Assessment of the Stability and Operability of Cobalt Phosphide Electrocatalyst for Hydrogen Evolution

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S *Supporting Information*

ABSTRACT: Transition metal phosphides have been investigated heavily as hydrogen evolution reaction (HER) catalysts. One of the most active transition metal phosphides, CoP, has been tested for its stability and operability under mild conditions that it may be exposed to in its applications (photoelectrochemistry and artificial photosynthesis). Surface-interrogation scanning electrochemical microscopy (SI-SECM) revealed that CoP HER catalyst is vulnerable to oxidation (by oxygen and chemical oxidants). The degradation mechanism was shown to be surface oxidation by dioxygen, followed by acid etching of the oxidized layer. The compositional integrity (unity ratio of cobalt and phosphorus) was maintained throughout the film decomposition progress.
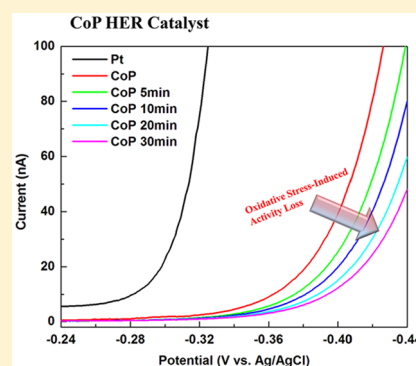
Solar-driven water electrolysis is a promising process for the renewable generation and storage of fuel (hydrogen).[1,2] Overall, solar water splitting devices have been developed,[3] and research efforts continue in order to minimize energy losses and cost associated with the components of the water splitting device, including the photoabsorber, separation membranes, and the redox catalysts. Considerable efforts have been devoted to finding an alternative to Pt, a highly effective, but expensive, hydrogen evolving electrocatalyst. Materials widely considered attractive for the hydrogen evolution reaction (HER; the reduction half-reaction of the water splitting process) are transition metal phosphides.[4] One of the best performing transition metal phosphide catalysts is the stoichiometric phosphide of cobalt, CoP, exhibiting approximately 80−100 mV overpotential for HER compared to platinum at the same current density.[5,6] A large number of papers have been published on this material's HER catalysis thus far; however, in all of the accounts the HER catalysis experiments were performed in H_2-saturated environments under an H_2 atmosphere and excellent stability of CoP was claimed. To the best of our knowledge, only a few reports in the literature address the limited stability of this material to date, including a recent contribution by Shao-Horn and co-workers, and even in these cases, the HER catalysis was performed in H_2 and the instability was associated with the oxidative stress imposed by the potential pulse provided at the electrode.[7] In the current work we assess the stability and the operability of the CoP material as a catalyst for the electrochemical HER. In this paper, the stability of the CoP catalyst was evaluated at varying flow rates of inert argon gas; the film dissolution progress was tracked by electrochemistry and elemental analysis, yielding some insight into the decomposition mechanism. The stability

and operability were also assessed as a function of pH of the solution, including efforts to protect the CoP film cathodically by application of a reducing bias. Finally, surface-interrogation scanning electrochemical microscopy (SI-SECM) was applied to the catalyst surface in attempts to investigate the surface chemistry during catalysis—similar to that in our previous explorations on other electrocatalytic surfaces.[8−12]

■ EXPERIMENTAL SECTION

General. All solutions were prepared using a Milli-Q deionized water (18.2 MΩ·cm, 4 ppb total oxidizable carbon). Boric acid (H_3BO_3, >99.5%, Fisher), sodium hypophosphite monohydrate ($NaPO_2H_2 \cdot H_2O$, >97% Fisher), cobalt chloride hexahydrate ($CoCl_2 \cdot 6H_2O$, 98% Aldrich), 1,1′-ferrocenedimethanol (98%, Acros), and iron chloride tetrahydrate ($FeCl_2 \cdot 4H_2O$, >99%, Acros) were used as received without further purification. Gold wires (99.99+%) of 25 μm diameter was purchased from Goodfellow (Devon, PA). The gold wire was used to fabricate the ultramicroelectrodes (UMEs) as described elsewhere.[8] Unless otherwise specified, all electrodes used were fabricated to an RG (RG = [radius of the electrode plus the glass sheath]/[radius of the electrode]) of about 1.3 and were polished with alumina paste on microcloth pads prior to use. The CoP hydrogen evolving catalyst films were deposited onto a gold UME by a published method with a minor modification—deposition time of 30 to 45 s was used instead of 15 min in order to ensure smooth and thin film.[6] For all
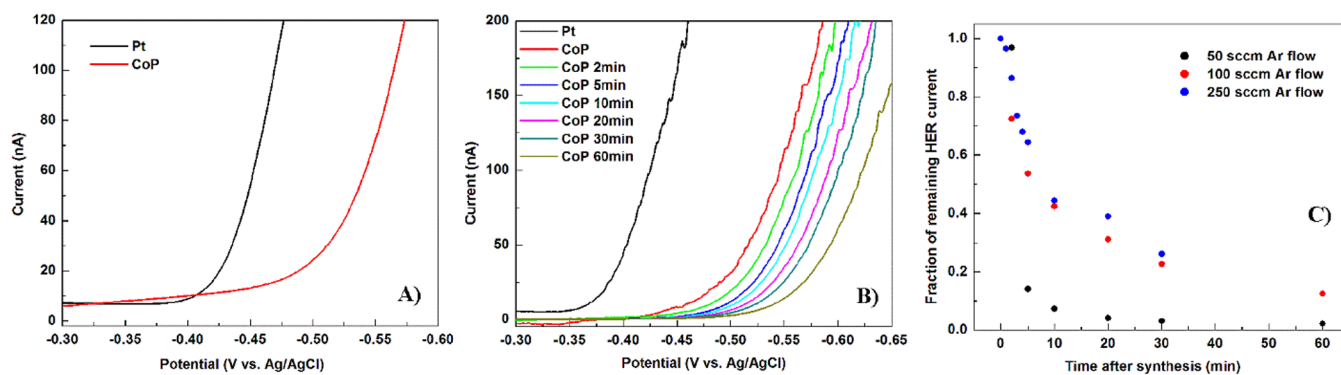
Figure 1. (A) Linear sweep voltammograms (LSVs) of Pt and CoP (on Au) UMEs (25 μm diameter) in the HER potential region (pH 2.8 sodium citrate−citric acid buffered water; scan rate of 10 mV/s employed). As reported in the literature,[5,6] approximately 80−110 mV overpotentials at the same current density compared to Pt were observed with usual electrode-to-electrode variation. (B) Series of HER LSVs for the CoP electrode after HER electrolyses. (C) HER current losses as a function of time are plotted at 50, 100, and 250 sccm Ar flow.
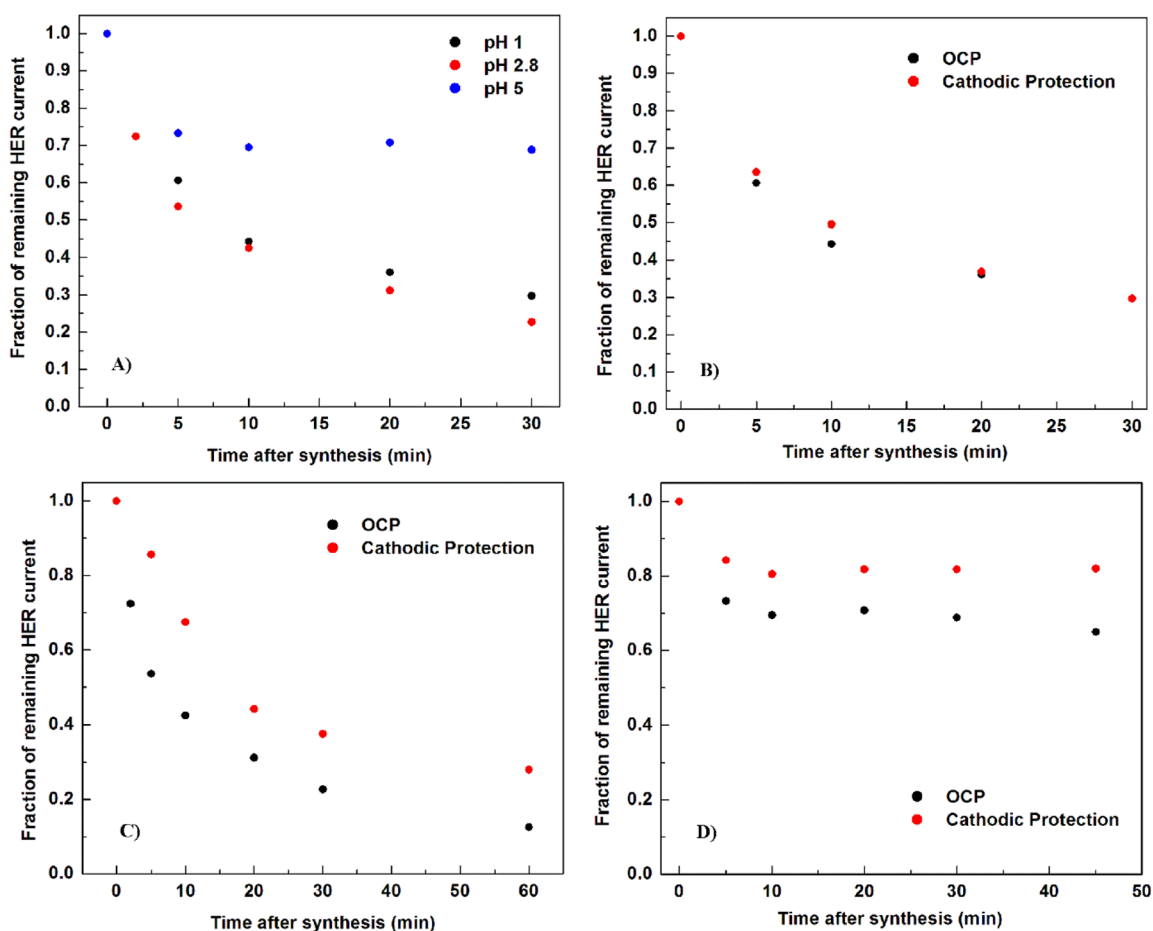

Figure 2. (A) Catalytic current losses of the CoP electrode as a function of time in solutions of pHs 1, 2.8, and 5. Similar rates of the HER current loss were observed in solution pHs of 1 and 2.8. Significantly retarded current loss was observed in pH 5. (B) HER catalytic current loss at varying operation times with and without cathodic electrode protection (pH 1). OCP denotes open circuit potential during time between experiments. (C) HER catalytic current loss at varying operation times with and without cathodic electrode protection (pH 2.8). (D) HER catalytic current loss at varying operation times with and without cathodic electrode protection (pH 5).

electrochemical measurements, an Ag/AgCl reference electrode and a platinum wire counter electrode were used.

Instrumentation. SEM micrographs were taken on a FEI Quanta 650 environmental SEM. Elemental analysis for the CoP samples was performed with an EDX mounted on the SEM. All electrochemical experiments excluding SECM measurements were performed on a CHI920C potentiostat.

All experiments were performed in a quartz glass reaction vessel containing the three-electrode system under inert gas flow (50, 100, or 250 sccm Ar). Total volume of the reaction solution (pH 1, 2.8, or 5) was controlled to 25−30 mL, with the working electrode 2−3 cm immersed in the solution. The top of the reaction vessel was open to ambient air with a circular opening with a diameter of 2.5 cm. SECM experiments were

conducted utilizing a CHI920C SECM station bipotentiostat and its built-in software (CH Instruments; Austin, TX). A rapid switching device for the fast SI-SECM titration experiments that was introduced recently[9] was employed in this work. Chronoamperometry (CA) was chosen as a detection technique in the SI-SECM experiments. The tip and the substrate electrodes (both 25 μm Au UME) were positioned at about 2.5−3.0 μm from one another, a distance at which generation-collection efficiency was greater than 90%. For each data point collected, the substrate was stepped to E_{subs} for a time t_{step} = 5 s, followed by a potential step back to open circuit. A respective detection by stepping the potential of the tip was performed immediately following the substrate open circuit. A total collection time of 15 s was selected for CA experiments. The redox mediator solutions employed in this work consisted of 2 mM $FeCl_2$ for pH 1 (0.1 M H_2SO_4), 1.8 mM $K_4Ru(CN)_6$ for pH 2.8 (50 mM citrate/citric acid buffer), and 1,1′-ferrocenedimethanol for pH 5 (50 mM phosphate buffer).

■ RESULTS AND DISCUSSION

Investigation of the HER Current Decay on a CoP Electrode as a Function of Inert Gas Flow. A cobalt phosphide HER catalyst film was deposited on a gold ultramicroelectrode (UME, 25 μm diameter) by a published method.[6] The electrochemical performance of the fabricated electrode was similar to that reported in the literature (Figure 1A), that is, 80−110 mV overpotentials were observed compared to a Pt electrode of the same size.[5,6] In our experiments, we tried to emulate a mild operating condition for the HER catalysis with 100 sccm of inert Ar gas flow with a circular reaction vessel opening (2.5 cm diameter) to air. The overall reaction solution volume was 30 mL (50 mM citrate buffered solution at pH 2.8), and the working electrode was immersed into the solution at a depth of 2−3 cm from the solution−air interface. Surprisingly a continued decay of the HER current from the CoP electrode was observed (Figure 1B) upon subsequent linear potential scans. The current decay was severe, such that 50% loss of activity was observed in about 10 min of operation. When the purging gas was exchanged to H_2 (100 sccm), the HER current decay was not mitigated significantly and the study hereon described was carried out under bubbling Ar atmosphere. To carefully study the CoP film decay process, Ar flow rate was varied to 50, 100, and 250 sccm. As seen in Figure 1C, CoP film deactivation was extremely fast in 50 sccm flow of Ar, losing 80−90% of the catalytic current within the first 10 min of operation. An Ar flow of 100 sccm prolonged the use of a CoP electrode as a HER catalyst; however, about 60% of the catalytic current was lost after 10 min of operation. A further increased Ar flow to 250 sccm marginally improved the stability of the electrode. From the observations described here, it is logical to derive the relationship between the dissolution of oxygen from the solution−air interface and the degradation rate of CoP, since inert gas flow rate generally is inversely related to the oxygen influx. It is known that transition metal phosphides are oxygen sensitive, however, we did not expect such hasty deactivation under vigorous flow of inert gas and a relatively small vessel opening. Notably, deactivation progressed even under H_2 bubbling, indicating that not only H_2 saturation of the solution but also headspace overpressure (such that oxygen is absent) is required for the sustainable operation of the CoP HER catalyst.[4−6]

Investigation of the HER Current Decay on a CoP Electrode as a Function of Solution pH. To further assess the stability and practical operability of the CoP HER catalyst, a pH variant analysis of the film decay was performed. Three different pH values pertinent to HER were adopted: pH 1 (0.1 M H_2SO_4), pH 2.8 (50 mM citrate/citric acid buffer, measured pH range of 2.6−3.0), and pH 5 (50 mM phosphate buffered water, measured pH range of 5.0−5.3). An Ar flow rate of 100 sccm was selected for the entire data set described here. As seen in Figure 2A, the HER current decay rate was proportional to the acidity of the solution; the rate of decay of the HER current was comparable in pHs 1 and 2.8, however, was significantly retarded in a pH 5 solution.

Associating the dependence of the HER current decay on the pH of the solution and that on the inert gas flow rate, it is deducible that the film loss mechanism is oxidation of the CoP film by the influx of oxygen followed by the acid-induced removal/dissolution of the oxide. Similar rate of the HER current loss in pHs 1 and 2.8 suggests that the acid removal of the catalyst film is sufficiently fast at pHs under 3, and that the oxygen dissolution and surface oxidation are the rate limiting processes. Physical removal of the catalyst film was indeed observed after extended operation times in the above-described conditions−see SEM images in Figure S1.

During practical applications of these types of catalysts, it is likely that the electrode is under constant reducing bias for continued operation, and therefore, should assist in cathodically protecting the catalyst from oxidative stress. We emulated such conditions and monitored the HER current loss under cathodic protection. An overpotential of −0.4 V (vs E^0 for HER at the respective pH) was constantly applied as the HER current decay was monitored in regular time intervals. As shown in Figure 2, cathodic potential had no protective effect in pH 1, presumably due to the fast dissolution of the oxidized layer. In a pH 2.8 solution, the application of a reducing bias extended the longevity of the HER current by the CoP electrode to a certain extent (40% current retention as opposed to 22% current retention in the open circuit case, after 20 min); however, the decay trend was similar to that of the open circuit case, therefore it is logical to conclude that even in pH 2.8 the cathodic protection method does not warrant a practical operation for extended periods of time. At pH 5, where acid removal of the oxidized layers is significantly retarded (see Figure 2), cathodic protection works to protect the CoP film quite well; in Figure 2, after a sharp drop in the HER current at short times, the cathodically protected CoP electrode exhibited stable HER in pH 5. The proposed surface processes based on these observations are initial formation of a surface oxide passivating layer as a consequence of the influx of oxygen, followed by acid etching of the oxide layer as a function of pH. The electrochemical reduction process of the passivating layer (the cathodic protection) is sufficiently fast at the proton concentration correlating to pH 5, however, is too slow to protect the film from etching in pHs 1 and 2.8. The collective data presented here suggest that oxygen diffusion and surface oxidation reaction are sufficiently fast even in 100 sccm purging of Ar and a relatively small opening (2.5 cm diameter) to air. Cobalt to phosphorus elemental ratio of the catalyst film was tracked as the film underwent decay (Table 1). The cobalt−phosphorus ratio remained 1:1 throughout the HER current loss process, in accordance with our other observations thus far described. The CoP decay process explained here in the presence of slow influx of oxygen is fundamentally different

Table 1. Cobalt to Phosphorous Elemental Ratio of the CoP Electrode at Various Operation Times

time of electrocatalysis (min)	fractional loss in the HER activity	Co/P ratio by EDX
0	0	1:0.95
10	0.56	1:1.04
20	0.63	1:1.05
30	0.70	1:1.07
60	0.88	1:1.09

from the one previously described deactivation process reported by Shao-Horn and co-workers,[7] in which they monitored the catalyst deactivation as a function of positive voltage applied prior to catalysis and discovered selective leaching of phosphorus at more positive potentials.

Application of Surface-Interrogation Scanning Electrochemical Microscopy (SI-SECM) to the CoP Catalyst Surface in Search of Reaction Intermediates. A SI-SECM investigation of the CoP HER catalyst surface was performed similar to those in our previous explorations of the surfaces of electrocatalysts employing the same technique.[8,10−13] A

condition for the stable operation of the catalyst described in the previous section (pH 5 with cathodic protection) was employed for this study. In the SI-SECM experiments, two UMEs (tip and substrate) are aligned such that the analyte generated by one electrode is quantitatively detected at the other. The electrochemical feedback delivered by the redox molecules in solution enables the quantitation of the surface adsorbed species (or surface charge distribution).[13] The operation principles are depicted in Figure 3A,B. Briefly, the substrate electrode was pulsed to a potential at which the surface species of interest (i.e., surface adsorbed H$^\bullet$, an intermediate during HER) are generated. The substrate electrode was then placed at open circuit to prevent continued generation of the surface adsorbates. This transience was probed at the tip electrode by applying an oxidizing bias, generating the oxidized form of the redox messenger molecule 1,1′-ferrocenedimethanol (FcDM$^+$). Tip-generated FcDM$^+$ then diffused down to the substrate electrode surface, oxidizing the surface species of interest and, in doing so, delivered redox feedback to the tip electrode (Figure 3A,B). The redox feedback loop deactivated upon full consumption of the surface
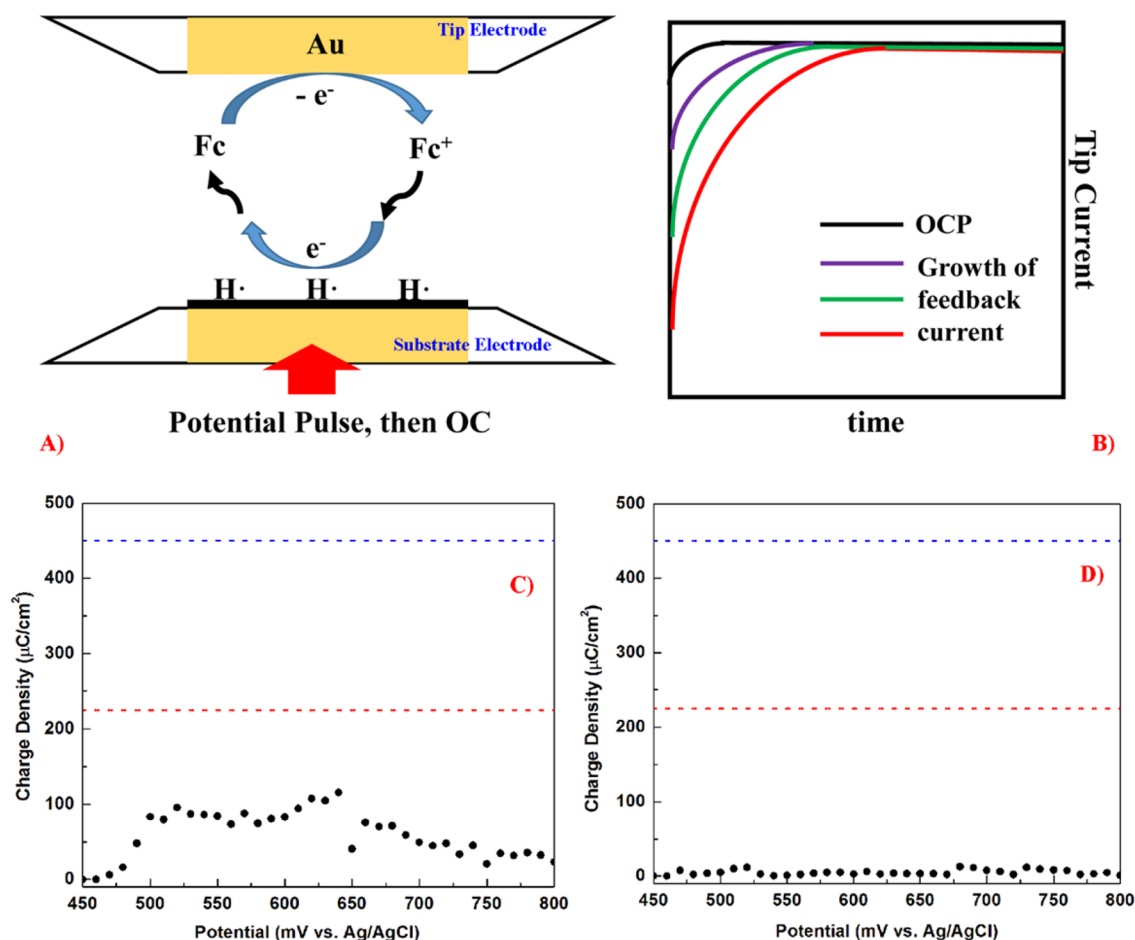

Figure 3. (A) Schematic depiction of the processes occurring during the surface titration experiments in a SI-SECM setup. Surface intermediate species (H$^\bullet$) are generated by potential pulses at the substrate electrode. Surface titration occurs as the solution redox messenger molecule (1,1′-ferrocenedimethanol, denoted Fc in the scheme) is oxidized at the tip electrode. (B) The resulting tip currents in a chronoamperogram is schematically shown. For a typical surface titration, a continuous increase (plateau at a certain potential) in the interrogation amperogram is obtained.[8,10,11] (C) A surface redox titration curve of CoP (charge density as a function of substrate electrode potential) is displayed. Typical charge density of a flat metal surface (Au (111); red dotted line) and that of a stable HER catalyst surface (MoS$_2$;[11] blue dotted line) are also shown as a reference. (D) A surface redox titration curve of CoP (second potential scan through) is displayed. A clear loss of the catalyst film and the resulting negative feedback was obtained.

species of interest, at which point the concentration of reacted surface species was quantifiable by the charge integration of the curve shown in Figure 3B.

A redox titration curve (plot of charge density−surface active species density as a function of the substrate electrode potential) obtained from the surface titration of CoP during HER is presented in Figure 3C. A reduction event can be seen starting from −450 mV and extends to about −650 mV, that is attributed to the titration of surface adsorbed H• on the CoP electrode. The collected charge density decreased gradually back to zero as the substrate potential increased to −800 mV and titration continued. In our previous investigations of catalyst surfaces, the collected charge density continued to increase (or at least plateau) as a function of more extreme (either oxidizing or reducing) substrate potential, due to the formation of more redox equivalents at the surface (increased surface concentration of H• atoms).[8,10−13] However, an atypical trend was observed for the case of CoP surface, that the collected charge density decreased with more reducing potentials. To further elucidate the phenomenon, a redox titration was performed for the second time on the same electrode. Surprisingly, no redox feedback response was observed resulting in a net zero charge density at all substrate potentials as shown in the second titration curve in Figure 3D. The substrate electrode was isolated after the SI-SECM experiments and was tested for HER, which revealed a behavior identical to that of a bare gold electrode. Removal of the CoP coating from the gold UME was also confirmed by optical microscopy and cyclic voltammetry (Figure S2). The aforementioned observations collectively suggest that the CoP catalyst film was oxidatively striped off of the underlying gold UME by the stress inflicted by the oxidizing potential of FcDM$^+$ (0.22 V vs Ag/AgCl or 0.42 V vs NHE). Such vulnerability to mild oxidative stress (unrelated to dioxygen) rendered it impossible for the surface interrogation to take place, and little information was obtained through the SI-SECM study. Attempts to interrogate the CoP surface were carried out in a pH 2.8 and pH 1 solutions using $Ru(CN)_6^{4-}$ and $FeCl_2$ redox mediators, respectively; however, a much faster oxidative stripping of the CoP film was observed in pH 2.8 with no attainable redox feedback (Figure S3) and due to the fast film dissolution, alignment of the two electrodes was impossible within the allotted time window in pH 1. All of the SI-SECM experiments described here were performed in an argon purging environment at a flow rate of ca. 25 sccm. The total solution volume was 5 mL, with a circular cell opening to air with a diameter of 0.5 cm. Such limited stability of the CoP catalyst film toward mild oxidative stress, both by oxygen and by chemical oxidants, seriously limits its applicability and operability in a photoelectrochemical or an artificial photosynthetic device of any scale.

CONCLUSIONS

In the present contribution, the stability of the CoP HER catalyst in mild operating conditions was evaluated. Even under high flow rates of inert gas, the oxidation of the catalyst film was surprisingly fast and the removal of the oxidized film by acid was confirmed. Overall, operability of the CoP HER catalyst film in a reasonable inert gas flow was generally limited to less than 20 min. Unlike in the case of decomposition induced by the oxidative voltage at the electrode,[7] the cobalt to phosphorus elemental ratio remained one to one throughout the decomposition process. Protection of the catalyst film by

applications of cathodic bias was unsuccessful in pH 1 and pH 2.8 solutions due to the fast acid etching of the oxidized film, but a successful implementation of the cathodic protection was feasible in a pH 5 solution in which the acid-driven etching process is significantly retarded. Surface-interrogation attempts of the CoP catalyst electrode were unsuccessful in all pH ranges tested (1, 2.8, and 5) due to the instability of the CoP catalyst; especially during the experiments in a pH 5 solution, the catalyst film revealed vulnerability toward chemical oxidative stress equivalent to ca. 0.4 V vs NHE, further limiting the potential scope of operation.

Although the two oxidants employed here, O_2 and ferrocenium ion, are quite different in nature (their oxidation mechanisms and involvement of protons), an electrocatalyst sensitive to both oxidative stimuli is problematic nonetheless. Dioxygen, in particular, is highly likely to be present in operational situations for the CoP catalyst, especially during extended operations; therefore, the limited stability toward such agent needs to be addressed. The limited stability of the CoP HER catalyst demonstrated in this work in imaginable and mild operating conditions calls for further work on the modification of the CoP catalyst for its tolerance in the working environment. Many preceding studies have demonstrated that materials with attractive functional properties can overcome operational sensitivities (to moisture, oxygen, and many other agents).[14−16] Similar endeavors are anticipated for the CoP catalyst in the near future.

ASSOCIATED CONTENT

ⓢ Supporting Information

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Notes
The authors declare no competing financial interest.

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