].

3.3. Electrochemical Measurements

Catalyst inks were prepared for each sample, consisting of approximately 7 mg of catalyst, 600 mg of H₂O, 600 mg of EtOH, and 15 mg of 5% Nafion ionomer. The mixture was then sonicated for 30 min to ensure uniform dispersion. A specific volume of 7 μ L of each ink was subsequently deposited by drop-casting onto the glassy carbon working electrode, resulting in a metal loading of approximately 5–6 μ g.

All glassware was cleaned with H₂O₂/H₂SO₄ concentrated solution overnight and rinsed several times with Milli-Q water before use. Cyclic voltammetry (CV) and linear scan voltage (LSV) experiments were carried out in a three-electrode system, composed of a glassy carbon disk (0.196 cm²) as working electrode (WE), a standard Ag/AgCl_{sat} reference electrode (RE), and a gold wire coated in a glass tube as counter-electrode (CE). An aqueous solution of 0.1 M KOH (prepared using Milli-Q water) was prepared and introduced into the cell. This solution was subsequently purged with N₂ gas for 30 min prior to conducting CV tests, or with H₂ for LSV experiments aimed at investigating the catalyst's performance for hydrogen oxidation reaction (HOR) and the hydrogen evolution reaction (HER). The half-cell potential was referenced to the reversible hydrogen electrode (RHE) using the Nernst Equation, given by $0.197 \text{ V (E}^\circ \text{ Ag/AgCl}_{\text{sat}}) + 0.059 \times \text{pH}$ and corrected for IR drop. The electrochemical tests were carried out using a Parstat 2273 (Princeton Applied Research, Oak Ridge, TN, USA, using the software "Power-Suite 2.58". CVs were recorded at a rate of 20 mV s^{−1} to calculate the electrochemical active surface area (ECSA) of the catalysts (m² g^{−1}). This was done by integrating the charge of the Pd-oxide reduction peak (A·V), dividing it by the scan rate of 0.02 V·s^{−1} to convert it into Coulombs (C), and then normalizing the result using the stripping factor of 405 μ C cm^{−2}. The HOR experiments were conducted at a scan rate of 1 mV s^{−1} and a WE rotating speed of 1600 rpm. The Tafel analysis was performed for each reaction to calculate the exchange current i^0 , expressed as A g^{−1}, as a measure of the catalytic activity and efficiency of the electrode materials involved in the electrochemical process. The frequency range of Electrochemical Impedance Spectroscopy (EIS) was from 100 kHz to 10 mHz in H₂-saturated 0.1 M KOH under 1600 rpm at 0.2 V vs. RHE. Nyquist plots of Pd/NiWO_{3−x}C, Pd/C, and NiWO_{3−x}C electrocatalysts were performed to study the kinetics of the HOR process.

3.4. Membrane Electrode Assembly (MEA) Preparation

HDPE-based radiation-grafted anion exchange membrane (thickness 29 μ m, IEC 2.65 ± 0.33 mmol g^{−1}) and ionomer (RG-AEMs and RG-AEIs, respectively), containing benzyltrimethylammonium (BTMA) functional groups, were used [49]. The electrodes were

fabricated using the sprayed catalyst-coated gas diffusion electrode (GDE) method [11,13,50]. The AEI powder, with an ion-exchange capacity (IEC) of $1.26 \pm 0.06 \text{ mmol g}^{-1}$, was ground with a pestle and mortar for 10 min. The preparation procedure for both the anode and cathode is the same: a specific amount of the desired catalyst and AEI powders (20 wt% of the total solid mass) were mixed with 1 mL of water and 9 mL of propan-2-ol. The obtained ink was homogenized by ultrasonication for 30 min and then sprayed onto a Toray TGP-H-60 carbon paper gas diffusion substrate (Alfa Aesar, Thermo Fisher Scientific, Ward Hill, MA, USA, 10% PTFE) using an Iwata spray gun, with intermittent (<10 s) drying on a hot plate (80 °C) and weighing to ensure the correct loadings. All electrodes and the HDPE RG-AEM [50] ($\text{IEC} = 2.56 \text{ mmol g}^{-1}$) were immersed in an aqueous KOH solution (1 mol L^{-1}) for 1 h, with an exchange of the KOH solution with a fresh solution midway through and then washed thoroughly in ultrapure water to remove excess KOH. The MEA (composed of the anode, cathode, and AEM) was then assembled and enclosed into a 5 cm^2 fuel-cell fixture (Scribner Associates, Southern Pines, NC, USA) at a 5 N m torque closing force.

3.5. Fuel Cell Testing

An 850e fuel cell test station (Scribner Associates, Southern Pines, NC, USA) was used for testing. The fuel-cell temperature was varied between 60 and 80 °C. H_2 and O_2 gas feeds, with flow rates of up to 1 L min^{-1} , were supplied to the anode and cathode, respectively, with no back-pressurization. The dewpoints for both the anode and cathode gas supplies were adjusted to determine the sensitivity of performance to changes in gas humidification. All the connecting lines between the fuel-cell tester and the fuel-cell fixture were heated to prevent premature condensation before the humidified gases entered the flow field. The MEAs were activated by discharging the cell at a constant voltage of 0.5 V during cell heating and leaving the cells at this voltage until a steady current density was observed. AEMFC performance data was collected under controlled potentiostatic conditions. The internal Ohmic resistances were estimated from the 850e instrument's internal current interrupt method.

4. Conclusions

In this work, we have synthesized and characterized a multiphase electrocatalyst with enhanced activity for the alkaline HOR and HER. Our recent investigations in this field have concentrated on enhancing the alkaline HOR with a minimum of PGM content. The development of AEMFCs as an alternative to the state-of-the-art PEMFC relies on overcoming the bottleneck of poor HOR kinetics of the anode catalysts utilized (usually Pt based). In this work, the Pd/NiWO_{3-x}C catalyst was designed to exploit the interaction of Pd with a W mixed oxide and Ni nanoparticle support to favor the HOR reaction. The two critical aspects of the HOR mechanism at high pHs are the hydrogen binding and hydroxyl binding processes. In this catalyst material, the optimum H binding of the Pd centers is combined with the OH binding favored by the WO_{3-x} material. The HOR activity is shown to be higher than for a Pd/C reference catalyst prepared with the same Pd content. We have also applied the catalyst to an AEM fuel cell. A peak power density of 900 mW cm^{-2} was achieved, and the system was tested for three days at 0.5 V cell potential. The results of these investigations have bolstered our understanding of strategies to improve HOR activity. Our future work will involve developing this NiWO_{3-x} material to host single Pd atom catalysts, thus reducing the PGM content to a minimum and coupling with non-PGM cathode catalysts in AEMFC testing.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/catal16080666/s1>, Figure S1: SEM images of (A) NiWO_{3-x}C and (B) Pd/NiWO_{3-x}C. Figure S2: Elemental composition of selected portions of the Pd/NiWO_{3-x}C

from HAADF image. (Values are atomic%). Figure S3: Pd and Ni elemental maps of a portion of the Pd/NiWO_{3-x}C nanostructured surface. A combined C, Ni, Pd and W map overlay on the same area. Figure S4: CVs of (A) NiWO_{3-x}C, (B) Pd/C and (C) Pd/NiWO_{3-x}C at scan rates of 10, 20, 30, 40, 50 mV s⁻¹ in 0.1 M KOH and (D–E) the corresponding capacitive current at 0.65 V vs. scan rates. Figure S5: Nyquist plots in N₂ saturated 0.1 M KOH at 0.3 V RHE with fitting of curves. NiWO_{3-x}C (Red); Pd/C (blue) and Pd/NiWO_{3-x}C (black). Figure S6: Accelerated stress testing of Pd/C (left) and Pd/NiWO_{3-x}C (right) in the HOR region. CVs in KOH 0.1 M at 50 mV s⁻¹ and 1600 rpm, 3000 cycles 0 to 0.9 V (RHE). Figure S7: LSVs in H₂-saturated KOH 0.1 M at 1 mV s⁻¹ and 1600 rpm. Table S1: Impedence data.

Author Contributions: Conceptualization, H.A.M.; resources, H.A.M.; writing—review and editing, H.A.M.; formal analysis, M.V.P.; investigation, M.V.P.; methodology, T.P. investigation, T.P.; methodology, M.B. investigation, M.B.; formal analysis, L.P.; investigation, L.P.; methodology. All authors have read and agreed to the published version of the manuscript.

Funding: The authors acknowledge the financial support provided by the FRESH project, funded by the European Union Horizon research and innovation program under grant agreement HORIZON-RIA-101069605. This research was also funded by the European Union NextGeneration EU through the Italian Ministry of Environment and Energy Security, POR H₂ AdP MMES/ENEA, with the involvement of CNR and RSE (PNRR—Mission 2, Component 2, Investment 3.5, “Ricerca e sviluppo sull’idrogeno”), L.A.3.1.6 and L.A. 1.1.24 (CUP: B93C22000630006).

Data Availability Statement: The raw data supporting the conclusions of this article will be made available by the authors on request.

Acknowledgments: The authors gratefully acknowledge the technical support and access to the facilities provided by the Interdepartmental Research Unit “Matchlab” of the University of Florence. They also thank Brunetto Cortigiani for his valuable technical assistance in the use of the platform.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Zahan, S.M.; Baranov, A.A.; Yassin, K.; Zhong, J.; Douglin, J.C.; Willdorf-Cohen, S.; Bhowmick, S.; Lilloja, J.; Tammeveski, K.; Tsur, Y.; et al. Can Anion-Exchange Membrane Fuel Cells Operate with Ambient Air? *ACS Energy Lett.* **2026**, *11*, 1688–1695. [\[CrossRef\]](#)
2. Li, L.; Yang, D.; Ying, L.; Liu, S. Recent Advances in Surface Oxophilicity Modification of Catalyst for Promoting Electrocatalytic Alkaline Hydrogen Oxidation Reaction. *J. Electroanal. Chem.* **2025**, *986*, 119100. [\[CrossRef\]](#)
3. Ren, J.T.; Chen, L.; Wang, H.Y.; Feng, Y.; Yuan, Z.Y. Hydrogen Oxidation Electrocatalysts for Anion-Exchange Membrane Fuel Cells: Activity Descriptors, Stability Regulation, and Perspectives. *Energy Environ. Sci.* **2024**, *17*, 3960–4009. [\[CrossRef\]](#)
4. Qiao, H.; Zhang, M.; Che, J.; Zhang, R.; Wen, B.; Huang, H.; Hu, J.; Li, H. Recent Advances of Hydrogen Oxidation: Reaction Mechanism, Catalytic Activity Enhancement, and Applications. *Int. J. Hydrogen Energy* **2026**, *201*, 152978. [\[CrossRef\]](#)
5. Cheng, Z.; Yang, Y.; Wang, P.; Wang, P.; Yang, J.; Wang, D.; Chen, Q. Optimizing Hydrogen and Hydroxyl Adsorption over Ru/WO_{2.9} Metal/Metalloid Heterostructure Electrocatalysts for Highly Efficient and Stable Hydrogen Oxidation Reactions in Alkaline Media. *Small* **2024**, *20*, 2307780. [\[CrossRef\]](#) [\[PubMed\]](#)
6. Gaur, A.; Lee, J.H.; Sharma, J.; Ryu, J.H.; Han, H.S. Significance of Oxophilic Site in Alkaline Hydrogen Evolution and Oxidation Reaction: Is It Playing the Same Role? *J. Mater. Chem. A Mater.* **2025**, *13*, 10296–10336. [\[CrossRef\]](#)
7. Wu, J.; Kang, Z.; Zhang, X. Recent Progress in Alkaline Electrocatalytic Hydrogen Oxidation Reaction: Mechanisms, Catalysts Design and Perspectives. *Coord. Chem. Rev.* **2025**, *528*, 216427. [\[CrossRef\]](#)
8. Li, L.; Tian, F.; Wu, F.; Qiu, L.; Geng, S.; Li, M.; Chen, Z.; Yang, W.; Liu, Y.; Yu, Y. Strong Electronic Metal-Support Interaction of Ni₄Mo/N-SrMoO₄ Promotes Alkaline Hydrogen Electrocatalysis. *Appl. Catal. B* **2025**, *361*, 124660. [\[CrossRef\]](#)
9. Peng, Y.; Nyaaba, A.A.; Liu, J.-Y.; Yang, L.; Liu, Y.-J.; Zhou, H.-B.; Ji, Z.-Y.; Zhou, B.; Zhong, Y.; Zhu, G.-X. Boosting Alkaline Hydrogen Oxidation by Tuning the Interface of WO₃-Ir. *Rare Met.* **2025**, *44*, 6246–6257. [\[CrossRef\]](#)
10. Miller, H.A.; Bellini, M.; Dekel, D.R.; Vizza, F. Recent Developments in Pd-CeO₂ Nano-Composite Electrocatalysts for Anodic Reactions in Anion Exchange Membrane Fuel Cells. *Electrochem. Commun.* **2022**, *135*, 107219. [\[CrossRef\]](#)
11. Bellini, M.; Pagliaro, M.V.; Lenarda, A.; Fornasiero, P.; Marelli, M.; Evangelisti, C.; Innocenti, M.; Jia, Q.; Mukerjee, S.; Jankovic, J.; et al. Palladium-Ceria Catalysts with Enhanced Alkaline Hydrogen Oxidation Activity for Anion Exchange Membrane Fuel Cells. *ACS Appl. Energy Mater.* **2019**, *2*, 4999–5008. [\[CrossRef\]](#)

12. Pagliaro, M.V.; Bellini, M.; Bartoli, F.; Filippi, J.; Marchionni, A.; Castello, C.; Oberhauser, W.; Poggini, L.; Cortigiani, B.; Capozzoli, L.; et al. Probing the Effect of Metal-CeO₂ Interactions in Carbon Supported Electrocatalysts on Alkaline Hydrogen Oxidation and Evolution Reactions. *Inorganica Chim. Acta* **2022**, *543*, 121161. [\[CrossRef\]](#)
13. Miller, H.A.; Pagliaro, M.V.; Bellini, M.; Bartoli, F.; Wang, L.; Salam, I.; Varcoe, J.R.; Vizza, F. Integration of a Pd-CeO₂/C Anode with Pt and Pt-Free Cathode Catalysts in High Power Density Anion Exchange Membrane Fuel Cells. *ACS Appl. Energy Mater.* **2020**, *3*, 10209–10214. [\[CrossRef\]](#)
14. Duan, Y.; Yu, Z.Y.; Yang, L.; Zheng, L.R.; Zhang, C.T.; Yang, X.T.; Gao, F.Y.; Zhang, X.L.; Yu, X.; Liu, R.; et al. Bimetallic Nickel-Molybdenum/Tungsten Nanoalloys for High-Efficiency Hydrogen Oxidation Catalysis in Alkaline Electrolytes. *Nat. Commun.* **2020**, *11*, 2789. [\[CrossRef\]](#) [\[PubMed\]](#)
15. Wang, Y.H.; Yang, Y.; Gao, F.Y.; Zhang, X.L.; Zhu, L.; Yan, H.K.; Yang, P.P.; Gao, M.R. Unraveling Stoichiometry Effect in Nickel-Tungsten Alloys for Efficient Hydrogen Oxidation Catalysis in Alkaline Electrolytes. *Angew. Chem. Int. Ed.* **2024**, *63*, e202407613. [\[CrossRef\]](#) [\[PubMed\]](#)
16. Miller, H.A.; Lavacchi, A.; Vizza, F.; Marelli, M.; Di Benedetto, F.; D'Acapito, F.; Paska, Y.; Page, M.; Dekel, D.R. A Pd/C-CeO₂ Anode Catalyst for High-Performance Platinum-Free Anion Exchange Membrane Fuel Cells. *Angew. Chem.* **2016**, *128*, 6108–6111. [\[CrossRef\]](#)
17. Zhou, Z.; Liu, Y.; Zhang, J.; Pang, H.; Zhu, G. Non-Precious Nickel-Based Catalysts for Hydrogen Oxidation Reaction in Alkaline Electrolyte. *Electrochem. Commun.* **2020**, *121*, 106871. [\[CrossRef\]](#)
18. Chen, T.; Zhang, B.; Yue, X.; Huang, S. Synthesis of NiMoW Ternary Alloy to Boost Hydrogen Oxidation Reaction in Alkaline Medium. *Int. J. Hydrogen Energy* **2024**, *53*, 919–924. [\[CrossRef\]](#)
19. Xiong, B.; Zhao, W.; Tian, H.; Huang, W.; Chen, L.; Shi, J. Nickel-Tungsten Nano-Alloying for High-Performance Hydrogen Electro-Catalytic Oxidation. *Chem. Eng. J.* **2022**, *432*, 134189. [\[CrossRef\]](#)
20. Shirke, Y.M.; Porel Mukherjee, S. Selective Synthesis of WO₃ and W₁₈O₄₉ Nanostructures: Ligand-Free PH-Dependent Morphology-Controlled Self-Assembly of Hierarchical Architectures from 1D Nanostructure and Sunlight-Driven Photocatalytic Degradation. *CrystEngComm* **2017**, *19*, 2096–2105. [\[CrossRef\]](#)
21. Cheng, H.; Klapproth, M.; Sagaltchik, A.; Li, S.; Thomas, A. Ordered Mesoporous WO_{2.83}: Selective Reduction Synthesis, Exceptional Localized Surface Plasmon Resonance and Enhanced Hydrogen Evolution Reaction Activity. *J. Mater. Chem. A Mater.* **2018**, *6*, 2249–2256. [\[CrossRef\]](#)
22. Yu, X.; Tian, H.; Fu, Z.; Pei, F.; Peng, L.; Meng, G.; Kong, F.; Chen, Y.; Chen, C.; Chang, Z.; et al. Strengthening the Hydrogen Spillover Effect via the Phase Transformation of W₁₈O₄₉ for Boosted Hydrogen Oxidation Reaction. *ACS Catal.* **2023**, *13*, 2834–2846. [\[CrossRef\]](#)
23. Pagliaro, M.V.; Wen, C.; Sa, B.; Liu, B.; Bellini, M.; Bartoli, F.; Sahoo, S.; Singh, R.K.; Alpay, S.P.; Miller, H.A.; et al. Improving Alkaline Hydrogen Oxidation Activity of Palladium through Interactions with Transition-Metal Oxides. *ACS Catal.* **2022**, *12*, 10894–10904. [\[CrossRef\]](#)
24. Kahraman, Z.; Güngör, A.; Buldu-Aktürk, M.; Tan, M.; Alp, E.; Erdem, E.; Genç, A. Phase-Dependent Optical, Photocatalytic and Capacitive Properties of Tungsten Oxide Nanowires. *Dalton Trans.* **2025**, *54*, 7376–7390. [\[CrossRef\]](#) [\[PubMed\]](#)
25. He, L.; Yu, C.B.; Lu, K.Q.; Yang, K.; Huang, W.Y.; Li, D. Recent Advances in Synthesis, Performance, and Application of Oxygen Vacancy-Enriched WO_{3-x} Photocatalysts. *Tungsten* **2025**, *8*, 8–36. [\[CrossRef\]](#)
26. Chen, P.; Baldwin, M.; Bandaru, P.R. Hierarchically Structured, Oxygen Deficient, Tungsten Oxide Morphologies for Enhanced Photoelectrochemical Charge Transfer and Stability. *J. Mater. Chem. A Mater.* **2017**, *5*, 14898–14905. [\[CrossRef\]](#)
27. Shpak, A.P.P.; Korduban, A.M.M.; Medvedskij, M.M.M.; Kandyba, V.O.O. XPS Studies of Active Elements Surface of Gas Sensors Based on WO_{3-x} Nanoparticles. *J. Electron Spectros. Relat. Phenom.* **2007**, *156–158*, 172–175. [\[CrossRef\]](#)
28. Cong, S.; Yuan, Y.; Chen, Z.; Hou, J.; Yang, M.; Su, Y.; Zhang, Y.; Li, L.; Li, Q.; Geng, F.; et al. Noble Metal-Comparable SERS Enhancement from Semiconducting Metal Oxides by Making Oxygen Vacancies. *Nat. Commun.* **2015**, *6*, 7800. [\[CrossRef\]](#) [\[PubMed\]](#)
29. Sinha, L.; Shirage, P.M. Surface Oxygen Vacancy Formulated Energy Storage Application: Pseudocapacitor-Battery Trait of W₁₈O₄₉ Nanorods. *J. Electrochem. Soc.* **2019**, *166*, A3496–A3503. [\[CrossRef\]](#)
30. Tian, X.; Ren, R.; Wei, F.; Pei, J.; Zhuang, Z.; Zhuang, L.; Sheng, W. Metal-Support Interaction Boosts the Stability of Ni-Based Electrocatalysts for Alkaline Hydrogen Oxidation. *Nat. Commun.* **2024**, *15*, 76. [\[CrossRef\]](#) [\[PubMed\]](#)
31. Jun, P.; Wu, Y.; Wei, Y.; Wang, W. First-Principle Study of Structural, Elastic, Mechanical, and Optical Properties of Wolframite NiWO₄ under Pressure. *Russ. J. Phys. Chem. A* **2025**, *99*, 3577–3585. [\[CrossRef\]](#)
32. Kuzmin, A.; Pankratov, V.; Kalinko, A.; Kotlov, A.; Shirmane, L.; Popov, A.I. UV-VUV Synchrotron Radiation Spectroscopy of NiWO₄. *Low Temp. Phys.* **2016**, *42*, 543–546. [\[CrossRef\]](#)
33. Bakradze, G.; Kalinko, A.; Kuzmin, A. Chemical-State Analyses of Ni, Zn, and W Ions in NiWO₄–ZnWO₄ Solid Solutions by X-Ray Photoelectron Spectroscopy. *J. Phys. Chem. Solids* **2022**, *161*, 110425. [\[CrossRef\]](#)

34. Zhang, B.; Qiu, X.; Chen, T.; Huang, C.; Yue, X.; Huang, S. Construction of Heterostructure between Ni₁₇W₃ and WO₂ to Boost the Hydrogen Oxidation Reaction in Alkaline Medium. *ACS Appl. Mater. Interfaces* **2024**, *16*, 3270–3278. [[CrossRef](#)] [[PubMed](#)]
35. Shi, H.; Dai, T.Y.; Sun, X.Y.; Zhou, Z.L.; Zeng, S.P.; Wang, T.H.; Han, G.F.; Wen, Z.; Fang, Q.R.; Lang, X.Y.; et al. Dual-Intermetallic Heterostructure on Hierarchical Nanoporous Metal for Highly Efficient Alkaline Hydrogen Electrocatalysis. *Adv. Mater.* **2024**, *36*, 2406711. [[CrossRef](#)] [[PubMed](#)]
36. Yu, H.; Davydova, E.S.; Ash, U.; Miller, H.A.; Bonville, L.; Dekel, D.R.; Maric, R. Palladium-Ceria Nanocatalyst for Hydrogen Oxidation in Alkaline Media: Optimization of the Pd–CeO₂ Interface. *Nano Energy* **2019**, *57*, 820–826. [[CrossRef](#)]
37. Lukaszewski, M.; Soszko, M.; Czerwiński, A. Electrochemical Methods of Real Surface Area Determination of Noble Metal Electrodes—An Overview. *Int. J. Electrochem. Sci.* **2016**, *11*, 4442–4469.
38. Wu, W.; Yang, S.; Qian, H.; Zhang, L.; Peng, L.; Li, L.; Liu, B.; Wei, Z. Interface Engineering of Advanced Electrocatalysts toward Alkaline Hydrogen Evolution Reactions. *Chin. J. Catal.* **2024**, *66*, 1–19. [[CrossRef](#)]
39. Shinagawa, T.; Garcia-Esparza, A.T.; Takanabe, K. Insight on Tafel Slopes from a Microkinetic Analysis of Aqueous Electrocatalysis for Energy Conversion. *Sci. Rep.* **2015**, *5*, 13801. [[CrossRef](#)] [[PubMed](#)]
40. Peng, Y.; Zhang, Y.; Guo, A.; Mao, M.; Wang, Y.; Long, Y.; Fan, G. Universal Low-Temperature Oxidative Thermal Redispersion Strategy for Green and Sustainable Fabrication of Oxygen-Rich Carbons Anchored Metal Nanoparticles for Hydrogen Evolution Reactions. *Chem. Eng. J.* **2022**, *433*, 133648. [[CrossRef](#)]
41. Ogada, J.J.; Ipadeola, A.K.; Mwonga, P.V.; Haruna, A.B.; Nichols, F.; Chen, S.; Miller, H.A.; Pagliaro, M.V.; Vizza, F.; Varcoe, J.R.; et al. CeO₂ Modulates the Electronic States of a Palladium Onion-Like Carbon Interface into a Highly Active and Durable Electrocatalyst for Hydrogen Oxidation in Anion-Exchange-Membrane Fuel Cells. *ACS Catal.* **2022**, *12*, 7014–7029. [[CrossRef](#)]
42. Singh, R.K.; Davydova, E.S.; Douglin, J.; Godoy, A.O.; Tan, H.; Bellini, M.; Allen, B.J.; Jankovic, J.; Miller, H.A.; Alba-Rubio, A.C.; et al. Synthesis of CeO_x-Decorated Pd/C Catalysts by Controlled Surface Reactions for Hydrogen Oxidation in Anion Exchange Membrane Fuel Cells. *Adv. Funct. Mater.* **2020**, *30*, 2002087. [[CrossRef](#)]
43. Cong, Y.; McCrum, I.T.; Gao, X.; Lv, Y.; Miao, S.; Shao, Z.; Yi, B.; Yu, H.; Janik, M.J.; Song, Y. Uniform Pd_{0.33}Ir_{0.67} Nanoparticles Supported on Nitrogen-Doped Carbon with Remarkable Activity toward the Alkaline Hydrogen Oxidation Reaction. *J. Mater. Chem. A Mater.* **2019**, *7*, 3161–3169. [[CrossRef](#)]
44. Miller, H.A.; Vizza, F.; Marelli, M.; Zadick, A.; Dubau, L.; Chatenet, M.; Geiger, S.; Cherevko, S.; Doan, H.; Pavlicek, R.K.; et al. Highly Active Nanostructured Palladium-Ceria Electrocatalysts for the Hydrogen Oxidation Reaction in Alkaline Medium. *Nano Energy* **2017**, *33*, 293–305. [[CrossRef](#)]
45. Douglin, J.C.; Singh, R.K.; Yang-Neyerlin, A.C.; He, C.; Yassin, K.; Miller, H.A.; Pagliaro, M.V.; Capozzoli, L.; Carbo-Argibay, E.; Brandon, S.; et al. Elucidating the Degradation Mechanisms of Pt-Free Anode Anion-Exchange Membrane Fuel Cells after Durability Testing. *J. Mater. Chem. A Mater.* **2024**, *12*, 10435–10448. [[CrossRef](#)]
46. Zheng, G.; Wang, J.; Liu, H.; Murugadoss, V.; Zu, G.; Che, H.; Lai, C.; Li, H.; Ding, T.; Gao, Q.; et al. Tungsten Oxide Nanostructures and Nanocomposites for Photoelectrochemical Water Splitting. *Nanoscale* **2019**, *11*, 18968–18994. [[CrossRef](#)] [[PubMed](#)]
47. Fairley, N.; Fernandez, V.; Richard-Plouet, M.; Guillot-Deudon, C.; Walton, J.; Smith, E.; Flahaut, D.; Greiner, M.; Biesinger, M.; Tougaard, S.; et al. Systematic and Collaborative Approach to Problem Solving Using X-Ray Photoelectron Spectroscopy. *Appl. Surf. Sci. Adv.* **2021**, *5*, 100112. [[CrossRef](#)]
48. Barlow, A.J.; Popescu, S.; Artyushkova, K.; Scott, O.; Sano, N.; Hedley, J.; Cumpson, P.J. Chemically Specific Identification of Carbon in XPS Imaging Using Multivariate Auger Feature Imaging (MAFI). *Carbon* **2016**, *107*, 190–197. [[CrossRef](#)]
49. Biancolli, A.L.G.; Herranz, D.; Wang, L.; Stehlíková, G.; Bance-Soualhi, R.; Ponce-González, J.; Ocón, P.; Ticianelli, E.A.; Whelligan, D.K.; Varcoe, J.R.; et al. ETFE-Based Anion-Exchange Membrane Ionomer Powders for Alkaline Membrane Fuel Cells: A First Performance Comparison of Head-Group Chemistry. *J. Mater. Chem. A Mater.* **2018**, *6*, 24330–24341. [[CrossRef](#)]
50. 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.* **2019**, *12*, 1575. [[CrossRef](#)]

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.