Bio-inspired Hydrogen Generation by Novel Bubble-Free Electro-Catalytic Systems

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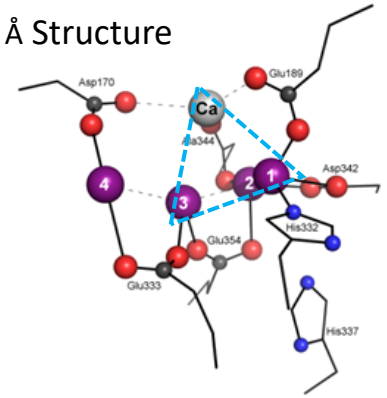
BACKGROUND:

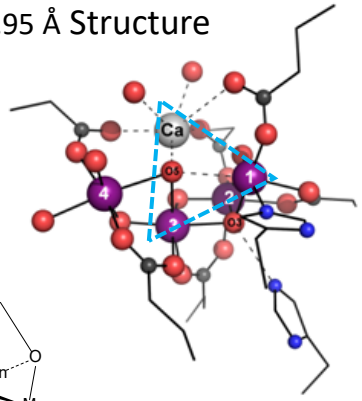
- to make hydrogen efficiently, a good oxygen-generating catalyst is needed at the other electrode …

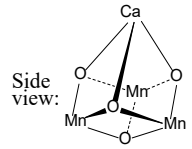
- The *Photosystem II–Oxygen Evolving Center* (*PSII-OEC*) that is found in all oxygenic photosynthetic organisms, is the most active water oxidation catalyst known at neutral pH
  (- up to 1,000 molecules of O_2 produced per second per *PSII-OEC*)

2.9 Å Structure



1.95 Å Structure





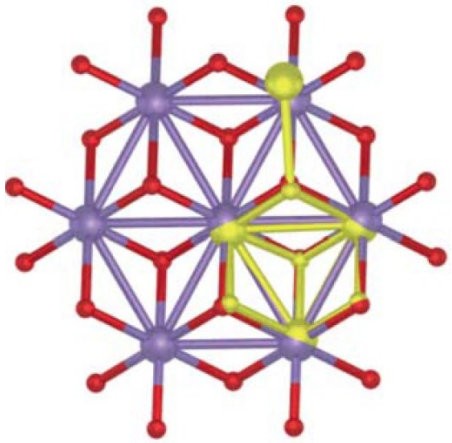
- To date, its catalytic mechanism remains uncertain and attempts to replicate its activity in man-made, abiological systems have been unsuccessful. In pH 7 water:
  - The onset voltage (at which catalysis starts) is far lower for the *PSII-OEC* than any non-biological catalyst
  - The catalytic activity of the *PSII-OEC* is significantly higher than any non-biological catalyst

- In particular, it is not clear why non-biological Mn oxides with a *birnessite* crystal structure that is identical to the catalytically active Mn_3O_3 core of the *PSII-OEC,* do not catalyze water oxidation as well as the *PSII-OEC* at pH 7

- **What is it about the *PSII-OEC* that makes it so much more catalytically active than non-biological analogues?**

- This project sought to address that profound question by developing high-performing non-biological catalysts that mimicked:
  - key active structures within the *PSII-OEC*, and
  - the '*bubble-free*' gas production exhibited by the *PSII-OEC*

Overlay of SEMs of *PSII-OEC* core and *birnessite* Mn oxide layer, showing close correspondence

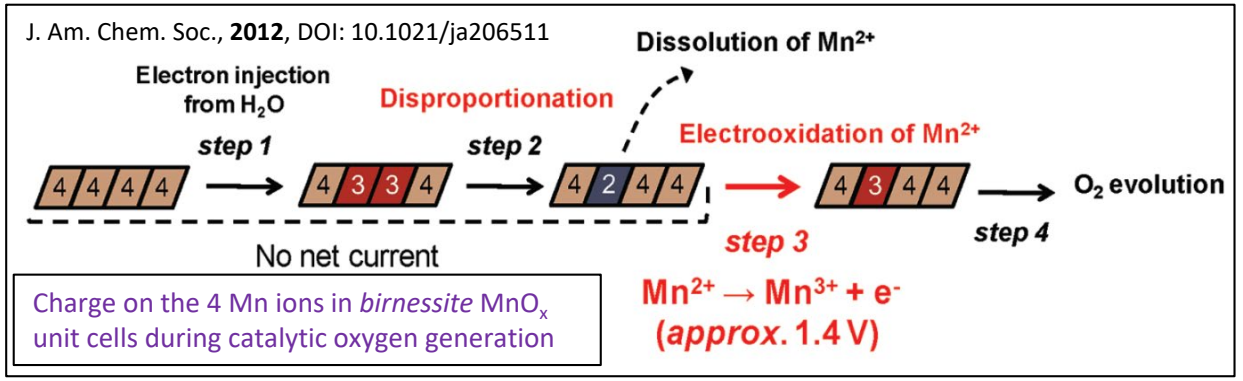


PROJECT AIMS (SUMMARIZED):

- To leverage: (1) computational advances at the ANU that revealed a key understanding of the *PSII-OEC* operation, and (2) advances at the University of Wollongong regarding '*bubble-free*' gas generation catalysis, to:
    - **develop electrodes that incorporate manganese/calcium components on conducting organic substrates, which mimic key structures within the *PSII-OEC*, to achieve high catalytic performance at neutral pH;**
    - **maximise their catalytic performance by incorporating gas diffusion layers that facilitate direct production of bulk oxygen gas without bubble formation (i.e. '*bubble-free*' gas generation);**
    - in parallel undertake further computational analysis to optimise the best system identified
- In so doing:
    - (Milestone 2): To achieve, within a 3-electrode system, high catalytic O_2-generation at near-neutral pH that exceeds present-day non-biological catalysts, including the best precious metal catalysts (and is preferably comparable to the *PSII-OEC*)
    - (Milestone 3): To scale up the best system into a 2-electrode, multi-cell prototype electrolyzer that demonstrates a potential pathway to near-neutral pH water electrolysis using renewable energy (where the O_2-generating anode performance is preferably comparable to the *PSII-OEC*)

PROJECT OUTCOMES (MIMICRY OF *PSII-OEC* STRUCTURES):

- What happens in non-biological *birnessite* MnO_x at pH 7?
  - In, *birnessite*, the catalytically active Mn^{3+} intermediate is unstable and disproportionates to an inactive Mn^{2+}. It only becomes catalytically active when a high voltage is applied to oxidise the Mn^{2+} back to Mn^{3+}



- Detailed computational analysis at ANU suggested that, by contrast, the active Mn^{3+} intermediate in the *PSII-OEC* is stabilized against disproportionation by the Ca and organic, protein environment about the *PSII-OEC* and that is why it is so much more active than non-biological Mn oxides (= the *'Low Oxidation State paradigm'*)

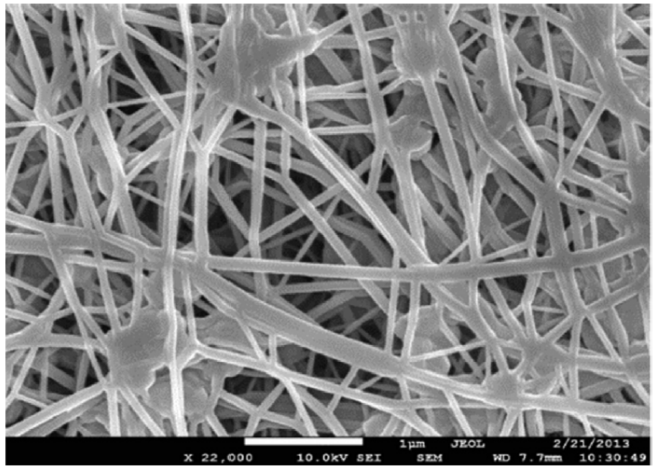
- To test that insight, we co-deposited a layer of *birnessite* MnO_x and Ca^{2+} on a conducting, organic, *liquid crystalline reduced graphene oxide (LCRGO)* capable of mediating electron transfer in the same way that redox-active tyrosine does in the *PSII-OEC*

- The resulting MnO_x/Ca/LCRGO composite catalysed O_2-generation at pH 7, in the form of gas bubbles, with:
  - **an onset overpotential (0.21-0.56 V) that was the same as that of the *PSII-OEC* (0.30-0.43 V)** and much better than unsupported *birnessite* MnO_x (0.71 V) or bare Pt (0.61 V)
  - Over 1 h at a fixed overpotential of 0.56 V, the Ca/MnO_x/graphene film was **1/10th-1/20th as active as the *PSII-OEC* operating at its maximum turnover rate (1000 O_2/s) with its optimum site density of 10^{14}/cm^2**.
  - Collection and GC studies of the gas bubbles produced confirmed that **the gas produced was pure oxygen**

Results are comparable to the *PSII-OEC* … They confirm the ANU computational work and demonstrate why the *PSII-OEC* is so much more active than non-biological MnO_x catalysts at neutral pH

PROJECT OUTCOMES (MIMICRY OF '*BUBBLE-FREE*' O_2-GENERATION BY *PSII-OEC*):

- To avoid gas bubble formation during catalytic oxygen generation, we fabricated electrodes that contained a *Gortex* gas diffusion layer
- *Gortex* is strongly hydrophobic ('*aerophilic*'), porous material that spontaneously extracts O_2 gas out of the catalyst layer as it is produced, before it can form gas bubbles (– *'bubble-free' gas production*)



SEM of *Gortex*

- First Experiments: We deposited conventional Raney Ni catalyst on *Gortex* and tested it as a *'bubble-free'* oxygen-generating electrode under near-neutral conditions (pH 12)
  - More catalytically active than the best precious metal catalyst, Pt, at all current densities
  - Demonstrated that avoidance of gas bubbles notably accelerates catalytic performance
- Then: deposited the bio-inspired Ca/MnO_x/graphene film on the Raney Ni, which was on *Gortex,* and tested it as a ***bio-inspired 'bubble-free'* oxygen-generating electrode under near-neutral conditions**
  - More catalytically active for O_2 production than all previous or control systems, including Pt on *Gortex*
  - **Catalytic performance exceeded *PSII-OEC* in all respects**, although this was, partly, because it was carried out at near-neutral (pH 12), not neutral (pH 7) conditions

Results confirm that '*bubble-free*' catalysis notably accelerates performance and can be used in a future bio-inspired, near-neutral pH water electrolyzer employing renewable energy

NEXT STEPS:

- (Milestone 3): Scale this system up into a 2-electrode, multi-cell prototype electrolyzer that demonstrates a potential pathway to near-neutral pH water electrolysis using renewable energy (where the O_2-generating anode performance is preferably comparable to, or better than the *PSII-OEC*).
- Evaluate prototype electrolyzer for possible commercialisation

FOR REFERENCE: Peer-Reviewed Papers Describing this Work

(1) "*Photo-Electrochemical Oxygen Evolution Reaction by Biomimetic $CaMn_2O_4$ Catalyst*"
(Published in *Appl. Sci.* **2019**, DOI:10.3390/app911219)

(2) "*Comparative Evaluation of the Structural and Other Features Governing Photo-Electrochemical Oxygen Evolution by Ca/Mn Oxides*"
(Published in *Catal. Sci. Techn*., **2020**, DOI: 10.1039/d0cy00105h).

(3) "*Insights into the Phenomenon of 'Bubble-Free' Electrocatalytic Oxygen Evolution from Water*"
(Published in *Sust. Energy Fuels*, **2020**, DOI: 10.1039/d0se01633k)

(4) "*Electronic structure modelling of the edge-functionalisation of graphene by Mn_xO_y particles*"
(Published in *Phys. Chem. Chem. Phys*., **2020**, DOI: 10.1039/d0cp04178e)

(5) "*The Prospects of Developing a Highly Energy-Efficient Water Electrolyzer by Eliminating or Mitigating Bubble Effects*"
(Published in *Sust. Energy Fuels*, **2021**, DOI: 10.1039/d0se01886d)

(6) "*A Bio-Inspired, Water Oxidation Catalyst that is 1/10th – 1/20th as Active as the Photosystem II - Oxygen Evolving Centre (PSII-OEC) in Neutral Water. New Insights into the Operation of the PSII-OEC*" (Submitted)

(7) "*Interaction of Graphene, MnO_x, and Ca^{2+} for Enhanced Biomimetic, 'Bubble-Free" Oxygen Evolution at mild pH*" (Submitted)