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## **A bio-inspired molecular water oxidation catalyst for renewable hydrogen generation: An examination of salt effects**

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## A bio-inspired molecular water oxidation catalyst for renewable hydrogen generation: An examination of salt effects

### Abstract

Most transport fuels are derived from fossil fuels, generate greenhouse gases, and consume significant amounts of water in the extraction, purification, and/or burning processes. The generation of hydrogen using solar energy to split water, ideally from abundant water sources such as sea water or other non-potable sources, could potentially provide an unlimited, clean fuel for the future. Solar, electrochemical water splitting typically combines a photoanode at which water oxidation occurs, with a cathode for proton reduction to hydrogen. In recent work, we have found that a bioinspired tetra-manganese cluster catalyzes water oxidation at relatively low overpotentials (0.38 V) when doped into a Nafion proton conduction membrane deposited on a suitable electrode surface, and illuminated with visible light. We report here that this assembly is active in aqueous and organic electrolyte solutions containing a range of different salts in varying concentrations. Similar photocurrents were obtained using electrolytes containing 0.0 - 0.5 M sodium sulfate, sodium perchlorate or sodium chloride. A slight decline in photocurrent was observed for sodium perchlorate but only at and above 5.0 M concentration. In acetonitrile and acetone solutions containing 10% water, increasing the electrolyte concentration was found to result in leaching of the catalytic species from the membrane and a decrease in photocurrent. Leaching was not observed when the system was tested in an ionic liquid containing water, however, a lower photocurrent was generated than observed in aqueous electrolyte. We conclude that immersion of the membrane in an aqueous solution containing an electrolyte concentration of 0.05 - 0.5M represent good conditions for operation for the cubium/Nafion catalytic system.

### Keywords

catalyst, renewable, hydrogen, generation, examination, bio, inspired, molecular, salt, water, effects, oxidation

### Disciplines

Life Sciences | Physical Sciences and Mathematics | Social and Behavioral Sciences

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# A bio-inspired molecular water oxidation catalyst for renewable hydrogen generation: An examination of salt effects

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## ABSTRACT

Most transport fuels are derived from fossil fuels, generate greenhouse gases, and consume significant amounts of water in the extraction, purification, and/or burning processes. The generation of hydrogen using solar energy to split water, ideally from abundant water sources such as sea water or other non-potable sources, could potentially provide an unlimited, clean fuel for the future. Solar, electrochemical water splitting typically combines a photoanode at which water oxidation occurs, with a cathode for proton reduction to hydrogen. In recent work, we have found that a bioinspired tetra-manganese cluster catalyzes water oxidation at relatively low overpotentials (0.38 V) when doped into a Nafion proton conduction membrane deposited on a suitable electrode surface, and illuminated with visible light. We report here that this assembly is active in aqueous and organic electrolyte solutions containing a range of different salts in varying concentrations. Similar photocurrents were obtained using electrolytes containing 0.0 - 0.5 M sodium sulfate, sodium perchlorate or sodium chloride. A slight decline in photocurrent was observed for sodium perchlorate but only at and above 5.0 M concentration. In acetonitrile and acetone solutions containing 10% water, increasing the electrolyte concentration was found to result in leaching of the catalytic species from the membrane and a decrease in photocurrent. Leaching was not observed when the system was tested in an ionic liquid containing water, however, a lower photocurrent was generated than observed in aqueous electrolyte. We conclude that immersion of the membrane in an aqueous solution containing an electrolyte concentration of 0.05 - 0.5M represent good conditions for operation for the cubium/Nafion catalytic system.

**Keywords:** Water oxidation, photosystem II, manganese cubane catalyst, salt effects, hydrogen, photocatalysis

## INTRODUCTION

Recent developments in renewable energy technologies, such as wind, photovoltaic, geothermal, tidal and wave, have led to a significant increase in the production of clean electricity. However, the challenge of producing low-carbon, renewable, transport fuels still remains. Hydrogen is a carbon-free, high-energy carrier that can be utilized efficiently in a range of applications. It remains one of the most promising fuels of the future. [1, 2]

Hydrogen can be produced using a variety of techniques and from a range of feedstocks. However, many of these rely on fossil fuels and the subsequent release of carbon dioxide into the atmosphere (for example, steam reforming from natural gas).[1] An ideal source of hydrogen gas is through the splitting of water using renewable energy sources ( $2\text{H}_2\text{O} \rightarrow \text{O}_2 + 2\text{H}_2$ ). This can be achieved by water electrolyzers that combine a water oxidation anode with a cathode for proton reduction. Of these two processes, the oxidation of water is thermodynamically very demanding:



The theoretical potential required to drive water oxidation falls to 0.82 V at pH 7. In practice, however, mechanistic complexity coupled with a substantial activation barrier means that a large electrochemical overpotential is needed to drive this reaction. Typical water electrolyzers therefore operate at ca. 2 V. For water splitting using renewable energy to be successful, catalysts are needed to lower the overpotential and, therefore also the overall voltage required to achieve water oxidation.

The most efficient known system for harnessing solar energy to oxidize water is the Photosystem II (PSII) complex that makes up part of the photosynthetic apparatus found in plants. At the core of Photosystem II is a tetra-manganese cluster referred to as the water oxidation complex (PSII-WOC).[3, 4] This cluster achieves efficient oxidation of water and is highly specific for water molecules. It is protected within a membrane bound protein active site that tightly controls the concentration of ions, such as  $\text{Cl}^-$ . This specificity has allowed photosynthetic organisms to flourish wherever there is a source of water. The oxidation process is achieved with a driving potential (provided by the light absorbing pigments) of 1.25 V vs SHE.[5]

We previously described a method for inducing a bio-inspired manganese cubane cluster  $[\text{Mn}_4\text{O}_4\text{L}_6]$ , ( $\text{L} = (p\text{-MeO-Ph})_2\text{PO}_2$ ) [6, 7] to undertake catalytic water oxidation when supported in a proton-conducting membrane, Nafion. [8] Investigation of the mechanism of catalysis suggests that water oxidation is achieved via an intra-molecular process where two of the core oxo ligands form an oxygen-oxygen bond resulting in the evolution of  $\text{O}_2$ . This is followed by the binding of water, which facilitate the regeneration of the cubane core coupled with the release of protons.[9] This process takes place at the hydrophobic/hydrophilic interface found within the channels of the Nafion membrane when it is cast as a thin layer upon a conducting electrode. The channels of Nafion are proton conductors and are selectively permeable to cations (and not anions) due to the lining of sulfonate anions (Figure 1).[10] In addition to providing an interface for the cluster to interact with water and the electrode, and for protecting the cluster from the bulk water solution, the Nafion sulfonate groups are thought to assist in the removal of protons arising from water in the catalytic process.[9]

A consistent photocurrent was observed for the cubium/Nafion system using a range of electrode materials, including Pt, glassy carbon and ITO, and in a range electrolytes at 0.1 M, including  $\text{Na}_2\text{SO}_4$ , NaF in water and  $\text{Bu}_4\text{NPF}_6$ ,  $\text{Bu}_4\text{NClO}_4$  in a water/acetonitrile mixture.[8] In the current study, we have investigated the influence of varying the ionic strength of aqueous and organic electrolytes, including sodium sulfate, sodium perchlorate, sodium chloride and tetrabutylammonium perchlorate ( $\text{Bu}_4\text{NClO}_4$ ), on the activity of the cubium,  $[\text{Mn}_4\text{O}_4\text{L}_6]^+/\text{Nafion}$  catalyst. The catalytic activity of this assembly was also investigated when immersed in an acetone.

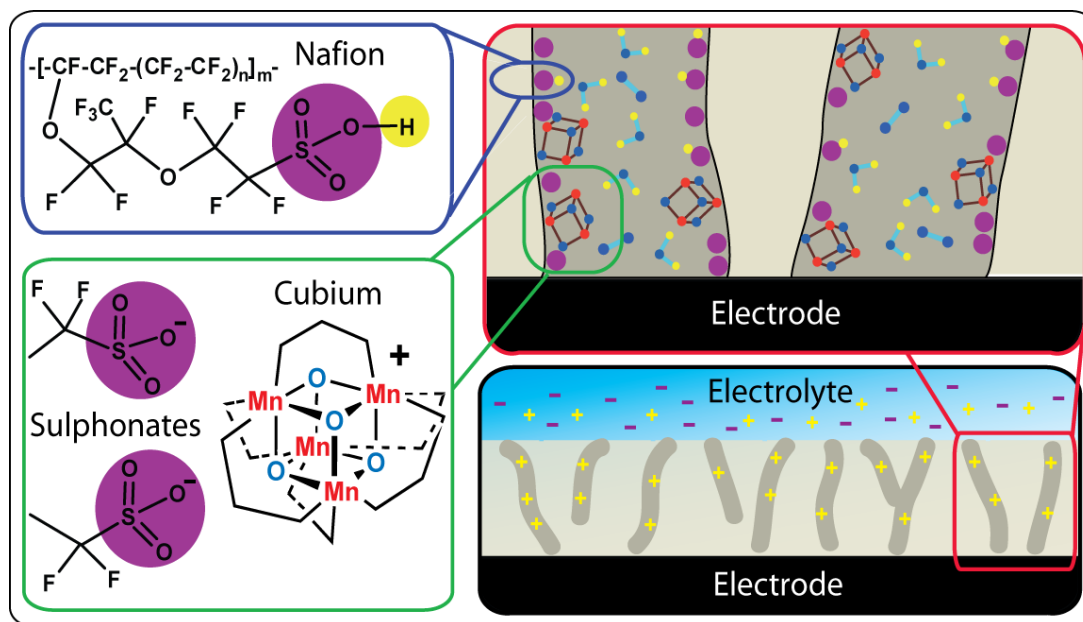


Figure 1. Schematic representation of the catalytic manganese cubium,  $[\text{Mn}_4\text{O}_4\text{L}_6]^+$  ( $\text{L} = (p\text{-MeO-Ph})_2\text{PO}_2$ ), suspended in a Nafion membrane. Figure adapted from Brimblecombe *et al.* 2009.[14]

## 1. EXPERIMENTAL SECTION

**Materials and Methods:** Bis(methoxyphenyl)phosphinic acid was purchased from Aldrich, and used without further purification. Tetrabutylammonium hexafluorophosphate ( $\text{Bu}_4\text{NPF}_6$ ) was obtained from GFS Chemicals and purified by a published procedure.[11] Nafion<sup>®</sup> was purchased from Dupont as a Nafion - PFSA polymer dispersion DE 1020, which is an aqueous dispersion of 10-12% Nafion. All other reagents were purchased from BDH or Aldrich and used as received. Cubane  $[\text{Mn}_4\text{O}_4\text{L}_6]$ , ( $\text{L} = \text{bis}(p\text{-methoxyphenyl})\text{phosphinate}$ ) and cubium  $[\text{Mn}_4\text{O}_4\text{L}_6]^+\text{ClO}_4^-$  were prepared as described in literature.[7]

**Electrochemistry:** Electrochemical experiments were conducted at  $22(\pm 2)^\circ\text{C}$  with BAS (Bio Analytical Systems) Epsilon CS3 or BAS 100B workstations. Cyclic voltammograms were obtained at scan rates of 5 to  $500\text{ mVs}^{-1}$  in a conventional three electrode electrochemical cell fitted with inlet and outlet ports for degassing solutions with nitrogen. Experiments in  $\text{CH}_2\text{Cl}_2$  or  $\text{CH}_3\text{CN}$  (0.1 M  $\text{Bu}_4\text{NPF}_6$ ), used an  $\text{Ag}/\text{Ag}^+$  (0.01 M  $\text{AgNO}_3$  in  $\text{CH}_3\text{CN}$ ) reference electrode, with a double glass frit separating the electrode from the test solution. The ferrocene/ferrocenium oxidation process was used to provide a reference potential calibration system for electrochemical studies in organic solvents (0.400 V vs NHE at  $25^\circ\text{C}$  [5]). Aqueous experiments were conducted in distilled water containing 0.1 M  $\text{Na}_2\text{SO}_4$  as the electrolyte. In this case, potentials were referenced against a BAS  $\text{Ag}/\text{AgCl}$  (3 M  $\text{NaCl}$ ) glass bodied reference electrode separated from the test solution by a Vycor frit, with a potential of 0.200 V vs NHE at  $25^\circ\text{C}$  (BAS reference electrode users manual). All voltammetric experiments used Pt wire or a Pt mesh auxiliary electrodes.

The working electrodes used were 3 mm diameter glassy carbon and Pt disc electrodes. The glassy carbon working electrode had an electroactive area of  $5.9\text{ mm}^2$  as determined by oxidation of 1.0 mM ferrocene in  $\text{CH}_3\text{CN}$  (0.5 M  $\text{Bu}_4\text{NPF}_6$ ) and use of the Randles-Sevcik equation [12] with a diffusion coefficient ( $D$ ) of  $1.7 \times 10^{-5}\text{ cm}^2\text{s}^{-1}$ .

**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  $120^\circ\text{C}$  for 20 min. Doping of the cast Nafion membrane with the cubium catalyst was achieved by immersion in a 2 mM  $\text{CH}_3\text{CN}$  solution of  $[\text{Mn}_4\text{O}_4\text{L}_6]^+\text{ClO}_4^-$ . Cubium in Nafion is reduced to cubane, at the initial potential used in cyclic voltammetry.

**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  $500\text{mW}/\text{cm}^2$ , measured at the electrode surface.

**Salt Concentration Film Testing:** The working, reference and counter electrodes were assembled together in a standard configuration and moved between the testing electrolytes as one unit. They were rinsed using the respective solvents and dried on transfer between individual electrolyte preparations. Aqueous electrolytes were prepared by dissolving appropriate quantities of various salts,  $\text{Na}_2\text{SO}_4$ ,  $\text{NaClO}_4$  or  $\text{NaCl}$ , in unbuffered distilled water (pH 6.7). Photocurrent measurements for the aqueous electrolyte were carried out at 1.00 V vs an Ag/AgCl reference electrode. All acetonitrile solutions contained 0.1 M  $\text{Bu}_4\text{NPF}_6$ . Distilled water was added to the acetonitrile or acetone solution containing 0.1 M  $\text{Bu}_4\text{NClO}_4$  electrolyte, and to a solution of 1-ethyl-3-methylimidazolium. $\text{BF}_4$  to achieve a 10% (v/v) solution.

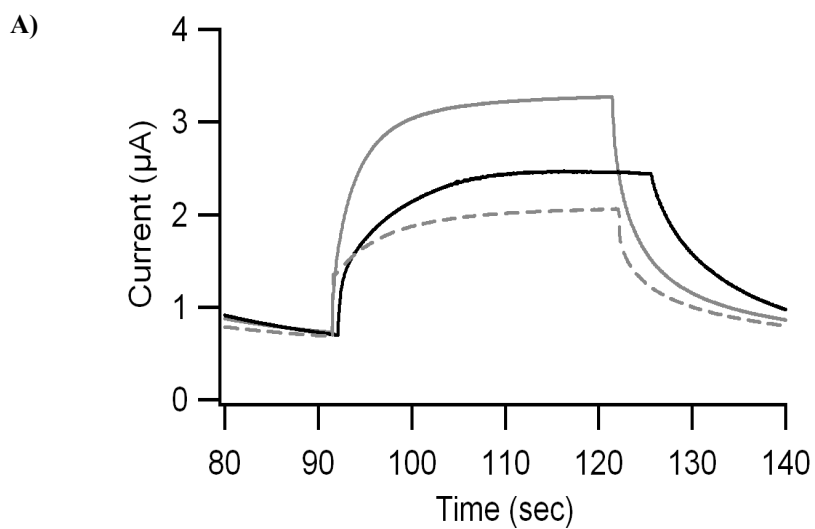
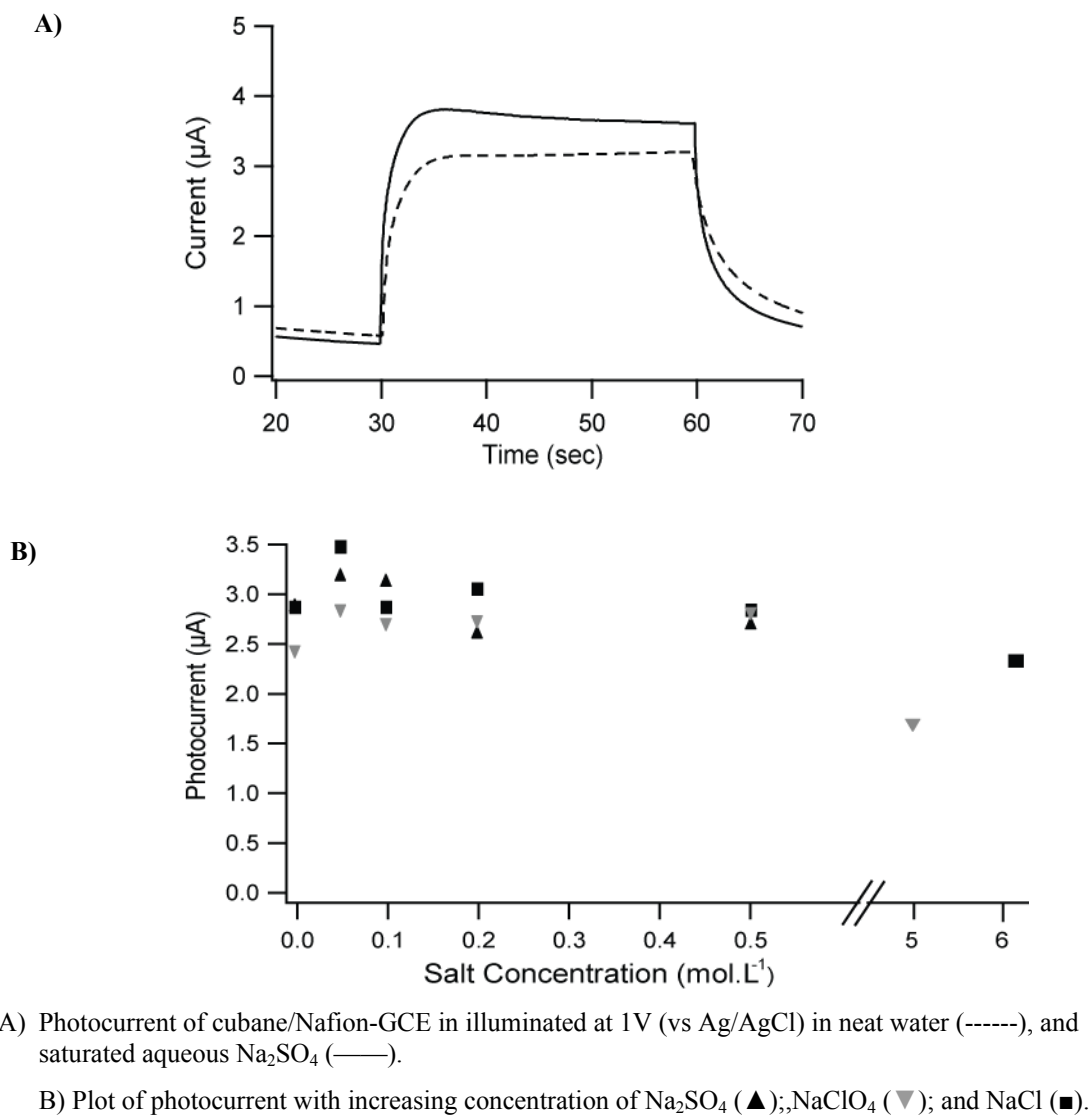
## 2. RESULTS AND DISCUSSION

### 2.1 Ionic Strength Dependence of Photocurrent

The observation that a reproducible photocurrent could be achieved for the cubium/Nafion catalytic system using a range of electrode materials, including Pt, glassy carbon and ITO, and in 0.1 M aqueous solutions of various electrolytes, including  $\text{Na}_2\text{SO}_4$ ,  $\text{NaF}$ ,  $\text{Bu}_4\text{NPF}_6$  and  $\text{Bu}_4\text{NClO}_4$ , [8] led us to further investigate the effect of the electrolyte on catalytic activity. Catalytic testing has now been undertaken using three salts,  $\text{Na}_2\text{SO}_4$  and  $\text{NaCl}$  (0 M – saturated), as well as  $\text{NaClO}_4$  (0 – 5 M).

The first series of experiments on the cubium/Nafion catalytic system were conducted using sodium sulfate and sodium perchlorate as electrolytes. As depicted in Fig. 2A, increasing the concentrations of these electrolytes had no significant effect on photocurrent for concentrations up to 0.5 M. A slight decrease in photocurrent was observed when the concentration of  $\text{NaClO}_4$  was raised to 5 M. We have previously demonstrated using cyclic voltammetry, that electrochemical conductivity is improved by the presence of protons.[11] This may be due to the ability of the cluster to migrate to the electrode surface to liberate electrons. During water oxidation, conductivity is maintained by the protons generated by the oxidation process, thereby enabling a photocurrent to be sustained over the short time scale displayed in Fig. 2. The photocurrent was found to increase with increasing pH as is expected from the relationship between water oxidation and proton concentration, with the potential required to oxidize water becoming 59 mV more positive for every decrease in pH unit. From the current investigation, we conclude the salt concentration has no observable effect on photocurrent at concentration lower than 1M and only a small negative effect at very high salt concentrations. This means that neither catalyst leaching from the Nafion film nor catalyst decomposition occur on the timescale of these experiments.

An alternative electrolyte approach is to operate the catalyst assembly in an organic solvent with dissolved water as a reagent. The photocurrent generated by the cubium/Nafion catalyst system in neat acetonitrile was previously found to be very small but to increase substantially as water was added to the electrolyte, reaching a plateau at 8-10% (v/v) water in the acetonitrile solution[8]. To investigate the potential of this approach and the influence of ionic strength, we tested photocurrent in an acetonitrile solution containing 10% water with increasing concentration of  $\text{Bu}_4\text{NClO}_4$  electrolyte. Direct comparison of the photocurrent arising from a cubane/Nafion-GCE immersed in water (0-1M  $\text{Na}_2\text{SO}_4$ ) and a 10% water (v/v) acetonitrile (0.1M  $\text{Bu}_4\text{NClO}_4$ ) solution revealed that the photocurrent was lower in the organic solution (Figure 3A). In addition to the lower water concentration at the reactive sites, a range of factors are thought to contribute to the lower photocurrent. Firstly, the proton content of the membrane is important in maintaining conductivity,[11] and thus we anticipate that immersion in an organic solvent, will lead to reduced proton conductivity especially within the Nafion. Secondly, the Nafion membranes tend to soften resulting in a weakening of the electrode adsorption when immersed in acetonitrile for extended periods. Thirdly, the swelling of the membrane in aqueous solution is believed to be important in maintaining the substructure of Nafion which assists in the catalytic process. The photocurrent was lost after extended immersion in a solution of acetonitrile/dichloromethane containing concentrated cationic species, due to leaching of the catalytically active cation species from the membrane.[8]



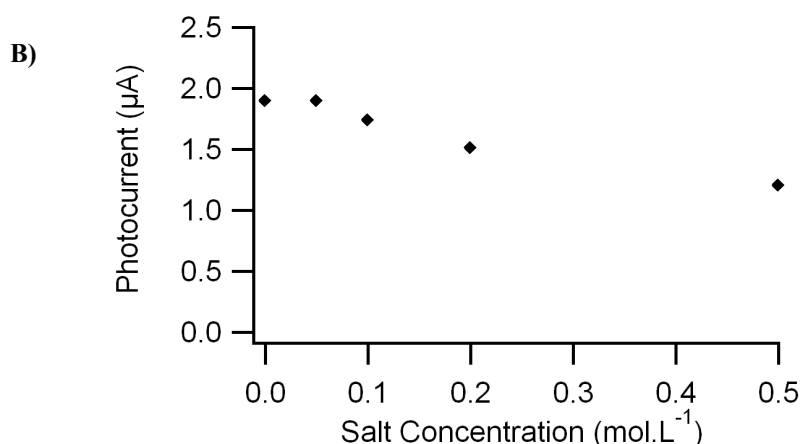


Figure 3. Photocurrent of cubane/Nafion-GCE membrane illuminated at 1V (vs Ag/AgCl) and:

A) Immersed in 0.1M  $\text{Na}_2\text{SO}_4$  aqueous electrolyte solution before (—) and after (-----) testing in acetonitrile and when immersed in a 0.1M  $\text{Bu}_4\text{NClO}_4$  acetonitrile solution containing 10%  $\text{H}_2\text{O}$  (—).

B) Immersed in acetonitrile containing 10%  $\text{H}_2\text{O}$  with increasing  $\text{Bu}_4\text{NClO}_4$  concentration.

Increasing the ionic strength of the electrolyte resulted in a slight decrease in photocurrent (Figure 3) which persisted even on subsequent re-immersion and testing of the membrane in aqueous electrolyte. This observation suggests that cations present in the organic electrolytes are able to leach the catalytic species more readily, resulting in the observed decrease in photocurrent. This was further investigated using a solution of 10% water (v/v) acetone (0.1M  $\text{Bu}_4\text{NClO}_4$ ) as the electrolyte (the cubane is more soluble in acetone than acetonitrile or water). The photocurrent generated on illumination of membranes immersed in acetone was significantly lower than that observed in aqueous electrolyte (Fig. 4). As in the acetonitrile electrolyte, photocurrent tests carried out in aqueous electrolyte following the organic testing revealed a decrease in photocurrent. In addition to increasing the solubility of the cluster, acetone is likely to swell the Nafion, further facilitating leaching of the cluster into the electrolyte.

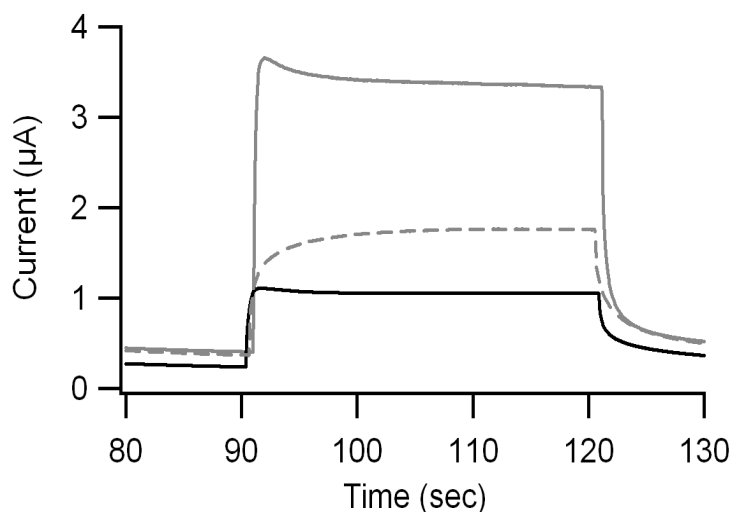


Figure 4. Photocurrent of cubane/Nafion-GCE film in illuminated at 1V (vs Ag/AgCl) and immersed in 0.1M  $\text{Na}_2\text{SO}_4$  aqueous electrolyte solution before (—) and after (-----) testing in acetone, and when immersed in a 0.1M  $\text{Bu}_4\text{NClO}_4$  acetone containing 10%  $\text{H}_2\text{O}$  (—).



The problems of leaching of the catalyst into the organic electrolyte led us to test the catalytic activity of the cubium/Nafion system in an ionic liquid, 1-ethyl-3-methylimidazolium.BF<sub>4</sub>, containing 10% (v/v) water. The measured photocurrent was 33% lower than that observed in aqueous electrolytes (Fig. 5). However, when the same membrane was re-tested in water, after the experiments in the ionic liquid, the photocurrent was found to correspond to that measured in the initial resting. This suggests either that leaching of the cluster does not occur or that it occurs at a much slower rate than observed in acetonitrile and acetone. The lower photocurrent observed in the ionic liquid electrolyte can be attributed to the much higher viscosity of this solvent system.

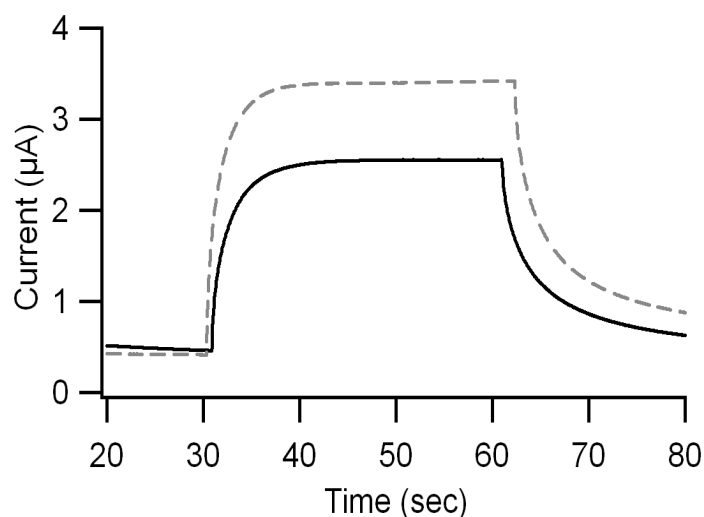


Figure 5. Photocurrent of cubane/Nafion-GCE in illuminated at 1V (vs Ag/AgCl), immersed in an aqueous solution containing 0.1M Na<sub>2</sub>SO<sub>4</sub> (-----) and immersed in a solution of 1-ethyl-3-methylimidazolium.BF<sub>4</sub> containing 10% water (v/v) (—).

### 3. CONCLUSIONS

The ionic strength of the supporting electrolyte in aqueous electrolyte appears to have no significant influence on the ability of the cubium/Nafion system to oxidize water at concentrations of 0.0 - 0.5 M. In electrolyte solutions of acetonitrile or acetone, in which the cubium is more soluble, the photocurrent decreases at higher ionic strength due to leaching of the catalyst from the membrane. Thus, these electrolyte configurations are not ideal for the application of this catalytic system. Leaching was not observed when the system was tested in an ionic liquid containing 10% water, however, the photocurrent measured was lower than observed in aqueous electrolyte. The cubium/Nafion catalytic system appears to operate best when the membrane is immersed in an aqueous solution containing an electrolyte concentration of 0.05 - 0.5M. In addition to providing the source of electrons, the aqueous environment is thought to be important for swelling of the Nafion membrane and facilitating conductivity within the membrane. As the catalytic cluster is insoluble in water the aqueous electrolyte also appears to assisting trapping the cluster within the membrane, maintaining electrochemical contact with the electrode. The salt concentration in the solution appears to assist with conductivity within the cell but we note, again, that significant photocurrent is observed in neat water. The optimum electrolyte concentration compares favorably with the concentrations of ions found in many common water sources, such as ground and sea water.

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