

Effects of aqueous buffers on electrocatalytic water oxidation with an iridium oxide material electrodeposited in thin layers from an organometallic precursor†

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A thin layer of an amorphous, mixed-valence iridium oxide (electrodeposited from an organometallic precursor, $[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3]^{2+}$) is a heterogeneous catalyst among the most active and stable currently available for electrochemical water oxidation. We show that buffers can improve the oxygen-evolution activity of such thin-layer catalysts near neutral pH, but that buffer identity and concentration, as well as the solution pH, remain key determinants of long-term electrocatalyst activity and stability; for example, phosphate buffer can reduce the overpotential by up to 173 mV.

The storage of solar energy in the form of chemical fuels requires a source of protons and electrons to take part in the reductive, fuel-forming chemistry. Water oxidation (eqn (1)), one half of overall water splitting,¹ is one possible source for these necessary electrons and protons:²



However, water-oxidizing chemistry presents mechanistic difficulties, as it is a four-proton, four-electron reaction, and has a high thermodynamic potential. This mechanistic complexity is reflected in the high electrochemical overpotential (denoted here as η) required to drive catalysts and electrocatalysts. Because water oxidation is required in most approaches³ to solar-fuel production, lowering the overpotential for oxygen evolution represents a significant opportunity for improvement in the efficiency of solar fuel formation.

Thus, there is currently a worldwide search underway for improved water-oxidation catalysts. Inspiration comes from Nature, which has provided the oxygen-evolving complex in

photosystem II as a benchmark system operating with turnover frequencies ($\text{mol O}_2 (\text{mol cata})^{-1} \text{s}^{-1}$) of *ca.* 100 t.o. s^{-1} at an “overpotential” estimated to be as small as 300 mV,⁴ although with limited lifetime. Synthetic systems rarely operate with appreciable rates at such overpotentials near neutral pH. Of such synthetic catalysts, those that are homogeneous have been extensively studied,⁵ but often undergo rapid decomposition, are incompatible with electrochemical oxidation, or have key mechanistic ambiguities.⁶ Heterogeneous catalysts seem to afford higher activity, but they have mechanisms of action that are more difficult to characterize and can suffer from pH incompatibilities or corrosion,⁷ depending upon the exact operating conditions.

Iridium oxides are well known for their excellent activity as electrocatalysts for water oxidation.⁸ They are found in dimensionally stable anodes (DSA)⁹ and are the active catalyst material in proton exchange membrane (PEM) water electrolyzers.¹⁰ The method of iridium-oxide preparation significantly affects the catalytic properties, including both activity and stability.¹¹ Differences in morphology, the availability of active sites on the surface, and effects of hydrated layers *versus* compact oxide phases could contribute to these differences in activity.

Anodic electrodeposition has been identified as a preferred method for the preparation of highly active cobalt,¹² manganese,¹³ and iridium-based heterogeneous catalysts.^{7c,14} We have reported the electrodeposition of an iridium oxide catalyst that is prepared by anodic oxidation of organometallic aqua cations bearing the Cp^* ligand, where Cp^* is pentamethylcyclopentadienyl.¹⁵ Specifically, electrodeposition of

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$[\text{Cp}^*\text{Ir}(\text{H}_2\text{O})_3]^{2+}$ (**1**) affords a blue layer on the anode that functions as a highly active water-oxidation electrocatalyst (**BL**). **BL** is not simply IrO_2 but rather an amorphous, electrochromic iridium oxide resembling Ir_2O_3 and having a complex structure that has not yet been fully elucidated.

BL can be deposited using either thick (*ca.* 2 μm) or thin (tens of monolayers) preparations. With extensive electrochemical quartz crystal nanobalance studies,¹¹ we have compared these thick and thin preparations of the catalyst, and shown that an unbuffered thick preparation operates with an overpotential¹⁶ around 200 mV, while a thin preparation invisible to the eye and with a surface coverage of only 35 nmol cm^{-2} gives a slight increase in required overpotential to 240 mV (at pH 3 in unbuffered solution).¹¹ Characterization of these thin layers is important because: (1) the cost of the iridium material is only U.S. \$0.45 per square foot (with Ir at \$14 000 mol^{-1}) as compared to over \$9 per square foot for the thick preparation,¹¹ but (2) the thin layers may be more susceptible to corrosion. Despite much work in this area, the stability and activity properties of such thin layers of amorphous iridium oxide are essentially unknown, especially under the complex, buffered aqueous conditions normally applying to oxygen evolution in solar-fuel production schemes.

In this study, we report the activity of **BL** over a wide range of conditions; we have varied the solution pH, type of aqueous buffer, and buffer concentration to optimize activity. Specifically, buffering conditions with phosphate have been found which enable sustained **BL**-catalyzed water oxidation at neutral pH. The improvement in behavior manifests at pH 7 as an overpotential that is 173 mV lower in the presence of phosphate than the analogous case lacking a buffer. High buffer concentrations were unexpectedly found to result in deactivation of the electrocatalyst, presumably due to accelerated corrosion processes of the thin layer. Because operation at near-neutral pH may be desirable, as it avoids the need for caustic or corrosive conditions,¹⁷ we discuss our results in the context of implementing direct photoelectrochemical water splitting.

Results

In our previous studies of thin layers of **BL**, we have found that the overpotential at pH 3 is *ca.* 240 mV. In this study, we began by expanding the scope of our pH-dependence studies with **BL** and found that the overpotential increases significantly at higher pH values. This is shown in Fig. 1.

The increase in overpotential beginning near pH 5 as shown in Fig. 1 suggests that a change in the operative mechanism and/or solution conditions above pH 5 play a key role in oxygen evolution. We first considered mass transport limitations to electrocatalysis (due to the generation of protons during vigorous oxygen evolution at the electrode surface) because differences between the pH near the electrode surface and the measured pH of the bulk solution would contribute to an apparent rise in overpotential. Thus, we employed a rotating disk electrode (RDE; rotated at 1500 rpm) to avoid local

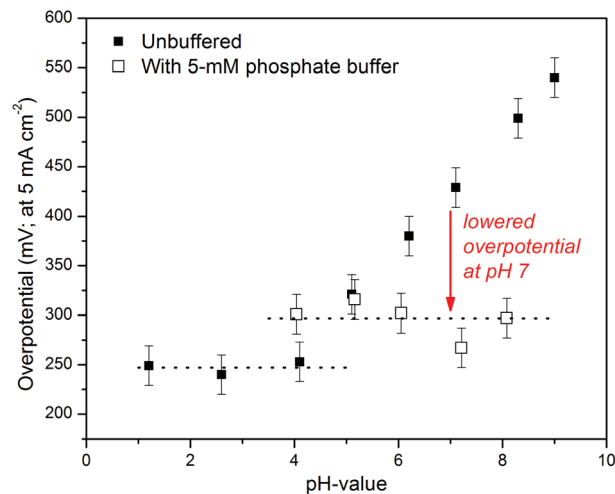


Fig. 1 Plot of overpotential versus bulk solution pH for **BL**-catalyzed water oxidation in the presence (solid squares) and absence (open squares) of phosphate buffer. The method of catalyst electrodeposition for both cases can be found in the ESI.† Dashed horizontal lines are guides for the eye and are a least squares fit to the experimental data as described in the main text. The arrow indicates the difference in overpotential at pH 7.

proton concentration gradients at the electrode surface. Moreover, the overpotential was measured at a fairly low current density of 0.5 mA cm^{-2} . During the experiments, the solution appeared well mixed. At higher current densities, though, extensive bubble formation is a symptom of a poorly mixed solution. Thus, even with the vigorous stirring afforded with the RDE, and generally low experimental current densities, we continued to observe increased overpotentials with higher solution pH.

Thus, we considered buffering the aqueous solution as a strategy for lowering the observed overpotential at higher pH values. A large part of the problem is no doubt that the deprotonation and consequent activation of water that occurs during the required steps of the water-oxidation reaction are mechanistically challenging. Previously, we have estimated the H/D kinetic isotope effect for electrochemical oxygen evolution with **BL** to be 2.68 ± 0.16 .¹¹ This KIE suggests that an O–H* bond is broken in the rate-determining step. Thus, in the case of our **BL**, as in many other catalysts, the management of protons during oxygen evolution is key. By facilitating deprotonation with a buffer, we expected a lower kinetic barrier and consequent lowering of the overpotential. In addition, the buffer should counter any local pH changes by increasing the capacity of the solution to accept protons.

Before screening any buffers, we consulted the Pourbaix diagram for IrO_2 , as the closest analogue to **BL**, to ensure our experiments would be conducted in pH and potential regions of predicted thermodynamic stability. The diagram⁷ predicts that iridium oxide is stable under water-oxidizing conditions well above neutral pH, but strictly up to around pH 11. At potentials of relevance to water oxidation beyond pH 11, corrosion of iridium oxide is predicted. Thus, we chose to explore the effects of various buffers with pK_a values ranging from 0 to 11.

The effects of buffer choice on catalytic activity for water oxidation are rarely discussed in the relevant literature.¹⁸ However, one notable recent study from Stahl *et al.*¹⁹ demonstrated some effects of buffer selection in the case of electro-deposited cobalt oxide as the catalyst. They noted that buffers can participate in detrimental side reactions, and our work mirrors this observation in some cases, because we find corrosion to be a problem under some conditions, presumably by buffer coordination and consequent solubilization of **BL**. This is consistent with some older work, which shows corrosion of iridium electrodes to form $[\text{IrCl}_6]^{2-}$ salts upon electrochemical oxidation in concentrated HCl solutions.²⁰

Phosphate at neutral pH ($\text{pK}_a(\text{HPO}_4^{2-}/\text{H}_2\text{PO}_4^-) = 7.2$) is one of the most popular buffers for use in catalytic water oxidation because it is not oxidizable^{12a} and buffers effectively near neutral pH. In the case of **BL**, we find that the presence of even dilute 5 mM phosphate (in addition to the 0.1 M KNO_3 supporting electrolyte) lowers the observed overpotential at pH 7.2 from 440 mV to 267 mV (Fig. 1, and Tafel plots in ESI†). Generally, the presence of phosphate buffer was shown to lower the overpotential for water oxidation for pH values between 6 and 8, as expected (Fig. 2).

However, particularly in the case of HPO_4^{2-} , the anion could coordinate the active metal sites, thereby deactivating the catalyst. This is demonstrated by the full Tafel plots (see ESI†) that show loss of activity upon reaching current densities near and above 1.0 mA cm^{-2} . Indeed, although phosphate was found to improve the catalytic performance of **BL**, solutions containing phosphate do not give stable oxygen evolution at high voltages. Phosphate ions are expected to bind more strongly to high-valent iridium intermediates, which are

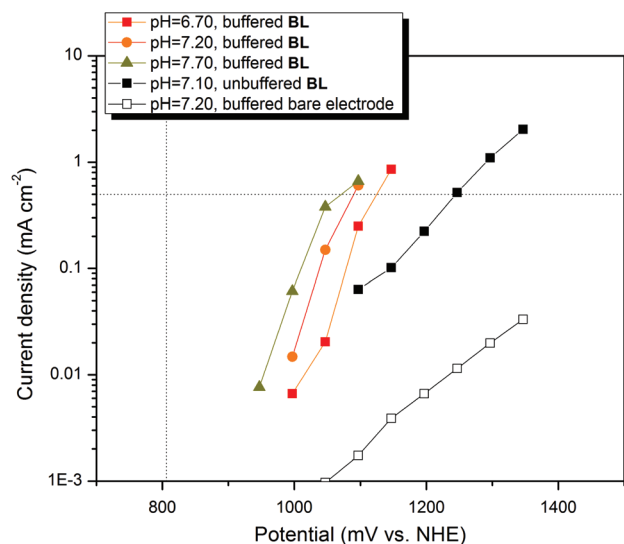


Fig. 2 Tafel plots for water oxidation catalysed by **BL** in the presence of 0.1 M phosphate buffer near pH 7. Vertical dash line shows the pH-adjusted thermodynamic potential for water oxidation (E° , 820 mV) under these conditions. Horizontal dashed line indicates a current density of 0.5 mA cm^{-2} . Conditions: thin preparation of **BL** (see ESI†) on Pt-disk rotating-disk electrode; rotation rate was 1500 rpm; Pt-wire counter electrode; Ag/AgCl reference electrode; 0.1 M KNO_3 as supporting electrolyte.

presumably dominant on the surface during vigorous water oxidation. This notion is further supported by the stirring-rate dependence of the phosphate buffered activity of **BL**. At 1500 rpm, current densities around 1 mA cm^{-2} can be achieved without observable corrosion in 5 mM phosphate solution. Without stirring, however, the effects of 5 mM phosphate are not observable, presumably due to the high proton concentrations at the electrode surface under these conditions, even at relatively modest current densities. With these results in hand, we moved to investigate the role of buffer concentration on catalyst activity.

Upon addition of 1 mM phosphate buffer, catalyst activity increases markedly. However, current densities of 0.5 mA cm^{-2} are not reached as in the case of 5 mM buffer. At phosphate concentrations $\geq 5 \text{ mM}$, **BL** shows a greatly lowered overpotential at 0.5 mA cm^{-2} , as shown in Fig. 1. However, at concentrations $>5 \text{ mM}$, **BL** is clearly deactivated during catalysis (Fig. 3). This trend of decreasing stability is especially marked at 50 and 100 mM phosphate.

Based on the data in Fig. 3, loss of activity begins at *ca.* 1.15 V *vs.* NHE. If the electrode is transferred to a phosphate-free solution following data collection at higher buffer concentrations, the anode showed no evidence for catalytic activity. Related chronoamperometry experiments in which the electrode's activity was tested in an unbuffered solution after several minutes of applied potentials above 1.15 V *vs.* NHE have shown that the phosphate-induced loss of activity with **BL** is irreversible. This strongly suggests loss of the electrocatalytic material from the electrode surface. Corrosion^{7a} is a likely mechanism for loss of activity, because phosphate could bind and solubilize the active iridium sites as in the case of the older work with concentrated HCl electrolytes.²⁰ Notably, the onset of corrosion is only 345 mV above the pH-adjusted thermodynamic potential for water oxidation, suggesting that addition of coordinating buffers perturbs the canonical corrosion characteristics of metal oxides as shown in Pourbaix diagrams (*i.e.*, the diagrams do not take into account the

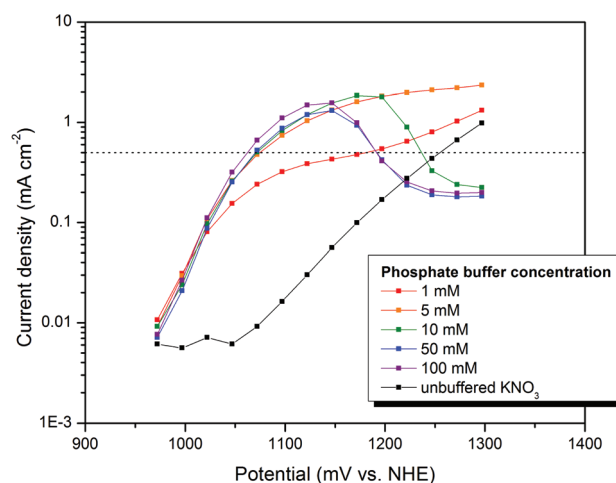


Fig. 3 Effect of phosphate buffer concentration on **BL** activity at pH 7.2.

presence of complexing agents or differences between **BL** and IrO_2).

However, because crystalline forms of iridium dioxide are electrochemically silent in voltammetry below the threshold voltage for oxygen evolution,¹¹ we cannot discount a coordination-induced morphology change that results in both loss of the internal redox chemistry of **BL** as well as electrocatalytic activity.

With our results on lowered overpotential in hand, we next moved to confirm that oxygen was the oxidation product of **BL** under these new, buffered conditions. In order to do this, we measured oxygen evolution in real-time during electrocatalytic water oxidation with a coupled Clark-type oxygen electrode.^{6,11,21} For this experiment, shown in Fig. 4, we applied 1.1 V vs. NHE, which is sufficient to drive **BL** under the buffered conditions but not in the corresponding unbuffered case. With this voltage, we observe that current passed (as shown on the Tafel plots in Fig. 2 and 3) results in oxygen evolution, and moreover, that there is a stoichiometric yield of O_2 for the current passed (*i.e.*, ~100% Faradaic yield). Appealingly, under our new conditions near pH 7, there is no oxygen evolved in the absence of the dilute phosphate buffer, demonstrating the key role of the phosphate under these conditions.

With these results in hand, we looked at other buffers in order to access lower overpotentials at other pH values. Buffers added at lower pH values (pH < 5, namely acetate, phosphate, and Na_2SiF_6) disrupt the electrocatalytic activity. This was manifested in increased or unimproved values for the overpotential. Additionally, unlike the case described above, Tafel slopes at low pH values were nearly identical to that of the unbuffered nitrate solution in the case of all buffers tested under these conditions including phosphate, acetate, and Na_2SiF_6 (see ESI†).

Acetate does not significantly affect the measured overpotential but does seem to accelerate corrosion. This is likely

caused by acetate's ability to coordinate Ir(III) and Ir(IV) , as in the case of Wilkinson's iridium acetate trimer.²² We have found that this trimer can be a precatalyst for chemically driven water oxidation.²³ We also encountered poor behavior in the case of hexafluorosilicate, which was previously found by Mallouk *et al.*²⁴ to be an effective buffering agent (HF/F^- is produced *in situ* and acts as the true buffer)²⁵ for iridium dioxide nanoparticles in a photochemically triggered system.

Borate ($\text{pK}_a = 9.2$) and carbonate ($\text{pK}_a = 10.3$) were also investigated. However, they operate near the corrosion region for iridium oxide, and thus distinguishing their intrinsic characteristics from the expected corrosion of an iridium material at high potentials and relatively high pH values is difficult.

Sodium bicarbonate buffer was not effective near its pK_a value (6.4), likely in part due to loss of the buffer through CO_2 bubble formation, apparent during experiments, but it does decrease the overpotential of the catalyst at pH 7.2 by 60 mV (see ESI, Fig. S4†). Based on the only slight changes in the Tafel slope in the case of work with bicarbonate, it is likely acting only to counter local pH effects and not to alter the operative mechanism of the reaction.

Trifluoromethanesulfonamide (TFMS) was previously explored as a buffer for electrodeposited cobalt oxide.¹⁹ Interestingly, we observed a decreased apparent overpotential for water oxidation by **BL** as compared to unbuffered catalyst near the lower pK_a of TFMS, which is 6.28.²⁶ In the previous study, it was noted that use of TFMS as a buffer did not result in stoichiometric oxygen evolution. This was indeed the case in our electrochemical experiments as monitored by Clark-type electrode, which showed significant deactivation of **BL** over the ten-minute time course of the experiment and an observed oxygen yield of only 88% (see ESI, Fig. S6†). A portion of the observed current is consumed in a process other than water

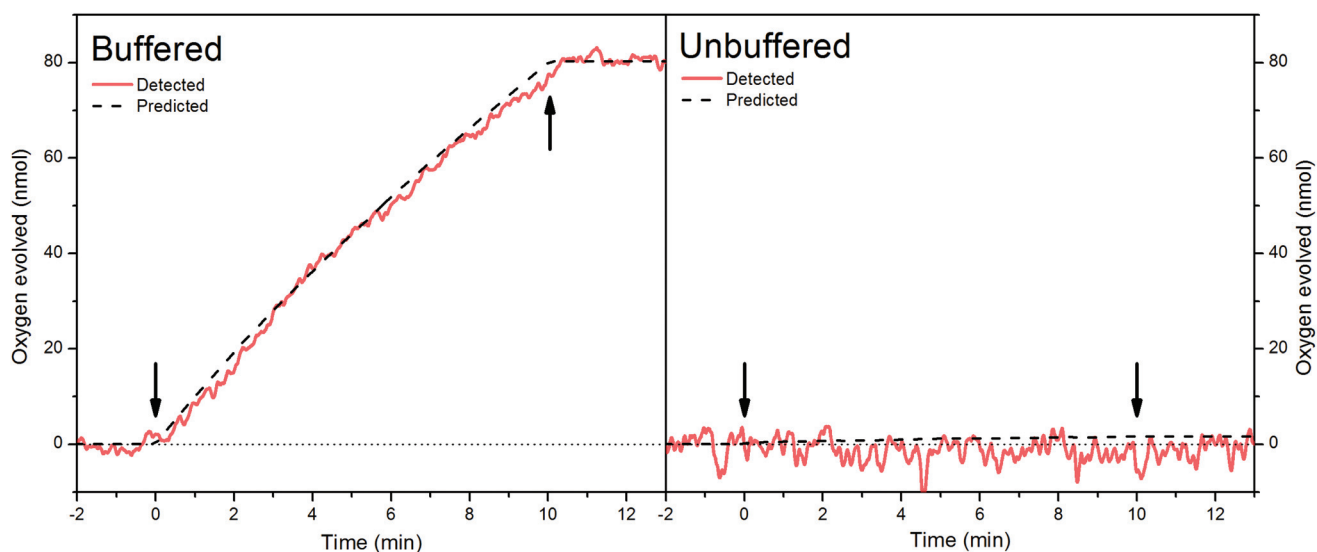


Fig. 4 Detection of oxygen produced by **BL** in the presence (left panel) and absence (right panel) of 50 mM phosphate buffer at pH 7.2. See Experimental section for details. No oxygen is produced under these conditions in the absence of **BL**. Dashed line shows predicted oxygen production based on charge transferred; red solid line shows the experimentally detected oxygen.

oxidation, most likely oxidation of TFMS. Furthermore, there was a noticeable deactivation or corrosion of **BL** during oxygen evolution with TFMS. Taken together, these data strongly suggest that any oxidizable organic buffer is not robust enough for use in water-oxidation catalysis, and may not only cause detrimental side reactions with the buffering media, but also destruction of the catalyst material. This is of special concern in systems such as our thin-layer of **BL**, where loss of any catalyst material is expected to strongly impact the activity.

Discussion

The choice of aqueous buffer is key when attempting to improve the performance of heterogeneous catalysts for water oxidation. Clearly, attempting to move across a wide pH range introduces multiple variables, including possible effects of the buffer itself on corrosion of the catalyst. In contrast to the findings of others on cobalt oxide,¹⁹ we have found unexpected corrosion tendencies in thin layers of our iridium **BL**. However, with judicious choice of concentrations and conditions, buffering **BL** at neutral pH is possible.

Of the buffers tested, only phosphate around its neutral pK_a was truly effective. Phosphate lowers the overpotential of **BL** for water oxidation by 173 mV as compared to unbuffered conditions. But corrosion was encountered at concentrations of phosphate buffer above 5 mM. Detrimental effects prevail at higher current densities, presumably due to the presence of high-valent metal intermediates in the catalytic cycle that we expect would tend to coordinate anionic bases instead of neutral substrate water. Upon coordination to the metal, the buffer could potentially block the catalyst's active site and disrupt its activity, or cause further corrosion. The exact mechanism of catalyst deactivation depends on the reversibility of anion binding. Meyer *et al.* have previously pointed to anion coordination in the case of the molecular "Blue dimer" ruthenium-based water oxidation catalyst as a mechanism of deactivation.²⁷ This supports an important parallel between homogeneous and heterogeneous catalysts for water oxidation. Similar mechanistic consequences of water *versus* chemical-oxidant coordination have been found in the case of our own manganese-terpyridine dimer.²⁸ Further work is needed in the area to clarify the exact mechanism(s) of electrocatalyst deactivation. One avenue for future work is the application of our gravimetric technique relying on a quartz crystal nanobalance (also known as a microbalance) to monitor electrode mass dynamically during electrocatalysis.^{6,11} Studies along this line could provide information about anion coordination as a function of potential, as well as corrosion processes.

Trifluoromethanesulfonamide (TFMS) was effective in lowering the overpotential of **BL**, but TFMS is undesirable due to its incompatibility with strong oxidizing conditions and the seeming capability of its oxidation products to deactivate **BL**. In all cases where catalyst deactivation was a problem, the rate of deactivation increased with increasing applied potential. This suggests that the high-valent metal intermediates

prevalent during active catalysis cause increased vulnerability of **BL** to coordination and deactivation.

In order to construct robust electrochemical or photoelectrochemical cells that produce solar fuel, all components will need to be optimized to operate under the required conditions. Thus, work is needed on water-oxidation catalysts that can operate under a variety of relevant conditions. Functionality at a wide range of pH values is one key factor, because caustic or corrosive conditions may not be practical in all schemes. Regardless, corrosion must be minimized to avoid loss of catalyst material during operation. Once such catalysts have been assembled, they can be utilized in the development of devices to generate solar fuels.

Conclusions

We have shown that a low overpotential for electrocatalytic water oxidation of 267 mV is attainable up to pH 4 and, with added phosphate buffer, at pH 7. Importantly, these low overpotentials are achieved with thin preparations (*ca.* 35 nmol cm⁻²) of **BL**. These very thin preparations are invisible to the eye and open the door to deployment of **BL** as a water-oxidation electrocatalyst for solar-fuel production at neutral pH. When the electrocatalytic layer is thin, no detrimental light-absorption is expected, favoring development of visible-light photoelectrochemical devices. Our screen of buffers here points to the issue of corrosion as a key parameter in the future development of thin-layer electrocatalysts; in line with older work on the effects of chloride, we find acetate and phosphate can induce corrosion of our thin-layer electrocatalyst. Taken together, the results suggest that cell conditions must be carefully selected for compatibility with the water-oxidation electrocatalyst, and by extension, other (photo)electrode components.

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