Electronic Supplementary Information

Electrochemically dealloyed nanoporous Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_{5}$ metallic glass for efficient and stable electrocatalytic hydrogen and oxygen generation

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Materials and methods

Experimental section

Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} master alloy ingots were prepared by arc melting high purity iron (Fe), Cobalt (Co), Nickel (Ni), Carbon (C), Fe\textsubscript{3}P, and Ni\textsubscript{2}P in a high purity argon atmosphere with Ti gettering. Fe\textsubscript{3}P and Ni\textsubscript{2}P compounds were used since phosphorous (P) are highly volatile in room temperature conditions. The stoichiometric equation for calculating the mass of raw materials for developing alloy ingot for Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} is given as 25 Fe + 5Fe\textsubscript{3}P + 10 Ni\textsubscript{2}P +20 Co+5C → Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5}. Each alloy ingots were remelted four times to ensure homogenous chemical composition throughout the whole ingot. The metallic glass amorphous ribbons were prepared by remelting the as-prepared alloy ingots and suddenly spraying the melt through a tube nozzle over a copper roller which is rotating at high speed. Thus the melt was rolled into ribbons of width 3mm and thickness 25 μm.

Materials characterization

The microstructural phase composition of the metallic glass ribbons was characterized by X-ray diffraction (XRD) using a Bruker D8 Advance high-resolution diffractometer with Cu Ka radiation (λ = 1.5406 Å, 40 k V and 40 mA). Surface morphology was analyzed using a scanning electron microscope (SEM: FEI Quanta 450FEG), Transmission electron microscope (TEM: JEM-2100F), and elemental analysis was carried out using Energy Dispersive analysis of X-ray (EDX) spectrometer attached to TEM and SEM. The temperatures associated with thermal transitions were obtained using the differential scanning calorimeter, DSC instrument (Perkin Elmer DSC 8000) at a heating rate of 5K/min under N\textsubscript{2} atmosphere. X-ray photoelectron spectroscopy (XPS-thermos K-Alpha+) was used to investigate the chemical states for the as-prepared MG ribbon and the 20 hour tested MG ribbons.
Electrocatalytic measurements

The HER and OER electrochemical performance of the MG catalyst Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} were tested in a three-electrode configuration on a Gamry 600 plus electrochemical workstation (USA). Ag/AgCl and Hg/HgO electrode were used as a reference electrode in 0.5 M H\textsubscript{2}SO\textsubscript{4} and 1M KOH, respectively, in acidic and alkaline media. Graphite carbon rod was used as the counter electrode in the acidic electrolyte, and a Pt tip electrode was used as a counter electrode in the alkaline electrolyte medium. The melt-spun ribbons were cut into 30 mm × 1 mm × 25 μm. The portion to be dipped in electrolyte solution was fixed as 0.4 cm, and the portion above the working part is wrapped by Teflon tape. It was assured that the electrolyte could not pass into the Teflon tape by properly pressing the Teflon tape. The active area of the metallic glass (MG) ribbon for electrochemical measurement is thus 0.08 cm\textsuperscript{2}. The ribbon samples were electrochemically dealloyed in 1M HCl by applying an optimized voltage of 0.2V for 30 minutes in a three-electrode configuration. After dealloying, samples were kept in a vacuum for 12 hours. The measurement for standard Pt and IrO\textsubscript{2} as working electrodes were prepared by dispersing 5mg of commercial Pt/C or IrO\textsubscript{2} powders in 650 μL deionized water and 350 μL isopropanol, 30 μL 5 wt% Nafion solution was added and sonicated for 30 min to form homogeneous dispersion. 5 μL ink was dropped on the surface of the GCE (surface area: 0.070685 cm\textsuperscript{2}) using a pipette and dried at 60 °C for 12 hr. Linear-sweep voltammetry with 95% iR compensation was carried out at a scan rate of 5 mV s\textsuperscript{-1} in 0.5 M H\textsubscript{2}SO\textsubscript{4} and 1.0 M KOH, respectively. The linear sweep voltammetry (LSV) curves of each sample were measured five times, and the final cycle was always used for analysis. To determine the double layer capacitance per unit area (C\textsubscript{dl}), a series cyclic voltammetry (CV) measurement was performed at various scan rates (200,150, 120, 100, 80, 60, 40, 20, and 10 mV.s\textsuperscript{-1}) in the non-faradaic region of polarization. The electrochemical active surface area, ECSA of the
MG electrocatalyst were calculated from the formula $ECSA = C_{dl}/C_s$, where $C_s$ is the specific capacitance of an atomically smooth surface, 40 $\mu$F.cm$^{-2}$. Electrochemical impedance spectra (EIS) were measured in the frequency range of 0.01 Hz to $10^5$ Hz by applying a dc voltage at the corresponding overpotential, $\eta_{10}$. The long-term durability test of HER was determined by chronoamperometry at the corresponding overpotential, $\eta_{10}$ and at a current density of 10 mA cm$^{-2}$. The cycling stability was tested by using Linear-sweep voltammetry after 2000 CV cycles with 100 mV s$^{-1}$ in the voltage range 0 to 2V.

All the potentials in this study were compensated by $iR_s$ as per the following equation (1):

$$E_{corr} = E_{meas} - iR_s$$  \hspace{1cm} (1)

of which, $E_{corr}$ is compensated postpotential, $E_{meas}$ is the measured potential during experiment and $R_s$ is the solution resistance measured by electrochemical impedance spectroscopy (EIS).

All the potentials were converted into reversible hydrogen electrode potential (RHE) as per the following equation (2. a-c)

HER in Acid media: $E_{(vs \ RHE)} = E_{(vs \ Ag/AgCl)} + 0.059\times pH (pH\sim0) + 0.197\ V$  \hspace{1cm} (2.a)

HER in alkaline media: $E_{(vs \ RHE)} = E_{(vs \ Hg/HgO)} + 0.059\times pH (pH\sim14) + 0.098\ V$  \hspace{1cm} (2.b)

OER in alkaline media: $E_{(vs \ RHE)} = E_{(vs \ Hg/HgO)} + 0.059\times pH (pH\sim14) + 0.098\ V$  \hspace{1cm} (2.c)

In 0.5M H$_2$SO$_4$ and 1M KOH, HER linear polarization curves were collected at a scan rate of 5 mV/s in the range of applied potential 0 to -2V vs. RHE. OER polarization curves were obtained at the same scan rate of 5 mV/s in the applied potential range 0 to 2V vs. RHE. The Tafel plot was derived from the corresponding LSV curve according to the Tafel equation (3):

$$\eta = a + b\log j$$  \hspace{1cm} (3)

where $\eta$ represents the overpotential, $b$ is the Tafel slope, $j$ is the current density and $a$ is the exchange current density.
Fig. S1 DSC spectrum for MG ribbon.
**Fig. S2** CV curves of electrochemically dealloyed Fe_{40}Co_{20}Ni_{20}P_{15}C_{5}. (a) HER acidic, (b) HER alkaline, (c) OER alkaline (d-f) Corresponding plots showing the double-layer capacitance (C_{dl}) per unit area.
Fig. S3 XPS spectra before and after chronoamperometric tests. (a-d) XPS spectra for P 2p. (e-h) XPS spectra for C 1s.
**Table S1.** HER performance of Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_{5}$ MG and other reported electrocatalysts in acidic electrolytes.

| Catalyst                        | Substrate          | $\eta_{10}$/mV | Tafel slope (mV.dec$^{-1}$) | Electrolyte                  | Ref.                                      |
|---------------------------------|--------------------|----------------|-----------------------------|------------------------------|-------------------------------------------|
| Glassy Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_{5}$/Dealloyed | Free-standing      | 128            | 67                          | 0.5 M H$_2$SO$_4$            | This work                                |
| 10wt. % Pt/C                    | Glassy carbon      | 42             | 24                          | 0.5 M H$_2$SO$_4$            | This work                                |
| FeP porous nanosheet            | Glassy carbon      | 240            | 67                          | 0.5 M H$_2$SO$_4$            | Chem. Commun. 2013, 49, 6656.            |
| CoP/NTs                         | Glassy carbon      | 130            | 60                          | 0.5 M H$_2$SO$_4$            | J. Mater. Chem. A 2014, 2, 14812         |
| NiCoP/rGO                       | Glassy carbon      | 59             | 51.2                        | 0.5 M H$_2$SO$_4$            | Adv. Funct. Mater. 2016, 26, 6785        |
| FeCo@FeCoP@C                    | Glassy carbon      | 65             | 60                          | 0.5 M H$_2$SO$_4$            | ACS Appl. Mater. Interfaces 2019, 11, 1267|
| Fe@Fe$_2$P/NCNT                 | Glassy carbon      | 78.2           | 52.2                        | 0.5 M H$_2$SO$_4$            | ChemElectroChem 2019, 6, 1413            |
| Ni$_2$P nanoparticles           | Glassy carbon      | 187            | 16                          | 0.5 M H$_2$SO$_4$            | J. Am. Chem. Soc. 2013, 135, 9267        |
| NiCoP nanowire                  | Glassy carbon      | 380            | 65                          | 0.5 M H$_2$SO$_4$            | Mater. Res. Express 2019, 6, 1150b3     |
| Porous hollow NiCoP polyhedra   | Glassy carbon      | 124            | 42                          | 0.5 M H$_2$SO$_4$            | ACS Appl. Mater. Interfaces 2017, 9, 5982|
| Mo$_2$C-porous                  | Glassy carbon      | 142            | 53                          | 0.5 M H$_2$SO$_4$            | Nat. Commun. 2015, 6, 6512               |
| Ni$_{12}$P$_5$                   | Titanium foil      | 107            | 63                          | 0.5 M H$_2$SO$_4$            | ACS Nano 2014, 8, 8121                   |
| MoS$_2$ nanosheets              | Glassy             | 180            | 55                          | 0.5 M H$_2$SO$_4$            | J. Am. Chem. Soc.                       |
|                  | Carbon Content | H₂SO₄ | Reference                  |
|------------------|----------------|-------|---------------------------|
| MoS₂/CoSe₂       | Glassy carbon  | 68    | 0.5 M H₂SO₄               | **Nat. Commun. 2015, 6, 5982** |
| MoP nanoparticles| Glassy carbon  | 125   | 0.5 M H₂SO₄               | **Adv. Mater. 2014, 26, 5702** |
| CoP nanoparticles| Glassy carbon  | 212.2 | 0.5 M H₂SO₄               | **J. Mater. Chem. A 2015, 3, 4255** |
Table S2. HER performance of Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} MG and other electrocatalysts in alkaline electrolytes.

| Catalyst                  | substrate          | $\eta_{10}$/ mV | Tafel slope (mV. dec\textsuperscript{-1}) | Electrolyte | Ref.                                      |
|---------------------------|--------------------|-----------------|------------------------------------------|-------------|-------------------------------------------|
| Glassy Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} Dealloyed | Free-standing     | 236             | 110                                      | 1 M KOH     | This work                                 |
| Crystallized Fe\textsubscript{40}Ni\textsubscript{20}Co\textsubscript{20}P\textsubscript{15}C\textsubscript{5} | Free-standing     | 312             | 95                                       | 1 M KOH     | This work                                 |
| 10wt. % Pt/C              | Glassy carbon     | 45              | 86                                       | 1 M KOH     | This work                                 |
| Ni/Mo\textsubscript{2}C/porous C | Nickel foam       | 179             | 101                                      | 1 M KOH     | *J. Mater. Chem. A* 2015, 4255          |
| FeP nanosheet/Ti          | Ti                | 95              | 64                                       | 1 M KOH     | *Appl. Catal. B Environ.* 2020, 260, 118156 |
| CoP                       | Carbon cloth      | 209             | 129                                      | 1 M KOH     | *J. Am. Chem. Soc.* 2014, 136 (21), 7587 |
| NiCo\textsubscript{2}P\textsubscript{x} nanowire | Carbon fiber      | 58              | 34.3                                     | 1 M KOH     | *Adv. Mater.* 2017, 29 (9), 1605502     |
| Mo\textsubscript{2}C-porous | Glassy carbon    | 151             | 59                                       | 1 M KOH     | *Nat. Commun.* 2015, 6 (1), 6512        |
| FeCoOH nanosheet          | Nickel foam       | 126             | N/A                                      | 1 M KOH     | *Chem. – A Eur. J.* 2018, 24 (18), 4724  |
| Ni/Mo\textsubscript{2}C/porous C | Glassy carbon    | 179             | 101                                      | 1 M KOH     | *Chem. Sci.* 2016, 7 (5), 3399          |
| Co(OH)\textsubscript{2}@PANI | Nickel           | 88              | 91.6                                     | 1 M NaOH    | *Adv. Mater.* 2015, 27                   |
| Material                  | Electrode Material | C (mAh g\(^{-1}\)) | I (mA g\(^{-1}\)) | KOH | Reference                        |
|--------------------------|--------------------|---------------------|-------------------|-----|----------------------------------|
| FeCoNiP@NC              | Glassy carbon      | 187                 | 52.2              | 1 M KOH | Sustain. Energy Fuels 2020, 4531 |
| Glassy Ni\(_{40}\)Fe\(_{40}\)P\(_{20}\) | Free-standing     | 270                 | 89                | 1 M KOH | Adv. Mater. Interfaces 2017, 1601086 |
| Ni/NiO                   | Glassy carbon      | 90                  | 101               | 1 M KOH | Natl. Sci. Rev. 2020, 27       |
| FeP array                | Glassy carbon      | 194                 | 75                | 1 M KOH | Chem. Commun. 2016, 2819       |
| FeP NAs/CC               | Glassy carbon      | 218                 | 146               | 1 M KOH | ACS Catal. 2014, 4065          |
| MoB                      | Glassy carbon      | 225                 | 59                | 1 M KOH | Angew. Chemie Int. Ed. 2012, 51, 12703 |
| FeP Nanotubes            | Glassy carbon      | 120                 | 60                | 1 M KOH | Chem. – A Eur. J. 2015, 18062  |
**Table S3.** OER performance of Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_5$ MG and other reported high performing electrocatalysts in alkaline electrolytes.

| Catalyst | substrate | $\eta_{10}$/mV | Tafel slope (mV.d ec$^{-1}$) | Electrolyte | Reference                      |
|----------|-----------|----------------|-------------------------------|-------------|--------------------------------|
| Glassy Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_5$/Dealloyed | Free-standing | 278          | 40                           | 1 M KOH     | This work                       |
| Crystallized Fe$_{40}$Ni$_{20}$Co$_{20}$P$_{15}$C$_5$ | Free-standing | 365          | 44                           | 1 M KOH     | This work                       |
| IrO$_2$ | Glassy carbon | 385          | 90                           | 1 M KOH     | This work                       |
| Co-P | Co foil | 345          | 47                           | 1 M KOH     | *Angew. Chemie Int. Ed.* 2015, 6251–6254 |
| Ni$_x$Co$_{3-x}$O$_4$ nanowire | Glassy carbon | 370          | 64                           | 1 M KOH     | *Angew. Chemie Int. Ed.* 2017,3897–3900 |
| NiFeO$_x$ | Carbon Fiber | 230          | 31.5                         | 1 M KOH     | *Nat. Commun.* 2015, 7261 |
| (Fe$_x$Ni$_{1-x}$)P | Nickel Foam | 156          | 66                           | 1 M KOH     | *Nano Energy* 2017, 38, 553 |
| Ni-P nanosheet | Glassy carbon | 300          | 64                           | 1 M KOH     | *Energy Environ. Sci.* 2016, 1246 |
| NiCoP@C | Glassy carbon | 297          | 58                           | 1 M KOH     | *Nanoscale* 2018, 10, 13555 |
| Ni-Co nanowire | Glassy carbon | 302          | 43.6                         | 1 M KOH     | *Adv. Energy Mater.* 2017, 1601492 |
| FeCoNiP@NC | Glassy carbon | 266          | 35.6                         | 1 M KOH     | *Sustain. Energy Fuels* 2020, 4531 |
| Material                          | Support   | Thickness | Current Density | Electrolyte | Journal/Ref          |
|----------------------------------|-----------|-----------|-----------------|-------------|----------------------|
| Glassy Fe54Ni30-xCoxNb6B9Cu1     | Free-standing | 274       | 37.4            | 1 M KOH     | J. Alloys Compd. 2021, 852, 156876 |
| NiCo2O4/NiO                      | Glassy carbon | 360       | 75              | 1 M KOH     | ACS Omega 2017, 2, 7559 |
| NiCo-LDH                         | Nickel Foam | 420       | 113             | 1 M KOH     | J. Power Sources 2015, 278, 445 |
| MoO2                             | Glassy carbon | 330       | 78              | 1 M KOH     | J. Phys. Chem. C 2020, 124, 20010 |
| NiFe Hydroxide                   | Glassy carbon | 245       | 28              | 1 M KOH     | Nat. Commun. 2015, 6, 6616 |
| NiCoFeP/C                        | Glassy carbon | 270       | 65              | 1 M KOH     | Chem. Commun. 2019, 55, 10896 |
| FeP/Fe3O4-CNT                    | Glassy carbon | 229       | 27.6            | 1 M KOH     | ACS Appl. Mater. Interfaces 2020, 12, 12783 |