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# From Wastewater to Hydrogen: Biorefineries Based on Microbial Fuel-Cell Technology

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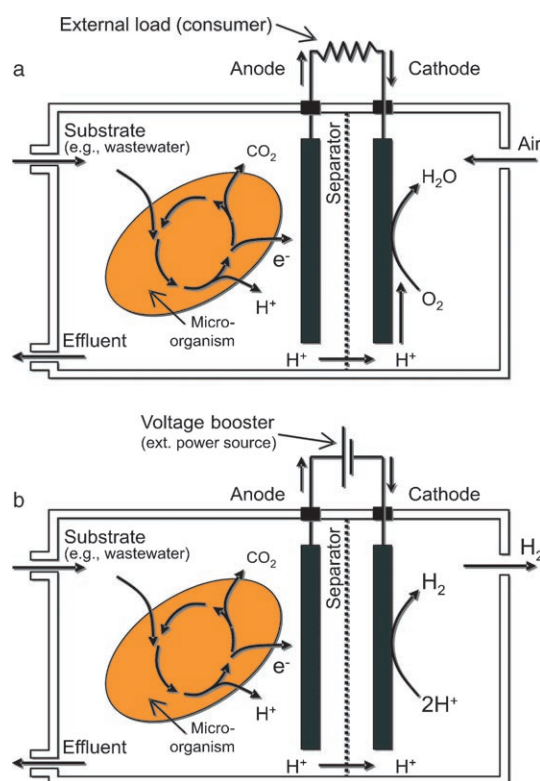
In light of the imminent climate change, the term “hydrogen economy”, as defined by Bockris and Appleby in the early 1970s,<sup>[1,2]</sup> has recently become a buzzword and a ray of hope for the development of technologies that lead to a responsible and sustainable handling of our world’s resources. The transition to such an economy requires the development of the respective technologies at the front end, namely for hydrogen production and storage,<sup>[3]</sup> and at the back end, that is, the technologies that use hydrogen as an energy carrier. The latter has lately seen considerable progress with, for example, the first hydrogen-powered vehicles becoming commercially available. The high-profile marketing of these products provides the public with the impression that society is on a successful way to reach the goal of a sustainable hydrogen economy in the near future. Yet, at the moment, an overwhelming amount of hydrogen is produced from fossil sources such as natural gas, which does not represent a sustainable path but rather simply relocates the CO<sub>2</sub> emissions from our streets to the hydrogen producer without providing a solution to the carbon dioxide problem.<sup>[4]</sup>

Owing to its ubiquity (in most regions of this world), water appear to be the future source for hydrogen; however, considerable amounts of energy, derived from sustainable sources yet to be found, have to be consumed for water splitting. As long as technologies such as nuclear fusion power generation remain a vision, this energy will most likely have

to be provided by a patchwork of different technologies, some already existent, some still to be developed. One important aspect is that mankind cannot afford to waste energy even if it is contained in streams that appear as worthless as sewage. However, although it has been estimated that municipal wastewater contains about nine times more chemical energy than is necessary for its treatment,<sup>[5]</sup> in conventional wastewater plants this energy still remains mainly untapped. Moreover, about 10% of municipal electricity consumption usually goes toward the treatment of wastewater.<sup>[6]</sup>

Recent developments suggest that microbial fuel cells (MFCs) may represent a promising technology for combining

wastewater treatment and energy recovery.<sup>[7–10]</sup> MFCs are electrochemical devices that convert the chemical energy contained in organic or inorganic matter into electricity by means of the catalytic (metabolic) activity of living anaerobic microorganisms. These organisms oxidize the substrate (fuel) and transfer the liberated electrons to the anode,<sup>[11]</sup> which is connected with the cathode—usually an oxygen electrode (see Figure 1a). It seems reasonable to use such a technology to produce not only electricity but also hydrogen. The first attempts in this direction go back to 1994, when Kreysa and co-workers proposed the combination of microbial fuel cells with water electrolysis.<sup>[12]</sup> As the voltage delivered by a biofuel cell does not suf-



**Figure 1.** Diagram of a) a microbial fuel cell (MFC) and b) a microbial electrolysis cell (MEC). Whereas the former type generates electricity, the latter cell produces hydrogen gas.

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fice for the water-splitting reaction, the authors used a stacked MFC configuration (10 fuel cells connected in two parallel series of five cells) to achieve sufficient power for the electrolysis of water. One of the greatest disadvantages of this approach was its low energy efficiency (about 11%), with the losses being caused, for example, by the irreversibility of the oxygen electrode of the fuel cell.

A recent report by Logan and Cheng<sup>[13]</sup> represents the summit of a new approach that goes back to almost simultaneous inventions and further developments by these authors at Penn State University (USA)<sup>[14]</sup> and a group at Wageningen University (The Netherlands).<sup>[15]</sup> The idea behind it is why have two separate devices—a fuel cell and an electrolyser—if one could merge them into one single device, a so-called microbial electrolysis cell (MEC; Figure 1b), thereby waiving unnecessary and efficiency-consuming parts like the fuel-cell cathode and the electrolyser anode. In particular, the cathodic oxygen reduction is considered to be a major bottleneck in the performance of microbial fuel cells,<sup>[16]</sup> and its direct replacement by the hydrogen-evolution reaction (HER) should result in a considerable increase in the overall energy efficiency of the hydrogen-generation process.

Again, the potential delivered by the microbial anode does not suffice to produce hydrogen at the cathode. A certain amount of extra voltage (minimum 0.13 V, in practice between 0.2 and 0.6 V<sup>[13–15,17–19]</sup>) has to be applied to reach the reduction potential of hydrogen and to produce hydrogen at sufficiently high rates. This voltage is low when compared to the voltage necessary for water electrolysis (in practice above 1.6 V<sup>[17]</sup>). Although the required potential in current laboratory-based systems is provided by a potentiostat, it should, of course, ideally be delivered by a microbial fuel cell.

In their report, Logan and Cheng<sup>[13]</sup> exploit the current state of the art and

knowledge of microbial fuel-cell research. They thus, for example, combine an optimized reactor design for a reduced internal resistance and chemically treated carbon as anode material for an improved biofilm electrode interaction.<sup>[20]</sup> This optimization can be seen as the main reason for the improvement of the hydrogen-generation efficiency to 82%, which constitutes a major progress in comparison to previous studies. The researchers underline the great potential of this technology by demonstrating efficient hydrogen production from carbon sources as varied as acetate, butyrate, lactate, glucose and even cellulose, all potential constituents of municipal, agricultural or industrial wastewaters.

Certainly, plenty of work remains to be done and issues need to be addressed. One such challenge is to increase the rate of hydrogen generation, another may be the replacement of platinum, which is used as the hydrogen-evolution catalyst, by noble-metal-free catalysts in order to decrease the costs of hydrogen production.

Despite all the enthusiasm, one has to keep in mind that the performance of bioelectrochemical hydrogen generation is confined by principle bottlenecks of the underlying microbial fuel-cell technology, like the limited rates of microbial metabolism and the rather restricted physical and chemical operational conditions (ambient temperature, near-neutral pH, low ionic strength).

Finally, a remark may be added concerning the confusing terminology of the new technique. As is the case with many new technologies, it is not always easy to find an unambiguous, catchy name that gives a quick impression of its nature and character. The name should be understandable for people from different sciences or different backgrounds. Since the first paper that describes bioelectrochemical hydrogen generation,<sup>[12]</sup> very different names and terms have been used for its description. It may be questioned if yet another term such as electrohydrogenesis is really necessary or

helpful, when terms such as bioelectrochemical hydrogen generation or bioelectrochemically assisted hydrogen generation already get to the point.

**Keywords:** electrochemistry · hydrogen · microbial fuel cells

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