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Biological-inorganic hybrid systems as a generalized platform for chemical production

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An expanding renewable energy market to supplant petrochemicals has motivated synthesis technologies that use renewable feedstocks, such as CO_2. Hybrid biological-inorganic systems provide a sustainable, efficient, versatile, and inexpensive chemical synthesis platform. These systems comprise biocompatible electrodes that transduce electrical energy either directly or indirectly into bioavailable energy, such as H_2 and NAD(P)H. In combination, specific bacteria use these energetic reducing equivalents to fix CO_2 into multi-carbon organic compounds. As hybrid biological-inorganic technologies have developed, the focus has shifted from phenomenological and proof-of-concept discovery towards enhanced energy efficiency, production rate, product scope, and industrial robustness. In this review, we highlight the progress and the state-of-the-art of this field and describe the advantages and challenges involved in designing bio- and chemo- compatible systems.

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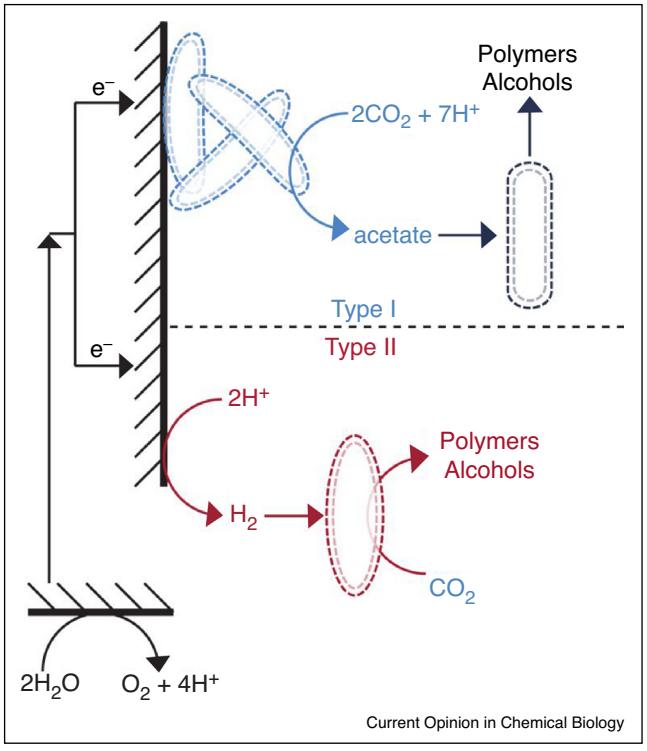
Introduction

Hybrid biological-inorganic (HBI) systems couple microorganisms with chemical catalysts to derive value-added products. These devices bypass many of the current problems facing traditional biomass-derived biofuels and biorefinery technologies through the use of abundant alternative feedstocks such as CO_2 and H_2O [1–3]. HBI systems overcome many of the challenges facing purely chemical approaches to CO_2 catalysis, such as the need to use concentrated CO_2 sources, poor selectivity between organic compounds over a narrow thermodynamic range, and the difficulty of performing multi-electron reductions for carbon-carbon bond formation [4]. The development of HBI devices could promote a synergistic relationship with sustainable energy generation leading to widespread adoption of both technologies. Here we describe the current progress in optimizing the performance of HBI systems, focusing on the improvements in biocompatibility of the reactors and genetic engineering of the microorganisms. We use a proposed set of standard metrics to benchmark systems against each other, setting standard reporting guidelines as in the photovoltaic field. We address the current state and future prospects of biological optimization and metabolic engineering to increase the efficiency and yields of HBI systems.

With the growing scope and ease of engineering microbes, there is increasing interest in their application to alternative energy technologies, particularly microbes that use CO_2 as their sole carbon source. Microbial CO_2 reduction in the context of HBI systems can be sorted into two main categories: Type I, where electrons are directly transferred to immobilized acetogenic bacteria [5–7], and Type II, in which electrons are indirectly transferred to organisms via electrochemical H_2 evolution from water splitting followed by microbial H_2 oxidation that is coupled to CO_2 reduction (Figure 1). Owing to a diverse group of autotrophic bacteria that use CO_2 as their sole carbon source with H_2 as a reducing equivalent, chemical synthesis from energy, air, and water is becoming a viable technology [8,9,10••]. The major challenges that dominate the design of Type I HBI devices involve promoting the intimate association of electrotrophs and high surface area electrodes [11•,12]. The mechanism of the difficult process of electron transfer from electrode to bacterium has only begun to be characterized [6], and the process of rationally designing Type I electrodes has remained empirical and challenging. The major challenge for Type II HBI devices is to maintain efficient H_2 evolution in the absence of toxic byproducts [9,10••]. Further advances in operational considerations, such as reactor design [13••,14••], have pushed this field closer towards practical implementation.

In addition to tolerating intermittent energy supply, devices that grow carbon-fixing bacteria contribute a reliable mechanism for fixing CO_2—annual anthropogenic production of which reaches 32 billion metric tons

Figure 1



Schematic overview of HBI systems. Two types of hybrids have emerged. Both couple water oxidation to CO_2 reduction. Type I systems establish a presumably direct interface through a microbial biofilm to produce acetate. This acetate requires downstream upgrading by a secondary fermentative microorganism to synthesize value-added chemical products. Type II systems initially electrochemically generate H_2. This H_2 is fed to autotrophic bacteria for CO_2 reduction directly to value-added chemicals, typically polymers and alcohols.

[15]. The use of H_2 and CO_2 to drive the metabolism of autotrophic microbes introduces the ability to enhance CO_2 reduction and circumvent the need for expensive feedstocks. In addition to higher cost, plant-derived carbon sources for heterotrophic growth (e.g., sugars, carbohydrates) intrinsically cap overall efficiency of the system to that of the plant solar-biomass conversion efficiency (approximately 1%) [16]. Powering microbes more directly with renewable energy (silicon-based photovoltaics: ~18% energy efficiency) dramatically raises the energetic ceiling for CO_2 reduction. However, biological synthesis of high-value products is currently one of the few economically feasible applications [17–20]. With further optimization of the biological-inorganic interface, HBI devices have the potential to compete with large-scale chemical production as well as a variety of fossil fuel derivatives.

Advances in genetic engineering have diversified the variety of microbes and products that can be synthesized by hybrid technologies. Such innovations enable a comprehensive path to replace petrochemical and biomass derived routes to chemical synthesis. Here, we highlight the opportunity for further work on the biological side of these hybrids to industrialize their native metabolisms and improve their chemocompatibility through genetic engineering approaches.

Enhancing biocompatibility: advances and challenges for high-rate and high-efficiency CO_2 reduction

Comparison between Type I and Type II HBI systems has been difficult due to different benchmarking conventions. For relevance to industrial scalability, we extracted the volumetric CO_2 reduction rate (g CO_2 L^{-1} d^{-1}) as a kinetic measure, and the energy efficiency ($\Delta G_{products} \Delta G^{-1}_{electrical\ energy\ input} \times 100\%$) as a thermodynamic measure of performance (Figure 2).

Based on these kinetic and thermodynamic metrics, both approaches currently have different advantages. Type I acetogen-based technologies, due to the direct association of bacteria with electrode, currently achieve a CO_2 reduction rate at ~1.3 g CO_2 L^{-1} d^{-1} to acetic acid [13]. This rise from ~0.067 g CO_2 L^{-1} d^{-1} in the first reports of this phenomena [21] in 2010 has largely been facilitated by the development of highly porous conductive electrodes (multi-walled carbon nanotubes on carbon supports) demonstrating high volumetric surface area for a high density of bacteria-electrode connections. Comparatively, Type II H_2-mediated technologies are making steady upwards progress (~0.24 g CO_2 L^{-1} d^{-1}) [10••], but face an intrinsic challenge arising from low H_2 solubility in water at ambient conditions. Exponential growth in a Type II reactor has been observed by increasing the driving voltage (from 2.0 V to 2.7 V) resulting in an excess of H_2 production at saturating concentrations (under ambient pressure). At this upper end of H_2 solubility, an instantaneous CO_2 fixation rate of ~0.98 g CO_2 L^{-1} d^{-1} was determined at a cell concentration of ~2.3 g cell dry weight (CDW) L^{-1} [22]. If this cell density could be sustained via a continuous culture reactor, Type II technologies could approach the kinetic performance of Type I systems. However, operating at such high driving forces may incur H_2 loss resulting in lowered energy efficiencies [22].

While cell densities as high as ~150 g CDW L^{-1} have been achieved with Type II organisms [23], the possibility of operating in this regime with growth on H_2 requires experimental validation. At this limit, an ambitious rate of ~20 g CO_2 L^{-1} d^{-1} is predicted, but achieving such rates will require new engineering schemes to ensure that the rates of H_2, CO_2, O_2 and other nutrient fluxes keep pace with each other. In the absence of high substrate solubility, Type II systems must overcome this kinetic barrier by increasing the number of reaction sites (high cell density) simultaneously with high mass transport. The point at which engineering improvements are unable to overcome fundamental limits on convective and diffusional