Towards Hydrogen Energy: Progress on Catalysts for Water Splitting

Gerhard F. Swiegers,\textsuperscript{A,D} Douglas R. MacFarlane,\textsuperscript{B,D} David L. Officer,\textsuperscript{A,D} Amy Ballantyne,\textsuperscript{A} Danijel Boskovic,\textsuperscript{A} Jun Chen,\textsuperscript{A} G. Charles Dismukes,\textsuperscript{C} Graeme P. Gardner,\textsuperscript{C} Rosalie K. Hocking,\textsuperscript{B} Paul F. Smith,\textsuperscript{C} Leone Spiccia,\textsuperscript{B} Pawel Wagner,\textsuperscript{A} Gordon G. Wallace,\textsuperscript{A} Bjorn Winther-Jensen,\textsuperscript{B} and Orawan Winther-Jensen\textsuperscript{B}

\textsuperscript{A}Intelligent Polymer Research Institute and ARC Centre of Excellence for Electromaterials Science, University of Wollongong, Wollongong, NSW 2522, Australia.
\textsuperscript{B}ARC Centre of Excellence for Electromaterials Science, Monash University, Clayton, Vic. 3800, Australia.
\textsuperscript{C}Department of Chemistry and Chemical Biology, Rutgers, The State University of New Jersey, Piscataway, NJ 08854, USA.
\textsuperscript{D}Corresponding authors. Email: Swiegers@uow.edu.au; Douglas.MacFarlane@monash.edu; DavidO@uow.edu.au

This article reviews some of the recent work by fellows and associates of the Australian Research Council Centre of Excellence for Electromaterials Science (ACES) at Monash University and the University of Wollongong, as well as their collaborators, in the field of water oxidation and reduction catalysts. This work is focussed on the production of hydrogen for a hydrogen-based energy technology. Topics include: (1) the role and apparent relevance of the cubane-like structure of the \textit{Photosystem II Water Oxidation Complex} (PSII-WOC) in non-biological homogeneous and heterogeneous water oxidation catalysts, (2) light-activated conducting polymer catalysts for both water oxidation and reduction, and (3) porphyrin-based light harvesters and catalysts.

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Introduction

The splitting of water into hydrogen and oxygen is a process that offers the prospect of a genuinely sustainable energy technology if the source of the energy is derived from sustainable solar, wind, tide, and hydro. The key to an energy efficient water splitting process is catalysts that can carry out the water oxidation and reduction reactions with minimal energy losses. Nature provides important insights in this respect in terms of structures and mechanisms that have evolved to carry out related processes in plants. A particularly key enzyme in this respect is the \textit{Photosystem II Water Oxidising Complex} (PSII-WOC) of photosynthesis, which facilitates the light-driven oxidation of water (H\textsubscript{2}O) into dioxygen (O\textsubscript{2}).\textsuperscript{[1,2]} The \textit{PSII-WOC} is, at the present time, the only known species capable of catalysing water oxidation in a sustained, efficient and light-driven form. Because of the remarkable versatility and efficiency of enzymes like the \textit{PSII-WOC}, a key task for chemists is to understand and apply Nature’s catalytic principles in artificial, non-biological systems. Breslow termed this quest ‘\textit{biomimetic chemistry}’ and defined it as:\textsuperscript{[3]}: ‘Imitating the style of enzyme catalysed processes in an effort to achieve some of the advantages, which Nature has realised by the use of enzymes.’ Its application to the specific case of the \textit{PSII-WOC} is widely spoken of as ‘\textit{Artificial Photosynthesis}’.

Taking a broader view of the mechanisms utilised by relevant enzymes informs the design of novel inorganic, polymer, and small molecule organic materials that are light harvesting, or catalytic in either or both of water oxidation and reduction. In the various forms that water splitting technology will ultimately take, all of these families of materials have a role to play and all are under active development at Monash and Wollongong Universities (ACES) and their collaborators. This article provides an overview of some of the recent developments in that research.

The Role of the Cubical Architecture of the \textit{Photosystem II Water Oxidising Complex} in Water Oxidation Catalysis

Fig. 1a depicts a model of the \textit{PSII-WOC} based on recent X-ray crystal structure data.\textsuperscript{[4–6]} As can be seen, the CaMn\textsubscript{3}O\textsubscript{4} core of the active site comprises a so-called \textit{cubane} structure in which the Ca and three of the Mn ions are positioned, with the four O atoms, in a cube-like arrangement. A fourth Mn ion lies on the outside of this cube. This structure is conserved in all known
photosynthetic organisms, raising questions as to its role and importance. Recent work has shown that several, recently-discovered, active Mn or Co molecular or inorganic water oxidation catalysts employ a cubane core that is structurally virtually identical to the catalytic core present in the PSII-WOC. Not only is the structural motif of the catalytic core of these species a cubane, but the actual physical dimensions of the cubane core also closely match those of the Mn₃O₄ unit which is capped by the Ca ion in the active site of the PSII-WOC. Examples in this respect include: (1) Nocera’s Co-pi catalyst, 

![Fig. 1.](image)

(a) Dimensionally accurate superimpositions of the CaMn₄O₄ core of the Photosystem II-Water Oxidising Complex (PSII-WOC) from the London, Berlin, and Osaka single crystal X-ray structures. The darkest depiction is that of the Osaka structure which was resolved to the highest resolution of 1.9 A. As can be seen, the core structures in these X-ray structures coincide to all intents and purposes. (b) Dimensionally accurate superimpositions of the EXAFS-derived structure of Co-pi (large structure), the London single crystal X-ray structure of the CaMn₄O₄ core of the PSII-WOC (dark small structure), and the XRD structure of the Co₄O₄ core of Hill’s Co polyoxotungstate catalyst (light small structure). The Ca ion in the PSII-WOC has been excluded for clarity (M = Mn or Co). (c) Dimensionally accurate superimpositions of the single crystal X-ray structure of the CaMn₄O₄ core of the London structure of the PSII-WOC (light structure) and the single crystal X-ray structure of the B-site of λ-Mn₄O₄ spinel (dark structure). The Ca ion in the PSII-WOC has been excluded for clarity (M = Mn or Co). (d) Surface formations of the Co₄O₄ and λ-Mn₄O₄ spinels that derive from the B-site (M = Mn or Co). Similar structures will exist at the surface of MnO₂ birnessite and Co-phosphate. (All images adapted and reproduced with permission; copyright the Royal Society of Chemistry: ref. [7]).

Gerry Swiegers is a Professor in the Intelligent Polymer Research Institute at the University of Wollongong. He is also an adjunct fellow of the ARC-funded Australian Centre for Electromaterials Science (ACES). His interests span bioinspired catalysis. He has been responsible for illuminating important fundamental aspects of chemical and biological catalysis.

Douglas MacFarlane is an ARC Federation Fellow at Monash University. He is also the program leader of the Energy Program in the ARC-funded Australian Centre for Electromaterials Science (ACES). His research interests include the development of ionic liquids for use in catalysis and energy storage.

David Officer is Professor of Organic Chemistry in the Intelligent Polymer Research Institute and the ARC Centre of Excellence in Electromaterials Science at the University of Wollongong, Wollongong, Australia (ACES). His research interests are in the areas of porphyrin and conducting polymer chemistry, nanomaterials, solar cells, and artificial photosynthesis.
(2) Frei and earlier workers’ Co₅O₄ spinel catalysts (B-site).[9]
(3) Spiccia and Hocking’s Mn₂O₃ birnessite,[10] (4) Hill’s recently discovered Co-polyoxotungstate catalyst,[11] (5) Dismuke’s λ-Mn₂O₃ spinel (B-site),[12] as well as (6) molecular Mn₄O₄ and Co₄O₄ cubanes.[12,13]

Fig. 1 illustrates these similarities. In Fig. 1a, the CaMn₃O₄ core of the PSII-WOC from the three most detailed single-crystal X-ray crystal structures of this enzyme, are superimposed upon each other. These are: (i) the so-called London structure by Barber, Iwata, and colleagues, which was resolved to 3.5 Å,[4] (ii) the so-called Berlin structure by Loll, Kern, and co-workers, which was resolved to 2.9 Å,[5] and (iii) the so-called Osaka structure by Umena, Kawakami, Shen, and Kamiya, that was resolved to 1.9 Å.[6] The Osaka structure provides the most detailed picture of the PSII-WOC core yet available. As can be seen in Fig. 1a, in all of these X-ray structures the CaMn₃O₄ core is essentially identical. The only significant difference is in the location of the fourth, outlying ‘dangler’ Mn ion. While there may have been radiation-induced variations in other parts of the (protein) structure, the CaMn₃O₄ core is invariant. This is so despite the differences in the technique used and, indeed, in spite of the diversity of the photosynthetic organisms involved.

This lack of evolutionary and structural diversity in the PSII-WOC core cubane arrangement implies that combinatorial biosynthesis in Nature has yielded only this one catalytic structure capable of facilitating sustained water oxidation catalysis. The question arises: why is that the case?


In fact, a Root Mean Square (RMS) ‘Goodness-of-Fit’ comparison indicates that there is a greater variation between the London, Berlin, and Osaka structures of the PSII-WOC than there is between the Osaka structure and the man-made catalysts mentioned above.[5] The active site structures of all of the above catalysts very closely match the Mn₃O₄ core in the PSII-WOC. Man-made efforts to develop new water oxidation catalysts therefore appear to have inadvertently also converged on a cubane structure that is, in large measure, not only qualitatively but also quantitatively identical to the cubane active site of the PSII-WOC.[7]

These apparent commonalities in an otherwise disparate and unconnected range of homogeneous, heterogeneous, and enzymatic catalysts are extraordinary. Human studies appear to be confirming the findings of combinatorial biosynthesis regarding the utility of the cubane structure in water oxidation catalysis.

The commonality may also extend to the actions of these catalysts. For example, several of these catalysts appear to undergo spontaneous dis-assembly and re-assembly of the cubane at an open face (or surface) during catalysis. Fig. 1d depicts the open-face structures that must exist in the Co₅O₄ and λ-Mn₂O₃ spinel catalysts.[7] Similar open faces are present in the Co-pi, Mn₂O₃ birnessite, and molecular cubane (immediately before O₂ formation, according to theoretical studies).[7] Given that Hill’s Co-polyoxotungstate also self-assembles, a library of associated, partially-assembled species must exist in solution; this would undoubtedly include an open-faced arrangement. We should observe also that Hill’s catalyst achieves the highest recorded turnover frequency of any abiological catalyst for catalytic water oxidation: >5 s⁻¹ at pH 8.[11] While short of the turnover frequencies achieved by the PSII-WOC, this nevertheless falls within the range of turnover frequencies typically achieved by enzymes: 1–10000 s⁻¹.

The only reasonable explanation for the fact that all of these heterogeneous, homogeneous, and enzymatic catalysts employ so similar a structure, is that the cubane arrangement is needed to guide the reactant (corner) O atoms along a single, optimum approach trajectory during the formation of the O-O bond of O₂. That is, the key commonality in all of these species likely involves a single approach trajectory and this manifests itself physically as a common catalytic structure in all catalytic classes.[14] If this is so, then it implies that the cubane structure must also allow vigorous, albeit constrained motion by the reactant O atoms at the corners of the cube (or open-faced half-cube). In the case of molecular species like the Mn₄O₄ or Co₄O₄ molecular cubanes, this would likely involve regular, repeated, conformational motion. However, in heterogeneous species like Co₄O₄ and the like, such motion would likely involve regular, repeated, oscillatory thermal motion at the surface of the catalyst.

This proposal is considerably strengthened by the finding from Rutgers University that the crystalline spinel LiMn₂O₄ becomes active in water oxidation only when the Li⁺ ions are removed, forming the isostuctural spinel λ-Mn₂O₃.[12] Delithiation presumably imparts freedom of motion to the bridging O atoms essential for catalysis. As can be seen in Fig. 1c, the cubical Mn₄O₄ units in λ-Mn₂O₃ are topologial identical to the Mn₄O₄ core found in the molecular ‘cubane’ catalysts (all O are dicordinate).

Most recently a direct comparison of cubic spinel vs layered polymorphs has provided the strongest evidence yet for the functional importance of the B₄O₄ cube topology for water oxidation.[15] Lithium cobalt oxides occur in two polymorphs of identical composition, Li₂Co₂O₄: cubic spinel (Fd3m) and layered (P₃m1) (Fig. 2; top), and are used as battery materials due to the high mobility of lithium.[16,17] The spinel polymorph contains Co₂O₄ cube subunits and forms above 350°C as the exclusive phase at this temperature. However, at temperatures greater than 500°C and longer calcination times, it transforms to the thermodynamically favoured layered polymorph.[18,19] This dichotomy between the two crystal structures made it possible to test the biospired hypothesis.[20] The higher calcination temperature and longer reaction times used to form the layered polymorph gives rise to increasing crystallite size.[19] To reduce this difference in particle sizes, the authors adapted a sol-gel method[21] that forms nano-particles (50–100 nm) and limited particle size differences to only two-fold. Powder X-ray diffraction (PXRD) confirmed the crystal structure transformation between 400 (all cubic), 500, 600, and 700°C (all layered), while the rate of oxygen evolution decreased to zero for this range, even when accounting for the surface area.[22]

¹Note added in proof: A higher turnover frequency has now been reported in L. Duan, F. Bozoglian, S. Mandal, B. Stewart, T. Privalov, A. Llobet, L. Sun, Nature Chem. 2012, advance article. doi: 10.1038/NCHEM.1301
and flexing/motion. Their active sites whilst ensuring dynamism in catalyst binding are now firmly established, both for the solid-state transition metal catalytic activity of the oxo-metallic cubes in water oxidation is still unclear. But the evidence for the intrinsic photo-absorption of the polymer enhances activity. The oxidation current-voltage characteristic shifts to lower potentials under exposure to light such that some oxidation current flows below the formal thermodynamic potential for water oxidation at the pH involved. This suggests that the effect of light is to generate a photo-voltage that is additive to the applied external bias.

Taking inspiration from the bulk heterojunction solar cells field, we have developed the concept of a conducting polymer based heterojunction photo-electrocatalyst. This notion involves photo-excitation in one conducting polymer followed by rapid charge separation across the junction such that recombination is suppressed. The effect has been demonstrated in the proton reduction reaction and further work explores the hetero-junction concept for other light enhanced electro-catalysed reactions (B. K. Colodziejczyk, D. R. MacFarlane, O. W. Winther-Jensen, 2012, unpubl. data).

Porphyris as Light Harvesters and Catalysts

Given the key roles that tetrapyroles such as chlorophylls play in photosynthetic light harvesting, electron transfer, and mediating water oxidation, it is no surprise that for more than 40 years researchers have been inspired to use synthetic chlorophylls (porphyrins) to develop processes that efficiently harvest light, and produce hydrogen and oxygen from water. Within ACES, we have been at the forefront of developing efficient light harvesting single porphyrins and porphyrin arrays, demonstrating their efficacy in the dye sensitised solar cell (DSSC). In 2007, in collaboration with Professor Michael
Grätzel, the inventor of the DSSC, we reported the highest efficiency porphyrin DSSC (7.1%) using functionalised porphyrins of the type shown in Fig. 3a. Grätzel and his other collaborators have subsequently gone on to show that, under the right set of cell conditions, porphyrins are the most efficient dyes for DSSCs (12.3% for one sun). We have demonstrated the value of using multiple porphyrins such as that depicted in Fig. 3b for light harvesting, proving that it is possible to harvest light and inject electrons into the device semiconductor from all the porphyrins in a porphyrin array attached to it, emulating the multichlorophyll light harvesting process in photosynthesis.

The efficacy of porphyrins as light harvesters, particularly nanostructured porphyrin arrays, has inspired us to investigate their potential to drive water splitting either as the light harvesting component, oxidation or reduction catalyst, or both. Previous work in this area has largely been concerned with using the photoexcited porphyrin to reduce a redox component such as methylviologen, which in turn reduces water (H₂) in the presence of a catalyst like platinum. A sacrificial electron donor or applied potential regenerates the oxidised porphyrin. As in the DSSC, the most commonly used light harvesting porphyrins are zinc porphyrins with a covalent attachment to the electron acceptor in order to ensure good electronic communication and effective charge separation. While some zinc porphyrins have been shown to effectively sensitise H₂ evolution from water, water-soluble tin porphyrins (Fig. 3c) have been most studied since, on photoexcitation, they form a relatively stable and long lived radical anion in the presence of an electron donor. The efficacy of such a porphyrin system has been recently demonstrated by Choi and his co-workers who showed that dihydroxytin(IV) tetrapyridylporphyrin in solution with platinum-decorated titanium dioxide nanoparticles and EDTA as a sacrificial electron donor produced H₂ across a broad pH range (pH 3–11) under visible light with a turnover number of 410; it was superior to a typical ruthenium complex adsorbed to the titanium dioxide.

While Choi’s work highlights the potential of porphyrins as practical sensitisers for H₂ production, it also emphasises the need to use expensive metal catalysts like platinum in any such system and, within ACES, we have been interested to develop catalytic systems that can enhance or even replace platinum. In the former respect, a 7-fold increase in H₂ production in 1M acid could be achieved by coating a platinum electrode with poly-pyrrole containing ferrocene sulfonate as counter-ion. In a more recent study, as described above, it has been shown that in the presence of an ion-coordinating polymer like polyethylene glycol (PEG), the polythiophene conducting polymer, PEDOT, has a comparable performance to platinum for the electrochemical catalytic production of H₂ from acidic electrolytes. This presents the opportunity to develop platinum-free photoactive porphyrin-sensitised H₂ generation and we are now investigating coupling tin porphyrins to these catalytic systems.

Photosensitisation of water oxidation catalysts has also been achieved albeit with high potential porphyrins. While this is of interest in relation to the photosensitisation of the manganese cubanes that ACES researchers and their collaborators have developed, we have rather focussed our attention on the development of porphyrin-based catalytic systems for water oxidation. In 1994, Naruta et al. reported for the first time oxygen evolution by a four electron oxidation of water using a rigid ortho linked manganese porphyrin dimer. The proximity of the two manganese atoms appeared to promote the formation of a peroxo bridge between the two oxidised manganese species leading to the formation of oxygen. This seemed analogous to the role of the two iron atoms in diferrocene catalysts for hydrogen production that were mirrored by the introduction of ferrocene sulfonate into polypyrrole, as described above.

Therefore, in a similar fashion, we electrochemically incorporated monomeric manganese tetrasulfonatophenylporphyrin into polythiophene films on indium tin oxide electrodes and demonstrated the production of oxygen from water on illumination of the composite electrode at a significantly reduced overpotential (0.09 V). This overpotential was low enough to allow the production of oxygen from seawater without the formation of chlorine. Given the high density of the porphyrin in the polythiophene, oxygen formation appears to arise in a

Fig. 3. Structures of porphyrins used as: (a and b) sensitisers for the dye sensitised solar cell, (c) sensitisers for water reduction, and (d) catalyst for water oxidation.
similar fashion to that proposed by Naruta and co-workers\(^{39}\) for the manganese porphyrin dimer. This result has opened up the possibility of a fully photosensitised porphyrin water oxidation catalyst and we are currently exploring this and other related opportunities.

**Conclusion**

The focus of the ARC Centre of Excellence for Electromaterials Science research program on a diverse range of electromaterials, from single organic molecules and inorganic complexes through to conducting polymers and nanostructured carbons, has made it a particularly suitable environment within which to develop exciting new materials for water splitting. Thus, the development of metal cubane complexes and subsequently a variety of related metal oxides has led to some very promising water oxidation catalysts that are also helping us to better understand the design of mimics for photosynthetic and other biological catalysts for use in practical devices. As the realisation of practical devices using such catalysts would currently require the use of expensive metals like platinum, we have also made inroads into the development of conducting polymer-based material replacements for platinum. These developments, coupled with our recent successes in the development of light harvesting porphyrins for solar cells and porphyrin catalysts has provided ACES researchers with important new approaches for the attainment of a truly bioinspired artificial photosynthetic water splitting system.

**References**