Self-supported porous heterostructure WC/WO$_{3-x}$ ceramic electrode for hydrogen evolution reaction in acidic and alkaline media

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Abstract: Tungsten carbide (WC)-based materials are widely considered as the hydrogen evolution reaction (HER) process catalysts due to their “Pt-like” electronic structure. Nonetheless, traditional powder electrodes have a high cost, and display problems related to the process itself and the poor stability over operation time. This paper presented a self-supported asymmetric porous ceramic electrode with WO$_{3-x}$ whiskers formed in situ on the walls of the finger-like holes and membrane surface, which was prepared by combining phase inversion tape-casting, pressureless sintering, and thermal treatment in a CO$_2$ atmosphere. The optimized ceramic electrode displayed good catalytic HER activity and outstanding stability at high current densities. More specifically, it demonstrated the lowest overpotentials of 107 and 123 mV and the lowest Tafel slopes of 59.3 and 72.4 mV·dec$^{-1}$ at 10 mA·cm$^{-2}$ in acidic and alkaline media, respectively. This superior performance was ascribed to the structure of the ceramic membrane and the charge transfer efficiency, which was favored by the in situ developed WC/WO$_{3-x}$ heterostructure and the oxygen vacancies.

Keywords: hydrogen evolution reaction (HER); porous ceramic membrane; WC/WO$_{3-x}$ heterostructure; self-supported electrode; oxygen vacancies

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1 Introduction

Nowadays, energy crisis and environmental pollution have increased the interest in developing sustainable and eco-friendly energy substitutes [1–4]. Hydrogen is a clean, sustainable, and zero-carbon emission energy source, which is widely considered to replace traditional fossil fuels [5–7]. Large-scale production of high-purity hydrogen can be obtained by the electrolysis of water [8,9]. Platinum (Pt)-based noble metals are the most effective hydrogen evolution reaction (HER) electrocatalysts, but their high cost and insufficient natural resources severely limit their wide application [10]. Therefore, new electrocatalysts with earth abundance, high efficiency, and high stability must be developed.

Tungsten carbide (WC)-based materials are considered as potential substitutes for Pt in the HER procedure, because they demonstrate a “Pt-like” d-band electron density state owing to the C that inserts into the W lattice [11–14]. WC has abundant resources, and it manifests high chemical stability and excellent electrical conductivity [15]. Traditional WC catalyst synthesis methods, such as W or W-based precursor carbonization process, which is used to prepare nano-WC particles, leading to poor crystallinity and low purity products and limiting the HER activity [11,16]. More importantly, in electrochemical tests or applications, the nano-WC particles need to be casted on the glassy carbon electrode with a polymer binder, which inevitably increases the resistance of charge transfer, buries the active sites, and weakens the catalytic efficiency [17]. Moreover, due to the weak physical contact between the catalyst and the glassy carbon electrode, the coated catalyst is easily peeled off from the electrode during long-term or high-current electrical operation, which severely restricts its stability and durability [18].

Strong attention has been paid on self-supported electrodes, where catalytic active phases could be in situ produced on their surfaces. This can improve stability and favor charge transfer and gas transport [17]. In addition, in self-supported electrodes, it is easier to construct the interface by in situ reactions and regulate the electronic structure near the interface. Compared with metal- and carbon-based substrates, porous conductive ceramic substrates gained attention recently because of their high chemical stability, tailor-made interconnected porous structure, and high mechanical strength [19,20]. Furthermore, it is worth noting that the inherent hydrophilicity of ceramic surfaces improves electrode/electrolyte contact, which favors charge transfer and bubble detachment [21–23].

Pore structure of electrode plays an important role in its electrocatalytic performance. Phase inversion tape-casting method could be successfully used to fabricate porous ceramic membranes with asymmetric structures [24,25], which could increase the HER performance significantly [19,20]. We combined phase inversion tape-casting and pressureless sintering to prepare the porous WC ceramic membranes with the asymmetric structure. The achieved membranes were suitable for HER; however, the electrocatalytic performance was not satisfactory. The construction of a high catalytic layer in the surface of WC membrane is very important.

Tungsten oxide is an n-type semiconductor material of transition metal oxides. It attracts strong attention in electrocatalysis because of its stability, abundant resources, and environmentally friendly nature [5,26–28]. Nevertheless, the electrocatalytic performance of hexavalent WO3 suffers from the large bandgap, resulting in poor electronic conductivity [29,30]. Furthermore, the oxide of WO3 can be partially reduced to produce non-stoichiometric WO3-x. The produced oxygen vacancies provide numerous effective electron transport paths. Therefore, they accelerate electron transport and improve electrical conductivity, as well as can act as active sites to improve the HER performance [2,31–33]. There are currently many methods for preparing WO3-x powders with various morphologies and compositions, such as carbothermal reduction [31], chemical gradient transport reaction [32], thermal evaporation [34], and solvothermal method [35]. Powder composite electrodes based on WO3-x and other active or conductive materials have also been produced, but they exhibit several problems, such as poor stability and compatibility, or complicated preparation processes [5,36,37]. Additionally, a literature survey reveals poor documentation on the in situ growth of WO3-x whiskers on WC ceramic membranes for preparing WC/VO3-x composite catalysts for HER.

This paper first prepared a WC ceramic membrane with abundant finger-like holes. Then, the produced WC ceramic membrane was partially oxidized under a CO2 atmosphere. The aim was to produce WO3-x whiskers with high compatibility to WC, where their in situ growth on the membrane surface and inside the
finger-like holes should occur, and be able to be applied to a novel HER self-supported electrode. The HER performance and the self-supported ceramic electrode’s long-term and high-current working stability in both acidic and alkaline media were evaluated.

2 Materials and experimental procedures

2.1 Preparation of WC/WO$_{3-x}$ heterostructure porous ceramic membrane

Commercially available WC (0.5–1 μm; Nangong Jingrui Alloy Material Co., Ltd., China) and tungsten trioxide (WO$_3$, 1 μm, chemical pure (CP); Sinopharm Chemical Reagent Co., Ltd., China) powders were used for preparing the skeleton of the ceramic membrane. Graphite powders (2 μm, CP; Sinopharm Chemical Reagent Co., Ltd., China) were used to construct the sacrificial layer at the bottom of the membrane. N-methyl-2-pyrrolidone (NMP, CP; Sinopharm Chemical Reagent Co., Ltd., China), polyvinylpyrrolidone (PVP, K30, CP; Sinopharm Chemical Reagent Co., Ltd., China), and polyethersulfone (PESf, Radel A-100; Solvay Advanced Polymers, USA) were used as the solvent, dispersant, and polymer binder of the ceramic slurry, respectively.

The porous WC ceramic membrane was prepared by phase inversion bilayer tape-casting and pressureless sintering, as illustrated in Fig. 1. The compositions of WC and graphite slurries are presented in Table S1 in the Electronic Supplementary Material (ESM). The slurries were obtained by 48-h ball-milling, and then degassed for 40 min. The tape-casting took place afterwards onto a Mylar sheet, using simultaneously two blade-gaps of 0.75 and 0.1 mm for WC and graphite slurries, respectively. The two-layer tape was transferred into a water bath for 6 h, where the phase inversion took place to transform the slurry into a green tape with an asymmetric structure. Then, the product was taken out from the water and dried. The green tape was cut to rectangular samples. The samples were heated at 800 °C for 3 h (the heating rate was 5 K·min$^{-1}$) to remove the polymer, and then the temperature was increased to 1600 °C, followed by holding at 1600 °C for 4 h in a graphite furnace under an Ar atmosphere. Then, the obtained WC ceramic membrane was placed in an alumina porcelain boat and heated at various temperatures between 700 and 1000 °C for 3 h (the heating rate was 5 °C·min$^{-1}$) in a tubular furnace under a CO$_2$ atmosphere to obtain the WC/WO$_{3-x}$ heterostructure ceramic membrane. The obtained samples are hereafter denoted as WC/WO$_{3-x}$-$T$ (where $T = 700, 800, 900, 1000$, representing the heating temperature).

2.2 Material characterization

The analysis of the crystalline phases developed in the samples was conducted by the X-ray diffractometer (Ultima IV, Rigaku, Japan) using Cu Kα radiation. Their morphologies were observed in a field emission scanning electron microscope (FE-SEM; GeminiSEM 300, ZEISS, Germany) and a transmission electron microscope (TEM; JEM-2100F, JEOL, Japan), equipped with the energy dispersive spectroscopy (EDS) and selected area electron diffraction (SAED) equipments that allowed chemical and crystallographic analysis of the samples.
The chemical compositions of the samples were thoroughly analyzed by the X-ray photoelectron spectroscopy (XPS) on a Model Kratos Axis Supra+ equipment (SHIMADZU, Japan) using Al Kα X-ray source. The electron paramagnetic resonance (EPR) spectra were recorded in a JEOL JES-FA200 EPR equipment (JEOL, Japan). The porosity was measured by Archimedes immersion method [25,38]. The mechanical strength of the membranes was estimated by three-point bending strength tests, using an Instron instrument (model 5567, UK, max load cell = 1 kN). Five different rectangular specimens were measured for each sample, and the bending strength (σ_F) was calculated by Eq. (1):
\[
\sigma_F = \frac{3FL}{2bh^2}
\]
where \( F \) is the fracture load, \( L \) is the fixture outer span (20 mm), and \( b \) and \( h \) are the width (10 mm) and thickness (0.6 mm) of the tested sample, respectively.

The water contact angle was measured on an Attention Theta equipment (Biolin Scientific, Sweden) at room temperature. The water permeability of the membrane was measured by a self-made device, which was used to evaluate the electrochemical active surface areas (ECSAs) of the electrocatalysts. The ECSA was calculated according to Eq. (5) [39]:
\[
\text{ECSA} = \frac{C_{dl}}{C_s}
\]
where \( C_s \) is the specific capacitance, and its value is 0.040 mF·cm⁻².

The Faradaic efficiency (FE) was calculated by Eq. (6) [40]:
\[
\text{FE}(H_2) = \frac{2n_1F_c \times 100\%}{It}
\]
where \( n_1 \) is the mole of hydrogen, \( F_c \) is the Faraday constant (\( 96,485 \) C·mol⁻¹), and \( I \) and \( t \) represent the current and time, respectively. The turnover frequency (TOF) was measured and calculated according to Eq. (7) [41]:
\[
\text{TOF} = \frac{j}{2F_n}
\]
where \( n_2 \) is the number of active sites. The \( n_2 \) values were measured and calculated by the CV test in a potential range of 0–0.6 V vs. RHE and a scan rate of 50 mV·s⁻¹. Then, by integrating the charge over the entire potential range of the CV curve, the half value of the charge was calculated, which represents the surface charge density \( (Q_s) \). The value of \( n_2 \) was calculated by Eq. (8):
\[
n_2 = \frac{Q_s}{F_c}
\]

3. Results and discussion

3.1 Membrane structure

Figure 2(a) presents the X-ray diffraction (XRD) patterns of WC and WC/WO_{3-x}–T. The oxidation products of WC after thermal treatment at 700, 800, 900, and 1000 °C were WO_{3} (JCPDS No. 20-1324), W_{19}O_{55}
With increasing the thermal treatment temperature, the diffraction peak intensity of $\text{WO}_3^{\text{−}x}$ gradually increased (Fig. 2(b)), while the O/W atomic ratio decreased from 3 to 2.72. Consequently, the thermal treatment temperature directly affected the composition of the produced phase.

Analysis with the XPS sheds light on the chemical states of the produced ceramic electrodes. According to the subsequent HER performance, the sample WC/\(\text{WO}_3^{\text{−}x}\)-900 was selected for further detailed analysis. Full XPS spectrum of WC/\(\text{WO}_3^{\text{−}x}\)-900 (Fig. S2 in the ESM) revealed the presence of C, N, O, and W elements. Nitrogen should result from the samples’ unavoidable exposure to the air. The O 1s spectrum of the WC ceramic membrane (Fig. S3(a) in the ESM) was fitted to two peaks with binding energies of 530.6 and 532.3 eV, corresponding to the W–O and C–O bonds, respectively [42]. This was a result of oxidation that occurred at the sample’s surface, along with the presence of a small amount of \(\text{WO}_3\) sintering additive [43]. In WC/\(\text{WO}_3^{\text{−}x}\)-900 electrode, the O 1s peak (Fig. 3(a)) could be deconvoluted into three peaks. The peak with a binding energy of 530.5 eV represented the W–O bond [31]. The second peak at 531.6 eV should be derived from the oxygen atoms in the region of oxygen vacancies [30,44]. This result further supported that there was a large number of oxygen vacancies on the membrane electrode surface, which could favor the catalytic reaction [44]. The peak at 532.8 eV corresponded to the C–O bond [36]. The O 1s spectra of WC/\(\text{WO}_3^{\text{−}x}\)-T membranes are presented in Fig. S4 in the ESM. There were no oxygen vacancy peaks in WC.
and WC/WO$_3$-x-700, which was consistent with the XRD and EPR results. However, the oxygen vacancy peak area percentages in WC/WO$_3$-x-800, WC/WO$_3$-x-900, and WC/WO$_3$-x-1000 were 22.6%, 32.5%, and 36.2%, respectively. This suggested that the increase of temperature favored the increase of oxygen vacancy content. The C 1s spectrum of WC/WO$_3$-x-900 electrode (Fig. 3(b)) had three strong peaks originating from the W–C, C–C, and C–O bonds, which were located at 282.7, 284.6, and 286.5 eV, respectively, similar to the WC membrane (Fig. S3(b) in the ESM) [36,45]. The C–O bond was due to the reaction with CO$_2$, and the C–O bond originally existed in the WC. The other weak peak, located at 288.9 eV, was assigned to the O–C=O bond, also due to the reaction with CO$_2$ [31].

The W 4f spectrum of WC/WO$_3$-x-y-900 electrode (Fig. 3(c)) could be deconvoluted into 4 characteristic peaks. Among them, a pair of peaks with binding energies centered at 31.7 and 33.8 eV were ascribed to the W–C$_{7/2}$ and W–C$_{5/2}$ bonds, respectively [10,15], while the two distinct peaks at 35.7 and 37.9 eV were attributed to the W–O$_{7/2}$ and W–O$_{5/2}$ bonds, respectively [42,46]. The plots of Fig. S5 in the ESM allow a comparison among the W 4f spectra of WC and WC/WO$_3$-x-T. More specifically, the intensity of W–O peaks in WC/WO$_3$-x-T gradually increased with the increase of thermal treatment temperature, suggesting that more tungsten oxide was forming by the reaction with WC at high temperatures. Moreover, the binding energy of W 4f in WC/WO$_3$-x-T decreased significantly with the increase of temperature. This revealed that WO$_3$ was reduced partially to produce WO$_{3-x}$ with oxygen vacancies, which was also consistent with the XRD results. Furthermore, in conjunction with the XRD results, the W–O bond in WC/WO$_3$-x-1000 exhibited stronger signals than that in the WC membrane. This provided evidence that WC was over-oxidized by CO$_2$ at 1000 °C. The results of the XPS analysis revealed the transfer of electrons at the WC/WO$_3$-x interface (Fig. S6 in the ESM). The binding energy of the characteristic peak of W–C in WC/WO$_3$-x-900 was lower than that of the single-phase WC, and the binding energy of W–O peaks was higher than that of the single-phase WO$_3$, suggesting that electrons were transferred from WO$_3$-x to WC at the WC/WO$_3$-x hetero-interface. Consequently, this electron transfer effect re-distributed the electrons at the interface and accelerated the charge transfer in electrocatalytic reactions.

Furthermore, the WC and WC/WO$_3$-x-700 membranes had no obvious signal in the EPR spectra (Fig. 3(d)). In contrast, in WC/WO$_3$-x-T ($T = 800$, 900, and 1000) electrodes, strong resonance lines appeared at the electron g factor of 2.003, which suggested the presence of oxygen vacancies. Moreover, the amount of oxygen vacancies gradually increased with the increase of the thermal-treatment temperature [40,47].

The morphological characteristics of the prepared ceramic electrodes are thoroughly outlined in Fig. 4. More specifically, the cross-section of the WC membrane (Fig. 4(a)) revealed an asymmetric double-layer structure, with a thickness of ~0.6 mm, composed of a skin layer (with a thickness of ~20 μm) and a finger-like porous layer. The finger-like porous layer consisted of many well-arranged micro-channels along the thickness direction. The pores were interconnected by interlacing crystal grains (Fig. S7 in the ESM). The microchannels were open at the bottom surface, had a diameter of ~60 μm, and were named “finger-like holes” after their shape (the inset in Fig. 4(a)). The skin layer at the upper part of the membrane was relatively dense. Its surface morphology, shown in Fig. 4(b), also consisted of interconnected pores formed by crystal grains, with a pore size of ~1 μm.

This unique structure is a result of the phase inversion process. In the water bath, the mutual diffusion of water and NMP destroys the inherent stability of the polymer slurry, resulting in phase separation. Continuous diffusion and phase separation finally lead to form the three-layer membrane structure, consisting of a dense sponge layer at the bottom, a finger-like porous layer in the middle, and a skin layer at the upper part (Fig. S8 in the ESM). Finally, the sponge layer (graphite) is removed after the high-temperature sintering. The skin layer and the finger-like porous layer are retained, forming the asymmetric porous membrane structure with an open bottom surface [48].

When the WC ceramic membrane was thermally treated at 700 °C in CO$_2$, a small number of whiskers with a 200–300 nm diameter grew on the top surface and inside the finger-like holes (Fig. 4(c) and Fig. S9(a) in the ESM). At 800 °C, the number of whiskers increased, the diameter increased to 200–400 nm, and they were apparently slightly larger (Fig. 4(d) and Fig. S9(b) in the ESM). When the temperature increased to 900 °C, more whiskers with a diameter of 300–500 nm were produced and uniformly distributed and interlaced.
Fig. 4 Microstructures of the ceramic electrodes. (a) Cross-section (the inset shows the bottom surface) and (b) top view of WC; top view of WC/WO$_3$-x membranes thermal-treated at (c) 700 °C, (d) 800 °C, (e) 900 °C, and (f) 1000 °C (the insets show the magnified views); and (g) top view, (h) cross-section showing the finger-like porous layer, and (i) bottom view of WC/WO$_3$-x-900 membrane.

to form interconnected pores, which completely covered the membrane surface and the finger-like hole walls (Figs. 4(e) and 4(g)–4(i)). At 1000 °C, the diameter of the whiskers was 1.4–2.2 μm, and large pores were formed by interlacing each other (Fig. 4(f) and Fig. S9(c) in the ESM).

At high temperatures, CO$_2$ should be decomposed into CO and O$_2$ through Reaction (9) [49]:

$$2\text{CO}_2 \rightleftharpoons \text{2CO} + \text{O}_2$$

where at 1000 K: the standard molar reaction Gibbs free energy $\Delta_f G_m^\theta = 391.25$ kJ·mol$^{-1}$, the standard equilibrium constant $K^\theta = 3.65 \times 10^{-21}$, partial pressure of CO $P_{\text{CO}} = 1.9 \times 10^{-7}$ atm; at 1200 K: $\Delta_f G_m^\theta = 356.49$ kJ·mol$^{-1}$, $K^\theta = 3.03 \times 10^{-16}$, $P_{\text{CO}} = 8.5 \times 10^{-6}$ atm.

The O$_2$ with low partial pressure can oxidize WC to WO$_3$. Through Reaction (10) [50,51]:

$$\text{WC} + 4\text{CO}_2 \rightleftharpoons 5\text{CO} + \text{WO}_3$$

where at 1000 K: $\Delta_f G_m^\theta = 65.57$ kJ·mol$^{-1}$, $K^\theta = 3.76 \times 10^{-4}$; at 1200 K: $\Delta_f G_m^\theta = 44.27$ kJ·mol$^{-1}$, $K^\theta = 1.18 \times 10^{-2}$.

Although the standard equilibrium constants at 1000 and 1200 K were lower than 1, Reaction (10) certainly took place spontaneously to the right, because the partial pressure of CO was very low.

The growth of whiskers should take place through the vapor–solid (VS) mechanism [52], because WO$_3$ sublimated easily. More specifically, CO$_2$ released trace amounts of oxygen at high temperatures, which should oxidize the WC surface to form the WO$_3$ crystal nuclei. The formed crystal nuclei grew along the preferred growth direction in the thermodynamic system. A small amount of WO$_3$ whiskers was produced after thermal treatment at 700 °C due to the very low partial pressure of O$_2$. As the temperature increased, the whiskers’ diameter increased due to the higher oxygen partial pressure. The thermal-treatment temperature of 900 °C lead to the formation of a large amount of W$_{24}$O$_{68}$ whiskers with appropriate diameter, which resulted in the best HER performance. Nonetheless, over-oxidation occurred at higher thermal treatment temperatures, where W$_{18}$O$_{49}$ whiskers were too large in diameter, and most of the surface was covered with oxide. When the temperature increased, the high-valence WO$_3$ should also be easily decomposed to produce low-valence tungsten oxides (W$_{24}$O$_{68}$, W$_{18}$O$_{49}$, etc.) [52,53]. The gradual decreased O/W atomic ratio in the
tungsten oxides produced at higher temperatures lead to an increase in oxygen vacancies [52,54].

The mechanical strength and the porosity of the prepared ceramic electrodes are shown in Fig. S10 in the ESM. The bending strength of the pristine WC ceramic membrane was 76.9 MPa, and the strength gradually decreased from 73.6 to 63.2 MPa with the increase of thermal-treatment temperature from 700 to 1000 °C. It should also be mentioned that all the bending strength values measured were high enough for its wide application. The porosity increased from 58.2% for WC to 67.1% for WC/WO$_3$-1000 membrane, attributed to the sublimation of WO$_3$.

Figure 5 shows the TEM analysis of WC/WO$_3$-900 electrode. More specifically, the W$_{24}$O$_{68}$ whiskers had a diameter of ~400 nm (the inset in Fig. 5(a)). Well-defined lattice fringes of the whiskers displayed good crystallinity with a lattice spacing of 0.379 nm, which corresponded to the (010) plane of W$_{24}$O$_{68}$ (Fig. 5(a)). The corresponding fast Fourier transform (FFT) image (the inset in Fig. 5(a)) revealed the (010) and the (−500) planes, suggesting the preferential growth of W$_{24}$O$_{68}$ whiskers along the (010) plane. The interface of WC/W$_{24}$O$_{68}$ heterostructure was clearly seen in Fig. 5(b). The lattice fringes had a spacing of 0.282 and 0.379 nm, which were assigned to the (001) plane of WC and the (010) plane of W$_{24}$O$_{68}$, respectively. The decomposition of WO$_3$ at high temperatures favored the formation of defects, such as lattice distortion, vacancies, and edge dislocation structures (Figs. 5(c), 5(d), and 5(e), respectively), which favored the catalytic activity of the membrane electrodes [55,56].

### 3.2 HER electrocatalytic activity

The HER electrocatalytic activity of the prepared ceramic electrodes was evaluated using a typical three-electrode system in 0.5 M H$_2$SO$_4$ and 1.0 M KOH media (Fig. S1 in the ESM). The HER catalytic performance of the prepared electrodes, along with the performance of Pt wire electrode in 0.5 M H$_2$SO$_4$, is illustrated in Fig. 6 and Table S2 in the ESM. The polarization curves (Fig. 6(a)) after IR compensation shows that Pt exhibited the lowest overpotential (defined as the overpotential when the current density reached 10 mA·cm$^{-2}$) of 34.8 mV. The bare WC ceramic electrode showed the weakest catalytic activity, with an overpotential of 216 mV. The presence of WO$_3$ significantly improved the catalytic activity, and WC/WO$_{3-x}$-900 showed the lowest overpotential of 107 mV. The improvement of the catalytic activity could be ascribed to the synergistic effect of tungsten oxide and WC.

![Fig. 5](image_url) TEM analysis of WC/WO$_{3-x}$-900 electrode. (a) HRTEM image of W$_{24}$O$_{68}$ (the insets are TEM (left) and FFT (right) images), (b) HRTEM image of WC/W$_{24}$O$_{68}$ heterostructure, and (c–e) TEM images of defects.
Fig. 6 HER performance of WC and WC/WO$_{3-x}$T ceramic membrane electrodes thermal-treated at 700, 800, 900, and 1000 °C and comparison with commercial Pt wire electrode in 0.5 M H$_2$SO$_4$ media. (a) Polarization curves, (b) Tafel slope plots, (c) capacitive current density ($\Delta j_{0.2}$ V) as a function of scan rate, and (d) EIS plots at an overpotential of 200 mV (the inset presents the equivalent circuit).

The Tafel slope is used to elucidate the kinetics of the electrocatalytic reaction process. The Tafel plots (Fig. 6(b)) demonstrated that the Tafel slope of Pt was 33.4 mV·dec$^{-1}$, which was close to the value reported in Ref. [57]. The Tafel slope of WC/WO$_3$-900 was 59.3 mV·dec$^{-1}$, which was superior to those of WC (113.1 mV·dec$^{-1}$), WC/WO$_3$-700 (91.7 mV·dec$^{-1}$), WC/WO$_3$-800 (67.5 mV·dec$^{-1}$), and WC/WO$_3$-1000 (73.5 mV·dec$^{-1}$), manifesting the fastest kinetics.

In an acidic medium, the HER process can be carried out through the following three basic steps [42]:

Volmer reaction: $\text{H}_3\text{O}^+ + e^- \rightarrow \text{H}_\text{ads} + \text{H}_2\text{O}$ (11)

Heyrovsky reaction: $\text{H}_2\text{O} + e^- + \text{H}_\text{ads} \rightarrow \text{H}_2\uparrow + \text{H}_2\text{O}$ (12)

Tafel reaction: $\text{H}_\text{ads} + \text{H}_\text{ads} \rightarrow \text{H}_2\uparrow$ (13)

According to the slope values, the Volmer–Heyrovsky mechanism should govern the HER process in WC/WO$_3$-900 electrode.

The exchange current density ($J_0$) is also an important parameter for evaluating the HER kinetics. It represents the hydrogen evolution rate per unit surface area at a certain potential, and can be calculated by extrapolating the Tafel diagram [58]. The results (Fig. S11 and Table S2 in the ESM) show that the exchange current density ($J_0$) of WC/WO$_3$-900 was 0.253 mA·cm$^{-2}$, which was markedly higher than that of bare WC, indicating the highest reaction efficiency. The ECSA was calculated by the $C_{dl}$ obtained by the CV test (Fig. S12 in the ESM) [36]. The electrode WC/WO$_3$-900 displayed the highest $C_{dl}$ of 181.8 mF·cm$^{-2}$ (Fig. 6(c)) and the largest ECSA of 4545.0 cm$^2$ (Table S3 in the ESM). These results suggested that it had the largest electrocatalytic effective surface area, leading to the best performance.

The Nyquist plots (Fig. 6(d)), which were fitted into an equivalent circuit containing solution resistance ($R_s$), were used to investigate the electrochemical activity of the electrocatalysts in H$_2$SO$_4$ media and estimated the values of charge transfer resistance ($R_{ct}$) and constant phase element (CPE). The smallest radius, i.e., $R_{ct} = 0.82 \, \Omega$, was recorded for WC/WO$_3$-900, which was much lower than that of WC (4.66 \, \Omega), suggesting its superior electrical conductivity and reaction kinetics at
the electrocatalyst–electrolyte interface (Table S2 in the ESM). The FE of the HER of WC/WO$_3$-$\cdots$-900 membrane electrode was evaluated, and the experimental measurement was consistent with the theoretically calculated amount of hydrogen, showing that the FE of the electrode was close to 100% (Fig. S13 in the ESM). The TOF was also measured to investigate the intrinsic activity of the electrodes. According to Fig. S14 in the ESM, the TOF value of WC/WO$_3$-$\cdots$-900 was 2.37 s$^{-1}$, which was more than 5 times that of WC (0.42 s$^{-1}$) when the overpotential was 200 mV.

During the operation process of HER catalyst, durability and stability are important parameters, which define the electrode’s performance. The linear sweep voltammetry (LSV) curves for WC/WO$_3$-$\cdots$-900 before and after 10,000 CV cycles (Fig. 7(a)) were almost overlapped, suggesting robust durability. In addition, the chronopotentiometric curve test at 30, 50, 100, 200, and 400 mA·cm$^{-2}$ was employed to evaluate the electrode stability (Fig. 7(b)). The overpotential remained almost constant under various current densities tested. Moreover, the overpotential of 30 mA·cm$^{-2}$ remained almost constant after 180 h of operation, suggesting good long-term stability. Furthermore, after the stability test, no change was detected in the morphology, phase composition, and the chemical state of WC/WO$_3$-$\cdots$-900, reflecting its excellent stability (Figs. S15 and S16 in the ESM). Considering the scouring and impact effect of water flow on the electrode in the actual process of water electrolysis, a water permeability test was performed on WC/WO$_3$-$\cdots$-900 (Fig. S17 in the ESM). The water permeation flux was 12.08×10$^3$ L·m$^{-2}$·h$^{-1}$·bar$^{-1}$, which remained stable under 3.0 bar for 4 h. In addition, the LSV curves almost coincided before and after the test, which reflected the stable and practical performance of the membrane electrode.

The LSV plots of the prepared electrodes in comparison with Pt in alkaline media are presented in Fig. 8(a). Compared to the 234-mV overpotential of the bare WC electrode, WC/WO$_3$-$\cdots$-900 manifested superior electrocatalytic activity with a low overpotential of 123 mV. The overpotential in alkaline solution was higher than that in acidic solution, which should be due to the protons provided by water dissociation under alkaline condition [59]. Moreover, the hydrophilicity of the electrode in acidic solution was better than that in alkaline solution, which should be conducive due to the full contact between the electrolyte and the electrode (Fig. S18 in the ESM) [41]. WC/WO$_3$-$\cdots$-900 electrode also had the smallest Tafel slope of 72.4 mV·dec$^{-1}$, suggesting that the Volmer–Heyrovsky mechanism governed the catalytic process (Fig. 8(b) and Table S4 in the ESM). Additionally, the highest exchange current density ($j_0$) of 0.363 mA·cm$^{-2}$ was recorded for WC/WO$_3$-$\cdots$-900, which justified its excellent catalytic performance among the produced catalysts (Fig. S19 and Table S4 in the ESM). From the CV curves (Fig. S20 in the ESM), the $C_{dl}$ of WC/WO$_3$-$\cdots$-900 was calculated as 168.3 mF·cm$^{-2}$, approximately 8 times as high as that of WC (21.9 mF·cm$^{-2}$) (Fig. S21 and Table S4 in the ESM), and the calculated ECSA was 4207.5 cm$^2$ (Table S3 in the ESM). These results confirmed that this electrode exposed the highest number of reactive sites in alkaline media.

According to the Nyquist plots (Fig. S22 in the ESM), the charge transfer resistance ($R_{ct}$) of WC/WO$_3$-$\cdots$-900 was 1.01 Ω, which was the smallest among the prepared electrodes. Moreover, the FE of WC/WO$_3$-$\cdots$-900 was close to 100%, reflecting its high catalytic performance.

Fig. 7 HER performance of WC/WO$_3$-$\cdots$-900 ceramic electrode in 0.5 M H$_2$SO$_4$. (a) Comparison of polarization curves before and after 10,000 CV cycles and (b) chronopotentiometry curve at 30, 50, 100, 200, and 400 mA·cm$^{-2}$ for 180 h.
Fig. 8 HER performance of WC and WC/WO_3-\(x\)-T thermal-treated at 700, 800, 900, and 1000 °C and the comparison with commercial Pt wire electrode in 1.0 M KOH media. (a) Polarization curves, (b) Tafel slope plots, (c) comparison of polarization curves before and after 10,000 CV cycles, and (d) chronopotentiometry curve at 30, 50, 100, 200, and 400 mA·cm\(^{-2}\) for 180 h for WC/WO_3-\(x\)-900 ceramic electrode.

(Fig. S23 in the ESM). Meanwhile, WC/WO_3-\(x\)-900 also showed the highest intrinsic activity with a TOF value of 2.19 s\(^{-1}\) at an overpotential of 200 mV (Fig. S24 in the ESM). There were no striking differences in the LSV curves of WC/WO_3-\(x\)-900 before and after 10,000 CV cycles in the 1.0 M KOH solution (Fig. 8(c)), suggesting that the electrode also had good long-term HER stability in alkaline media. In addition, in the chronopotential curve test (Fig. 8(d)) at current densities of 30, 50, 100, 200, and 400 mA·cm\(^{-2}\), the overpotential of 30 mA·cm\(^{-2}\) remained almost constant after 180 h of operation, suggesting its superior long-term stability in alkaline media. As expected, the morphology and phase composition of WC/WO_3-\(x\)-900 electrode were almost unaffected by the long-term stability test (Figs. S15 and S16 in the ESM).

The HER performance of WC/WO_3-\(x\)-900 was compared with the previously reported TC-based catalysts in acidic and alkaline media (Tables S5 and S6 in the ESM, respectively). The HER performance of WC/WO_3-\(x\)-900 electrode exceeded those of many TC-based electrocatalysts. Most importantly, WC/WO_3-\(x\)-900 was a strong self-supported electrode prepared through a simple and scalable production method.

The above experimental results showed that the WO_3-\(x\) whiskers produced by the reaction of WC with CO_2 should play an important role. The in situ developed WC/WO_3-\(x\) heterostructure interface synergistically modulated the electronic structure and the charge transfer, favoring the acceleration of the HER electrochemical process and the maintenance of high stability [22,60,61]. The appropriate number and diameter of WO_3-\(x\) in WC/WO_3-\(x\)-900 lead to the best HER performance. Furthermore, the abundance of oxygen vacancies in the non-stoichiometric WO_3-\(x\) provided many effective electron transfer paths, which could accelerate the electron transfer, and could also play the role of active sites to improve the HER performance [2,31,56]. They could also modulate the electronic structure and reduce the band gap of WO_3, and often generate interband states for WO_3, thereby improving conductivity [40,62]. Moreover, the in situ
high-temperature reaction generated many defects, which could modulate the electronic structure and surface properties of the electrodes, thereby optimizing the H adsorption step in the HER [63]. The high superhydrophilicity (Fig. S18 in the ESM) and the asymmetric structure favored the charge transfer between the electrode and the electrolyte as well as the easy removal of the bubbles from the electrode surface.

4 Conclusions

A self-supporting porous WC ceramic electrode was produced with WO$_{3-x}$ whiskers produced in situ on the surface and inside the finger-like hole structure. WC/WO$_{3-x}$-900 electrode displayed outstanding HER activity in both acidic and alkaline media (overpotentials of 107 and 123 mV and Tafel slopes of 59.3 and 72.4 mV·dec$^{-1}$, respectively), and good long-term stability and durability. The superior HER performance was attributed to the WC/WO$_{3-x}$ heterostructure interface, the abundance of oxygen vacancies, the superhydrophilicity, and the asymmetric structure of the finger-like holes. The self-supporting electrodes were also produced easily. Thus, they manifest good prospects for large-scale production and a wide application in water splitting in conjunction with their good properties.

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Electronic Supplementary Material

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