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Editor's Choice paper

Photocatalytic oxygen evolution from non-potable water by a bioinspired molecular water oxidation catalyst

Robin Brimblecombe[a], Jun Chen[b], Pawel Wagner[b], Timothy Buchhorn[b], G. Charles Dismukes[c], Leone Spiccia[a,*], Gerhard F. Swiegers[b,*]

[a] ARC Centre of Excellence for Electromaterial Science and School of Chemistry, Monash University, Clayton, Victoria 3800, Australia
[b] ARC Centre of Excellence for Electromaterial Science and Intelligent Polymer Research Institute, University of Wollongong, Wollongong NSW 2522, Australia
[c] Department of Chemistry and Chemical Biology, Waksman Institute of Microbiology, Rutgers, The State University of New Jersey, 190 Frelinghuysen Road, Piscataway, NJ 08854, USA

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ABSTRACT

We report that a model complex of the *Photosystem II-Water Oxidizing Complex* (*PSII-WOC*) facilitates, exclusively, photocatalytic water oxidation from non-potable water sources like seawater, under suitable conditions. When the manganese *cubane* cluster $[Mn_4O_4L_6]^+$, (L = (p-MeO-Ph)$_2$PO$_2$), 1^+, is incorporated within a Nafion membrane deposited on an electrolytic anode that is poised at 1.00 V (vs. Ag/AgCl) and illuminated with light, catalysis of only water oxidation is observed in aqueous solutions of sodium chloride, including seawater. No chlorine formation can be detected. This effect is comparable to the ability of the *PSII-WOC* in marine and hypersaline organisms to catalyze, exclusively, water oxidation with chloride present within the WOC as an essential cofactor for activity. It stands in clear contrast to commercial water electrolyzers which generate chlorine gas at their anodes when filled with seawater. Investigations suggest that this effect originates largely in electrostatic repulsion of anionic chloride ions by the Nafion support. In this respect it also appears similar to the *PSII-WOC*, which harnesses a proteinaceous, proton-conducting environment with high cation affinity in its active site. Solar seawater electrolysis of this type offers a potentially unlimited source of clean hydrogen fuel for a future, pollution-free economy.

1. Introduction

Hydrogen is widely considered to be an ideal "fuel of the future" due to its potential to replace fossil fuels like gasoline or diesel in transportation applications. Photocatalytic water-splitting offers a promising route to the clean, renewable, and cost-effective production of hydrogen. While water is an essential part of human life, it is also becoming an increasingly scarce and precious resource. The critical value of water is demonstrated by the fact that the extraction, production, and delivery of fossil fuels like gasoline and diesel, require a surprisingly large input of water. It has been estimated that, on average, ca. 12.5 gal of water are needed to extract, refine, and deliver 1 gal of gasoline [1]. This includes water that is consumed in the refinery cooling cycles and for washing, as well as water employed in other aspects of production and distribution. An automobile with a gas consumption of 20 mile/gal of gasoline will, consequently, also have a water consumption of 1.6 mile/gal of water (or 0.63 gal of water/mile). One way to reduce the amount of water consumed would be to use hydrogen as the fuel. Thus, for example, if hydrogen from the steam reforming of natural gas was used instead of gasoline, this would equate to a consumption of only 0.07 gal of water/mile. Hydrogen produced by water electrolysis using a renewable energy source like wind or solar, has an even lower water intensity, equating to a mere 0.03 gal water/mile. Hydrogen from coal-powered water electrolysis would, however, require ca. 13 gal water/mile because of the large amount of water needed for cooling in coal power stations. One source of water that is not affected by scarcity is seawater, which is available in plentiful supply. Seawater electrolysis offers the possibility of almost unlimited generation of hydrogen. However, electrolytic cleavage of seawater normally yields the toxic gas chlorine, Cl_2, not oxygen, at the anode [2–8]. While water oxidation is thermodynamically favored over chloride oxidation, its high overpotential causes chlorine to be preferentially formed whenever chloride ions are present in the electrolyte. In this work we report that a model complex $[Mn_4O_4L_6]^+$ (1^+, L = (p-MeO-Ph)$_2$PO$_2$) [9] of the *Phostosystem II Water Oxidizing Complex* (*PSII-WOC*), immobilized within a Nafion layer on a conducting electrode which is then poised at 1.00 V (vs. Ag/AgCl) and illuminated with sunlight, facilitates photocatalytic

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* Corresponding authors. Tel.: +61 242215577.
E-mail addresses: leone.spiccia@monash.au (L. Spiccia), swiegers@uow.edu.au (G.F. Swiegers).

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generation of exclusively O_2 in aqueous solutions saturated with chloride ions. No chlorine formation is observed at the anode.

2. Experimental

2.1. Materials and methods

Bis(methoxyphenyl)phosphinic acid was purchased from Aldrich, and used without further purification. Tetrabutylammonium hexafluorophosphate (Bu_4NPF_6) was obtained from GFS Chemicals and purified by a published procedure [9]. Nafion® was purchased from Dupont as an aqueous Nafion – PFSA polymer dispersion (DE 1020), which comprises 10–12% Nafion. All other reagents were purchased from BDH or Aldrich and used as received. Cubane 1 $[Mn_4O_4L_6]$, (L = bis(*p*-methoxyphenyl)phosphinate) and *cubium* 1^+ $[Mn_4O_4L_6]^+ClO_4{}^-$ were prepared as described elsewhere [10].

2.2. Electrochemistry

Electrochemical experiments were conducted at 22(±2) °C with BAS (Bio Analytical Systems) Epsilon CS3 or BAS 100B workstations. Cyclic voltammograms were obtained at scan rates of 5–500 mV s^{-1} in a conventional three electrode electrochemical cell containing inlet and outlet ports for degassing solutions with nitrogen. Experiments in CH_2Cl_2 or CH_3CN (0.1 M Bu_4NPF_6), used a Ag/Ag^+ (0.01 M $AgNO_3$ in CH_3CN) reference electrode, with a double glass frit separating the electrode from the test solution. The ferrocene/ferrocenium oxidation process was used to provide an internal reference potential calibration system for electrochemical studies in organic solvents (0.400 V vs. NHE at 25 °C [11]). Aqueous experiments were conducted in distilled water containing 0.1 M Na_2SO_4 as the electrolyte. In this case, potentials were referenced against a BAS Ag/AgCl (3 M NaCl) glass-bodied reference electrode separated from the test solution by a Vycor frit, with a potential of 0.200 V vs. NHE at 25 °C (BAS reference electrode users manual). All voltammetric experiments used Pt wire or a Pt mesh auxiliary electrode.

The working electrodes were 3 mm diameter glassy carbon and Pt disc electrodes. The glassy carbon working electrode had an electroactive area of 5.9 mm^2, as determined by oxidation of 1.0 mM ferrocene in CH_3CN (0.5 M Bu_4NPF_6) and use of the Randles–Sevcik equation [11] with a diffusion coefficient (D) of 1.7×10^{-5} cm^{-2} s^{-1}.

2.3. Film deposition and Nafion doping

Nafion modified electrodes were prepared by drop-casting a suspension of 10% Nafion onto the working electrode and heating in a laboratory oven at 120 °C for 20 min. Doping of the cast Nafion membrane was achieved by immersion in a 2 mM CH_3CN solution of 1^+ $ClO_4{}^-$.

2.4. Light source

The Xenon light source used for these experiments generated white light with a stable output over the range 250–750 nm, from a Rofin Australia-Polilight PL6, passed through a 1 m long liquid light guide. Illumination experiments were conducted at a light intensity of approximately 500 mW/cm^{-2}, measured at the electrode surface.

2.5. Salt concentration film testing

The working, reference and counter electrodes were fixed together in a standard configuration and moved between the testing electrolytes as one unit, with rinsing on transfer between individual electrolyte preparations, using the respective solvents. Aqueous electrolytes were prepared by dissolving Na_2SO_4, $NaClO_4$ or NaCl in unbuffered distilled water (pH 6.5). Seawater samples were collected at Towradgi Beach in Wollongong, NSW, Australia. Photocurrent was measured using the aqueous electrolyte at 1.00 V vs. Ag/AgCl reference electrode. All acetonitrile solutions contained 0.1 M Bu_4NPF_6. Distilled water was added to the acetonitrile 0.1 M Bu_4NPF_6 electrolyte to achieve a 10% (v/v) solution. $Bu_4NCl{\cdot}H_2O$ was added to the acetonitrile 0.1 M Bu_4NPF_6 electrolyte to a concentration of 0.1 M. Chlorine (Cl_2) tests were conducted using Merck analytical chlorine test strips, which could detect chlorine down to 0.5 mg/L.

3. Results and discussion

3.1. The role of non-potable water as a source of hydrogen from electrolysis

Recent developments in renewable energy technologies like wind, photovoltaic, geothermal, tidal and wave energies, have resulted in a significant increase in the production of clean electricity. However, the challenge of producing low-carbon, renewable, transportation fuels remains unresolved. Hydrogen is a carbon-free, high-energy carrier that can be used in numerous applications, including transportation applications [12,13]. Hydrogen can be produced using a variety of processes, however many of these rely on the consumption of fossil fuels with a resulting overall release of carbon dioxide into the atmosphere. An example in this respect is the manufacture of hydrogen using steam reforming of natural gas, which generates one CO_2 molecule for every two H_2 molecules formed [12]. An ideal source of hydrogen is to split water using renewable energy sources, according to the equation:

$$2H_2O \rightarrow O_2 + 2H_2 \tag{1}$$

This is achieved by water electrolyzers that combine a water oxidizing anode (which generates O_2) with a proton reducing cathode (which generates H_2). Of these two half-reactions, water oxidation at the anode is, thermodynamically, the more demanding [11]:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \quad 1.00\ \text{V at pH 0; 0.62 V at pH 7} \quad \text{(vs. Ag/AgCl)} \tag{2}$$

In practice, the mechanistic complexity of the water oxidation half-reaction and the large activation barrier that exists, means that a substantial electrochemical overpotential must be applied to drive the reaction. For this reason, typical commercial water electrolyzers operate at an applied potential of >2.00 V. The accompanying energetic inefficiency has, to date, largely rendered water electrolysis unviable as a technique for large-scale hydrogen generation. Catalysts which lower the overpotential for water oxidation and, therefore, also, lower the overall voltage required for electrolysis, are needed for water splitting driven by renewable energy to become competitive.

In most electrolyzers, the water feedstock needs to be quite pure to prevent corrosion [12]. If one takes into account the large number of commuter miles traveled worldwide each day, this requirement means that a very substantial investment in clean water would be needed if we were to meet transportation demands using hydrogen from electrolysis. The challenge in sustainably producing hydrogen from water is therefore not only to develop catalysts that dramatically reduce the energy requirement, but also to develop catalysts that are capable of producing hydrogen sustainably from non-potable water sources.

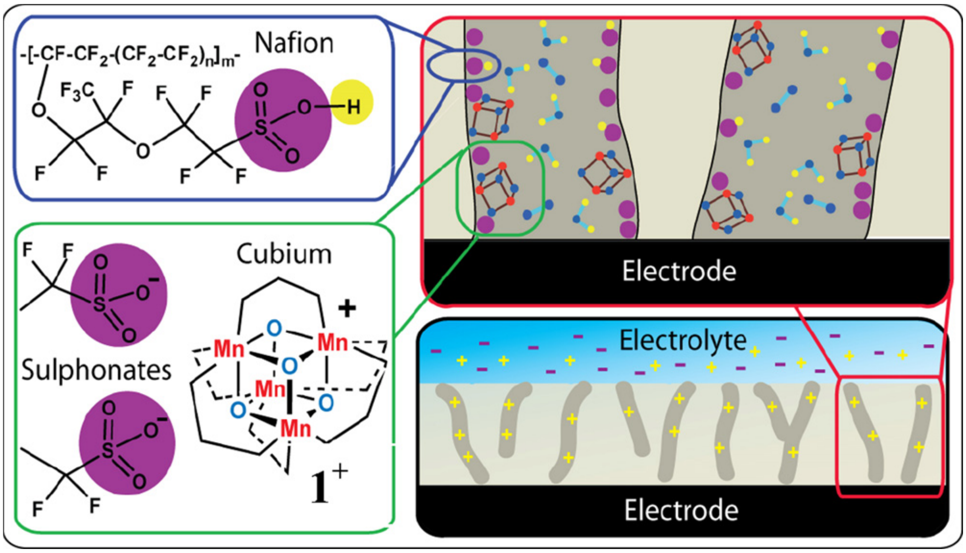

Fig. 1. Schematic representation of the manganese *cubium*, $[Mn_4O_4L_6]^+$ 1^+ (L = (*p*-MeO-Ph)$_2$PO$_2$), suspended in a Nafion membrane. Figure adapted from reference [25].

3.2. Seawater as a source of hydrogen from electrolysis

Seawater is one of the most abundant and accessible resources on Earth. It contains a multiplicity of inorganic ions, organic molecules and biological materials, whose concentrations vary, often dramatically, around the world. Typical seawater contains common ions like Cl^-, Na^+, Mg^{2+}, $SO_4{}^{2-}$, Ca^{2+}, K^+ and $HCO_3{}^-$ (listed in order of decreasing concentration). Of these, Cl^- and Na^+ are the most abundant, with standard mean chemical concentrations of [Cl^-] 0.55 M and [Na^+] 0.47 M, respectively [14]. If subjected to electrolysis, seawater may undergo a variety of oxidation processes, of which the most important is:

$$2Cl^- \rightarrow Cl_2 + 2e^- \quad 1.16 \quad V(vs. Ag/AgCl) \tag{3}$$

While thermodynamically less favorable than water oxidation (reaction (2)) [14], this half-reaction has a substantially lower overpotential. For this reason, chloride oxidation occurs readily and selectively at the anode in the presence of chloride ions within a standard, commercial electrolysis cell operating at >2.00 V. In so doing, it: (a) reduces the efficiency of the cell, (b) consumes a significant portion of the applied energy, and (c) generates the undesirable by-product of chlorine gas, Cl_2, which is highly poisonous.

Efficient electrolysis of seawater requires a catalyst at the anode that drastically diminishes the overpotential required for Eq. (2) and is, thereby, selective for water oxidation, yielding O_2. Several catalysts have been developed to selectively oxidize water instead of chloride in seawater. Particularly prevalent in this respect have been oxides of Mn–Mo–Fe, and Mn–Mo–W which yield high proportions of dioxygen as the anodic product [2–8]. Coating of such catalysts with a thin layer of the polymer Nafion, which electrostatically repels anionic chloride ions, has been shown to enhance their selectivity for oxygen generation, albeit with diminished overall catalytic activity [2]. Immobilized enzymes and homogeneous Mo complexes, that are capable of selectively oxidizing water in seawater, have also been described [15,16]. The types of precious metal catalysts that are typically used at the anode in commercial water electrolyzers, like Pt, Ir and Ru, do not preferentially oxidize water and are not suitable for seawater electrolysis [17,18].

The most efficient catalyst that employs solar energy to oxidize water is the *Photosystem II Complex* (*PSII*), which forms part of the photosynthetic apparatus found in plants [19]. At the core of *Photosystem II* is a tetra-manganese oxo cluster referred to as the *Water Oxidation Complex* (*WOC*) [20,21]. This cluster facilitates efficient oxidation of water and is highly specific for water molecules as reactants. It is protected within a membrane-bound protein active site that tightly controls the concentration of ions such as chloride, Cl^-. This specificity allows photosynthetic organisms to flourish wherever there is a source of water, including in the oceans. The oxidation process involves a driving potential of 1.05 V vs. Ag/AgCl, which is provided by the light absorbing pigments [22].

In previous work we described a method to facilitate catalytic water oxidation using a bio-inspired manganese *cubane* cluster $[Mn_4O_4L_6]^+$, (L = (*p*-MeO-Ph)$_2$PO$_2$), known colloquially as "*cubium*" (1^+) (Fig. 1) [9,23–26]. When 1^+ is incorporated within a thin layer of the proton-conducting membrane, Nafion, deposited on a conducting surface which is then biased at 1.00 V (vs. Ag/AgCl) and illuminated with light, the system readily and actively oxidizes water to generate O_2 (Fig. 1). The channels of Nafion are proton conductors and selectively permeable to cations, not anions, due to the presence of a lining of sulfonate anions (Fig. 1) [27]. The Nafion sulfonate groups are also thought to assist the catalytic process by transporting away the protons that are released by the water reagents during cycling [9].

In the present study, we investigate the influence on the photocatalytic process of high concentrations of three different salts in the water electrolyte; namely, sodium sulfate, sodium perchlorate and sodium chloride. The ability of the system to preferentially oxidize water in seawater is also examined. This work extends upon and elaborates abbreviated data that was published in a conference proceeding [28].

3.3. Ionic strength and photocurrent

We previously reported that consistent photocurrents deriving from photocatalytic water oxidation, were observed for the 1^+/Nafion system deposited on a range of electrode substrates, including Pt, glassy carbon and ITO [26]. Our initial studies involved electrolytes comprising neat water or 0.1 M solutions of salts such as Na_2SO_4, NaF, Bu_4NPF_6, and Bu_4NClO_4 [26]. To further investigate the effect of the electrolyte on the photocurrent, catalytic testing was then carried out using aqueous electrolytes saturated with Na_2SO_4 or NaCl, as well as with 5 M $NaClO_4$ and, later, seawater.

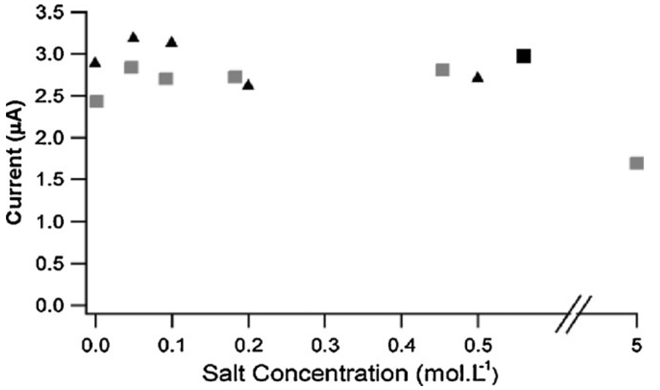

Fig. 2. Plot of the photocurrent of 1^+/Nafion-glassy carbon electrode illuminated at 1.00 V (vs. Ag/AgCl) as a function of increasing Na_2SO_4 (▲) and $NaClO_4$ (▨) concentration. The use of seawater as electrolyte yielded data (■) which was in the same range (within 10%) as that obtained at <0.5 M salt concentration.

The first experiments were conducted using sodium sulfate and sodium perchlorate electrolyte and reported in our previous conference proceeding [28]. As noted, increasing the concentrations of these salts up to 0.5 M in the electrolyte solution had no noticeable influence on the observed photocurrent (Fig. 2). A slight decrease in photocurrent was observed when the concentration of $NaClO_4$ was raised to 5 M (Fig. 2) [28].

We have previously demonstrated, using cyclic voltammetry, that electrical conductivity in the 1^+/Nafion system is improved by increasing the concentration of protons in the solution [9]. This is believed to be because the protons compete with 1^+ for the ion-exchange sites in the Nafion, thereby increasing the dynamism of the 1^+-Nafion interactions and allowing the catalyst to more readily migrate to the electrode surface where it can release electrons and cycle. During water oxidation, conductivity is maintained because protons are produced during the oxidation process. These protons enable the photocurrent to be sustained. We have also demonstrated that the absolute size of the photocurrent increases linearly with increasing pH; this is to be expected given that the potential required to oxidize water is known to become 59 mV more positive for each one unit decline in pH [25]. From the data in Fig. 2, we conclude that the concentration of the electrolyte salt, by contrast, produces no observable effect on the photocurrent of the system at concentrations below 1 M. At extremely high salt concentrations, only a trivially small, negative effect is observed.

3.4. Catalytic selectivity

The 1^+/Nafion catalytic assembly has previously also been shown to yield no photocurrent when neat acetonitrile is used as an electrolyte [9,26]. As aliquots of water are titrated into the acetonitrile, however, the photocurrent progressively increased up to ca. 8% water (v/v). Beyond 8% water, the current ceased increasing and remained constant. This experiment demonstrated that the absolute magnitude of the photocurrent is proportional to the concentration of the oxidizable water substrate within the membrane. This behavior is highly characteristic of saturation kinetics of the type observed in many enzymes, where it is known as Michaelis–Menten kinetics.

The cubanes are also able to oxidize simple organic molecules, like thioethers, hydrocarbons, alkenes, benyzl alcohol and benzaldehyde, when dissolved in organic solution [29]. The cubane 1 has, moreover, been reported to oxidize Me_3SiCl (present in large excess) to chlorine, Cl_2, in O_2-free organic solution [19]. This led us to examine whether the 1^+/Nafion system is able to photocatalytically oxidize benzyl alcohol when present in an aqueous solution.

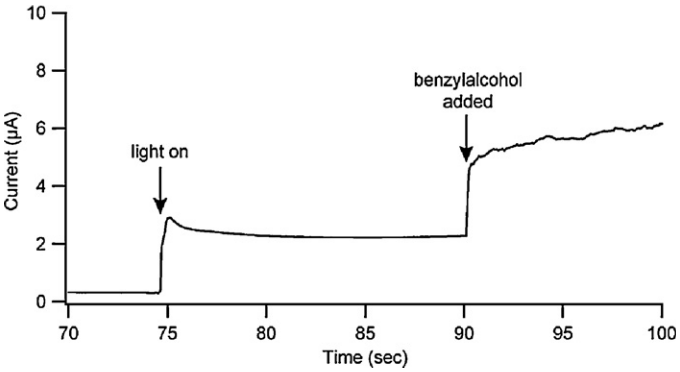

Fig. 3. Photocurrent of 1^+/Nafion on glassy carbon in 0.1 M Na_2SO_4 aqueous solution (10 mL) at 1.00 V (vs. Ag/AgCl), before and after the addition, with no stirring, of benzyl alcohol (0.5 mL).

As can be seen in Fig. 3, the photocurrent was found to dramatically increase on the addition of benzyl alcohol to the aqueous electrolyte. The oxidation of organic molecules like benzyl alcohol is energetically less demanding than the oxidation of water. Thus, we conclude that the photocurrent is dependent on the rate at which the 1^+/Nafion system is able to catalyze the oxidation of individual substrates.

For the 1^+/Nafion system to operate successfully in non-potable water like seawater, the system must be able to preferentially catalyze the oxidation of water rather than chloride (Cl^-) ions (which are typically present at concentrations of ~0.5 M in seawater). As noted earlier, surface-cast Nafion layers, being cation-exchange resins, have been reported to electrostatically repel and block transport of anionic Cl^- ions to the surface of electrolyzer anodes, thereby enhancing the rate of water oxidation relative to chloride oxidation [2]. We were therefore interested to see how a glassy carbon electrode, coated with a layer of Nafion of the same thickness as that used in our 1^+/Nafion electrodes, would behave in an aqueous solution saturated with NaCl.

Fig. 4(a) shows that some limited Cl^- oxidation does occur in such a system, over the potential range 1.20–1.40 V (vs. Ag/AgCl). At potentials positive of 1.50 V, the oxidation of the bulk water solution becomes overwhelmingly prevalent. Thus, in our system at least, the presence of a thin Nafion layer is not sufficient to entirely block Cl^- transport to the electrode surface. It, undoubtedly, *hinders* movement of Cl^- to the electrode – as attested by the fact that water oxidation predominates above 1.50 V – but it clearly does not halt it completely. This would be in line with previous studies which showed that surface-cast Nafion layers facilitated, at best, 80% dioxygen and 20% chlorine generation in seawater [2].

Fig. 4(b) displays comparable data when the Nafion coating contains 1^+ and is illuminated with light. As can be seen, the presence of the catalyst is confirmed by the large redox peak that appears at 0.85–1.15 V, peaking at approximately 0.95 V. Between 1.00 and 1.20 V, chloride ions are, moreover, not catalytically converted to chlorine by the underlying electrode surface (Fig. 4(a)). Thus, by maintaining the system at a potential within the range 1.00–1.20 V, all of the gaseous products formed at the anode will derive exclusively from water oxidation photocatalysis in Nafion. In other words, it is possible to determine whether the catalyst favors photocatalytic O_2 or Cl_2 formation by studying the ratio of product gases from 1^+/Nafion catalyst in the presence of aqueous Cl^- at a fixed bias of 1.00 V and under illumination by light.

Fig. 5(a and b) depicts the photocurrent of a glassy carbon electrode coated with 1^+/Nafion and illuminated at 1.00 V (vs. Ag/AgCl) in the presence of increasing Cl^- concentration up to saturated NaCl. As can be seen in Fig. 5(b), the photocurrent is unaffected by the chloride concentration, even in saturated chloride solution.

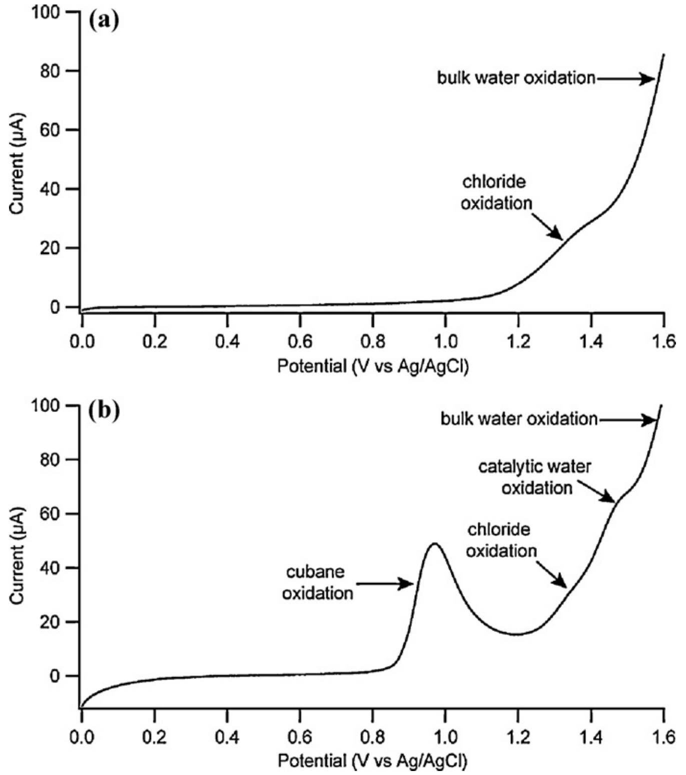

Fig. 4. Linear sweep voltammetry in aqueous 0.1 M Na_2SO_4 and 0.05 M NaCl at a scan rate of 10 mV s^{-1} of: (a) Nafion on a glassy carbon electrode, (b) 1^+/Nafion on a glassy carbon electrode.

Experiments using seawater yielded data and results that were very similar (Fig. 5(b)). Fig. 2 shows the photocurrent for seawater relative to the Na_2SO_4 and $NaClO_4$ electrolytes. Tests using Merck analytical chlorine test strips, after two days of continuous water oxidation at 1.00 V (vs. Ag/AgCl) in a sealed cell, confirmed that no chlorine was detected. The strips are accurate down to 0.5 mg/L Cl_2.

These experiments suggest that the catalyst in Nafion either does not catalyze the oxidation of Cl^- in aqueous solutions or, at least, it very substantially prefers to oxidize water even in the presence of Cl^- ions.

To further investigate the ability of the catalyst to catalyze the oxidation of Cl^-, we immersed the 1^+/Nafion-glassy carbon electrode system in a solution of acetonitrile (0.1 M Bu_4NPF_6) and then systematically added Bu_4NCl. As mentioned earlier, 1 is known to oxidize Me_3SiCl to chlorine, Cl_2, in O_2-free organic solution [19].

Fig. 6 shows, however, that the addition of Cl^- in the form of Bu_4NCl did not generate a noticeable photocurrent. In fact, essentially no photocurrent was observed at all. The small increase in current after the start of illumination that was observed for the acetonitrile – $Bu_4NCl{\cdot}H_2O$ electrolyte (Fig. 6(a)), compared to the acetonitrile – Bu_4NPF_6 electrolyte (Fig. 6(b)), is thought to be due to the small amount of water of hydration from the Bu_4NCl salt.

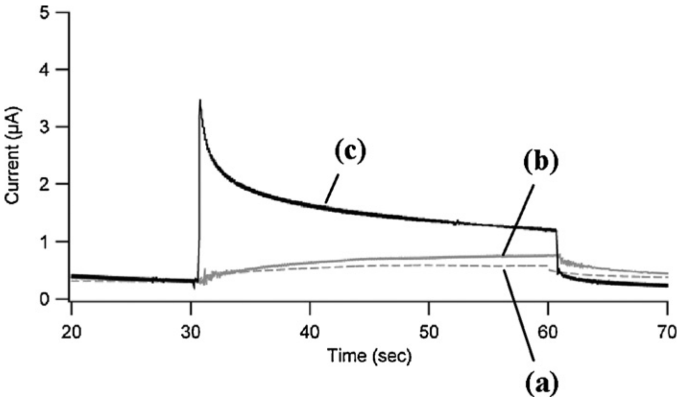

Fig. 6. Photocurrent from a 1^+/Nafion glassy carbon electrode, poised at the oxidation potential of the cubane (1.00 V vs. Ag/AgCl), (a) in acetonitrile with 0.1 M Bu_4NPF_6 (– – – –), (b) in acetonitrile with $Bu_4NCl{\cdot}H_2O$ (————), and (c) in acetonitrile with 10% (v/v) water (—).

By contrast, the addition of even tiny aliquots of water to the acetonitrile solution dramatically increased the observed photocurrent. Water is clearly a highly preferred reactant in the catalysis.

Since no significant photocurrent was seen in the presence of Cl^- and no increase in photocurrent was observed in aqueous solutions saturated with NaCl, we propose that the 1^+/Nafion system does not catalyze the oxidation of Cl^- at the 1.00 V (vs. AgCl) potential needed to catalyze water oxidation. This is likely due largely to the repellant nature of the Nafion and the fact that the catalyst is buried within it, not merely at its surface (as in previous studies [2]). It is also possible, however, that the oxidation of Cl^- commences at potentials more positive than the potential required to oxidize the cubane in aqueous solution. That is, it is also possible that the catalyst diminishes the overpotential of the water oxidation reaction, to thereby facilitate it at a potential lower than that required for Cl^- oxidation. The fact that the free cubane (not embedded within Nafion) is known to react spontaneously with Me_3SiCl to yield Cl_2, contends against this possibility however.

While the precise origin of the specificity remains uncertain, it is nevertheless clear that 1^+/Nafion preferentially and exclusively oxidizes water over chloride ions in non-potable water and seawater when biased at 1.00 V and illuminated with light. In short, the system is highly selective for water oxidation during photocatalysis.

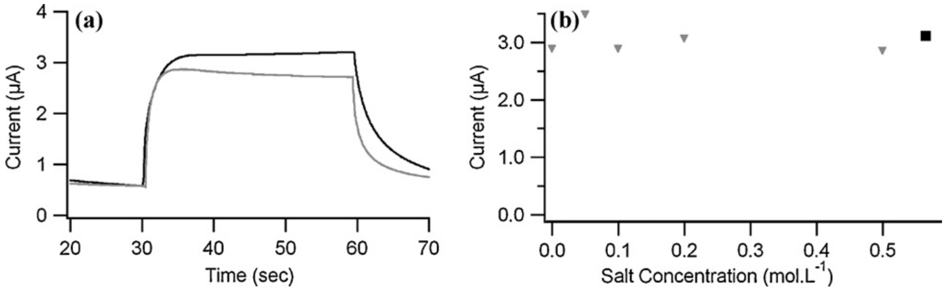

Fig. 5. (a) Photocurrent of 1^+/Nafion on glassy carbon electrode illuminated with light at 1.00 V (vs. Ag/AgCl) in neat water (—), and saturated aqueous NaCl (————). (b) Plot of the photocurrent in (a) with increasing NaCl (▼) concentration. The use of seawater as electrolyte yielded data (■) which was in the same range (within 10%) as the data depicted in (b).

4. Conclusions

The presence of large concentrations of chloride ions in the supporting electrolyte of photocatalytic water-splitting systems based on a 1^+/Nafion-glassy carbon anode, appear to have essentially no influence on the rate of water oxidation or on the mixture of product gases at an applied bias of 1.00 V (vs. Ag/AgCl). Under illumination with light, the only catalytic product is dioxygen, O_2. Competitive chlorine formation is not observed at all. Thus, 1^+/Nafion appears to be highly selective for water oxidation over chloride oxidation. This result is qualitatively similar to the *PSII-WOC*, which also facilitates only water oxidation in non-potable water sources like seawater. Like the *PSII-WOC*, which operates at a driving potential of 1.05 V vs. Ag/AgCl, the active site in 1^+/Nafion is surrounded by a proton conducting environment with high cation affinity. This result stands in direct contrast with conventional, commercial water electrolyzer systems which generate largely chlorine gas at the anode when using chloride-containing non-potable water or seawater as electrolyte. The origin of this effect appears to derive largely from the electrostatically repulsive nature of the Nafion support for anions like Cl^-. The cation specificity of the Nafion membrane may limit the concentration of Cl^- ions at the catalyst active sites.

As the system does not oxidize Cl^- and is unaffected by ionic concentrations observed in abundant water sources such as seawater, we propose that a range of non-potable water sources could be used for the practical operation of this system.

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