#### CHEMISTRY & SUSTAINABILITY

# CHEMSUSCHEM

#### **ENERGY & MATERIALS**

# **Accepted Article**

Title: Preparation of yolk-shell structured CoxFe1-xP and their enhanced OER performances

Authors: Song Yue, Shanshan Wang, Qingze Jiao, Xueting Feng, Kun Zhan, Yiqing Dai, Caihong Feng, Hansheng Li, Tongying Feng, and Yun Zhao

This manuscript has been accepted after peer review and appears as an Accepted Article online prior to editing, proofing, and formal publication of the final Version of Record (VoR). This work is currently citable by using the Digital Object Identifier (DOI) given below. The VoR will be published online in Early View as soon as possible and may be different to this Accepted Article as a result of editing. Readers should obtain the VoR from the journal website shown below when it is published to ensure accuracy of information. The authors are responsible for the content of this Accepted Article.

To be cited as: ChemSusChem 10.1002/cssc.201901604

Link to VoR: http://dx.doi.org/10.1002/cssc.201901604



WILEY-VCH

www.chemsuschem.org

# Preparation of yolk-shell structured Co<sub>x</sub>Fe<sub>1-x</sub>P and their enhanced OER performances

Song Yue <sup>[a]</sup>, Shanshan Wang <sup>[a]</sup>, Qingze Jiao <sup>[a,b]</sup>, Xueting Feng <sup>[a]</sup>, Kun Zhan <sup>[a]</sup>,

Yiqing Dai<sup>[a]</sup>, Caihong Feng<sup>[a]</sup>, Hansheng Li<sup>[a]</sup>, Tongying Feng<sup>[b]</sup>, and Yun Zhao<sup>\*[a]</sup>

<sup>[a]</sup> School of Chemistry and Chemical Engineering, Beijing Institute of Technology,

Beijing, 100081, China

<sup>[b]</sup> School of Materials and Environment, Beijing Institute of Technology, Zhuhai,

519085, China

\*Corresponding author. School of Chemistry and Chemical Engineering, Beijing Institute of Technology, Beijing 100081, China.

E-mail address: zhaoyun@bit.edu.cn (Y. Zhao).

## **Abstract:**

The design and development of low-cost, highly efficient and stable electrocatalysts to take the place of noble metal catalysts for oxygen evolution reaction (OER) remain a significant challenge. We report the synthesis of yolk-shell structured binary transition metal phosphide ( $Co_xFe_{1-x}P$ ) with different Co/Fe ratios through a phosphidation process using cobalt ferrite as precursors. Furthermore, as-synthesized Co<sub>x</sub>Fe<sub>1-x</sub>P catalysts are used for OER. All yolk-shell structured  $Co_xFe_{1-x}P$  catalysts with different Co/Fe ratios show much better performances than the solid one. It is found that the formation of Co oxides on the catalyst surface during OER and the optimal Co/Fe ratio are critical to their activity. Among the as-prepared  $Co_xFe_{1-x}P$  catalysts, the catalyst with the Co/Fe ratio of 0.47/0.53 (Co<sub>0.47</sub>Fe<sub>0.53</sub>P) exhibits the best performances. Co<sub>0.47</sub>Fe<sub>0.53</sub>P possesses an overpotential of 277 mV at the current density of 10 mA · cm<sup>-2</sup>, a Tafel slope of 37 mV · decade<sup>-1</sup> and superior stability in an alkaline medium. The outstanding performances are partly ascribed to the transfer of valence electrons from Co to P and Fe. The Co<sub>0.47</sub>Fe<sub>0.53</sub>P matrix with excellent conductivity and Fe phosphate which is stable on the surface of the catalyst are also helpful for the OER performance. In addition, the yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  increases the contact area between electrolyte and catalyst. These characteristics of Co<sub>0.47</sub>Fe<sub>0.53</sub>P greatly improve its performances for OER. This optimized binary transition metal phosphide will provide a novel approach for the design of non-precious metal electrocatalysts.

# Introduction

With the increase in energy demand and the intensification of environmental pollution, energy conversion technologies on the basis of renewable energy have caused enormous concern.<sup>[1]</sup> Electrolysis of water to generate oxygen and hydrogen is considered to be the most efficient way to use renewable energy.<sup>[2]</sup> Due to the slow proton coupled electron-transfer reaction and the formation of rigid O-O double bonds, oxygen evolution reaction (OER) usually requires a small overpotential, therefore OER is still considered to be a bottleneck in the overall water decomposition system.<sup>[3]</sup> Up to date, IrO<sub>2</sub> and RuO<sub>2</sub> have been widely used as catalysts for OER because of their high efficiency and low overpotentials.<sup>[4]</sup> However, their applications have been largely limited due to their low reserves and high costs. It is quite necessary to develop OER catalysts with low cost, abundant reserves and superior performances.<sup>[5]</sup> In the past few years, researchers have been working hard to explore new OER catalysts as substitutes for IrO<sub>2</sub> and RuO<sub>2</sub>, and have made some significant progresses.<sup>[6]</sup>

Various metal oxides and metal hydroxides, including cobalt oxides,<sup>[2c, 7]</sup> Ni-Co oxides,<sup>[8]</sup> Ni-Fe-Co oxides,<sup>[9]</sup> nickel hydroxides<sup>[10]</sup> and cobalt-chromium hydroxides<sup>[11]</sup> have been intensively studied as OER catalysts. Qiao and colleagues synthesized hollow Co<sub>3</sub>O<sub>4</sub> microtube arrays by a self-assembly method.<sup>[12]</sup> Bell and colleagues explored the reasons for prominent OER activities of Ni–Fe oxides.<sup>[13]</sup> The large charge transfer resistance of these materials due to their low intrinsic conductivity results in poor OER performances.<sup>[14]</sup> More recently, metal sulfides are used as OER catalysts because of their better intrinsic electrical conductivity. Shanmugam and co-workers prepared CoS<sub>2</sub> (400)/N, S-GO, which possessed more excellent electrocatalytic performance compared to the precious metal catalysts.<sup>[15]</sup> Zhang and co-workers prepared urchin-like NiCo<sub>2</sub>S<sub>4</sub> submicron spheres integrated with micro-sized and nano-sized structures using a

facile one-pot method, which delivered efficient OER activities.<sup>[16]</sup> Although metal sulfides show higher OER performances, their poor structural stability during the OER process limits the implementation in OER-related applications.<sup>[9, 17]</sup> In the past three years, transition metal phosphides (TMPs) have caused researchers' concern because of their excellent OER properties<sup>[9]</sup> (e.g., high activity, outstanding durability, and low cost). Chang et al. synthesized the surface oxidized CoP nanorods/C as OER catalysts. Its overpotential was comparable to IrO<sub>2</sub>, and the Tafel slope was only  $71 \text{ mV} \cdot \text{dec}^{-1}$ , which was smaller than that of IrO<sub>2</sub>.<sup>[18]</sup> Hao et al. found that binary transition metal phosphides (BTMP) had superior electrocatalytic properties due to the availability of more active sites.<sup>[19]</sup> The Co-Fe-P foam reported by Kim et al. possessed outstanding OER activity ( n i=10mA · cm-2 = 330 mV(vs. RHE) ), which was better than that of Co-P  $(\eta_{i=10mA} \cdot m_{-2}=382 \text{ mV})$ .<sup>[20]</sup> The spindle structured Co<sub>0.17</sub>Fe<sub>0.79</sub>P/N-doped carbon reported by Chen et al. possessed good OER performance ( n<sub>i=10mA</sub>. m-2=299 mV).<sup>[21]</sup> Du et al. reported that CoFeP hollow microspheres showed overpotential of 350mV at the current density of 10mA · cm<sup>-2</sup> for OER, which was better than that of Pt/C ( $\eta_{i=10\text{mA} \cdot \text{cm}-2}=510 \text{ mV}$ ).<sup>[22]</sup> Even though a variety of BTMP catalysts show superior performances, it is quite necessary to optimize their structure and composition to exert more excellent properties. In addition, the reaction mechanism of BTMP as OER catalysts is unknown due to their complex compositions. Therefore, further research is still required.

In this work, yolk-shell structured cobalt iron phosphide microspheres ( $Co_xFe_{1-x}P$ ) were prepared by phosphiding yolk-shell structured cobalt ferrites. Their OER performances were compared to those of CoFeP solid spheres (CoFeP-S). The influence of Co/Fe molar ratios for yolk-shell structured  $Co_xFe_{1-x}P$  on the OER properties was also investigated and the optimum Co/Fe molar ratio was determined. Moreover, the reaction mechanism of  $Co_xFe_{1-x}P$  as OER catalysts was discussed. It is found that as-prepared yolk-shell structured  $Co_{0.47}Fe_{0.53}P$ microspheres possessed superior performances, for example, small overpotentials, low Tafel slopes, and good durability. The results indicate that yolk-shell structured  $Co_{0.47}Fe_{0.53}P$ microspheres are promising candidates to substitute the noble metal catalysts for OER.

### **Results and Discussion**

#### The structures and compositions of Co<sub>x</sub>Fe<sub>1-x</sub>P microspheres.

A series of yolk-shell structured  $Co_xFe_{1-x}P$  microspheres were synthesized by the phosphidation process for their corresponding cobalt ferrites. As depicted in Figure 1, X-ray powder diffraction (XRD) patterns of  $Co_xFe_{1-x}P$  are consistent to that of CoP (JCPDS No. 29-0497) except that positions of diffraction peaks are shifted. The peaks at 31.6, 36.3, 46.2, 48.1 and 56.7° correspond to the (011), (111), (112), (211) and (301) reflections respectively.<sup>[9]</sup> These can be attributed to a composite phosphide phase with a CoP-like structure. Compared to XRD patterns of cobalt ferrite precursors (Figure S1), no diffraction peaks for cobalt ferrites are observed for  $Co_xFe_{1-x}P$ . It indicates that  $Co_xFe_{1-x}P$  were successfully synthesized by phosphiding their corresponding cobalt ferrites. X-ray photoelectron spectroscopy (XPS) analysis is used to determine the composition of as-synthesized  $Co_xFe_{1-x}P$ , which are denoted as  $Co_{0.63}Fe_{0.76}P$  (phosphidation of Cobalt ferrite-1),  $Co_{0.47}Fe_{0.53}P$  (phosphidation of Cobalt ferrite-2), and  $Co_{0.24}Fe_{0.76}P$  (phosphidation of Cobalt ferrite-3).



Figure 1. XRD patterns of FeP, CoP, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P and Co<sub>0.24</sub>Fe<sub>0.76</sub>P microspheres.

Low-magnification scanning electron microscope (SEM) images (Figure 2A<sub>1</sub>, B<sub>1</sub> and C<sub>1</sub>) of  $Co_xFe_{1-x}P$  reveal microspheres with the diameter of 1.1~1.8µm (the average particle diameters of  $Co_{0.63}Fe_{0.37}P$ ,  $Co_{0.47}Fe_{0.53}P$  and  $Co_{0.24}Fe_{0.76}P$  microspheres are 1.7, 1.4 and 1.2µm, respectively). As the Fe content increases, the size of  $Co_xFe_{1-x}P$  microspheres decreases. High-magnification SEM images (Figure 2A<sub>2</sub>, B<sub>2</sub> and C<sub>2</sub>) further indicate that  $Co_xFe_{1-x}P$  are microspheres composed of nanoparticles. Compared to SEM images of cobalt ferrite precursors (Figure S3A<sub>1</sub>, A<sub>2</sub>, B<sub>1</sub>, B<sub>2</sub>, C<sub>1</sub> and C<sub>2</sub>), the diameter and morphology of  $Co_xFe_{1-x}P$  microspheres are not changed significantly, but the surface of  $Co_xFe_{1-x}P$  is smoother than that of precursors. However, as-prepared CoP microspheres with the diameter of 1.9-2.2µm exhibit irregular shape, uneven particle size and obvious agglomeration (Figure S4B<sub>1</sub> and B<sub>2</sub>). As-prepared FeP microspheres show similar surface features to  $Co_xFe_{1-x}P$  microspheres with the diameter of 0.8-1.1µm (Figure S4A<sub>1</sub> and A<sub>2</sub>). Obviously, the introduction of Fe benefits the formation of regular  $Co_xFe_{1-x}P$  microspheres and the

spherification ability of  $Co_xFe_{1-x}P$  microspheres is evidently influenced by the content of Fe. If the molar ratios of Co to Fe are lower than 1:1, perfect spheres can be obtained. Energy dispersive X-ray spectroscopy (EDS) mappings (Figure 2A<sub>3</sub>, B<sub>3</sub> and C<sub>3</sub>) indicate that Fe, Co, and P are distributed homogeneously on the  $Co_xFe_{1-x}P$  microspheres. Transmission electron microscopy (TEM) images (Figure 3A<sub>1</sub>, B<sub>1</sub> and C<sub>1</sub>) present that  $Co_xFe_{1-x}P$  microspheres possess a yolk-shell structure with the inner spheres of 300-400 nm in diameter. High-resolution TEM (HRTEM) images (Figure 3A<sub>2</sub>, B<sub>2</sub> and C<sub>2</sub>) also present lattice fringes corresponding to an interplanar distance of 1.90Å, 2.44Å and 2.77Å that can be attributed to the (211) (111) and (011) plane of the  $Co_xFe_{1-x}P$  phase, suggesting the formation of  $Co_xFe_{1-x}P$  microspheres. It is worth noting that Cobalt ferrite-2 microspheres also possess the yolk-shell structure (Figure S5). It indicates that the phosphidation process does not have an influence on the morphology of the samples.  $Co_xFe_{1-x}P$  microspheres maintain the yolk-shell morphology of their precursors. The SEM and TEM images of cobalt iron phosphide solid microspheres (denoted as CoFeP-S) are shown in Figure S6. Most of as-prepared CoFeP-S are solid microspheres with a diameter of 200-400 nm, although a little amount of small solid spheres with a diameter of less than 100nm are observed.



**Figure 2.** SEM images at different magnification and EDS mappings of Co<sub>0.24</sub>Fe<sub>0.76</sub>P (A),Co<sub>0.47</sub>Fe<sub>0.53</sub>P (B) and Co<sub>0.63</sub>Fe<sub>0.37</sub>P microspheres (C).



Figure 3. TEM and HRTEM images of Co<sub>0.24</sub>Fe<sub>0.76</sub>P (A), Co<sub>0.47</sub>Fe<sub>0.53</sub>P (B) and Co<sub>0.63</sub>Fe<sub>0.37</sub>P microspheres (C).

#### The OER catalytic performance evaluation of Co<sub>x</sub>Fe<sub>1-x</sub>P microspheres.

The OER activity of various catalysts (including  $Co_xFe_{1-x}P$ , CoP, FeP, CoFeP-S and commercial IrO<sub>2</sub>) were tested using a rotating disk electrode (RDE) technique in 1 M KOH aqueous solution. Linear sweep voltammograms (LSV) curves of various catalysts are shown in Figure 4A. Compared with cobalt ferrite, CoP, FeP and commercial IrO<sub>2</sub>,  $Co_xFe_{1-x}P$  microspheres show significantly superior performance, which is characterized by a lower overpotential. The overpotential value reaching 10 mA·cm<sup>-2</sup> is typically used as a parameter to evaluate the OER performance of the catalyst, specifically, the lower the overpotential of the catalyst reaching 10 mA·cm<sup>-2</sup>, the better the activity of the catalyst.<sup>[23]</sup> In Figure 4A, the overpotentials of  $Co_xFe_{1-x}P$  catalysts reaching 10 mA·cm<sup>-2</sup> are 297 ( $Co_{0.24}Fe_{0.76}P$ ), 277 ( $Co_{0.47}Fe_{0.53}P$ ) and 288 ( $Co_{0.63}Fe_{0.37}P$ ) mV, respectively, which are much smaller than those of the CoP (340 mV), FeP (480 mV), CoFeP-S (310 mV), and commercial IrO<sub>2</sub> (364 mV), Cobalt ferrite-2 (458 mV). Comparing the properties of  $Co_xFe_{1-x}P$  catalysts with different Co/Fe ratios,  $Co_{0.47}Fe_{0.53}P$  with Co/Fe ratio of 0.47:0.53 shows the most outstanding OER capability with the lowest overpotential of 277 mV.



Figure 4. (A) OER polarization curves and (B) Tafel plots of Co<sub>0.24</sub>Fe<sub>0.76</sub>P, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P, FeP, CoP, Cobalt ferrite-2 microspheres, CoFeP-S, and IrO<sub>2</sub>. (C) Nyquist plots of Co<sub>0.24</sub>Fe<sub>0.76</sub>, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P, CoP, FeP, and Cobalt ferrite-2 microspheres. (D) Plots of the capacitive currents *vs.* the scan rates of Co<sub>0.24</sub>Fe<sub>0.76</sub>P, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P, CoP, FeP, Cobalt ferrite-2 microspheres, and CoFeP-S at 1.28V in 1M KOH.

Generally, a catalyst with a lower Tafel slope will result in a more excellent kinetic process for the OER reaction.<sup>[24]</sup> As can be seen from the Tafel plots (Figure 4B), the Tafel slope of  $Co_{0.47}Fe_{0.53}P$ is 37 mV·dec<sup>-1</sup>, significantly smaller than those of Cobalt ferrite-2 (81 mV·dec<sup>-1</sup>), CoP (66 mV·dec<sup>-1</sup>), FeP (92 mV·dec<sup>-1</sup>),  $Co_{0.63}Fe_{0.37}P$  (44 mV·dec<sup>-1</sup>),  $Co_{0.24}Fe_{0.76}P$  (47 mV·dec<sup>-1</sup>), CoFeP-S (54 mV·dec<sup>-1</sup>), and commercial IrO<sub>2</sub> (69 mV·dec<sup>-1</sup>). The lowest Tafel slope of  $Co_{0.47}Fe_{0.53}P$  may be attributed to the highly active sites on its surface. As the potential increases, the OER rate of  $Co_{0.47}Fe_{0.53}P$  can increase rapidly.<sup>[25]</sup> The lowest Tafel slope of  $Co_{0.47}Fe_{0.53}P$  indicates the best electrocatalytic activity and its potential application.

The ion transport kinetics of these catalysts is analyzed by the electrochemical impedance spectroscopy (EIS) analyses, and results are presented in Figure 4C. The simplified equivalent electrical circuit fitting the Nyquist plots are presented in Figure S8,<sup>[26]</sup> and the parameters R<sub>s</sub>, R<sub>ct</sub> and C<sub>dl</sub> represent the uncompensated series resistance, the charge transfer resistance, and the accompanying double-layer capacitance, respectively. The R<sub>s</sub> values of Co<sub>0.47</sub>Fe<sub>0.53</sub>P, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.24</sub>Fe<sub>0.76</sub>P, CoP, Cobalt ferrite-2 and FeP microspheres are similar, indicating a consistent experimental configuration. As can be seen from Figure 4C, the R<sub>ct</sub> values follow the order of Co<sub>0.47</sub>Fe<sub>0.53</sub>P<br/>Co<sub>0.63</sub>Fe<sub>0.37</sub>P</br>Co<sub>0.47</sub>Fe<sub>0.53</sub>PCo<sub>0.24</sub>Fe<sub>0.76</sub>PCoPCobalt ferrite-2FeP. The minimum R<sub>ct</sub> indicates a high charge transfer efficiency occurs at the Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres owing to its abundant

active sites and excellent electronic conductivity, which facilitates the improvement of charge transport capability and further improves OER performances.<sup>[26]</sup>

Cyclic voltammetry (CV) was performed with different scan rates in the non-Faradaic regions to measure  $C_{dl}$  (in Figure S9),<sup>[20]</sup> which is proportional to the electrochemical active surface area (ECSA). As shown in Figure 4D,  $C_{dl}$  decreases in the order of  $Co_{0.47}Fe_{0.53}P$  (98 mF·cm<sup>-2</sup>) >  $Co_{0.63}Fe_{0.37}P$  (86 mF·cm<sup>-2</sup>) >  $Co_{0.24}Fe_{0.76}P$  (62 mF·cm<sup>-2</sup>) > CoP (53 mF·cm<sup>-2</sup>) > CoFeP-S (9  $mF \cdot cm^{-2}$ ) > Cobalt ferrite-2 (5  $mF \cdot cm^{-2}$ ) > FeP (2  $mF \cdot cm^{-2}$ ). Therefore, Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres obviously have more active sites than other catalysts, which is useful to improve the OER performances. More importantly, the Cdl values of CoxFe1-xP are much higher than those of CoP and FeP, indicating that the interaction between Co and Fe may cause more active sites.<sup>[27]</sup> It is worth noting that the C<sub>dl</sub> of yolk-shell structured Co<sub>x</sub>Fe<sub>1-x</sub>P (62, 86, 98 mF·cm<sup>-2</sup>) microspheres are also much larger than that of CoFeP-S (9 mF·cm<sup>-2</sup>), suggesting the enormous ECSA of yolk-shell structure. Meanwhile, the mass activity, and turnover frequency (TOF) are also calculated (calculation methods are seen in the experimental section) in order to measure the inherent activity of different catalysts.<sup>[28]</sup> As seen in Table 1, the mass activity of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres is 238  $A \cdot g^{-1}$ , which is significantly larger than other catalysts. It indicates that the yolk-shell structured Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres possess the most excellent catalytic performance. Furthermore, the TOF values of various samples are compared. The premise of this evaluation is to assume that all Co and Fe ions are catalytically active.<sup>[27]</sup> As presented in Table 1, the TOF of Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P, Co<sub>0.24</sub>Fe<sub>0.76</sub>P, CoP and FeP at the overpotentials of 290mV are 0.0053, 0.0107, 0.00315, 0.00075 and 0.000033 s<sup>-1</sup>, respectively. The  $Co_{0.47}Fe_{0.53}P$  microspheres have the largest TOF, suggesting its enhanced OER performances. In summary, the excellent OER activity of yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  microspheres is ascribed to the large active area, highly active sites in unit area, and high turnover frequency.

microspheres.			
Catalyst	$\eta$ at J=10mA $\cdot$ cm $^{-2}[mV]$	mass activity at η=0.29V[A·g <sup>-1</sup> ]	TOF at η=0.29V[s <sup>-1</sup> ]
$Co_{0.63}Fe_{0.37}P$	288	117	0.0053
$Co_{0.47}Fe_{053}P$	277	238	0.0107
$Co_{0.24}Fe_{0.76}P$	297	71	0.00315
CoP	340	17	0.00075
FeP	480	0.7	0.000033

Table 1. OER Activity Data for	Co <sub>0.24</sub> Fe <sub>0.76</sub> P, Co <sub>0.63</sub> Fe <sub>0.37</sub> P, Co <sub>0.47</sub> Fe <sub>0.53</sub> P, FeP and CoP
	minnomhana

The long-term stability is a crucial concern for all catalysts. The commercial IrO<sub>2</sub> catalyst has poor stability in a strong alkaline environment due to the strong oxidation process of the OER reaction.<sup>[29]</sup> First of all, we tested the electrochemical stability of as-prepared  $Co_{0.47}Fe_{0.53}P$  catalyst by the chronoamperometry (i-t) method. As shown in Figure 5A, the current density retention of  $Co_{0.47}Fe_{0.53}P$  catalyst after 11 h of testing is almost 98 %, while it is 55% for the commercial IrO<sub>2</sub> electrode. It reveals the enhanced stability of  $Co_{0.47}Fe_{0.53}P$  catalyst. By comparing the LSV curves before and after the stability test, the overpotential of the  $Co_{0.47}Fe_{0.53}P$  catalyst reaching 10 mA • cm<sup>-</sup> slightly increases by 3 mV (Figure S10A), while the IrO<sub>2</sub> catalyst increases by 30 mV (Figure S10B), further demonstrating the superior stability of  $Co_{0.47}Fe_{0.53}P$  catalyst. Compared with  $Co_{0.47}Fe_{0.53}P$ , less than 50% of the current density retention rates after only 30000 s of OER for CoP and FeP (Figure 5A) exhibits the poor stability of monometallic phosphides. Wang et al. also proposed that for cobalt iron phosphide, stable iron phosphates during the OER can contribute to the stability and activity of the active sites (cobalt oxides).<sup>[30]</sup> Therefore, it is preliminarily concluded that the bimetallic system contributes to the stabilization of the active sites. However, further studies are still required to reveal the deeper mechanism for this stabilization. Furthermore, the stability of  $Co_{0.47}Fe_{0.53}P$  catalyst was investigated by the accelerated degradation test. By comparing LSV curves before and after continuous CV for 1000 cycles (Figure 5B), the OER activity of  $Co_{0.47}Fe_{0.53}P$  catalyst does not change significantly, and the overpotential reaching 10 mA · cm<sup>-2</sup> slightly increases by 17 mV. All of the above tests indicate that as-prepared  $Co_{0.47}Fe_{0.53}P$  catalyst possesses the excellent activity and stability during the OER process. In addition, compared with Co-, Fe-, and Ni-based oxide/phosphide catalysts reported in literatures (Table S1), yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  microspheres exhibit the best OER performances.



**Figure 5.** (A) Chronoamperometric test of Co<sub>0.47</sub>Fe<sub>0.53</sub>P, CoP, FeP microspheres, and IrO<sub>2</sub> at a constant overpotential. (B) Accelerated stability of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres.

The catalytic activity of  $Co_xFe_{1-x}P$  microspheres may be associated with the valence of elements and coordination environment of the  $Co_xFe_{1-x}P$  catalyst.<sup>[5]</sup> In order to understand the reasons of the outstanding catalytic performance of  $Co_{0.47}Fe_{0.53}P$ , X-ray photoelectron spectroscopy (XPS) analysis is executed and compared with  $Co_{0.63}Fe_{0.37}P$  and  $Co_{0.24}Fe_{0.76}P$  (Figure 6A, B and C). For P 2p spectra, the binding energies of 129.4 and 130.3 eV are assigned to the P  $2p_{3/2}$  and P  $2p_{1/2}$  of phosphides, respectively. There are also two peaks located at 133.9 and 134.8 eV assigned to the phosphates, which could be caused by oxidation. For Fe 2p spectra, two peaks at 723.9 and 710.8 eV correspond to the Fe  $2p_{1/2}$  and Fe  $2p_{3/2}$ , while the peaks of Fe<sup>2+</sup> and Fe<sup>3+</sup> appear at 712.8 and 710.2 eV, respectively. According to previous reports, the surface Fe of the  $Co_{0.47}Fe_{0.53}P$  catalyst tends to bind with phosphate.<sup>[30]</sup> In comparison to the Fe  $2p_{3/2}$ , P  $2p_{3/2}$  and Co  $2p_{3/2}$  reference peaks,<sup>[20, 31]</sup> the P  $2p_{3/2}$  and Fe  $2p_{3/2}$  has a positive shift of 0.8 eV. The shifts demonstrate a cationic state of Co atoms, and it is consistent with the anionic state of the P and Fe atoms by electron transfer from Co to P and Fe<sup>[19]</sup>, which is responsible for the enhanced catalytic activity of  $Co_{0.47}Fe_{0.53}P$  microspheres.<sup>[32]</sup> In addition, positive shifts of binding energies signify the reduced

electron occupation leading to a robust electron-accepting site. Co  $2p_{3/2}$  binding energies of  $Co_{0.47}Fe_{0.53}P$  exhibit a larger positive shifts (0.8 eV) compared to  $Co_{0.63}Fe_{0.37}P$  (0.5 eV) and  $Co_{0.24}Fe_{0.76}P$  (0.3 eV), which means that more electron transfer take place in the  $Co_{0.47}Fe_{0.53}P$ .<sup>[19]</sup> Therefore, the Co of  $Co_{0.47}Fe_{0.53}P$  is able to act as a more robust electron-accepting site.<sup>[20]</sup> In another words, the high-valence state of Co ions enhances the OH sorption capacity of the electrocatalyst,<sup>[31]</sup> which is greatly beneficial to improve the performance of OER. Therefore,  $Co_{0.47}Fe_{0.53}P$  microspheres exhibit better catalytic activity for OER.



Figure 6 XPS spectrum of Co 2p, Fe 2p, and P 2p for  $Co_{0.24}Fe_{0.76}P(A)$ ,  $Co_{0.47}Fe_{0.53}P(B)$  and  $Co_{0.63}Fe_{0.37}P$  microspheres (C).

It should be noted that the surface area and pore size distribution are critical aspects for improving OER performances. Therefore, the surface characteristics of  $Co_{0.47}Fe_{0.53}P$  were investigated by the N<sub>2</sub> adsorption-desorption isotherm and pore size distribution curves. As depicted in Figure S11B, the adsorption-desorption isotherm of  $Co_{0.47}Fe_{0.53}P$  shows a type-II isotherm with H3 hysteresis loop. The pore size distribution of  $Co_{0.47}Fe_{0.53}P$  shows that the pore size is mainly distributed over a wide range of 25-200 nm with a predominant peak of 56 nm, representing the coexistence of mesopores and macropores in the samples. According to previously published works, abundant mesopores can serve as a reservoir for electrolytes, facilitating the internal reflex space for fast ion transmission and related reactions;<sup>[27]</sup> while the presence of macropores can provide open spaces to the infiltration of electrolyte, and facilitate the efficient diffusion of gas products (O<sub>2</sub>).<sup>[33]</sup> This type of hierarchical porous structure can provide a large amount of active sites on the surface of the electrocatalysts and facilitate mass transport channels for the reactions.<sup>[25]</sup> Based on

the Barrett-Joyner-Halenda (BJH) and the Brunauer-Emmett-Teller (BET) methods, the pore volumes of  $Co_{0.63}Fe_{0.37}P$ ,  $Co_{0.47}Fe_{0.53}P$  and  $Co_{0.24}Fe_{0.76}P$  are calculated to be 0.139, 0.219 and 0.226 cm<sup>3</sup>·g<sup>-1</sup>, respectively. The specific surface areas of  $Co_{0.63}Fe_{0.37}P$ ,  $Co_{0.47}Fe_{0.53}P$  and  $Co_{0.24}Fe_{0.76}P$  are 24.323, 24.389 and 24.352 m<sup>2</sup>·g<sup>-1</sup>, respectively. By comparison with the pore volume, specific surface area and the pore size distribution (Figure S11), it can be found that different  $Co_xFe_{1-x}P$  samples possess similar pore size distribution, similar specific surface area, and a little bit different pore volume, which may be due to their similar structural characteristics. However, the specific surface area of CoFeP-S is calculated to be 17.172 m<sup>2</sup>·g<sup>-1</sup>. Compared with CoFeP-S, the yolk-shell structured  $Co_xFe_{1-x}P$  microspheres possess larger specific surface area. Thus, the abundant porosity and the suitable specific surface area of  $Co_{0.47}Fe_{0.53}P$  microspheres contribute to the increase of electrolyte-electrode contact area and the reduction of diffusion path for ions,<sup>[34]</sup> thereby improving electrochemical performances.

#### The OER catalytic mechanism analysis of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres.

CV scans were performed in order to explore the conversion of  $Co_{0.47}Fe_{0.53}P$  during the OER. Figure S12 shows the CV curves of  $Co_{0.47}Fe_{0.53}P$ , FeP and CoP microspheres. It is worth noting that the CV behavior of  $Co_{0.47}Fe_{0.53}P$  is similar to that of CoP, which proves that cobalt ions are vigorously involved in the reaction. At the same time, it is observed that there is no peak in the catalytic range (1.4 - 1.8V) in the situation of FeP, so it is inferred that the influence of iron ions in the catalytic process may be mostly synergistic.<sup>[35]</sup> According to the possible OER catalytic mechanism of Co-based catalysts in alkaline medium proposed by Chou et al,<sup>[36]</sup> the electro transfer peaks in the range of 1.1 and 1.4 V in the CV curve of  $Co_{0.47}Fe_{0.53}P$  may correspond to the

conversion of  $Co(OH)_2 + OH^- \rightarrow CoOOH + H_2O + e^-$ . Besides, at higher potential, CoOOH can be

further oxidized to Co oxides with outstanding OER performances.<sup>[37]</sup> Based on previous reports,<sup>[30, 35a]</sup> it can be speculated that Co oxides formed on the surface of catalysts are main active sites for the OER.



# Figure 7 High resolution spectra of Co 2p, Fe 2p and P 2p for Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres after 11 h stability test.

To confirm the conversion of Co<sub>0.47</sub>Fe<sub>0.53</sub>P, EDS, SEM, XPS, TEM, and HRTEM tests were performed after the long-term durability test for 11 h. As depicted in Figure S13A and B, the initial particle size and surface morphology of Co<sub>0.47</sub>Fe<sub>0.53</sub>P are maintained after 11 h. It is worth noting that the EDS elemental mapping in Figure S13C exhibits the uniform distribution of Fe, Co, P and O, where the significant decrease of P element and the uniform distribution of O elements may be related to the formation of metal oxide. In order to investigate the electronic state conversions after the 11 h durability test, the XPS analysis was performed (Figure 7). For Co 2p spectra, the presence of Co 2p<sub>3/2</sub> peaks at 780.3 and 782.3 eV probably indicates the change of Co phosphides to Co phosphates and Co oxides during the long-term stability test. According to previous reports, Co oxides formed on the surface of the catalyst during the OER are primarily in charge of high reactivity, while Co phosphates contribute little to the activity of the catalysts.<sup>[30]</sup> For P 2p spectra, the P  $2p_{1/2}$ and P 2p<sub>3/2</sub> peaks corresponding to phosphides(in Figure 6B) disappear, while only two P 2p peaks assigned to phosphates exist, which is coincident with the change of the Co 2p spectrum. The oxidation of phosphides during the 11 h durability test agrees well with previously published work.<sup>[30, 38]</sup> No significant peak changes for Fe 2p are observed after durability test, suggesting that the structure of Fe phosphate is maintained during the OER test. These stable Fe phosphate might be helpful to the durability of the catalyst.<sup>[30]</sup> Noting that Fe phosphate is a poor catalyst, nevertheless, the existence of Fe phosphate can boost the reactivity of Co oxides through probable synergistic effects.<sup>[30]</sup> According to previous reports, the phosphate groups on the surface of the catalyst possess the enhanced surface wettability, which contributes to form more open coordinate sites, thereby promoting the OH<sup>-</sup> adsorption capacity of the catalyst.<sup>[39]</sup> At the same time, the phosphate ion group on the electrocatalytically active interface can improve the interfacial protontransfer kinetics, assisting the deprotonation step from -OOH to -OO\* on the active center of cobalt oxides during the OER.<sup>[40]</sup> It can be seen from Figure 8A that the overall yolk-shell structure of the microspheres do not change substantially after 11h test. Nevertheless, as observed in detailed figure (Figure 8B), a layer of substances with uneven thickness are formed on the surface of microspheres (denoted as S-A). In the HRTEM image (Figure 8C) of the S-A region, the (311) and (111) crystal plane of Co<sub>3</sub>O<sub>4</sub> with an interplanar spacing of 2.45Å and 4.62Å are clearly observed, at the same time, a large area of amorphous portion are detected in the S-A region. The amorphous substances might be cobalt/iron phosphates.<sup>[41]</sup> Based on the analysis of TEM and HRTEM tests, it can be inferred that Co<sub>3</sub>O<sub>4</sub> formed on the surface of the microspheres serves as active sites during the OER process, consistent with the previous reports.<sup>[41-42]</sup> In addition, the formation of surface S-A can effectively increase the contact area between the active sites and the electrolyte since the S-A are fluffy and uneven, which is beneficial to the improvement of OER performance.



Figure 8 TEM and HRTEM images of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres after 11h stability test.

The changes of  $Co_{0.47}Fe_{0.53}P$  microspheres before and after the 11 h durability test match our speculation and further reveal that Co oxides formed on the surface of catalysts can be the main active sites for OER, while iron ions act through possible synergistic effects. Moreover, the OER reactivity of the  $Co_{0.47}Fe_{0.53}P$  catalyst is much higher than that of the cobalt ferrite. This phenomenon can be ascribed to the formation of an outer layer/inner layer of  $CoO_x/CoFeP$  structure during OER as reported in previous literature.<sup>[35a, 41, 43]</sup> Based on the published work<sup>[36]</sup> and our results, the OER catalytic mechanism of  $Co_xFe_{1-x}P$  catalysts in an alkaline media is proposed as shown in Figure 9.



Figure 9 Proposed mechanism of OER catalysis of Co<sub>x</sub>Fe<sub>1-x</sub>P.

Firstly, Co atoms on the surface of  $Co_xFe_{1-x}P$  are partially oxidized to  $Co(OH)_2$ , which are then oxidized to form  $Co_3O_4$  as the active sites. These active sites can accelerate the oxidation of

absorbed  $OH^-$  into  $O_2$ . Then, at a higher potential,  $Co_3O_4$  will be further oxidized to form  $CoO_2$ , which are more efficient species for OER process.<sup>[43]</sup>

The details are as follows. During the OER process, the function of the active sites mainly includes adsorption of the elementary species (O, OH) and catalyzing the conversion reaction of the adsorbed species to  $O_2$ . During the elementary step, the active sites adsorb the elementary species of O and OH according to the following scheme:<sup>[44]</sup>

$$\mathbf{OH}^- + \mathbf{*} \to \mathbf{OH}^* + \mathbf{e}^- \tag{1}$$

$$OH^* + OH^- \to O^* + H_2O + e^-$$
 (2)

As the species are adsorbed onto the catalytic active sites, the conversion reaction from the elementary species ( $O^*$ ,  $OH^*$ ) and the intermediate ( $OOH^*$ ) to  $O_2$  proceeds continuously at the active sites:

$$0^* + 0H^- \to 00H^* + e^-$$
 (3)

$$00H^* + 0H^- \to 0_2 + H_20 + e^-$$
(4)

During this step, the active sites can promote the production of  $O_2$  by reducing the energies required for the conversion reaction.

At the same time, the phosphate ion group on the electrocatalytically active interface can promote the OH<sup>-</sup> adsorption capacity of the catalyst<sup>[39]</sup> and assist the deprotonation step from -OOH to -OO\* on the active center of cobalt oxides during the OER.<sup>[40]</sup> In addition, the binary transition metal phosphides of the inner layer possess superior conductivity to cobalt ferrite (as shown in Figure 4C), which can provide conductive supports for the oxide active sites of the outer layer, thereby promoting the electron transfer;<sup>[9, 30, 35a]</sup> On the other hand, the binary transition metal phosphides help to stabilize the active sites on the outer layer, preventing their depletion and subsequent activity degradation.<sup>[35a]</sup> In summary, the enhanced adsorption capacity and the interfacial proton-transfer kinetics of the phosphate groups in combination with the superior conductivity and stability of CoFeP and the catalytic conversion ability of cobalt oxides result in the improvement of the catalytic activity for the Co<sub>x</sub>Fe<sub>1-x</sub>P catalyst. However, further research is needed to investigate the electron-transfer between the inner layer phosphide and outer layer oxides during OER and the synergistic interactions between Co and Fe to promote OER.

#### Conclusions

In summary, extremely efficient and stable yolk-shell structured  $Co_xFe_{1-x}P$  catalysts for the OER were successfully fabricated by a template method and phosphidation process. Among asprepared  $Co_xFe_{1-x}P$  (including  $Co_{0.63}Fe_{0.37}P$ ,  $Co_{0.47}Fe_{0.53}P$  and  $Co_{0.24}Fe_{0.76}P$ ), CoP, FeP, CoFeP-S, cobalt ferrite microspheres and commerical IrO<sub>2</sub>, yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  microspheres exhibit the most excellent OER performances including small overpotential (277 mV), low Tafel slope (37 mV · decade<sup>-1</sup>), and superior stability in an alkaline medium. The Co oxides formed on the surface of catalysts during OER are found to be the main active sites, while the existence of inner layer CoFeP and surface Fe phosphate may also improve the OER capability of the catalyst. The transfer of valence electrons from Co to P and Fe can enhance the OH<sup>-</sup> adsorption capacity of the

catalyst. In addition, the unique yolk-shell structure of  $Co_{0.47}Fe_{0.53}P$  increases the contact area between the electrolyte and the active material, which is also beneficial for the OER. This work exhibits huge potential for obtaining a range of materials with controllable compositions through scalable synthesis. Together with the excellent performance and low cost, yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  microspheres are expected to be a promising alternative for precious metal-based electrocatalysts.

## **Experimental Section**

#### Materials

All chemicals were of analytical grade and used without further purification. Anhydrous glucose, cobalt sulfate heptahydrate ( $CoSO_4 \cdot 7H_2O$ ), ferrous ammonium sulfate hexahydrate ( $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$ ) Super-P and ethanol were purchased from Sinopharm Chemical Reagent Co. Ltd, (Beijing, China). Sodium hypophosphite (NaH<sub>2</sub>PO<sub>2</sub>) were purchased from Aladdin Reagent Co. Ltd (Shanghai, China). Nafion (5 wt%) were purchased from Alfa Aesar Chemical Co. Ltd, (Shanghai, China).

#### Synthesis of yolk-shell structured Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres

First of all, cobalt ferrite microspheres were synthesized according to a previously reported method with some modification.<sup>[45]</sup> In brief, 15 g anhydrous glucose, 15 mM Fe(NH<sub>4</sub>)<sub>2</sub>·(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O and 30 mM CoSO<sub>4</sub>·7H<sub>2</sub>O were dissolved in 100mL deionized water. The mixture was stirred for 40 min and then transferred into a stainless-steel Teflon-lined autoclave. The autoclave was sealed and maintained at 160°C for 24 h. The precipitates were collected, washed using water, then dried at 80°C for 6 h. As-obtained black solids were dispersed in a porcelain boat, placed in a muffle furnace, raised to 450°C at a heating rate of  $2^{\circ}C \cdot \min^{-1}$ , calcined for 3h, and then raised to 550°C at a heating rate of 2°C·min<sup>-1</sup>, calcined for 3h. The final product was designated as cobalt ferrite-2. When the mole ratio of  $Fe(NH_4)_2 \cdot (SO_4)_2 \cdot 6H_2O$  and  $CoSO_4 \cdot 7H_2O$  were 1/4 and 2/1, the final products were designated as cobalt ferrite-1 and cobalt ferrite-3, respectively. For comparison, iron/cobalt oxide was prepared by dissolving 45 mM of Fe(NH<sub>4</sub>)<sub>2</sub>·(SO<sub>4</sub>)<sub>2</sub>·6H<sub>2</sub>O or 45mM of CoSO<sub>4</sub>·7H<sub>2</sub>O with 15g anhydrous glucose in 100mL deionized water following the same reaction conditions. In the typical metal phosphide synthesis process,<sup>[9, 42, 46]</sup> 400mg of NaH<sub>2</sub>PO<sub>2</sub> and 10mg of cobalt ferrite-2 were separately placed in a tube furnace with NaH<sub>2</sub>PO<sub>2</sub> at the upstream position, then raised to 350°C at a heating rate of 5°C min<sup>-1</sup>. The phosphidation process was run at  $350^{\circ}$ C for 3h in the N<sub>2</sub> flow. NaH<sub>2</sub>PO<sub>2</sub> thermally decomposed and released PH<sub>3</sub> gas at above 200°C. Upon heating, since NaH<sub>2</sub>PO<sub>2</sub> was at the upstream of the tube furnace, the PH<sub>3</sub> gas released by thermal decomposition of NaH<sub>2</sub>PO<sub>2</sub> was transported by the N<sub>2</sub> gas stream to Cobalt ferrite-2 at the downstream. The yolk-shell structured Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres were formed by the reaction of PH<sub>3</sub> with Cobalt ferrite-2.<sup>[46]</sup> The FeP, CoP, Co<sub>0.63</sub>Fe<sub>0.37</sub>P and Co<sub>0.24</sub>Fe<sub>0.76</sub>P were prepared by replacing cobalt ferrite-2 with iron oxide, cobalt oxide, cobalt ferrite-1 and cobalt ferrite-3, following the same phosphidation process.

For comparison, solid microspheres of CoFeP-S was prepared by phosphiding cobalt ferrite solid microspheres. Cobalt ferrite solid microspheres were synthesized based on the published method.<sup>[47]</sup> 90 mM of NH<sub>4</sub>Ac, 7.5 mM Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and 15 mM Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O were dissolved in 50 mL ethylene glycol. Then the mixture was transferred into a stainless-steel Teflon-lined autoclave. The autoclave was sealed and maintained at 180°C for 24 h. After cooling down, the

precipitates were collected, washed and dried at 80°C for 6 h. CoFeP-S was then obtained using the same phosphidation process as yolk-shell structured  $Co_xFe_{1-x}P$  microspheres.

#### Characterizations

The structures of catalysts were analyzed by XRD, which was carried out using  $CuK_{\alpha}$  radiation. The morphology and size of samples were observed using SEM and TEM. The crystalline structure and lattice fringes of the catalysts were observed by HRTEM. The valence analysis, elemental analysis and Co/Fe molar ratios were performed by XPS. The elemental distribution information was collected by EDS. The pore size distribution and surface area of catalysts were studied by BET. **Electrochemical measurements** 

Electrochemical measurements were conducted on a CHI760E electrochemical workstation (CH Instruments, Inc., Shanghai). All the tests were conducted using tri-electrode system, with strong alkaline medium (1M KOH) as electrolyte, a platinum sheet as pair electrode, a Hg/ HgO electrode as reference electrode and a glassy carbon (GC) RDE as working electrode. The measured potentials vs. Hg/HgO were transformed into the RHE scale based on the following formula:

$$E_{RHE} = E_{Hg/Hg0} + 0.098 + PH \cdot 0.0591 \tag{5}$$

Working electrode was prepared as follows: The samples (5mg), Super-P (5mg) and Nafion (100 $\mu$ L, 5wt%) were dispersed into ethanol (900 $\mu$ L) by sonication for 1h to form a homogeneous ink. The electrocatalyst suspension (10 $\mu$ L) was loaded onto a GC electrode, causing a mass loading of 0.5 mg·cm<sup>-2</sup>. The control materials, including Co<sub>0.63</sub>Fe<sub>0.37</sub>P, Co<sub>0.24</sub>Fe<sub>0.76</sub>P, CoP, FeP, IrO<sub>2</sub>, and cobalt ferrite, were studied using the identical mass loading.

Before the measurements, the GC electrode was polished with alumina powder. The CV scans were applied using a scan rate of  $100 \text{mV} \cdot \text{s}^{-1}$  until the signals were stable. The polarization curves were obtained by the LSV scans from 0.2 to 0.8 V(vs. Hg/ HgO) using the scan rate of 5 mV  $\cdot \text{s}^{-1}$ . The GC electrode was stirred at 1600 rpm constantly to release the emerging oxygen bubbles during the testing. The EIS measurements were carried out at room temperature under the same condition. Tafel slopes were calculated on the basis of plot overpotential ( $\eta$ ) – log(J). CV scans for 1000 cycles were performed with a scanning rate of  $100 \text{mV} \cdot \text{s}^{-1}$  to test the accelerated stability of catalysts. The durability was measured by chronoamperometry. Cyclic voltammograms at distinct scan rates were measured to investigate the ECSA of the catalysts.

The overpotential ( $\eta$ ), turnover frequency (TOF), and mass activity (A $\cdot g^{-1}$ ) were calculated as follows:

$$\eta = E(vs. RHE) - 1.23V \tag{6}$$

Mass activity = 
$$J/m$$
 (7)

$$TOF = SJ/(4nF)$$
(8)

Where m represented the mass of the loaded catalysts  $(mg \cdot cm^{-2})$ ; J represented the measured current density  $(mA \cdot cm^{-2})$ ; n represented the molar amount of ions, supposing all Co and Fe ions were active for OER; S represented the surface area of GC RDE (0.196 cm<sup>2</sup>); F represented the Faraday constant (96485.3 C · mol<sup>-1</sup>).<sup>[24]</sup>

# **Associated Content**

#### Supporting Information

XRD, SEM and TEM of cobalt ferrite microspheres; SEM and TEM of FeP and CoP microspheres; XRD, SEM and TEM of CoFeP-S; EDS spectrum of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres; CV measurements at distinct scan rates and equivalent circuit of Co<sub>0.24</sub>Fe<sub>0.76</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P, Co<sub>0.63</sub>Fe<sub>0.37</sub>P, CoP, FeP, Cobalt ferrite-2 microspheres and CoFeP-S; LSV curves of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres and IrO<sub>2</sub> before and after 11h stability test for OER; BET of Co<sub>0.24</sub>Fe<sub>0.76</sub>P, Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres; CV curves of Co<sub>0.47</sub>Fe<sub>0.53</sub>P, microspheres; SEM and EDS analysis of Co<sub>0.47</sub>Fe<sub>0.53</sub>P microspheres after 11h stability test; A table of comparison of OER electrocatalytic parameters with the reported literatures.

# Acknowledgements

The authors of this paper would like to thank the National Natural Science Foundation of China (No. 21376029) and the Analysis & Testing Center, Beijing Institute of Technology for sponsoring this research. This research was also supported by Beijing Key Laboratory for Chemical Power Source and Green Catalysis, Beijing Institute of Technology.

**Keywords:** Transition metal phosphides, Yolk-shell structured microspheres, OER, Noble-metal-free electrocatalyst, Alkaline media

# References

- a) J. Yan, Z. Yao, J. Mietek, Q. S. Zhang, *Chemical Society Reviews* 2015, *46*, 2060-2086; b) M. S.
   Faber, S. Jin, *Energy & Environmental Science* 2014, *7*, 3519-3542; c) Q. Li, T. Wang, D. Havas,
   H. Zhang, P. Xu, J. Han, J. Cho, G. Wu, *Advanced Science* 2016, *3*, 1600140.
- [2] a) H. Xiaopeng, C. Fangyi, Z. Tianran, Y. Jingang, H. Yuxiang, C. Jun, Advanced Materials 2014, 26, 2047-2051; b) T. Chun, C. Ningyan, P. Zonghua, X. Wei, S. Xuping, Angew Chem Int Ed Engl 2015, 54, 9351-9355; c) J. Wang, W. Cui, Q. Liu, Z. Xing, A. M. Asiri, X. Sun, Advanced Materials 2016, 28, 215-230; d) J. Tian, Q. Liu, N. Cheng, A. M. Asiri, X. Sun, Angewandte Chemie 2014, 126, 9731-9735.
- [3] a) T. Reier, Z. Pawolek, S. Cherevko, M. Bruns, T. Jones, D. Teschner, S. Selve, A. Bergmann, N. N. Hong, R. Schlögl, *Journal of the American Chemical Society* 2015, *137*, 150910115801001;
  b) B. Wurster, D. Grumelli, D. Hötger, R. Gutzler, K. Kern, *Journal of the American Chemical Society* 2016, *138*, 3623; c) X. F. Lu, P. Q. Liao, J. W. Wang, J. X. Wu, X. W. Chen, C. T. He, J. P. Zhang, G. R. Li, X. M. Chen, *Journal of the American Chemical Society* 2016, *138*, jacs.6b03125;
  d) L. Gong, D. Ren, Y. Deng, B. S. Yeo, *Acs Applied Materials & Interfaces* 2016, *8*, 15985.
- [4] a) Y. Pi, N. Zhang, S. Guo, J. Guo, X. Huang, *Nano Letters* 2016, *16*, 4424-4430; b) T. Reier, M. Oezaslan, P. Strasser, *Acs Catalysis* 2012, *2*, 1765–1772; c) X. Qiao, S. Liao, R. Zheng, Y. Deng, H. Song, D. Li, *Acs Sustainable Chemistry & Engineering* 2016, *4*, 4131-4136.
- [5] T. Zhang, J. Du, P. Xi, C. Xu, Acs Applied Materials & Interfaces 2016, 9.
- [6] I. Roger, M. A. Shipman, M. D. Symes, *Nature Reviews Chemistry* **2017**, *1*, 0003.

- [7] a) A. Bergmann, E. Martinezmoreno, D. Teschner, P. Chernev, M. Gliech, J. F. de Araújo, T. Reier, H. Dau, P. Strasser, *Nature Communications* 2015, *6*, 8625; b) A. Ganassin, A. Maljusch, V. Colic, L. Spanier, K. Brandl, W. Schuhmann, A. Bandarenka, *Acs Catalysis* 2016, *6*; c) E. L. Tae, J. Song, A. R. Lee, C. H. Kim, S. Yoon, I. C. Hwang, G. K. Min, K. B. Yoon, *Acs Catalysis* 2015, *5*, 150814121556001.
- [8] a) L. Han, X. Y. Yu, X. W. Lou, Advanced Materials 2016, 28, 4601-4605; b) Y. Yang, H. Fei, G. Ruan, C. Xiang, J. M. Tour, Acs Nano 2014, 8, 9518-9523.
- [9] K. Liu, C. Zhang, Y. Sun, G. Zhang, X. Shen, F. Zou, H. Zhang, Z. Wu, E. C. Wegener, C. J. Taubert, Acs Nano 2017, 12, 158-167.
- [10] H. Liang, F. Meng, M. Caban-Acevedo, L. Li, A. Forticaux, L. Xiu, Z. Wang, S. Jin, *Nano Lett* 2015, 15, 1421-1427.
- [11] C. Dong, X. Yuan, X. Wang, X. Liu, W. Dong, R. Wang, Y. Duan, F. Huang, *Journal of Materials Chemistry A* **2016**, *4*.
- [12] Y. P. Zhu, T. Y. Ma, M. Jaroniec, S. Z. Qiao, *Angewandte Chemie International Edition* 2016, 56, 1324.
- [13] M. W. Louie, A. T. Bell, Journal of the American Chemical Society **2013**, 135, 12329-12337.
- [14] a) Y. Matsumoto, E. Sato, Materials Chemistry & Physics 1986, 14, 397-426; b) B. S. Yeo, A. T. Bell, Journal of the American Chemical Society 2011, 133, 5587-5593.
- [15] S. Shanmugam, P. Ganesan, M. Prabu, J. Sanetuntikul, Acs Catalysis 2015, 5, 3625-3637.
- [16] Z. Zhang, X. Wang, G. Cui, A. Zhang, X. Zhou, H. Xu, L. Gu, Nanoscale 2014, 6, 3540-3544.
- [17] A. Dutta, N. Pradhan, Journal of Physical Chemistry Letters 2016, 8, 144-152.
- [18] J. Chang, Y. Xiao, M. Xiao, J. Ge, C. Liu, W. Xing, Acs Catalysis **2015**, *5*, 6874-6878.
- [19] J. Hao, W. Yang, Z. Zhang, J. Tang, *Nanoscale* **2015**, *7*, 11055-11062.
- [20] H. W. Kim, S. K. Oh, E. A. Cho, H. S. Kwon, *Acs Sustainable Chemistry & Engineering* **2018**, *6*, 6305-6311.
- [21] J. Chen, Y. Zhang, H. Ye, J.-Q. Xie, Y. Li, C. Yan, R. Sun, C.-P. Wong, ACS Applied Energy Materials 2019, 2, 2734-2742.
- [22] Y. Du, H. Qu, Y. Liu, Y. Han, L. Wang, B. Dong, *Applied Surface Science* **2019**, *465*, 816-823.
- J. Yang, G. Zhu, Y. Liu, J. Xia, Z. Ji, X. Shen, S. Wu, Advanced Functional Materials 2016, 26, 4712 4721.
- [24] X. Feng, Q. Jiao, L. Tong, Q. Li, M. Yin, Z. Yun, H. Li, C. Feng, Z. Wei, *Acs Sustainable Chemistry & Engineering* **2017**, *6*, acssuschemeng.7b03236.
- [25] F. Li, Y. Bu, Z. Lv, J. Mahmood, G. F. Han, I. Ahmad, G. Kim, Q. Zhong, J. B. Baek, Small 2017, 13, 1701167.
- [26] J. Jiang, C. Yan, X. Zhao, H. Luo, Z. Xue, T. Mu, *Green Chemistry* **2017**, *19*, 3023-3031.
- [27] F. Xueting, J. Qingze, C. Huiru, Y. Mengmeng, L. Qun, Z. Yun, L. Hansheng, Z. Wei, F. Caihong, ACS Applied Materials & Interfaces.
- [28] M. Gong, Y. Li, H. Wang, Y. Liang, J. Z. Wu, J. Zhou, J. Wang, T. Regier, F. Wei, H. Dai, Journal of the American Chemical Society 2013, 135, 8452-8455.
- [29] Alessandro Minguzzi, F.-R. F. Fan, Alberto Vertova, Sandra Rondinini, A. J. Bard, *Chemical Science* **2012**, *3*.
- [30] T. Wang, W. Chao, J. Yue, A. Sviripa, J. Liang, J. Han, Y. Huang, Q. Li, W. Gang, *Journal of Materials Chemistry A* 2017, 5, 10.1039.C1037TA08720A.
- [31] T. Zhang, J. Du, P. Xi, C. L. Xu, Acs Applied Materials & Interfaces 2016, 9, 362-370.

- [32] a) J. Tian, Q. Liu, A. M. Asiri, X. Sun, *Journal of the American Chemical Society* 2014, *136*, 7587-7590; b) P. Jiang, Q. Liu, Y. Liang, J. Tian, A. M. Asiri, X. Sun, *Angewandte Chemie* 2015, *126*, 13069-13073.
- [33] J.-T. Ren, G.-G. Yuan, C.-C. Weng, Z.-Y. Yuan, *Electrochimica Acta* 2017, 261, 454-463.
- [34] Y. Li, X. Liu, H. Li, D. Shi, Q. Jiao, Y. Zhao, C. Feng, X. Bai, H. Wang, Q. Wu, Journal of Power Sources 2019, 422, 122-130.
- [35] a) A. Mendoza-Garcia, D. Su, S. Sun, Nanoscale 2016, 8, 3244-3247; b) M. Bajdich, M. Garcíamota, A. Vojvodic, J. K. Nørskov, A. T. Bell, Journal of the American Chemical Society 2013, 135, 13521-13530.
- [36] N. H. Chou, P. N. Ross, A. T. Bell, T. D. Tilley, *ChemSusChem* **2011**, *4*, 1566-1569.
- [37] S. Du, Z. Ren, Y. Qu, J. Wu, W. Xi, J. Zhu, H. Fu, *Chemical Communications* **2016**, *52*.
- [38] a) L.-A. Stern, L. Feng, S. Fang, X. Hu, *Energy & Environmental Science* 2015, *8*, 2347-2351; b) J.
   Nan, Y. Bo, S. Meili, S. Yujie, *Angewandte Chemie* 2015, *127*, 6349-6352.
- [39] B. Yuan, F. Sun, C. Li, W. Huang, Y. Lin, *Electrochimica Acta* **2019**, *313*, 91-98.
- [40] C. Yang, C. Laberty-Robert, D. Batuk, G. Cibin, A. Grimaud, *Journal of Physical Chemistry Letters* 2017, *8*, 3466.
- [41] P. Wang, F. Song, R. Amal, Y. H. Ng, X. Hu, *Chemsuschem* **2016**, *9*, 472-477.
- [42] L. Jiao, Y. X. Zhou, H. L. Jiang, Chemical Science 2016, 7, 1690-1695.
- [43] P. Chen, K. Xu, Z. Fang, Y. Tong, Y. Xie, Angew Chem Int Ed Engl 2016, 54, 14710-14714.
- [44] M. Bajdich, M. García-Mota, A. Vojvodic, J. K. N?rskov, A. T. Bell, Journal of the American Chemical Society 2013, 135, 13521-13530.
- [45] S. Zhang, Z. Qi, Y. Zhao, Q. Jiao, X. Ni, Y. Wang, Y. Chang, C. Ding, Journal of Alloys and Compounds 2017, 694, 309-312.
- [46] R. Zhang, X. Wang, S. Yu, T. Wen, W. Hu, Advanced Materials 2016, 29, 1605502.
- [47] H. Peng, L. Yu, A. Zuo, C. Guo, F. Yuan, *Journal of Physical Chemistry C* 2009, 113, 900-906.

# **Entry for the Table of Contents**



Yolk-shell structured  $Co_{0.47}Fe_{0.53}P$  microspheres exhibited enhanced OER performances.