Insights into the High Activity of Ruthenium Phosphide for the Production of Hydrogen in Proton Exchange Membrane Water Electrolyzers

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The demand of green hydrogen, that is, the hydrogen produced from water electrolysis, is expected to increase dramatically in the coming years. State-of-theart proton exchange membrane water electrolysis (PEMWE) uses high loadings of platinum group metals, such as Pt in the electrode where hydrogen is produced. Alternative electrodes based on phosphides, sulfides, nitrides, and other low-cost alternatives are under investigation. Herein, a simple process for the preparation of RuP electrodes with high activity for the hydrogen evolution reaction (HER) in acidic electrolyte is described. A straightforward one-pot synthesis that yields RuP nanoparticles with fine-tuned composition and stoichiometry is presented, as determined by multiple characterization techniques, including lab- and syn-chrotron-based experiments and theoretical modeling. The RuP nanoparticles exhibit a high activity of 10 mA cm⁻² at 36 mV overpotential and a Tafel slope of 30 mV dec⁻¹, which is comparable to Pt/C. Moreover, a RuP catalyst-coated membrane (CCM) with a low Ru loading of 0.6 mg_{Ru} cm⁻² is produced and tested in a PEMWE cell configuration, yielding 1.7 A cm⁻² at 2 V.

1. Introduction

It is expected that green hydrogen will play a key role in the transition to meet the 1.5 °C target of Paris Agreement. Green hydrogen, that is, the hydrogen obtained from carbon-decoupled sources using renewable energy, is the ideal candidate for the intermediary storage state between the harvesting and

deployment of renewable energies and for the insertion of the renewable energies in key sectors such as transport, industry, and heat.^[1,2] As a consequence, it is projected that the global production and demand of renewable hydrogen will increase exponentially in the coming years.^[3,4] At present, water electrolysis is the most suitable technology to meet with the demands of large-scale hydrogen production.^[5] Water electrolyzers are electrochemical devices that use (renewable) electricity to split H₂O and generate H₂ (via the hydrogen evolution reaction, HER) and O₂ (via the oxygen evolution reaction, OER). Proton exchange membrane water electrolysis (PEMWE) is one of the most promising technologies currently under investigation and development for large-scale hydrogen production based on renewable electricity; this is due

to highly favorable features such as its compact design, fast response, high rate of current, low gas crossover rate, and low cell ohmic losses. $^{[6,7]}$

However, state-of-the-art (SoA) PEMWEs have certain drawbacks that can jeopardize their wider implementation. Perhaps most critically: the electrodes are based on scarce, ill-distributed platinum (Pt/C) in the cathode (HER) and iridium (IrO_x) in the

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anode (OER). Recently there has been a large effort aimed at the development of either 1) platinum group metals (PGM)-free electrocatalysts or 2) significant decreases in the PGM loading on the electrodes.^[8]

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To date, several types of active and durable catalysts have been reported for the HER in acidic media; these include metal sulfides, nitrides, phosphides, and carbides.^[9-11] However, in most cases, their performances are still far below Pt/C. Among those, transition metal phosphides (TMP) are gaining interest in the scientific community. Not only do TMPs exhibit HER activity comparable to that of SoA Pt-based electrodes, but their loading on the electrode can be tuned (without loss in performance), which leads to a drastic reduction in the amount of expensive PGMs used in the state-of-the-art PEMWEs.^[10] Furthermore, some TMPs exhibit stable HER activity for several voltammetry cycles or for several hours by applying a constant current or a constant potential in a half-cell or single-cell system. For instance, Li et al. developed porous CoP/N-doped carbon networks that demonstrate good stability over 2000 cyclic voltammograms (CV) in 0.5 M H₂SO₄ measured in a rotating disk electrode (RDE).^[12] On the other hand, Sapountzi et al. reported high durability of FeP under constant polarization at 2 V for 100 h in PEMWE.^[13] To date, the majority of investigations on TMPs for the HER only report RDE data. However, due to the very fast kinetics of the HER, mass-transport effects may dominate the activities obtained in the RDE configuration, preventing the proper assessment of catalytic activities of highly active HER catalysts.^[14] To date, only very few reports demonstrate the use of TMPs as a cathodic electrocatalyst in an actual membrane electrode assembly (MEA) configuration.^[13,15–25]

TMPs can be prepared in a wide range of compositions and structures, which in principle provides a platform for fine tuning the electrode HER performance. This could be achieved for instance by optimizing the transition metal element (TM), its local (interfacial) coordination environment, and the TM-to-P stoichiometry.^[26] To the best of our knowledge, the synthesis of TMPs for the HER has been conducted by one of the following three approaches: 1) cathodic electrodeposition (CE),^[17,20] 2) gas-solid reaction (GS-R)^[27,28] and 3) using organophosphorus reagents, such as trioctylphosphine (TOP), as a P source.^[29,30] Although these approaches have been successful for the synthesis of TMPs, they present certain drawbacks. For instance, during the CE approach, the TMPs are formed at the surface of the electrodes and therefore cannot be deposited on the polymeric membrane. In the case of GS-R, NaH₂PO₂ decomposes into PH₃, which is an extremely toxic chemical byproduct. Finally, the TOP approach is conducted in the presence of toxic and flammable organic solvents. Therefore, it is desirable to develop a simple and cost-effective method for synthesizing TMPs as high-performance cathode materials for the HER.

In this work we developed an easy and scalable synthesis of pure RuP with very high HER activity and durability in both RDE and PEMWE configurations. RuP was synthesized by a dry chemistry method, by simply mixing the Ru and P precursors and subjecting the mixture to a thermal treatment under vacuum. The RuP obtained was thoroughly characterized by both experimental and theoretical approaches and exhibited a higher HER activity than similar TMPs, close to the value reported for Pt/C in the RDE configuration.^[31–33] Additionally, RuP has been tested to assess its practical applicability in PEMWE. A single cell with a catalyst-coated membrane (CCM), in which RuP has been deposited as a cathodic electrode, has a performance of 1.73 A cm^{-2} at 2 V, comparable to that reached by Pt-based materials between 1.7 and 3 A cm⁻² at 2 V. Furthermore, investigation of the RuP durability indicates a high stability for the electrode, even in harsh corrosion conditions; the single-cell setup has been tested up to 2 A cm⁻² demonstrating its high stability. It is noteworthy that in these materials the durability is usually evaluated at lower current densities of 1 A cm⁻².

2. Results and Discussion

2.1. Structure, Composition, and Morphology

The crystallographic structure of RuP was determined by XRD. The Rietveld refinement of the RuP crystal structure is presented in **Figure 1a**. The experimental pattern confirms that the sample displays a pure single phase with orthorhombic *Pnma* space group (# 62). The cell parameters are a = 5.5261(5) Å, b = 3.1619(3) Å, c = 6.1244(6) Å and the volume is V = 107.01(2) Å³. Both Ru and P atoms are in 4c (x ¼ z) sites. It is a compact structure with a mixture of RuP₆ distorted octahedra sharing faces along the ac plane and sharing edges along the bc plane (Inset Figure 1a). The shorter Ru–Ru distances appear between RuP₆ octahedra sharing faces (around 2.82 Å), while the longer Ru–Ru distance observed between octahedra sharing edges is ≈ 3.16 Å (Figure 1b). We note that the shorter Ru–Ru distances are similar to Ru–Ru (2.67–2.73 Å) in metallic Ru,^[34] suggesting the pseudometallic character of Ru in the phosphide.

A representative TEM image of RuP is depicted in Figure 1c. The micrograph reveals that the material is formed by homogeneous aggregates of particles, partially sintered and with a nondefined shape, see also Figure S1, Supporting Information. The HRTEM image in Figure 1d shows the crystallographic planes of RuP, indicating that the particles are crystalline.

The surface composition and relative surface abundance of Ru and P in RuP were analyzed by recording high-resolution XPS spectra of C 1*s*, P 2*p*, Ru 3*d*, and Ru 3*p* core-level regions. Charge effects were accounted for by setting the C 1*s* peak at 284.6 eV.

Figure 2a shows the XPS spectrum of the P 2p core-level region of RuP. The spectrum displays two main peaks with maxima at \approx 129.7 and 133.2 eV. These peaks correspond to P in two different oxidation states (environments). The peak at higher binding energy (BE) (133.2 eV) indicates the presence of oxidized phosphorus species, whereas the peak at lower BE (129.7 eV) corresponds to metal phosphides. The presence of phosphates at the surface of the sample (atomic ratio of P in phosphides/ phosphates $\approx 0.75/1.0$ indicates the oxidation of a fraction of the surface P atoms due to air exposure.^[28,35] Since XPS is a surface-sensitive technique, these results only indicate the presence of phosphate species at the surface. As further evidenced later, we found that the oxidation process is limited to the surface region, which further supports the conclusion that oxidation results from air exposure. A closer inspection of each peak reveals the presence of two components, which correspond to the P $2p_{3/2}$ and P $2p_{1/2}$ components with a spin-orbit splitting



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Figure 1. a) XRD pattern (black line), Rietveld refinement (red crosses), and residue (blue line) of the RuP crystal structure. Inset: schematic view of the RuP crystal structure with the Ru atoms represented as gray spheres, P atoms as blue spheres, and RuP₆ octahedra as blue polyhedrons. b) Representation of the Ru—Ru and Ru—P main bond distances. c) Representative TEM image of RuP; inset: electron diffraction pattern of RuP. d) HRTEM images of a particle showing the (002) crystallographic planes of RuP.



Figure 2. XPS spectra of RuP. a) P 2*p* core-level region. Purple and green peaks correspond to the P $2p_{3/2}$ and $2p_{1/2}$ levels of phosphides and phosphates, respectively. b) Ru 3*d* core-level (green and purple doublets) and C 1s (blue peaks) core-level regions.

of \approx 0.7 eV. The P 2*p*_{3/2} BE of the metal phosphide (129.7 eV) is negatively shifted compared to elemental P (130.2 eV), which suggests a slight partial anionic state of P in the phosphide.

Figure 2b shows the XPS spectrum of the Ru 3d and C 1s corelevel regions. The Ru region displays two doublets, with Ru $3d_{5/2}$ peak at 279.8 and 282.1 eV and with the $3d_{3/2}$ peak at 284.0 and 285.9 eV, respectively. The low-BE doublet can be ascribed to metallic Ru most likely in RuP; however, the presence of anhydrous RuO₂ cannot be ruled out since both species display the main Ru 3d_{5/2} peak at similar BEs, namely, 279.9–280.2 eV for Ru⁰ and 280.5–280.7 eV for RuO₂. In addition to the main photoelectronic peaks, the spectrum of RuO₂ should display two satellite peaks due to core-hole screening at \approx 1.8 eV higher BE than the main peaks, that is, the Ru $3d_{5/2,sat}$ should appear at ${\approx}281.6\,\text{eV}^{[36]}$ This value is lower than the actual value observed for the second Ru $3d_{5/2}$ doublet in our spectrum, which occurs at 282.1 eV. Consequently, we do not ascribe the second doublet to satellite peaks of the main doublet of RuO₂, but to an actual oxidized Ru species at the surface of the phosphide. In the literature, Ru $3d_{5/2}$ peaks at around 282.5 eV have been ascribed to Ru³⁺ compounds such as Ru(OH)₃ or Ru(NO)(NO₃)₃; in this case, we assign it to Ru-PO_x phases. The Ru $3p_{3/2}$ core-level region (Figure S2, Supporting Information) shows two components at 461.1 and 463.6 eV. These values are typically observed for Ru⁰ and oxidized Ru, respectively.^[36] Note that the BE 463.6 eV is 1 eV higher than that expected for RuO₂ of 462.6 eV, being closer to the values expected for Ru³⁺ species.^[36] Regardless of the actual nature of the species at high BE, the analysis of the Ru 3p core-level region excludes the presence of RuO₂. The relative surface atomic abundance of RuP/oxidized Ru is \approx 3.

The assignment of Ru oxidation states close to metallic but partially charged in RuP is consistent with the NEXAFS data and DFT analysis. For analysis and characterization of the NEXAFS part of the spectrum, we computed the theoretical P K-edge spectrum of RuP using DFT and the Fermi golden Rule. A comparison of the experimental and theoretical spectrum is provided in **Figure 3**a,b. It should be noted that due to wellknown limitations associated with the evaluation of absolute energy values in DFT, the edge of the theoretical spectrum has been aligned to the experimental edge.

The theoretical spectrum reproduces the first main peak of the experimental spectrum at 1.5 eV from the edge (Figure 3b). To understand the origin of this peak we performed a PDOS analysis on the RuP ground-state structure in the presence of a core hole. The PDOS of the adsorbing P atom, with the core-hole potential, is denoted P(h) and colored blue, and the PDOS of nonadsorbing P atoms are colored orange. The spin-resolved PDOS demonstrates a clear downshift in the energy of the states of the P ion with a core hole with respect to the remaining (unperturbed) P ions in the lattice. The energetic lineup between these states in the PDOS and the theoretical P K-edge spectra suggests that the first main peak is due to a transition from the 1s orbitals to a p-like orbital of the absorbing atom P(h) (i.e., the P ions with a core hole) mixed with nonlocal electronic transitions to p-like orbitals associated with the other P ions. This accounts for the broad peak and is consistent with the RuP phase being metallic.

What is clear from the comparison between the experimental P K-edge spectrum and the theoretical K-edge spectrum of RuP is that the second main peak at 8.8 eV from the edge is not well

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Figure 3. a) Plots of the experimental NEXAFS spectra, red and black lines are the TEY and TFY spectrum, respectively. Plots of DFT-simulated NEXAFS spectra for the b) RuP and c) Ru₂P₆O₁₈ compounds considered. We also plot the spin-resolved DOS, projected onto the p-orbitals of the X-ray-absorbing P atoms with a core-hole potential P(h) (blue) and neighboring P atoms (orange). Spin up (down) contributes to positive (negative) values. Inset shows the local coordination environments of the P atoms in the RuP and Ru₂P₆O₁₈ systems (P: orange; Ru: blue; O: red). d) A plot of the bulk-phase RuP spin-resolved total DOS (gray shaded) and projected DOS for Ru *d* (red) and P *p* (blue) states.

reproduced by the simulation. Differences in the relative intensities of the two main peaks have been observed in the absorption spectra collected with TEY and TFY corrected for self-absorption. The higher intensity of the second peak for TEY collection mode (which has a higher surface sensitivity) further suggests that this peak could be associated with a secondary oxidized phase present at the surface of the RuP particles, as confirmed by other surfacesensitive characterization techniques such as XPS (see above). To explore this possibility we also computed the theoretical P

K-edge spectrum of two different Ru/P-oxidized phases, which contain octahedrally coordinated Ru(III) bonded to tetrahedral $[PO_4]^-$ moieties; the unit cells for two phases were Ru₄P₁₂O₃₆ and Ru₂P₆O₁₈. The simulated P K-edge spectra of the Ru₂P₆O₁₈ are plotted in Figure 3c. Again, we applied a rigid shift to the computed absorption energy to align the theoretical absorption edge with the second main peak of the experimental spectrum. It is worthwhile to highlight that the energetic separation of the two peaks (7.3 eV) is consistent with the expected shift associated with the change in oxidation state between a phosphide and a phosphate ion,^[37] and analogous shifts have been observed for S K-edge NEXAFS on minerals.^[38]

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The theoretical spectrum for both of the oxide phases we considered satisfactorily reproduces the second peak in the experimental measurement. In other words, the structural similarities between the two different materials make it impossible to identify the exact crystal phase of the oxidized surface of RuP without further experimental structural characterization. However, based on further PDOS analysis, it is possible to infer that the second adsorption peak in the spectrum is mainly due to local transitions between the 1s orbitals and a p-like orbital of a P(h) ion within a tetrahedrally coordinated oxide environment. As depicted in Figure 3c by the peak in the PDOS as 12-14 eV, nonlocal transitions to other P ions occur at higher energy ($\approx 4 \text{ eV}$) with a significantly lower intensity.

To elucidate the catalytic performance of the RuP (see below) we further characterized its bulk phase by DFT simulations. The valence band DOS (shaded grey) and Ru (red) and P (blue) PDOS are plotted in Figure 3d; the position of the Fermi level within the band clearly demonstrates the metallic behavior of RuP. Closer inspection of the PDOS suggests a strong degree of hybridization between the Ru 4*d* and P 3*p* manifolds. In fact, the decomposition of the total electron density via Bader partitioning reveals computed positive and negative charges for Ru (0.12 *e*) and P (-0.12 e) respectively, in agreement with the XPS results for the RuP phase. It is worthwhile to point out that the Bader charges computed for the bulk phase agree with the values also reported by Bonita et al (0.11/-0.11 e).^[39]

2.2. Catalytic Performance

Figure 4a shows the polarization curve (with iR compensation) for RuP in 0.1 M HClO₄ between 0.05 and -0.1 V. The polarization curve obtained for a Pt/C catalyst (Pt/C, 20 wt%, Johnson Matthey) recorded under the same conditions is shown for comparison. The catalytic activity of RuP was benchmarked by determining the overpotential needed to reach a current density (j_{geo}) value of 10 mA cm⁻² (η_{10}), as recommended in previous works.^[40,41] Consistent with previous measurements in the literature, the Pt/C has an $\eta_{10} = 21$ mV.^[42] As observed in Figure 4a, for RuP we measure an $\eta_{10} = 36$ mV, which remarkably is within 15 mV of the SoA Pt/C benchmark.

The role of the surface on the catalysis of the HER should not be downplayed. In the absence of atom-resolved data on the exact exposed facets of the RuP in the present work, we consider the results of previous simulations carried out by Wang et al. to further analyze our results.^[43] The catalytic activity for the HER can be linked to the BE of H to the surface, Wang et al computed H adsorption energy for the RuP (011) surface comparable to Pt, which is therefore consistent with the excellent activity of RuP manifested in our work. On the other hand, the slight charge observed by several techniques on the Ru and P atoms inside the phosphide can increase the electron transfer rate, thus promoting the catalytic process toward HER. It has been previously reported that several Ru–P phases present more activity than metallic Ru due to optimized electron transfer.^[31]

Durability is a key factor for the implementation of an electrocatalyst in commercial electrolyzers. We examined the stability of RuP during the HER in acidic media by recording 8000 consecutive cycles between 0.05 and -0.1 V (Figure 4a) and by monitoring the potential needed to maintain a current density (j_{geo}) of 10 mA cm⁻² during a 15 h period (Figure 4b). The activity is stable, with a constant value of *E* in chronopotentiometry and ΔE (at 10 mA cm⁻²) of 19 mV in the polarization curves, between the initial polarization curve and after 8000 cycles.

Figure 4c compares the HER overpotential at 10 mA cm⁻² (η_{10}) of the RuP catalyst reported in this work (green star) with other ruthenium phosphides reported in the literature (red circles)^[26,31,32,44,45] and other TMPs (blue rhombuses)^[27,33,46–48] under acidic conditions. In many works, the catalyst loading was not specified or is higher than in the present study. The HER activity obtained in this work for RuP is among the best reported for ruthenium phosphides or in general for any of the TMPs electrocatalysts, as demonstrated by its comparably lower η_{10} value, see Figure 4c.

The Tafel slope is a representative value of the activity of the electrocatalyst, with small slopes characterizing faster kinetics. Furthermore, it can provide additional information on the reaction mechanism. We obtained a Tafel slope of $39.8 \pm 0.5 \text{ mV dec}^{-1}$ (Figure 4a inset). The Tafel slope calculated for RuP is among the lowest reported in the literature for similar TMPs catalysts, see Figure 4c. It is well established that the HER can take place via the so-called Tafel, Heyrovsky, or Volmer ratedetermining steps (RDS), characterized by Tafel slopes of \approx 30, 40, or 120 mV dec⁻¹, respectively.^[49] However, these values are only correct when considering that the symmetry factors for Volmer (β_1) and Heyrovsky (β_2) steps are equal to 0.5.^[50] Additionally, correctly extracting Tafel slopes is inherently challenging and it comes with associated errors. This is because it depends on the range from which the value is extracted, the presence of mechanism changes or overlapping mechanisms at different overpotentials, and there may even be discrepancies if voltammetry is the best method for determining the Tafel slope.^[51] Also, Tafel slopes reported in the literature for different TMPs (Figure 4c) are not consistent with the theoretical ones. For all of this, it is important to study in more detail the mechanistic aspects of the HER on RuP and in general for the TMPs, for a better understanding of the HER over these catalysts.

To the best of our knowledge, very few papers in the literature report exhaustive experimental studies on the mechanism and kinetics of the HER with TMP electrodes.^[52] EIS furnishes additional information to that obtained in the voltammetric measurements. EIS can be used to determine the reaction mechanism and the kinetic parameters such as the individual symmetry factors of each electrochemical step. To this end, we carried out EIS measurements at different overpotentials (η), ranging from 10 to 50 mV. The Nyquist plots obtained display two capacitive arcs

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Figure 4. a) Polarization curves, 1st and 8000th cycle, for the HER in H₂-saturated 0.1 \times HClO₄ at 1600 rpm and 10 mV s⁻¹ for the RuP catalyst. The HER activity recorded for Pt/C (20 wt%, JM) is shown for comparison. b) Chronopotentiometry at the potential for RuP where *j* = 10 mA cm⁻², during 15 h. c) Comparison of the HER current density at η_{10} and the Tafel slopes of the RuP catalyst reported in this work (green star) with other Ru phosphides reported in the literature (red circles) and other TMPs (blue rhombuses) under acidic conditions. Horizontal dashed lines represent the three theoretical Tafel slopes when the values of β_1 or β_2 are 0.5. d) EIS measurements at different overpotentials, from 10 to 50 mV. Inset: Equivalent circuit used for the HER. e) Dependencies of $\log(R_{ct})$, $\log(R_{h})$, and $\log(CPE_{h})$ on overpotentials from EIS data.

(Figure 4d), consistent with equivalent circuits reported for the HER.^[53] In the equivalent circuit shown in the inset of Figure 4d, the Faradaic impedance (Z_f) corresponds to the connection of

the charge transfer resistance, $R_{\rm ct}$, in series with the parallel connection of $R_{\rm h}$ and $C_{\rm h}$, where $R_{\rm h}$ and $C_{\rm h}$ are the equivalent resistance and capacitance, respectively, both associated with

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the adsorption of protons. The total impedance includes the solution resistance (R_s) and the double-layer capacitance (C_{dl}). Generally, the capacitances are replaced by constant phase elements (*CPE*) to represent the nonuniform current distribution on the electrode surface due to microscopic roughness of the electrode.^[54] Therefore, for the accuracy of the fitting results, C_{dl} and C_h of the equivalent circuit were replaced by CPE_{dl} and CPE_h. The impedance of CPE can be expressed as

$$Z_{\rm CPE} = \frac{1}{(j)^{\varphi} T} \tag{1}$$

where *j* is the imaginary unit, ω is the angular frequency of the ac perturbation, φ is an empirical constant representing the behavior of the CPE, and *T* is the CPE capacitance.

The dependencies of the equivalent circuit elements R_{ct} , R_h , and CPE_h with the electrode potential from EIS spectra are presented in Figure 4e. These dependencies on overpotential vary depending on the limiting step, as the Tafel slope does.^[53] We have tested all combinations with our results and, by comparing them with the Tafel slope, we have been able to confirm that RuP has Heyrovsky as the limiting step. When the Heyrovsky step is the RDS, the dependencies of the equivalent circuit elements with η are expressed in Equation (3)–(5) (see ref. [53] for more information).

$$\frac{d\eta}{d\log R_{ct}} = \frac{\ln(10)}{\beta_1 f} = 59(\beta_1)^{-1} \,\mathrm{mV}\,\mathrm{dec}^{-1}\,(\mathrm{at}\,25\,^\circ\mathrm{C}) \tag{2}$$

$$\frac{d\eta}{d\log R_h} = \frac{\ln(10)}{(1+\beta_2)f} = 59(1+\beta_2)^{-1} \,\mathrm{mV}\,\mathrm{dec}^{-1}\,(\mathrm{at}\,25\,^\circ\mathrm{C}) \tag{3}$$

$$\frac{d\eta}{d\log C_h} = -\frac{\ln(10)}{f} = -59 \,\mathrm{mV}\,\mathrm{dec}^{-1}\,(\mathrm{at}\,25\,^\circ\mathrm{C}) \tag{4}$$

Values of 0.79 and 0.5 for β_1 and β_2 , respectively, were obtained from Equation (3) and (4). Note that since the Volmer step is in equilibrium and the Heyrovsky is the RDS, the Tafel slope should be coincident with Equation (3). Through this rigorous study, we have demonstrated that RuP follows the Volmer–Heyrovsky mechanism, with Heyrovsky

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being the limiting step. Under these conditions, only β_2 has a real impact on the reaction kinetics, and it does not deviate from the ideal value of 0.5. However, β_1 deviates significantly, unlike most electrochemical reactions. This deviation of the nonlimiting step, which can only be observed and confirmed through the dependencies of the different elements in the equivalent circuit, is of great importance and it can contribute to a better understanding of these types of catalysts and aid in their subsequent treatment in computational modeling.

Finally, the specific activity of the catalyst was calculated by normalizing the current density to the surface area of the catalyst. Several different approaches to calculate the surface area of catalytic oxide and phosphide particles have been proposed in the literature. In this work, we have used two approaches, the mass-specific surface area (A_s) method (see experimental section) and the electrochemical surface area (ECSA) where ECSA = $C_{\rm dl}/C_{\rm s}$. We used the $C_{\rm s}$ value of 0.040 mF cm⁻², and $C_{\rm dl}$ has been determined from the CPE_{dl} obtained from the EIS.^[55]

$$C_{\rm dl} = T^{\frac{1}{\varphi}} (R_{\rm s}^{-1})^{1 - \frac{1}{\varphi}} \tag{5}$$

The C_{dl} and ECSA values obtained for RuP are 1.5 mF cm⁻² and 36.0(1) cm², respectively.

The C_{dl} value obtained for our catalyst is smaller than previously reported for similar phosphides (see Table S1, Supporting Information), probably because most works in the literature calculate C_{dl} values by recording cyclic voltammetry at different scan rates. However, this approach assumes that capacitance does not depend on the polarization potential of the electrode. In addition, the capacitance can be a function of the scan rate, making it difficult to extract accurate C_{dl} values.^[56] In order to avoid this issue, we have used EIS to determine the C_{dl} . We have calculated area-specific activity normalized to the ECSA, see Figure S3, Supporting Information.

The HER performance was assessed in a conventional PEMWE. CCMs containing a loading of $0.8 \,\mathrm{mg_{cat}}\,\mathrm{cm}^{-2}$ of RuP as cathode and $1 \,\mathrm{mg_{cat}}\,\mathrm{cm}^{-2}$ of Ir_{black} as anode were prepared. The cell was tested by recording a galvanostatic polarization curve up to $2 \,\mathrm{A}\,\mathrm{cm}^{-2}$, obtaining an E_{cell} value of 2.07 V



Figure 5. a) Cell potential (E_{cell}) with respect to the current density (*j*) recorded galvanostatically up to 2 A cm^{-2} . The comparison with reference performance values reached by different SoA TMPs is indicated with a red line. b) E_{cell} evolution over time (*t*) at a constant current density of 2 A cm^{-2} (nominal load). The measurements were carried out at 80 °C and ambient pressure.

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Nation 117

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Catalyst	<i>j</i> @ 2 V A ^{−1} ·[cm ^{−2}]	Mass loading [mg _{cat} cm ⁻²]	T [°C]	Durability
RuP – This work	1.70	0.8	80	Stable 60 h @ 2 A cm ⁻²
FeP/CP ^{[16]b)}	1.48	7	90	Only shows 3 cycles
Ni ₅₅ P ₃₄ B ₁₁ /CF/CP ^{[17]b)}	1.08	-	90	-
Ni _{71.} ⁵ Mo _{26.5} P _{2.0} ^{[18]b)}	1.87	-	90	Stable 46 h at 1 A cm^{-2}
CoP/CP ^{[19]b)}	1.89	6.12 to 6.19	90	-
Ni ₁₂ P ₅ -Ni ₂ P ^{[25]b)}	0.2@1.653 V	16.6	80	$120 h @ 0.2 A cm^{-2}$
FeP ^{[13]a)}	0.2@2.06 V	0.4	22	Stable at 2 V for 100 h
NiP ₂ ^{[15]b)}	0.05@1.86 V	0.4	25	Stable at 1.9 V for 48 h

4 5

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^{a)}Catalyst deposited over the membrane; ^{b)}Catalyst deposited over the PTL

0.95

1.86@2.27 V

1 31

0.5@1.82V

1@1.9V

DVANCED

FeCoP-300/CF/CP^{[20]b)}

Sulfur doped MoP^{[23]b)}

CoP^{[21]b)}

Ni₇₈P₂₂^{[22]b)}

 $Ni_{0.46}P_{0.54}^{[24]b)}$

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(Figure 5a). At each applied current density, the cell potential is measured under steady-state conditions. The performance at 2 V was chosen to benchmark the RuP activity. As shown in Figure 5a and in Table 1, the activity of RuP compares well with that of the SoA TMPs, displayed as a red line in Figure 5a. It should be noted that unlike most published TMPs, the catalyst was spray coated over the Nafion membrane, which allows a large-scale application. To the best of our knowledge the only other example of the cathode deposited over the membrane was in the case of FeP.^[13] Furthermore, only FeP and NiP₂ cathodes have been tested with lower loadings.^[13,15] The mass loading of the cathode investigated in this work is low, $0.6 \text{ mg}_{Ru} \text{ cm}^{-2}$, a Ru loading that suffices for reaching catalytic performances comparable to commercial loadings of Pt, see Table S2, Supporting Information.

Moreover, a durability test was carried out at a constant current density of \approx 2 A cm⁻² at 80 °C and *P*_{amb}. Figure 5b shows that even under severe corrosion conditions this MEA has demonstrated an almost a constant activity for at least 60 h.

3. Conclusion

In this work we report a simple, one-pot synthesis of RuP with controlled composition via thermal treatment of commercially available ruthenium and phosphorous under vacuum. The RuP particles display a strong degree of hybridization between Ru 4d and P 3p, with a slight charge distribution between Ru and P atoms that can increase the electron transfer rate and therefore the HER performance. The activity for the HER of the RuP particles was first assessed in a thin-film rotating ring disk electrode configuration, obtaining a low overpotential of 36 mV to achieve a current density of 10 mA cm^{-2} , a value that compares well with that of state-of-the-art Pt/C catalysts. In view of this performance, a CCM was produced with a low Ru loading of $0.6 \text{ mg}_{\text{Ru}} \text{ cm}^{-2}$ in the cathode and tested for hydrogen production in a PEMWE configuration, yielding 1.73 A cm^{-2} at a potential of 2 V. Moreover, a constant current density of 2 A cm^{-2} at 80 °C is recorded for at least 60 h of operation, which is among the best results reported in the literature for Pt-free PEMWEs.

8h@2V

Several studies. Active during thousands of hours

24 h @ 1.85 V

 $1 \,\mathrm{A\,cm^{-2}}$ for 16 h

4. Experimental Section

90

50

90

80

90

Synthesis of RuP: The stoichiometric amounts of Ru powder (0.2 g, ruthenium black, Merck) and red phosphorus (0.061 g, Merck) were mixed in a mortar inside a glove box in N₂ atmosphere. The mixture was introduced in a Pyrex tube. The tube was sealed under vacuum and it was subjected to thermal treatment at a heating rate of 0.7 $^{\circ}$ C min⁻¹, reaching a temperature of 525 °C. It was maintained at this temperature for 24 h.

Characterization: Phase identification and crystal size were determined by X-ray powder diffraction (XRD) in a Bruker-axs D8 Advanced diffractometer (40 kV, 30 mA) in Bragg-Brentano reflection geometry with Cu Ka radiation ($\lambda = 1.5418$ Å). The data were obtained between 10° and 64° 2θ in steps of 0.05°. The patterns were analyzed with the Rietveld method $^{\left[57\right]}$ using the Fullprof program $^{\left[58\right]}$ In the refinements, a pseudo-Voigt function was used for the shape of the peaks.

Transmission electron microscopy (TEM) images, high-resolution TEM (HRTEM), and X-ray energy dispersive spectra (EDS) were recorded in a JEOL 2100 field-emission gun transmission electron microscope operating at 200 kV and equipped with an EDS spectrometer Oxford INCA Energy 2000 system. The phosphides were deposited on Cu grids supporting a lacey carbon film.

X-ray photoelectron spectroscopy (XPS) was collected using a SPECS customized system equipped with a nonmonochromatic X-ray source XR 50 and a hemispherical energy analyzer PHOIBOS 150. X-ray MgK line (1253.6 eV) was used as the excitation (operating at 200 W/12 kV). The energy regions of the photoelectrons of interest were scanned at increments of 0.1 eV and fixed pass energy of 20 eV. Charge effects were accounted for by setting the C 1s core-level peak at 284.6 eV. Spectra were analyzed using the XPSCasa Software.^[59] A Shirley-type background was used for peak analysis. XPS peaks were deconvoluted using a combination of Gaussian/Lorentzian curves. Asymmetric peaks were used for the fitting of the Ru 3d and 3p peaks.

X-ray absorption spectroscopy (XAS) measurements at room temperature were carried out at the B07 (VerSoX) B branch beamline of Diamond Light Source, the UK synchrotron facility.^[60,61] Near-edge X-ray absorption fine structure (NEXAFS) measurements at the P-edge were carried out at the B07 VerSoX beamline. Data was collected in total electron yield (TEY) and total fluorescence yield (TFY) modes to differentiate between surface and bulk components: TEY is considered as a surface-sensitive (top few

nm) measurement while TFY is more bulk sensitive (tens to hundreds of nm). The spectra were corrected with the I0 signal from the last mirror to remove the effects of absorption from beamline optical components. A linear baseline was subtracted and the spectra were normalized such that the edge jump was 1. The TFY spectra were corrected for self-absorption with ATHENA software.^[62]

4DVANCED

Computational Methods: All simulations in this work have been carried out using the Quantum ESPRESSO software suite, version 6.8.^[63–65] Quantum ESPRESSO implements density functional theory (DFT) within the pw.x code using the planewave and pseudopotential approach in periodic boundary conditions.^[63] Simulations were carried out using lattice and geometric parameters as determined experimentally via XRD.

For description of the core electrons, we made use of ultrasoft pseudopotentials, distributed as part of the pslibrary.^[66] More specifically, to facilitate X-ray absorption calculations, the pseudopotentials Ru.pbe-spn-rrkjus.UPF, P.pbe-n-rrkjus.UPF, and O.pbe-nl-rrkjus.UPF were modified to include GIPAW reconstruction of the core-level wavefunctions.^[67] In addition, a further pseudopotential Pstar1s.pbe-n-rrkjus_gipaw.UPF was created, which contains a core hole in the P 1s orbital. All pseudopotentials used in this work are available from the authors upon request.

Electronic wave functions have been expanded in the planewave basis set with a kinetic energy cutoff of 120 Ry, while the electronic density was expanded up to 1200 Ry. We used the Perdew–Burke–Ernzerhof functional to describe electron exchange and correlation interactions.^[68] For the various systems considered, we used regular, automatically generated k-point meshes of $4\times6\times4~$ (Ru₄P₄), $3\times1\times2~$ (Ru₄P₁₂O₃₆), and $7\times4\times3~$ (Ru₂P₆O₁₈) respectively. We found that these simulation parameters yielded sub-5 meV convergence on the computed total energy.

Theoretical NEXAFS spectra were computed by solving the Fermi golden rule as implemented within the xspectra.x code of the Quantum ESPRESSO software suite.^[69-72] All NEXAFS simulations of the P K-edge were calculated within the dipole transition approximation, using the electronic structure computed in the presence of a core-hole potential in the P 1s orbital. The final presented theoretical spectra for each material were constructed from the sum of simulations with the polarization vector aligned along each of three Cartesian directions, and a constant broadening of 0.8 eV was applied to each of the spectra. To understand the origin of the peaks we observed in the theoretical X-ray absorption spectrum, we computed the (empty) conduction band projected density of states (PDOS) for each of the compounds considered, including the presence of a core-hole potential on one of the P atoms. In the PDOS analysis, the eigenstates of the Kohn-Sham Hamiltonian were projected onto orthogonalized atomic wavefunctions, resolved by atom and orbital angular momentum, which allowed us to distinguish the contributions to the DOS from p orbitals on the adsorbing P atom (with a core hole) and those from neighboring P atoms. Furthermore, to inform on the metallicity of the RuP ground state (no core-hole potential), we performed DOS and PDOS analysis, considering the valence and conduction manifolds.

Electrochemical Characterization: An Autolab PGstat 302N potentiostat/ galvanostat was used to test the electrochemical performance in the HER. The measurements were performed using a standard three-compartment glass cell and an RDE (Pine Research Instruments). A graphite bar and an Ag/AgCl (3.5 M) were used as counter and reference electrodes, respectively. Potentials were reported versus the reversible hydrogen electrode (RHE). As recommended, to convert the experimental potentials to RHE, an experimental calibration of the reference electrode was done before each measurement.^[40] Briefly, for the calibration, CVs were made in the voltage range of HER/hydrogen oxidation reaction using a Pt electrode in H₂-saturated solution of the desired electrolyte.

The catalyst under study was deposited onto the working electrode by means of an ink. The ink was prepared by mixing RuP (4.5 mg) and Black Pearls 2000 (1 mg, BP, Cabot, Lot-4 854 640). BP is used to improve the electrical conductivity. The solids were ultrasonically dispersed in a mixture of water (670 μ L), ethanol (300 μ L, absolute, Pharmapur), and 5%wt Nafion (30 μ L, Aldrich) using an Ultrasonic Processor UP50H (Hielscher). 10 μ L of the ink were dropped onto a 0.196 cm⁻² glassy carbon electrode, with a final catalyst loading of 0.23 mg_{oxide} cm⁻².

To assess the catalyst' activity for HER, a series of voltammograms were recorded between 0.05 and -0.1 V versus RHE at 5 mV s⁻¹. The measurements were performed in an H₂-saturated H₂SO₄ (0.5 M) electrolyte at a rotation rate of 1600 rpm. The HER polarization curves were *iR* corrected using the formula *E*·*iR*_{corrected} = *E*_{applied}-*iR*. In this formula *i* is the current and *R* is the ohmic electrolyte resistance (*R* = 5 Ω) as obtained from electrochemical impedance spectroscopy (EIS). Impedance measurements were carried out in a frequency range from 10 kHz to 0.1 Hz (10 points per decade) with an amplitude signal of 10 mV at overpotentials ranging from 10 to 50 mV. The value of ECSA can be obtained by applying the equation ECSA = *C*_{dl}/*C*_s, where *C*_s is the specific capacitance for a flat surface. We used the value of C_s = 0.040 mF cm⁻² typically used in these types of materials at these conditions.^[22,24]

CCM Preparation and PEMWE Measurements: The CCMs were prepared with a wet spraying technique using a vacuum heating table (Fuel Cell Store) to hold the Nafion 212 PEM substrate in place and heat it up to 100 °C during deposition. The distance between spraying nozzle and substrate was kept at 6 cm, and the ink deposition rate was limited to $2-3 \text{ min mL}^{-1}$. The inks were prepared by mixing the catalyst (1 mg) in ultrapure H₂O (1 mL, MiliQ, 18 M Ω cm⁻¹) and the desired amount of Nafion D521 solution (5 wt% in lower aliphatic alcohols and water) to achieve an ionomer content of 25 and 30 wt% in the dry anode and cathode layer, respectively. The mixture was sonicated for at least 1 h until the catalyst was well dispersed. Isopropanol (1 mL, IPA, ACS reagent, >99.5%) was added and the mixture was sonicated for 15 min to reach the adequate dispersion and homogeneity of the ink. This process was scaled up to the desired volume of ink. After spraying and drying, the CCM was hot pressed at 5 MPa and 125 °C. The resulting loading of Ir at the anode was 1 mg cm^{-2} and the cathode was prepared with 0.8 mg cm^{-2} of the RuP synthetized in this work.

Long-term testing of the CCMs was performed using the conventional PEMWE configuration; here, deionized water was fed via natural convection. This ensured stable, steady conditions for recording long-term polarization curves measurements. On both the anode and cathode side, the porous transport layer (PTL) was a Ti porous sintered layer (PSL) on Ti mesh produced by diffusion bonding^[73] and coated with Pt.^[74] On the cathode, an extra carbon paper sheet (Spectracarb 2050A-1050) was placed in contact with the catalyst layer. On both sides Ti bipolar plates (BPPs) were used. The cell active area was 4 cm² and tests were carried out at 80 °C and ambient pressure. The polarization curves were measured galvanostatically according to the JRC EU-harmonized procedure^[75] employing a dwell and consecutive recording period of 10 s for each current step.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

catalyst-coated membranes, green hydrogen, hydrogen evolution reaction, proton exchange membrane water electrolysis, RuP

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