Charles Dismukes, 2022 Catalysis & Biocatalysis Research Programs at Rutgers University

2020-2022

Group Members

Dr. Anders Laursen
$RenewCO_2$ LLC

Dr Mahak Dhiman
postdoc

Krishani Teeluck
PhD Candidate

Apostolos Zournas
PhD Candidate

Hengfei Gu
PhD Candidate

Yifei Li
PhD Candidate

Zachary Clifford
PhD Candidate

Christopher Turner
Grad Student

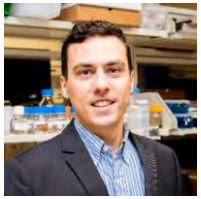
Recent Alumni

Shinjae Hwang
Applied Materials
Semi-conductor Industry

Karin Calvinho
$RenewCO_2$ LLC
Start-up

Joshua Flynn
Chemours
Chemical Industry

Spencer Porter
Global Foundry
Semi-conductor Industry



Graeme Gardner
Visikol
Start-up

Paul Smith
Valparaiso U.
Faculty

Yuan Zhang
Berkley Nat. Lab
Postdoc

Colin Gates
Loyola U.
Faculty

Dr Gennady Ananyev
Research Professor

Anagha Krishnan
Colorado School of Mines
Postdoc

Xiao Qian
Cipher Gene LLC
Industry

Tiago Guerra
A4F
Start-up

Kelsey McNeely
Exxon Mobil
Chemical Industry

Nick Bennette
Counterbalance Capital
Investment

David Robinson
BASF
Environmental Catalysis

Jyotishman Dasgupta
TIFR
Faculty

Undergraduate Student Alumni (2020-2018)
Dismukes Laboratories, Rutgers University

Current 2021:

Hiba Shaqra
Andrew Hsieh
Gnaneswar Chundi
Ethan Black
Julia Burns
Joyce Yu
Michael Stringer
Brooklyn Castillo

Alexander Kim
2022

Sofia Dvinskik
2022

Kye Mani
2021

Mathiaas Miller
Rutgers MBS

Kyra Yap
Stanford

Sunjay Melkote
Stanford National Lab

Devan Solanki
Yale

Lauren Ostopowickz
Arizona State

Edward Izett
Opus12

Anika Jalil
UC Santa Barbara

Tim Goetjen
Northwestern

Jonah Williams
McDermott

Jack Weber
Columbia

Ajay Kashi
Opus12

Waksman Institute of Microbiology

Chemistry Dept,

Research in Collaboration with….

Martha Greenblatt: Solid state materials synthesis and chemistry

Eric Garfunkel: novel photovoltaic materials; low power materials for nanoelectronics

Katherine Ayers: Electrocatalysis Proton Energy Systems Director of Research,

Todd G. Deutsch: Tandem Absorbers for Economical Solar H_2 Production & CO_2 reduction

David Case: Theoretical chem biomolecules, electronic structure of transition-metal complexes

Andrew M. Rappe: Theoretical chemistry of materials

Sagar Khare: Computational and experimental studies of molecular recognition

Petra Fromme: Biochemistry & Crystallography

Desmond Lun: Computer design of microbial metabolism, computational systems biology

Debashish Bhattacharya: Algal genomics & Evolution,

Charles Musgrave: Theoretical chemistry of electrocatalysis

Paul G. Falkowski: Biogeochemical cycles, photosynthesis, biological oceanography

Laura Fabris: application of plasmonic nanoparticles

RUTGERS
UNIVERSITY | NEW BRUNSWICK

2021
CHANCELLOR'S AWARD FOR PIONEERING RESEARCH

This award honors a faculty member whose research contributions have transformed the field, including highly cited scholarship or practiced patents.

Charles Dismukes

Distinguished Professor

Chemistry & Chemical Biology

School of Arts and Sciences

Publications, 2018-2021

1. Hwang, S., S.H. Porter, M. Li, R. Thorpe, A.B. Laursen, A. Safa-ri, M. Greenblatt, E. Garfunkel and G.C. Dismukes, *Thin-film SrNbO2N photoanode: in situ synthesis of photo-stable inter-faces and the influence of thickness and roughness on performance* ***J. Phys. Chem.****, 2022.* ***in press.***
2. Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes, *Quantifying the oxidation states of manganese in the water oxidation cycle of Photosystem II by chemical reduction of ultrapure PSII microcrystals.* ***Photosyn. Res*** *, , 2022.* ***in preparation.***
3. Gates, C., G. Ananyev, S. Roy-Chowdhury, B. Cullinane, M. Miller, P. Fromme and G.C. Dismukes, *Why Did Nature Choose Manganese Exclusively to Make Oxygen on Earth?* ***J. Phys. Chem. C****, 2022.* ***in press.***
4. Dismukes, G.C., *Beyond biofuels, a need for solutions to overcome Nature's inefficiency. in review, 2022.*
5. Dismukes, G., A. Laursen and K. Calvinho, *"Nickel Phosphide Catalysts For Direct Electrochemical Co2 Reduction To Hydrocarbons",* ***USPTO,*** *Editor. 2021 filed.*
6. Zournas, A., J.A.E. ten Veldhuis and G.C. Dismukes, *CO2 throttle-points and bottle-necks in photosynthetic electron transport and their influence on CO2 carboxylation rate as revealed by chlorophyll fluorescence transients.* ***Photosyn. Res****. In preparation, 2021.*
7. Mani, K., A. Zournas and G.C. Dismukes, *Bridging the gap between Kok-type and kinetic models of photosynthetic electron transport within Photosystem II.* ***Photosynth Res,*** *2021.* ***Aug 16.***

Publications, 2018-2021

8. Laursen, A.B., K.U. Calvinho, T.A. Goetjen, K.M. Yap, S. Hwang, H. Yang, E. Garfunkel and G.C. Dismukes, *CO2 electro-reduction on Cu3P: Role of Cu (I) oxidation state and surface facet structure in C1-formate production and H2 selectivity. Electrochimica Acta, 2021.* ***391: p. 138889.***
9. Gabr, A., A. Zournas, T.G. Stephens, G.C. Dismukes and D. Bhattacharya, *Evidence for a robust photosystem II in the photosynthetic amoeba Paulinella. New Phytologist, 2021.* ***IN PRESS.***
10. Calvinho, K.U.D., A.W. Alherz, K.M.K. Yap, A.B. Laursen, S. Hwang, Z.J.L. Bare, Z. Clifford, C.B. Musgrave and G.C. Dismukes, *Surface Hydrides on Fe2P Electrocatalyst Reduce CO2 at Low Overpotential: Steering Selectivity to Ethylene Glycol. J Am Chem Soc, 2021.* ***143(50): p. 21275-21285.***
11. ten Veldhuis, M.-C., G. Ananyev and G.C. Dismukes, *Symbiosis extended: exchange of photosynthetic O2 and CO2 mutually power metabolism of lichen symbionts. Photosyn. Res, 2020*
143: p. 287–299.
12. Potkay, A., M.C. Ten Veldhuis, Y. Fan, C.R.C. Mattos, G. Ananyev and G.C. Dismukes, *Water and Vapor Transport in Algal-Fungal Lichen: Modeling constrained by Laboratory Experiments, an application for Flavoparmelia caperata. Plant Cell Environ, 2020.* ***43(4): p. 945-964.***
13. Hwang, S., Young, J.L., Mow, R., Garfunkel, E., Dismukes, G.C., *Highly efficient and durable III-V semiconductor-catalyst photocathodes: Via a transparent protection layer. Sustainable Energy and Fuels, 2020.* ***4(3): p. 1437–1442.***

Publications, 2018-2021

14. Gates, C., G. Ananyev and G.C. Dismukes, *Realtime kinetics of the light driven steps of photosynthetic water oxidation in living organisms by "stroboscopic" fluorometry. Biochim Biophys Acta Bioenerg, 2020.* ***1861(8): p. 148212.***
15. Dismukes, G.C., A. Laursen, M. Greenblatt and K. Calvinho, *Continuation in Part to Nickel phosphide catalysts for direct electrochemical CO2 reduction to hydrocarbons, USPTO, Editor. 2020.*
16. Dismukes, G.C., A. Laursen, M. Greenblatt and K. Calvinho, *Nickel phosphide catalysts for direct electrochemical CO2 reduction to hydrocarbons, USPTO, Editor. 2020, US Patent 10,676,833.*
17. Calvinho, K.U.D., A.W. Alherz, K.M.K. Yapa, A.B. Laursen, S. Hwang, Z.J.L. Bare, C.B. Musgrave and G.C. Dismukes, *Hydride-driven Electrocatalytic Reduction of CO2 to Ethylene Glycol on Fe2P. submitted, 2020.*
18. Shevela, D., G. Ananyev, A.K. Vatland, J. Arnold, F. Mamedov, L.A. Eichacker, G.C. Dismukes and J. Messinger, *"Birth defects' of photosystem II make it highly susceptible to photodamage during chloroplast biogenesis. Physiologia Plantarum, 2019.* ***166(1): p. 165-180.***
19. Kumaraswamy, K.G., A. Krishnan, G. Ananyev, S.Y. Zhang, D.A. Bryant and G.C. Dismukes, *Crossing the Thauer limit: rewiring cyanobacterial metabolism to maximize fermentative H-2 production. Energy & Environmental Science, 2019.* ***12(3): p. 1035-1045.***
20. Jalil, A.F., K.U. Calvinho, A.B. Laursen and G.C. Dismukes. *Development of Falling Thin Film Liquid Phase Electrolyzer for CO 2 Reduction. in 2019 AIChE Annual Meeting. 2019. AIChE.*

Publications, 2018-2021

21. Hwang, S., S.H. Porter, A.B. Laursen, H. Yang, M. Li, V. Manichev, K.U.D. Calvinho, V. Amarasinghe, M. Greenblatt, E. Garfunkel and G.C. Dismukes, *Creating stable interfaces between reactive materials: titanium nitride protects photoabsorber–catalyst interface in water-splitting photocathodes. Journal of Materials Chemistry A, 2019.* ***7(5): p. 2400-2411.***
22. Ananyev, G., S. Roy-Chowdhury, C. Gates, P. Fromme and G.C. Dismukes, *The Catalytic Cycle of Water Oxidation in Crystallized Photosystem II Complexes: Performance and Requirements for Formation of Intermediates. Acs Catalysis, 2019.* ***9(2): p. 1396-1407.***
23. Vinyard, D.J., G.M. Ananyev and G.C. Dismukes, *Desiccation tolerant lichens facilitate in vivo H/D isotope effect measurements in oxygenic photosynthesis. Biochimica et Biophysica Acta (BBA) - Bioenergetics, 2018.* ***1859(10): p. 1039-1044.***
24. Qian, X., Y. Zhang, D.S. Lun and G.C. Dismukes, *Rerouting of Metabolism into Desired Cellular Products by Nutrient Stress: Fluxes Reveal the Selected Pathways in Cyanobacterial Photosynthesis. ACS Synthetic Biology, 2018.* ***7(5): p. 1465-1476.***
25. Laursen, A.B., R.B. Wexler, M.J. Whitaker, E.J. Izett, K.U. Calvinho, S. Hwang, R. Rucker, H. Wang, J. Li and E. Garfunkel, *Climbing the volcano of electrocatalytic activity while avoiding catalyst corrosion: Ni3P, a hydrogen evolution electrocatalyst stable in both acid and alkali. ACS Catalysis, 2018.* ***8(5): p. 4408-4419.***
26. Krishnan, A., X. Qian, G. Ananyev, D.S. Lun and G.C. Dismukes, *Rewiring of cyanobacterial metabolism for hydrogen production: Synthetic biology approaches and challenges. Synthetic Biology of Cyanobacteria, in Adv Exp Med Biol. , W.Z.a.X. Song, Editor. 2018, Springer: Singapore. p. 171-213.*

Publications, 2018-2021

27. Greenblatt, M. and G.C. Dismukes, *Spinel Catalysts for Water Oxidation/Water Splitting. 2018.*
28. Dismukes, G., K. Calvinho and A. Laursen. *Bioinspired heterogeneous electrocatalysts for CO2 reduction: Energy-efficient carbon-carbon coupling rivaling enzymes. in ABSTRACTS OF PAPERS OF THE AMERICAN CHEMICAL SOCIETY. 2018. AMER CHEMICAL SOC 1155 16TH ST, NW, WASHINGTON, DC 20036 USA.*
29. Chen, H., G.C. Dismukes and D.A. Case, *Resolving Ambiguous Protonation and Oxidation States in the Oxygen Evolving Complex of Photosystem II. The Journal of Physical Chemistry B, 2018.* ***122(37): p. 8654-8664.***
30. Chen, H., D.A. Case and G.C. Dismukes, *Reconciling Structural and Spectroscopic Fingerprints of the Oxygen-Evolving Complex of Photosystem II: A Computational Study of the S2 State. The Journal of Physical Chemistry B, 2018.* ***122(50): p. 11868-11882.***
31. Calvinho, K.U., A.B. Laursen, K.M. Yap, T.A. Goetjen, S. Hwang, N. Murali, B. Mejia-Sosa, A. Lubarski, K.M. Teeluck and E.S. Hall, *Selective CO 2 reduction to C 3 and C 4 oxyhydrocarbons on nickel phosphides at overpotentials as low as 10 mV. Energy & Environmental Science, 2018.* ***11(9): p. 2550-2559.***
32. Ananyev, G., C. Gates and G.C. Dismukes, *The multiplicity of roles for (bi)carbonate in photosystem II operation in the hypercarbonate-requiring cyanobacterium Arthrospira maxima. Photosynthetica, 2018.* ***56(1): p. 217-228.***

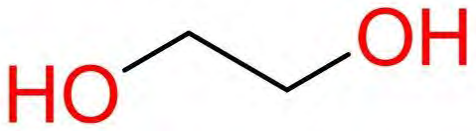
Artificial Photosynthesis is the path to a sustainable Energy Future

First renewable chemicals

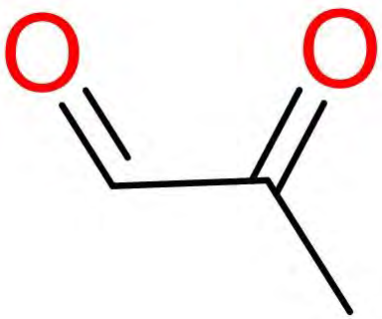
Scale-up Feasible

RENEW CO_2

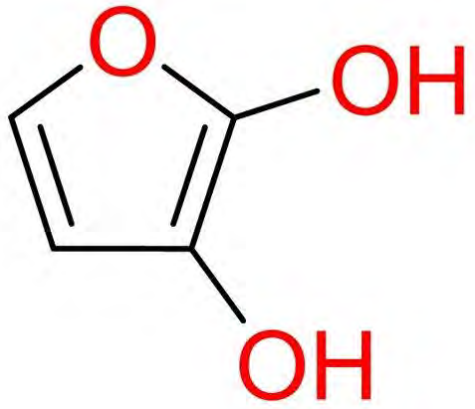
Rutgers Startup



Mono-ethylene glycol



Methyl glyoxal

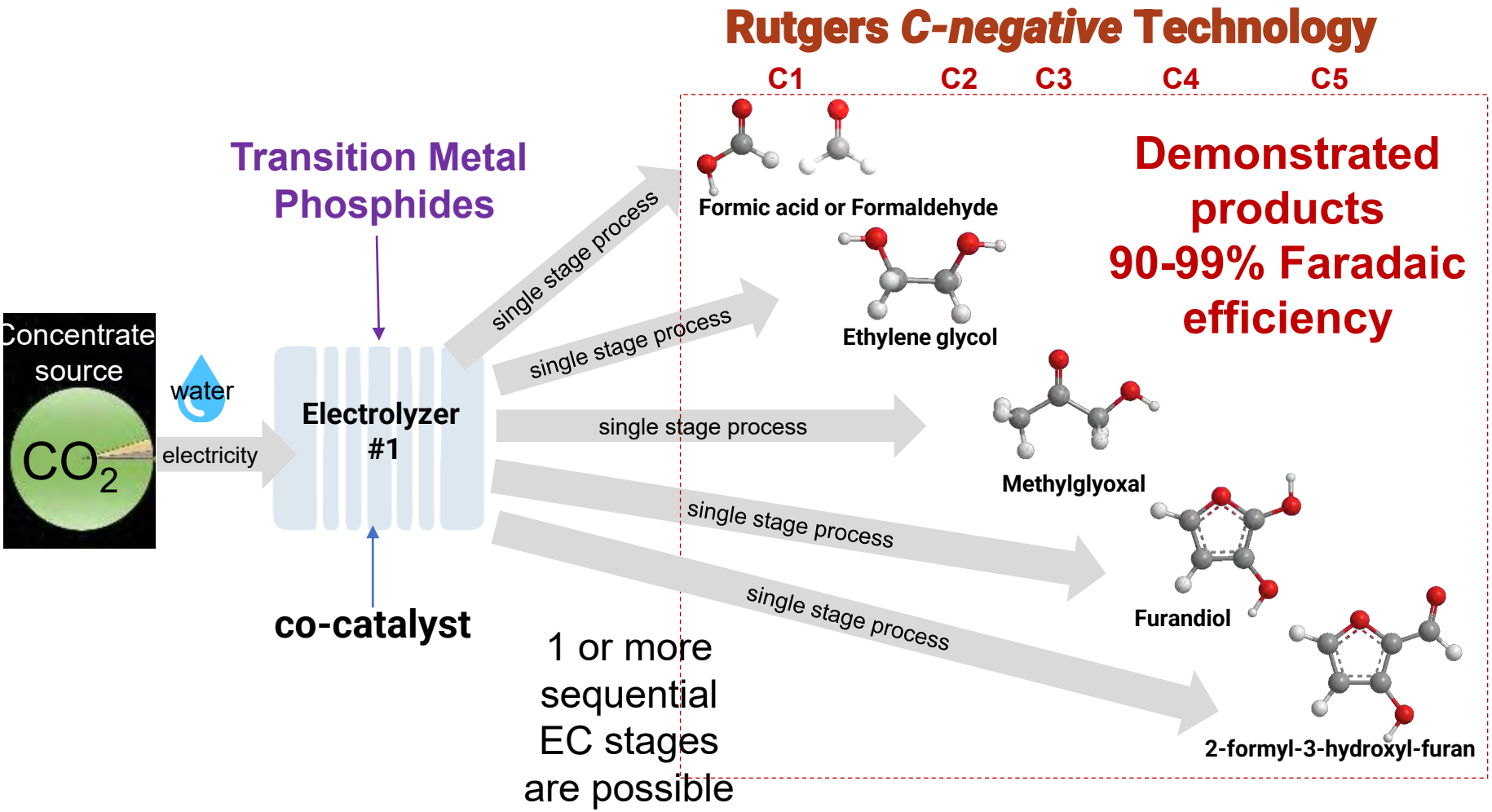


Furandiol

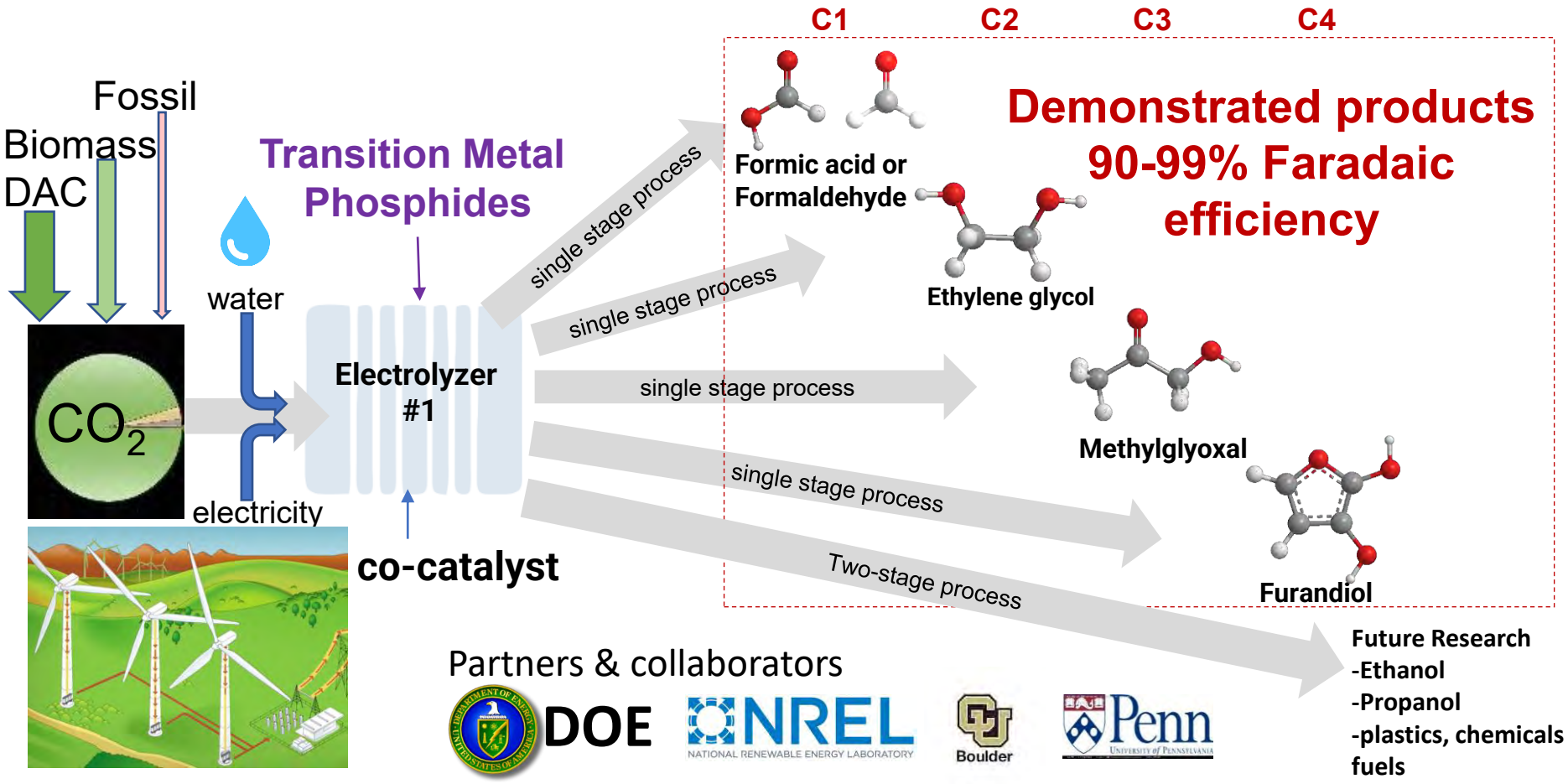
Dr. Anders Laursen
Research associate &
CEO RenewCO_2 LLC

Karin Calvinho
CTO RenewCO_2

Artificial Photosynthesis beats Natural Photosynthesis



CO_2→ Bulk Chemicals & Fuels : *Rutgers CO_2-Negative Technology*



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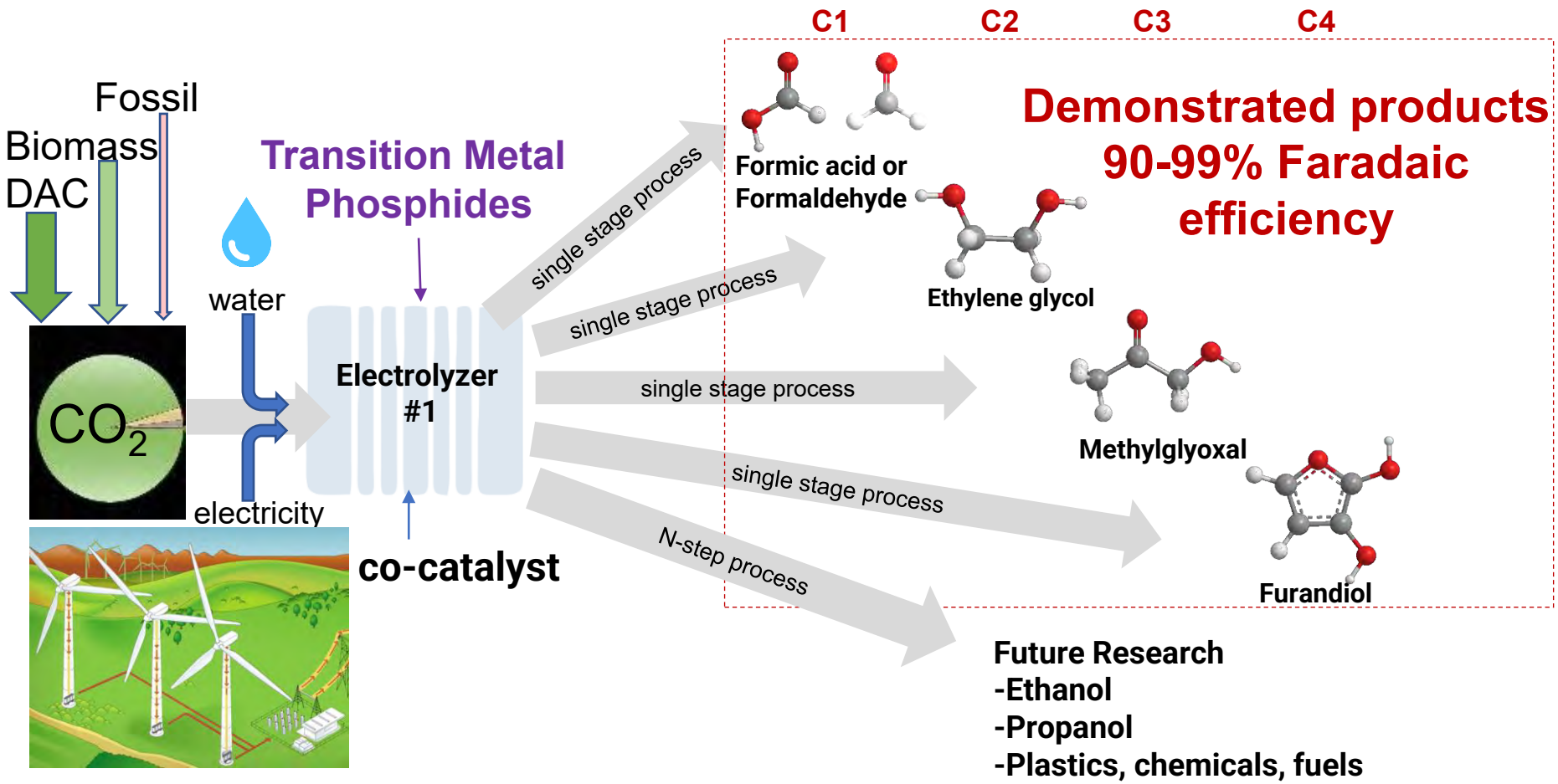
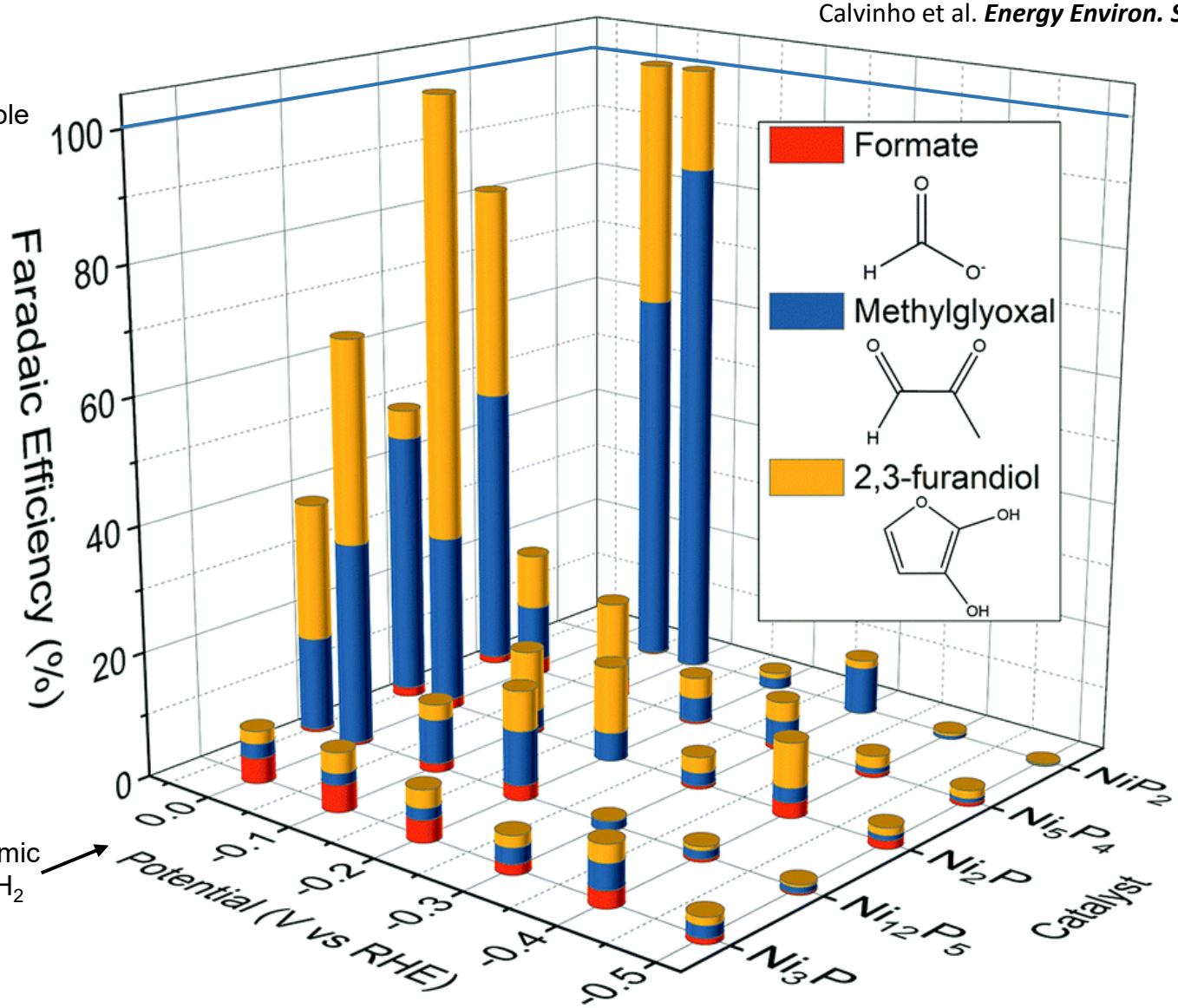


Saving Planet Earth
Nickel Phosphides: Bioinspired CO_2 Reduction Catalysts

Calvinho et al. ***Energy Environ. Sci.***, 2018,

H_2 is the sole remaining product



Thermodynamic potential for H_2 evolution

Reaction conditions: pH 7.5, 0.5 M $KHCO_3$(aq), 25°C, 1 atm CO_2

JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
pubs.acs.org/JACS
Article

Surface Hydrides on Fe_2P Electrocatalyst Reduce CO_2 at Low Overpotential: Steering Selectivity to Ethylene Glycol

Karin U. D. Calvinho,[⊥] Abdulaziz W. Alherz,[⊥] Kyra M. K. Yap,[⊥] Anders B. Laursen, Shinjae Hwang, Zachary J. L. Bare, Zachary Clifford, Charles B. Musgrave,* and G. Charles Dismukes*

Cite This: *J. Am. Chem. Soc.* 2021, 143, 21275−21285
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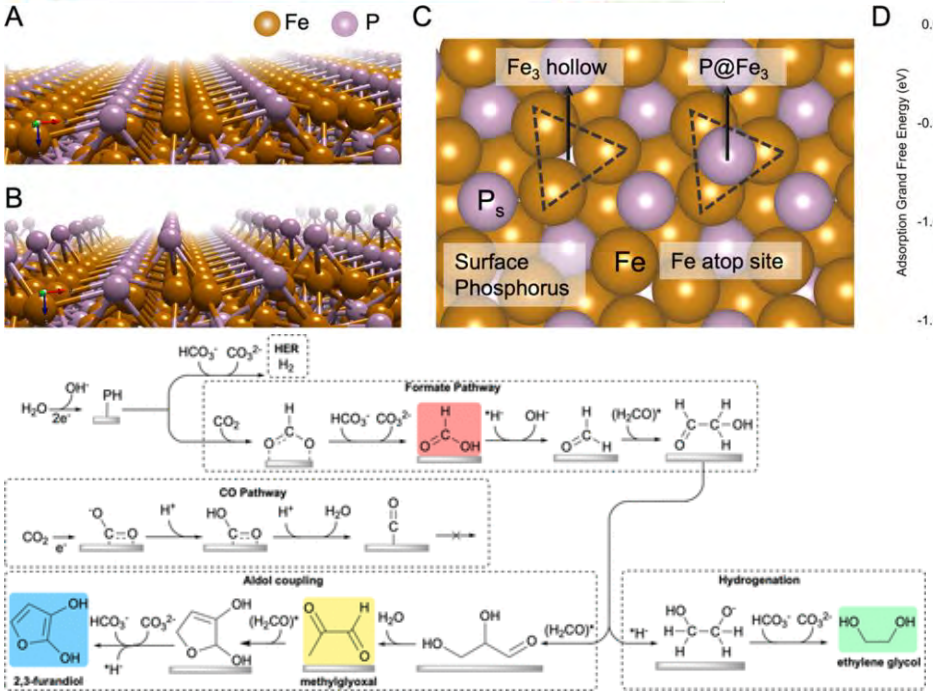
DOI: 10.1021/jacs.1c03428

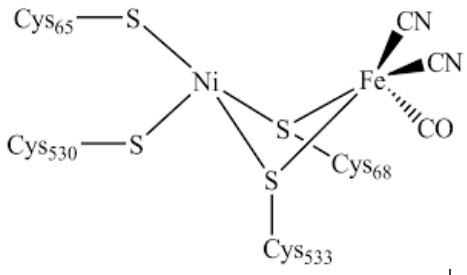


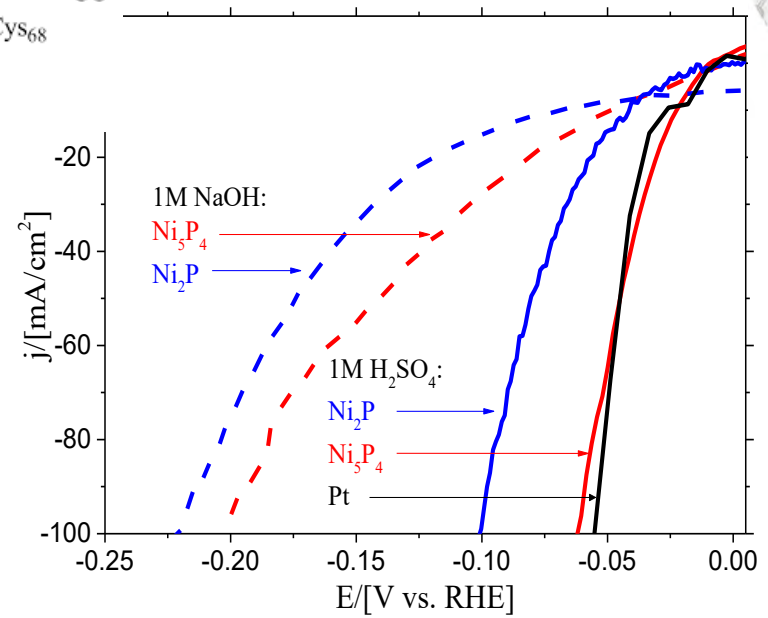
A) Fe_2P (0001) side view showing the clean surface and (B) reconstructed surfaces. (C) Fe_2P (0001) top view

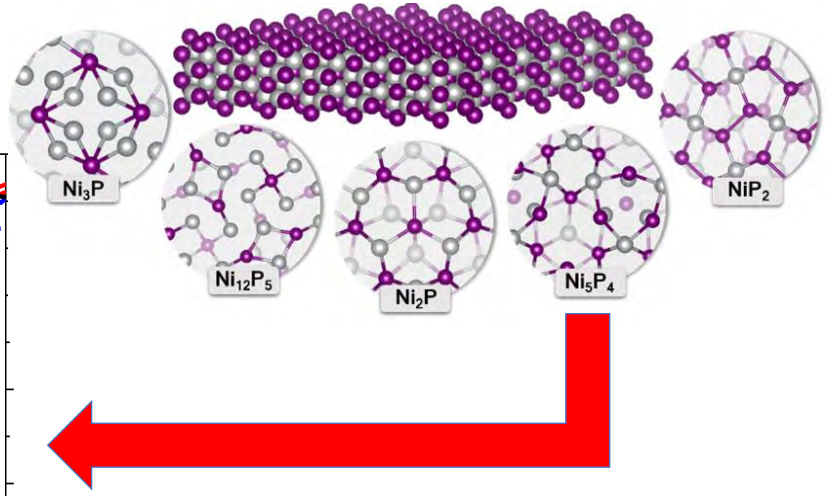
**C_2 precursor to produce ethylene glycol is also the precursor to the C_3 and C_4 products. The *C_2 aldol precursor (glycolaldehyde) simply reacts faster with *H to produce more ethylene glycol as the bias decreases than it reacts with the decreasing amount of *C_1 via a slower, entropically disfavored step*

Transition Metal Phosphides: Bioinspired H2 Evolution Catalysts

NiFe-Hydrogenase → Ni-organometallic models (fragile) → Ni_xP_y solid state catalysts (Robust)







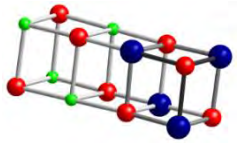
Activity = PGM performance

Stability in both acidic and basic media (>24h, no degradation)

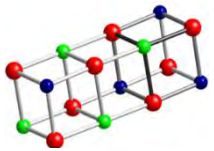
Laursen, A.B., K.R. Patraju, M.J. Whitaker, M. Retuerto, T. Sarkar, N. Yao, K.V. Ramanujachary, M. Greenblatt and G.C. Dismukes, *Energy & Environmental Science, 2015. 8: p. 1027-1034.*

A. B. Laursen, R. B. Wexler, M. J. Whitaker, E. Izett, R. Rucker, H. Wang, J. Li, M. Greenblatt, A. M. Rappe and G.C. Dismukes, *ACS Catalysis, 2018(8): p. 4408−4419.*

Water Splitting
PGM-free catalysts



(*Fd-3m*)



(*R-3m*)

Cubic

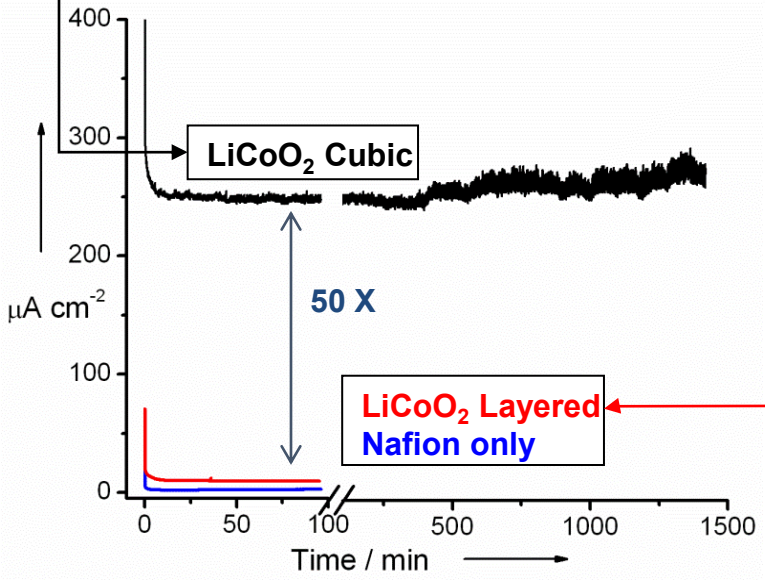
Layered

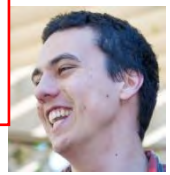
$LiCoO_2$

$½O_2 + 2H^+$

H_2O

H_2O





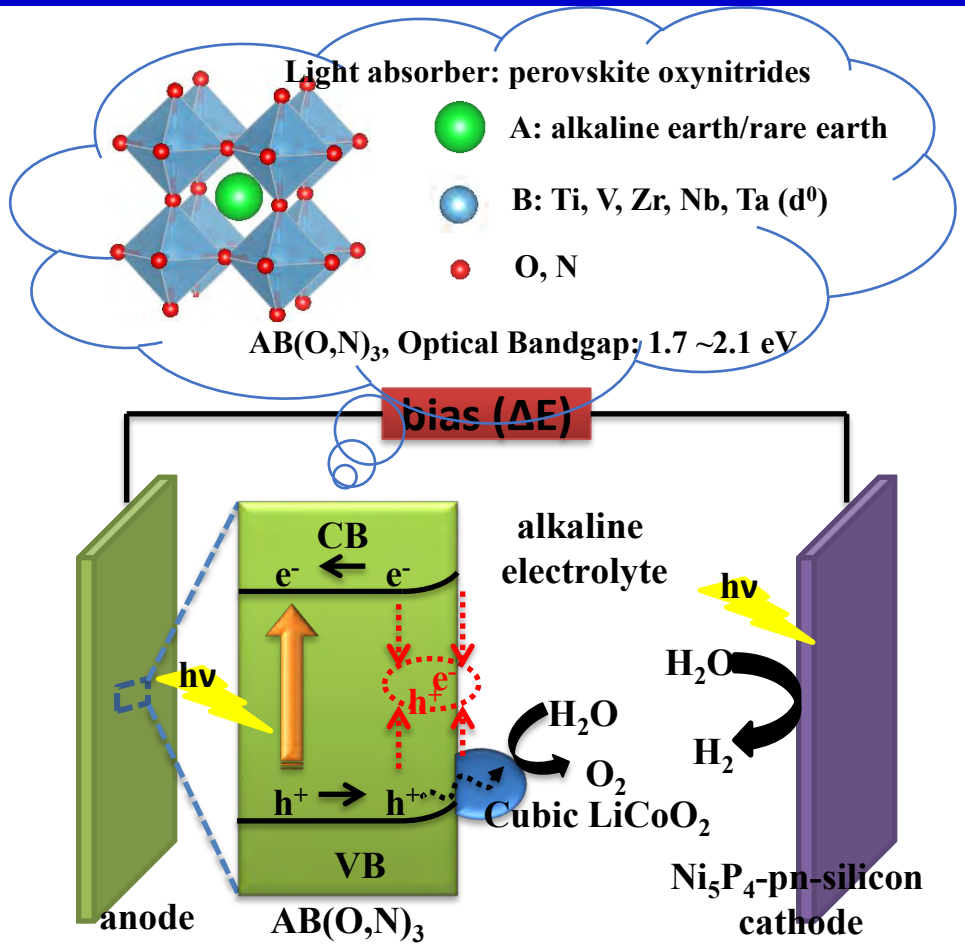
Graeme Gardner

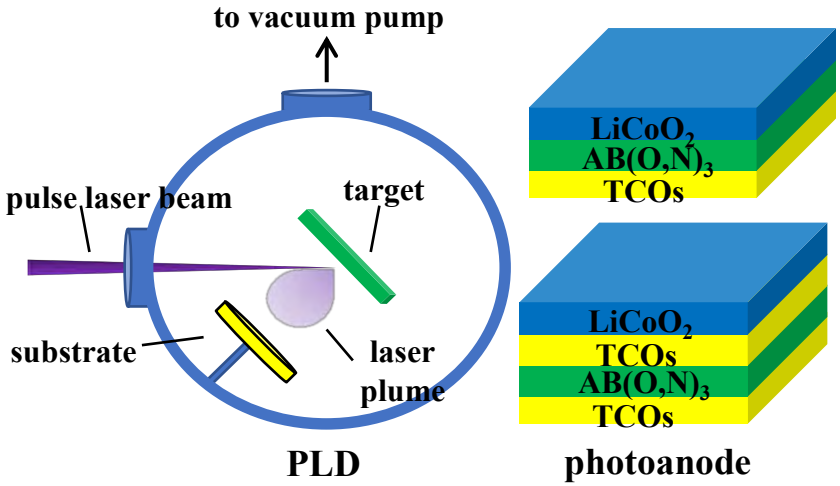
Gardner, Robinson, Smith, Go, Greenblatt, Dismukes (2012) ***Angew Chemie***, 51, 1616

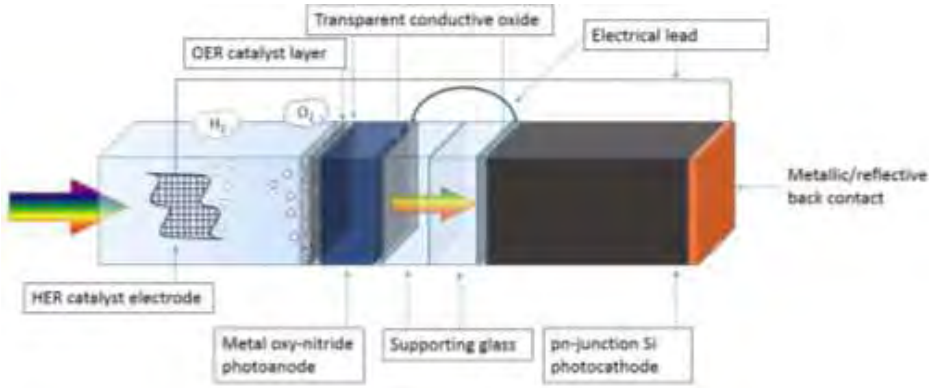
Gardner, Al-Sharab, Danilovic, Go, Ayer, Greenblatt and Dismukes, (2016) ***Energy Environ. Sci.,.*** 9: p. 184--192.

Hydrogen from Water & Sunlight: Photoanode-Photocathode-Catalysts

GC Dismukes (PI) and E Garfunkel (coPIs), Rutgers University. DOE/NSF-1433492







- Synthesize and investigate selected phase-pure members of perovskite oxynitride series $AB(O,N)_3$.
- Characterize the optical bandgaps and photoinduced carrier lifetime of these materials in preparation of attaching OER catalyst.

- Using pulsed laser deposition, prepare photoanode with thin film structures shown above.
- Fabricate photocathode of pn-silicon and Ni5P4 HER catalyst
- Investigate two electrolytes system: aqueous alkaline electrolyte solution (pH=14) and alkaline exchange membrane

Dismukes Waksman lab projects

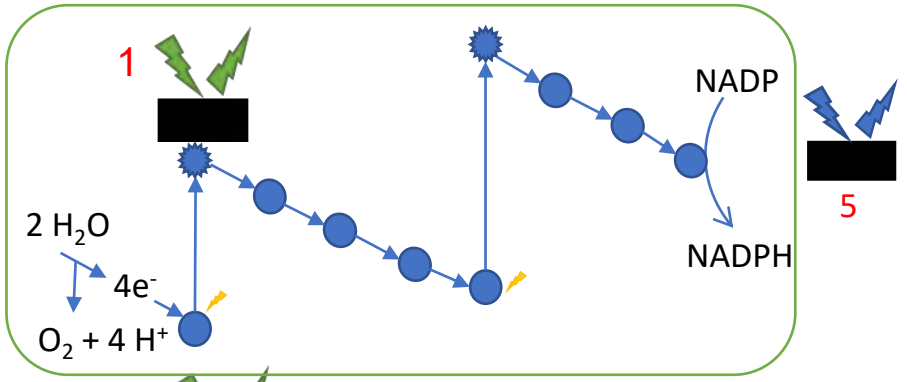
Bioenergy from Biomass - Natural Photosynthesis

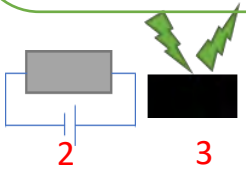
- Photosynthetic Adaptation to Carbon Dioxide
- Metabolomics – Experimental Isotopic Fluxes by Mass Spectrometry
- Computational Modelling of Metabolism

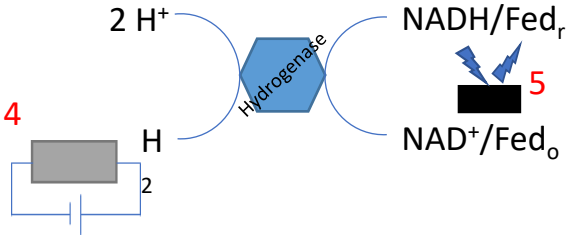
Biocatalysis

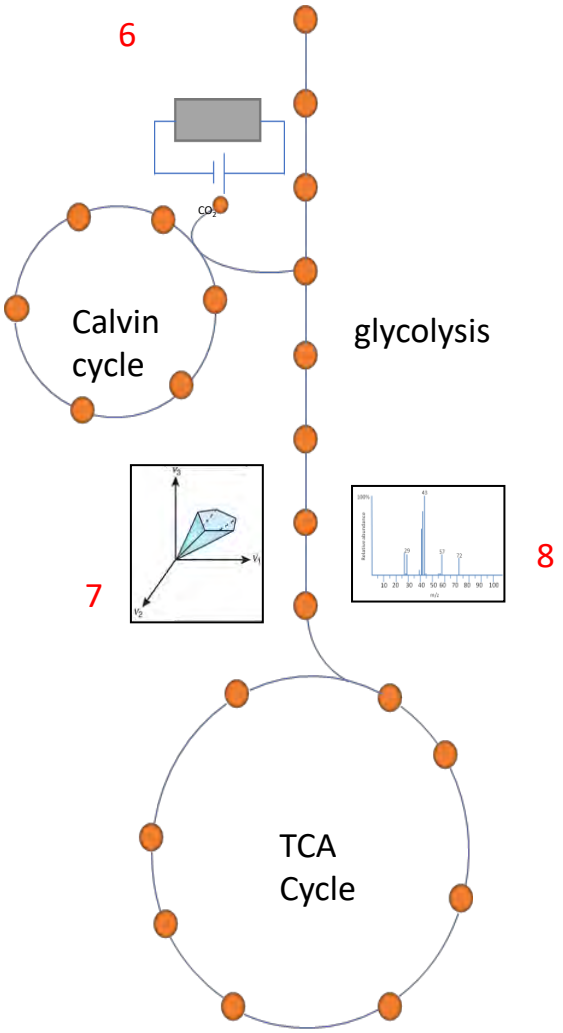
- Photosystem II and Water Oxidation Catalysis
- Overcoming Limitations in Carboxylation

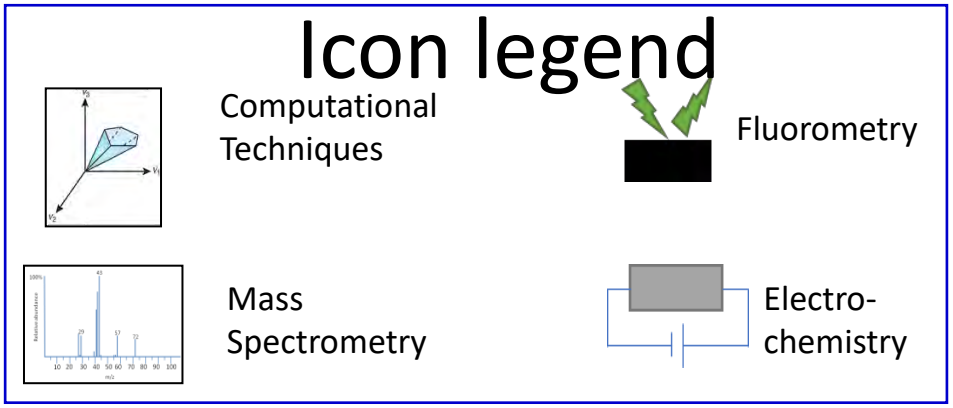
Dismukes Waksman lab analytical toolbox





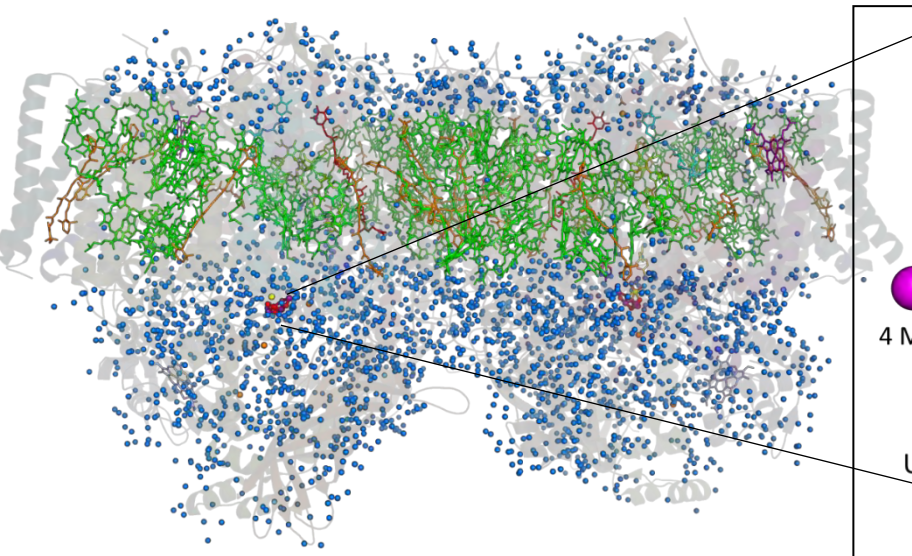


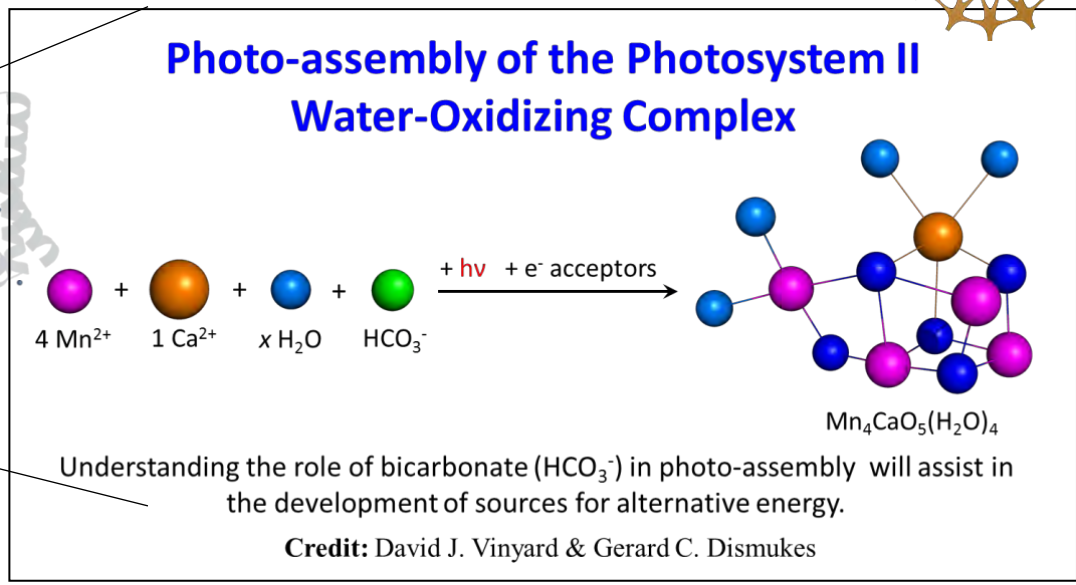




Powerful tools developed in our laboratory offer unique insights into biology

Bioinorganic Chemistry



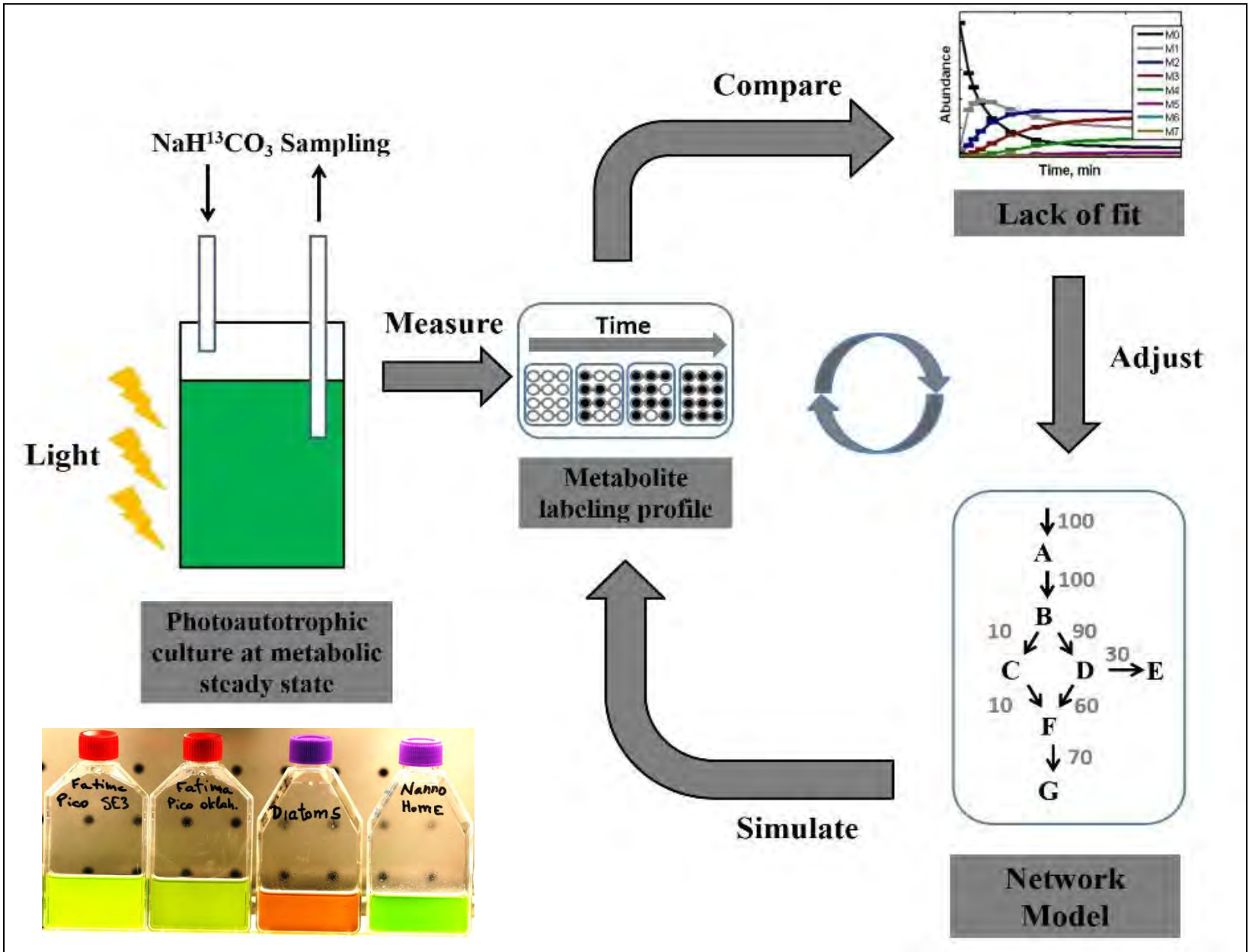


Project Background: Photosystem II uses manganese to split water in all oxygenic phototrophs on Earth.

For the first time we have succeeded in replacing Mn with cobalt in PSII. This opens the door to understanding the chemistry of water oxidation and O_2 production on Earth.

Vinyard, D.J., J.S. Sun, J. Gimpel, G.M. Ananyev, S.P. Mayfield and G.C. Dismukes, Natural isoforms of the Photosystem II D1 subunit differ in photoassembly efficiency of the water-oxidizing complex. Photosynthesis research, 2015: p. 1-10.

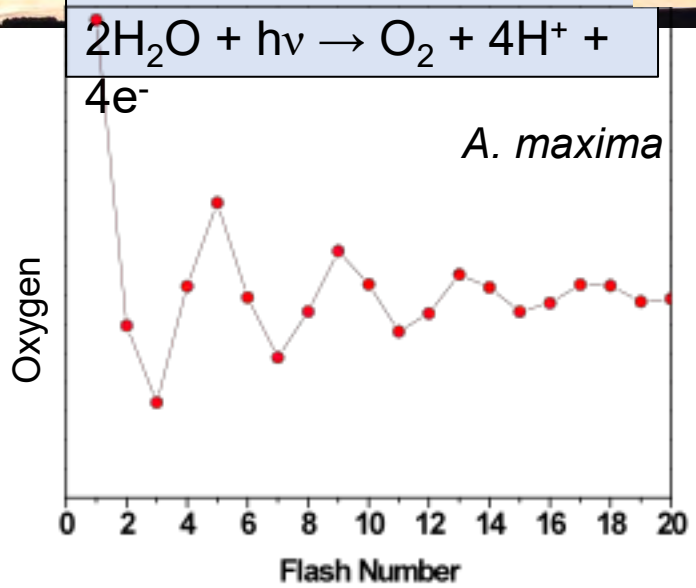
Can We Unlock the Power of Photosynthetic Metabolism?
Kinetic Flux Profiling of Photoautotrophic Metabolism



Oximetry
Flash oxygen electrode (Clark-type), membrane-bound platinum-iridium

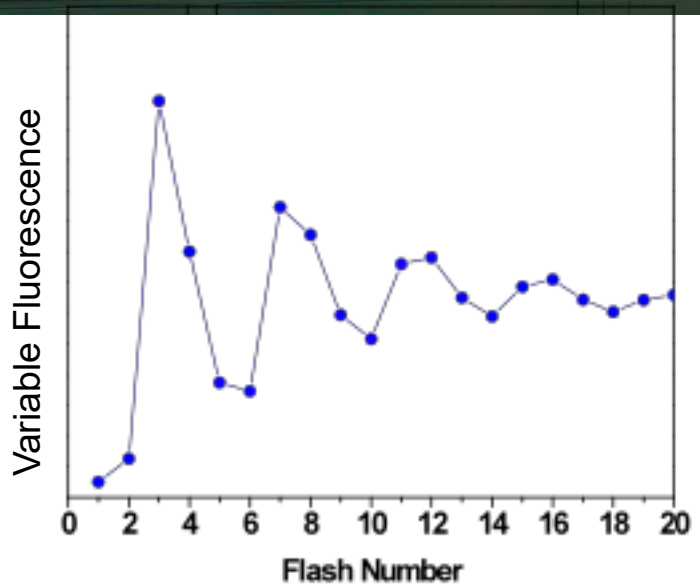
$2H_2O + h\nu \rightarrow O_2 + 4H^+ + 4e^-$

A. maxima



Chl Fluorescence Induction
Fast repetition rate fluorometer

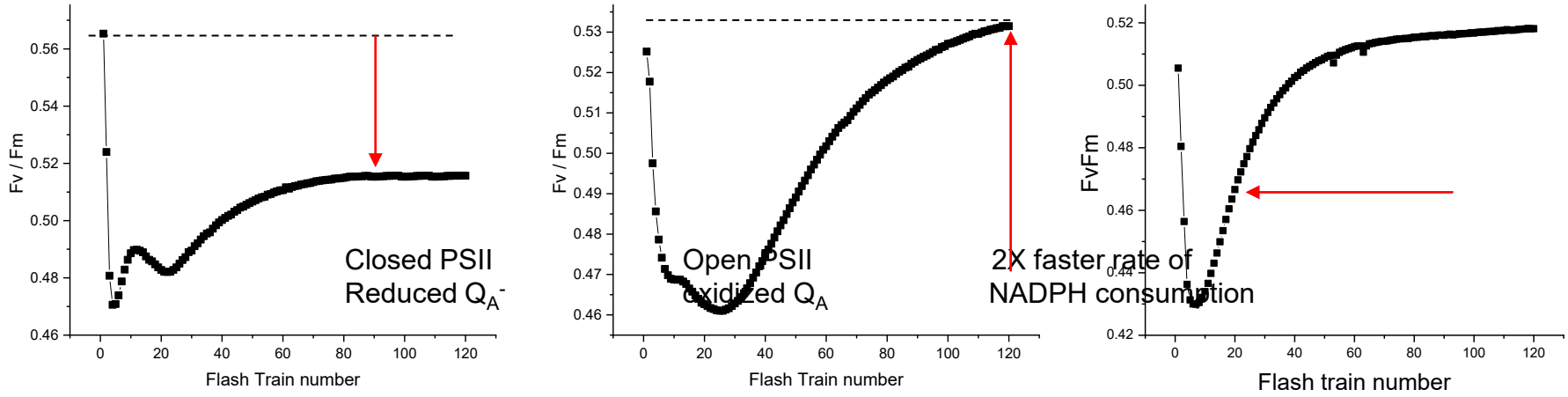
Chl Fv/Fm



CO_2 -Dependent Chlorophyll Variable Fluorescence Yield & Rate

Constant growth conditions: Air 0.04% CO_2
Variable CO_2 in headspace (no bicarb added)
Nannochloropsis Oceania –green alga

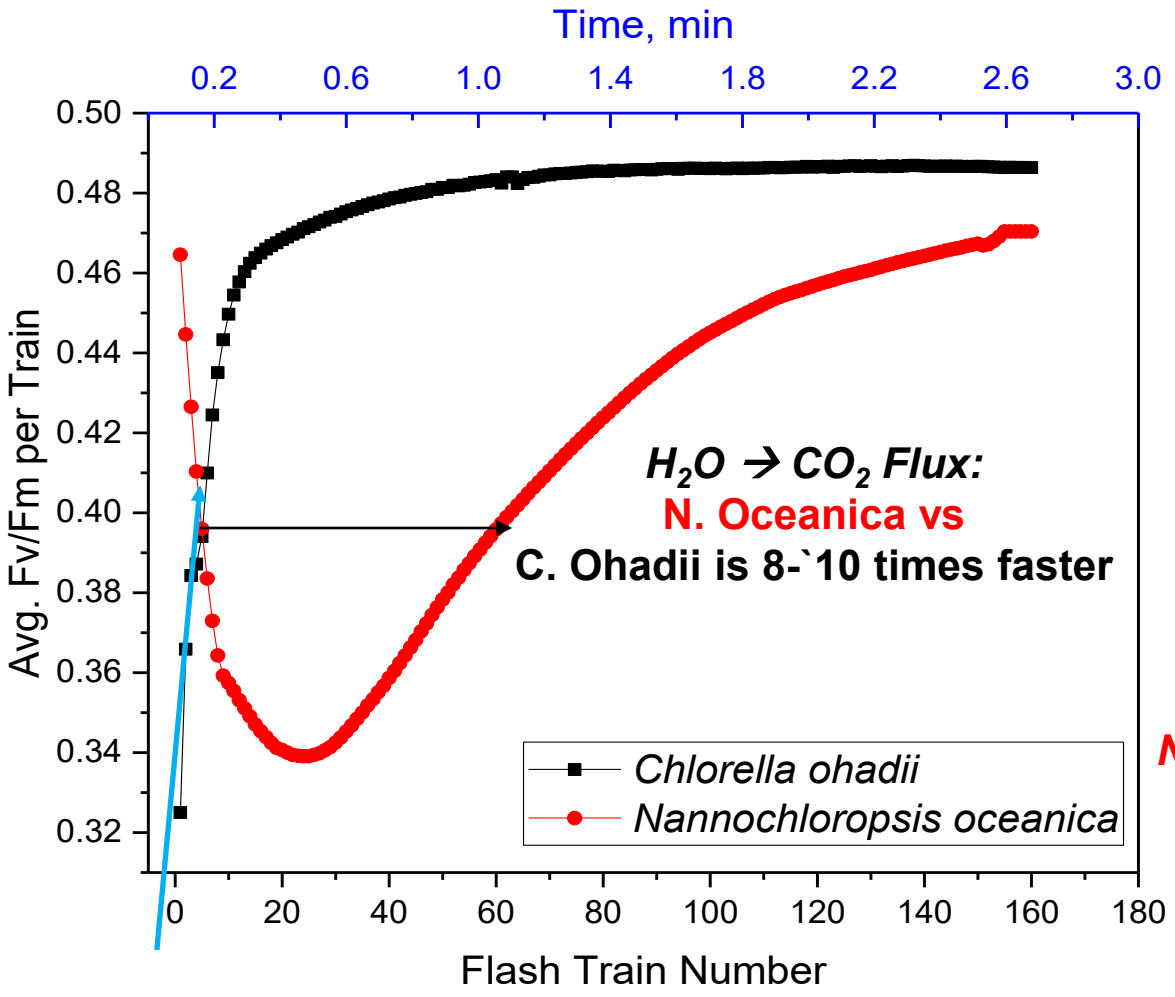
Measure: Air 0.04% CO_2 2 % CO_2 10 % CO_2



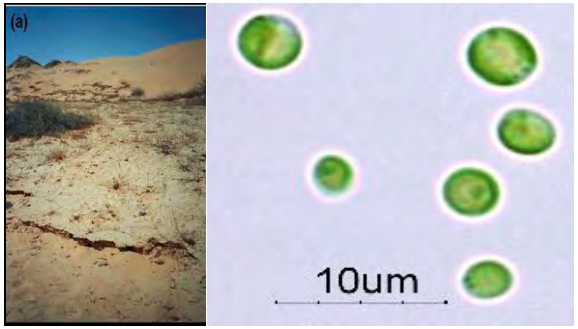
- ✓ 2% + 10% CO_2 opens closed PSII centers (QA-) to the full dark-adapted level
- ✓ 10% CO_2 accelerates the rate of NADPH consumption (~50 → 25 FT)
- ✓ Slow CO_2 diffusion rate
- ✓ RuBisCO is ponderously slow and highly inefficient (+ATP)

The Usain Bolt of Photosynthesis: *Chlorella Ohadii*

Algal Tree of Life: *Chlorella ohadii* Possesses the Fastest Carbon Fixation Mechanisms Among Eukaryotic Phototrophs:



C. ohadii: from the Negev Desert, Israel ***Treves et al. (2013)***



***N. oceanica*: marine heterokont alga slow growing lipid producer**

Ananyev, G., C. Gates, A. Kaplan & G.C. Dismukes, BBA-Bioenergetics, *2016. 1858(11):873-*

Photosynthetic Adaptation to Carbon Dioxide Gradients in Yellowstone: A glimpse into the future of climate change?

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