

Article

TiO₂-Doped Hydrochar Derived from *Phoenix dactylifera*: Synthesis and Electrocatalytic Performance for Alkaline Hydrogen Production

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Abstract

Cost-effective, durable, and environmentally friendly electrocatalysts to be used for the alkaline hydrogen evolution reaction (HER) represent one of the key challenges facing green hydrogen generation. In this context, a TiO₂-doped hydrochar derived from *Phoenix dactylifera* L. Deglet Nour (date pits) was synthesized and incorporated into a graphite-based electrode to improve HER performance in a 1 M KOH solution. Three TiO₂ loadings (1, 3, and 6 wt%) were systematically studied and compared using electrochemical techniques to evaluate the influence of oxide incorporation on HER kinetics. In parallel, physicochemical characterization analyses were performed to acquire an in-depth understanding of the morphology, composition, and surface properties of biomass-derived carbonaceous materials and to establish correlations with their electrochemical behavior. The G/HC-3% TiO₂ electrode exhibited the most pronounced electrocatalytic performance, with an overpotential of 194 mV at $-10 \text{ mA} \cdot \text{cm}^{-2}$ and a Tafel slope of $67 \text{ mV} \cdot \text{dec}^{-1}$, indicating favorable interfacial charge transfer kinetics. The present work demonstrates that biomass-derived TiO₂-doped hydrochar has significant potential as a sustainable and high-performance electrocatalyst in alkaline water electrolysis.

Keywords: hydrogen evolution reaction (HER); alkaline water electrolysis; sustainable electrocatalyst; non-noble catalysts; hydrochar-based electrodes



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1. Introduction

The global transition toward sustainable energy systems requires the development of efficient and environmentally benign technologies for hydrogen production. Hydrogen has been identified as a clean high-energy-density fuel with the potential to supplement renewable sources that are intermittent, like solar and wind power [1,2]. Alkaline water electrolysis (AWE) is one of the oldest and most widely used systems in production technology due to its low cost, long-term stability, and ability to use non-precious metal catalysts. By applying an electric current through an alkaline electrolyte, typically a KOH or NaOH

solution, hydrogen forms at the cathode and oxygen at the anode. Water molecules are considered to be the source of protons under alkaline conditions, and hydrogen production follows the Volmer–Heyrovsky or Volmer–Tafel process [3].

Nonetheless, the general effectiveness of this process is restricted by the slow kinetics of the hydrogen evolution reaction (HER), especially in alkaline conditions [4,5], where overpotentials of more than 200–400 mV are generally necessary due to the extra energy required to dissociate water molecules before protons can be reduced. Consequently, to surmount such kinetic barriers, cost-effective and durable electrocatalysts are of great importance [6]. Noble metals like platinum exhibit excellent HER activity (overpotentials of 30–50 mV at 10 mA/cm²) but suffer from high cost and scarcity, restricting their large-scale implementation [7,8]. As a result, the creation of other types of materials relying on earth-available elements, with customized surface chemistry and conductivity to promote catalyst activity, has been an active research focus [7–9].

Carbon-based materials showed good potential due to their high electrical conductivity, adjustable porosity, and chemical stability [10,11]. Among them, hydrochar, the hydrothermal product of biomass carbonization, provides an environmentally friendly pathway to the functionalized carbon rich in oxygen-containing functional groups, hierarchical porosity, and reactive surfaces [12–14]. These surface functionalities allow for the anchoring of metal oxides or nanoparticles, which results in synergistic composite materials. In this respect, titanium dioxide (TiO₂) has gained a lot of interest because of its high chemical stability and the capacity to offer a high number of active sites to absorb hydrogen [15]. Nevertheless, it has inherent low electrical conductivity (~10^{−12} S/cm for bulk TiO₂) which restricts its inherent catalytic capability [16]. This limitation can be mitigated by incorporating TiO₂ with a conductive carbon matrix to enhance the transfer of charges and provide more catalytic interfaces into contact [17]. The incorporation of TiO₂ into a biomass-based hydrochar system is thus an encouraging approach to achieving effective, low-cost and sustainable electrocatalysts for the HER [10,17]. The date pit waste (*Phoenix dactylifera* L.) carbon matrix offers a renewable supply of carbon with a high oxygen surface area and functional oxygen groups, and TiO₂ nanoparticles facilitate better catalytic activity [18]. These robust interfaces between the two phases, especially the Ti–O–C bonds, may facilitate the movement of electrons and support the Volmer step ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^*_{\text{ads}} + \text{OH}^-$) during the alkaline HER [8,19].

The aim of the current study is achieving the synthesis and characterization of graphite–hydrochar–TiO₂ composite electrodes with different TiO₂ loadings (1, 3, and 6 wt%) to understand the correlation between the structure and electrocatalytic activity. Specifically, we aim to: (i) describe crystallinity, morphology, and interfacial bonding; (ii) ascertain the electrochemical characteristics of the samples using electrochemical impedance spectroscopy, Tafel analysis, and linear sweep voltammetry; and (iii) evaluate the effect of TiO₂ content on electrical conductivity, charge transfer, the accessibility of active sites and HER kinetics in 1 M KOH aqueous solution.

2. Materials and Methods

2.1. Chemicals and Reagents

All chemicals used were of analytical grade and employed without any further purification. Titanium dioxide (TiO₂, anatase), ethanol (≥99.8%), and potassium hydroxide (KOH) were supplied by Sigma-Aldrich (St. Louis, MO, USA). The hydrochar used in this study was synthesized from *Phoenix dactylifera* L. Deglet Nour (date pits), and deionized water was used in all preparation and electrochemical steps.

Figure 1 shows a schematic illustrating the role of each component in the composite electrode.

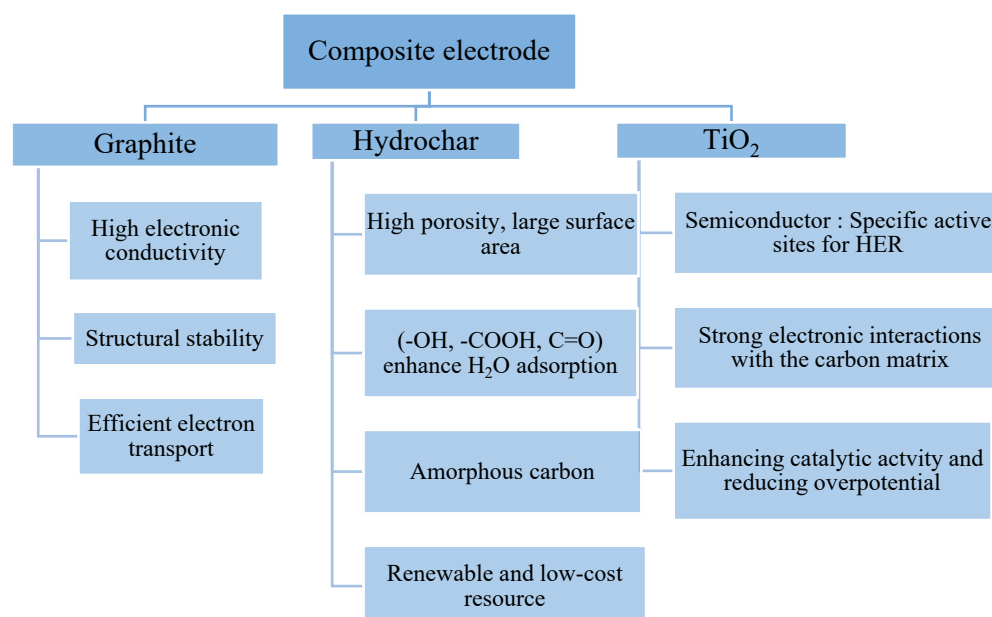


Figure 1. The synergistic contributions of graphite, hydrochar, and TiO₂ components in the composite electrode.

Graphite ensures conductivity, hydrochar provides porosity and active sites, and TiO₂ enhances electron transfer and catalytic activity [20,21].

2.2. Preparation and Doping of Hydrochar

Hydrochar was synthesized from *Phoenix dactylifera* L. (date pits) according to the procedure described in Figure 2 and subsequently doped with titanium dioxide (TiO₂) using a dispersion method [22]. The preparation of hydrochar involved several steps. First, date pits were washed with distilled water three to four times to remove impurities, adhering dust, and water-soluble substances. After washing, the raw material was dried at 80 °C for 24 h to remove residual moisture. The dried pits were then ground into a fine powder using a blade mill (model 07251842 from Grosseron, Saint-Herblain, France). The resulting product was sieved to obtain different particle sizes using sieves with different mesh sizes. To ensure uniform particle size, only fractions with a diameter of 250 µm were retained for the preparation of hydrochar.

The hydrothermal carbonization of the biomass was carried out in a 30 mL Teflon-lined stainless-steel autoclave reactor. For each batch, 2.5 g of biomass was mixed with 25 mL of distilled water (solid-to-liquid ratio of 1:10 g mL^{−1}). This reactor was heated to 230 °C for 8 h and then left to cool naturally to room temperature. This procedure was repeated ten times under the same conditions to obtain a sufficient amount of hydrochar for the subsequent activation and electrode preparation. The obtained hydrochar was filtered, rinsed, and dried at 80 °C for 24 h. The mass yield of the material was calculated for each batch using $\eta (\%) = \frac{m_f}{m_i} * 100$. Through the repetition of the hydrothermal process, a consistent mass yield of 56% was obtained, with a standard deviation of only 0.7%.

For chemical activation, 5 g of the carbonized sample was carefully impregnated with 85% phosphoric acid at an impregnation mass ratio of 1:2 (sample:acid). The acid was added gradually to ensure distribution over the sample surface, forming a thin, uniform layer of phosphoric acid on the carbon surface. This step aimed to enhance the porosity and surface area of the carbon material, essential for improving its adsorption capabilities. After impregnation, the sample was dried overnight at 80 °C to remove any residual moisture. Once dried, the impregnated sample was calcined at 550 °C for 90 min in a nitrogen atmosphere. After calcination, the sample underwent a final rinse with deionized water.

until the washing solution reached a neutral pH (~ 7), indicating the complete removal of residual acid. This was followed by vacuum filtration to separate the solid from the liquid phase. The filtered sample was then dried again at $80\text{ }^{\circ}\text{C}$ for 24 h, yielding a stable, activated carbon material which was stored in a desiccator until further use.

For TiO_2 doping, an appropriate amount of TiO_2 was mixed with hydrochar at different mass ratios (5, 15 and 30 wt% TiO_2 relative to the total mass). The mixture was dispersed in an ethanol solution under magnetic stirring for 2 h at room temperature, then dried and calcined at $300\text{ }^{\circ}\text{C}$ for 2 h.

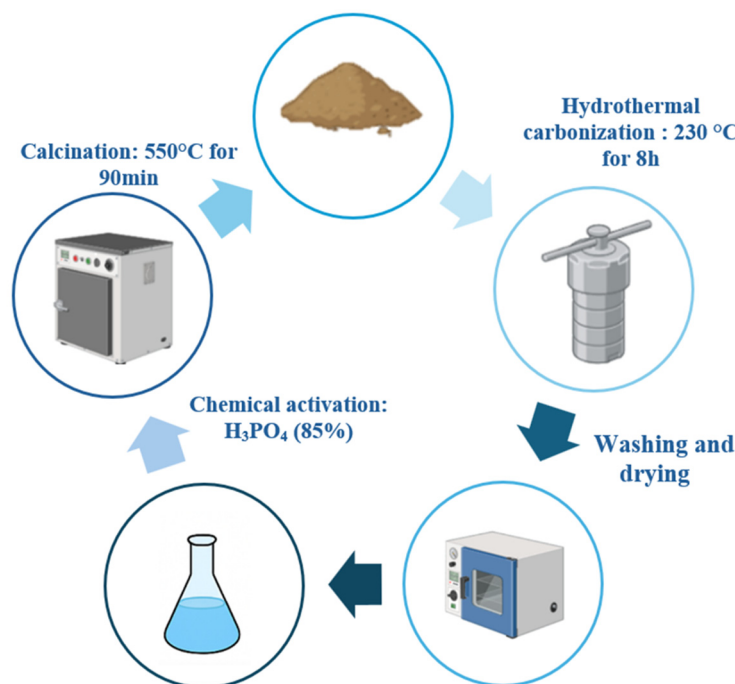


Figure 2. Hydrochar synthesis process.

2.3. Electrode Preparation

The working electrodes were prepared in two phases, using the graphite paste method. The hydrochar derived from *Phoenix dactylifera* date pits was used as a carbonaceous modifier; it was first doped with TiO_2 at nominal mass ratios of 5, 15, and 30 wt% (relative to the hydrochar mass) to form the HC- TiO_2 composite. In the second step, the final working electrode was prepared by mixing 80 wt% of graphite with 20 wt% of the previously synthesized composite, as shown in Table 1 [23,24]. This solid mixture was then homogenized with paraffin oil as a binder, using a solid-to-binder mass ratio of 74:26 (w/w). The paste was then packed into the cavity of a 1 mL insulin syringe with a surface area of 0.166 cm^2 . A copper wire was inserted into the paste to ensure electrical contact while remaining protected from the electrolyte. Before each electrochemical measurement, the electrode surface was polished using emery paper and rinsed with distilled water to ensure reproducibility.

Table 1. Composition and nominal loading of different electrodes.

Sample Name	TiO_2 in Composite (wt%)	Composite in Electrode (wt%)	Actual TiO_2 in Electrode (wt%)
G/HC-5% TiO_2	5%	20%	1%
G/HC-15% TiO_2	15%	20%	3%
G/HC-30% TiO_2	30%	20%	6%

2.4. Electrochemical Characterization

A combination of complementary characterization techniques was used to obtain a comprehensive understanding of the TiO₂-doped hydrochar electrodes (Figure 3). Electrochemical experiments were performed with an EC-lab software (version 12.0)-controlled Bio-Logic SP150 potentiostat (Bio-Logic Science Instruments, Seyssinet-Pariset, France). All electrochemical measurements were carried out using three electrodes, a working electrode (WE), a platinum electrode as the counter electrode (CE) and a saturated calomel electrode (SCE), in an alkaline solution of 1 M KOH.

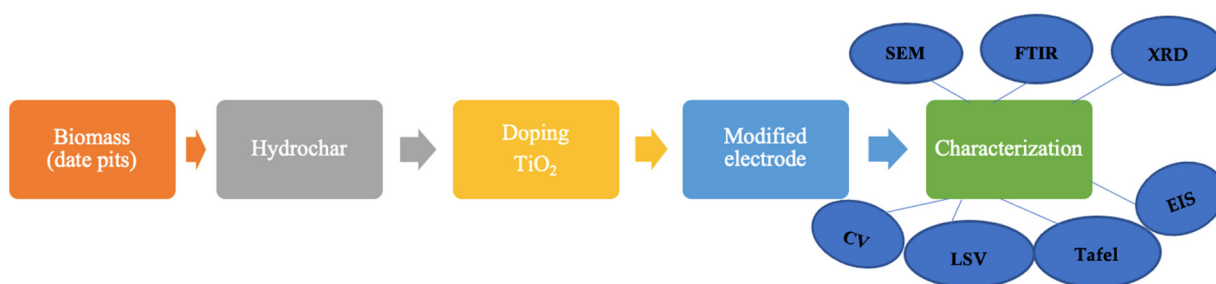


Figure 3. Schematic representation of experimental workflow for preparation of hydrochar/TiO₂-modified electrodes and their structural and electrochemical characterizations.

To study the hydrogen evolution reaction (HER), all measurements were carried out in the negative potential range (−1.6 to 0 V vs. SCE), focusing exclusively on the cathodic region to observe reduction processes. Based on the equation $E_{\text{RHE}} = E_{\text{SCE}} + 0.241 + 0.059 \times \text{pH}$, all potentials were converted to the reversible hydrogen electrode (RHE), and the current densities were normalized to the geometric area of the working electrode. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were performed at a sweep rate of 10 mV·s^{−1}, and electrochemical impedance spectroscopy (EIS) measurements were carried out over a frequency range from 100 kHz to 0.1 Hz with a perturbation amplitude of 10 mV. All electrochemical measurements were repeated three times on different days under identical experimental conditions. The obtained results showed only minor fluctuations, confirming the reproducibility of the electrochemical data.

3. Results and Discussion

3.1. Structural and Chemical Characterization

To determine the specific pore surface of hydrochar, a BET analysis was conducted. As presented in Table 2, activated hydrochar exhibits the most favorable properties, with a high specific surface area of 254.28 m²/g and a well-developed porous structure. These characteristics make it highly suitable for demanding applications such as electrocatalysis. In contrast, raw hydrochar shows more moderate adsorptive properties (33.04 m²/g), while the starting biomass possesses a very small surface area (0.22 m²/g) and negligible microporosity.

In this section, the synthesized catalysts are referred to as HC-5%, HC-15% and HC-30%, where the percentage denotes the initial TiO₂ doping level used during the synthesis of hydrochar from date pit biomass.

Figure 4 presents the FTIR spectra of the three TiO₂-doped hydrochar catalysts, and the analysis reveals characteristic functional groups and confirms the gradual incorporation of TiO₂ within the composite matrix. A broad absorption band appears at 3359.94 cm^{−1} for the HC/5% TiO₂ composite and at 3229.96 cm^{−1} for the 15% TiO₂ sample. This band corresponds to the O–H stretching vibrations of surface hydroxyl groups from TiO₂, oxygenated functional groups from hydrochar, and adsorbed water molecules. The transition to lower

wavenumbers accompanied by increasing TiO₂ content indicates stronger hydrogen bonding and enhanced interaction between hydroxyl groups and the metal oxide surface. A weak peak at 2917.46 cm⁻¹, which appears for the 30% TiO₂ composite, is due to the C–H stretching vibrations of the remaining methylene groups of the hydrochar. Its low intensity indicates a high level of carbonization of the material. All three composites exhibit an intense band around 1574 cm⁻¹ (1574.57 cm⁻¹ for 5% and 1574.20 cm⁻¹ for 15%), assigned to the vibrations of carboxylate groups (COO⁻) and aromatic C=C bonds in the hydrochar. The presence of this band even at 5% TiO₂ suggests the formation of carboxylate–titanium complexes, providing evidence of a chemical interaction between the two components.

Table 2. BET characteristics of analyzed materials.

Parameters	Biomass	Raw Hydrochar	Activated Hydrochar
Specific Surface Area (m ² /g)			
Single-Point Surface Area	0.2146	33.0493	232.7693
BET Surface Area	0.2208	33.0497	254.2808
Langmuir Surface Area	0.4177	52.5552	807.4454
t-Plot Micropore Area	-	15.3367	60.8747
t-Plot External Surface Area	0.2492	17.7131	193.4981
BJH Adsorption Cumulative Surface Area	-	6.4499	782.4208
Pore Volume (cm ³ /g)			
t-Plot Micropore Volume	−0.000005	0.008573	0.03193
BJH Adsorption Cumulative Volume	-	0.004034	0.521714
Pore Size (nm)			
BJH Adsorption Average Pore Diameter	-	2.5016	2.8672

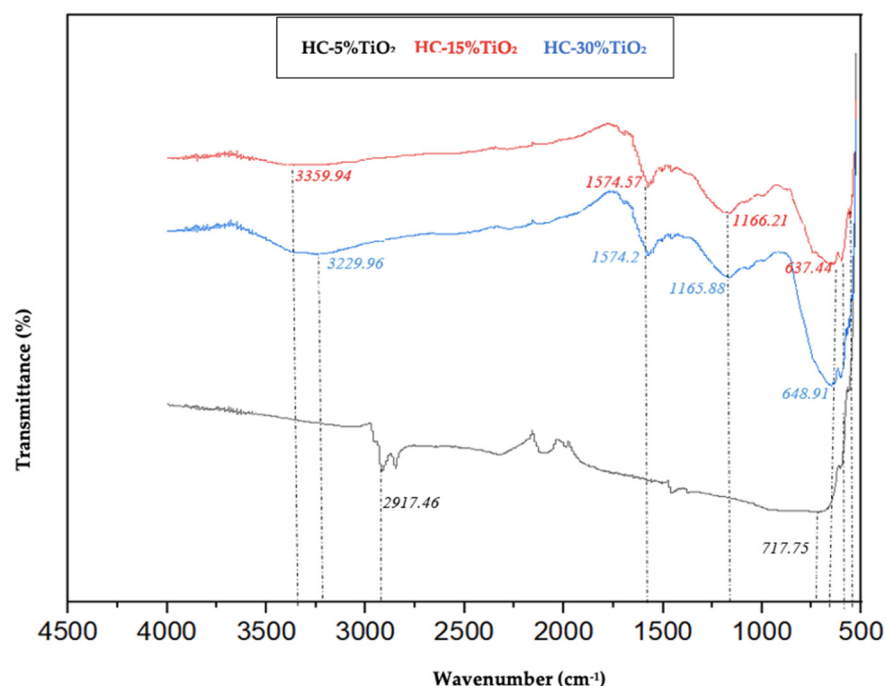


Figure 4. FTIR spectra of hydrochar/TiO₂ composite electrodes with different TiO₂ loadings (5, 15, and 30 wt%).

The bands at 1166.21 cm^{-1} (5%) and 1165.88 cm^{-1} (15%) result from the overlapping of C–O vibrations (alcohols, ethers, esters) from hydrochar and Ti–O–Ti vibrations from TiO_2 , confirming the coexistence of organic and inorganic phases.

The bands observed at 837.44 cm^{-1} and 717.75 cm^{-1} are attributed to aromatic C–H deformation and Ti–O vibrations, respectively.

This region provides the most direct evidence of TiO_2 incorporation. The bands at 717.75 cm^{-1} and 648.91 cm^{-1} are characteristic of Ti–O and Ti–O–Ti vibrations corresponding to the anatase phase of TiO_2 . The progressive increase in intensity in this region ($5\% < 15\% < 30\%$) confirms the controlled and quantitative incorporation of TiO_2 . For the 30% TiO_2 composite, transmittance decreases drastically, indicating a high abundance of Ti–O bonds.

The main structural and functional effects revealed by FTIR analysis and their contribution to the improved HER activity of the HC– TiO_2 composites are summarized in Figure 4.

All in all, the FTIR analysis demonstrates that TiO_2 is successfully incorporated into the composite through the formation of carboxylate–titanium interfacial bonds. This structure evolution, in terms of improved surface functionality and hybrid interfaces, is likely to have a very significant impact on the electrochemical behavior of the electrodes, as discussed in the next section.

The correlated analysis of the EDX spectra and elemental mappings of the SEM micrographs was conducted on the hydrochar– TiO_2 composite powders before mixing them with graphite in order to confirm the successful incorporation of TiO_2 into the hydrochar matrix. Figure 5 shows the progressive structural and chemical evolution of the bio-based electrodes doped with TiO_2 with respect to the oxide content.

At 5 wt% TiO_2 , the carbon matrix derived from biomass retains a porous and lamellar texture, composed of carbon aggregates of a few micrometers in size. TiO_2 is presented in the form of extremely fine, submicrometric particles, which are evenly distributed throughout the carbon network without forming perceptible clusters. At this scale, the oxide does not form a distinct phase, since the particles are small and adequately dispersed to influence the overall morphology. This is confirmed by the EDX quantifications showing titanium only in trace amounts and by the elemental maps where the Ti signal appears as isolated points.

According to the SEM characterizations of TiO_2 nanoparticles obtained from the 15 wt% sample, the development of oxide-related features drastically increased in magnitude and definition when compared to the prior sample of 5 wt% TiO_2 . In addition, there is a marked change in the microstructural composition of the sample, resulting in a more defined biphasic structure. Furthermore, SEM characterizations demonstrate that the 15 wt% sample possesses a higher number of granular deposits and submicrometric to micro-aggregates than the 5 wt% sample and does not completely occlude the pore structure of the composite. The EDX analyses, in turn, validate a consistent rise in titanium content ($\approx 10.11\text{ wt}\%$), whereas the elemental mappings prove the dense yet highly uniform distribution of Ti, which reflects the creation of a long interfacial network between the conductive carbon matrix and oxide particles. This structuring imparts a hierarchy of functions within the composite: electronic conduction ensured by the continuous carbon matrix and an increased density of active sites provided by TiO_2 . At this stage, morphological integrity is preserved, and the interfacial connection probably promotes efficient charge transfer, conditions normally associated with good electrochemical performance.

At 30 wt% TiO_2 , the capacity of the carbon matrix is exceeded, resulting in widespread restructuring and a significant increase in particle size. EDX measurements show that there are high levels of titanium (around 35 wt% Ti), and elemental mapping also shows that

there are significant areas with high concentrations of titanium, which corroborate the fact that there was intense segregation and loss of dispersion.

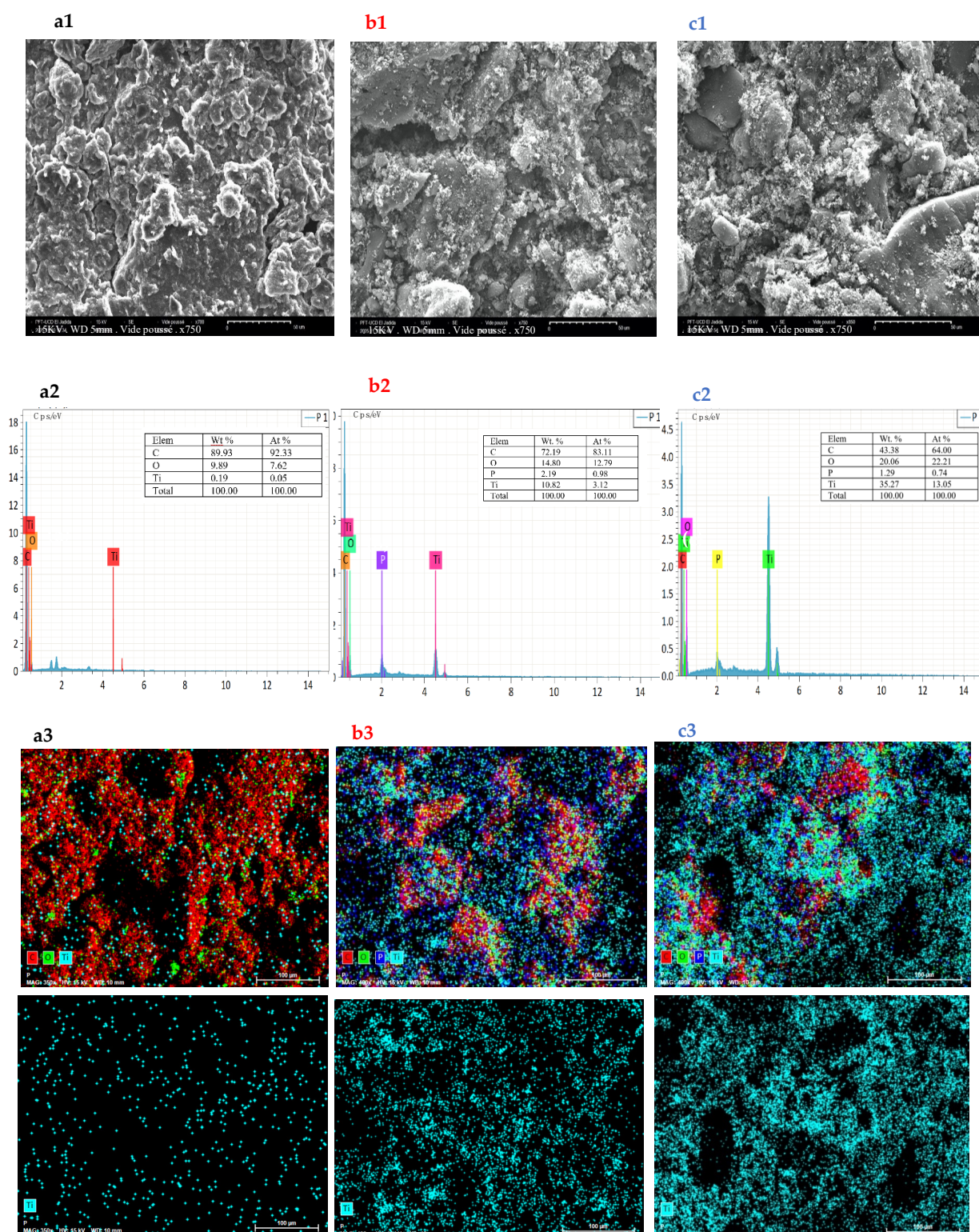


Figure 5. The SEM–EDX analysis of the morphology and elemental composition of HC–TiO₂ composites with varying TiO₂ loadings: HC–5%TiO₂: (a1) SEM image, (b1) EDX spectrum, and (c1) elemental mapping. HC–15%TiO₂: (a2) SEM image, (b2) EDX spectrum, and (c2) elemental mapping. HC–30%TiO₂: (a3) SEM image, (b3) EDX spectrum, and (c3) elemental mapping. Scale bars correspond to 50 μ m.

Figure 6 presents the X-ray diffraction patterns of the HC/ $x\%$ TiO₂ composites with various amounts of the oxide (5 wt%, 15 wt% and 30 wt%). This analysis confirms the formation of a highly crystallized hydrochar/TiO₂ composite in the anatase phase, as evidenced by the presence of characteristic diffraction peaks. The diffractogram of the sample containing 5% TiO₂ is dominated by a carbon peak, which is attributed to the (002) plane and is centered around $2\theta \approx 26^\circ$. The peaks associated with TiO₂ are either weak or hard to detect, which is explained by the low TiO₂ content that restricts their XRD detectability. When the TiO₂ content rises to 15 wt%, the diffractogram shows multiple additional peaks, most notably at approximately $2\theta \approx 37^\circ$ (004), 48° (200), 54° (105), 62° (204), and 68° (116). These peaks represent the distinctive crystallographic phase of the anatase phase of TiO₂. The appearance of these reflections indicates the formation of distinct TiO₂ crystallites within the carbon matrix. The anatase-related peaks in the sample with 30 wt% TiO₂ become noticeably more intense and well-defined, indicating an increase in crystallinity and the amount of oxide in the composite. Additionally, no extra peaks that would indicate secondary phases or impurities were observed, showing that a relatively pure HC/TiO₂ composite was successfully formed. The evolution of the spectra reveals a clear correlation between oxide content and structural response: from the 5% sample to the 30% sample, the intensity of the peaks increases considerably, indicating a higher density of active crystalline sites. This well-defined anatase structure provides optimized charge transfer pathways and a more effective catalytic surface for proton adsorption, in contrast to amorphous phases that restrict conduction.

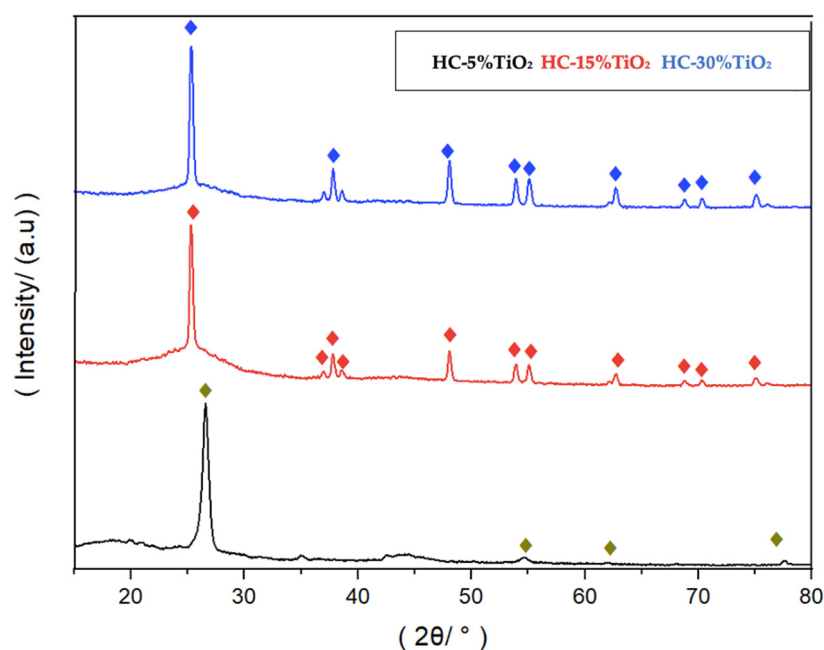


Figure 6. X-ray diffraction (XRD) analysis of HC- $x\%$ TiO₂ composites.

3.2. Electrochemical Analysis

For the electrochemical study, the fully assembled electrodes are designated as G/HC-1%TiO₂, G/HC-3%TiO₂ and G/HC-6%TiO₂. These electrodes were prepared using the previously described HC-5%, HC-15% and HC-30% catalysts, respectively, integrated into the graphite matrix at specific mass loadings.

The cyclic voltammograms (Figure 7) clearly demonstrate the effect of TiO₂ incorporation on the electrocatalytic behavior of hydrochar under an applied potential range of -0.53 to 1.07 V vs. RHE at a scan rate of $10 \text{ mV} \cdot \text{s}^{-1}$. In order to better understand the role of TiO₂, reference electrodes based on pure graphite and undoped hydrochar were also

studied. Pure graphite and the undoped hydrochar (G/HC-0%TiO₂) exhibit the lowest cathodic current densities, reaching only approximately −11 mA and −26 mA respectively. The modified electrode (G/HC-1%TiO₂) exhibits modest catalytic improvement, with a cathodic current density not exceeding −32 mA, reflecting sluggish hydrogen evolution reaction (HER) kinetics. This minimal addition (1 wt%) of TiO₂ suggests a limited contribution to the creation of additional active sites, and the overall effect remains marginal. At an intermediate doping level of 3 wt%, a remarkable enhancement is observed, with the current density reaching −80 mA. This substantial increase is consistent with a favorable interfacial interaction between the porous hydrochar matrix and the TiO₂ nanoparticles: the hydrochar provides a high surface area and a conductive carbon framework, while TiO₂, despite its semiconducting nature, appears to act as an interfacial modifier that facilitate charge redistribution at the electrode/electrolyte interface through Ti-O-C coupling rather than as a direct electronic conductor. This enhancement is supported by the non-monotonic dependence of performance on TiO₂ loading, which cannot be attributed to a simple surface area effect alone. Nevertheless, when TiO₂ loading is further increased to 6 wt%, activity is reduced significantly (−30 mA). This deterioration is attributed to particle agglomeration and partial pore blocking, which reduces the available electroactive surface area. Moreover, excessive TiO₂ loading introduces an additional resistive barrier that impedes the charge transfer, consistent with the character of the oxide at high concentrations, thereby negating its catalytic contribution. Overall, these results show that 3 wt% TiO₂ doping provides the best balance between interfacial modification, porosity preservation, and charge transfer efficiency [25].

The linear sweep voltammetry (LSV) curves in Figure 8 indicate significant variations in electrocatalytic activity between the modified electrodes, in full accordance with the cyclic voltammetry (CV) data. Pure graphite and the undoped hydrochar (G/HC-0%TiO₂) exhibit the lowest cathodic current densities, reaching about −20 mA/cm² and −29 mA/cm² respectively. With a cathodic current density of approximately −120 mA/cm² at −0.53 V vs. RHE, the G/HC-3%TiO₂ electrode exhibits the best electrocatalytic performance, suggesting more efficient processes of charge transfer and increased access to the catalytic sites of the electrode/electrolyte interface. Conversely, electrodes with 1% and 6% TiO₂ exhibit intermediate activity. At low TiO₂ concentration (1%), the number of titanium-based active sites is not high enough to effectively catalyze the step involving the dissociation of water, which is rate-limiting under alkaline conditions. On the other hand, at high TiO₂ loading (6 wt%), performance decreases, consistent with reduced charge transfer efficiency, particle agglomeration, and the partial filling of the porous graphite/hydrochar structure.

In 1 M KOH, the LSV curves of the G/HC-*x*%TiO₂ electrodes show the following hierarchy: G/HC-3%TiO₂ has the highest current densities across the entire potential window, followed by G/HC-1%TiO₂ and the undoped hydrochar (G/HC-0%TiO₂), while pure graphite and G/HC-6%TiO₂ show the lowest performance. At −10 mA·cm^{−2}, the overpotentials follow the order G/HC-3%TiO₂ ($\eta_{10} = 194$ mV) < G/HC-1%TiO₂ ($\eta_{10} = 198$ mV) < G/HC-6%TiO₂ ($\eta_{10} = 373$ mV) < G/HC-0%TiO₂ ($\eta_{10} = 401$ mV) < G ($\eta_{10} = 486$ mV). Pure graphite exhibits the highest overpotentials, suggesting that moderate doping levels significantly improve catalytic activity. At higher overpotentials ($\eta \gtrsim 300$ mV), G/HC-3% continues to outperform the other electrodes, reaching current densities of approximately −120 mA·cm^{−2}. This behavior likely indicates an optimal balance between the density of doping-induced active sites, the electrical conductivity of the graphite/hydrochar composite, and the efficiency of mass transport and gas bubble evacuation [26,27].

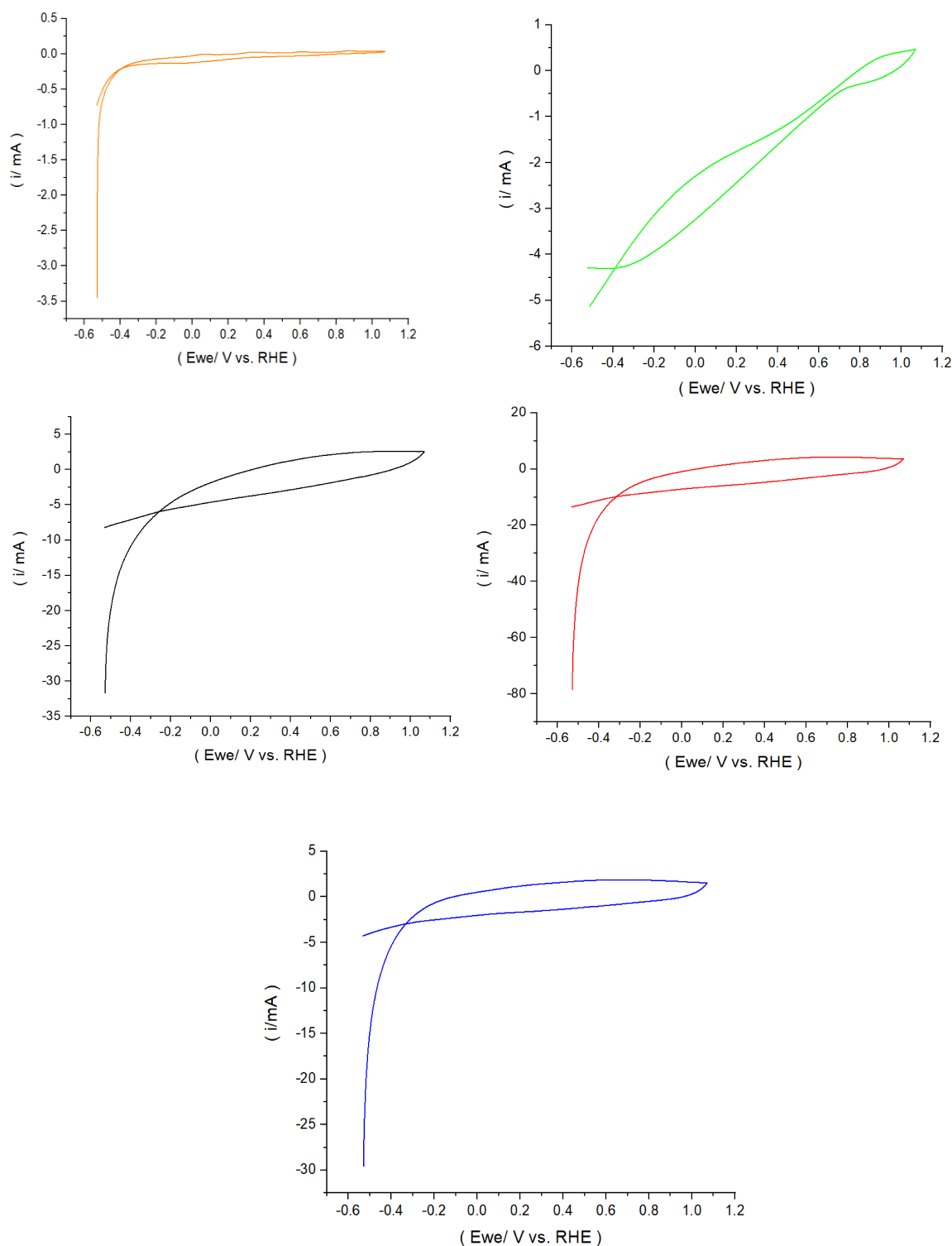


Figure 7. Electrochemical performance of TiO_2 -doped electrodes: cyclic voltammetry (CV) curves.

Linear sweep voltammetry (LSV) and Tafel slope analysis were used to determine the electrocatalytic activity of the electrodes prepared for catalyzing the hydrogen evolution reaction (HER). According to the LSV results, the overpotential decreases considerably in the presence of $\% \text{TiO}_2$; the undoped hydrochar (G/HC-0%) exhibits a high overpotential of 401 mV, reflecting low initial thermodynamic activity. Conversely, the G/HC-1% TiO_2 electrode exhibits a clear reduction in overpotential to 198 mV, with the polarization curve shifting toward more favorable potentials. The Tafel slopes were extracted to study the reaction kinetics in more detail. Figure 9 shows that the G/HC-0% electrode has a Tafel

slope of $141 \text{ mV} \cdot \text{dec}^{-1}$. Although the introduction of 1% TiO_2 substantially lowers the overpotential, it yields a larger slope of $395 \text{ mV} \cdot \text{dec}^{-1}$, suggesting that charge transfer becomes a limiting factor as current density increases for this specific loading level. This increase in the Tafel slope may indicate a complex modification of the electrode/electrolyte interface. At this relatively low loading, TiO_2 particles may partially block the intrinsic active sites or the natural porosity of the hydrochar without providing a sufficient density of additional catalytic sites to compensate this loss. In addition, due to the semiconducting nature of TiO_2 , local potential barriers may be introduced, hindering the initial charge transfer step and resulting in slower reaction kinetics. The G/HC-3% TiO_2 composite represents the optimal among the electrocatalysts, combining the lowest overpotential with the lowest Tafel slope of $67 \text{ mV} \cdot \text{dec}^{-1}$, consistent with a Volmer–Heyrovsky mechanism, in which the rate of the reaction is controlled by the electrochemical desorption of hydrogen. In the 6% loading of TiO_2 , performance declines, with the Tafel slope increasing to $304 \text{ mV} \cdot \text{dec}^{-1}$. This deterioration is due to the semiconductor properties of excess TiO_2 , which increases the overall ohmic, making interfacial charge transfer increasingly difficult. These findings suggest that 3% TiO_2 doping presents the best balance between the effect of the porosity of the hydrochar matrix and catalytic sites on enhancing the HER in an alkaline medium.

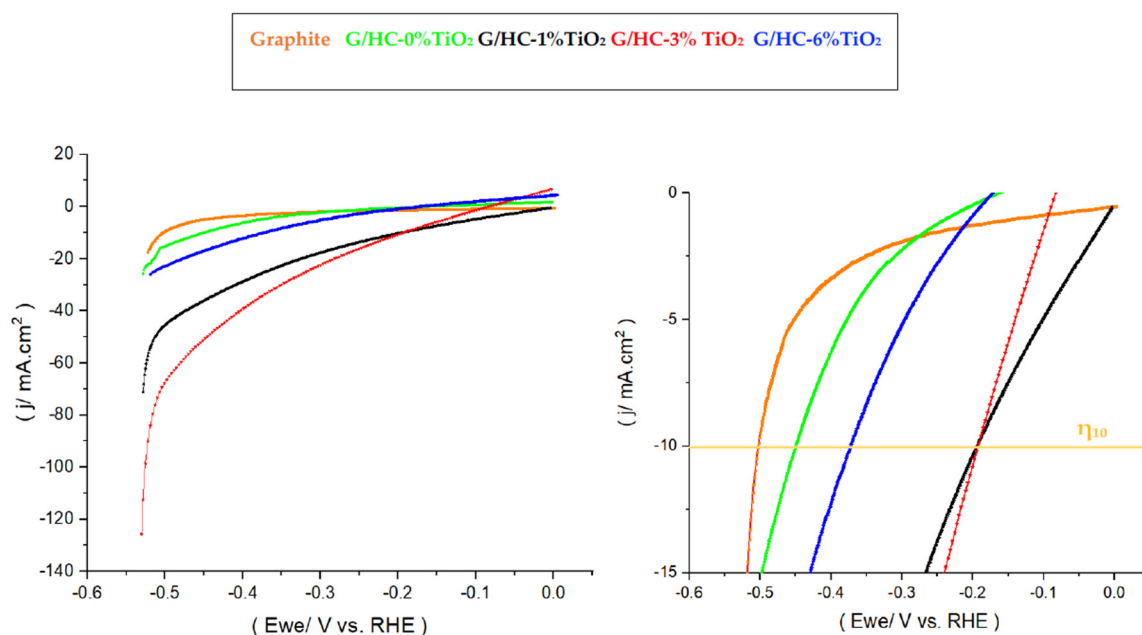


Figure 8. Linear sweep voltammetry polarization curves. The horizontal line indicates the reference current density ($-10 \text{ mA} \cdot \text{cm}^{-2}$) used for the extraction of η_{10} , and the vertical dashed lines mark the corresponding potentials for each sample.

In alkaline media, the hydrogen evolution reaction (HER) generally follows the Volmer–Heyrovsky or Volmer–Tafel mechanism [28]. The Volmer step corresponding to water dissociation and hydrogen adsorption ($\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_{\text{ads}} + \text{OH}^-$) is typically the rate-determining step due to the high energy required to cleave the O–H bond [28,29]. The Tafel slopes obtained in this study are consistent with a Volmer–Heyrovsky mechanism, in which the Volmer step is followed by electrochemical desorption ($\text{H}_{\text{ads}} + \text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}_2 + \text{OH}^-$) [28,30]. At the optimal concentration, TiO_2 is considered to catalyze the water dissociation step owing to its favorable adsorption affinity toward water molecules and hydroxide ions. The Tafel slope achieved for G/HC-3% TiO_2 is comparable to those reported for non-noble Ni-based catalysts ($60\text{--}80 \text{ mV} \cdot \text{dec}^{-1}$) and significantly superior to those of most modified carbon-based materials ($100\text{--}200 \text{ mV} \cdot \text{dec}^{-1}$) [31,32], demonstrating

the effectiveness of the incorporation of TiO₂ in enhancing the intrinsic kinetics of carbon-based HER electrocatalysts.

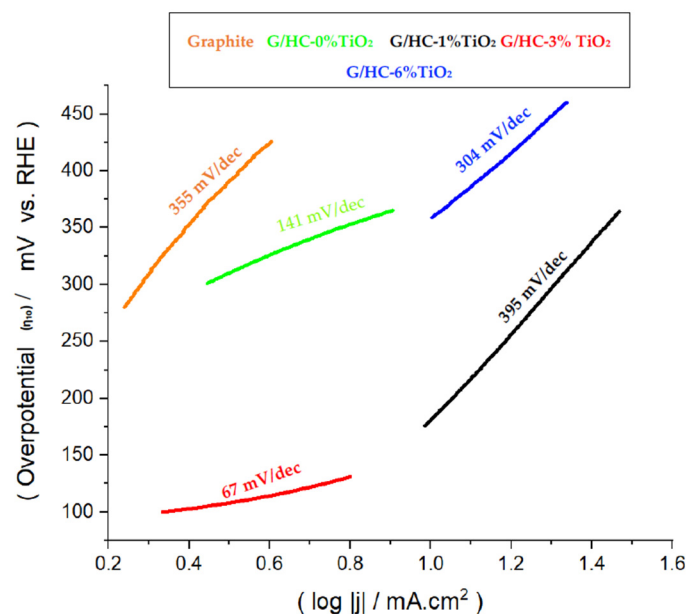


Figure 9. Tafel plots of TiO₂-doped electrodes.

Figure 10A illustrates the relationship between the capacitive current density (i) and the scan rate (ν), while Figure 10B depicts the variation in the same current as a function of the square root of the scan rate ($\sqrt{\nu}$).

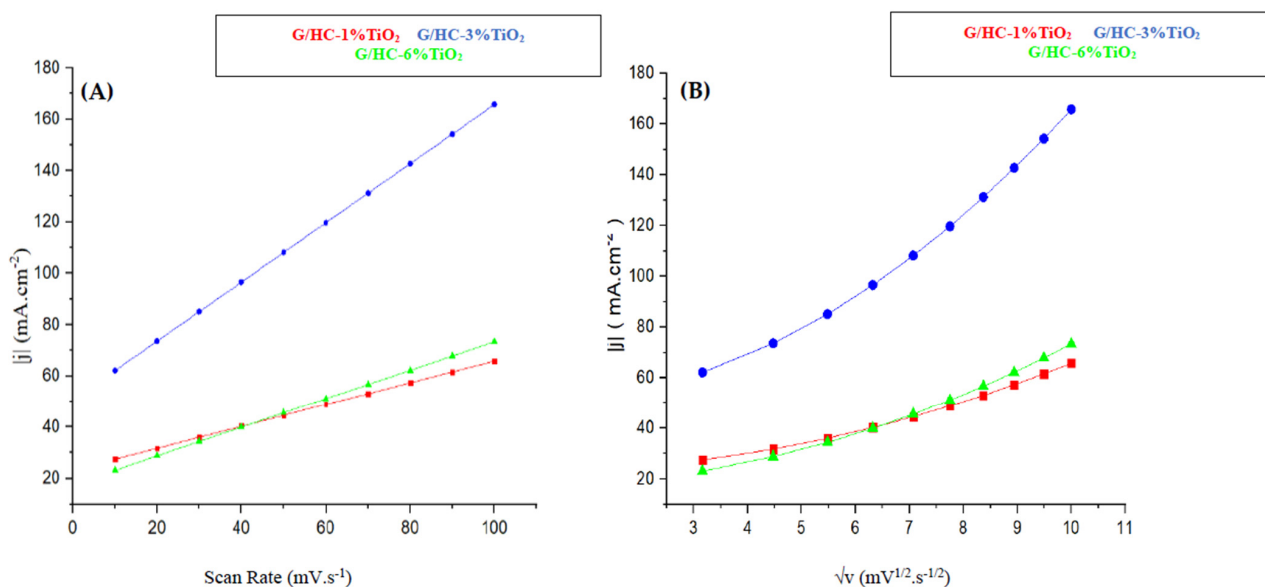


Figure 10. Electrochemical performance of TiO₂-doped electrodes; (A): scan rate and (B): square root of scan rate.

The nearly perfect linearity observed between the capacitive current (i) and the scan rate (ν) for all modified electrodes (G/Hc-1% TiO₂, G/Hc-3% TiO₂, and G/Hc-6% TiO₂), with correlation coefficients $R^2 \approx 1.00$, indicates the dominance of a surface-controlled capacitive process characterized by rapid and reversible charge accumulation at the electrode/electrolyte interface [33]. This linear i vs. ν relationship is a diagnostic feature of electrochemical double-layer capacitance (Cdl), which is directly proportional to the electrochemically active surface area (ECSA) [34].

To further quantify the electrochemical behavior of the electrodes, the linearity of the current response was assessed by comparing the coefficient of determination (R^2) obtained from the linear fitting of (j), as summarized in Table 3. The dominant charge storage mechanism was determined based on which relationship yielded the higher R^2 value.

Table 3. Quantitative analysis of electrochemical behavior.

Electrode	R^2 (i vs. v)	R^2 (i vs. $\sqrt{v}$)	Dominant Behavior
G/HC-1% TiO ₂	0.990	0.978	Mainly capacitive
G/HC-3% TiO ₂	1.000	0.978	Perfectly capacitive
G/HC-6% TiO ₂	1.000	0.979	Perfectly capacitive

The extracted C_{dl} values were 0.45, 1.22, and 0.57 mF/cm² for the 1%, 3%, and 6% TiO₂ electrodes, respectively. It should be noted that the conversion of C_{dl} to absolute ESCA values using a fixed specific capacitance (C_s of a value of 40 μ F/cm²), commonly adopted for carbon-based materials, may not be fully appropriate for composite systems such as graphite/hydrochar/TiO₂, where the heterogenous nature of the surface renders C_s inherently uncertain. Accordingly, C_{dl} values are used here primarily as a relative indicator of electrochemically active surface area trends rather than as absolute quantitative estimates.

In contrast, the relationship between i and $v^{1/2}$ demonstrates moderate linearity ($R^2 \approx 0.978$), indicating a minor contribution from diffusion-controlled faradaic processes [35]. This behavior implies that while charge storage is predominantly surface-controlled, a secondary component includes ion transport within the porous hydrochar structure, typical of hierarchical nanoporous materials. Each of the electrodes therefore has a mixed pseudocapacitive–faradaic response with dominant capacitive behavior, a feature of high-surface-area carbon-based materials [36]. The relatively higher C_{dl} values and effective charge transfer dynamics are beneficial to the HER [37,38]. The increased surface area is characterized by many active sites involved in water dissociation and hydrogen adsorption, and capacitive behavior makes sure that the charge is redistributed faster across the electrode surface under applied potential [39,40]. Notably, the G/HC-3%TiO₂ electrode, which exhibits the highest C_{dl} , demonstrates optimal synergy between the electronically conductive graphite/hydrochar matrix and the catalytically active TiO₂ nanoparticles [41]. Such materials combine the rapid charge storage properties of supercapacitors and the faradaic activity of electrocatalysts, which creates a strong synergy between charge storage and catalytic hydrogen production [40].

To establish the kinetics of charge transfer at the electrode/electrolyte interface, measurements of the electrochemical impedance spectroscopy were conducted within the frequency range of 100 kHz to 0.1 Hz (Figure 11). Nyquist diagrams display depressed semicircles, indicating that the hydrogen evolution reaction is predominantly controlled by charge transfer processes. A modified Randles equivalent circuit ($R_1 + Q_2/R_2 + W_2$) was used to fit the spectra, yielding excellent agreement with the experimental data and confirming the validity of the selected model. The quantitative analysis indicates that the G/HC-3%TiO₂ electrode exhibits the lowest R_{ct} value of 6.22 Ω , approximately 50% lower than that of the undoped hydrochar (12.68 Ω). This reduction suggests an enhancement in interfacial charge transfer kinetics upon TiO₂ incorporation. Given the intrinsically low electronic conductivity of the oxide, this improvement is not attributed to direct conductivity enhancement but rather to the establishment of Ti-O-C bonds that facilitate local charge redistribution between the TiO₂ phase and the carbon matrix. The evolution of R_{ct} —decreasing from 12.68 Ω to 6.22 Ω , then rising to 10.11 Ω —is consistent with this interpretation, as a simple conductivity or surface area effect would not be expected to

produce such a trend. The increase in R_{ct} noted for the 6% sample ($10.11\ \Omega$) is attributed to particle agglomeration and the increasing dominance of resistive pathways associated with excess semiconducting TiO_2 , which limits electrocatalytic performance.

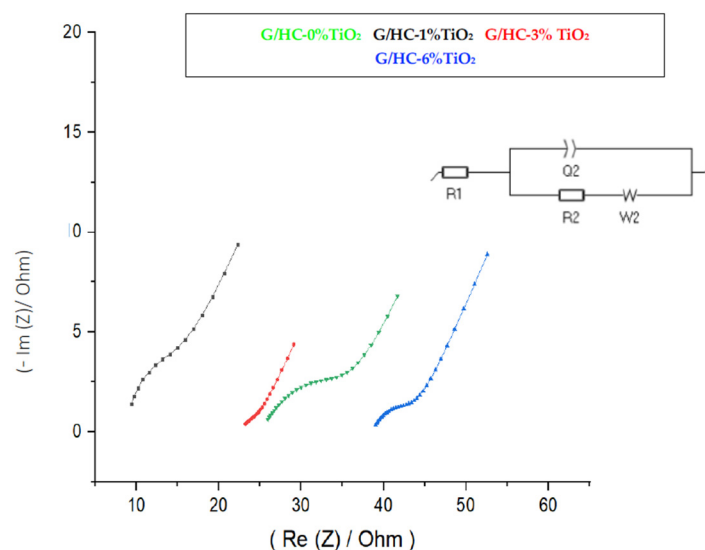


Figure 11. Nyquist plots of the various composite electrodes in 1 M KOH solution.

The electrochemical long-term stability of the composite electrode G/Hc-3% TiO_2 was tested via chronoamperometry at a constant potential of $-1.2\ \text{V}$ (which corresponds to approximately $-0.13\ \text{V}$ vs. RHE in 1 M KOH) for 120 min. The current stabilized to about $-10\ \text{mA}\cdot\text{cm}^{-2}$ after the initial 5 to 10 min, as depicted in Figure 12. This steady plateau suggests that the electrode possesses good electrochemical stability toward the alkaline HER. This stable current response is in agreement with the LSV data recorded in Figure 8, and the ability of performance to be reproducible over time also indicates that the active layer of the electrode does not lose its structural or conductive integrity, and there is no significant degradation. These findings confirm the appropriateness of G/Hc-3% TiO_2 as a robust and stable electrocatalyst.

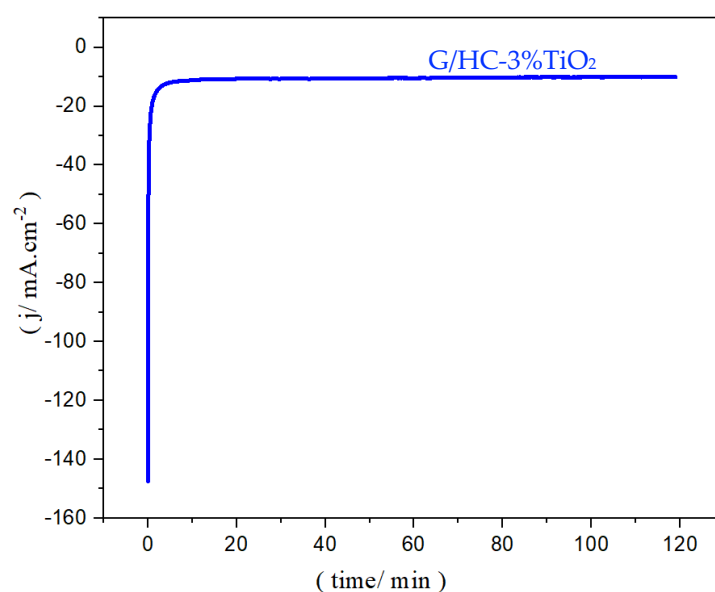


Figure 12. Chronoamperometric stability curve of G/Hc-3% TiO_2 electrode.

The G/HC-TiO₂ composite electrodes designed in this study have a number of main merits which render them good prospects in the applied applications of alkaline water electrolysis. In addition to their electrochemical performance, from a financial perspective, the G/HC-TiO₂ system offers a high cost-benefit compared to traditional HER catalysts since it does not contain any noble metals, which significantly minimizes the cost of raw materials. This waste valorization strategy not only minimizes production costs but also addresses biomass residue management challenges. Moreover, titanium dioxide is a low-cost earth-abundant oxide with an estimated price below \$5 per kilogram, several orders of magnitude lower than that of noble-metal-based catalysts. The combination of low-cost and readily available materials makes the G/HC-TiO₂ system economically attractive for large-scale hydrogen production.

The environmental advantages of the G/HC-TiO₂ system are equally remarkable. The hydrochar component is derived from date pit biomass, transforming an agricultural by-product of low commercial value into a functional electrode material. The carbon matrix originates from renewable resources, specifically date pit waste, aligning with circular economic principles. All constituent materials (graphite, hydrochar, and TiO₂) are non-toxic and environmentally harmless, and there are no concerns about any heavy metal contamination or hazardous waste generation. Furthermore, these materials exhibit excellent chemical stability in alkaline media, suggesting prolonged operational lifetimes and reduced electrode replacement frequency, thereby minimizing the associated environmental impacts.

As summarized in Table 4, the hydrochar-based electrodes developed in this work exhibit remarkable hydrogen evolution reaction (HER) activity in alkaline medium compared with other biomass-derived and non-noble catalysts. To ensure a rigorous and reliable comparison, all catalysts selected for Table 3 were tested under consistent experimental conditions, specifically in a 1 M KOH electrolyte. Furthermore, all reported overpotentials were evaluated at a current density of -10 mA/cm^2 , which is the standard benchmark for comparing HER electrocatalysts.

The G/HC-3%TiO₂ electrode delivers an overpotential of 194 mV at $10 \text{ mA}\cdot\text{cm}^{-2}$ with a Tafel slope of $67 \text{ mV}\cdot\text{dec}^{-1}$, which is comparable to NiFe LDH (100–200 mV) and Ni-Mo alloys (50–100 mV) and significantly superior to most reported carbon-based catalysts such as N-doped biochar (143–184 mV, $164 \text{ mV}\cdot\text{dec}^{-1}$). This enhanced performance implies that an intermediate level of TiO₂ results in a good ratio between oxide-assisted active site formation and the maintenance of electronic conductivity and porosity in the hydrochar-based composite. In contrast, excessive TiO₂ loading (6 wt%) leads to partial pore blockage and increased interfacial resistance, explaining the decline in catalytic activity. The performance hierarchy of G/HC-*x*%TiO₂ electrodes (3% > 1% > 6%) thus highlights the importance of maintaining a balanced composition between conductivity, active site density, and porosity.

When compared to noble metal catalysts such as Pt/C and Ru@CQDs ($\eta_{10} = 10\text{--}65 \text{ mV}$), the hydrochar-based composites remain competitive, especially considering their low cost, environmental sustainability, and metal-free nature. All of these results show that carbon-oxide composites obtained from biomass are a worthy useful substitute for traditional noble catalysts in large-scale alkaline water electrolysis.

The understanding of the improvement in and evolution of the HER performance of the G-HC/TiO₂ electrodes presented in the table depends on the mechanistic analysis presented below. Hydrochar is used as a modifier, as well as an electron transfer catalyst: the partially graphitized carbon structure of the material enhances conductivity, whereas the oxygenated functional groups facilitate the redistribution of charges, thus decreasing the resistance to charge transfer at the electrode-electrolyte interface. In addition to these electronic effects, the porous structure of hydrochar enhances the electrochemically accessible

surface area, providing more active sites for hydrogen adsorption and the electrochemical infiltration of electrolytes, which leads to HER kinetics.

Table 4. HER performance comparison of biomass-derived carbon-based and noble metal catalysts in alkaline medium.

Catalyst/Electrode	Biomass Source/Structure	Modification	η_{10} (mV)	Tafel Slope (mV·dec ⁻¹)	References
Biomass-derived and non-noble catalysts					
G/HC-3% TiO ₂	Graphite + hydrochar	TiO ₂ dispersion (n wt%) + calcination 300 °C	194	67	
Wood residue	Carbonized wood	Ni ₃ S ₄ /CW	280	122	[42]
Willow catkins	Biomass fiber	NiFe LDH/(NiFe)S _x /CMT	169	105	[43]
Willow catkins	Biomass fiber	NiFe LDH/CMT	333	140	[43]
Willow catkins	Biomass fiber	NiFeS _x /CMT	266	139	[43]
Cattail spike	Plant fiber	Ni/NBCF-1-H ₂	47	58	[44]
Sulfur self-doped	Camella japonica flowers		154	89	[45]
NiP/Poplar wood	Poplar wood	Phosphorization	83	73	[46]
Mo ₂ C@SNC	Sunflower seeds	Porous carbon doped with Mo	60	71	[47]
NiFe LDH	Synthetic	NiFe layered double hydroxide	100–200	80–120	[48]
MoO ₃ /AC	Human hair		353	124	[49]
Noble metal catalysts (for benchmarking)					
Pt/C	Carbon black	Pt nanoparticles	~30	30–40	[50]
Ru@CQDs	Carbon quantum dots	Ru nanoparticles	10–65	47–63	[51]

In alkaline conditions, the hydrogen evolution reaction generally conforms to a Volmer–Heyrovsky mechanism, where the initial step of water dissociation (Volmer: $\text{H}_2\text{O} + \text{e}^- \rightarrow \text{H}^* + \text{OH}^-$) frequently serves as the rate-limiting step, especially on carbon-based substrates. Within Butler–Volmer formalism, the Tafel slope (b) is used as a diagnostic criterion to determine the rate-limiting step:

- $b \simeq 120 \text{ mV} \cdot \text{dec}^{-1}$ indicates Volmer-limited kinetics.
- $b \simeq 40 \text{ mV} \cdot \text{dec}^{-1}$ reflects Tafel recombination control.
- Intermediate values near $40\text{--}120 \text{ mV} \cdot \text{dec}^{-1}$ are consistent with the Heyrovsky limitation.

The measured Tafel slope of $141 \text{ mV} \cdot \text{dec}^{-1}$ for G/HC-0%TiO₂ indicates that the Volmer step is rate-limiting, which is anticipated for carbon-based substrates with low water activation ability. The apparent decrease in overpotential and the Tafel slope value of $67 \text{ mV} \cdot \text{dec}^{-1}$ for G/HC-3%TiO₂ indicate that the incorporation of TiO₂ catalyzes the Volmer step, causing the mechanism to shift to a regime where the electrochemical desorption step (Heyrovsky) becomes rate-determining. This enhancement is fundamentally supported by the textural properties of the activated hydrochar. The high BET surface area ($254.28 \text{ m}^2/\text{g}$) and significant pore volume ($0.521 \text{ cm}^3/\text{g}$) of the support provide a robust accessible framework that ensures the superior dispersion of TiO₂ nanoparticles, thereby increasing the density of active sites available for the reaction. This mechanistic shift is further supported by the corresponding decrease in charge transfer resistance (R_{ct}) measured by EIS. The evolution of the Tafel slope therefore reflects improved water activation and a more favorable hydrogen adsorption–desorption balance at the electrode surface.

Besides the intrinsic characteristics of the hydrochar, further improvements are achieved by incorporating TiO₂ into the matrix, which facilitates interfacial charge separation and enables electron flow between the conductive carbon network and the electrolyte. The enhanced performance is attributable to the formation of Ti-O-C interfacial bonds between the TiO₂ nanoparticles and the carbon structure of the hydrochar. These connections generate local charge polarization and strengthen the electronic interactions between the semiconducting TiO₂ phase and the conductive carbon matrix. At the physicochemical level, TiO₂ exhibits Lewis acid character at surface Ti⁴⁺ sites, which polarizes adsorbed water molecules and lowers the energy needed to break the O-H bond—an effect well-documented for TiO₂-based catalysts in the alkaline hydrogen evolution reaction. Meanwhile, the Ti-O-C covalent bond is expected to alter the local work function at the interface, rearranging electron density from the carbon matrix to the adsorbed water intermediates. In this configuration, TiO₂ plays a dual role:

- As a catalytic site, it lowers the energy required to break the O-H bond.
- As a surface modifier, its hydrophilic character improves electrode wetting and the local concentration of OH[−], maximizing interfacial chemistry and facilitating gas bubble removal.

The transition of the Tafel slope from 141 mV·dec^{−1} for G/HC-0% TiO₂ to 67 mV·dec^{−1} for G/HC-3%TiO₂ directly reflects this mechanistic change, where the accelerated Volmer step allows the reaction to be governed by electrochemical desorption (Heyrovsky step).

It should be acknowledged that the mechanistic role attributed to Ti-O-C interfacial bonds, especially in relation to charge redistribution and its impact on the Volmer step, is an inference based on indirect electrochemical evidence and not direct structural or spectroscopic proof. However, the substantial reduction in R_{ct} upon the incorporation of 3 wt% TiO₂, coupled with the non-monotonic dependence of catalytic performance on TiO₂ loading, lends support to this interpretation. The ultimate confirmation of the formation of Ti-O-C bonds and their electronic implications would require complementary characterizations, such as XPS and Raman spectroscopy, to identify H* intermediates, and these analyses are logical extensions of the present study and are currently under consideration.

Nevertheless, it is important to maintain a balanced composition: while an intermediate TiO₂ content results in a high density of active sites, overloading at 6 percent causes the partial blockage of pores and higher interfacial resistance, as the electronically conductive properties of the composite eventually become limited by the intrinsic semiconducting nature of anatase TiO₂. At high loading, this introduces insulating percolation pathways that increase R_{ct} and negate the catalytic gains of Ti-O-C coupling.

4. Conclusions

This work highlights the remarkable potential of bio-derived resources, in this case, date pit biomass (*Phoenix dactylifera* L.), for the development of sustainable electrodes that are dedicated to the production of green hydrogen. By converting high-volume agricultural residue into a TiO₂-functionalized hydrochar, this study is fully consistent with the principles of the circular economy, biomass valorization at the local level, and the minimization of the carbon footprint of electrocatalyst materials.

The combination of structural, chemical and electrochemical analyses indicates that the controlled incorporation of TiO₂ into the carbon matrix enables the development of effective composite electrodes without the involvement of noble elements, which have historically been required for an efficient hydrogen evolution reaction (HER). An intermediate TiO₂ loading of 3 wt% provides an optimal balance between charge transfer efficiency, oxide dispersion, and active site accessibility while maintaining long-term stability. This composition

represents the best HER kinetics and the lowest charge transfer resistance among the tested formulations, supporting the relevance of the applied interfacial engineering strategy.

Beyond electrochemical performance, the use of a renewable, low-cost, and locally available precursor provides clear environmental and socioeconomic advantages. Replacing critical raw materials with new and recyclable carbon–TiO₂ composites derived from agricultural waste represents a meaningful step toward accessible, sustainable, and low-impact electrolyzer technologies that can contribute to carbon-neutral energy pathways. The simplicity of synthesis, the moderate energy requirements, and the absence of scarce metals further strengthen the prospects for large-scale deployment with a minimized ecological footprint. Overall, this study demonstrates that sustainability-driven material development can yield competitive electrocatalysts for green hydrogen production. Future research explores cleaner synthesis routes, the addition of other earth-abundant elements, and the extension of this concept to various biomass types in order to create the next generation of fully sustainable electrochemical materials in support of the global energy transition.

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