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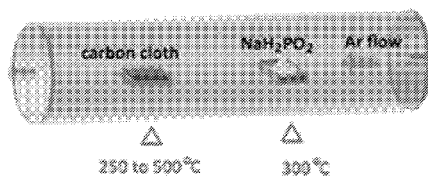


Fig. 2A

(57) Abstract: The present disclosure provides for methods of phosphidation, catalysts formed from phosphidation, and methods of producing H<sub>2</sub>.



## METHODS OF PHOSPHIDATION AND STRUCTURES MADE THEREFROM

### CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to US provisional application serial 62/116,715 entitled "METHODS OF PHOSPHIDATION AND STRUCTURES MADE THEREFROM" filed on February 16, 2015, which is entirely incorporated herein by reference.

### BACKGROUND

Hydrogen is a clean energy carrier for replacing petroleum fuels to relieve issues associated with global warming. Water splitting by electrolyzer is one of the most promising and efficient methods to produce hydrogen on demand. Among many different cathode materials, pure Platinum (110) exhibits the highest efficiency in the hydrogen evolution reaction (HER), where its Tafel slope is as low as ~30 mV/dec. However, the high cost and limited source of Pt retards its large scale applications. Recent research efforts have focused on several more economical materials which may be suitable replacements for Pt cathodes, such as molybdenum sulfide, Mo<sub>2</sub>C, MoB, MoN and metal phosphides. It is recently noted that the HER efficiency of transition metal phosphides of Mo, W, Fe, Co and Ni have shown significant advances. The content for Fe, Ni, Co, Mo and Pt in the Earth's crust is estimated to be 50000, 80, 20, 1.5 and 0.003 ppm respectively. It is apparent that Fe, the fourth most common element in the Earth's crust, is a very attractive material for large-scale catalysis. Hence, the possibility of using iron phosphide as a HER catalyst has been extensively studied. FeP<sub>2</sub> was obtained by the pyrolysis of ferrocene and red phosphorous. Nanoporous FeP nanosheets were prepared by ion-exchange synthesis using Fe<sub>18</sub>S<sub>25</sub> and trioctyl-phosphine as sources. Alternatively, FeP nanoparticles were synthesized by gas phase phosphidation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles at 350 °C. These reports have demonstrated a Tafel slope ranging from 59 to 67 mV/dec. Very recently, dense FeP nanowire array has been achieved by chemical phosphidation of the hydrothermally grown FeOOH nano array, where the Tafel slope of the system has been further lowered to 38 mV/dec.

### SUMMARY

Embodiments of the present disclosure provide methods of phosphidation, a catalyst, methods of producing H<sub>2</sub>, and the like.

An embodiment of the present disclosure includes a method of phosphidation, comprising: electroplating of a metal (M) on a substrate, converting the M to MOOH, M oxide, or a combination, and converting the MOOH and/or M oxide to nanocrystalline metal phosphide (MP). In an embodiment, the metal is selected from the group consisting of: Fe, Co, and Ni. In an embodiment, the metal phosphide is selected from the group consisting of: FeP, CoP, and NiP. In an embodiment, converting the M to MOOH, M oxide, or a combination includes converting M to MOOH and/or M oxide, where M on the substrate can be converted to MOOH or M oxide or where a portion of the M can be converted to MOOH and another portion can be converted into M oxide. In a particular embodiment, the metal phosphide has a rugae-like morphology. In an embodiment, the substrate is a carbon-based substrate. In a particular embodiment, the substrate is a carbon cloth.

An embodiment of the present disclosure includes a catalyst, comprising a nanocrystalline metal phosphide (MP) having a rugae-like morphology. In an embodiment, the nanocrystalline metal phosphide is selected from the group consisting of FeP, CoP, and NiP. In an embodiment, the nanocrystalline metal phosphide is FeP and has a HER performance having a Tafel slope of about 28 to 30, about 29, or about 29.4 mV/dec. In a particular embodiment, the active site density for FeP can be about 10 to 50 or more times higher than that of Pt foil. In an embodiment, the FeP is disposed on a carbon cloth.

An embodiment of the present disclosure includes a method of producing H<sub>2</sub>, comprising exposing H<sub>2</sub>O to a catalyst and producing H<sub>2</sub>.

Other compositions, apparatus, methods, features, and advantages will be or become apparent to one with skill in the art upon examination of the following drawings and detailed description. It is intended that all such additional compositions, apparatus, methods, features and advantages be included within this description, be within the scope of the present disclosure, and be protected by the accompanying claims.

### **BRIEF DESCRIPTION OF THE DRAWINGS**

Figure 1A is an SEM image for the FeOOH formed after oxidation of the electroplated Fe on carbon cloth. In Fig. 1B, the XRD pattern shows the presence of  $\alpha$ - and  $\gamma$ -phase FeOOH as indexed.

Figure 2A is a schematic illustration for the phosphidation process. Fig. 2B shows XRD patterns and SEM images for the FeOOH/carbon cloth samples after phosphidation at varied temperatures.

Figures 3A-D are graphs. Fig. 3a shows the polarization curves for the catalysts prepared at different phosphidation temperatures, where the current is normalized by the geometrical area of carbon cloth and the potential is after internal resistance correction. Fig. 3B are Tafel slopes extracted from the polarization curves in Fig. 1A. Fig. 3C shows double-layer capacitance for the corresponding catalysts prepared at different phosphidation temperatures. Fig. 3D shows time-dependent HER performance for the FeP phosphidated at 300 °C.

Figure 4 is a collection of TEM images for the FeP catalyst phosphidated at 300°C.

Figure 5A illustrates the current–voltage scan for the FeP catalyst formed at 300 °C (Scan procedure: from positive to negative and then positive voltages). The electrochemical processes UPD, OPD, OPD-stripping and UPD-stripping are observed in sequence. Fig. 5B illustrates charges required to strip the Cu deposited at different underpotentials.

Figure 6 is the XRD pattern of the Fe<sub>2</sub>O<sub>3</sub> on carbon cloth obtained after heated at 400 °C in air for 4 h. The red curve is the XRD pattern for the sample after phosphidation at 300 °C for 1 h.

Figure 7A shows the polarization curves for the Fe<sub>2</sub>O<sub>3</sub> on carbon cloth after 300 °C phosphidation. Fig. 7B demonstrates that the Tafel slope for the sample is 42 mV/dec.

Figures 8A-D are cyclic voltammograms (CV) of FeP catalysts prepared at different phosphidation temperatures, where the curves are taken in a potential window without faradaic processes in a 0.5 M H<sub>2</sub>SO<sub>4</sub>.

Figure 9 graphs voltammetric scans. After the UPD of Cu on FeP catalysts at various underpotentials (0.22, 0.24, 0.26, 0.28, 0.30 and 0.32 V), linear voltammetric scans were then performed from the set underpotential to a point at which all of the UPD copper had been oxidized at a scan rate of 5 mV·s<sup>-1</sup>. It is observed that curves for the UPD at 0.22V and 0.24V show an OPD-stripping peak, meaning that some overpotential-deposited Cu is involved. The curve for UPD at 0.26V is used to extract the charge quantity  $Q_{Cu^{2+}}$ .

Figure 10 demonstrates RHE voltage calibration. The calibration was performed in the high purity hydrogen saturated electrolyte with a Pt wire as the working electrode. The current-voltage scans were run at a scan rate of 5 mV·s<sup>-1</sup>, and the average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. Our result shows that the E(Ag/Ag/Cl) is lower than E(RHE) by 0.225V. This value is consistent with the value 0.218V from Nernst equation as described in experimental section.

## DETAILED DESCRIPTION

Before the present disclosure is described in greater detail, it is to be understood that this disclosure is not limited to particular embodiments described, as such may, of course, vary. It is also to be understood that the terminology used herein is for the purpose of describing particular embodiments only, and is not intended to be limiting, since the scope of the present disclosure will be limited only by the appended claims.

Where a range of values is provided, it is understood that each intervening value, to the tenth of the unit of the lower limit (unless the context clearly dictates otherwise), between the upper and lower limit of that range, and any other stated or intervening value in that stated range, is encompassed within the disclosure. The upper and lower limits of these smaller ranges may independently be included in the smaller ranges and are also encompassed within the disclosure, subject to any specifically excluded limit in the stated range. Where the stated range includes one or both of the limits, ranges excluding either or both of those included limits are also included in the disclosure.

Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs. Although any methods and materials similar or equivalent to those described herein can also be used in the practice or testing of the present disclosure, the preferred methods and materials are now described.

As will be apparent to those of skill in the art upon reading this disclosure, each of the individual embodiments described and illustrated herein has discrete components and features which may be readily separated from or combined with the features of any of the other several embodiments without departing from the scope or spirit of the present disclosure. Any recited method can be carried out in the order of events recited or in any other order that is logically possible.

Embodiments of the present disclosure will employ, unless otherwise indicated, techniques of chemistry, catalysis, material science, and the like, which are within the skill of the art. Such techniques are explained fully in the literature.

The following examples are put forth so as to provide those of ordinary skill in the art with a complete disclosure and description of how to perform the methods and use the compositions and compounds disclosed and claimed herein. Efforts have been made to ensure accuracy with respect to numbers (*e. g.*, amounts, temperature, *etc.*), but some errors

and deviations should be accounted for. Unless indicated otherwise, parts are parts by weight, temperature is in °C, and pressure is in bar. Standard temperature and pressure are defined as 0 °C and 1 bar.

Before the embodiments of the present disclosure are described in detail, it is to be understood that, unless otherwise indicated, the present disclosure is not limited to particular materials, reagents, reaction materials, manufacturing processes, or the like, as such can vary. It is also to be understood that the terminology used herein is for purposes of describing particular embodiments only, and is not intended to be limiting. It is also possible in the present disclosure that steps can be executed in different sequence where this is logically possible.

It must be noted that, as used in the specification and the appended claims, the singular forms “a,” “an,” and “the” include plural referents unless the context clearly dictates otherwise. Thus, for example, reference to “a support” includes a plurality of supports. In this specification and in the claims that follow, reference will be made to a number of terms that shall be defined to have the following meanings unless a contrary intention is apparent.

### Definitions

Phosphidation, as used herein, is a process of synthesizing transition metal phosphides (MP) using heat and/or electrochemical techniques and a reagent.

Hydrogen evolution reaction (HER), as used herein, is the process of producing hydrogen ions via water electrolysis.

### General Discussion

Embodiments of the present disclosure provide for methods of phosphidation, catalysts formed from phosphidation, methods of producing H<sub>2</sub>, and the like. Embodiments of the present disclosure may be advantageous since the catalyst formed has a relatively large surface area, has a Tafel slope that of about 28 to 30 mV/dec (*e.g.*, better than that of Pt foil), and the active site density for the FeP described herein can be about 10 to 50 times or more higher than the Pt foil.

In an embodiment, the method of phosphidation includes electroplating of a metal (M) on a substrate. In an embodiment, the metal can include Fe, Co, or Ni. In an embodiment, the substrate can be a carbon-based substrate such as a carbon cloth. The metal can then be converted into MOOH and/or M oxide (either or a mixture can be present),

which can have a rugae-like morphology. Subsequently, the MOOH and/or M oxide is converted into a nanocrystalline metal phosphide (MP), which can have a rugae-like morphology. In an embodiment, the MP can be FeP, CoP, or NiP.

In a particular embodiment, the method of phosphidation includes electroplating of Fe onto a substrate. In an embodiment, the substrate can be a carbon-based substrate such as a carbon cloth. The Fe can then be converted into FeOOH and/or Fe<sub>2</sub>O<sub>3</sub>, which can have a rugae-like morphology. In a particular embodiment, the Fe is converted into FeOOH. Next the FeOOH and/or Fe<sub>2</sub>O<sub>3</sub> can be converted into nanocrystalline FeP, which can have a rugae-like morphology.

In an embodiment, converting can include a vapor phase phosphidation that is carried on in a two-zone chemical vapor deposition (CVD) furnace. A compound such as NaH<sub>2</sub>PO<sub>2</sub>, or a result equivalent alternative, can be evaporated at about 250 to 350 °C or about 300 °C and brought to the FeOOH and/or Fe<sub>2</sub>O<sub>3</sub> at the downstream site, which can be set at a desired reaction temperature (*e.g.*, about 250-300° C).

In a specific embodiment, iron phosphide can be synthesized by vapor phase phosphidation of the FeOOH obtained by electroplating. The rugae-like morphology formed during the electroplating provides a large surface area. The subsequent phosphidation at about 300 °C converts the FeOOH to nanocrystalline FeP while maintaining the rugae morphology. The Tafel slope reaches about 28 to 30, about 29, or about 29.4 mV/dec, which is better than that of Pt foil. The active site density for our FeP can be about 10 to 50 times or 50 times higher than the Pt foil, suggesting that the high HER performance for FeP is strongly related to its large number of active sites. Although not intending to be bound by theory, it is believed that the nanocrystalline structure and the rugae-like surface contribute to its high HER performance. Additional details are provided in Example 1.

In an embodiment, the catalyst can include a nanocrystalline metal phosphide (MP) having a rugae-like morphology. In an embodiment, the substrate can be a carbon-based substrate such as a carbon cloth. In an embodiment, the MP can be FeP, CoP, or NiP. In an embodiment, the MP is FeP, where FeP has a HER performance having a Tafel slope of about 29.4 mV/dec and has an active site density for FeP is 50 times higher than the Pt foil. Additional details and embodiments are provided in the following Example.

An embodiment of the present disclosure provides for a method of producing H<sub>2</sub>. In general, the method includes exposing H<sub>2</sub>O to a catalyst such as those described herein, which can produce H<sub>2</sub>.

## **EXAMPLES**

Now having described the embodiments of the disclosure, in general, the examples describe some additional embodiments. While embodiments of the present disclosure are described in connection with the example and the corresponding text and figures, there is no intent to limit embodiments of the disclosure to these descriptions. On the contrary, the intent is to cover all alternatives, modifications, and equivalents included within the spirit and scope of embodiments of the present disclosure.

### **Example 1**

In this Example, we perform the electroplating of Fe on carbon cloth and convert it to FeOOH or Fe<sub>2</sub>O<sub>3</sub> at various oxidation temperatures. Systematic gas phase phosphidation reveals that nanocrystalline FeP, rather than highly crystalline FeP and FeP<sub>2</sub>, leads to the best HER performance (Tafel slope = 29.4 mV/dec), which is comparable to that of Pt at low overpotential. The required overpotential to reach 10 mA/cm<sup>2</sup> is 39 mV, even lower than 46 mV of our best Pt foil. The Tafel slope we obtained is also the lowest among the reported for metal phosphides.

The electroplating of Fe on carbon cloth is performed in a 0.1M FeSO<sub>4</sub> solution and the subsequent oxidation in air forms a uniform coating on the fibrous structure as shown in the scanning electron microscopy (SEM) images (Figure 1A). The magnified SEM image reveals the rugae-like structure, which is beneficial for catalytic reaction owing to its high surface area. Figure 1B displays the X-ray diffraction (XRD) pattern, which is well indexed to the polycrystalline  $\alpha$ - and  $\gamma$ -FeOOH. The vapor phase phosphidation is carried on in a two-zone chemical vapor deposition (CVD) furnace, where the NaH<sub>2</sub>PO<sub>2</sub> is evaporized at 300 °C and brought to the rugae-like FeOOH at the downstream site which can be set at a desired reaction temperature such as 250, 300, 400, and 500 °C.

Figure 2A schematically illustrates the set-up for the gas phase phosphidation. We observe that the rugae-like FeOOH structures can be easily phosphidated with the vapor phase reaction at the temperature >250 °C. The XRD results in Figure 2B show that the orthorhombic FeP crystals form after phosphidation at 400°C and some FeP<sub>2</sub> also appears after 500 °C phosphidation. All peaks are well indexed to orthorhombic FeP or FeP<sub>2</sub>.<sup>[7g]</sup> When the phosphidation temperature is at 300 °C or lower, the diffraction peaks are relatively broader, suggesting that the resulted crystals are small in size. The SEM photos in inset of Figure 2B



show the surface morphology of the sample phosphidated at each temperature, where the rugae-like morphology still sustains after phosphodiation at 250 or 300 °C. A higher temperature such as 400 and 500 °C wrecks the rugae-like structures.

It is noted that the gas phase phosphidation of FeOOH is more efficient than Fe<sub>2</sub>O<sub>3</sub>. We have separately converted the electroplated Fe to Fe<sub>2</sub>O<sub>3</sub> by heating the sample to 400 °C in air for 4 h. The subsequent phosphidation at 300 °C cannot efficiently convert Fe<sub>2</sub>O<sub>3</sub> to FeP. The XRD result in supporting Figure 6 demonstrates that Fe<sub>2</sub>O<sub>3</sub> structure still remains and only part of the Fe<sub>2</sub>O<sub>3</sub> is converted to Fe<sub>3</sub>O<sub>4</sub> and FeP. The HER performance for the obtained catalyst is rather poor (Tafel slope is 42 mV/dec; Supporting Figures 7A-B) and thus we will focus our discussions on the catalysts prepared from FeOOH only.

Figure 3A shows the polarization curves (measured current normalized by the geometrical area of the sample) for the catalysts prepared at different phosphidation temperatures. Note that the potential (V) used here is already after internal resistance compensation. Meanwhile, it is worthy that the RHE calibration is crucially important to ensure that the overpotential is correct (see experimental section for details). We observe that the HER current decreases with the increasing phosphidation temperature from 300 to 500 °C, indicating that the highly crystalline FeP or FeP<sub>2</sub> is not necessarily better for HER. The Pt foil we used exhibits consistently good performance (overpotential of -46 mV, -55 mV and -78 mV vs. RHE at -10 mA/cm<sup>2</sup>, -20 mA/cm<sup>2</sup> and -100 mA/cm<sup>2</sup> respectively). Interestingly, the corresponding overpotential for the catalyst phosphidated at 300 °C is -39 mV, -49 mV and -80 mV. The result is surprising since it is already superior to the performance of Pt at a low overpotential, a proper regime used to evaluate the intrinsic property of the HER catalysts. Nevertheless, the performance of Pt becomes better than FeP when the overpotential is larger than 75 mV. It is suspected that the transport of ionic species on ion phosphides may be limited, which requires further study. Figure 3B shows that the Tafel slope for the sample prepared at 400 °C (FeP) and 500 °C (FeP + FeP<sub>2</sub>) is 39.0 and 51.4 mV/dec respectively. Surprisingly, the Tafel slope for the samples phosphidated at 300 °C is around 29.4 mV/dec, which is comparable to that of Pt. Supporting Table S1 compiles the HER characteristics for the metal phosphides from existing reports, where our catalyst seems to possess superior performance. We perform the scanning rate measurement for these samples to extract their capacitance of the double layer at the solid-liquid interface (see supporting Figures 8A-D for details). Figure 3C summarizes the obtained capacitance, from which we conclude that a lower Tafel slope correlates to a higher capacitance. This implies

that the HER efficiency variation is related to the difference in capacitance. Note that the capacitance is a rather nice gauge for the interfacial area between the surface of the electrode and an electrolyte. In other words, the effective surface area of the catalysts based on highly crystalline FeP or FeP<sub>2</sub> is lower than the samples phosphidated at 300 °C. The capacitance results are also in line with the SEM observation as shown in Figure 2B. In addition to the high HER efficiency, the catalyst also presents excellent stability in acidic solutions as shown in the time dependent measurement (Figure 3D). The transmission electron microscopy (TEM) images in Figure 4 demonstrate that the sample phosphidated at 300 °C consists of rich FeP nanocrystallites with irregular shapes, where the crystallites are only few nanometer in lateral size. Electron diffraction (ED) tells that these crystallites are randomly oriented. It is likely that the high surface area from rugae-like morphology together with the large number of nanocrystallites contribute to the high performance HER.

The underpotential deposition (UPD) of copper has been used to extract the density of active sites for Pt<sup>[9]</sup> and WS<sub>2</sub>,<sup>[10]</sup> where they observe that the coverage and surface density of the copper is the same as that for adsorbed hydrogen on the HER catalyst surface. Hence, the surface activity of HER catalysts can be determined by measuring the charges exchanged during the stripping of the copper deposited at the underpotential regions. The optimal condition for measuring active sites of our FeP is in a solution with 0.5 M H<sub>2</sub>SO<sub>4</sub> and 20 mM CuSO<sub>4</sub>. Figure 5a displays the current–voltage scan for FeP formed at 300 °C, where the regions for UPD, overpotential deposition (OPD) and their stripping are clearly observed. Figure 5B shows the charges required to strip the Cu (Q<sub>Cu2+</sub>) deposited at different underpotentials. We find that the Q<sub>Cu2+</sub> for the UPD at 0.22 and 0.24 V has already involved OPD of Cu (see Figure 9 for details). The Q<sub>Cu2+</sub> plateau in between UPD 0.26V and 0.32V allows us to extract the active sites number. The Q<sub>Cu2+</sub> at UPD 0.26 V is 0.1328 C, meaning that 6.68x10<sup>-7</sup> mol of Cu (0.1328/96500/2) has been deposited. Since the electrode area of our FeP is 1 cm<sup>2</sup>, the active site density is estimated as 6.68x10<sup>-7</sup> mol/cm<sup>2</sup> = 4.14 x 10<sup>17</sup> sites/cm<sup>2</sup>. Note that the active site density for the Pt foil estimated using the same method is 7.9 x 10<sup>15</sup> sites/cm<sup>2</sup>, which is in the same order of magnitude as the number 1.5 x 10<sup>15</sup> sites/cm<sup>2</sup> reported elsewhere.<sup>[10]</sup>

In summary, iron phosphide was synthesized by vapor phase phosphidation of the FeOOH obtained by electroplating. The rugae-like morphology formed during the electroplating provides a large surface area. The subsequent phosphidation at 300 °C converts the FeOOH to nanocrystalline FeP while maintaining the rugae morphology. The Tafel slop

reaches 29.4 mV/dec, better than that of Pt foil. The active site density for our FeP is 50 times higher than the Pt foil, suggesting that the high HER performance for FeP is strongly related to its large number of active sites. We believe the nanocrystalline structure and the rugae-like surface contribute to its high HER performance.

### Experimental Section

**Materials:** All chemical reagents used in this experiment were of analytical grade. Ferrous sulfate heptahydrate ( $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ ), sodium hypophosphite ( $\text{NaH}_2\text{PO}_2$ ), sodium hydroxide ( $\text{NaOH}$ ), nitric acid ( $\text{HNO}_3$ ), sulfuric acid ( $\text{H}_2\text{SO}_4$ ) and ethanol were used as received without further purification. The water used throughout all experiments was purified through a Millipore system.

**Synthesis of FeOOH on carbon cloth:** The carbon cloth (CC, 1 cm  $\times$  2.5 cm) was repeatedly washed using deionized water and ethanol to remove impurities and maintain the wettability of the CC. The CC was then quickly inserted into 0.1 M  $\text{FeSO}_4$  (immersed geometric area 1 cm<sup>2</sup>) as a working electrode. The 0.1 M  $\text{FeSO}_4$  was prepared by dissolving 1.112 g (4 mmol)  $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$  in 40 mL Milli-Q water at room temperature ( $\sim 23$  °C). Pt foil and Ag/AgCl (in 3 M KCl solution) electrode were used as the counter and reference electrodes, respectively. Constant current electroplating was conducted at  $-10 \text{ mA} \cdot \text{cm}^{-2}$  in a PGSTAT 302N Autolab workstation. Freshly prepared samples were then exposed to air for overnight.

**Preparation of FeP on carbon cloth:** In a typical experiment, the  $\text{NaH}_2\text{PO}_2$  in a porcelain boat was put in the upstream side and FeOOH/CC in another boat was placed at the downstream side in a furnace. First, the acquired samples were heated to different temperatures with a heating speed of 2 °C/min in an Ar flowing atmosphere (60 sccm). Subsequently, the  $\text{NaH}_2\text{PO}_2$  was quickly heated to the temperature of 260 °C in 10 min, and then slowly raised to 300 °C with a heating speed of 1 °C/min to transport the generated  $\text{PH}_3$  to the substrate. After the reaction, the samples were immersed into 0.5 M  $\text{H}_2\text{SO}_4$  and Milli-Q water for 20 min respectively to dissolve the impurities. After dried in vacuum oven, the loading of FeP on CC was determined to be  $4.9 \text{ mg} \cdot \text{cm}^{-2}$  using a high precision microbalance.

**Electrochemical Measurements:** The electrochemical measurements were performed in a PGSTAT 302N Autolab Potentiostat/Galvanostat (Metrohm) at room temperature. Graphite rod and Ag/AgCl (in 3 M KCl solution) electrode were used as counter and reference electrodes, respectively. The reference electrode was calibrated for the reversible hydrogen potential in the electrolyte solution purged with Ar for 30 min prior to

measurements. In a 0.5 M H<sub>2</sub>SO<sub>4</sub> solution,  $E$  (RHE) =  $E$  (Ag/AgCl) + 0.197 + 0.059 pH. The pH value for our solution is 0.35 and hence the equation becomes  $E$  (RHE) =  $E$  (Ag/AgCl) + 0.218. The validity of the Nernst equation used in our study has been verified by our separate RHE calibration. The calibration was done in a high purity hydrogen saturated electrolyte with a Pt wire as the working electrode (see Supporting Figure 10 for details), where the measurement (0.225 V offset) agrees well with the value 0.218V mentioned above.

The electrocatalytic activity of FeP towards HER was examined by obtaining polarization curves using linear sweep voltammetry (LSV) at a scan rate of 0.5 mV · s<sup>-1</sup> in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. The time dependent current density of the FeP was tested in 0.5 M H<sub>2</sub>SO<sub>4</sub> at an overpotential of 85 mV (vs. RHE). All data have been corrected for a small ohmic drop (~1.7 Ω) based on impedance spectroscopy.

**Estimation of Active Site Density:** All copper UPD experiments were carried out in a 0.5 M H<sub>2</sub>SO<sub>4</sub> and 20 mM CuSO<sub>4</sub> solution. After electrochemical cleaning in a H<sub>2</sub>SO<sub>4</sub> solution, the FeP electrode was transferred into solution containing dissolved cupric ions and then polarized at various underpotentials (from 0.22 V to 0.32 V) for 120 s. A linear voltammetric scan was then performed from the set underpotential to a point at which all of the UPD copper had been oxidized at a scan rate of 5 mV · s<sup>-1</sup>. Charges obtained for copper stripping were corrected by subtracting the charge obtained for the same electrode under the same conditions in the absence of any cupric ions in solution (i.e. 0.5 M H<sub>2</sub>SO<sub>4</sub>).

**Characterization:** The morphologies of the catalysts were determined by field-emission scanning electron microscope (FESEM, FEI Quanta 600) and transmission electron microscopy (FEI Titan ST, operated at 300 KV). The crystalline structure of the samples was analyzed by X-ray diffraction (XRD, Bruker D8 Discover diffractometer, using Cu Kα radiation, λ = 1.540598 Å).

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### Supporting Materials for Example 1

**Table S1.** Summary of HER performance for Iron-based catalysts published recently. It is noted that particular attention should be paid when comparing the overpotential ( $\eta_{10}$  and  $\eta_{20}$ ) and exchange current density since they are strongly affected by the potential calibration for reference electrodes. The Ag/AgCl reference electrodes are used in reference [5] and [10], where the potential calibration equation is  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.197 + 0.059\text{pH}$ . For example, the pH value for a 0.5 M  $\text{H}_2\text{SO}_4$  solution is around 0.35; hence the calibration equation becomes  $E(\text{RHE}) = E(\text{Ag/AgCl}) + 0.218$ . If a saturated calomel electrode (SCE) electrode is used the potential calibration is  $E(\text{RHE}) = E(\text{SCE}) + 0.241 + 0.059\text{pH} = E(\text{SCE}) + 0.262$  (for  $\text{pH} = 0.35$ ), which is used in references [7] and [14]. However, in references [2] [3] [4] and [13] the potential calibration was taken as  $E(\text{RHE}) = E(\text{SCE}) + 0.281$ , meaning that the values of  $\eta_{10}$  and  $\eta_{20}$  in these references are further lowered by 19 mV and the exchange current density value is expected to be higher due to the calibration.

Catalyst	substrate	Catalyst loading (mg/cm <sup>2</sup> )	$\eta_{10}$ (mV)	$\eta_{20}$ (mV)	Tafel slope (mV/dec)	$J_0$ (mA/cm <sup>2</sup> )	Electrolyte Conc. (H <sub>2</sub> SO <sub>4</sub> )
<b>FeP</b> <sup>(this work)</sup>	Carbon cloth	4.9	39	49	29.4	0.47	0.5 M
<b>FeP</b> <sup>[1]</sup>	Ti foil	1	50	61	37	0.43	0.5 M
<b>FeP</b> <sup>[2]</sup>	Ti foil	0.6	85		60		0.5 M
<b>FeP</b> <sup>[3]</sup>	carbon cloth	4.2		54	32	0.59	0.5 M
<b>FeP</b> <sup>[4]</sup>	Ti foil	3.2	55	72	38	0.42	0.5 M
<b>FeP<sub>2</sub></b> <sup>[5]</sup>	GCE	0.425			66	1.75×10 <sup>-3</sup>	0.5 M
<b>porous FeP</b> <sup>[6]</sup>	GCE	0.28	-80	~110	67		0.5 M
<b>FeP/Graphene</b> <sup>[7]</sup>	GCE	0.28	123		50	0.12	0.5 M
<b>Fe<sub>2</sub>P/N-graphene</b> <sup>[8]</sup>	GCE	1.71	138	164	67	9.2×10 <sup>-2</sup>	0.5 M
<b>Ni<sub>2</sub>P</b> <sup>[9]</sup>	Ti foil	1	117	130	46	3.3×10 <sup>-3</sup>	0.5 M
<b>Ni<sub>2</sub>P</b> <sup>[10]</sup>	GCE	0.38		140	87		1.0 M
<b>CoP</b> <sup>[11]</sup>	Ti foil	2		85	50		0.5 M
<b>Ni<sub>12</sub>P<sub>5</sub></b> <sup>[12]</sup>	Ti foil	3	107	141	63		0.5 M
<b>CoP/CNT</b> <sup>[13]</sup>	GCE	0.285	122		54	0.13	0.5 M
<b>CoP</b> <sup>[14]</sup>	Carbon cloth	0.92	67	100	51		0.5 M

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It should be noted that ratios, concentrations, amounts, and other numerical data may be expressed herein in a range format. It is to be understood that such a range format is used for convenience and brevity, and thus, should be interpreted in a flexible manner to include not only the numerical values explicitly recited as the limits of the range, but also to include all the individual numerical values or sub-ranges encompassed within that range as if each numerical value and sub-range is explicitly recited. To illustrate, a concentration range of “about 0.1% to about 5%” should be interpreted to include not only the explicitly recited concentration of about 0.1 wt% to about 5 wt%, but also include individual concentrations (e.g., 1%, 2%, 3%, and 4%) and the sub-ranges (e.g., 0.5%, 1.1%, 2.2%, 3.3%, and 4.4%) within the indicated range. In an embodiment, the term “about” can include traditional rounding according to significant figures of the numerical value. In addition, the phrase “about ‘x’ to ‘y’” includes “about ‘x’ to about ‘y’”.

It should be emphasized that the above-described embodiments of the present disclosure are merely possible examples of implementations, and are set forth only for a clear understanding of the principles of the disclosure. Many variations and modifications may be made to the above-described embodiments of the disclosure without departing substantially from the spirit and principles of the disclosure. All such modifications and variations are intended to be included herein within the scope of this disclosure.



## CLAIMS

We claim at least the following:

1. A method of phosphidation, comprising:  
electroplating of a metal (M) on a substrate,  
converting the M to MOOH, M oxide, or a combination thereof, and  
converting the MOOH, M oxide, or both to nanocrystalline metal phosphide (MP).
2. The method of claim 1, wherein M is selected from the group consisting of: Fe, Co, and Ni.
3. The method of claim 1, wherein MP is selected from the group consisting of: FeP, CoP, and NiP.
4. The method of claim 1, 2, or 3, wherein the MP has a rugae-like morphology.
5. The method of claim 1, 2, 3, or 4, wherein the substrate is a carbon-based substrate.
6. The method of claim 1, 2, 3, or 4, wherein the substrate is a carbon cloth.
7. A method of phosphidation, comprising:  
electroplating of Fe on a substrate,  
converting the Fe to FeOOH, Fe<sub>2</sub>O<sub>3</sub>, or a combination thereof, and  
converting the FeOOH, Fe<sub>2</sub>O<sub>3</sub>, or both to nanocrystalline FeP.
8. The method of claim 7, wherein the FeP has a rugae-like morphology.
9. The method of claim 7, wherein converting includes converting Fe to FeOOH.
10. The method of claim 7 or 9, wherein converting includes a vapor phase phosphidation carried out in a two-zone chemical vapor deposition (CVD) furnace, where NaH<sub>2</sub>PO<sub>2</sub> is evaporated at about 300 °C and brought to the FeOOH at the downstream site.

11. The method of claim 10, wherein the reaction temperature is about 250 to 300° C.
12. The method of claim 7, wherein the substrate is a carbon cloth.
13. A catalyst, comprising: a nanocrystalline metal phosphide (MP) having a rugae-like morphology.
14. The catalyst of claim 13, wherein MP is selected from the group consisting of: FeP, CoP, and NiP.
15. The catalyst of claim 14, wherein the MP is FeP, wherein FeP has a HER performance having a Tafel slope of about 29mV/dec.
16. The catalyst of claim 14, wherein an active site density for FeP is about 10 to 50 times higher than that of Pt foil.
17. The catalyst of claim 14, wherein the FeP is disposed on a carbon cloth.
18. A method of producing H<sub>2</sub>, comprising:  
exposing H<sub>2</sub>O to a catalyst, wherein the catalyst is a nanocrystalline metal phosphide (MP) having a rugae-like morphology, and  
producing H<sub>2</sub>.
19. The method of claim 18, wherein MP is selected from the group consisting of: FeP, CoP, and NiP.
20. The method of claim 19, wherein the FeP is disposed on a carbon cloth.

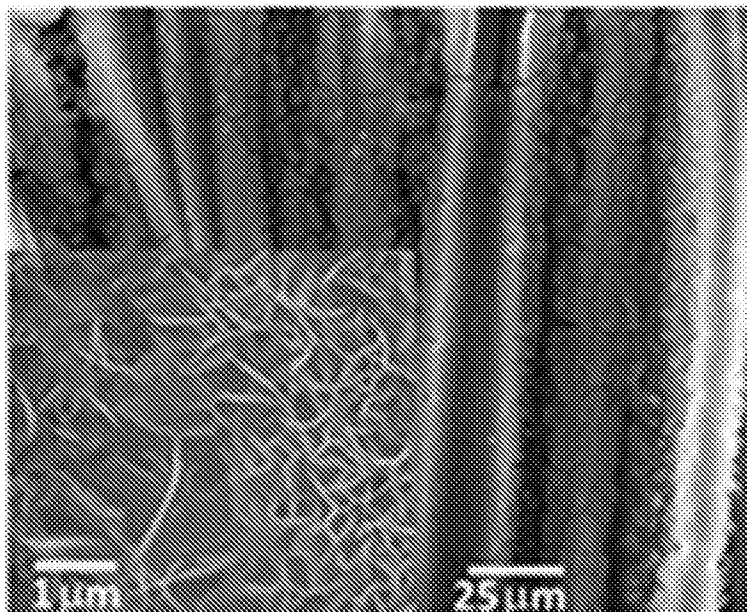


Fig. 1A

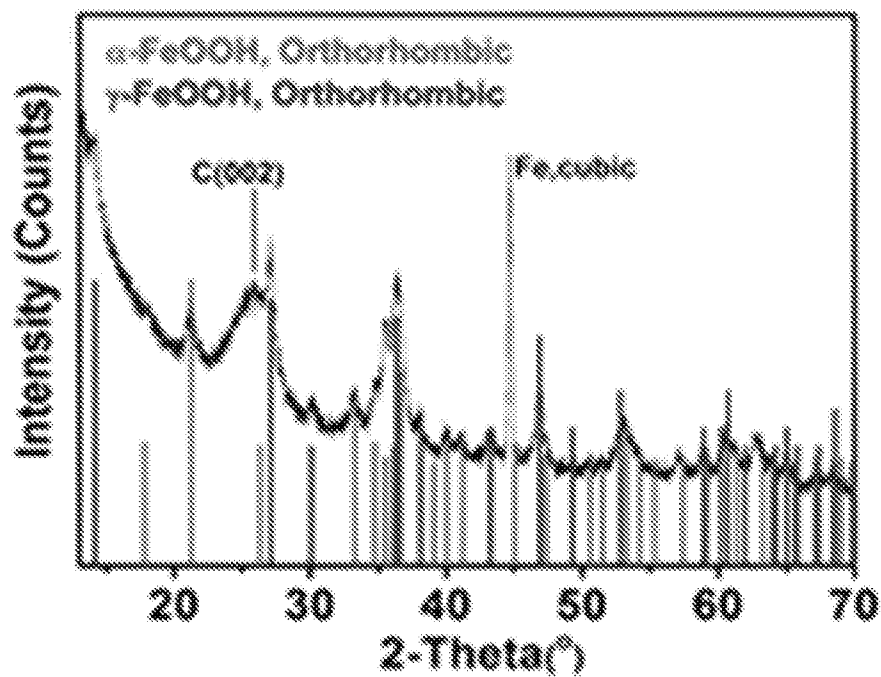


Fig. 1B

Fig. 2A

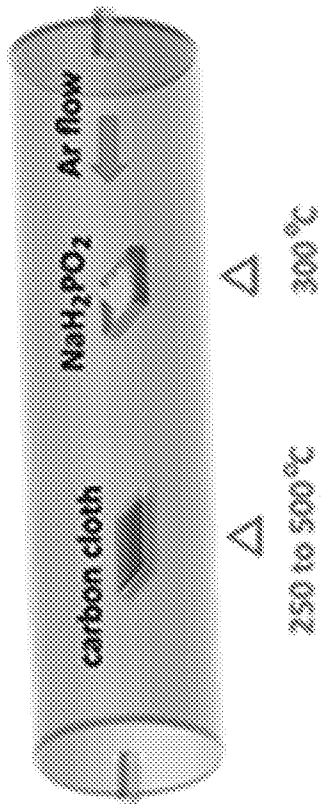
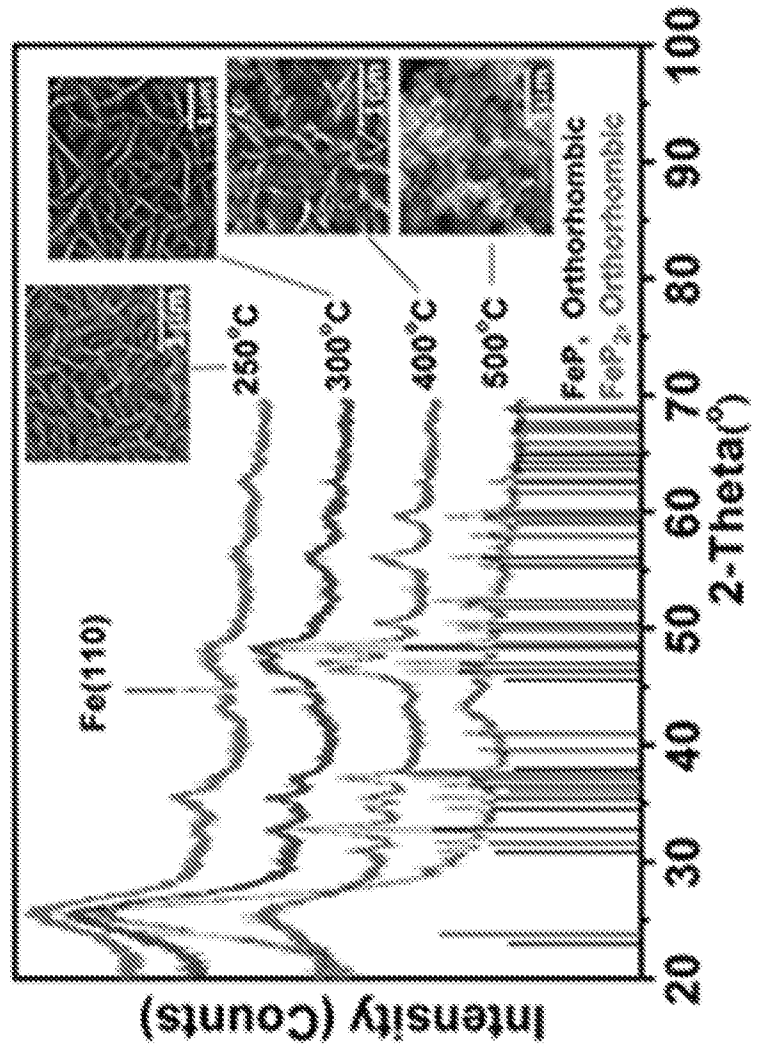


Fig. 2B



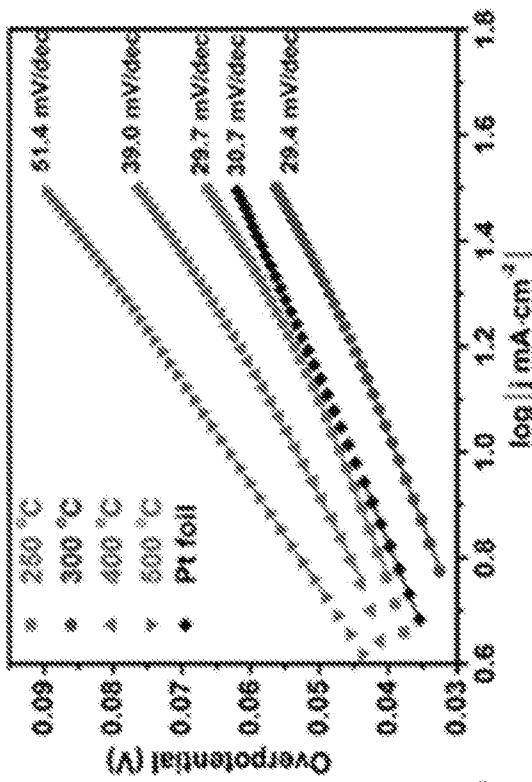


Fig. 3B

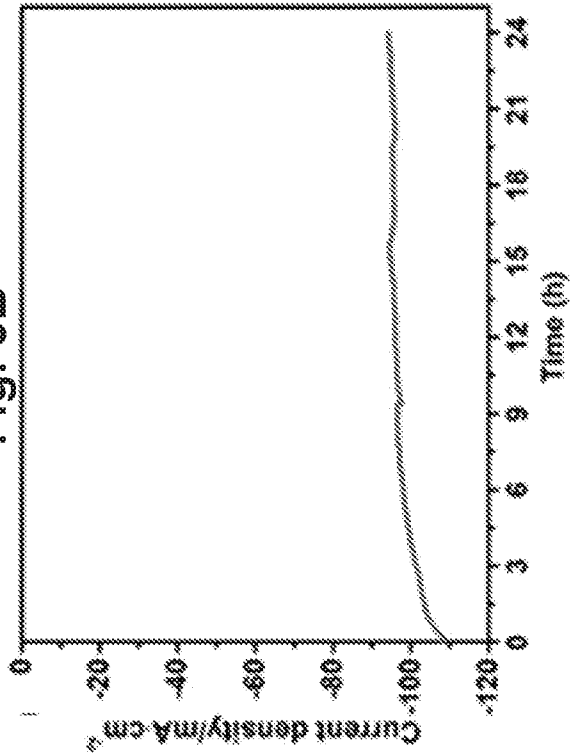


Fig. 3D

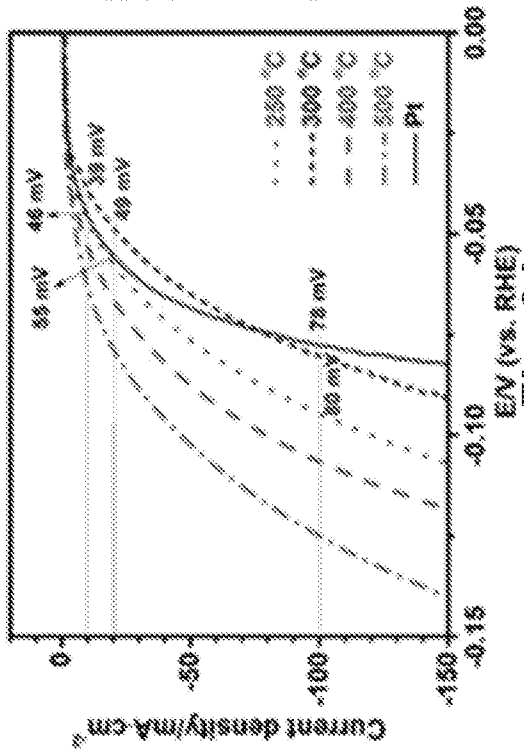


Fig. 3A

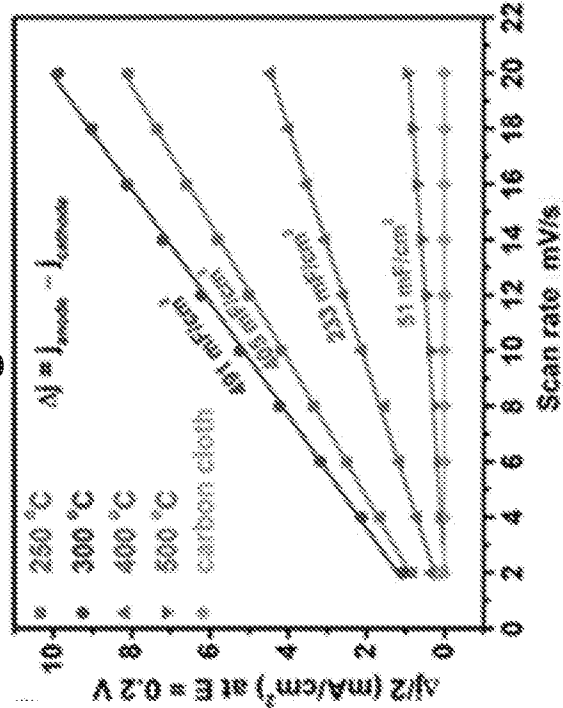


Fig. 3C

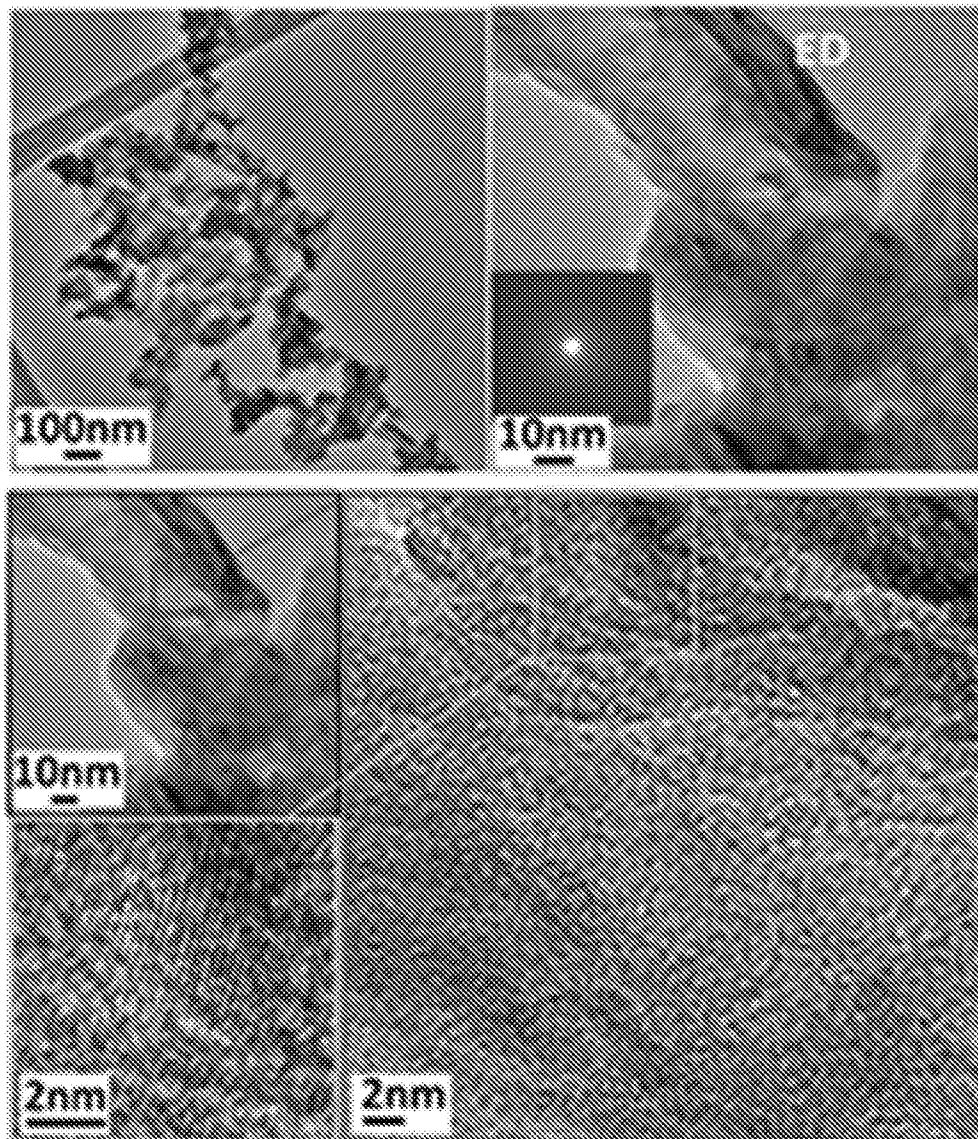


Fig. 4

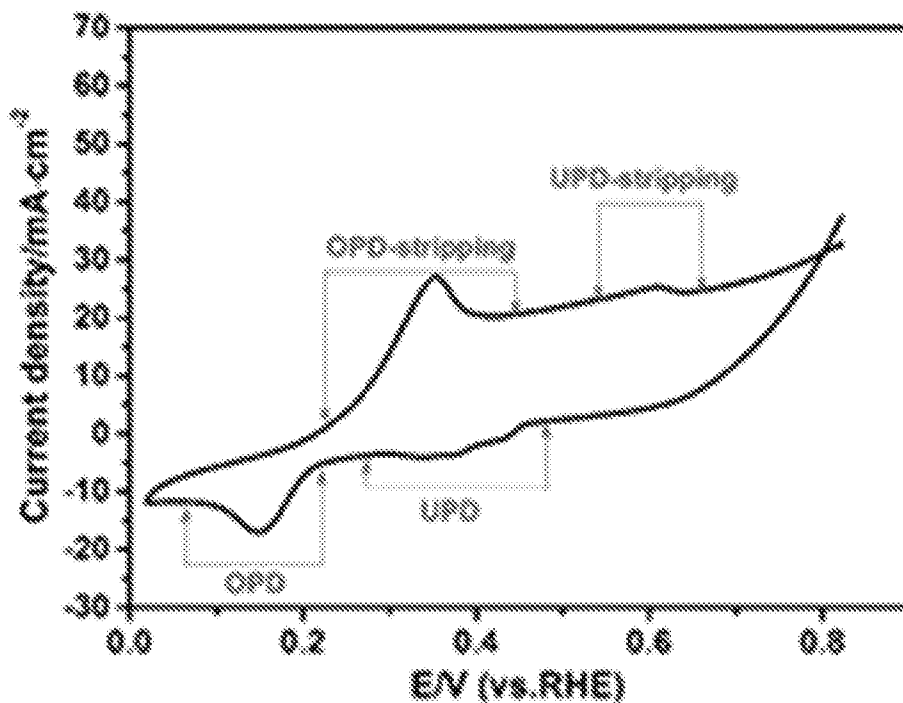


Fig. 5A

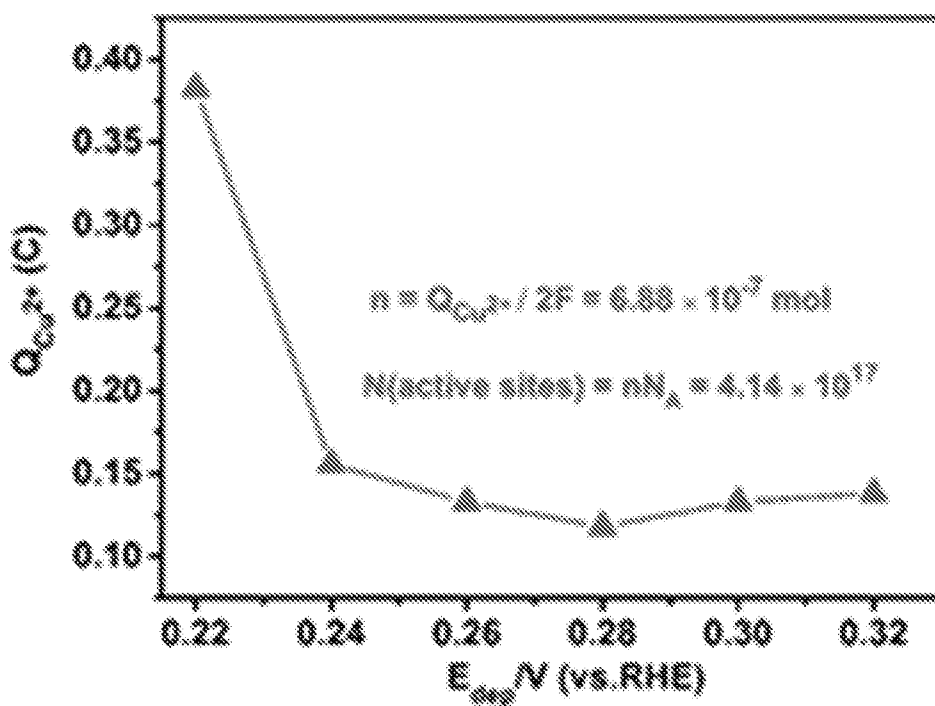


Fig. 5B

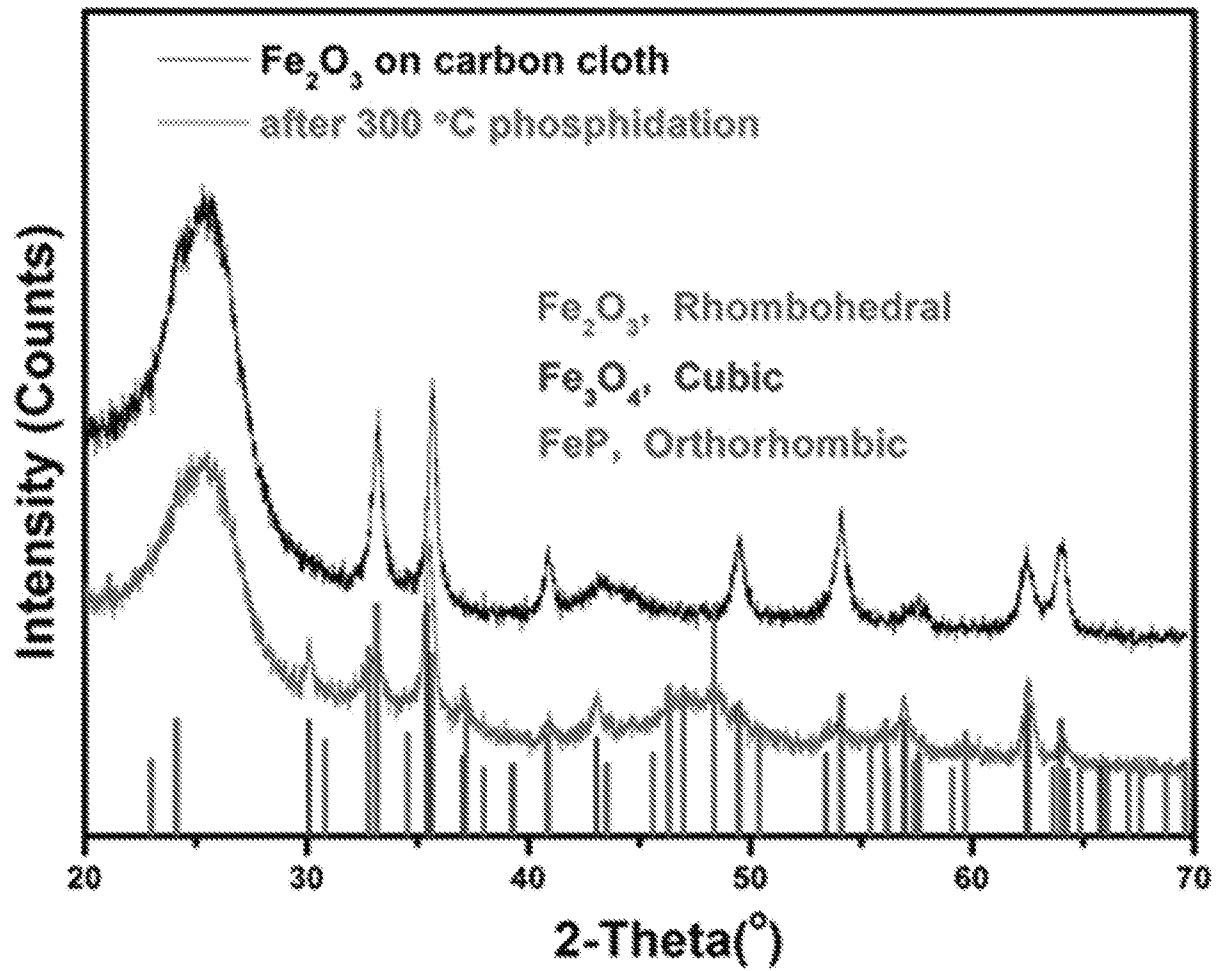


Fig. 6



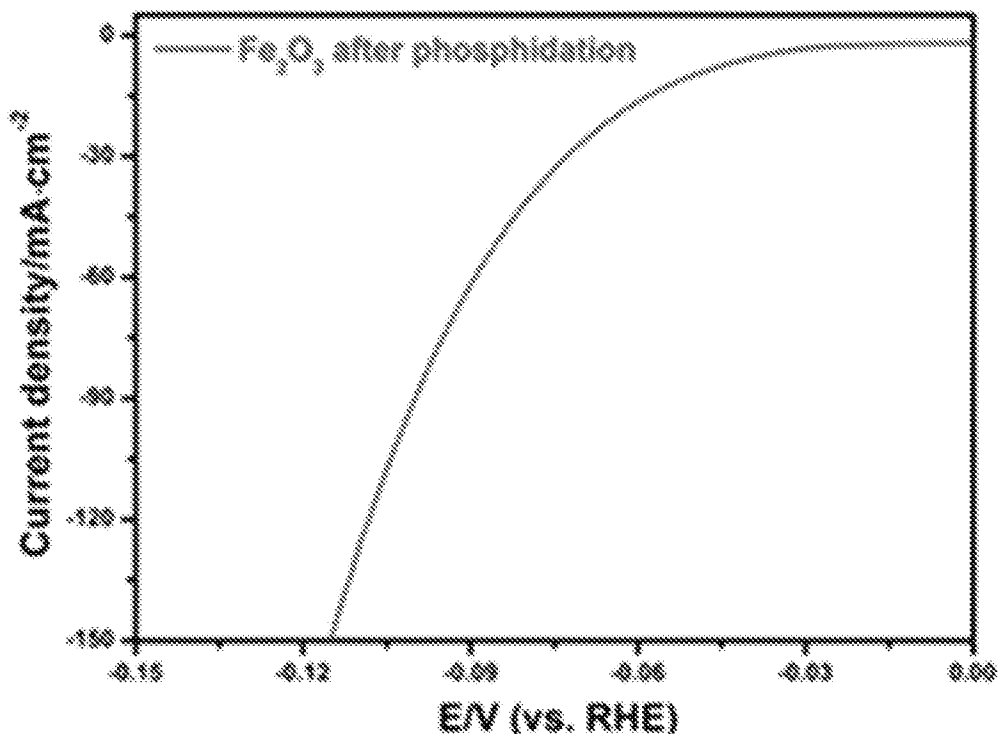


Fig. 7A

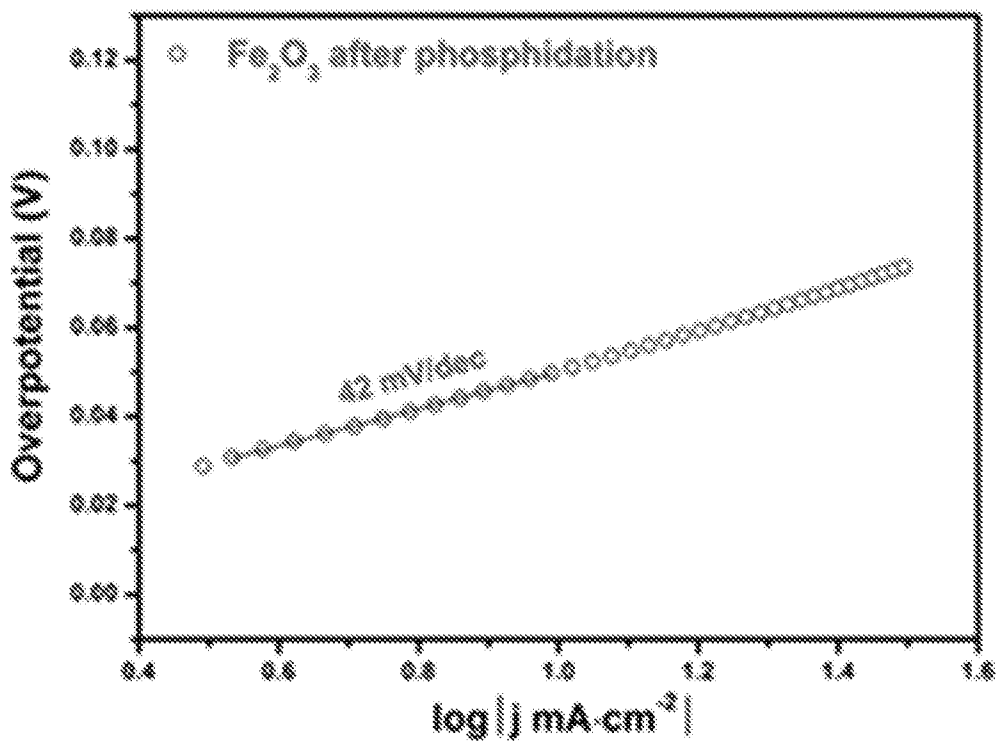


Fig. 7B

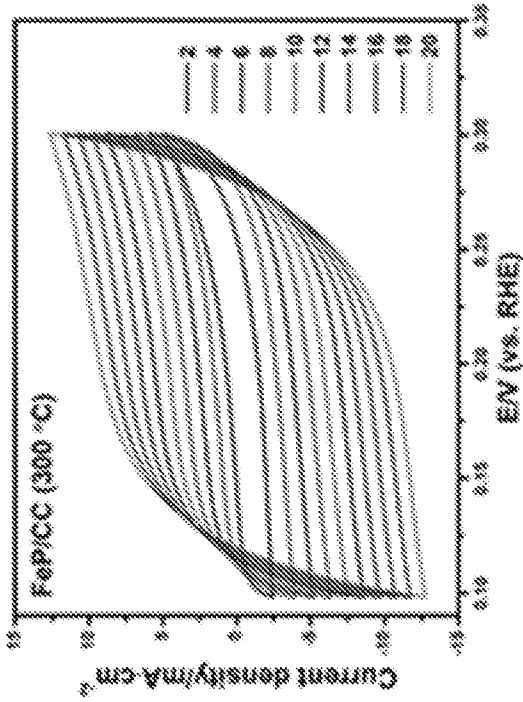


Fig. 8B

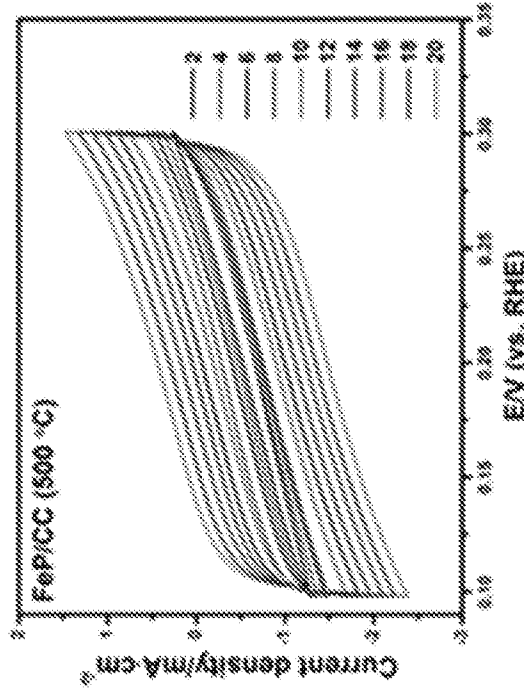


Fig. 8D

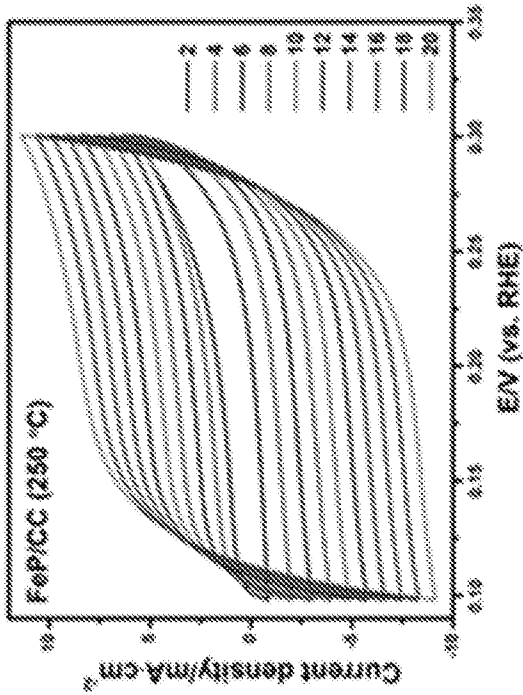


Fig. 8A

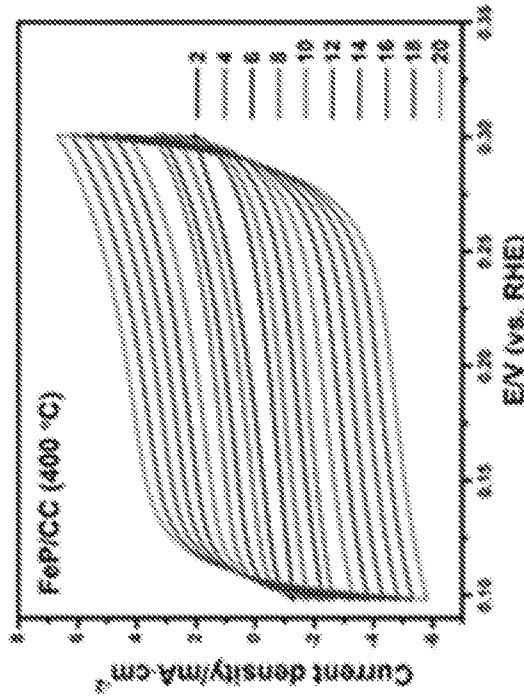


Fig. 8C

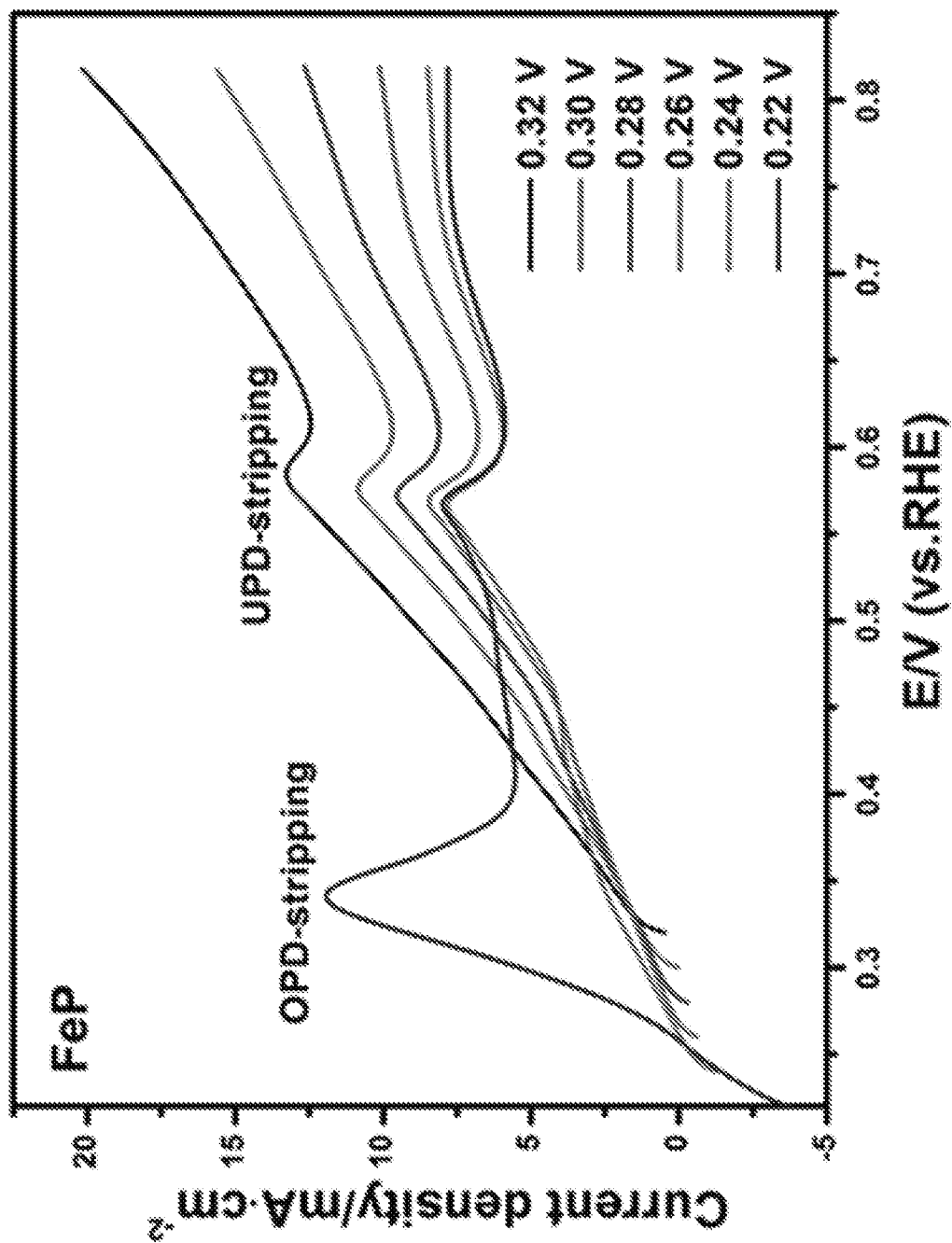


Fig. 9

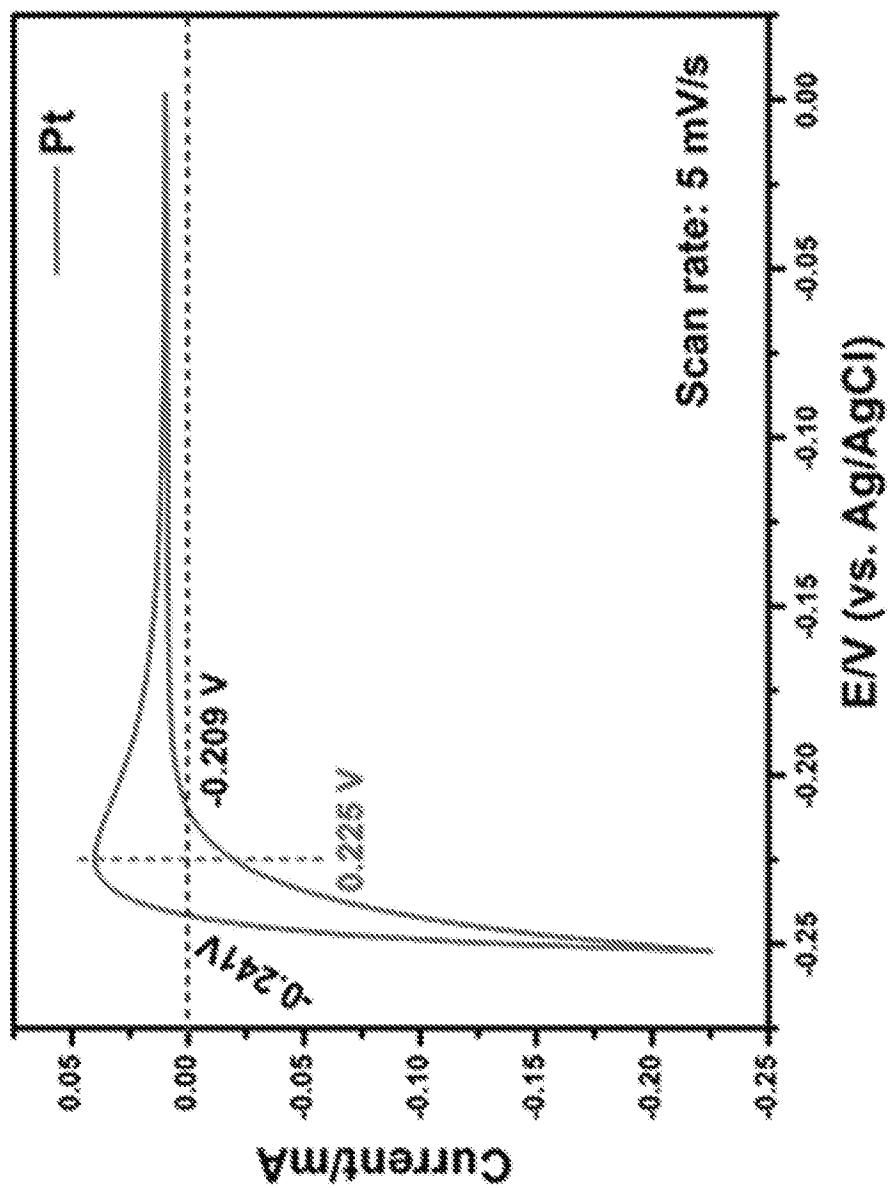


Fig. 10

**INTERNATIONAL SEARCH REPORT**

International application No PCT/IB2016/050767
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<b>A. CLASSIFICATION OF SUBJECT MATTER</b> INV. C25D5/48 C25D5/54 ADD. C25D3/20		
According to International Patent Classification (IPC) or to both national classification and IPC		
<b>B. FIELDS SEARCHED</b> Minimum documentation searched (classification system followed by classification symbols) C25D		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) EPO-Internal, WPI Data		
<b>C. DOCUMENTS CONSIDERED TO BE RELEVANT</b>		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	PING JIANG ET AL: "A Cost-Effective 3D Hydrogen Evolution Cathode with High Catalytic Activity: FeP Nanowire Array as the Active Phase", ANGEWANDTE CHEMIE INTERNATIONAL EDITION, vol. 53, no. 47, 24 September 2014 (2014-09-24), pages 12855-12859, XP055266378, DE ISSN: 1433-7851, DOI: 10.1002/anie.201406848 abstract figures 2a, 3b page 12855, right-hand column, line 42 - page 12856, right-hand column, line 24 -/--	1-12
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input checked="" type="checkbox"/> See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search		Date of mailing of the international search report
20 April 2016		04/07/2016
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer  Lange, Ronny

## INTERNATIONAL SEARCH REPORT

International application No

PCT/IB2016/050767

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
	<p>-&amp; Ping Jiang ET AL: "Supporting Information A Cost-Effective 3D Hydrogen Evolution Cathode with High Catalytic Activity: FeP Nanowire Array as the Active Phase**",  24 September 2014 (2014-09-24),  XP055267011,  Retrieved from the Internet:  URL:http://api.onlinelibrary.wiley.com/asset/v1/doi/10.1002/anie.201406848/asset/supinfo/anie_201406848_sm_miscellaneous_information.pdf?l=SkaBT8QEx2qMKFzmpntImv1Y6SM+cDa2MQA08Mce/XBM/Q4Z+zkF0iVTKwQTXayUGxtwOCP5Mrd/e93RluHkq0Txd1yr9+m9ByByip3993FLfTVR9duDKA==  [retrieved on 2016-04-20]  page 1</p>	
Y	<p>-----  JINGQI TIAN ET AL: "Self-Supported Nanoporous Cobalt Phosphide Nanowire Arrays: An Efficient 3D Hydrogen-Evolving Cathode over the Wide Range of pH 0-14",  JOURNAL OF THE AMERICAN CHEMICAL SOCIETY,  vol. 136, no. 21, 28 May 2014 (2014-05-28),  pages 7587-7590, XP055266351,  US  ISSN: 0002-7863, DOI: 10.1021/ja503372r  abstract  figure 1e  page 7587, right-hand column, lines 14-16  page 7588, left-hand column, lines 19-22</p>	1-7
Y	<p>-----  JUAN F. CALLEJAS ET AL: "Electrocatalytic and Photocatalytic Hydrogen Production from Acidic and Neutral-pH Aqueous Solutions Using Iron Phosphide Nanoparticles",  ACS NANO,  vol. 8, no. 11,  25 November 2014 (2014-11-25), pages  11101-11107, XP055266364,  US  ISSN: 1936-0851, DOI: 10.1021/nn5048553  abstract  page 11102, left-hand column, lines 20-24</p>	1-12
Y	<p>-----  US 2010/092865 A1 (KANNO RYOJI [JP] ET AL)  15 April 2010 (2010-04-15)  abstract  example 1</p>	1-12
A	<p>-----  IL 39 659 A (INT NICKEL LTD [GB])  31 August 1975 (1975-08-31)  claim 1</p> <p>-----</p>	1-12

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/IB2016/050767

## Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claims Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
  
2.  As all searchable claims could be searched without effort justifying an additional fees, this Authority did not invite payment of additional fees.
  
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

see annex

### Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.

**FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210**

This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-12

Invention I concerns a method of phosphidation, comprising: electroplating of a metal on a substrate, converting the M to MOOH, M oxide, or a combination thereof, and converting the MOOH, M oxide, or both to nanocrystalline metal phosphide.

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2. claims: 13-20

Invention II concerns a catalyst, comprising: a nanocrystalline metal phosphide having a rugae-like morphology. Invention II also concerns a method of producing H<sub>2</sub>, comprising: exposing H<sub>2</sub> O to a catalyst, wherein the catalyst is a nanocrystalline metal phosphide (MP) having a rugae-like morphology, and producing H<sub>2</sub> .

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No PCT/IB2016/050767
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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