



Transition metal phosphide catalysts for hydrogen oxidation reaction

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ABSTRACT

A series of transition metal phosphides consisting of tungsten (WP), cobalt (CoP), nickel (NiP), nickel-tungsten (Ni-WP), cobalt-tungsten (Co-WP) and cobalt-molybdenum (Co-MoP) was prepared by a temperature-programmed reduction process. Hydrogen oxidation activities for the phosphide compounds were studied. The hydrogen oxidation reaction (HOR) was determined using a half-cell rotating disc electrode in a 0.5 M H₂SO₄ electrolyte. In addition, the passivity of the phosphides in an acidic environment was studied by ICP. The Co-WP demonstrated the highest activity for the HOR based on chronoamperometry and the exchange current density. The single WP exhibited a low HOR activity, but the incorporation of Ni or Co enhanced the activity. In contrast, WP exhibited a high passivity, while NiP and CoP dissolved in the 0.5 M H₂SO₄. The high activities over Co-WP and Ni-WP were attributed to the role of WP in preventing the Co and Ni from corroding in the acidic media.

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1. Introduction

Fuel cells utilize hydrogen gas to generate clean and useful energy by the electrocatalytic oxidation of hydrogen (HOR). At present, the best and most practical catalyst for the HOR is the Pt-alloy catalysts. However, because these catalysts are expensive, current studies are concentrated on exploring a more economical catalyst based on non-noble materials, for example, carbides and perovskites. One of the non-noble catalysts considered as a potential candidate is the transition metal phosphide, which is generally known to demonstrate excellent activity for hydrodesulfurization (HDS) and hydrodenitrogenation (HDN) in the petroleum industries. In addition to its activity, these materials exhibit excellent physical and mechanical properties [1–5], for instance, electric conductivity, hardness, wear and corrosion resistance. Recently, monometallic phosphides have been studied for their use in electrode reactions, porous anode catalysis and in Li electrodes [6]. Daimon and Kurobe [7] reported that the addition of phosphorus to Pt–Ru resulted in a higher catalytic activity due to the effective particle size reduction of Pt–Ru. Phosphides have also recently been used for methanol oxidation in DMFCs [8]. In the present study, we investigated the HOR activities for some single and binary phosphide compounds. The phosphides were also investigated for their resistivity in acidic media due to the highly acidic environment of the PEFC.

2. Experimental

2.1. Catalyst preparation

The precursors of the metal phosphides (WP, CoP or NiP) were prepared by combining stoichiometric quantities of ammonium metatungstate ((NH₄)₆H₂W₁₂O₄₀·nH₂O), cobalt nitrate (Co(NO₃)₂·nH₂O) or nickel nitrate (Ni(NO₃)₂·nH₂O) with an aqueous solution of diammonium phosphate ((NH₄)₂HPO₄). For the bimetallic phosphides (Ni-WP and Co-WP), ammonium metatungstate or ammonium molybdate was added to cobalt nitrate, (Co(NO₃)₂·nH₂O) or nickel nitrate together with diammonium phosphate. As for the Co-MoP, the same starting material was used except that ammonium metatungstate was replaced with ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·nH₂O). The bimetallic ratios of Ni to W, Co to W and Co to Mo were set constant at 1:1. The solids were dissolved in water at 313 K with stirring and then dried at 393 K. The catalysts were ground before being calcined for 5 h at 773 K. These oxide precursors were then reduced at temperatures shown in Table 1 at a ramping rate of 1 K min^{−1} in a stream of H₂ and maintained at the final temperature for 2 h. Prior to phosphidation, temperature-programmed reduction (TPR) was carried out in a flow of hydrogen, and the evolution of water (*m/z* = 18) was measured online using a quadrupole mass spectrometer (Baltzer). The mixture was then cooled and passivated under a stream of 1% O₂/He. The dissolution of the metal phosphides in acid was carried out by adding 2 mg of the catalyst to 10 mL of 0.5 M H₂SO₄, then followed by mixing in a tube mixer for 24 h prior to analysis by inductively coupled plasma spectroscopy (ICPS, Shimadzu).

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Table 1

The properties and HOR activities of the transition metal phosphides measured by a half-electrode cell, and the concentrations of the respective metals after mixing for 24 h in 0.5 M H₂SO₄ solution.

Metal phosphides	Reduction temperature (K)	BET area (m ² /g)	Exch. Curr. j_0 (μA/cm ²)	Oxidation current (μA/μg)	Conc. in 0.5 M H ₂ SO ₄ (ppm)	
					Co or Ni	W or Mo
WP	923	9	2.01	0.0001	–	1 ^(W)
NiP	823	10	0.67	0.0010	>100 ^(Ni)	–
NiWP	873	10	2.46	0.0027	6 ^(Ni)	1 ^(W)
CoP	823	n.m.	n.m.	0.0030	>100 ^(Co)	–
CoWP	873	10	3.03	0.0087	29 ^(Co)	4 ^(W)
CoMoP	873	5	0.44	0.0041	97 ^(Co)	51 ^(Mo)

n.m.: not measured.

2.2. Characterization

The bulk structure of the phosphide catalyst was examined by XRD (30 kV, 28 mA). The diffraction pattern was obtained using an RINT2000 (Rigaku Co.) with Cu Kα radiation ($\lambda = 1.542 \text{ \AA}$). The peaks were identified by the JCPDS card references for WP (PDF#29-1364), NiP (PDF#03-953), CoP (PDF#32-0306), NiWP (PDF#47-1346) and CoMoP (PDF#32-299). The specific surface area of the catalyst was determined using an Omnisorp 100CX (Beckman Coulter Co.) at liquid nitrogen temperature after the catalyst was evacuated at 473 K for 2 h. XPS was performed by an ESCA-3200 (Shimadzu Corp.) using Mg Kα radiation at the power of 240 W (30 mA, 8 kV). The peak shift correction was based on the binding energies of C 1s (284.6 eV). The baseline correction for the peak fitting was carried out by the Shirley method using Kratos software preinstalled with the ESCA-3200. The W 4f spectra were deconvoluted using the area ratios of 1.33 [9] for a spin-orbit splitting of 2.1 eV. The atomic ratios were determined using the sensitivity factors provided by the manufacturer.

2.3. Electrochemical measurements

The voltammetric measurements were performed using an RDE (HZ-5000, Hokuto Denko) apparatus composed of a platinum counter, a standard calomel reference (SCE), and the phosphides on a glassy-carbon disk as the working electrode. Fifty mg of the catalyst was well dispersed in a 35% ethanol solution (1 mL) and then sonicated to form a 0.05 cat.-g mL⁻¹ solution. Ten μL of the ethanol-catalyst solution was then dropped onto the glassy-carbon disk. After the catalyst was applied to the disk at 26 μg cm⁻¹ (5 μg based on the electrode area), a 5-μL aliquot of a 5 wt% 2-propanol solution containing Nafion (Aldrich) was dropped onto the glassy-carbon disk. The RDE attached to a three-compartment electrochemical cell was placed in a 0.5 M H₂SO₄ solution. The measurement was carried out at room temperature and a rotation speed of 2000 rpm at 50 mV s⁻¹ for the cyclic voltammetry (CV) and at 5 mV s⁻¹ for the slow scan voltammetry (SSV) with scans from -0.2 to 1.0 V to determine the current density in Ar and H₂ (21.8 mL min⁻¹). The scanning was carried out several times to obtain the steady state values. The current densities were obtained from the current normalized to the sample's geometric area (0.196 cm²) and with the current normalized to the electrode BET area. All the potential values in this measurement are obtained with respect to the SCE unless specified.

3. Results and discussion

3.1. TPR

The evolution of water during the TPR of MoP, WP, CoP, Co-WP and Co-MoP is presented in Fig. 1. The maximum evolution of water for CoP was at 823 K, while that for the WP and MoP was between 923

and 973 K. However, the maximum for the bimetallic Co-WP and Co-MoP was around 873 K, which was lower than that for WP and higher than those for NiP and CoP. Since Clark et al. [10] reported that the high surface area and CO uptake follow the trends of the water evolution profiles; therefore, the final temperatures in the present study as listed in Table 1 were determined by the highest evolution of water during the TPR. Although Stinner et al. [11] synthesized binary phosphides (Co-MoP) at 1023 K, the present study by TPR showed that Co-MoP is also formed at 873 K; thus high temperature is not necessary for the preparation. The addition of Co or Ni probably enhanced the phosphidation probably by assisting the dissociation of hydrogen and lowered the reduction temperature for phosphidation. Furthermore, in a previous paper, the low phosphidation temperature of Ni-MoP has shown to result in a higher catalytic activity for HDS than those of higher temperature [12].

3.2. XRD and physical properties

The XRD patterns of the WP, NiP and Ni-WP metal phosphides are shown in Fig. 2a, and those of WP, CoP and Co-WP are shown in Fig. 2b. The WP showed peaks at $2\theta = 21.0^\circ$, 28.6° , 31.0° , 43.1° , 44.5° and 46.4° that perfectly matched the reference. The peaks of NiP and CoP corresponded well to dinickel phosphide and dicobalt phosphide. The NiP crystallites undergo simultaneous crystallization because the preparation temperature for NiP is the lowest (823 K) compared to the other phosphide catalysts. This conclusion was corroborated in the thermokinetic studies by Budniok and Matyja [13]. Ni-WP showed XRD peaks that are difficult to assign because of the presence of WP and NiP. However, in this study, three peaks at $2\theta = 35.2^\circ$, 39.8° and 43.8° were observed. The main peak shifted to 39.8° and another peak appeared at $2\theta = 35.1^\circ$ due to the formation of the NiW bimetallic phosphide.

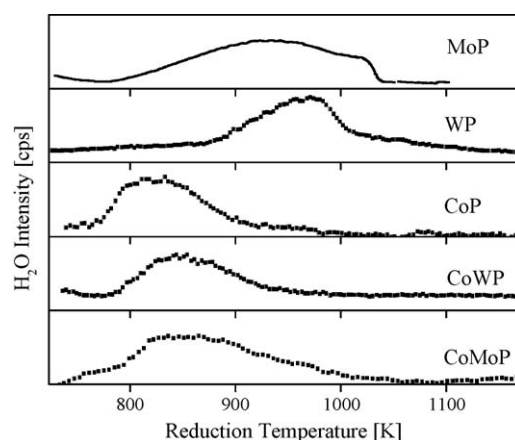


Fig. 1. The evolution of H₂O ($m/z = 18$) during temperature-programmed reduction in hydrogen gas measured using an online mass spectrometer for MoP, WP, CoP, Co-WP and Co-MoP.

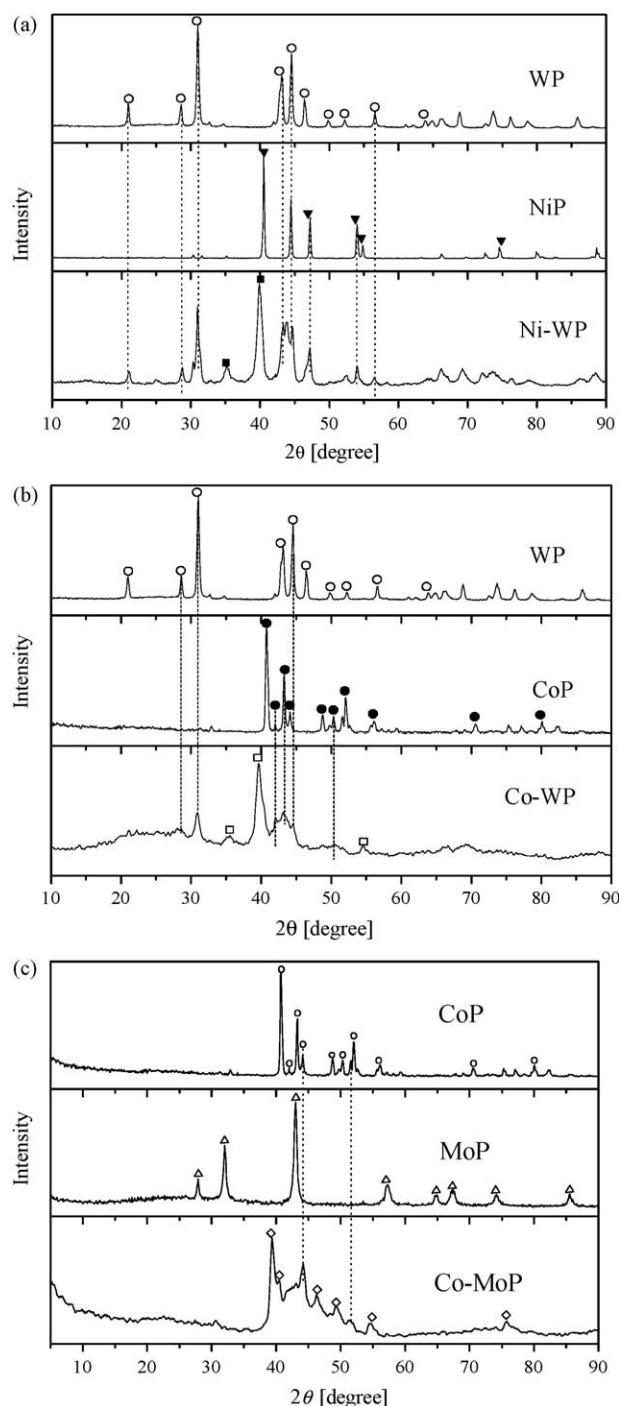


Fig. 2. XRD measurements of the phosphide catalysts prepared by the temperature-programmed reduction method. (a) WP (○), NiP (▼) and NiWP (■); (b) WP, CoP (●) and CoWP (□); (c) CoP, MoP (△) and Co-MoP (◇).

The XRD peaks at $2\theta = 31.0^\circ$, 43.2° and 44.5° for Co-WP were attributed to WP. However, the larger peaks at $2\theta = 35.2^\circ$ and 39.6° were attributed to the presence of the Co-WP bimetallic phosphides. The introduction of Co to WP leads to a shift in the WP peaks (40.7°) to lower angles (39.6°) due to the formation of the Co-WP alloy [14]. The wide peak in the angular range of $38^\circ < 2\theta < 52^\circ$ indicates the presence of fine crystalline phases of the Co-WP catalysts. The Co-MoP catalyst showed main peaks at $2\theta = 39.3^\circ$, 40.4° and 49.4° that are consistent with the data in literature [11].

The BET surface areas of the transition metal phosphides are shown in Table 1. The surface areas of all the phosphide catalysts were found to range from 5 to $10 \text{ m}^2 \text{ g}^{-1}$ and are consistent with those reported by Stinner et al. [11]. The addition of Co or Ni to the WP did not significantly change the surface area. However, the surface area of Co-MoP was half that of the tungsten-based phosphides. This could be due to the lower initial surface area of the MoP; thus the further incorporation of cobalt resulted in some increase in the surface area.

3.3. XPS analysis

The XPS spectra of the CoP, CoWP and WP are shown in Fig. 3a–c. The binding energy at 777.6 eV corresponds to elemental cobalt, while peaks at 779.9 and 781.6 eV indicate the presence of Co^{2+} and Co^{3+} , respectively. In Fig. 3a, the analysis showed that approximately 31% of total cobalt present in the Co-WP surface is in the form of elemental cobalt, while 49 and 20% of the cobalt are in the forms of Co^{2+} and Co^{3+} , respectively. Fig. 3b shows the P 2p spectrum for the analysis of the phosphorus states, suggesting three species of phosphorous present at the surface. The P $2p_{1/2}$ peaks at 129.3, 131.4 and 133.0 correspond to elemental phosphorous, P^+ and P^{5+} , respectively [2]. Fig. 3c shows that the XPS peaks of W 4f were deconvoluted to various valence states. Quantitative analysis using XPS yields the atomic ratio of CoP, WP and Co-WP. The atomic ratios of P/W for WP, P/Co + W for Co-WP and P/Co for Co-P were 0.47, 0.33 and 0.50, respectively, and corresponded well with the nominal composition of the phosphides. In addition, the average valences of cobalt and tungsten for the Co-WP were slightly higher than those of WP and CoP. This indicated the existence of the bimetallic phosphides of CoW at the catalyst surface.

3.4. Phosphide catalyst dissolution in H_2SO_4

The dissolution of the catalyst in 0.5 M H_2SO_4 after 24 h of vigorous mixing is shown in Table 1. The higher the concentration of the metal in H_2SO_4 solution measured by ICPS represents a higher dissolution of the catalyst, thus corresponding to a low resistance in acid environment. In this study, NiP and CoP showed an extremely high Ni and Co concentration ($>100 \text{ ppm}$) and therefore exhibited a high dissolution in acid. Krolkowski and Butkiewics [15] reported that NiP exhibited a distinctly better corrosion resistance than the pure Ni, although their test was performed in NaCl instead of H_2SO_4 . WP showed only a 1-ppm concentration of dissolved W and exhibited a remarkable resistance to H_2SO_4 . This is due to the nature of the WP that is extremely stable in an acidic medium similar to those of ordinary metallic compounds such as tungsten carbide, nitrides, borides and silicides. In the case of Ni-WP and Co-WP, the concentrations of Ni and Co were significantly low compared to those of a single metal phosphide. The concentrations of Ni and Co were 6 and 29 ppm, respectively, indicating good stability in the acidic environment. The WP in both Co-WP and Ni-WP probably has the role of a corrosion inhibitor and prevented Ni and Co from corrosion by forming a stable WP-rich amorphous phase. When Mo was substituted for W as in the Co-MoP, the concentrations of Co and Mo in the acid were four times greater than that of Co-WP. This result showed that WP had a greater ability to prevent corrosion compared to MoP, although Mo also prohibited Co from corrosion.

3.5. HOR activity by voltammetric measurement

The HOR activity over the metal phosphide catalysts was evaluated by chronoamperometric methods as a current–time plot as illustrated in Fig. 4. When the gas was changed from Ar to H_2 , the

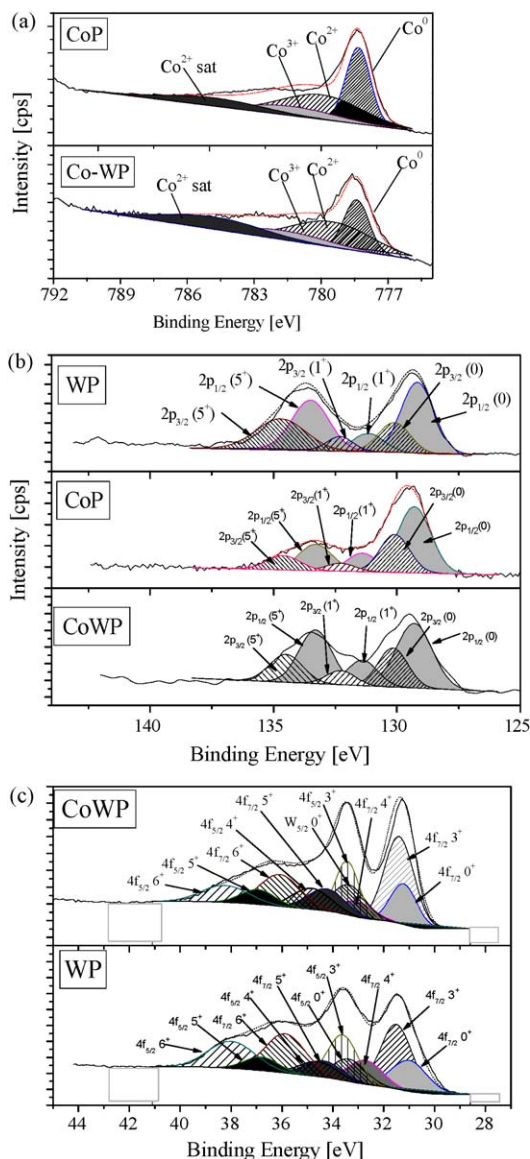


Fig. 3. Deconvolution of the XPS patterns of the CoP, CoWP and WP catalysts. (a) Co 2p, (b) P 2p and (c) W 4f.

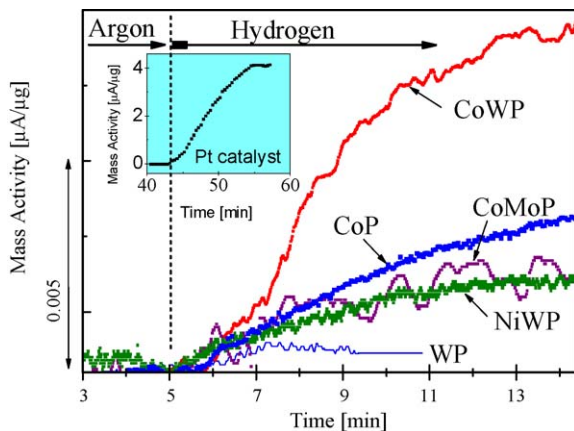


Fig. 4. The oxidation currents of Co-WP, Ni-WP, Co-P, WP, Co-MoP and Pt (inset figure) during CA in 0.5 M H₂SO₄ saturated in argon and hydrogen gases at room temperature. A potential of 0.1 V (RHE) was constantly applied to the working electrode.

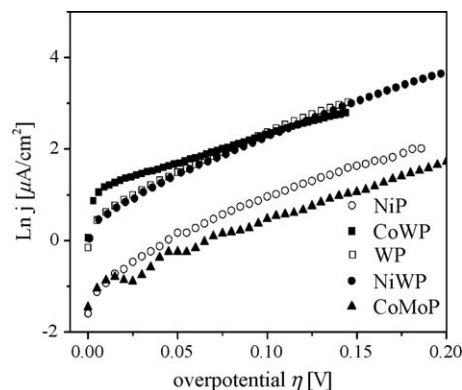


Fig. 5. The anode polarization curves of Co-WP, Ni-WP, WP and Co-MoP during slow scan voltammetry in 0.5 M H₂SO₄ saturated with H₂ gas at room temperature.

mass activity of the metal phosphides gradually increased until it reached a steady state after approximately 5–10 min. The mass activity indicates the HOR activity over the phosphide catalysts. The Co-WP exhibited the largest increase in mass activity ($0.087 \mu\text{A} \mu\text{g}^{-1}$) compared to the other metal phosphides. To reaffirm this, slow scan voltammetry measurement of the metal phosphide catalysts was conducted and is illustrated in Fig. 5. The exchange current density (j_0) was determined using the linearized Butler–Volmer rate law, $j = j_0 n f \eta$ (where $f = F/RT$), assuming limited charge transfer kinetics at low potential deviations from equilibrium. The j_0 values of the phosphides catalysts are shown in Table 1. The results indicated that the Co-WP catalyst showed the highest j_0 value ($3.03 \mu\text{A} \text{cm}^{-2}$) in agreement with that obtained from chronoamperometry. Studies conducted by Popczyk et al. [16] and Budniok and Kupka [17] have also reported high activities of the phosphides containing Co and/or Ni for hydrogen and oxygen evolution reactions in alkaline solution. Similarly, in this study, the electrocatalytic activity of the phosphided CoW, CoMo and NiW materials increased due to the presence of Co and Ni on the surface of the crystals that functioned as the catalytically active component. The passivity towards corrosion is conferred by the W and Mo components dissolved in the catalyst phase. Also shown in Table 1 is the HOR activity over bimetallic Co-MoP and Ni-WP which values were 0.0041 and $0.0027 \mu\text{A} \mu\text{g}^{-1}$, respectively. The bimetallic phosphide exhibited significantly higher activity than the tungsten phosphide. The addition of tungsten significantly increased the HOR activity and reduced the dissolution of NiP and CoP. The HOR activity of a commercial Pt catalyst (Electrochem) was also measured using chronoamperometry and is illustrated in the inset in Fig. 4. The mass activity obtained over the Pt catalyst was $3.92 \mu\text{A} \mu\text{g}^{-1}$ and is 3 orders of magnitude higher than that of Co-WP. However, the bimetallic phosphides such as Co-WP and Ni-WP displayed good passivity in acidic media. The activity of the phosphides depended on the metal promoter used; thus, the combination with other metal compounds can improve the HOR activity providing the probability for using transition metal phosphides as an electrocatalyst for fuel cell anodes.

4. Conclusion

WP, NiP, CoP, Ni-WP, Co-WP and Co-MoP were prepared by the temperature-programmed reaction method and studied for their HOR activities using a half-cell RDE in a 0.5 M H₂SO₄ electrolyte and their passivity in an acidic environment by ICP. The XRD results showed the crystalline phase of the Ni-P and WP compared to the Co-WP and Co-MoP. The surface areas of the phosphides were very similar and no significant change was observed with the incorporation of Ni or Co. The HOR activity was

the highest over the Co–WP. The enhanced HOR activity over the metal phosphides can be attributed to the presence of Ni and Co. The dissolution of the metal phosphides in 0.5 M H₂SO₄ was lower for the WP and Co–WP. Although NiP and CoP showed high dissolution, the tungsten addition significantly enhanced the stability. WP had the function of protecting Co and Ni from corrosion in acidic media.

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