Proton-Coupled Electron Transfer: The Engine of Energy Conversion and Storage

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ABSTRACT: Proton-coupled electron transfer (PCET) underpins energy conversion in chemistry and biology. Four energy systems are described whose discoveries are based on PCET: the water splitting chemistry of the Artificial Leaf, the carbon fixation chemistry of the Bionic Leaf-C, the nitrogen fixation chemistry of the Bionic Leaf-N and the Coordination Chemistry Flow Battery (CCFB). Whereas the Artificial Leaf, Bionic Leaf-C, and Bionic Leaf-N require strong coupling between electron and proton to reduce energetic barriers to enable high energy efficiencies, the CCFB requires complete decoupling of the electron and proton so as to avoid parasitic energy-wasting reactions. The proper design of PCET in these systems facilitates their implementation in the areas of (i) centralized large scale grid storage of electricity and (ii) decentralized energy storage/conversion using only sunlight, air and any water source to produce fuel and food within a sustainable cycle for the biogenic elements of C, N and P.

INTRODUCTION

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Chemical and biological energy conversions are rooted in the coupling of electrons and protons. Coupling between the electron and proton is difficult because, unlike electrons, which can tunnel over long distances, the 2000-fold more massive proton can only tunnel over very short distances. Despite this inherent quantum mechanical difference between the two particles, they must both tunnel together for their coupling.

Proton-coupled electron transfer (PCET) has largely been treated as a thermodynamic issue dating back to Pourbaix's classification of the pH dependence of redox potentials, culminating in the construction of the Pourbaix diagram,¹ which plots the Nernstian potential as a function of the proton concentration. In biology, the electron was connected to the proton by Peter Mitchell with his description of the chemiosmotic principle² where the energy released from an electron transfer network is translated into a chemical transmembrane potential of a proton gradient.

The kinetics facet of PCET was originally inferred indirectly from kinetic isotope effects (KIEs), as pioneered by Westheimer's examination of chemical and biochemical transformations.³ Subsequently, the approach to utilizing KIEs to offer insight into a variety of reaction mechanisms was adopted, most prominently by Meyer and co-workers in their work to elucidate small molecule activation reactions.⁴ Ironically it was Westheimer who contextualized the difference between the indirect determination of PCET mechanism by KIE measurements versus direct kinetics measurements as follows.⁵ Imagine a plate of food (reactant) and then a plate of the final result of that processed food (product). Would you guess that there was a human in between those two plates? The point here is that the conversion of reactant to product typically involves a complicated cascade of events (e.g., equilibria, intermediates that are often not identified). Relying on KIEs to inform on PCET kinetics and mechanism assumes a rate-determining PCET event that does not have to be deconvolved from a medley of reaction events. We were able to isolate PCET and directly measure kinetics for the first time by creating supramolecular donor-acceptor complexes incorporating proton hopping pathways (Figure 1A).⁶ The PCET coupling enters because the rate of the electron transfer depends on the position of the proton within the interface. The design of symmetric proton interfaces gave way to asymmetric interfaces^{7,8} where the proton position could be evaluated spectroscopically.^{9,10} These experimental kinetics measurements stimulated our concurrent development of the first complete theoretical framework for PCET.¹¹ In the initial formulation of a PCET framework,¹² the electron and the proton were described in terms of four diabatic states (e⁻ and H⁺ on a donor, e⁻ and H⁺ on acceptor, and e⁻ on donor/ H^+ on acceptor and vice versa), as accommodated by a "square scheme" for PCET (Figure 1B).¹³ PCET involves a given solvent fluctuation to produce a state with a significant probability for the electron and proton to transfer together. The electron and the proton are treated on the same footing in a 2D tunneling space of Figure 1B, where r_e and r_n are the positions of the electron and proton, respectively. Owing to the mass difference between the electron and proton, the proton does not move on the time scale of the electron (i.e., Born-Oppenheimer principle), but there is an optimal position that the proton assumes to allow for the electron to tunnel, giving rise to the zigzag path in the 2D tunneling space expressed in Figure 2C; this tunneling path is parametric on the solvent.^{14,15} This

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Figure 1. Proton coupled electron transfer experiment and theory. (A) Donor–acceptor supramolecular assemblies that permit the direct measurement of PCET kinetics, which is initiated upon light excitation. The electron transfer rate depends on the position of the proton within a hydrogen bonded interface. (B) The path for PCET tunneling between the initial and final states for the electron (I,F) and proton (i,f), and r_e and r_p are the positions of the electron and proton, respectively. Wavy arrow denotes electron tunneling when the proton assumes a position within the interface to symmetrize the potential energy surface. The path is parametric on the solvent coordinate. (C) Design of the hangman catalyst construct where a proton is positioned in the secondary coordination sphere to enable its coupling to electron transfer at the metal center (M) to facilitate small molecule (X) activation.

theoretical framework of the four diabatic states of PCET has been subsequently expanded within a multistate continuum model in which mixed electronic/proton vibrational free energy surfaces are obtained as functions of two collective solvent coordinates corresponding to ET and PT.^{16,17} The net result from these experimental and theoretical studies is that, for strong coupling to occur, electron transfer must be coupled to short proton hops.

Quantitative and conceptual frameworks have emerged from these fundamental studies in PCET that are now informing diverse approaches in chemical and biological sciences. Notably, PCET plays a central role in radical enzymology¹⁸ and attendant studies in biophysics and biomimetic systems,^{19–21} electrochemistry²² and photochemistry,²³ as well as bond activation reactions.^{24–26} For most energy applications, the coupling between electron and proton must be strong so that energetic barriers may be reduced and thus high energy efficiencies are achieved. However, not all energy applications require tight coupling. Below are four energy applications and technologies



Figure 2. Coordination Chemistry Flow Battery for aqueous electrical storage. (A) Potential landscape for H_2 generation when the electron and proton are coupled vs when the electron is uncoupled from the proton and reduction occurs by outer-sphere electron transfer via H. (B) Coordination Chemistry Flow Battery where the ligands encapsulating a Ti³⁺ negolyte enforces H⁺ reduction by outer-sphere electron transfer, leading to the ability to store electrons at a high potential in aqueous solution.

that have resulted from controlling PCET. The discovery of the Coordination Chemistry Flow Battery (CCFB) requires the complete decoupling of the electron and proton so as to avoid the parasitic energy-wasting hydrogen evolution reaction. Conversely, strong coupling between the proton and electron underpins the water splitting chemistry of the Artificial Leaf, the carbon fixation chemistry of the Bionic Leaf-C and nitrogen fixation chemistry of the Bionic Leaf-N. The proper design of PCET in these systems facilitates their implementation in the areas of the centralized grid storage of solar electricity and decentralized energy storage/conversion with the use of only sunlight, air and any water source to produce fuel and food.

COORDINATION CHEMISTRY FLOW BATTERY FOR LARGE-SCALE GRID STORAGE

A flow battery is a solution-based battery where the potential for the electricity-to-chemical electrolytic redox couple (charge) is generated with a renewable energy input and the chemical-toelectricity galvanic redox couple (discharge) is then collected upon flowing solution over a current collecting cell-stack.^{27,28} The redox active electrolytes in which oxidizing and reducing equivalents are stored (posolyte and negolyte, respectively) are contained in separate external tanks. Unlike conventional batteries (e.g., Li-ion battery), energy and power density are decoupled in a flow battery and hence may be independently scaled. The energy density is determined by the amount of redox electrolytes (concentrations and sizes of tanks) whereas the power density is determined by the nature of current collection (flow rate and size of the current collecting cell-stack). The decoupling of energy density from power density is particularly attractive to meet the changing demand of electricity on the grid and thus the flow battery is a preferred method of renewable energy storge for power companies,²⁹ and is additionally attractive owing to their inherent safety, stability, long cycle lifetimes and the ability to rely on the grid for regeneration. Indeed, the home solar panel provides a source of regeneration and thus the need for incentives for solar power installation is diminished owing to the ability of the power company to absorb installation costs in the consumer's buy back cost of electricity.

Voltage is a singular parameter that directly relates to cost, and hence viability, of a given flow battery technology. Since power is directly proportional to voltage, a higher voltage translates directly into a lower cost for the membrane-electrode(stack)assembly. The ability to attain high voltages in water is challenged by the thermodynamic potential of water splitting to generate oxygen and hydrogen at 1.23 V vs NHE. Oxygen generation is kinetically complex, involving a 4e^{-/}4H⁺ PCET reaction accompanied by O-O bond formation, and thus may easily be circumvented in the design of the posolyte. Conversely, hydrogen generation is problematic to the design of the negolyte as it is a facile $2e^{-}/2H^{+}$ PCET reaction that occurs at low overpotentials. Consequently, to avoid parasitic hydrogen generation at high voltages, many fundamental science studies have examined redox couples in nonaqueous solution. However, the most cursory technoeconomic analysis shows that the cost of the large volumes of nonaqueous solvent needed for grid storage makes a nonaqueous flow battery untenable.^{30,31} The question then becomes-can high voltages be achieved in aqueous solution?—or from the perspective of PCET—can the electron be decoupled from the proton? If proton reduction proceeds by sequential one-electron steps that are completely uncoupled, then H₂ generation from water confronts the large energetic barrier imposed by the H- intermediate, as schematically illustrated in Figure 2A. On the NHE reference scale, the first reduction of an uncoupled electron and proton proceeds with an uphill potential of 2.3 V to produce $\hat{H_{\cdot}}$;^{32,33} the addition of a second electron and proton then proceeds with a downhill potential of 2.3 V. Thus, despite an overall thermodynamic potential of 0 V for the $2e^{-}/2H^{+}$ coupled reaction, a 2.3 V energy barrier is confronted if the protons are not coupled to the twoelectron process.

The large energetic barrier shown in Figure 2A for H_2 generation may be realized by designing a negolyte that can only react with the proton by a Marcus outer-sphere electron transfer. Redox couples with d-electron counts of d^0/d^1 , $d^3/$ d^4 (high spin) and d^6 (low spin)/ d^7 (low spin) are particularly attractive, as they give rise to large negative reduction potentials in a (pseudo)octahedral ligand field. Accordingly, the Coordination Chemistry Flow Battery (CCFB) was developed in which a Ti³⁺ ion was coordinated by a chelating and bulky ligand.³⁴ The bulky ligand hinders association of water and protons to the metal center, and thus restricts electron transfer exclusively to an outer-sphere mechanism. Accordingly, the CCFB operates at a 1.70 V while averting hydrogen production (Figure 2B). The design of the CCFB is in contrast to flow batteries using typical coordination compounds (such as the vanadium flow battery) and organic electrolytes where water molecules or protons are coordinated to inorganic or organic redox center; in these instances, cell voltages are much smaller to avoid hydrogen generation by PCET.³⁵ Additionally, anionic

ligands of the CCFB allow the posolyte and negolyte to be highly negatively charged, thus resulting in increased solubility and relaxed constraints on the membrane that prevents crossover of the anolyte and posolyte. As a result of these benefits, the CCFB has been successfully commercialized for large-scale grid storage.³⁶ The CCFB concept is being advanced with the continued design of increased potentials for aqueous redox couples,³⁷ which directly results in increased power density. An important frontier is the development of CCFBs with multi-electron couples in aqueous solution to allow for increased energy density.

ARTIFICIAL LEAF: SOLAR WATER SPLITTING WITH NO WIRING

The strong coupling between proton and electron that is required to minimize reaction barriers of small molecule activation was captured with the creation of "hangman" catalysts. The hangman catalyst places a proton transfer relay in the secondary coordination sphere of a redox active metal platform at which small molecules bind (Figure 1C). The initial hangman complex featured an iron porphyrin (PFe) with water molecule bound between the PFe(III)OH redox center and a carboxylic acid on a xanthene backbone to form a structurally well-defined proton transfer network that is reminiscent to those found in heme proteins.³⁸ Accordingly, PFe hangman porphyrins were shown to support catalase-like and cytochrome P450-like small molecule transformations.³⁹⁻⁴³ Subsequent hangman catalysts promoted a variety of reductive small molecule activation reactions operating by PCET⁴⁴⁻⁴⁷ including the hydrogen evolution reaction (HER), $^{48-52}$ oxygen reduction reaction (ORR),⁵³⁻⁵⁷ and carbon dioxide reduction reaction $(CO_2 RR)$. ^{58,59} The secondary sphere coordination strategy has subsequently been generalized to a variety of metal complexes,⁶⁰ especially for the purposes of promoting HER.^{61–71} With regard to the oxidative PCET transformation of water splitting, catalyst stability is paramount. Here again, a secondary coordination sphere is beneficial to managing the concomitant release of 4H⁺ and $4e^-$ upon the generation of O_2 from H_2O . For this transformation, corroles provide a privileged alternative to porphyrins, as they possess a trianionic ligating core and thus are able to stabilize metals in high formal oxidation states, which is desired for catalytic oxidations.^{72,73} A molecular system may be stabilized by the heroic replacement of all the C-H bonds around the corrole periphery with C-F bonds, and the meso positions of the corrole ring may been covered by pentafluorophenyl substituents to result in a stable OER operation at a noteworthy overpotential and turnover frequency.⁷⁴ Other synthetic strategies may also be explored for the design of stable molecular catalysts under the harsh oxidative conditions of OER,⁷⁵ but all are synthetically intensive.

The arduous synthetic challenges required to realize stable molecular catalysts have led to the discovery of all inorganic OER catalysts.^{76–78} Phosphate (P_i) and borate (B_i) oxoanions facilitate the dimensional reduction of extended metal oxides by capping cluster growth to give rise to metalate oxygen evolving catalysts (M-OECs) that exhibit high OER activity (Figure 3A). The all-inorganic cobalt metalate cluster CoP_i^{79} is a member of a palette of M-OEC catalysts,^{77,78,80,81} including Mn^{82,83} and Ni⁸⁴ metalate cluster congeners and alloys.^{85–90} The M-OECs range from 10 to 50 metal centers as deduced from X-ray pair distribution function (PDF) analysis of heterogeneous films.^{91–94} The molecular nature of the M-OECs has allowed the OER mechanism of catalysis to be defined at a molecular and



Figure 3. Self-healing OER catalysts. (A) Chemical structures of the extended solid LiCoO₂, and the molecular cobaltate cluster Co-OEC (blue, red, bronze and gray spheres denote Co, O, Li and H atoms, respectively). The Co-OEC is a dimensionally reduced molecular fragment of the extended LiCoO₂ structure and results from capping the edges of the cluster with phosphate (P_i) or borate (B_i) to furnish CoP_i and CoB_i, respectively. (B) Self-healing is achieved if the potential for self-assembly is less than the potential for water spitting catalysis. Blue spheres represent the Co-OEC catalyst shown in (A).

atomistic level. Isotopic measurements using differential electrochemical mass spectrometry (DEMS)⁹⁵ together with electrokinetic^{96–98} and spectroscopic⁹⁹ studies establish that O–O bond formation occurs by PCET at the edges of the metalate clusters. The conductivity and current–voltage characteristics of the film are consistent with a model in which the PCET of OER is managed by coupling the transport of electrons that delocalize within the metalate cluster to transport of protons/ions at cluster edge sites.^{100,101}

An important property of the M-OEC catalysts is their "self-healing" nature, 102-104 thus allowing them to operate in neutral and natural water sources.^{105,106} In the oxygen evolution reaction (OER), the four-electron oxidation of water to oxygen is accompanied by the release of four protons, which are neutralized in strong base. In neutral and natural water, however, the concentration of hydroxide is small and the strongest base in water is the oxide itself. Metal oxides are basic, as indicated by the Lux classification of bases,¹⁰⁷ and they readily react with acid. Excluding critical elements (e.g., Ru, Ir), reaction of acid with the oxides of earth-abundant metals (e.g., first row transition metals) thus leads to corrosion by the leaching of metal ions and dissolution of the oxide. The self-healing Co, Mn and Ni metalate cluster catalysts balance their self-assembly in the presence of phosphate (P_i) or borate (B_i) anions with OER catalysis such that the equilibrium for self-assembly (i.e., catalyst regeneration) lies energetically within that of OER catalysis (Figure 3B). Owing to these energetics, the self-healing catalyst is distinguished by turnover number that is infinite; i.e., as long as the catalyst is operating, it is able to heal itself. Because these self-healing catalysts continually renew themselves during OER, they can operate in neutral and natural water.

Self-healing enables OER catalysts to be interfaced with materials under noncorrosive conditions. Simple transparent conducting oxides (TCOs) such as indium- and fluorinated- tin

oxides provide an ohmic interface between catalyst and silicon and at the same time protect Si from oxidation by O_2 generated from OER.¹⁰⁸ Because the metalate cluster catalysts allow OER to be performed under benign conditions, the TCOs are stable, unlike the case if they were to be subject to acidic or basic conditions. Additionally, nonprecious metals are stable under benign HER conditions and therefore may be used in place of Pt to produce hydrogen. For instance, dealloying a NiMoZn cathode furnishes a high surface area material that can support HER under neutral conditions at high current densities as does a cobalt phosphide Co-P(6%) alloy.¹⁰⁹

The ability to easily interface water splitting catalysts to Si allowed for the creation of the Artificial Leaf,¹¹⁰ which is the first stand alone, wireless water splitting device (Figure 4). The



Figure 4. Artificial Leaf. The p-side of a triple junction amorphous Si solar cell is coated with a transparent conducting oxide (TCO) protective layer and a Co-OEC OER catalyst. The n-side is coated with a Co-P HER catalyst. Similar to the Kok cycle in Photosystem II, the absorption of four photons to produce oxidizing and reducing equivalents are translated into energy storge via the water splitting reaction.

Artificial Leaf comprises a silicon wafer that is engineered to absorb the entire solar spectrum. The top layer of the wafer is amorphous Si (a-Si). The strained lattice of a-Si opens the band gap of the semiconductor, resulting in an absorption spectrum in the blue spectral region with a maximum of ~400 nm. Doping a-Si with its larger Group 14 counterpart, Ge, allows the lattice to be relaxed and the band gap decreased and thus the absorption maximum to be controlled with the level of doping. When sunlight impinges on the silicon wafer of the Artificial Leaf through the Co-OEC/TCO layer, a wireless hole/electron current is created that is passed to the respective OER and HER catalyst coatings on the silicon wafer. As in the Kok cycle of natural photosynthesis,¹¹¹ after the accumulation of four units charge, one at a time, water is split to hydrogen and oxygen. When the Artificial Leaf is immersed in any water source and exposed to sunlight, hydrogen and oxygen bubble from each side of the wafer coatings at a rate that is commensurate with the solar flux impinging on the silicon. Owing to the low solubility of



Figure 5. Bionic Leaf-C. (A) The water splitting function of the photosynthetic membrane may be replaced with water splitting chemistry of the Artificial Leaf. (B) In a hybrid-inorganic-biological (HIB) system, Photosystem II and Photosystem I are effectively replaced with a hydrogenase, which allows the hydrogen produced from inorganic water splitting to be interfaced to a biological organism. In the Bionic Leaf-C, the hydrogen from water splitting powers cellular biosynthesis in carbon-fixing organisms to produce biomass or liquid fuels via metabolically engineered pathways. (Inset, lower right) Solar energy efficiencies for *C. necator*, under CO₂ (solid bar) and air (hatched bar), interfaced to hydrogen from water splitting performed with CoP₁ and Co-P driven by a photovoltaic device of 20% efficiency (biomass = *C. necator*, PHB = polyhydroxybutyrate, C₃ol = isopropanol and C₄ + C₅ols is a combination of isobutanol and isopentanol).

 O_2 and H_2 in water, the solar-to-fuels conversion process may be driven with the use of only a separator. Overall solar-to-fuels efficiencies (SFE) were observed to be as high as 4.7% (for a 7.7% solar cell) when Ohmic losses are minimized. Even further increases in SFE may be realized by engineering designs that minimize Ohmic resistances such as flow-cells and optimized of cell-geometries.^{112,113} Noting that the overall solar-to-fuels efficiency is a product of the overall efficiency for water splitting and solar cell efficiency, SFE(%) = $\varphi(SE) \cdot \varphi(WS)$, $\varphi(WS)$ is 60% and thus overall cell efficiencies (>10%) may be readily achieved with the use of PV materials with solar-to-electricity efficiencies $\varphi(SE) > 16\%$. The net result of these studies is that the Artificial Leaf duplicates the direct solar process of

photosynthesis—the splitting of water to hydrogen and oxygen using light from neutral water, at atmospheric pressure and room temperature. However, because the artificial system can absorb light and separate charge at efficiencies much greater than Photosystems II and I,¹¹⁴ its solar-to-fuels (hydrogen—oxygen) efficiencies are much greater than that achieved by the photosynthetic membrane for water splitting.

BIONIC LEAF-C: ARTIFICIAL PHOTOSYNTHESIS AT EFFICIENCIES GREATER THAN NATURAL PHOTOSYNTHESIS

Photosynthesis is masterful in managing PCET in view of the extraordinary number of protons and electrons that must be

accommodated to drive the fixation of CO_2 to biomass, represented here as $(CH_2O)_{n\nu}$

Sunlight +
$$nH_2O + nCO_2 \rightarrow (CH_2O)_n + nO_2$$
 (1)

For instance, the reduction of CO_2 to glucose is a $24e^- \mid 24H^+$ process. Such management of PCET is unparalleled in chemical CO₂ reduction systems. The HER is kinetically much easier to achieve versus the activation of the stable carbon-oxygen double bond of CO_2 . Thus, controlling PCET such that HER is suppressed relative to CO₂ reduction is a major challenge for chemical reduction strategies,¹¹⁵ even for simple catalytic chemical reactions such as CO_2 to CO, which only involves only $2e^-$ and $2H^+$.^{116,117} Indeed, selectivity for CO in this reaction reduces to an issue of decreasing the efficacy of H_2 generation relative to a constant potential dependence of CO generation.^{115,118} Nature overcomes the challenge confronting chemical systems by separating H^+/e^- generation from CO_2 reduction. The proton and electron equivalents are obtained from the light reaction of photosynthesis—the splitting of water (Figure 5A). The oxygen half-reaction of water splitting is accomplished at Photosystem II. The electron and proton equivalency released from that half reaction are transported along the photosynthetic membrane to Photosystem I where they are combined to produce Nature's form of hydrogen, NADPH/H⁺, and ATP is generated from the resulting proton gradient through F-ATPase.¹¹⁹ NADPH and ATP are then appropriated as a hydrogen (hydride/proton) source and energy supply, respectively, in driving the separate dark reactions that fix CO_2 by carboxylation in the so-called Calvin-Benson (CB) cycle:

light: Sunlight +
$$nH_2O \rightarrow nH_2(2H^+/2e^-) + \frac{n}{2}O_2$$

(2)

dark: $nH_2(2H^+/2e^-) + nCO_2 \rightarrow (CH_2O)_n + \frac{n}{2}O_2$

(3)

Once H_2 (NADPH/H⁺) is produced, light is not needed, as the reduction of CO_2 to nearly any biomass/fuels product is thermoneutral to exergonic¹²⁰ and thus may be performed in the dark. Nonetheless, most photoelectrochemical approaches combine the light and dark reactions in one step, i.e., water oxidation at the anode and CO₂ reduction at the cathode. Conversely, the spatial separation of water splitting to generate reducing proton and electron equivalents from the CO₂ reduction machinery permits Nature to manage the multiple electrons and protons needed for CO₂ fixation. This separation of the solar (water splitting) and CO₂ fixation (dark reaction) is a key lesson offered by Nature in designing an artificial photosynthesis, together with other key advantages inherent to biology including carbon-carbon bond formation to furnish products with high selectivity within a narrow energetic window (most CO₂ reduction products to fuels/biomass are within a 200 mV exergonic window). Despite these advantages, solar light absorption and the energetics associated with the water splitting reaction in Photosystems II/I present a roadblock with regard to the overall efficiency of stored solar energy. Simple models predict that carbon fixation pathways, limited by enzyme concentrations and rates, can use only 3-18% of the absorbed light,^{121,122} and consequently the highest solar-to-biomass efficiencies offered by plant biomass are only $\sim 1\%$.¹¹ Conversely, the solar-to-electrical and solar-to-hydrogen efficiencies powered by photovoltaic materials integrated with

water splitting catalysts have increased significantly in recent years,¹¹³ far exceeding the efficiencies of Photosystems II/I. Consequently, a hybrid inorganic-biological (HIB) approach emerges as a viable artificial photosynthesis where photoelectrochemistry is used to produce the electron and proton donors from water splitting either directly in the form of H₂ or indirectly via small molecule organic or redox mediators.¹²³ The electron donor can then be used in tandem with CO_2 as a carbon source to feed lithoautotrophic microorganisms and produce biomass and fuels. With an HIB approach, the energy efficiency associated with producing the electron and proton equivalents with solar photovoltaic materials/catalysts overcomes the constraining energy efficiencies of Photosystems I/II while simultaneously exploiting the ability of biology to fix carbon in complex molecules with high selectivity.

Hydrogen is an especially effective donor for HIB systems because it can be translated via hydrogenases as a natural 2H⁺/ 2e⁻ source for carbon fixing cycles. Initial work on Pseudomonas hydrogenomonas established that autotrophs could survive in combination with water electrolysis,¹²⁴ and accordingly the H₂ produced from the catalysts of the Artificial Leaf either directly from a buried junction (as shown in Figure 4) or indirectly via photovoltaics is an effective nutrient source. In this hybrid approach, as illustrated in Figure 5A, the entire photosynthetic assembly for water splitting that produces O₂ and NADPH is replaced by inorganic solar water splitting. On this basis, the Bionic Leaf-C was created where the microorganism C. necator converts carbon dioxide from air, along with the hydrogen produced from the catalysts of the Artificial Leaf, into biomass and liquid fuels using the tools of synthetic biology.¹²⁵ Here, the only "food" source for the bioorganism to grow or make liquid fuels is hydrogen, which it metabolized to NADPH via hydrogenases (Figure 5B). The NADPH/H⁺ offers the reductant for the fixation of carbon dioxide from air, which has been established by ${}^{13}CO_2$ isotopic labeling studies. ¹²⁶ In the implementation of the Bionic Leaf-C, the interface between inorganic materials and biology must be properly designed to attain high energy efficiencies. Initial implementation of the hybrid system used a NiMoZn alloy for an HER catalyst.¹²⁷ The formation of H₂O₂ and other ROS from O₂ reduction at the cathode at low potentials between 1.8-2.3 V resulted in attenuated cell growth. High cell growth could only be achieved at 2.7–3.0 V, an applied potential at which hydrogen evolution outcompeted the formation of reactive oxygen species (ROS). However, such high overpotentials directly results in low overall energy efficiency thus necessitating a cathode that suppressed ROS, leading to the development of a cobalt–phosphorus alloy cathode (Co-P(6%)).¹⁰⁹ The Co–P cathode, which works synergistically with the self-healing CoP_i anode to result in negligible metal ion concentrations in solution, is highly active for H_2 production at neutral pH and applied voltages <2.0 V, thus furnishing high electricity-to-biomass yields, $\eta_{\rm ECE}$, shown in Figure 5B (inset). A solar-to-biomass yield of $\eta_{\text{SFE}} = \eta_{\text{PV}} \times \eta_{\text{ECE}} =$ 10.8% is achieved with a typical Si photovoltaic efficiency of $\eta_{\rm PV}$ = 20%. The $\eta_{\rm SFE}$ is an authentic efficiency, as $\eta_{\rm ECE}$ includes limitations arising from H₂ generation, H₂ solubility, and the energy efficiency associated with biomass maintenance and growth. Moreover, the $\eta_{\rm ECE}$ = 20% for the HIB system operating in air is only 2.7 times lower than η_{SFE} in pure CO₂, despite a CO_2 concentration difference between air and pure CO_2 of 2500. The high product yield obtained for the HIB system in air demonstrates the advantages offered by carbon-concentrating mechanisms (CCMs, carbonic anhydrases, CO₂/HCO₃⁻ trans-

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Figure 6. Bionic Leaf-N. (A) The Bionic-Leaf N combines H_2 from solar water splitting with CO_2 to produce polyhydroxybutyrate (PHB) and (B) then draws on the PHB as internal energy and hydrogen supply to power the nitrogen fixation cycle to produce ammonia and solid N biomass (ref 154). Once PHB is produced, a solar source is no longer needed, and the organism can be introduced into soil and perform fertilization. When grown in the presence of wastewater, the organism will also sequester P in the form of cyclic and linear polyphosphate (polyP) (ref 156). The process allows for the sustainable and distributed production of fertilizer from sunlight, atmospheric CO_2 and N_2 and wastewater.

porters and carboxysomes)¹²⁸ to alleviate mass transport limitations, absorb solubilized CO_2 and maintain high intracellular CO_2 concentrations. The Bionic Leaf-C produces biomass without the need for agricultural land and owing to high solar-to-biomass efficiencies greatly reduces the required land surface area, which for the HIB system is defined by the area of the photovoltaic device, as the biomass is grown in a dark reactor.

The Bionic Leaf-C may be extended to deliver longer-chain alcohols with metabolically engineered *C. necator*. The carbon flux within *C. necator* at the juncture of acetyl coenzyme A may be redirected along pathways that result in the synthesis of liquid alcohols.¹²⁹ Hydrogen driven biosynthesis ($E_{appl} = 2.0$ V) of engineered *C. necator* into isopropanol (C_3), isobutanol (C_4) and isopentanol (C_5) occurs at high η_{ECE} 's and thus high η_{SFE} 's, as summarized in Figure 5B (inset). Beyond fuels, the HIB approach has implications along two paths: (1) a general strategy for renewable chemical synthesis^{130–132} and (2) "fast biomass", i.e., biomass growth at energy efficiencies exceeding natural biomass, thus opening an interesting opportunity for carbon sequestration if the biomass were to be buried irreversibly.

The introduction of electrons and protons within a HIB framework may occur by other means than H₂. Small molecule organic mediators may serve as electron and proton sources but from the perspective of energy storage they must be made renewably at high energy efficiency. Alternatively, reducing equivalents may be supplied to the biological organism either directly from an electrode¹³³ or indirectly with reversible mediators¹³⁴ such as $Fe^{3+/2+135,136}$ or neutral red dye^{137,138} to carry electrons (and possibly protons in the case of neutral red¹³⁹) from the electrode to the cell. For direct electron transfer, a nanostructured electrode has typically been employed that is run at constant current.¹⁴⁰ To maintain that current, the applied voltage of a typical potentiostat will be driven to any voltage (and may be in excess of 10 V). Thus, the overall energy efficiency and, ultimately, $\eta_{\rm ECE}$, for these constant current-driven HIB systems may be extremely small.¹⁴¹ Moreover, at high applied potentials, there is a large overpotential for H₂ generation and if there are hydrogenases present in the organism, then the HIB system may indeed be using H_2 as the electron and proton carrier vs the nanostructured electrode. An authentic electrical connection with the interior of a cell may be established in "exoelectrogen" bacteria such as Shewanella and Geobacter, which use protein scaffolds to form a conducting contact between electrodes and extracellular electron transport chains.^{142–145} In combination with techniques of synthetic biology, these bacteria have been genetically engineered to produce organic fuels using reducing equivalents obtained directly from cathode surfaces.¹⁴⁶ Finally, the inorganic interface in HIB systems need not be an electrode. Nanoparticle semiconductors have been shown to deliver charge equivalents into enzymes,¹⁴⁷ and purportedly into bacterial cells for CO₂ fixation to acetate.¹⁴⁸ However, bacteria are opportunistic species, and it has been shown¹⁴⁹ for the latter that neither the semiconducting nanoparticle nor light are involved in CO₂ fixation. Instead, the bacteria uses cysteine present in the medium as the carbon source for acetate production.

BIONIC LEAF-N: A DISTRIBUTED HABER-BOSCH NITROGEN FIXING SYSTEM

The Bionic Leaf-C is a carbon fixing organism that sequesters CO_2 from air using CCMs. Nitrogen is another atmospheric gas that has enormous consequences to energy consumption and climate change. The industrial synthesis of ammonia results in CO₂ emissions that are greater than any other chemical-making reaction.¹⁵⁰ Depending on the fossil-fuel source (gas, naptha, oil, coal \rightarrow 1.6, 2.5, 3.0, and 3.8 ton CO₂ per ton NH₃, respectively) for hydrogen generation, the global average of CO₂ emitted per ton NH₃ produced is 2.87 tons,¹⁵¹ translating approximately to 1.2% of global anthropogenic CO_2 emissions¹⁵² and consuming 1.8% of global energy output.¹⁵⁰ These values are lower limits as the CO_2 -equivalent (CO_2e) emissions for the extraction and transport of fossil fuel feedstocks are not included nor is the CO₂e emission for fertilizer distribution. In addition to the high carbon balance and energy intensity, chemical fertilizers easily dissolve in surface runoff and groundwater, resulting in significant environmental impacts on air, water and a multitude of ecosystems.¹⁵³

Nitrogen is bioavailable to natural organisms operating the nitrogenase-catalyzed reduction of nitrogen to ammonia. Here again, biology manages a significant electron and proton budget in the PCET reduction of the kinetically inert N₂ molecule,

$$N_2 + 16ATP + 8H^+ + 8e^-$$

 $\rightarrow 2NH_3 + 16ADP + 16P_i + H_2$ (4)

Note that biological nitrogen fixation is typically admired for its ability to proceed at room temperature and pressure. However, it is seldom recognized that the biological reaction is run at significant overpotential. The free energy for reduction of N₂ by $3H_2$ to $2NH_3$ is exothermic, $\Delta G(298 \text{ K}) = -7.96 \text{ kcal mol}^{-1}$ at room temperature and pressure. The 16 ATP energy input per nitrogen molecule is 107.3 kcal mol $^{-1}$ ($\Delta G(ATP \rightarrow ADP + Pi) = -7.3 \text{ kcal mol}^{-1}$) with the formation of one molecule of H_2 at pH = 7 accounted for, or an equivalent voltage input for N₂ reduction in excess of 4.5 V. Accordingly, although there are a multitude of nitrogen fixing organisms, they all down-regulate nitrogen fixation as the overall PCET conversion (4) is essentially too exhausting for the microbe to maintain.

To overcome this roadblock of energy balance in nitrogen fixation, the three-step process summarized schematically in Figure 6 was developed for the autotrophic and nitrogen-fixing bacteria Xanthobacter autotrophicus (X.a.), which has parallel Cand N-fixing pathways and may be directly grown from hydrogen.¹⁵⁴ To this end, X.a. is able to combine hydrogen produced from the catalysts of the Artificial Leaf with CO₂ from air to produce polyhydroxybutyrate (PHB). The PHB biopolymer that is stored within the bacteria is a nascent source of intracellular energy (ATP) and hydrogen (NADPH/H⁺). With its own internal energy and hydrogen supply, down regulation of nitrogen fixation in X.a.-PHB is mitigated and nitrogen fixation occurs unencumbered as reflected in an acetylene assay, which reveals exceptionally high nitrogenase activity (turnover frequency of 1.9×10^4 s⁻¹ per bacterial cell and turnover number of ~9 × 10⁹ bacterial cell⁻¹).¹⁵⁴ When the NH₃ assimilation pathway within X.a. is disrupted with a glutamine synthetase inhibitor, direct production of extracellular NH₃ is observed; ¹⁵N isotope labeling experiments confirm that the generated NH_3 is from N_2 .

With solar light effectively stored in PHB as energy and as a source of protons and electrons for the PCET reaction 4, N_2 fixation may occur in the dark. Accordingly, *X.a.* may be introduced into soil where it is able to draw N_2 from air and convert PHB into the ATP and NADPH/H⁺ sources needed to perform nitrogen fixation from air, and in turn directly fertilize crops. Indeed, as shown in a field trial of lettuce and corn (Figure 7), *X.a.*-PHB (20% by cellular weight) functions as a living biofertilizer and may replace between 50–80% of chemical fertilizer while maintaining yield and quality.

The Bionic Leaf-N living biofertilizer results in significant reduction in the carbon budget. The growth of the crops shown in Figure 7 requires 130 lb N per acre. A 3.8 lb CO₂ emission per lb of N(urea)¹⁵⁵ translates to 197,600 lb of CO₂ released in the manufacturing of fertilizer for a 400-acre farm; in the case of nitrate, the CO₂ is 6.7 lb per lb N (ammonium nitrate)¹⁵⁵ and therefore 348,400 lbs of \overline{CO}_2 are released into the atmosphere. Thus, the replacement of 50% chemical fertilizer with the living biofertilizer in Figure 7 results in the mitigation of 98,800 lb of emitted CO₂ for the crops grown with urea and 174,000 lb of emitted CO₂ for the crops using ammonium nitrate as a fertilizer source. Additionally, the decomposition of PHB results in carbon sequestration into the soil (at 20% loading of PHB by weight, 0.4 lb CO₂e per lb on N), and thus the use of Bionic Leaf-N as a living biofertilizer is a carbon negative process. Additionally, it has been shown that *X.a.* is able to fix phosphorus from waste streams in the form of linear and cyclic polyphosphates.^{154,156} Thus, the use of Bionic Leaf-N as a living biofertilizer permits a cyclic and renewable rotation of the biogenic elements of C and N from air and P from wastewater, and thus beyond fertilization, has applications for land restoration.



Figure 7. Crop fertilization by Bionic Leaf-N. Lettuce and corn plants grown with (A) 100% synthetic fertilizer urea-ammonium nitrate (UAN) and (B) with 50% UAN replaced by the organic biofertlizer of Bionic-Leaf N.

CONCLUDING REMARKS

The efficiencies of energy conversion and storage at an atomistic level depend on how electrons and protons are coupled. For most applications, including the conversion of small molecules of energy consequence, strong coupling is required to ensure a low energy barrier for the transformation, and hence attain high energy conversion efficiencies. Owing to the very disparate length scales for electron and proton tunneling, catalysts, whether they be homogeneous or heterogeneous, must be designed to accommodate short proton hopping pathways coupled to longer electron transfer pathways. However, for some applications, "reversed engineered" PCET pathways are needed to engender high energy barriers to prevent parasitic energy wasting reactions. This is the case for the design of flow batteries, which demand an aqueous environment and high voltage (i.e., reduced cell stack cost as power = current \cdot voltage) for technological feasibility. The combination of aqueous solution and high voltage biases hydrogen production, which is a parasitic reaction that degrades both power and energy efficiency of the flow battery. By decoupling the electron and proton, a large kinetic barrier imposes a significant penalty on hydrogen generation.

The other challenge beyond coupling in PCET transformations is the management of significant electron and proton inventories. The water splitting reaction, which is kinetically challenging, involves only a 4 electron/proton equivalency. For $\rm CO_2$ reduction to C5 to C8 fuels require 30–50 electron/proton equivalencies. Chemical catalysis approaches confront the significant challenge of having to manage such large proton and electron inventories while avoiding the more facile PCET reaction of hydrogen production. Biology has evolved to manage such large proton and electron inventories while circumventing hydrogen generation, thus providing an imperative for HIB systems where the proton and electron equivalents are provided by solar water splitting of inorganic catalyst/photoabsorber and passed on to a biological organism, which manages their

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Notes

The author declares the following competing financial interest(s): The author was Founder of Sun Catalytix Corporation, which developed the Coordination Chemistry Flow Battery (CCFB). The assets of Sun Catalytix were acquired by Lockheed Martin, and the CCFB is currently being commercialized under GridStar Flow. Sun Catalytix Corporation is defunct, and the author has no financial interests in the CCFB or Lockheed Martin Corporation. The author is Founder and has financial interests in Kula Bio, which is currently commercializing a living biofertilizer offered by the approach of the Bionic Leaf-N.

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combination with CO_2 to produce biomass and liquid fuels. In this carbon neutral, artificial photosynthetic approach, the inorganic system replaces the solar energy expending processes of natural photosynthesis thus engendering energy storage efficiencies for the artificial system that far exceed that of the natural system. Extending the HIB approach to carbon- and nitrogen-fixing organisms, a carbon negative organic biofertilization may be achieved that results in significant carbon emission savings. The Bionic Leaf-C and Bionic Leaf-N rely on only sunlight, air and wastewater to create distributed and renewable systems to produce fuel and food within a sustainable cycle for the biogenic elements of C, N and P. These discoveries are particularly useful to the poor of the world,¹⁵⁷ where large infrastructures for fuel and food production are not tenable. Although the Artificial Leaf, Bionic Leaf-C and Bionic Leaf-N are decentralized energy storage/conversion systems as opposed to the centralized energy storage system of a flow battery, all require proper coupling and management of electrons and protons to accelerate discovery to technology so that energy efficiencies are maximized and engineering attendant to the production of undesirable products for a given application is minimized.

Beyond energy conversion and storage, PCET is at the frontier of placing society on a path to restructuring a chemical manufacturing infrastructure from one based on carbon to one based on renewable energy. Photo- and electro-redox catalysis have emerged as powerful strategies to perform organic synthesis under mild conditions by taking advantage of photons or electrons to generate highly reactive intermediates by PCET that are otherwise difficult to access with traditional methods.^{158–165} The precipitous drop in cost of Si has made solar-generated energy costs competitive with traditional energy generation in many markets,^{166,167} opening the way for solar powered electro- and photo-catalytic redox processes. However, the energy efficiency of photo- and electro-redox processes must be considered,^{168,169} as it directly contributes to the capex cost of renewable energy generation. To date, most photoredox processes occur with high energy light and low quantum yields or, in the case of electroredox processes, high overpotentials and low faradaic efficiencies. The realization of higher efficiencies relies on averting nonproductive pathways of PCET intermediates, 170,171 providing an imperative for precisely defining reaction intermediates and mechanisms. Complementing traditional chemical synthesis, the powerful tool of synthetic biology allows the HIB approach to be generalized to a renewable chemical synthesis platform, depending on the biomachinery to which water-splitting is coupled.¹³² High throughput will demand high mass fluxes of electron/proton reducing equivalents to be matched to that of the oxidant to achieve production rates needed for manufacturing. Whether abiotic or biotic in approach, PCET is a crucial cog in the engine of fundamental science that will drive the transition to global energy and chemical infrastructures powered by the sun.

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