DEPARTMENT OF Chemistry & Biochemistry

TCU COLLEGE OF SCIENCE & ENGINEERING

Using Surface Polymer Networks to Connect DSPEC Components for a High Solar Energy Conversion Efficiency

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Introduction — Alternative Fuel from Water

It is extremely important in our age to look for alternative, more environmentally favorable energy sources. The Sun is a largely unused and widely available energy source to power human industry, and it can be utilized in different ways. Conversion of solar energy into chemical fuel by means of water splitting into oxygen and hydrogen — a strategy inspired by natural photosynthesis — is currently a promising and actively researched approach. However, reaching a high energy conversion efficiency, which is essential for industrial implantation of the method, remains a primary goal. Our research focuses on the creation of electropolymer interfaces to achieve a more direct electron transfer between the components of a photochemical water splitting system, thus leading to a higher solar energy conversion efficiency.

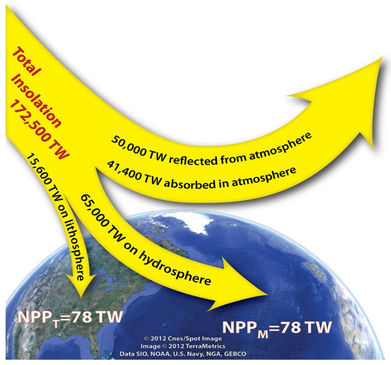
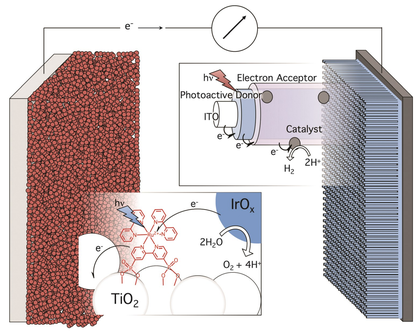


Figure 1. Energy from the sun reaches Earth at a substantial rate. From the total 172,500 TW insolation, around 15,600 TW falls on land. A small fraction of this is stored as chemical energy for the biosphere, the net primary production (NPP).[1]

Figure 2. Scheme of a possible dual absorbing dye-sensitized photoelectrochemical cell (DSPEC), capable of 8-photon, 4-electron water splitting.[2] DSPECs are specifically designed for using solar energy to generate hydrogen and oxygen from water.



Water-oxidation at the anode:

$2\ H_2O \rightarrow O_2 + 4\ e^- + 4\ H^+$

H^+-reduction at the cathode:

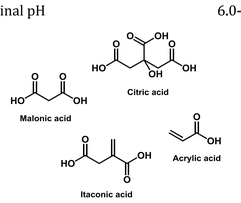
$4\ H^+ + 4\ e^- \rightarrow 2\ H_2$

Overall water splitting: $2\ H_2O \rightarrow O_2 + 2\ H_2$

Iridium-Oxide Suspensions

We have prepared several novel iridium-oxide nanoparticle suspensions, using two different synthetic methods, to serve as the water-oxidation catalysts in our system. During the synthesis, the nanoparticles are functionalized with specific capping groups that contain terminal double bonds, through which they can be incorporated to the surface polymer electrochemically.

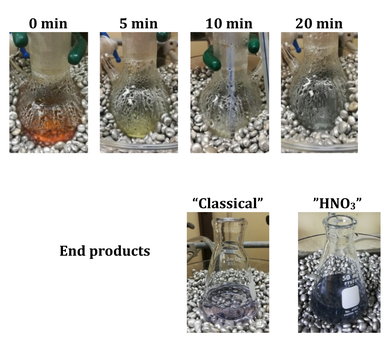
	"Classical-Synthesis"	"HNO_3-Synthesis"
Capping group: 'Ir' molar ratio	10:1	1:10
Initial pH	10.5-11.5	12.0-13.0
Final pH	6.0-7.5	1.0-2.0



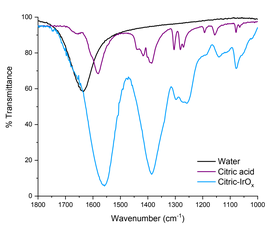
+ K_2IrCl_6 (aq)

90 °C

End products



Figures 3. (**Right**) The FT-IR spectrum of Citric-IrO_x (blue) proves the presence of Citric acid of the Citric-IrO_x nanoparticle suspension.



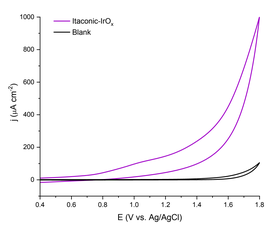
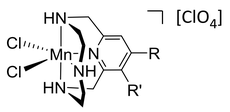


Figure 4. (**Left**) CV of Itaconic-IrO_x (in 0.1 M KNO_3, 0.1 V/s), proving its catalytic activity for water-oxidation.

"Is this an efficient water-oxidation catalyst?"

Established by Sherman et al. in 2016, the two electrode Collector-Generator (CG) method is an efficient electrochemical technique for the detection of electrochemically or photoelectrochemically produced oxygen. We specifically used it for proving (or rather disproving) the catalytic activity of a mononuclear manganese (III) complex with a 12-membered tetraaza-pyridinophane ligand, towards water oxidation.



R, R' = H

Figure 5. (**Left**): Structure of the *cis*-Mn(III) complex ($[Mn^{III}(\mathbf{L})Cl_2][ClO_4]$).

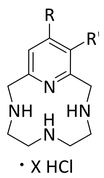
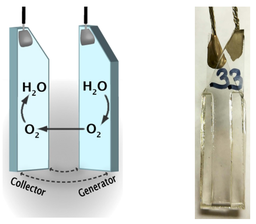


Figure 6. (**Right**): Structure of the tetraazapyridinophane ligand (**L**) of the manganese(III) complex.



Above: (**Left**) Scheme of a Collector-Generator cell. At the Generator, O_2 is produced via oxidation of water if the electrode is poised with a positive enough potential. The Collector electrode then "collects" the oxygen, and reduces it back to water, if poised with a negative enough potential. (**Right**) A hand-made Collector-Generator cell, consisting of two FTO electrodes facing each other with their conductive sides, separated by a 1 mm thick spacer.

Figure 7-8. (Below) (**Left**): Cyclic voltammograms (CVs) of the mononuclear Mn(III) complex shown in Figure 5 above, in 20 mM phosphate buffer at pH 6.7, at 0.1 V/s scan rate, with five segments, starting from 0 V to negative potentials, at an FTO electrode. (**Right**): Proposed mechanism of the catalytic water-oxidation cycle of the manganese complex.

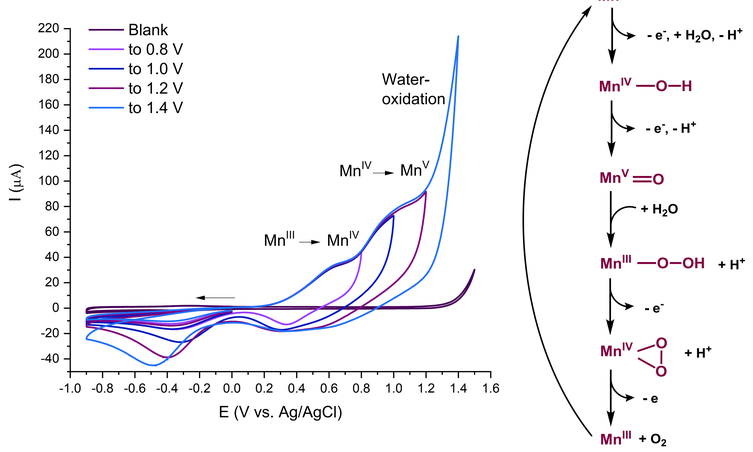


Figure 9. CVs taken at a planar FTO electrode in 20 mM phosphate buffer with 0.5 M $NaClO_4$ at pH 6.7, saturated with nitrogen (black) or air (blue). Upon comparison of the two scans, we find that the onset potential of O_2-reduction is about –0.3 V.

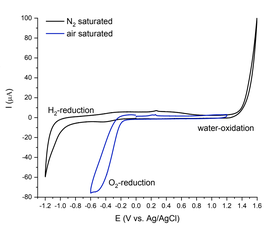


Figure 10. As the potential is scanned further positive (maximum anodic potential of each scan indicated in the legend), currents for O_2-reduction are observed. (20 mM phosphate buffer, pH 11, N_2 saturated, FTO electrode.)

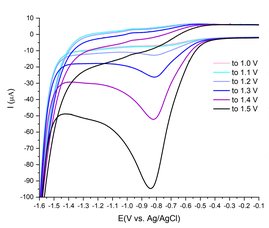


Figure 11. Chronoamperometric I-t analysis of the Mn(III) complex vs. Blank, using a two-electrode Collector-Generator cell. The Generator was poised at 1.4 V, while the Collector was poised at –0.8 V vs. Ag/AgCl.

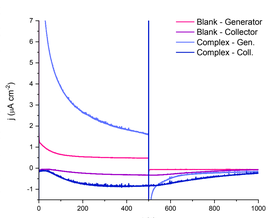


Table 1. Farradaic efficiency of the manganese complex from 8 different trials.

1) **0 %**	3) **36 %**	5) **0 %**	7) **36 %**
2) **0 %**	4) **40 %**	6) **19 %**	8) **24 %**

Conclusion: The studied Mn(III) complex with a 12-membered tetraazapyridinophane ligand was disproved of being an efficient catalyts for water oxidation.

References

1) Sherman, B.D., *et al. Photosynthesis Research*, 2013, doi: 10.1007/s11120-013-9795-4.

2) Swierk, J. R. and Mallouk, T. E. *Chem. Soc. Rev.*, 2013, 42: 2357.

3) Sherman, B.D., *et al. Anal. Chem.*, 2016, 88: 7076.

Electropolymerized Interfaces

We are pursuing the formation of photoanodes with polymer surface coatings prepared by electropolymerization. The polymer interfaces are designed to promote directional electron transfer at the interface, thereby resulting in a better solar energy conversion efficiency.

Using acrylic acid and acrylamide as small molecule precursors, electro-polymer coatings have been prepared on FTO (fluorine-doped tin oxide) surfaces. The structure of the surface polymers enables the incorporation of catalyst units to the interface.

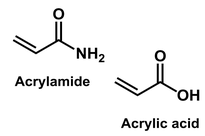
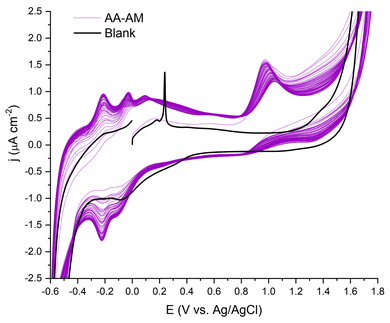
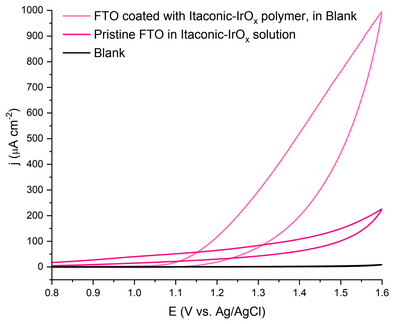


Figure 13. (**Below**) Electropolymerization of an acrylic acid – acrylamide (50 mM of each) solution onto an FTO electrode, via 150 scan segments at 0.01 V/s (~12 hours).





As water flows spontaneously from high to lower altitudes, so do the electrons from high to lower energy electronic states.

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Figure 14. (**Below**) CV of an FTO, coated with itaconic-IrO_x polymer, in Blank solution (0.1 M KNO_3) proves the success of the previous electropolymerization step.

Future Directions

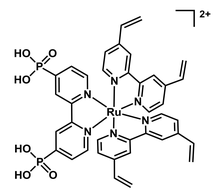
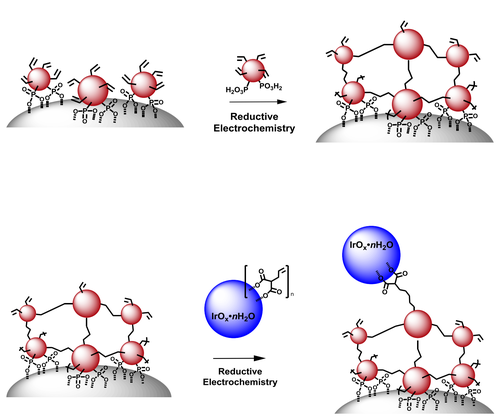
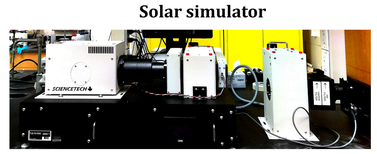


Figure 15. Tris(bipyridine)ruthenium(II) chromophore functionalized with vinyl groups for preparing electropolymerized dye -catalyst interfaces.



Future research work will involve the incorporation of functionalized iridium oxide nanoparticles in the poly(acrylic acid/acrylamide) films and the characterization of their catalytic activity toward water oxidation. The method will then be extended to tin-oxide and titanium-dioxide semiconductor electrodes for preparing photo-active interfaces. Studies using a solar simulator (shown below) will then be performed on the dye-sensitized photoelectrochemical cells assembled from the previously optimized components in order to validate their solar energy conversion efficiency.

Solar simulator



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