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MINI-REVIEW

The Artificial Leaf: Recent Progress and Remaining Challenges

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Abstract

The prospect of a device that uses solar energy to split water into H_2 and O_2 is highly attractive in terms of producing hydrogen as a carbon-neutral fuel. In this mini review, key research milestones that have been reached in this field over the last two decades will be discussed, with special focus on devices that use earth-abundant materials. Finally, the remaining challenges in the development of such "artificial leaves" will be highlighted.

Abstrak

Daun Buatan: Perkembangan Terkini dan Tantangannya. Masa depan perangkat yang memanfaatkan energi matahari untuk memisahkan molekul air menjadi H_2 dan O_2 sangat menarik, terutama dalam hal produksi hidrogen sebagai bahan bakar netral karbon. Dalam tinjauan singkat ini, penelitian penting yang telah dicapai dalam bidang ini selama duapuluh tahun terakhir akan dibahas, dengan perhatian khusus terhadap perangkat-perangkat yang menggunakan bahan yang banyak terkandung dalam tanah. Terakhir, tantangan lainnya dalam pengembangan "Daun Artifisial" juga akan digarisbawahi.

Keywords: artificial photosynthesis, electrochemistry, hydrogen production, sustainable hydrogen, water splitting

The principles of the artificial leaf

An artificial leaf operates by using light-energy input to split water into hydrogen and oxygen according to the following equations:

$2H_2O \rightarrow O_2 + 4e^- + 4H^+$ (E = +1.23 V *vs.* NHE): the oxygen evolution reaction (OER)

$2e^- + 2H^+ \rightarrow H_2$ (E = 0 V *vs.* NHE): the hydrogen evolution reaction (HER)

where NHE indicates the normal hydrogen electrode. Schematics of two archetypal artificial leaves are shown in Figure 1. The light harvesting part of the leaf might be a buried photovoltaic device (Figure 1A), or the light harvesting function might be performed by semiconductor films on each electrode immediately underneath the electrocatalysts (Figure 1B). All true artificial leaves are monolithic devices; i.e., the light harvester(s) and the electrodes comprise a single entity (as opposed to an electrolyzer being powered by remote solar panels). Within these confines, the majority of artificial leaves reported to date are "wireless" devices (Figure 1A), whereby the electrochemical circuit is completed by protons (or hydroxide under basic conditions) traveling through the solution that surrounds the leaf. Devices such as these are useful for proof-of-concept, but they may present problems for larger-scale implementation because it is more difficult to keep the product gases (O_2 and H_2) separate (there is a greater chance of gas "crossover"). Hence practical artificial leaves will probably incorporate a gas-impermeable membrane, such as Nafion, through which electrolyte charge carriers can pass but that is electrically insulating. The electrochemical circuit is then completed by external wires connecting the anode and cathode in a "wired" configuration (Figure 1B).

Ideally, the electrocatalysts used to drive the OER and the HER should be composed solely of earth-abundant elements, so that large surface area artificial leaves can be produced using readily-available materials at low cost. "Earth abundant" in this sense therefore generally means first row transition metals and their compounds. Depending on the pH of the electrolyte, different materials make suitable OER or HER electrocatalysts. In terms of

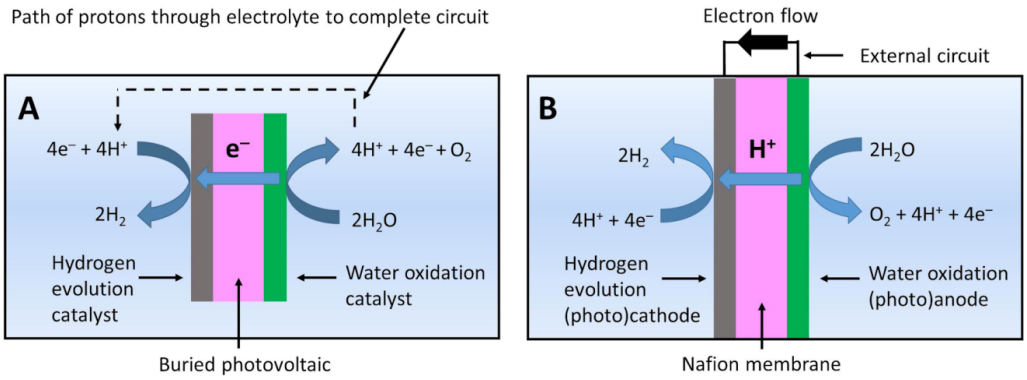

Figure 1. Two Generic Representations of Artificial Leaves. A) A Wireless Configuration with no Separation of the Product Gases. B) A Wired Configuration in which the Electrical Circuit is Completed by External Wiring. In this Latter Conformation, one or both of the Electrodes will also Incorporate Light-harvesting Semiconductors, making a Photo-Catalytic Ensemble

the OER, mixed NiFe oxides make excellent oxygen evolution catalysts at high pH [1], whereas at neutral pH, cobalt oxides show considerable promise [2]. There are currently no good first-row transition metal catalysts for the OER that work at low pH, and this is an area in which further research is urgently required.

For the HER, Ni-Mo alloys work well at high pH [3], and metal chalcogenides (such as MoS_2) display good activity across the entire pH range [4]. For more information on electrocatalysts for the OER and HER, the reader is referred to other, more in-depth recent reviews [5-8]. The semiconductors used in artificial leaves of the sort shown in Figure 1B should also be composed of earth-abundant elements, for similar reasons of scalability and cost. Moreover, these semiconductors should have bandgaps of between 1.6 and 2.4 eV (corresponding to the absorbance of light of wavelengths of 500-800 nm) in order to match the region of the greatest power output from the sun (which is in the visible region) [9]. However, perhaps the dominating factor in the choice of semiconductor materials at the current time is the stability of these materials to aqueous electrolytes. This restricts the choice of semiconductors rather severely, but some attractive candidates are now beginning to emerge. For the HER, p-type silicon [10] has been used extensively as an underlying semiconductor material onto which electrocatalysts can be deposited, and more recently, Cu_2O has been shown to be effective in this role as well [11]. For the OER, the most studied earth-abundant semiconductors that absorb light in the visible region are hematite (Fe_2O_3) [12] and $BiVO_4$ [13].

Selected examples of artificial leaves

In 1998, Rocheleau, *et al*. reported a wireless artificial leaf in which a triple junction amorphous Si solar array (to provide the electrical driving force for the reaction) was covered on one side with a CoMo alloy as the HER catalyst and on the opposite side with an OER catalyst based on $NiFe_yO_x$ species [14]. The photoelectronchemical solar-to-hydrogen conversion efficiency was stated as being an impressive 7.8% at a pH of 14, where solar-to-hydrogen conversion efficiency is defined as the ratio of energy that would be released upon recombining the H_2 and O_2 produced by the leaf to the energy in the incident light used to split the H_2O in the first place. This seminal work demonstrated the feasibility of direct solar-to-hydrogen devices that work using sunlight alone.

However, although the electrolyte employed in this initial example (1 M KOH) is suitable for laboratory demonstrations, it is rather less suitable for applications over large areas due to its corrosive nature. With this in mind, Nocera, *et al*. developed a wireless artificial leaf able to split water into hydrogen and oxygen under solar irradiation that operated at near-neutral pH [15]. This leaf used buried triple-junction silicon as the photovoltaic light-absorber, onto which a protective ITO (indium-tin oxide) coating was deposited by sputtering. A cobalt oxy-hydroxide catalyst for the OER was then electrodeposited on this ITO layer, producing the anode on one side of the leaf. Meanwhile, the HER catalyst on the cathode side of the leaf was a novel ternary NiMoZn material (formed by electrodeposition onto the cathode from an aqueous solution of the metal salts). Irradiation of this device with simulated solar light in potassium borate buffer at a pH of 9.2 (mild electrolyte conditions compared to Rocheleau's system) allowed the OER and HER to be performed simultaneously with a 2.5% solar-to-hydrogen conversion efficiency. However, again, no attempt was made to prevent the product gases from mixing.

More recently, Verlage, *et al*. reported a prototype artificial leaf using a tandem-junction GaAs/InGaP light harvester (which perhaps might not qualify as "earth abundant") in combination with an NiMo HER catalyst and a nickel-based OER catalyst [16]. Under 1 Sun illumination in 1 M KOH, the authors found a solar-to-

hydrogen conversion efficiency of 8.6% for this device in a wireless configuration (as in Figure 1A). Crucially, however, the design of this leaf also took into consideration the potential for mixing of the product gases by embedding the leaf in an anion-permeable membrane, which thus separated the anode and cathode compartments from each other. Indeed, this lowered the levels of H_2 found in the anode-side O_2 stream (and the O_2 in the H_2 stream on the cathode side) below 0.5%, which is well below the 4% explosion threshold for mixtures of these gases. Such a strategy could be vital for the construction of commercial artificial leaves, in which safety and product purity will be key concerns.

Another factor that will be most important in the realization of mass-produced artificial leaves is cost. In this regard, Kim, *et al*. have demonstrated a monolithic artificial leaf that they claim demonstrates a "meaningful advancement in performance and cost" compared to devices based on triple-junction solar cells (as in the Nocera leaf), on account of employing a single-junction perovskite photovoltaic (which is itself amenable to solution processing at modest cost) [17]. Their system uses two different light absorbers arranged in series: the single-junction perovskite solar cell already mentioned (based on $CH_3NH_3PbI_3$) and a $BiVO_4$ semiconductor that is doped with molybdenum. On top of this, a cobalt carbonate-based oxygen evolution catalyst is deposited. Together, this constitutes the photoanode of the leaf, which is able to achieve a current density for the OER of 4.8 mA/cm^2 at 0 V overpotential under simulated sunlight. The device can be operated in both wired and wireless configurations, giving solar-to-hydrogen efficiencies of 4.3% and 3.0%, respectively under simulated 1 Sun illumination.

The final example that we shall consider takes an alternative approach to lowering the cost of artificial leaves by using organic light-harvesting polymers as the buried photovoltaics [18]. Such organic photovoltaics often present the advantages of improved flexibility and lower production costs (e.g., by employing roll-to-roll printing methods) compared to inorganic photovoltaics. In the system under discussion here, Janssen, *et al*. found that a triple-junction polymer solar cell decorated on the anode side with Co_3O_4 and on the cathode side with NiMoZn achieved a solar-to-hydrogen conversion efficiency of 4.9% (albeit over only very small cell areas). However, the demonstration that organic photovoltaics can work efficiently in artificial leaves is nevertheless valuable, and it suggests one route by which this field may develop in the future.

Key challenges

Several challenges remain before the use of artificial leaves becomes widespread. First, solar power is both diffuse and intermittent, so that low current densities (~10 mA cm^{-2} is an often-quoted benchmark [19]) are to be expected for the water- splitting process. Low current densities in turn equate to slow gas production rates, which can lead to extensive mixing of product gases, even when "gas-impermeable" membranes, such as Nafion, are employed [20]. In the more extreme case, gas mixing presents an explosion hazard, which would require the electrolyser to be shut down. In a less extreme case, hydrogen crossing to the anode side of the cell is oxidised to protons and electrons in a parasitic side reaction, while oxygen on the cathode side is reduced to water. These reactions prevent the build-up of dangerous head-space compositions, but they also consume energy (and the products of water splitting) and thus greatly reduce the overall solar-to-collected hydrogen (i.e., Faradaic) efficiency [21]. Approaches such as that used by Verlage, *et al*. do indeed seem to reduce gas crossover, but it has yet to be shown that such measures are sufficient for safe operation over extended timeframes (thousands to tens-of-thousands of hours), as would be required in a commercial device.

A second challenge in the realisation of a practical artificial leaf concerns how the hydrogen is harvested. Low current densities for hydrogen production mean that large surface area arrays will be required in order to make useful amounts of hydrogen on practical timescales, and collecting this gas (at a correspondingly low pressure) might well prove inefficient. The generation of hydrogen at a point source would make the most effective use of any hydrogen evolution catalyst and would also facilitate pressurisation for storage.

With regard to these two challenges in particular, the electron-coupled-proton buffer (ECPB) offers a potential route by which gas mixing can be reduced and hydrogen collection can be facilitated [22-24]. The general concept (see Figure 2), allows water to be oxidised to produce O_2 without any hydrogen being produced at the cathode at the same time. Instead, the counter-electrode reaction during water oxidation is the reversible reduction and protonation of the ECPB. In a subsequent step, this reduced ECPB can be re-oxidised to produce hydrogen and re-generate the ECPB in its original form.

In an artificial leaf, this system could be used (for example) to generate oxygen from water at a photoanode under solar irradiation, whereas the corresponding cathode reaction would be reduction of the ECPB. No hydrogen would be produced during this step, and hence there would be no danger of gases mixing inside the solar-harvesting array. The reduced ECPB could then be transferred to a purely electrochemical device and subjected to re-oxidation at high current densities using an external voltage input, thereby generating hydrogen.

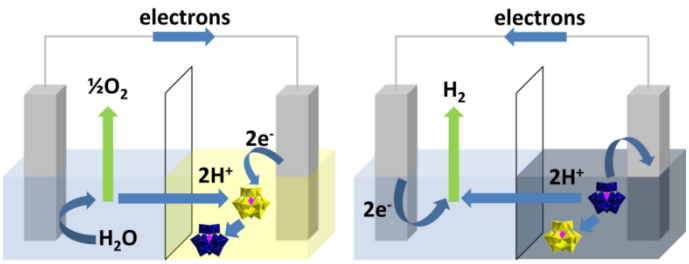

Figure 2. An Illustration of the Concept of the Electron-coupled-proton buffer (ECPB). On the Left Hand Side, Water is Oxidized to give O_2, whereas the Protons and Electrons released Reversibly Protonate and Reduce the Buffer. Later on (Right Hand Side), the Reduced Buffer is Re-oxidized at an Anode, Liberating Protons and Electrons, which go on to Form H_2 at the Cathode

Higher current densities in this purely electrochemical step would allow the H_2 to be produced much more rapidly than was the oxygen that was evolved during the photo-driven step and would also allow an electrolysis cell of much smaller dimensions than the solar harvesting array to be used. This would make more effective use of any hydrogen evolution catalyst that might be employed and would facilitate pressurisation of the product gas. A demonstration system capturing some of these advantages has been reported recently [25].

Yet further challenges remain for artificial leaves. In particular, the cost of the components (membranes, electro-catalysts, and light harvesters) must be reduced, especially if large area arrays are to be deployed. For this reason, we have focused in this mini review on systems that employ only earth-abundant electrocatalysts. However, much work still needs to be done if artificial leaves are to be economically competitive as a way of storing energy by making hydrogen. Moreover, all of the examples discussed herein have been operated for only relatively short periods of time (typically no more than a few tens of hours). Any truly mass-produced (or mass-producible) artificial leaf will need to demonstrate sustained hydrogen production under intermittent sunlight for several thousands (if not tens of thousands) of hours. This puts considerable constraints on the materials and conditions that can be used (strongly basic or acidic environments may not be suitable) and thus represents a considerable materials and engineering challenge.

Outlook

We end this minireview by noting the tremendous promise that artificial leaves have as a means for promoting the development of the non-legacy world. With both rising populations and increasing levels of affluence in many developing economies, the demand for energy is also rising rapidly [26]. Solar energy is geographically well-distributed and is essentially free. Hence the capture of solar energy and its conversion to storable fuels (such as hydrogen) in artificial leaves has great potential as a means by which this increasing energy demand can be met in a sustainable and environmentally-friendly manner. We hope that this minireview will go some way towards inspiring others, especially those in the non-legacy world, to develop new artificial leaf devices that meet the needs and aspirations of their societies.

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