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Enhancing the efficiency of the hydrogen evolution reaction utilising Fe₃P bulk modified screen-printed electrodes *via* the application of a magnetic field†

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We report the fabrication and optimisation of Fe₃P bulk modified screen-printed electrochemical platforms (SPEs) for the hydrogen evolution reaction (HER) within acidic media. We optimise the achievable current density towards the HER of the Fe₃P SPEs by utilising ball-milled Fe₃P variants and increasing the mass percentage of Fe₃P incorporated into the SPEs. Additionally, the synergy of the application of a variable weak (constant) external magnetic field (330 mT to 40 mT) beneficially augments the current density output by 56%. This paper not only highlights the benefits of physical catalyst optimisation but also demonstrates a methodology to further enhance the cathodic efficiency of the HER with the facile application of a weak (constant) magnetic field.

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Introduction

Electricity produced from renewable sources such as wind turbines, solar PV and tidal power can be converted to chemical energy in the form of green hydrogen gas.^{1,2} The energy density of green hydrogen gas (140 MJ kg⁻¹) is greater than fossil fuels such as: coal (24 MJ kg⁻¹), natural gas (55 MJ kg⁻¹) and petrol (44 MJ kg⁻¹) making it a promising alternative energy source.³ Green hydrogen is generated within an electrolyser and has no direct carbon by-products, whereas 'grey' hydrogen is produced in processes such as natural gas reformation and coal or biomass gasification where the by-products are CO₂ and CO.^{4,5} The cathodic reaction within a proton exchange membrane (PEM) electrolyser is the hydrogen evolution reaction (HER; 2H⁺ + 2e⁻ → H₂), where protons are electrochemically reduced to hydrogen gas formed at the surface of a suitable cathode.^{6,7}

Platinum (Pt) based cathodic materials are commonly required within commercial electrolysers to carry out efficient water splitting, given that they are highly active and stable catalysts for electrolytic applications.⁸ However, the application of Pt based materials within electrolysers is limited by their high cost and low abundance,^{9–11} therefore research is directed towards discovering active and stable non-precious metals (NPM) cathodic catalysts.^{12–15} Transition metal phosphides (TMPs) are regarded as promising cathodic catalysts, composed

of active transition metals such as Ni,^{16–18} Co^{19–21} and Fe^{22–24} which are stabilized when alloyed with phosphides.¹⁶ An interesting study by Schipper *et al.*²⁵ reported on the effects of phase transition of FeP, Fe₂P and Fe₃P films electrodeposited on the surface of fluorine doped tin oxide (FTO). An increase in ferric content within the phases led to increased activity towards the HER, resulting in low HER overpotentials of 116, 83, 49 and 8 mV (*vs.* RHE) for FeP, Fe₂P, Fe₃P and Pt, respectively. The films exhibited high achievable current densities, in excess of –100 mA cm⁻² and promising stability within acidic conditions during chronoamperometric measurements at –120 mV (*vs.* RHE) for 20 hours. Iron phosphides contain exposed stepped surfaces of 3-fold Fe and Fe–Fe bridge sites that are thought to exhibit affinity for H⁺ ions.²⁶ FeP is mainly composed of Fe–P sites (which result in weak adsorption), where up to six P atoms are covalently bonded to an Fe^{III} centre in an orthorhombic crystal system.²⁷ Fe₂P consists of a combination of tetrahedral Fe^I and pyramidal Fe^{II} sites, each site arranged in a hexagonal crystal system where there are a maximum of four Fe–P interactions per Fe atom.^{28,29} Within the iron phosphides, Fe₃P contains the weakest covalent bonds, but the strongest ionic interactions, metallicity and contains the largest number of Fe–Fe interactions.³⁰ This is a result of Fe₃P consisting of Fe^I centres arranged in a tetragonal crystal system where the increase in ferric content leads to a maximum of three Fe–P covalent bonds and an increase in favourable Fe–Fe interactions.³¹ Clearly, Fe₃P is a very interesting material to study towards the HER.

In addition to material optimisation, as reported above for iron phosphides, another interesting approach to increase the cathodic efficiency of electrolysis is by using an external magnetic field.^{32,33} This is due to Lorentz force induced convection *via* magnetohydrodynamic (MHD) and micro-MHD

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effects,³⁴ in which the former results in diffusion layer thinning, improving the mass and charge transfer of H⁺ and e⁻ ions. In the latter, a perpendicular magnetic field can induce flow patterns at very small scales, close to the electrode surface (*i.e.* within the diffusion layer), which is impossible through mechanical agitation and regulates bubble removal at the electrode surface in the clockwise or anticlockwise direction, leading to the reduction of ohmic loss, and the increased availability of active sites.^{34–37} Elias *et al.*³² have studied the effect of a magnetic field on the HER by applying magnetic flux densities (B) between 0.1–0.4 T to enhance HER efficiency in Ni–W alloy electrodes. It was found that the HER onset potential of –1.35 V (*vs.* SCE) for the Ni–W electrode when $B = 0$, was reduced to –1.01 V (*vs.* SCE) when $B = 0.4$ T. Additionally, there was an increase in current density from –0.70 to *ca.* –0.82 A cm⁻² at $B = 0.1$ T and $B = 0.4$ T, respectively. Ferromagnetic materials such as Fe, Ni and Co³⁸ are highly affected by an applied magnetic field and amplify the Lorentz effect, whereas materials such as Pt (paramagnetic) and graphite (diamagnetic) are largely unaffected.³⁹ This is due to the Zeeman effect where the distortion of electron orbitals within magnetic materials in the presence of a magnetic field leads to decreased energy barriers and enhanced electron transfer.⁴⁰ Fe₃P is a robust ferromagnetic material, hence exhibits magnetic properties that are required to enhance HER efficiency within water electrolysis.⁴¹

The assessment criteria of a NPM cathodic catalysts' suitability for use in PEM electrolysis is dependent upon a number of critical factors; proficient HER catalysis, high achievable current density and stability in acidic media. Another important factor, often forgotten, is the ability to translate research outputs to industry – mass-printable screen-printed electrodes can help this transition. Consequently, in this paper, we report the incorporation of Fe₃P variants into SPES and optimise their performance as HER catalysis in acidic conditions; the effect of applying a weak magnetic field is also explored and found to provide beneficial outputs to the HER.

Experimental section

Chemicals

All chemicals used were of analytical grade from Sigma Aldrich and were without need of any further purification. The Fe₃P powder (product code: 691593; Sigma Aldrich, UK) and Fe₂P powder (product code: 691658; Sigma Aldrich, UK) utilised were of 99.5% purity (trace metals basis, –40 mesh avg. part. size). These are referred to in the text with a subscript “raw” to indicate that they were used, raw, without any treatment.

The Fe₃P powder was wet ball milled in a Retsch PM 100 planetary ball mill over the following time intervals: 5, 10, 20 and 50 h in a 50 mL zirconium oxide (ZrO₂) grinding jar (Retsch, Germany). Ball milling was carried out with 2 mm yttrium stabilized zirconia beads (Retsch, Germany) at 150 rpm, where 2 g Fe₃P was placed in 30 mL methanol to form a milling slurry. The 2 mm diameter of the zirconia beads and milling speed have been previously shown to result in the finest powder dispersion.⁴² Electrochemical measurements were performed in

0.5 M H₂SO₄, which was of the highest possible purity from Sigma Aldrich (99.999%, double distilled for trace metal analysis).

Electrochemical measurements

The electrolyte (0.5 M H₂SO₄) was made using deionized water (resistivity 18.2 MΩ cm), which was degassed with high purity nitrogen before electrochemical measurements. It is common within research conducting HER experiments to remove any trace of oxygen, to prevent the onset of the competing ORR. An Autolab Compact™ (Switzerland) potentiostat was used to carry out electrochemical measurements. A three-electrode system was used to take measurements with modified and bare graphitic screen printed electrodes (SPES) with a working area diameter of 3.1 mm used as working electrodes, with a carbon counter and a saturated calomel electrode (SCE) reference. The neodymium ring magnets (30 × 10 × 10 I.D. mm, magnetic field strength: 0.44 T, First4Magnets, product code: F3010DM-1) used for electrochemical measurements were placed in incremental distances from the electrode surface, highlighted in the ESI Table T1.† The screen-printing process used to produce the Fe₂P and Fe₃P SPES utilised within this study is explained within the ESI† and is also described in more depth in previous studies.^{11,43–45} Herein, the potential is referenced to the reversible hydrogen electrode (RHE) utilising the following equation, as is common within the literature:^{46–48} $E_{\text{RHE}} = E_{\text{SCE}} + 0.059\text{pH} + 0.242$ V (at 25 °C).

Physicochemical characterisation of the raw and ball milled Fe₃P powders

It was important to assess the particle size and distribution of the raw Fe₃P powder using Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray (EDX) elemental mapping to compare against the (wet) ball-milled variants. In the ESI, Fig. S1(A₁)† shows an SEM image of the raw Fe₃P powder, where the average particle size is *ca.* 400 μm. SEM images in Fig. S1(A_{2–3})† depict the reduction in particle size of the ball milled Fe₃P powders. The average particle size of the 5, 10 and 20 h ball-milled Fe₃P powders is >10 μm, whereas the Fe₃P powder ball milled for 50 h is <1 μm. After 20 h of ball milling, a cold welding process has likely occurred and the Fe₃P particles have aggregated changing the microscopic structure from crystalline to amorphous, which is also shown in the EDX elemental mapping images in Fig. S1(B_{1–5})†. The corresponding EDX elemental analysis is exhibited in ESI Table T2,† showing elemental compositions of carbon, oxygen, iron and phosphorous. The initial ratio of Fe : P is shown to be 8 : 1, which could be a result of the non-uniform distribution due to the (relatively) large average particle size. The Fe : P ratio is steadily reduced as the ball-milling duration increases, where a ratio of 5 : 1 is observed at 50 h. The percentage composition of oxygen within the Fe₃P powders increases with ball milling duration, where raw Fe₃P contains 3.5% and 50 h ball milled Fe₃P contains 11.5% oxygen. It is expected that ball-milling in an air atmosphere, as employed here, will lead to an increase in oxygen concentration and the ball milled Fe₃P powders will likely be



covered with a thin oxide layer. The thin oxide layer is thought to make the powder particles brittle, therefore resulting in a finer dispersion when the amorphous powder is agitated.⁴⁹ The presence of carbon within the raw and ball milled Fe₃P powders is a result of the wet milling process in the presence of methanol.

X-ray Diffraction (XRD) analysis can be used more accurately to assess the crystallinity of the raw and ball milled Fe₃P powders. Fig. S2(A)† exhibits the characteristic diffraction peaks of raw Fe₃P at $2\theta = 35.9^\circ, 40.5^\circ, 41.2^\circ, 42.2^\circ, 43.1^\circ, 44.6^\circ, 45.4^\circ, 46.0^\circ, 47.5^\circ, 49.9^\circ, 51.3^\circ, 52.0^\circ, 53.1^\circ$ and 54.5° , which are indexed towards the following single crystal faces of Fe₃P, respectively; (301), (321), (330), (112), (420), (141), (400), (222), (110), (530), (620), (541), (422) and (212).^{50,51} Fig. S2(B–E)† exhibit XRD spectra of the ball milled variants of Fe₃P powder in the time intervals 5, 10, 20 and 50 h, respectively. The spectra become increasingly convoluted, hence show a reduction in the crystallinity of Fe₃P as the ball-milling time increases. The following single crystal faces within the milled powders are detected; (301), (330), (420), (141), (222), (530), (541) and (212). This suggests a transformation from crystalline to amorphous, as observed above.

Raman Spectroscopy was used to further characterise the raw and ball milled Fe₃P powders. Fig. S3(A)† shows the Raman spectrum for raw Fe₃P, exhibiting characteristic vibrational bands at *ca.* 655 and 1339 cm⁻¹, which correspond to the Fe–O (A_g1) symmetric stretching mode and first order carbon (D) band.⁵² The Fe–O and carbon vibrational bands are likely present as a result of the methanol milling within the presence of air. The Raman spectra of the 5, 10, 20 and 50 h ball milled Fe₃P powders are shown in Fig. S3(B)–(E)†, respectively. Additional characteristic vibrational bands are present within the spectra for each of the milled Fe₃P variants at *ca.* 214, 391 and 488 cm⁻¹ corresponding to Fe–O symmetric stretching modes. Vibrational bands at 291 and 523 cm⁻¹ within the milled Fe₃P samples indicate Fe–O asymmetric bending modes (T_g2).⁵²

X-ray Photoelectron Spectroscopy (XPS) was used to assess the surface elemental composition of the raw and ball milled Fe₃P powders. The XPS profiles of Fe 2p_{3/2}, Fe 2p_{1/2} and P 2p shown in Fig. S4† are consistent with the findings in literature.^{53–55} The Fe spectra in Fig. S4(A_{1–5})† correspond to Fe³⁺ as they exhibit well-defined satellite peaks that are approximately 8 eV from the centre of the main Fe 2p_{3/2} peak at 710 eV. The Fe 2p_{1/2} bands at *ca.* 720 and 725 eV correspond to Fe²⁺ (Fe–O) and Fe³⁺ (Fe–P), respectively.⁵⁶ The P 2p spectra in Fig. S4(B_{1–5})† exhibit peaks at 128.6 and 129.9 eV, which correspond to 2p_{3/2} and 2p_{1/2}, respectively, where the peak at 129.9 eV is a result of Fe–P bonding within Fe₃P.⁵⁴ The peak at 133.0 eV corresponds to P⁵⁺, indicating P–O bonding in FePO₄, which is also suggested in the Fe 2p spectra through the presence of Fe³⁺.^{57,58} The XPS findings are consistent with the Raman spectroscopy, where partial surface oxidation is suggested. The above physicochemical characterisation techniques have confirmed the presence of crystalline and amorphous Fe₃P within the raw and ball-milled samples.

Results and discussion

Exploring Fe₂P and Fe₃P bulk modified screen-printed electrodes (SPEs) towards the hydrogen evolution reaction (HER)

The HER activity of Fe₂P and Fe₃P bulk modified SPEs, fabricated as described in detail in the Experimental section, were first evaluated within acid media (0.5 M H₂SO₄). Fig. 1(A) shows linear sweep voltammetry (LSV) obtained for the different % Fe₂P SPE_{Raw} variants (5, 10, 20 and 40%), which have been benchmarked against a bare SPE (no Fe₂P) and a polycrystalline Pt electrode. Note that the subscript “Raw” is given to these, as the untreated raw powder, is utilised. The polycrystalline Pt electrode, as expected, exhibits optimal HER activity with an onset of -0.01 V (*vs.* RHE). HER onset potential values of -0.53 , -0.21 , -0.20 , -0.19 and -0.17 V (*vs.* RHE) are exhibited by the bare SPE, 5% Fe₂P SPE_{Raw}, 10% Fe₂P SPE_{Raw}, 20% Fe₂P SPE_{Raw} and 40% Fe₂P SPE_{Raw}, respectively (NB: the HER onset potential is defined as the point at which the observed current deviates from the background current by $-25 \mu\text{A cm}^{-2}$).⁵⁹ The most electronegative HER onset potential is displayed by the bare SPE, where the graphitic carbon layer is solely responsible for the observed HER catalysis; this response is as expected and observed previously. The closest HER onset potential to the Pt electrode is obtained using the 40% Fe₂P SPE_{Raw}, which possesses the highest loading of the Fe₂P catalyst, therefore the highest number of electroactive sites. The polycrystalline Pt electrode also exhibits the optimal achievable current density, requiring -0.06 V (*vs.* RHE) to reach -10 mA cm^{-2} . None of the Fe₂P SPEs reached the -10 mA cm^{-2} current density standard, marked as a dashed line in Fig. 1.

Fig. 1(B) also shows LSV obtained for the 5% Fe₃P SPE_{Raw}, 10% Fe₃P SPE_{Raw}, 20% Fe₃P SPE_{Raw} and 40% Fe₃P SPE_{Raw}, again, benchmarked against a bare SPE and a polycrystalline Pt electrode. HER onset potential values of -0.53 , -0.14 , -0.13 , -0.11 and -0.11 V (*vs.* RHE) were exhibited by the bare SPE, 5% Fe₃P SPE_{Raw}, 10% Fe₃P SPE_{Raw}, 20% Fe₃P SPE_{Raw} and 40% Fe₃P SPE_{Raw}, respectively. The least electronegative HER onset potential was exhibited by the 20 and 40% Fe₃P SPE_{Raw} due to the higher loading of Fe₃P catalyst within SPEs. A higher achievable current density is observed within the Fe₃P SPEs compared to the Fe₂P SPEs, where the 20% Fe₃P SPE_{Raw} and 40% Fe₃P SPE_{Raw} required -1.13 and -1.24 V (*vs.* RHE) to reach -10 mA cm^{-2} . This is likely due to the increase in ferric content, where a greater number of Fe–Fe bridge sites result in a faster heterogeneous electron transfer (HET) rate.²⁵ It is evident that a 20% incorporation of Fe₃P within SPEs is the optimal mass loading with no significant improvement with 40%, and in fact, is worse than the 20% incorporation, which is likely due to partial blockage of active sites at the electrode surface and reduced conductive electronic pathways within the graphite electrode.^{6,11,43} Note that further loadings of the Fe₃P result in difficulties in screen-printing due to the change in rheology and represents the limit; this has been seen multiple times for materials incorporated into bulk SPEs by our group. Given that the 20% Fe₃P SPE_{Raw} is the nearest in HER activity to the optimal Pt



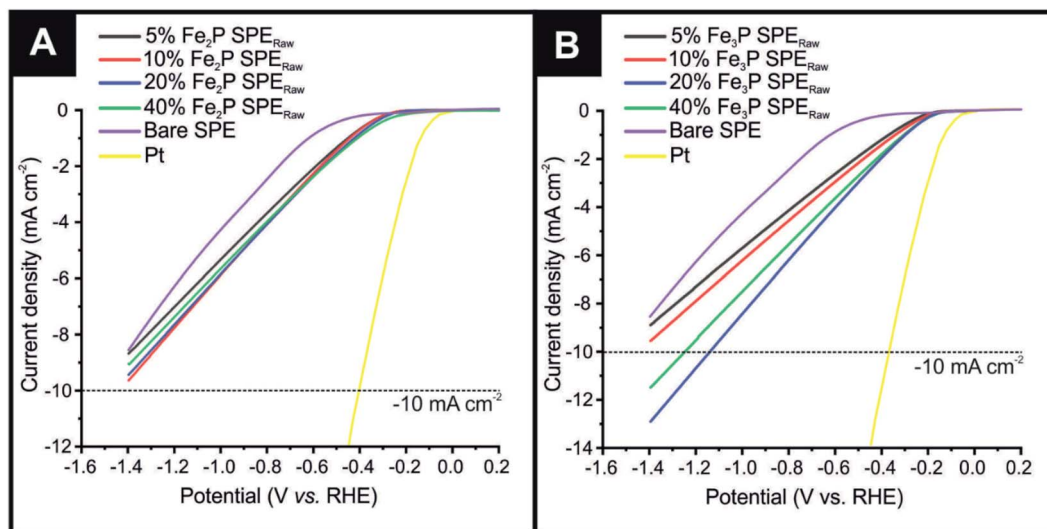


Fig. 1 (A) Linear sweep voltammetry (LSV) exhibiting the onset potential of the HER, in the potential range +0.2 to -1.4 V (vs. RHE) for the Fe_2P SPEs produced from raw powder: Fe_2P SPE_{5%}, Fe_2P SPE_{10%}, Fe_2P SPE_{20%}, Fe_2P SPE_{40%}, bare/unmodified SPE and polycrystalline Pt. (B) And for the Fe_3P SPEs produced from raw powder: Fe_3P SPE_{5%}, Fe_3P SPE_{10%}, Fe_3P SPE_{20%}, Fe_3P SPE_{40%} bare/unmodified SPE and polycrystalline Pt. Scan rate: 25 mV s^{-1} (vs. RHE) in $0.5 \text{ M H}_2\text{SO}_4$.

electrode, this mass loading of Fe_3P only was taken forward for further exploration towards the HER.

Next, ball-milling was utilised to try and tune/improve the HER kinetics of the Fe_3P further, which is facilitated by reducing the average particle size and increasing porosity; such an approach has been previously reported for other materials.^{60–62} Consequently, raw Fe_3P powder was ball milled over various time intervals (5, 10, 20 and 50 h) and the resultant powders incorporated into the bulk of bespoke SPEs and benchmarked against the HER within acidic media. Note that a full physicochemical characterization was performed on the raw and ball milled Fe_3P powders utilized, as it is the focus of HER exploration within this paper (see Experimental section and ESI†), but not performed on the Fe_2P powders.

Fig. 2 shows LSVs obtained for the Fe_3P SPE_{5 h BM}, Fe_3P SPE_{10 h BM}, Fe_3P SPE_{20 h BM} and Fe_3P SPE_{50 h BM}, benchmarked against a bare SPE and a polycrystalline Pt electrode. HER onset potential values of -0.53 , -0.12 , -0.11 , -0.11 and -0.12 V (vs. RHE) are exhibited by the bare SPE, Fe_3P SPE_{5 h BM}, Fe_3P SPE_{10 h BM}, Fe_3P SPE_{20 h BM} and Fe_3P SPE_{50 h BM}, respectively. The applied potentials of: -1.04 , -0.91 , -0.84 and -1.14 V (vs. RHE) were required to reach -10 mA cm^{-2} for the Fe_3P SPE_{5 h BM}, Fe_3P SPE_{10 h BM}, Fe_3P SPE_{20 h BM} and Fe_3P SPE_{50 h BM}, respectively. The HER onset potentials displayed by the ball milled Fe_3P SPEs show that the HER kinetics of each SPE have remained stable as a result of increased ball milling time. The applied potential required to reach -10 mA cm^{-2} for all Fe_3P electrodes was greatly reduced with milling time, excluding the Fe_3P SPE_{50 h BM}, which has marginally increased. It is evident that there is an optimal duration of ball milling, where a 25.7% reduction in applied potential to reach -10 mA cm^{-2} is exhibited by the Fe_3P SPE_{20 h BM} compared to the unmilled variant. This is due to increasing ball-milling time leading to an increase in specific surface area and a decrease in crystal size and micropore diameter of the Fe_3P powder. Note,

that as the micropore diameter is reduced, porosity is increased with respect to increased micropore ratio. It is likely that the micropore diameter (nm) decreases up to 20 h of ball milling, then begins to plateau or increase moving towards 50 h. This is because there is an increase in the maximum distribution of nanoparticles (P_{max}) after which porosity is reduced as a result of cluster formation.⁶³ The Fe_3P powder ball milled for 20 h

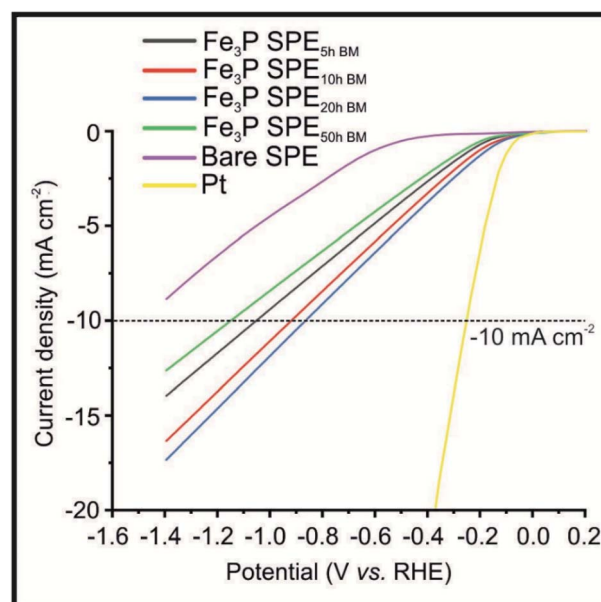


Fig. 2 Linear sweep voltammetry (LSV) exhibiting the onset potential of the HER, in the potential range +0.2 to -1.4 V (vs. RHE) for the 20% Fe_3P SPEs produced from ball milled (BM) powder: Fe_3P SPE_{5 h BM}, Fe_3P SPE_{10 h BM}, Fe_3P SPE_{20 h BM}, Fe_3P SPE_{50 h BM}, bare/unmodified SPE and polycrystalline Pt. Scan rate: 25 mV s^{-1} (vs. RHE) in $0.5 \text{ M H}_2\text{SO}_4$.



possesses the greatest porosity and therefore the higher ratio of Fe–Fe bridge sites to Fe–P sites. The Fe₃P SPE_{5 h}, Fe₃P SPE_{10 h}, Fe₃P SPE_{20 h} and Fe₃P SPE_{50 h} exhibit specific activities of 0.296, 0.297, 0.314 and 0.306 A cm⁻², respectively, hence displaying the optimal ball milling time of 20 h. Tafel analysis was used in a qualitative manner, in order to assess whether there was an alteration in the HER reaction mechanism as the ball milling time increased. Tafel analysis extrapolated from the faradaic regions of the LSVs presented in Fig. 2 with values of 118.1, 88.5, 101.4, 95.6 and 96.4 mV dec⁻¹ are exhibited by the bare SPE, Fe₃P SPE_{5 h}, Fe₃P SPE_{10 h}, Fe₃P SPE_{20 h} and Fe₃P SPE_{50 h}, respectively. This suggests that there is no change in the rate limiting HER step, which closely matches that expected for the Volmer step/mechanism. Last, the current literature has been surveyed with respect to transition metal phosphides (TMPs), as shown in the ESI (ESI Table T3†) where all other approaches have utilised drop-casting. It is evident that our Fe₃P bulk modified SPEs perform comparably with previous TMPs with our approach potentially offering a greater transition from academia to industry based upon that fact that these Fe₃P SPEs can offer mass production and scales of economy.

Electrochemical performance of the Fe₃P SPEs towards the HER under a weak (constant) magnetic field

The optimised Fe₃P SPEs were next explored towards the HER under the effect of a weak (constant) magnetic field applied perpendicular (*B*–). As shown in Fig. 3, the 20% Fe₃P SPE_{Raw} displayed the following potential values to reach –10 mA cm⁻² of –1.13, –1.07, –1.09, –1.11 and –1.13 (vs. RHE) which correspond to the *B* values of: 0 (magnet off), 0.29, 0.33, 0.15 and 0.04 T, respectively.

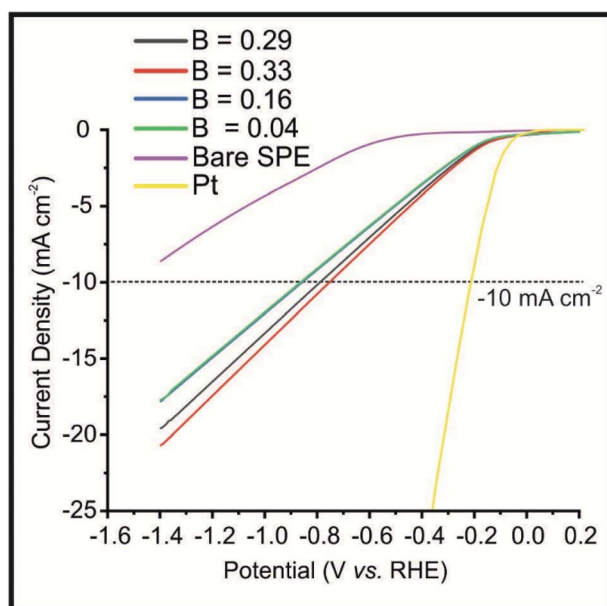


Fig. 3 Linear sweep voltammetry (LSV) exhibiting the onset potential of the HER under an applied magnetic field, in the potential range +0.2 to –1.4 V (vs. RHE) for the Fe₃P SPE_{20 h BM} at the following magnetic flux densities: 0.29, 0.33, 0.16 and 0.04 T. Scan rate: 25 mV s⁻¹ (vs. RHE) in 0.5 M H₂SO₄.

0.04 T, respectively. The potential values for the 20% Fe₃P SPE_{20 h BM} to reach –10 mA cm⁻² of –0.84, –0.77, –0.74, –0.82 and –0.84 V (vs. RHE) correspond to the *B* values listed above. It is evident that applying a larger magnetic flux density beneficially alters the HER catalysis exhibited by the 20% Fe₃P SPE_{Raw} where a 56% improvement, compared to the bare SPE, is observed at the maximum flux density (*B*).

The increase in HER activity can be visually observed, *via* being held at a potential of –0.50 (vs. RHE) in the ESI (see Video S1†), using the Fe₃P SPE_{20 h BM}. It is evident that hydrogen bubbles are produced at a faster rate upon the surface of the Fe₃P SPE_{20 h BM}, as the magnetic flux density is increased, when the magnet is brought closer to the electrode surface. A suitable way to demonstrate this increased rate of hydrogen gas output is calculating the hydrogen turnover frequency (ToF) with and without the effect of magnetic field. ToF calculations, shown in the ESI,† for the Fe₃P SPE_{20 h} with and without a magnetic field, exhibit values of 2.72 × 10⁻⁷, 5.61 × 10⁻⁷, 5.67 × 10⁻⁷, 4.17 × 10⁻⁷ and 3.30 × 10⁻⁷ H₂ per s per active site, corresponding to the following values of *B*: 0, 0.29, 0.33, 0.15 and 0.04 T respectively; this suggests that applying a magnetic field enhances the kinetics of the HER.

Commercial PEM electrolysis requires the use of cathodic catalysts that exhibit long-term stability and current retention in acidic conditions. Therefore, chronoamperometry, shown in ESI (Fig. S5†), was carried out using the Fe₃P SPE_{20 h BM} at –0.50 V (vs. RHE) for a duration of 24 h in 0.5 M H₂SO₄, in the presence of a magnetic field (*B* = 0.33 T). It is clear that the Fe₃P SPE_{20 h BM} retains nearly 100% of its current density at 2.98 mA cm⁻² for 24 h, in exception to a drop in current density at 15 h to ca. 2 mA cm⁻² until 20 h, where the current density returns to 2.98 mA cm⁻².

Last, the reason for the increase of 56% and the improvement of the ToF under the application of a weak (constant) magnetic field needs to be surmised. It is important to ascertain whether the observed response (beneficial signal output with regards to a greater achievable HER current density) is due to the application of the magnetic field improving the electron transfer/heterogeneous rate kinetics between the electrode surface and the proton, or other factors. It is likely that the following factors contribute: (1) ferromagnetic materials, such as Fe₃P utilised here, exhibit increased electron transfer efficiency due to higher energy electrons (as a result of the external magnetic field) within the conductive graphitic substrate transferring to the Fe₃P active sites at a faster rate; (2) Fe₃P possesses greatest porosity and larger surface area, after 20 h ball milling, therefore a higher number of distributed Fe–Fe bridge active sites where high energy electrons will have an increased number of electronic pathways to active sites; (3) the application of the magnetic field may also be attributed to the Lorentz force, which induces convection *via* magnetohydrodynamic [MHD] and micro-MHD effects, resulting in diffusion layer thinning and removal of hydrogen gas bubbles from the electrode surface, increasing the availability of active sites on the electrode surface and increasing the ToF. Since hydrogen gas is diamagnetic, the direct effect of the magnetic field is likely to be relatively negligible. Thus, based on the



observations herein, it is likely that the effect of the magnetic field improving the hydrogen evolution reaction is not kinetic/charge transfer in nature but rather that of mass-transport. This is a truly interesting field worthy of further insight.

Conclusions

To summarise, we have demonstrated the proficient activity of Fe₃P SPE's towards the HER in an acidic electrolyte where the Fe₃P material was incorporated into bulk modified SPEs. Ball-milling of the raw Fe₃P powder prior to incorporation into the SPEs was utilised as a means to tune the HER kinetics of the Fe₃P SPEs, by reducing average particle size. An external magnetic field was utilised to further optimise the HER activity exhibited by the ball-milled Fe₃P SPEs, where a weak magnetic flux density resulted in a beneficial increase of 56%. The Fe₃P SPE_{20 h BM} exhibited excellent stability over the course of a 20 h chronoamperometric measurement at -0.50 V (vs. RHE) under a magnetic field (0.33 T), retaining 100% of its current density. The proficient HER activity and long term stability of the ball milled Fe₃P SPEs in acidic conditions, under weak magnetic control, represents the first instance of SPEs utilised within a magnetic field, where applying a weak magnetic field reduces the requirement for costly magnetic components. This work opens up an entire field of unexplored research and demonstrates an advancement in the field of PEM electrolysis, helping transition this work closer to industrial uptake as the Fe₃P bulk modified SPEs can be mass-produced and have scales of economy.

Conflicts of interest

The authors declare no competing financial interest.

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References

- 1 S. E. Hosseini and M. A. Wahid, *Renewable Sustainable Energy Rev.*, 2016, **57**, 850–866.
- 2 I. Dincer and C. Acar, *Int. J. Hydrogen Energy*, 2015, **40**(34), 11094–11111.
- 3 World Nuclear Association, *Heat Values of Various Fuels*, <https://www.world-nuclear.org/information-library/facts-and-figures/heat-values-of-various-fuels.aspx>, accessed 16/01/2020.
- 4 F. Isorna, F. Segura and J. A. Marquez, *Green hydrogen production methods. A review of solar-driven water splitting techniques*, 2018.
- 5 T. R. Ayodele and J. L. Munda, *Int. J. Hydrogen Energy*, 2019, **44**(33), 17669–17687.
- 6 J. P. Hughes, F. D. Blanco, C. E. Banks and S. J. Rowley-Neale, *RSC Adv.*, 2019, **9**(43), 25003–25011.
- 7 P. S. Adarakatti, M. Mahanthappa, J. P. Hughes, S. J. Rowley-Neale, G. C. Smith, S. Ashoka and C. E. Banks, *Int. J. Hydrogen Energy*, 2019, **44**(31), 16069–16078.
- 8 M. Karuppanan, Y. Kim, S. Gok, E. Lee, J. Y. Hwang, J.-H. Jang, Y.-H. Cho, T. Lim, Y.-E. Sung and O. J. Kwon, *Energy Environ. Sci.*, 2019, **12**(9), 2820–2829.
- 9 S. J. Rowley-Neale, D. A. C. Brownson, G. C. Smith, D. A. G. Sawtell, P. Kelly and C. E. Banks, *Nanoscale*, 2015, **7**(43), 18152–18168.
- 10 S. Rowley-Neale, M. Ratova, L. Fugita, G. Smith, A. Gaffar, J. Kulczyk-Malecka, P. Kelly and C. Banks, *ACS Omega*, 2018, **3**(7), 7235–7242.
- 11 S. J. Rowley-Neale, C. W. Foster, G. C. Smith, D. A. C. Brownson and C. E. Banks, *Sustainable Energy Fuels*, 2017, **1**(1), 74–83.
- 12 G. Hu, J. Li, P. Liu, X. Zhu, X. W. Li, R. N. Ali and B. Xiang, *Appl. Surf. Sci.*, 2019, **463**, 275–282.
- 13 J. Hao, W. Yang, Z. Zhang and J. Tang, *Nanoscale*, 2015, **7**(25), 11055–11062.
- 14 B.-W. Ahn, T.-Y. Kim, S.-H. Kim, Y.-I. Song and S.-J. Suh, *Appl. Surf. Sci.*, 2018, **432**, 183–189.
- 15 A. Sumboja, T. An, H. Y. Goh, M. Lübke, D. P. Howard, Y. Xu, A. D. Handoko, Y. Zong and Z. Liu, *ACS Appl. Mater. Interfaces*, 2018, **10**(18), 15673–15680.
- 16 A. R. J. Kucernak and V. N. N. Sundaram, *J. Mater. Chem. A*, 2014, **2**(41), 17435–17445.
- 17 J.-S. Moon, J.-H. Jang, E.-G. Kim, Y.-H. Chung, S. J. Yoo and Y.-K. Lee, *J. Catal.*, 2015, **326**, 92–99.
- 18 B. You, N. Jiang, M. Sheng, M. W. Bhushan and Y. Sun, *ACS Catal.*, 2016, **6**(2), 714–721.
- 19 F. Du, Y. Zhang, H. He, T. Li, G. Wen, Y. Zhou and Z. Zou, *J. Power Sources*, 2019, **431**, 182–188.
- 20 Z. Zhu, Y. Yang, Y. Guan, J. Xue and L. Cui, *J. Mater. Chem. A*, 2016, **4**(40), 15536–15545.
- 21 Y. Li, S. Niu, D. Rakov, Y. Wang, M. Cabán-Acevedo, S. Zheng, B. Song and P. Xu, *Nanoscale*, 2018, **10**(15), 7291–7297.
- 22 F. Wang, X. Yang, B. Dong, X. Yu, H. Xue and L. Feng, *Electrochem. Commun.*, 2018, **92**, 33–38.
- 23 H. Du, S. Gu, R. Liu and C. M. Li, *Int. J. Hydrogen Energy*, 2015, **40**(41), 14272–14278.
- 24 Z. Gao, Q. Gao, Z. Liu, C. Zhang, X. Zhang, X. Liu, R. Wang and N. Li, *RSC Adv.*, 2016, **6**(115), 114430–114435.
- 25 D. E. Schipper, Z. Zhao, H. Thirumalai, A. P. Leitner, S. L. Donaldson, A. Kumar, F. Qin, Z. Wang, L. C. Grabow, J. Bao and K. H. Whitmire, *Chem. Mater.*, 2018, **30**(10), 3588–3598.
- 26 D. E. Schipper, Z. Zhao, H. Thirumalai, A. P. Leitner, S. L. Donaldson, A. Kumar, F. Qin, Z. Wang, L. C. Grabow, J. Bao and K. H. Whitmire, *Chem. Mater.*, 2018, **30**(10), 3588–3598.
- 27 K. Persson, *Materials Data on FeP (SG:62) by Materials Project*, Energy, U. S. D. o., Ed., 2015.



- 28 E. Kha, S. Bhat, S.-C. Lee and S. Bhattacharjee, *Cu-substituted Fe₂P: An emerging candidates for magnetic RAM application*, 2019.
- 29 K. Persson, *Materials Data on Fe₂P (SG:189) by Materials Project*, Energy, U. S. D. o., Ed., 2016.
- 30 J. Wu, X. Y. Chong, R. Zhou, Y. H. Jiang and J. Feng, *RSC Adv.*, 2015, 5(100), 81943–81956.
- 31 K. Persson, *Materials Data on Fe₃P (SG:82) by Materials Project*, Energy, U. S. D. o., Ed., 2016.
- 32 L. Elias and H. A. Chitharanjan, *Electrocatalysis*, 2017, 8(4), 375–382.
- 33 F. A. Garcés-Pineda, M. Blasco-Ahicart, D. Nieto-Castro, N. López and J. R. Galán-Mascarós, *Nat. Energy*, 2019, 4(6), 519–525.
- 34 V. Gatard, J. Deseure and M. Chatenet, *Curr. Opin. Electrochem.*, 2020, 23, 96–105.
- 35 Y. Li, L. Zhang, J. Peng, W. Zhang and K. Peng, *J. Power Sources*, 2019, 433, 226704.
- 36 M. Sheikholeslami and D. D. Ganji in *External Magnetic Field Effects on Hydrothermal Treatment of Nanofluid*, ed. M. Sheikholeslami and D. D. Ganji, William Andrew Publishing, 2016, pp. 1–47.
- 37 N. Leventis and X. Gao, *Anal. Chem.*, 2001, 73(16), 3981–3992.
- 38 M. D. Kuz'min and M. Richter in *Encyclopedia of Materials: Science and Technology*, ed. K. H. J. Buschow, R. W. Cahn, M. C. Flemings, B. Ilshner, E. J. Kramer, S. Mahajan and P. Veysière, Elsevier, Oxford, 2007, pp. 1–7.
- 39 M.-Y. Lin, L.-W. Hourng and C.-W. Kuo, *Int. J. Hydrogen Energy*, 2012, 37(2), 1311–1320.
- 40 Z. Zeng, T. Zhang, Y. Liu, W. Zhang, Z. Yin, Z. Ji and J. Wei, *ChemSusChem*, 2018, 11(3), 580–588.
- 41 E. J. Lisher, C. Wilkinson, T. Ericsson, L. Haggstrom, L. Lundgren and R. Wappling, *J. Phys. C: Solid State Phys.*, 1974, 7(7), 1344–1352.
- 42 H. Shin, S. Lee, H. S. Jung and J.-B. Kim, *Ceram. Int.*, 2013, 39(8), 8963–8968.
- 43 S. J. Rowley-Neale, D. A. C. Brownson, G. C. Smith, D. A. G. Sawtell, P. J. Kelly and C. E. Banks, *Nanoscale*, 2015, 7(43), 18152–18168.
- 44 S. J. Rowley-Neale, G. C. Smith and C. E. Banks, *ACS Appl. Mater. Interfaces*, 2017, 9(27), 22539–22548.
- 45 A. G.-M. Ferrari, C. W. Foster, P. J. Kelly, D. A. C. Brownson and C. E. Banks, *Biosensors*, 2018, 8(2), 53.
- 46 K. Li, C. Zhang, X. Li, Y. Du, P. Yang and M. Zhu, *Catal. Today*, 2018, 335, 173–179.
- 47 C. Wang, W. D. Wu, Y. Wang, D. Xu and F. Yan, *New J. Chem.*, 2017, 41(15), 7392–7399.
- 48 X. Wang, W. Xiao, J. Zhang, Z. Wang and X. Jin, *Electrochem. Commun.*, 2019, 102, 52–56.
- 49 B. Madavali, J.-H. Lee, J. K. Lee, K. Y. Cho, S. Challapalli and S.-J. Hong, *Powder Technol.*, 2014, 256, 251–256.
- 50 E. Lisher, C. Wilkinson, T. Ericsson, L. Haggstrom, L. Lundgren and R. Wappling, *J. Phys. C: Solid State Phys.*, 2001, 7, 1344.
- 51 X. Lai, F. Zhu, Y. Liu, W. Bi, J. Zhao, E. E. Alp, M. Y. Hu, D. Zhang, S. Tkachev, M. H. Manghnani, V. B. Prakapenka and B. Chen, *Earth Planet. Sci. Lett.*, 2020, 531, 115974.
- 52 C. Pirim, M. A. Pasek, D. A. Sokolov, A. N. Sidorov, R. D. Gann and T. M. Orlando, *Geochim. Cosmochim. Acta*, 2014, 140, 259–274.
- 53 Y. Wang, L. Zhang, H. Li, Y. Wang, L. Jiao, H. Yuan, L. Chen, H. Tang and X. Yang, *J. Power Sources*, 2014, 253, 360–365.
- 54 C. Y. Son, I. H. Kwak, Y. R. Lim and J. Park, *Chem. Commun.*, 2016, 52(13), 2819–2822.
- 55 T. Plachy, E. Kutalkova, M. Sedlacik, A. Vesel, M. Masar and I. Kuritka, *J. Ind. Eng. Chem.*, 2018, 66, 362–369.
- 56 F.-X. Ma, C.-Y. Xu, F. Lyu, B. Song, S.-C. Sun, Y. Y. Li, J. Lu and L. Zhen, *Adv. Sci.*, 2019, 6(3), 1801490.
- 57 G. Cho, H. Kim, Y. S. Park, Y.-K. Hong and D.-Y. Ha, *Int. J. Hydrogen Energy*, 2018, 43(24), 11326–11334.
- 58 S. Yao, V. Forstner, P. W. Menezes, C. Panda, S. Mebs, E. M. Zolnhofer, M. E. Miehlich, T. Szilvási, N. A. Kumar, M. Haumann, K. Meyer, H. Grützmacher and M. Driess, *Chem. Sci.*, 2018, 9(45), 8590–8597.
- 59 J. Scremin, I. V. J. d. Santos, J. P. Hughes, A. G.-M. Ferrari, E. Valderrama, W. Zheng, X. Zhong, X. Zhao, E. J. R. Sartori, R. D. Crapnell, S. J. Rowley-Neale and C. E. Banks, *Nanoscale*, 2020, (12), 18214–18224.
- 60 M. Ma, K. Chen, J. Jiang, X. Yang, H. Wang, H. Shao, J. Liu and L. Ouyang, *Inorg. Chem. Front.*, 2020, 7(4), 918–929.
- 61 L.-F. Zhang, X. Ke, G. Ou, H. Wei, L.-N. Wang and H. Wu, *Sci. China Mater.*, 2017, 60(9), 849–856.
- 62 X. Liu, Y. Guo, W. Zhan and T. Jin, *Catalysts*, 2019, 9, 240.
- 63 T. T. Bui, X. Q. Le, D. P. To and V. T. Nguyen, *Adv. Nat. Sci.: Nanosci. Nanotechnol.*, 2013, 4(4), 045003.

