

Amorphous Mixed Metal Oxides for Photoelectrochemical Water Splitting



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Abstract

Photoelectrochemical (PEC) water splitting is a promising solution to the world's approaching energy and climate crisis. PEC cells produce a solar fuel, hydrogen, by electrochemically splitting water with a single monolithic device using sunlight, the most abundant renewable energy source. Photoelectrolysis requires a semiconductor material that has 1) an adequate band gap (~1.6-2.2 eV), 2) a band edge alignment that straddles the H₂ and O₂ reaction potentials, 3) high conversion efficiency, and 4) stability in the operating environment. Currently, no known material satisfies all the necessary photoelectrode criteria. Some traditional semiconductor materials have shown conversion efficiencies above 10% but are unstable, while oxide semiconductors have demonstrated long term stability but are generally less than 1% efficient. One such material, copper oxide (Cu₂O), has shown good conduction band edge position but insufficient valence band edge position. The valence band can be shifted via band gap engineering by alloying in other oxides (group III oxides in this case) that have good valence band position. These mixed metal oxide thin film samples were prepared at NREL's National Center for Photovoltaics using reactive radio frequency magnetron sputtering. Tungsten trioxide (WO₃) samples from the Hawaii Natural Energy Institute were characterized in parallel to provide a reference for good oxide performance. The samples were made into photoelectrodes and tested for band gap, flat-band potential, and corrosion resistance. All samples showed indirect-like band gaps with most having acceptable band gap magnitudes. The valence band edge positions were not positive enough to drive the oxygen half reaction but all samples had acceptable conduction band edge positions. However, the measured current densities were 1-3 orders of magnitude lower than that of WO₃, making them unsuitable as a PEC material in the amorphous form. Recent electronic structure theory calculations predict that mixed metal oxides with a delafossite crystal structure should have higher charge mobilities and thus higher current densities. Future research should include characterization of delafossites for their PEC performance.

Objectives and Requirements

Characterize amorphous mixed metal oxide films and evaluate their suitability as a PEC electrode material by comparing to tungsten trioxide, an "ideally performing" oxide material:

Band edges must straddle O₂ and H₂ half reaction potentials

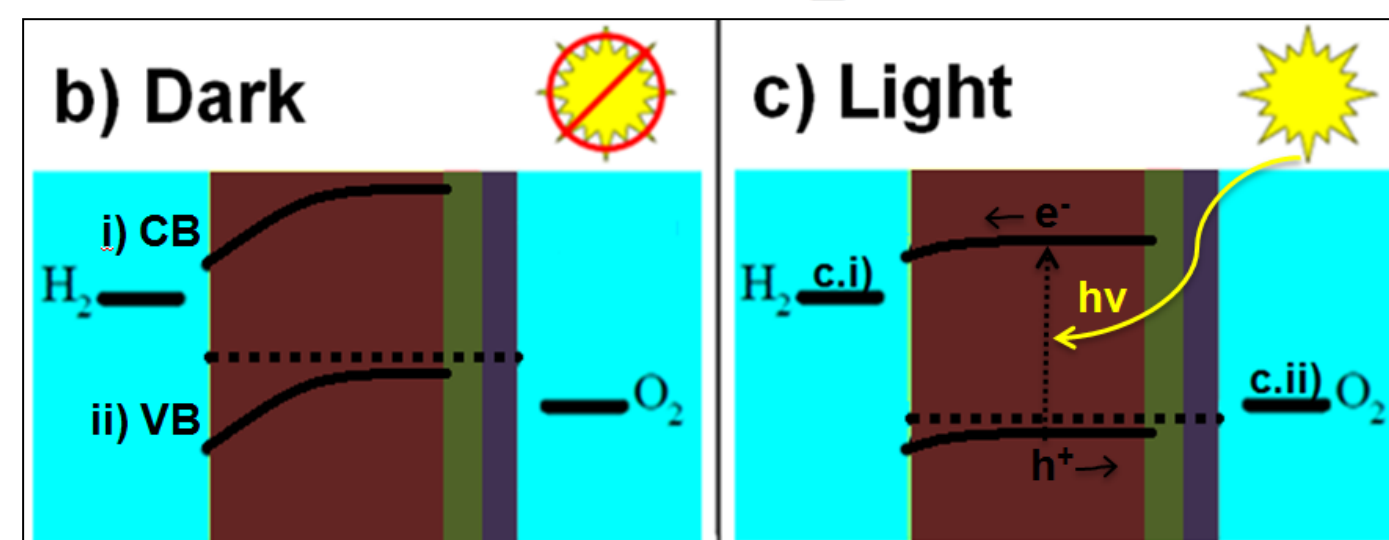
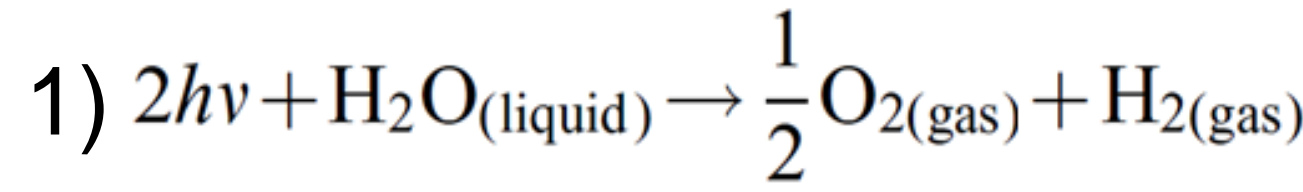
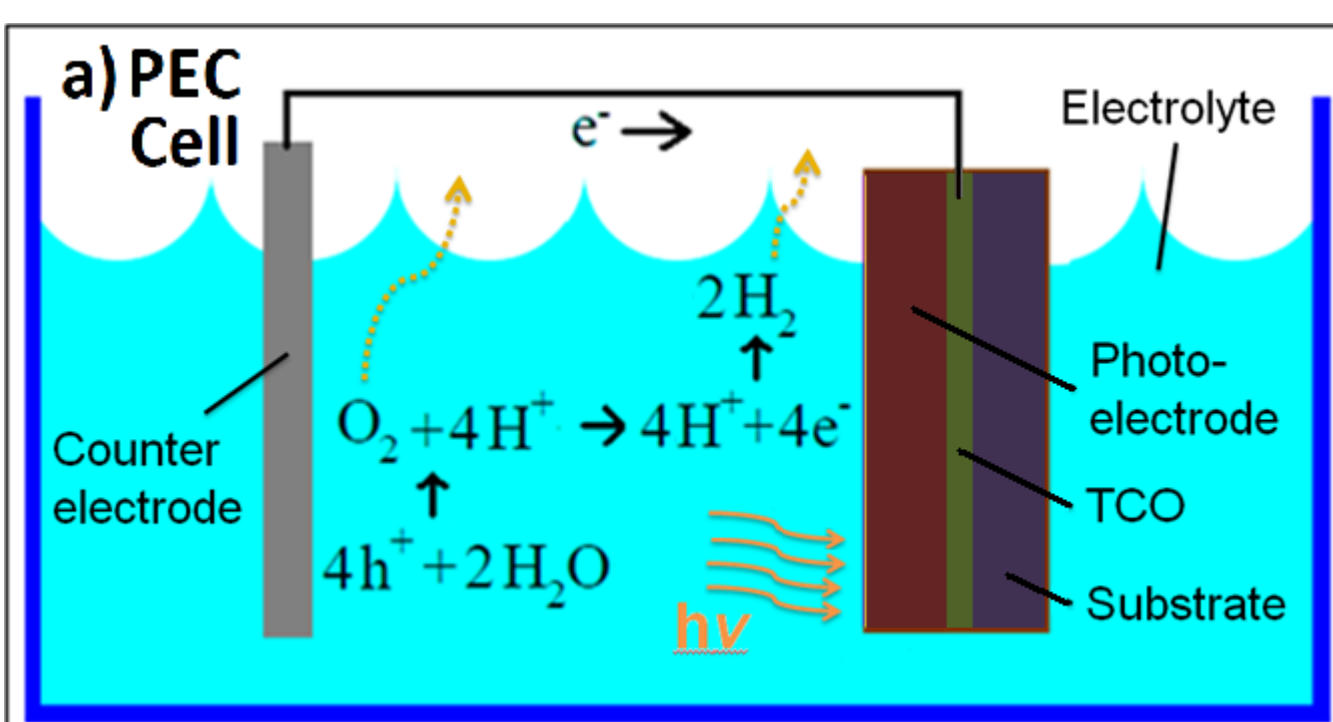
Band gap (E_g) ≈ 1.6-2.2 eV

Photocurrent density: >1 mA/cm²

Minimal degradation in current density over 1,000 hours

PEC Background and Theory

Photoelectrochemical (PEC) cells produce hydrogen by splitting water via photoelectrolysis where light drives the reaction in Equation 1. Photoelectrolysis is the only way to convert solar energy directly into hydrogen fuel using a single monolithic device and can be 30% more efficient than a photovoltaic/electrolysis separated system [1].

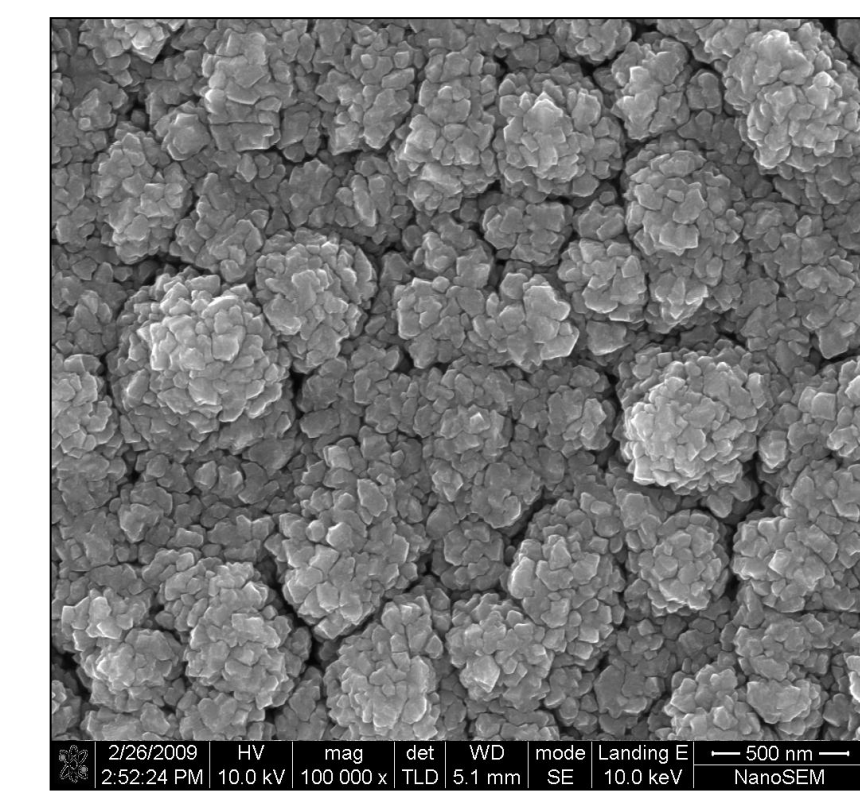


A PEC cell uses light energy (hv) to drive an electrochemical reaction (Equation 1) to split water into hydrogen (H₂) and oxygen (O₂) gas. For a PEC cell with a p-type photoelectrode (a), H₂ is produced at the photoelectrode and O₂ at the counter electrode. For these reactions to occur, the conduction band (CB) edges (b.i) and valence band (VB) edges (b.ii) must be respectively above the H₂ reaction potential (c.i) and below the O₂ reaction potential (c.ii) [2].

Amorphous Mixed Cu-M-Oxides

It is known that copper oxide (Cu₂O) provides relatively good conduction band edge position but insufficient valence band edge position for PEC water splitting. It is possible to mix Cu₂O with other oxides that have good valence band positions (band gap engineering) to produce an oxide that has both good valence and conduction band edge positions. Titanium dioxide (TiO₂) is known to exhibit valence and conduction band edge positions capable of splitting water, but the valence band is much lower than necessary, reducing the amount of visible light absorbed. The band gap of TiO₂ is also too large to absorb most of the solar spectrum [3]. It has been theorized that mixed oxides can provide both a more suitable valence band edge position and band gap.

Amorphous mixed oxide films were prepared by co-sputtering copper and a group III metal oxide (Cu-M-Oxides where M = Ti, Al, Ga, or In) onto a transparent conducting oxide (TCO) coated glass substrate. The amorphous nature allows variations in the Cu/M ratio without phase separation.



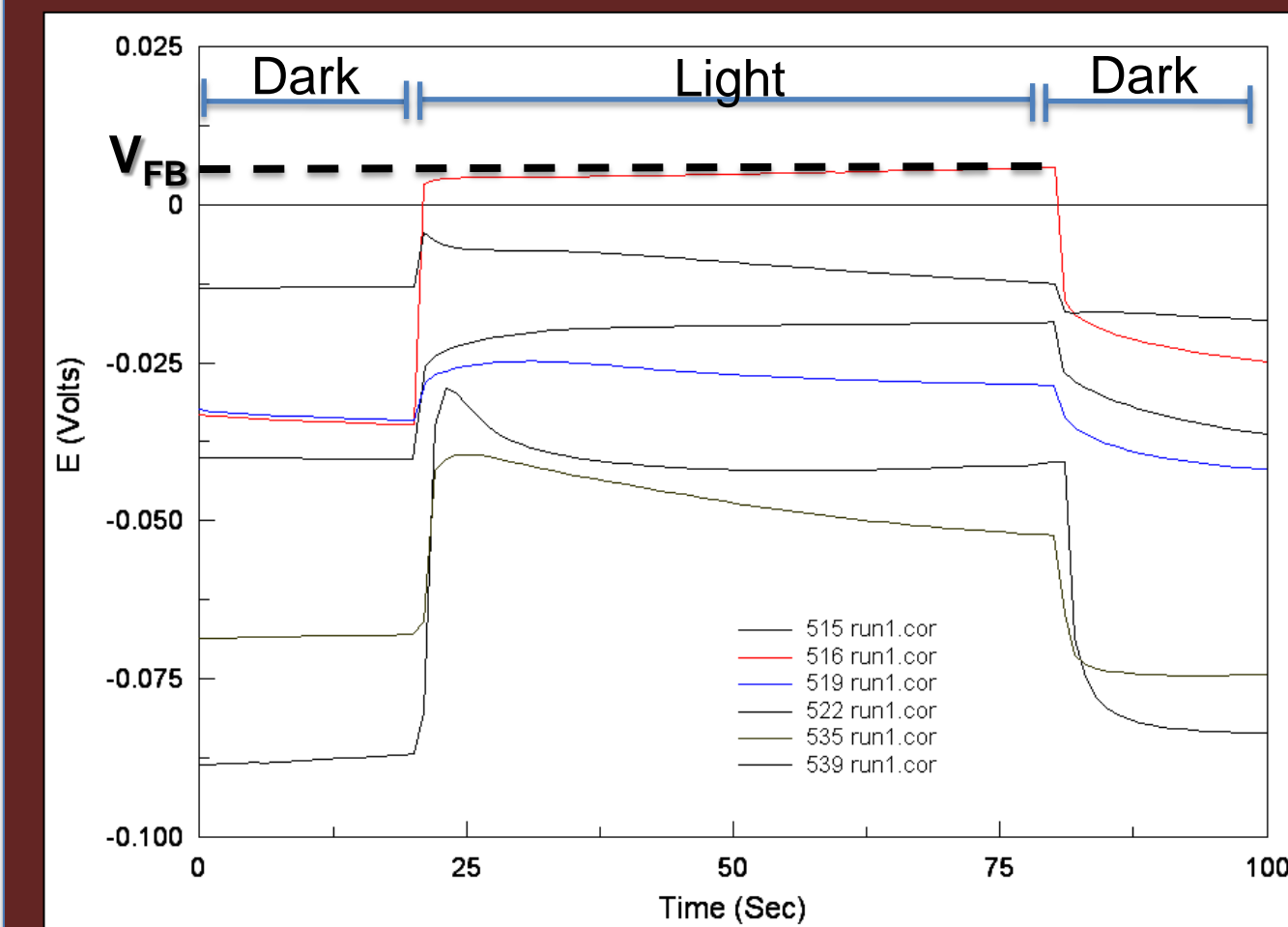
SEM image of an amorphous mixed copper oxide thin film. This particular sample's surface morphology provides large area to accommodate more photocatalytic reactions than a smooth surface.

Characterization: Methods → Results

Four techniques were used to characterize the amorphous mixed metal oxide films for the purpose of evaluating their suitability as PEC electrode materials. All experiments were performed using a three-electrode setup consisting of a photoelectrode constructed from each Cu-M-Oxide sputtered substrate, Pt counter electrode, and Ag/AgCl reference electrode. Based on Pourbaix (potential/pH) diagrams, a pH 10 solution (0.5 M potassium sulfate in carbonate buffer) was selected as the PEC cell electrolyte for all experimental measurements.

Illuminated Open-circuit Potential

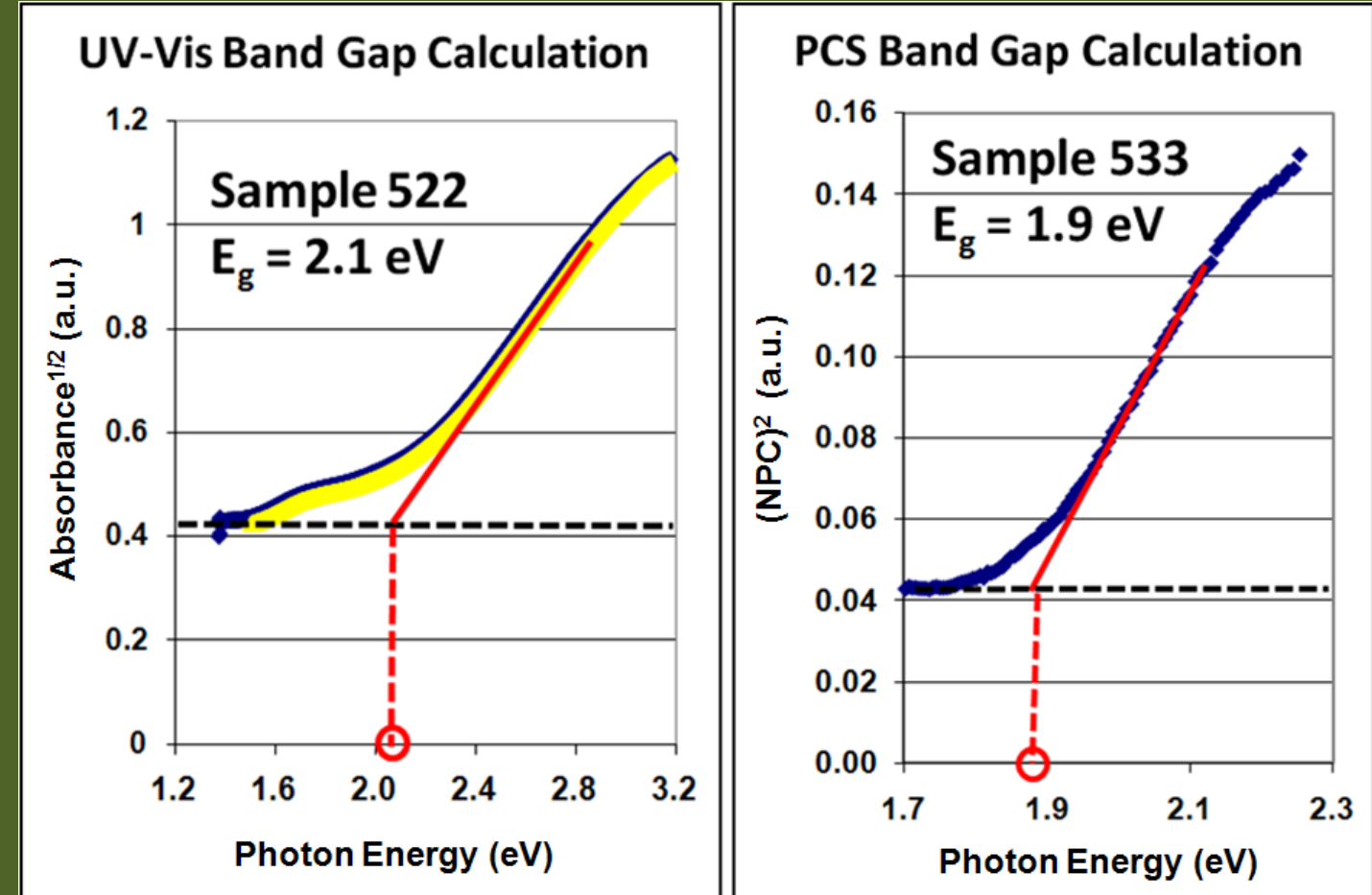
Voltage response to saturated illumination shows conductivity type and measures flat-band potential (V_{FB})



Open-circuit potential measurements show voltage over a 100 second period (20 dark, 60 light, 20 dark). A positive deflection during illumination indicates p-type conductivity (all samples). The maximum value is V_{FB}.

UV-Vis and Photocurrent Spectroscopy

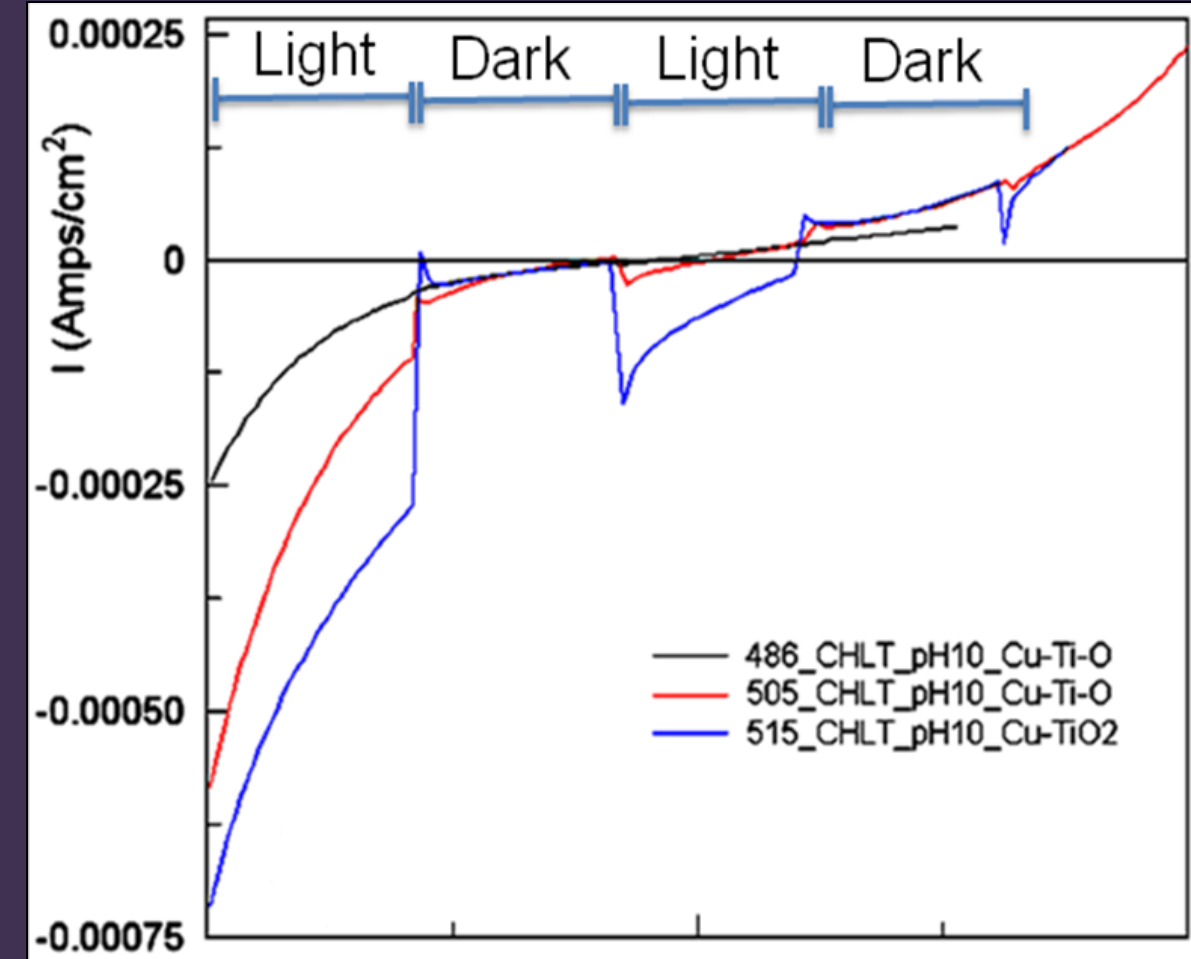
Absorption/photocurrent vs. incident photon energy for band gap (E_g) extrapolation and determining transition type



UV-Vis absorbance spectrum and band gap extrapolation for an indirect gap (absorbance^{1/2} vs. hv) semiconductor (left). Band gap extrapolation for a direct gap (normalized photocurrent (NPCP)² vs. hv) semiconductor (right). All samples had indirect gap transitions.

Linear Voltammogram

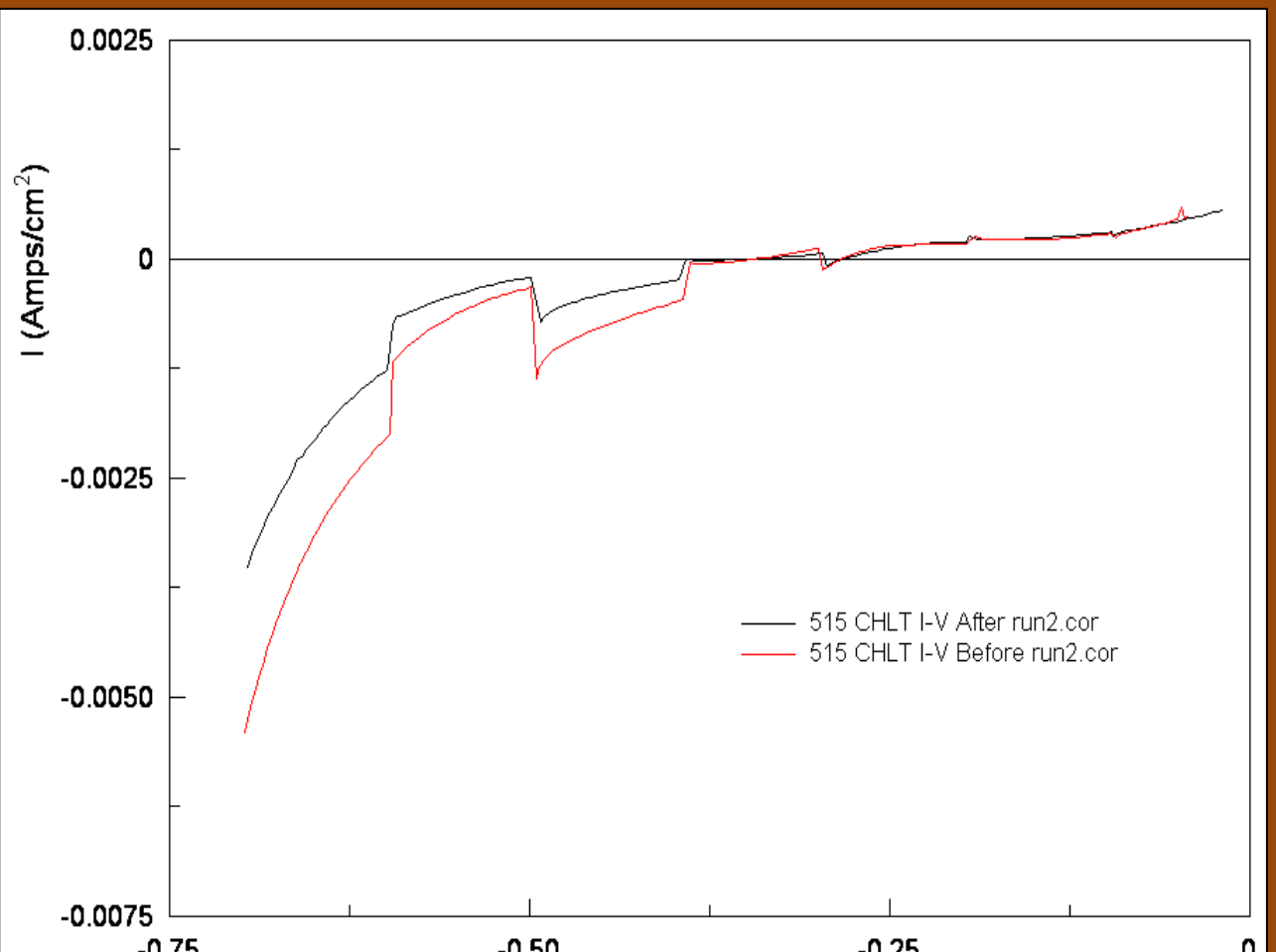
A linear voltage sweep is applied to measure the photocurrent and dark current density responses



The current-voltage curves show photocurrent and dark current densities for an applied bias range of -0.5 V to 0 V vs. reference.

Potentiostatic Durability

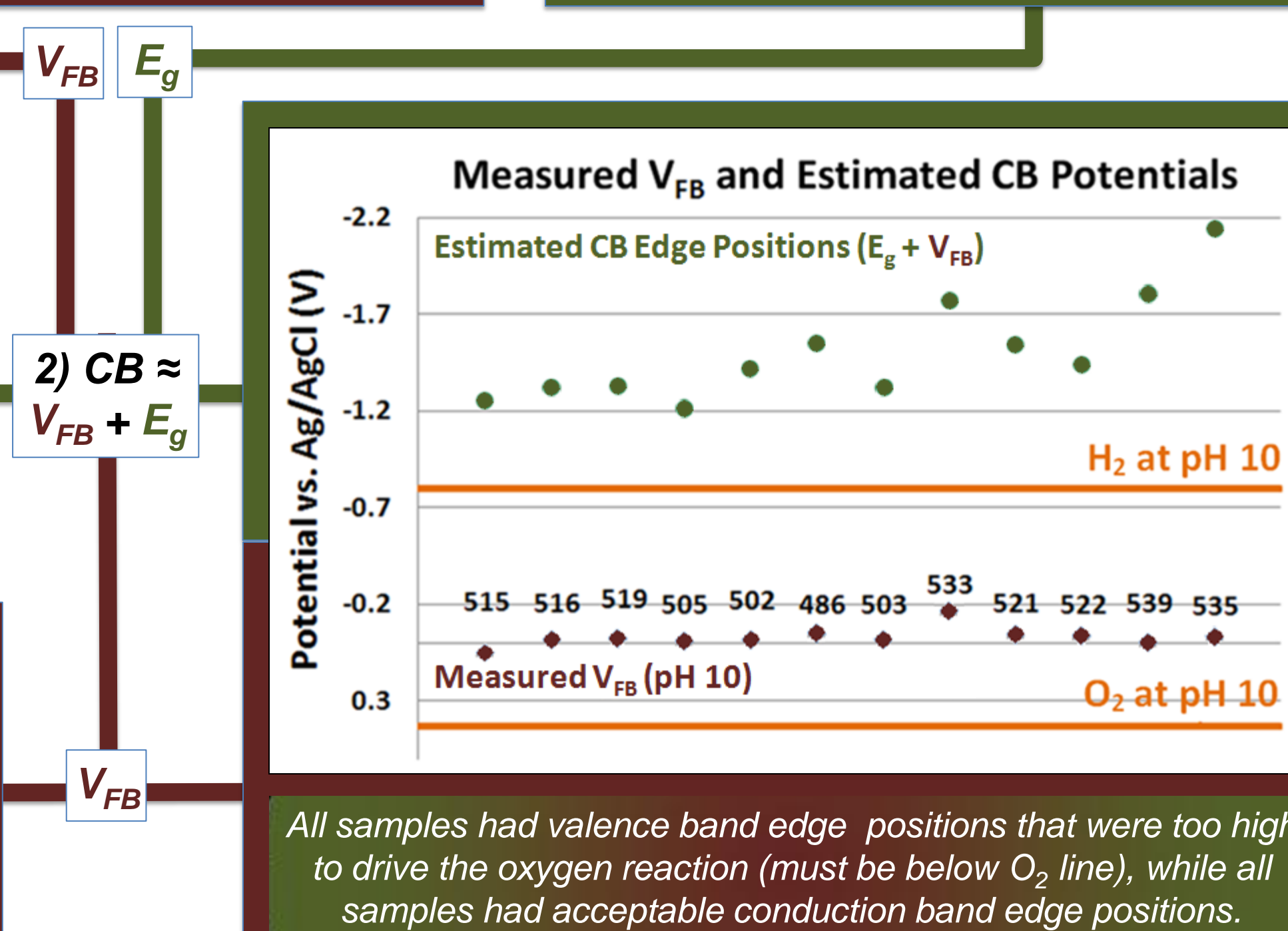
Linear voltammogram before and after a one hour potentiostatic test shows operating stability



Current-voltage curves for sample 515 before (red) and after (black) one hour potentiostatic (-0.4 V vs. reference) durability testing are shown.

All samples were within or near the desired E_g range. Equation 2 (right) was used to estimate the conduction band (CB) positions.

Assuming valence band (VB) ≈ V_{FB}, the VB edges were too high to straddle the O₂ reaction potential.



All samples had valence band edge positions that were too high to drive the oxygen reaction (must be below O₂ line), while all samples had acceptable conduction band edge positions.

Fabrication Parameters										Characterization Results			
Sample ID	Co-Sputter Material	Substrate	O ₂ (sccm)	Ar (sccm)	Cu (wt.%)	Co-Sputter Material Power (W)	V _{FB} (V)	Transition Type	Band Gap (UV-Vis)	Band Gap (PCS)	CHLT-I-V At -0.40 V (A/cm ²)	Stability	
515*	Ti	150C	5	5	200	100	0.05	Indirect	1.4	1.9	3.0E-04	stable	
516*	Ti	150C	5	5	200	100	-0.02	Indirect	1.4	1.9	2.0E-04	stable	
519	Ga ₂ O ₃	150C	5	5	120	-	-0.03	Indirect	1.4	1.3	7.5E-05	decr., level	
505	Ti	150C	5	5	150	200	-0.01	?	1.4	1.6	5.0E-05	unstable	
502	Ti	150C	5	5	100	200	-0.02	?	1.4	1.9	2.0E-05	unstable	
486	Ti	150C	5	5	60	200	0.05	?	1.5	2.3-2.5	1.0E-02	n-type	
503	Ti	150C	5	5	100	200	-0.02	Indirect	1.3-1.4	2.4-2.5	1.0E-05	unstable	
533	Al	RT	5	5	60	150	-0.17	Indirect	1.6-1.7	1.9	1.0E-05	stable	
521	In ₂ O ₃	150C	5	5	120	-	-0.04	?	1.5-1.6	1.8-2.1	5.0E-06	decr., level	
522	In ₂ O ₃	RT	8	2	120	-	-0.04	Indirect	2.1	2.05	3.5E-06	stable	
535	Al	RT	5	5	80	250	-0.01	Indirect	1.8-1.9	2	1.5E-05	unstable	
538	Al	RT	5	5	60	200	-0.04	Indirect	2.1-2.2	2.3	1.0E-05	decr., level	
528	Ga ₂ O ₃	RT	5	5	100	250	none	Indirect	1.9-2.0	1.9-2.0	1.0E-05	linear	
WO ₃ **	-	-	-	-	-	-	-	Indirect	2.6	2.65	3.0E-03	stable	

*TiO₂ was deposited as a film before the Cu, **WO₃ was used as an "ideal" reference oxide

The current densities were on the order of μA/cm² (under AM 1.5G) while WO₃ is typically on the order of mA/cm² making the Cu-M-Oxides unsuitable as a PEC material in the amorphous form.

The four most stable samples during OCP were further tested for durability. The 50% decrease in photocurrent magnitude over just one hour is considerably worse than the stability requirements.

Conclusions and Future Work

The amorphous mixed metal oxides are not suitable as PEC electrode materials because their valence band edge positions are too high, their photocurrent densities are low, and they are not stable.

Good conduction band edge but not valence band edge



All are within or near the required E_g range



Photocurrent density 1-3 orders or magnitude too low



Current degradation of 50% over only one hour of testing



Future Work: It was shown that the sputtering conditions used consistently produce samples with p-type conductivity. The fact that the Cu-M-Oxide materials retain their p-type nature despite alloying is beneficial because there are few known p-type oxide semiconductors, and p-type materials used in PEC cells can be resistive to oxidative corrosion. Like all amorphous materials, these oxides have significantly lower charge mobilities than crystalline materials because of the inherent pervasiveness of defects. Recent theory calculations by M. N. Huda et al. have shown that crystalline, particularly the delafossite crystal structure, mixed metal oxides (Cu-M-Oxides where M = group IIIA or IIIB) are also p-type and have excellent hole mobilities. Such delafossites should be evaluated in future work (CuLaO₂ is expected to have the best performance) as they have potential to provide good current densities while benefiting from p-type stability.



References

- 1) T. Bak, J. Nowotny, M. Rekas, C. C. Sorrell, Photo-electrochemical hydrogen generation from water using solar energy, Materials-related aspects. International Journal of Hydrogen Energy, 2002. Vol. 27. p. 991-1022.
- 2) J.D. Beach Jr., In,Ga,N For Photoelectrochemical Water Splitting, PhD Thesis - Colorado School of Mines, 2001.
- 3) P. E. de Jongh, D. Vanmaekelbergh, J. J. Kelly, PEC of Electrodeposited Cu₂O. Journal of The Electrochemical Society, 2000.
- 4) Deutsch, Todd. The Sustainable Hydrogen Economy. National Renewable Energy Laboratory. June 23, 2010.