G. Charles Dismukes
Rutgers University
Dept Chemistry & Chemical Biology
The Waksman Institute
2023-2024 Annual Report

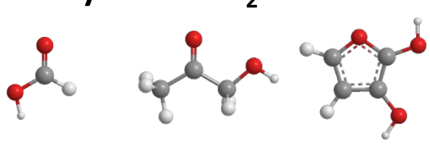
The Dismukes research group conducts fundamental and applied research in the areas of catalysis, renewable energy, and sustainable production of chemicals via biological and chemical approaches. The biological approach focuses on investigations of the light reactions and central carbon metabolism in photosynthetic microorganisms. The chemical approach involves synthesis of bioinspired electrocatalysts and their integration within electrolyzers and artificial photosynthetic systems. The disciplinary approaches used are genetic engineering, materials synthesis by design, electrochemistry and catalysis. The goal is to produce sustainable processes for producing renewable fuels and biomass at high energy efficiency. Our laboratories are located in the Waksman Institute of Microbiology and the Chemistry and Chemical Biology Laboratory at Rutgers University. Additionally, Dr Dismukes is a member of the graduate training faculties in Chemical and Biological Engineering (SOE), Biochemistry and Microbiology (SEBS), and Earth and Planetary Sciences (SAS). In the 2023-June 2024 period the group was comprised of 23 researchers and interns.

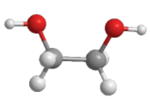
Our Laboratories and Research Programs:

Energy for an overcrowded planet
Department of Chemistry & Chem Biology

Electro-Catalysts for Water Oxidation
-H^+ & e^- from water

Carbon-Negative Synthesis from Scratch
Electro-Catalysts for CO_2 Conversion

-2018 

-2023 

-2024 C-negative polymers from CO_2

Food for an overcrowded planet
Waksman Institute of Microbiology

Improving Photosynthesis in Vivo:
-Eliminating flux chokepoints

Chokepoints in CO_2 Carboxylation:
-RuBisCO/ Calvin-Benson Cycle

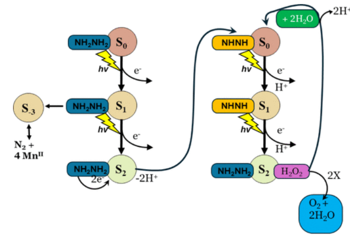
Catalysis by Photosynthetic Enzymes:
-Photosystem II/Water Oxidation

Rutgers Startup from 5 RU patents

RENEW CO_2

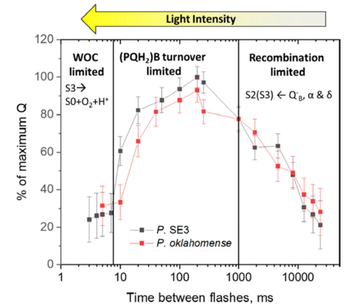
Current Research Projects (2023-September 2024):

Converting the 4-Flash Photosynthetic O_2 Evolution Cycle to a 2-Flash Catalytic Cycle with a Simple Co-catalyst: Counting Electrons and Holes Directly and Transparently.



We apply a direct electron-counting method and two classes of reducing agents capable of single- vs multielectron H atom transfer reactions (nH) to probe the oxidation states of manganese in ultrapure Photosystem II (PSII) microcrystals (PSIIX) during the 4-flash catalytic cycle of O2 evolution…
Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes,
ACS Catalysis, 2024. https://doi.org/10.1021/acscatal.4c03896

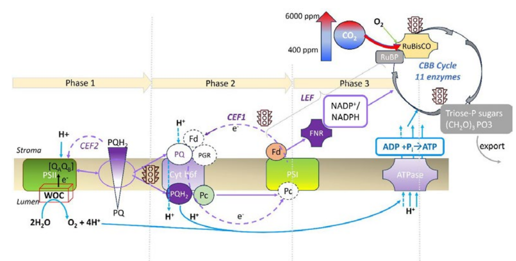
Exceptional Quantum Efficiency Powers Biomass Production in Halotolerant Algae *Picochlorum* sp.^



The green algal genus *Picochlorum* is of biotechnological interest because of its robust response to multiple environmental stresses. We compared the metabolic performance of *P.* SE3 and *P. oklahomense* to diverse microbial phototrophs and observed exceptional performance of photosystem II (PSII) in light energy conversion in both *Picochlorum* species…
Colin Gates, Gennady Ananyev, Fatima Foflonker, Debashish Bhattacharya, G. Charles Dismukes. **Photosynthesis Research, 2024.**
https://link.springer.com/article/10.1007/s11120-024-01075-9

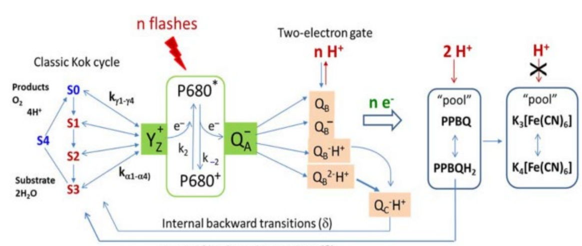
Comment on: "Photosynthesis. Electronic structure of the oxygen-evolving complex in photosystem II prior to O-O bond formation. *Dismukes, G.C. and R. Stranger*
The publication by Cox et al. [1] used the electron spin echo method to assign the electronic spin of the ground state of the tetra-manganese cluster of a photosynthetic oxygen-evolving complex, concluding spin S = 3. We report an error in their application of the method that resulted in an appreciably larger value of S than the correct value and describe possible sources of the discrepancy…
Science, 2024. doi/10.1126/science.1254910#elettersSection.

Adaptation of plant photosynthetic metabolism to extreme CO2 levels in Yellowstone revealed by in vivo fluorescence dynamics. *ten Veldhuis, J.A.E. and G.C. Dismukes,*



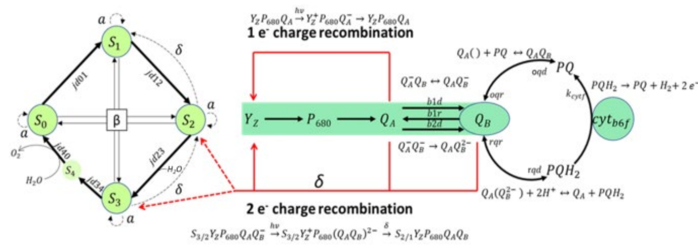
How plants adapt to elevated CO_2 levels is a much-studied question that has returned ambiguous answers. Whether photosynthesis can favorably adapt to extreme CO_2 remains yet unknown. Here, we investigate changes in photosynthetic metabolism in a C_3 plant growing near sources of high CO_2 emission in Yellowstone NP…
Plant Cell Environ, 2024. Under review; Research Square: https://www.researchsquare.com/article/rs-3235087/v1

Regulation of light energy conversion between linear and cyclic electron flow within photosystem II controlled by the plastoquinone/quinol redox poise.



Ultra-pure Photosystem II complexes crystalize as uniform microcrystals (PSIIX) of unprecedented homogeneity that allow observation of details previously unachievable, including the longest sustained oscillations of flash-induced O_2 yield over > 200 flashes and a novel period-4.7 water oxidation cycle. We provide new evidence for a molecular-based mechanism for PSII-cyclic electron flow that accounts for switching from linear to cyclic electron flow within PSII as the downstream PQ/PQH_2 pool reduces in response to metabolic needs and environmental input…
Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes, **Photosynth Research 2023.**
https://link.springer.com/article/10.1007/s11120-022-00985-w

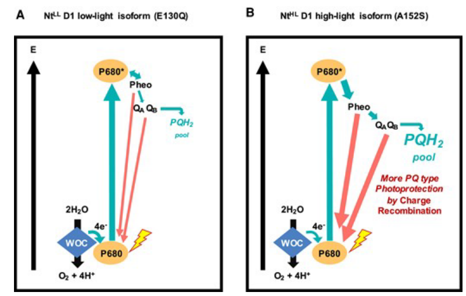
Cyclic electron flow around photosystem II in silico: How it works and functions in vivo.



To date, cyclic electron flow around PSI (PSI-CEF) has been considered the primary (if not the only) mechanism accepted to adjust the ratio of linear vs cyclic electron flow that is essential to adjust the ratio of ATP/NADPH production needed for CO2 carboxylation. Here we provide a kinetic model showing that cyclic electron flow within PSII (PSII-CEF) is essential to account for the accelerating rate of decay in flash-induced oscillations of O-2 yield as the PQ pool progressively reduces to PQH(2)…

Zournas, A., K. Mani and G.C. Dismukes, **Photosynthesis Research, 2023.** https://link.springer.com/article/10.1007/s11120-023-00997-0

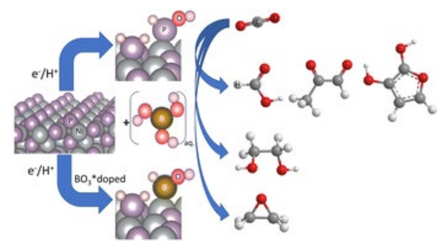
Cyanobacterial photosystem II reaction center design in tobacco chloroplasts increases biomass in low light.



The D1 polypeptide of the photosystem II (PSII) reaction center complex contains domains that regulate primary photochemical yield and charge recombination rate. Many prokaryotic oxygenic phototrophs express two or more D1 isoforms differentially in response to environmental light needs, a capability absent in flowering plants and algae. We report that tobacco (Nicotiana tabacum) plants carrying the Synechococcus (Synechococcus elongatus PCC 7942) low-light mutation (LL-E130Q) in the D1 polypeptide (NtLL) acquire the cyanobacterial photochemical phenotype: faster photodamage in high light and significantly more charge separations in productive linear electron flow in low light…

Zhang, Y., G. Ananyev, A. Matsuoka, G.C. Dismukes and P. Maliga, **Plant Physiol, 2023.** https://academic.oup.com/plphys/article/191/4/2229/6891079

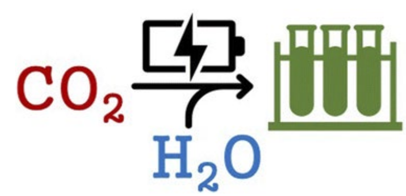
Tunable product selectivity on demand: Mechanism-guided Lewis acid co-catalyst for CO2 electroreduction to ethylene glycol.



Bioinspired nickel phosphide electrocatalysts can produce more complex multi-carbon products than natural photosynthetic enzymes but controlling C-product selectivity and suppressing H_2 evolution remain open challenges. Here, we report a significant shift in the CO_2RR product distribution on Ni_2P in the presence of boric acid/borate, a soluble Lewis acid/base co-catalyst that shifts product selectivity to ethylene glycol (EG) with an 85% CO_2-Faradaic efficiency...

Li, Y., K. Calvinho, A. Laursen, M. Dhiman, D. Santorelli, Z. Clifford and G.C. Dismukes, **EES Catalysis, 2024. https://pubs.rsc.org/en/content/articlelanding/2024/ey/d3ey00237c**

Enabling technologies for the continuous electrically driven conversion of CO2 and water to multi-carbon products at high current densities.

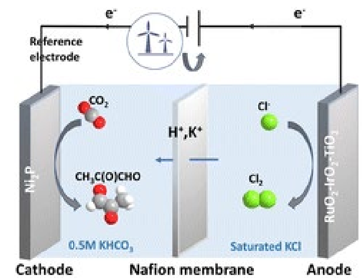


Herein, we demonstrate greatly improved conversion of CO2 using a gas diffusion electrode (GDE) with flowing electrolyte configuration for CO2 gas delivery in combination with a high surface area nickel phosphide electrocatalyst. This configuration achieves 40–50% selectivity for total carbon products over H2 formation (HER) at total current densities ranging from 50 to 300 mA cm−2…

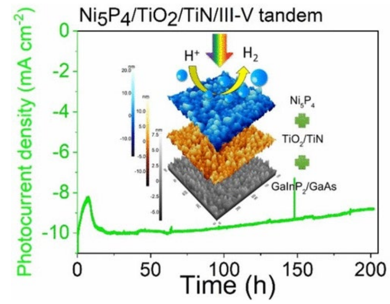
Dhiman, M., Y. Chen, Y. Li, A.B. Laursen, K.U.D. Calvinho, T.G. Deutsch and G.C. Dismukes, **Journal of Materials Chemistry A, 2023. https://pubs.rsc.org/en/content/articlelanding/2023/ta/d2ta08173c**

Remodeling the chlor-alkali electrolysis process to co-generate useful reduction products from CO2. Converting CO2 into usable chemicals and fuels electrochemically is a promising method to close the carbon cycle and store intermittent renewable energy. However, on combining it with a typical anode, the oxygen

evolution reaction (OER), results in both high energy consumption and produces only oxygen of little commercial value. Conversely, the chlor-alkali process is an established and profitable electrochemical process that produces Cl_2 and alkali (KOH). Herein, we demonstrate the feasibility of integrating the chlorine evolution reaction (CER) together with the CO2 reduction reaction (CO2RR) to co-generate C4 (2,3-furandiol) and C3 (methylglyoxal) products…
Li, Y., A.B. Laursen, M. Dhiman and G.C. Dismukes, **Journal of Materials Chemistry A, 2023.**
https://pubs.rsc.org/en/content/articlelanding/2023/ta/d3ta03202g

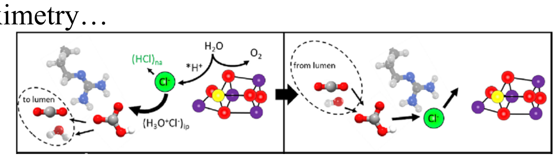


TiO2/TiN Interface Enables Integration of Ni5P4 Electrocatalyst with a III–V Tandem Photoabsorber for Stable Unassisted Solar-Driven Water Splitting.
H2 production by direct photoelectrochemical (PEC) water splitting has remained unachievable commercially, mainly due to rapid failure at the interface between the photoabsorber(s) and catalyst(s). PEC devices made from multijunction III–V semiconductors with platinum group metal (PGM) catalysts have yielded impressive initial solar-to-H2 (STH) efficiency >19%, which rapidly corrodes in aqueous electrolytes. Here, TiO2/TiN layers were fused to create a bifunctional interface between a GaInP2/GaAs III–V tandem photoabsorber and a polycrystalline Ni5P4 HER catalyst…

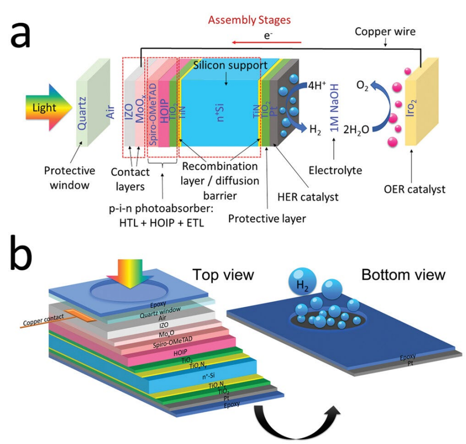


Hwang, S., H. Gu, J.L. Young, M.A. Steiner, A.B. Laursen, R.A. Crichton, Y.-W. Yeh, P.E. Batson, L.C. Feldman, M. Li, K. Wyatt, A. Safari, T.G. Deutsch, E. Garfunkel and G.C. Dismukes, **ACS Energy Letters, 2024.** https://pubs.acs.org/doi/10.1021/acsenergylett.3c02606

How chloride functions to enable proton conduction in photosynthetic water oxidation: Time-resolved kinetics of intermediates (S-states) in vivo and bromide substitution
Chloride (Cl−) is essential for O_2 evolution during photosynthetic water oxidation. Two chlorides near the water-oxidizing complex (WOC) in Photosystem II (PSII) structures from Thermosynechococcus elongatus (and T. vulcanus) have been postulated to transfer protons generated from water oxidation. We monitored four criteria: primary charge separation flash yield (P* → P+QA−), rates of water oxidation steps (S-states), rate of proton evolution, and flash O2 yield oscillations by measuring chlorophyll variable fluorescence (P* quenching), pH-sensitive dye changes, and oximetry…
Colin Gates, Jonah M. Williams, Gennady Ananyev, G. Charles Dismukes, **BBA - Bioenergetics**, 2023.1864 (4) https://doi.org/10.1016/j.bbabio.2023.148998



Interfacial Connections between Organic Perovskite/n+ Silicon/Catalyst that Allow Integration of Solar Cell and Catalyst for Hydrogen Evolution from Water.
The rapidly increasing solar conversion efficiency (PCE) of hybrid organic–inorganic perovskite (HOIP) thin-film semiconductors has triggered interest in their use for direct solar-driven water splitting to produce hydrogen. However, application of these low-cost, electronic-structure-tunable HOIP tandem photoabsorbers has been hindered by the instability of the photovoltaic-catalyst-electrolyte (PV+E) interfaces. Here, photolytic water splitting is demonstrated using an integrated configuration consisting of an HOIP/n+silicon single junction photoabsorber and a platinum (Pt) thin film catalyst…



Gu, H., F. Zhang, S. Hwang, A.B. Laursen, X. Liu, S.Y. Park, M. Yang, R.C. Bramante, H. Hijazi, L. Kasaei, L.C. Feldman, Y.-W. Yeh, P.E. Batson, B.W. Larson, M. Li, Y. Li, K. Wyatt, J.L. Young, K. Teeluck, K. Zhu, E. Garfunkel and G.C. Dismukes, **Advanced Functional Materials, 2023**. https://doi.org/10.1002/adfm.202301196

Scholarship (2023-2024): 1 published patent, 2 submitted Notice of Inventions; 14 submitted or published manuscripts in peer reviewed journals, 1 PhD thesis.

PhD Theses: Yifei Li, PhD thesis in SAS-CCB: "Electrochemical CO_2 Reduction On Nickel Phosphides"

Patents and NOI Disclosures:

1. Dismukes, G.C., A. Laursen and K. Calvinho, *Lewis/Bronsted Acid/Base And Nickel Phosphide Binary Catalyst-System (Co-Catalysts) For Direct Electrochemical Co_2 Reduction To Hydrocarbons*, in **USPTO**, patent # US-20230193481-A1, International.
2. Dismukes, G.C. and M. Dhiman, *Provisional Patent Application #: 63/567,121 "Electroreduction of Carbon Dioxide (CO2) to Multi-Carbon Products on Electrocatalyst Comprised of Molybdenum Diphosphide (MoP2) and Its Doped Derivatives"*, in *Rutgers University*. 2023.
3. Dismukes, G.C. and C.W. Cady, *Notice of Invention Disclosure "Catalysts for the selective partial oxidation of natural gas to methanol and hydrocarbons to alcohols"*, in *Rutgers University*. 2023.

Peer Reviewed Publications, Period 2023-2024 (September)

1. ten Veldhuis, J.A.E. and G.C. Dismukes, *Adaptation of plant photosynthetic metabolism to extreme CO2 levels in Yellowstone revealed by in vivo fluorescence dynamics.* **Plant Cell Environ,** 2024. Submitted.
2. Yifei Li, Abdulaziz Alherz, Mahak Dhiman, Karin Calvinho, Tom Emge, Charles Musgrave, Eric Garfunkel and G.C. Dismukes, *Electrocatalytic CO2 reduction on single crystal NiP2 facets: Surface intermediates and mechanism revealed by in situ Raman spectroscopy and GC-DFT quantum mechanical calculations.* **EES Catalysis**, Submitted.
3. Li, Y., K. Calvinho, A. Laursen, M. Dhiman, D. Santorelli, Z. Clifford and G.C. Dismukes, *Tunable product selectivity on demand: Mechanism-guided Lewis acid co-catalyst for CO2 electroreduction to ethylene glycol.* **EES Catalysis**, 2024. **2,** p. 823-833.
4. Hwang, S., H. Gu, J.L. Young, M.A. Steiner, A.B. Laursen, R.A. Crichton, Y.-W. Yeh, P.E. Batson, L.C. Feldman, M. Li, K. Wyatt, A. Safari, T.G. Deutsch, E. Garfunkel and G.C. Dismukes, *TiO2/TiN Interface Enables Integration of Ni5P4 Electrocatalyst with a III–V Tandem Photoabsorber for Stable Unassisted Solar-Driven Water Splitting.* **ACS Energy Letters,** 2024. **9**(3): p. 789-797.
5. Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes, *Converting the 4-Flash Photosynthetic O_2 Evolution Cycle to a 2-Flash Catalytic Cycle with a Simple Co-catalyst: Counting Electrons and Holes Directly and Transparently.* **ACS Catalysis,** 2024. **14**: p. 15073−15087.
6. Gates, C., G. Ananyev, F. Foflonker, D. Bhattacharya and G.C. Dismukes, *Exceptional Quantum Efficiency Powers Biomass Production in Halotolerant Algae Picochlorum sp.* **Photosynthesis Research**, 2024. 10.1007/s11120-024-01075-9.
7. Dismukes, G.C. and R. Stranger *Comment on: "Photosynthesis. Electronic structure of the oxygen-evolving complex in photosystem II prior to O-O bond formation".* **Science**, 2024. doi/10.1126/science.1254910#elettersSection.
8. Zournas, A., K. Mani and G.C. Dismukes, *Cyclic electron flow around photosystem II in silico: How it works and functions in vivo.* **Photosynthesis Research**, 2023. **156**(1): p. 129-145.
9. Zhang, Y., G. Ananyev, A. Matsuoka, G.C. Dismukes and P. Maliga, *Cyanobacterial photosystem II reaction center design in tobacco chloroplasts increases biomass in low light.* **Plant Physiol**., 2023. **191**(4): p. 2229-2244.
10. ten Veldhuis, M.-C., G. Ananyev and G.C. Dismukes, *Adaptation of plant photosynthetic metabolism to extreme CO2 levels in Yellowstone: living on the edge.* **Research Square**, 2023, https://www.researchsquare.com/article/rs-3235087/v1.
11. Li, Y., A.B. Laursen, M. Dhiman and G.C. Dismukes, *Remodelling the chlor-alkali electrolysis process to co-generate useful reduction products from CO2.* **Journal of Materials Chemistry** A, 2023. **11**(40): p. 21694-21701.
12. Gu, H., F. Zhang, S. Hwang, A.B. Laursen, X. Liu, S.Y. Park, M. Yang, R.C. Bramante, H. Hijazi, L. Kasaei, L.C. Feldman, Y.-W. Yeh, P.E. Batson, B.W. Larson, M. Li, Y. Li, K. Wyatt, J.L. Young, K. Teeluck, K. Zhu, E. Garfunkel and G.C. Dismukes, *Interfacial Connections between Organic Perovskite/n+ Silicon/Catalyst that Allow Integration of Solar Cell and Catalyst for Hydrogen Evolution from Water.* **Advanced Functional Materials**, 2023. **33**(25): p. 2301196.

13. Gates, C., G. Ananyev, S. Roy-Chowdhury, P. Fromme and G.C. Dismukes, *Regulation of light energy conversion between linear and cyclic electron flow within photosystem II controlled by the plastoquinone/quinol redox poise.* **Photosynth Res**, 2023. **156**(1): p. 113-128.
14. Dhiman, M., Y. Chen, Y. Li, A.B. Laursen, K.U.D. Calvinho, T.G. Deutsch and G.C. Dismukes, *Enabling technologies for the continuous electrically driven conversion of CO2 and water to multi-carbon products at high current densities.* **Journal of Materials Chemistry** A, 2023. **11**(2): p. 717-725.
15. Colin Gates, Jonah M. Williams, Gennady Ananyev, G. Charles Dismukes, *How chloride functions to enable proton conduction in photosynthetic water oxidation: Time-resolved kinetics of intermediates (S-states) in vivo and bromide substitution,* **BBA - Bioenergetics,** 2023.1864 (4), doi.org/10.1016/j.bbabio.2023.148998.

Invited and Contributed Presentations:

March 2024 CSNY Spring Symposium, *March 13,* New Jersey Institute of Technology, Newark, NJ.
- Ethylene Glycol Production on Transition Metal Phosphides from CO_2 by Electrolysis: A Carbon Negative Path to Sustainable Plastics
- Transition Metal Pnictides: Bioinspired Electrocatalysts for Converting CO_2 to Multi-carbon Products from Scratch
- Electrocatalytic CO_2 Reduction on Single Crystal NiP_2 Facets: Surface Intermediates and Mechanism Revealed

April 2024, Life Sciences Initiative Competition, Rutgers University, NJ.
Improving photosynthesis under climate stress by multigene bioengineering

April 2024, Eastern Regional Photosyn Conf. Woods Hole, MA.
- "Direct Reductive Titrationsof PSIIX-WOC to Free Mn^{II} Reveals the Lowest Redox State is S_{-3}"
- "Increasing biomass production via mutagenesis of Pyruvate-Ferredoxin Oxidoreductase (PFOR) and PEP Carboxylase (PPC): Consequences on flux through the PET Chain of a model cyanobacterium"

May 2024, Grossman Innovation Prize Competition, Rutgers University. NJ.
Plastics Made from Scratch: Carbon-Negative Manufacturing from Waste CO_2

June 2024, APS2 North American Photosynthesis Conference, Atlanta GA, Jun 2-6.
"70 Years since Calvin-Benson: Where are the bottlenecks? Which phototrophs can sprint? Any marathoners?"

August 2024 Gordon Research Conference: C1 Metabolism, 11-16 August in Waterville Valley, NH. "Manipulating Microbial Metabolism for More Biomass and BioSolarH_2: What Nature Teaches Us to Do and to Avoid"

Sept 2024, Waksman Institute of Microbiology Retreat, Rutgers University, NJ.
"Investigating the role of Pyruvate-Ferredoxin Oxidoreductase (PFOR) in regulating photosynthetic carbon flux and cell growth in the cyanobacteria *Synechococcus elongatus* PCC. 7002"

May 2023, Gordon Research Conference, CO2 Assimilation in Plants from Genome to Biome, Ciocca, Italy:
- Direct Measurement of CO_2 Carboxylation Kinetics across the Photosynthetic Tree of Life: Finding the Chokepoints and Validation by Microkinetic Modelling
- Investigating the impact of elevated CO_2 on photosynthetic metabolism from the long-term adaption of plants to naturally high CO_2 sources in the environment: Yellowstone NP

June 2023, American Chemical Society National Meeting, Los Angeles, CA. *Green Chemistry & Engineering Symposium*, Long Beach, CA. "Chemicals Made from Scratch: A Carbon-Negative, Renewably Powered Future without Biofuels"

April 2023, Eastern Regional Photosynthesis Conference, Woods Hole, MA. "How plants adapt to extreme environmental CO_2 levels: What Yellowstone can teach us."

Feb 2023, Dept of Chemistry, University Richmond, VA; “Chemicals Made from Scratch: A Carbon-Negative, Renewably Powered Future without Biofuels”