

ELECTROCHEMICAL REACTIONS IN POWER SOURCES AND SINKS: PERSONAL REFLECTIONS ON PROGRESS AND FUTURE PROSPECTS

ASHOK K. VIJH*

Institut de recherche d'Hydro-Québec (IREQ), Varennes, Qué. JOL 2PO (Canada)

Summary

The basis of all electrochemical power sources such as fuel cells, batteries, and photoelectrochemical devices is the energy-producing *electrochemical reactions*, whose high rates, to the exclusion of all parasitic or deleterious reactions, is the paramount goal desired in all research and development work in electrochemical energy conversion and storage. A subjective evaluation of the status of some of these key electrochemical reactions is undertaken in relation to the materials problems involved; an outline of the recent progress is given together with the current focus and future possibilities. An elementary examination of the fundamental aspects of some of these reactions, *e.g.*, the electrocatalysis of the hydrogen and the oxygen reaction is carried out in a manner which emphasizes their salient features both in the configuration of a power source, (*i.e.*, fuel cell) and that of the complementary power sink (*i.e.*, electrolyzer).

It is observed that considerable progress has been made in the electrocatalysis of the hydrogen and oxygen evolution reactions with the discovery of the so-called BP electrocatalysts by Brown *et al.* recently. The earlier DSA catalysts for the chlorine evolution reaction are also clearly a milestone. Much progress has also been made in the commercialization of phosphoric acid fuel cells for utilities, in the exploratory materials work on photoelectrochemical cells, and in understanding the fundamental constraints and the materials problems of several storage batteries.

Future progress is urgently needed in the nearly intractable problem of the stable and active non-noble metal electrocatalysts for the oxygen reduction reaction. The promise of much future activity and perhaps some breakthroughs are clearly indicated in the following areas: photoelectrochemical cells — both for photoelectrolyses, and, the electrochemical photovoltaics; commercialization of Li-SOCl₂ primary batteries and related systems; optimization and commercial availability of some of the currently researched batteries for vehicular and load-levelling applications; development of the entire area of conducting polymer electrodes and ionic poly-

meric electrolytes; chemically modified (derivitized) electrode surfaces; and the development of concepts treating living beings as electrochemical power sources.

Introduction

This article originated from an invitation from John Broadhead, the U.S. Regional Editor of the *J. Power Sources*, asking me, and some other scientists and technologists, "to pause for a moment and contemplate..." on major questions or problems bearing on power sources — the progress made and the possible productive lines of future intensified study. Finding such an invitation to pontificate quite irresistible, we seized upon the opportunity, without being bothered too much either by our lack of a spectacular track record in such matters or by our manifest absence of oracular gifts.

First of all these personal reflections pertain to *electrochemical* power sources, and will thus exclude other important non-mechanical power sources such as the "dry" photovoltaics. Second, the focus will be on some fundamental electrochemical aspects of the *electrode reactions*, which constitute the heart of such power sources; this is the reason why the somewhat unusual title deals with the *power sources* and *sinks* together since, in many cases, the source and the sink are the opposite faces of the same coin and their behaviour is governed by very similar materials properties and electrochemical kinetic considerations. Consider the familiar "simple" reaction:



An electrochemical cell operating in a fuel cell mode to sustain reaction (1) is a power source; however, the same device in the electrolysis mode is a power *sink*. Although the above simple depiction deliberately ignores the critical parameters that make the above reaction into a *device*, *i.e.*, an optimum fuel cell or an electrolysis unit, it does emphasize the point that the basic factors involved in the two situations such as good electrocatalysis, absence of electrode corrosion and aging effects, *etc.*, are the same. Hence, any progress (or future prospects) in the basic electrochemical aspects of power sources cannot be correctly understood or completely appreciated without making an appropriate reference to the similar progress in the analogous power sinks, *i.e.*, the electrolyzers. One possible approach is to outline the progress and future possibilities in the *key* electrochemical reactions and materials problems involved in both situations, *i.e.*, the power source and the power sink; this approach, although quite unorthodox in the power sources

field, is adopted here since it focuses on the *electrochemical reactions* which are responsible for the production (in a source) and the consumption (in a sink) of power. Other vital aspects such as the design and engineering of the devices and their performance characteristics will be covered, it is hoped, in other reviews here.

1. The hydrogen reaction

The electrocatalytic oxidation of hydrogen is the basis of an H_2-O_2 fuel cell; its converse is the electrolysis of water, *viz.*, eqn. (1) here. There have been countless studies on the factors determining the rates of this reaction on metals and alloys, as reviewed previously [1]. Based on some earlier work on gas-phase heterogeneous catalysis, electrochemists formed the notion that rates of the hydrogen evolution reaction on metals are influenced by their electronic configurations, more particularly by their percentage d-character. Following the penetrating analysis of Ehrlich [2] for the gas-phase reactions, we have examined this question critically for the electrocatalysis of the hydrogen evolution reaction on metals [3] and alloys [4, 5]. It has thus been shown that for metals and their alloys [3, 5], there is no correlation between their percentage d-character and either the magnitude of the M-H (surface atom of the metal-chemisorbed hydrogen atom) interaction energy or the value of the exchange current density. It was further indicated that in rationally chosen alloys (*e.g.*, Pd-Ag alloys), the rate of the electrolytic hydrogen evolution reaction is determined more by the atomic composition of the electrode surface than by the electronic configuration of the bulk material [4, 5]. Among the workers in this area, the issue is far from settled although it is not clear as to how one could obtain an unambiguous resolution of this controversy.

The practical goal in the present context is to obtain an electrocatalyst which provides high rates of reaction at low or negligible overpotentials, and is stable, inexpensive, and abundantly available. Such an electrocatalyst has recently been reported from the British Petroleum (BP) laboratories [6] and has been recently confirmed by us [7] regarding its spectacular claims. The BP electrocatalysts of Brown *et al.* are based on Ni-Mo metallic coatings on nickel mesh substrates; these electrodes are extremely stable, do not show visible aging, and exhibit a typical overpotential of 48 mV at an apparent current density of 100 mA cm^{-2} . The high electrocatalytic activity is intrinsic and is further (apparently) enhanced by the high area of the electrocatalyst. These non-noble metal electrodes contain all the features we could hope to expect in an ideal electrode and it is rumoured that these electrocatalytic surfaces are already being used (under confidential licensing agreements) in the new generations of electrolyzers of some well-known manufacturers on the international market.

In principle, one should be able to use these electrodes in fuel cells also, for the oxidation of hydrogen. In practice, however, since *anodic* potentials

(on the hydrogen scale) are needed to carry out this reaction, problems from corrosion and surface oxide formation, etc., may be expected on these non-noble metal electrodes. However, the discovery of the BP electrodes, after long and frustrating struggles on similar lines by many workers, has ignited the hope that similar success may be achieved for the oxidation of hydrogen. In any case, in any hydrogen-oxygen fuel cell the critical problem is not the discovery of a new electrocatalyst for the oxidation of hydrogen but, rather, the need for a new electrocatalyst for cathodic reduction of oxygen (see below).

2. The oxygen reaction

The anodic evolution of oxygen is of great practical interest in commercial electrolyzers since it is the main source of power loss owing to the poor catalysis of this reaction on most electrodes. In addition, since this reaction proceeds at high anodic potentials, problems such as electrode corrosion, non-conducting or semi-conducting oxide formation on the anodic surface (*i.e.*, the *demetallization* of the electrode), and aging effects associated with long-term slow changes in the electrode characteristics, assume enhanced proportions. A recent breakthrough, however, claims highly electrocatalytic electrodes showing remarkable electrode stability [8]; these electrodes are constituted, typically, of NiCeMo in the ratio of 59.5:14.9:25.6 and exhibit an electrode potential of +1.48 *vs.* RHE at an apparent current density of 500 mA/cm² at 70 °C in 30% KOH solution.

Future progress is indicated in the direction of establishing the fundamental factors responsible for the incredibly high electrocatalytic activity and stability of these electrodes for the evolution of hydrogen [6] and oxygen [8]; such studies, it is believed, would lead to a better theoretical framework for the understanding of electrocatalysis, and the development of new electrode materials for a variety of electrochemical reactions.

The reverse of the oxygen evolution reaction, namely, the complete reduction of oxygen involving a rupture of the oxygen-oxygen bond and the transfer of four electrons in the overall reaction, *viz.*,



represents perhaps the most challenging problem in electrocatalysis today. Despite much work, there is hardly a good electrocatalyst for this reaction; even platinum, which is the best and the stablest electrocatalyst known for this reaction, is far from satisfactory because of its low exchange current density and, of course, its cost and scarcity. The electroreduction of oxygen, if achieved efficiently and inexpensively, is bound to lead to dramatic advances not only in the hydrogen-oxygen fuel cells but also in metal-air batteries, and in the chloralkali industry — through the use of the so-called “oxygen depolarized cathode”; similar improvements can also be expected in some other commercially-important electrolyses.

Reflecting on the future avenues of progress in the electrocatalysis of this reaction, one cannot help being pessimistic in view of the considerable number of fundamental and empirical studies on the subject. It would appear, however, that empirical approaches such as those of Brown *et al.*, which have recently achieved spectacular successes for the hydrogen [6] and the oxygen [8] evolution reactions after many years of blind alleys, should hold some promise for the oxygen reduction reaction also. This would be particularly so if one could succeed in developing a theoretical framework for understanding the root causes of previous successes [6, 8], thus serving as guidelines for the future work on electrocatalysis. The recent interesting approaches of Anson *et al.* [8(a)] involving dimeric metalloporphyrins such as dicobalt cofacial porphyrin linked by four-atom bridges, exhibit four electron reduction of oxygen and bring out some novel theoretical aspects of this reaction; these materials are not stable, however, and it appears unlikely that they can be modified to yield stable electrocatalysts of possible commercial interest.

3. Some other electrode reactions and materials

One of the most important power "sinks" is the chloralkali industry in that it "converts" an enormous quantity of electric power to chlorine and caustic every year. Dramatic progress in the power savings in this industry was achieved by the discovery of the DSA (for dimensionally-stable anode) electrodes which are based on the isostructural oxides, TiO_2 and RuO_2 . These materials yield highly catalytic and stable electrodes for the anodic evolution of chlorine.

Electrolyses involving organic molecules are of great interest not only in electro-organic syntheses but also in fuel cells involving direct oxidation of simple molecules such as methanol and hydrazine. A fundamental difficulty in all such reactions is that either the intermediates or the products of the reaction inhibit the electrode process (usually by forming chemisorbed layers or "filming" the electrode) so that the reaction rate tends towards unacceptably low values within a few minutes (or hours) of the initiation of the electrolysis. A recent dramatic discovery in which the platinum metal is deposited on a solid polymer electrolyte to give a Pt-SPE electrode shows a way in which the initial high activity of platinum for the oxidation of methanol is mostly maintained even after long periods of electrolysis; for example, the Pt-SPE (Nafion) electrode showed activity for the anodic oxidation of methanol which is about twenty times greater than on a platinumized-platinum electrode, even after twenty hours of electrolysis [9]. Much future progress may be expected from similar approaches involving polyelectrolyte coatings [10], polymer films [11] or related chemical modifications on the electrode surfaces [12]. New electrodes involving such modified surfaces are, inevitably, bound to find their way into imaginative novel applications in electrochemical energy conversion and storage devices.

An important new class of materials, just beginning to find applications in the power sources field, is constituted by organic metals and semiconductors; polyacetylene and its derivatives are examples of these materials which are rapidly attracting much research interest [13].

4. Electrochemical energy storage: batteries

Although both primary and secondary batteries "store" power, only secondary batteries may be treated as true storage devices.

The current situation for primary batteries has been well encapsulated by Brodd [14]: "As in the 1960's when alkaline cells were introduced with 5 - 7 times the energy density of Leclanché at high drains, again today a new system, Li-SOCl₂, offers a similar improvement in energy density". There are about four or five primary lithium systems under intense development and some of them (*e.g.*, Li-SO₂, Li-MnO₂, and Li-CF_x) are being sold commercially. Further progress would be aimed at optimization and improvement of these batteries and an examination of some other closely related systems.

As regards secondary batteries, many promising systems are currently being developed as indicated here in Table 1, taken from Jensen and Tofield [15]. It is impossible to predict as to which is the "most promising" future system; it is likely that a number of competing systems aimed at specific segments of the market will emerge. All the current systems involve some materials problems, despite various attractive features; several analyses of these battery systems are available in which their current status and future promise have been elucidated, compared, and commented upon [14 - 20]; there is no need to re-capture these "status-reports" here, especially since no clear predictions regarding future progress can be ventured.

Some brief comments of a subjective nature, however, are in order on some of the "newer" system. The intoxication of some years ago of an all-solid battery based on super-ionic conductors such as RbAg₄I₅ wore off as intractable problems associated with the electrode-electrolyte interfaces were encountered. The materials problems of sodium-sulphur and lithium-metal sulphide batteries would appear to have not been completely resolved, despite a very considerable amount of work. The commercial possibilities initially attributed to the intercalation batteries seem not to have been realized. The exceedingly complex plumbing of a Zn-solid chlorine (*i.e.*, Zn-Cl₂ CH₂O) battery would clearly be expected to be a source of problems during its mobile operation such as in an electrical vehicle. These formidable problems are not seen, however, as insurmountable by investigators developing their pet systems.

Recently, novel types of batteries based on ionic polymeric electrolytes have commanded attention in some circles. In the initial work, problems associated with poor adhesion at the Li/polymer interface, low ionic conductivity of the ionic polymer at room temperature, and the difficulty in elimi-

TABLE 1

A summary of the major organizations engaged in the development of commercial storage batteries around the world: taken from Jensen and Tofield [15]

Battery	Temperature of operation	Organizations developing battery (examples)
Ni-Fe	ambient	Westinghouse, Eagle-Pitcher (USA), Swedish National Development Co. (Sweden)
Ni-Zn	ambient	Gould, General Motors, Yardney, Eagle-Pitcher, Energy Research Corporation, NASA-Lewis (USA), D.A.U.G. (Germany), Lucas (UK)
Zn-Cl ₂ ·6H ₂ O	ambient	Energy Development Associates (USA)
Zn-air	ambient	C.G.E. (France), Toyota, Nissan (Japan)
Zn-Br ₂	ambient	G.E., Exxon (USA), Magneti-Marelli (Italy)
Fe-air	ambient	Westinghouse (USA), Siemens (Germany), Royal Swedish Institute of Technology (Sweden), Matsushita (Japan)
Ni-H ₂	ambient	COMSAT, Energy Research Corp., Tyco Labs (USA), SAFT (France), Harwell (UK)
Li-water	ambient	Lockheed (USA)
Li-TiS ₂	ambient	Exxon (USA)
Na-S	300 - 400 °C	Ford, G.E., Dow (USA), Yuasa (Japan), C.G.E. (France), Brown-Boveri, Battelle (Germany), Chloride Silent Power, British Rail, Harwell (UK)
Li-FeS	400 °C	A.N.L., Gould, Atomics International, General Motors (USA), Varta (Germany), Admiralty (UK)

nating the partial transport by anions have been identified [21]. Some other results on an all-polymeric solid state battery based on polyacetylene electrodes and polyethylene oxide complexes as electrolytes have also been reported [22]. These new materials undoubtedly offer exciting opportunities for further activities in the battery field; it is too early to surmise whether such activities would lead to some notable progress.

5. Photoelectrochemical energy conversion and storage

Following the seminal paper of Honda and Fujishima [23] on the photoelectrochemical cleavage of water molecules, an explosive surge of activity has taken place in this area and a steadily increasing stream of papers on photoelectrochemical cells (PEC's) has appeared in the literature [24 - 32] since 1975. Typically, a photoelectrochemical cell contains a semiconducting electrode (the "working" electrode) under suitable illumination immersed in an electrolyte solution containing a second (counter) electrode. When the semiconducting surface is illuminated with a light energy equal to or greater than the band gap of the semiconductor, a photon is captured and an electron-hole pair is created. The electron and hole thus produced are

separated by the electrical field within the space charge layer of the semiconductor at the semiconductor–electrolyte interface, and used to drive the usual electrode reactions at the cathode (reduction) and anode (oxidation), respectively. At least four distinct cases of photoelectrochemical cells can arise and they are as follows [30]:

(i) *Liquid junction photovoltaics*

These devices are also known as the electrochemical photovoltaics or regenerative cells. These cells utilize a single redox couple in the electrolyte and the oxidation at the anode is exactly opposite to the reduction at the cathode. The net free energy change in the overall cell reaction is zero. In such cells, the absorbed optical energy increases the free energy of electrons in the semiconductor electrode; the useful electrical work is done when these electrons traverse the external circuit to maintain the two electrochemical reactions. These cells are energy conversion devices in which optical energy is converted to electrical energy; no energy storage is involved.

(ii) *Photoelectrolysis cells*

One such cell is shown in Fig. 1 [31] for the photoelectrochemical decomposition of water to give H_2 and O_2 . The light is absorbed at the semiconducting anode (e.g., *n*-type TiO_2) and an electron–hole pair is formed. The hole is driven to the semiconductor surface and oxidizes OH^- to give O_2 . The electrons are conducted through the external circuit to the cathode (platinum) where they reduce protons to gaseous hydrogen. The overall reaction is driven in an uphill direction, i.e., the free energy change

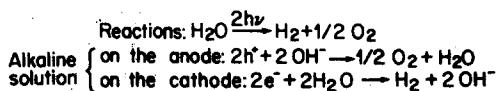
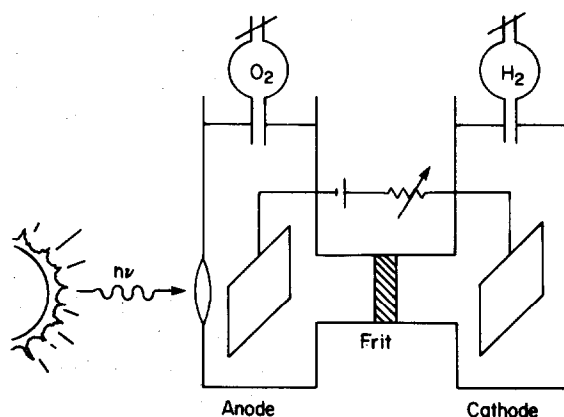


Fig. 1. Schematic diagram of a photoelectrolysis cell for the decomposition of water; after Tomkiewicz and Fay [31].

is positive. The solar (optical) energy is thus *stored* as chemical energy of the products, *i.e.*, H_2 and O_2 . These photoelectrolysis cells are thus energy storage devices.

(iii) Photoelectrocatalytic cells

In these cells, an electrochemical reaction is thermodynamically feasible (*i.e.*, the free energy change in the overall reaction is negative) but kinetically very slow. The light energy absorbed at the semiconductor electrode is used to overcome the energy of activation of the electrochemical reaction. An example of such a reaction is the anodic oxidation (*e.g.*, on an *n*-type TiO_2) of cyanide ions, of interest in the decomposition of waste materials. Another example is the photo-Kolbe reaction where acetic acid is oxidized to ethane. The optical energy is neither converted nor stored but is used to catalyse a slow reaction to usefully high rates.

(iv) Photogalvanic cells

In photogalvanic cells, the optical energy is absorbed by the solution species (rather than the electrodes) such as a suitable dye molecule in the electrolyte; this is followed by a charge transfer process to an electrode. The optical energy is converted to the electrical energy (as in electrochemical photovoltaics) here also, except that the primary event of photon absorption and an electron-hole creation resides on an electrolyte species rather than the electrode surface.

The field of photoelectrochemical cells is in its infancy and is yet at the stage of fundamental materials research. The range of problems and possibilities is wide and the complexity of theoretical and experimental approaches immense. The key materials problems are encapsulated below.

(v) Fundamental materials considerations in photoelectrochemical cells [24, 30]

Since photoelectrocatalytic reactions involve neither conversion nor storage of energy, they will not be considered further here. Also, photogalvanics may be treated as a special case of photovoltaics except that the seat of optical absorption is displaced towards the electrolyte side of the semiconductor-electrolyte interface. The material problems to be examined here thus pertain to the regenerative cells and to the photoelectrosynthetic cells.

The performance of electrochemical photovoltaics is determined by two critical parameters: the band gap of the semiconductor electrode, which determines its absorption characteristics; and the flat-band potential (this is the potential at which the bands at the semiconductor-electrolyte interface show no bending and are, hence, flat — this is the situation of zero *net* charge in the interphase), which governs the maximum attainable photovoltage of these cells. Also, semiconducting electrodes usually exhibit corrosion under illumination and, hence, corrosion prevention becomes the third critical consideration.

The problems of electrochemical stability of the photoelectrode are much more severe in photoelectrosynthetic cells (Fig. 1), however.

Also, here again, the band gap of the semiconductor electrode is important since it determines the absorption characteristics and thence the ultimate conversion efficiency possible. The flat-band potential is also a central parameter since it affects the conversion efficiency by establishing the external bias requirements. The current materials available for these cells are unsatisfactory in regards to one or more of the three criteria, *i.e.*, they show photocorrosion, exhibit poor sunlight absorption in the visible spectrum, and need external bias.

In practice, only oxides are the likely candidates for photoanodes since compound semiconductors formed by anions (*e.g.*, S, Se, Te, As, P, etc.) show pronounced corrosion under photoelectrolytic conditions. However, the oxides which are electrochemically stable (*e.g.*, $n\text{-TiO}_2$) have invariably high band gaps and thence poor absorption in the visible range of sunlight; or, the external bias requirements are so high that the photoelectrolysis has virtually no advantage over the conventional electrolysis.

It has been observed that for oxides,

$$E_g + V_b \cong 3.2 \text{ eV}$$

where V_b is the minimum external bias. When the $V_b = 1.2 \text{ eV}$, this approaches the conditions of conventional electrolysis, since the difference between the reversible potentials for the hydrogen evolution and the oxygen evolution reactions is 1.23 V at room temperature. Thus the requirement for positive bias should be less than 1.2 V (*i.e.*, the E_g should be $>2 \text{ eV}$) for useful harnessing of the solar energy. Ideally a *negative* external bias is desirable; this would be for oxides with $E_g \geq 3.2 \text{ eV}$. These oxides absorb very poorly however in the visible region and show good absorption characteristics in the ultraviolet region only.

Several approaches have been attempted to reconcile these complex, and to some extent contradictory, requirements for these photoelectrode materials and these are as follows [24 - 32]:

(a) Hetero-structures such as CdS or CdSe (good photoabsorbers) covered by TiO_2 or SrTiO_3 (to protect against corrosion) have been used. When these structures show photoresponse, it is found to be due to the substrate CdS or CdSe being exposed to the illumination through pores in the oxide coating, and, thence, the high corrosion. When the TiO_2 or SrTiO_3 coatings are pore-free, the photoresponse is due to these oxides only and, hence, quite poor.

(b) Attempts to increase photoresponse by incorporating inclusions of transition metals (*e.g.*, Cr) in a stable oxide such as TiO_2 have led to quite insufficient improvements.

(c) Coatings of transition metal oxides, *e.g.*, lanthanum chromate on TiO_2 , have been concluded to lead to some improvement in photoresponse and acceptable corrosion stability. This approach may show some promise, although it needs much further exploration, especially regarding long-term electrode stability.

(d) Dyes, sensitizers, "super-sensitizers", and other organic coatings and surface groups that show good absorption in the visible range have been coated on stable electrodes such as TiO_2 . These layers show rapid degradation of the photoresponse and undergo oxidation, bleaching, and visible destruction. Also, sufficiently thick coatings of the dye needed for a good photoresponse (at least *initially*) tend to inhibit the electrochemical charge transfer, since they form choking, insulating layers.

(e) Photoanodes based on layered compounds such as WS_2 , WSe_2 , ZnS_2 , ZnSe , and HfSe have been suggested. It has been argued that the electron-hole transition in these compounds occurs between two levels (*i.e.*, two different d levels) of the same atom, *i.e.*, the cation, instead of the usual valence band (anion) to the conduction band (cation) transition that leads to the weakening of the cation-anion bonds and thence the corrosion. It has been pointed out, however, that if the corrosion begins by the formation of a surface state on the surface of the semiconductor to which the electrolyte solution species attach (and then cause it to detach from the lattice), the mode of charge transfer within the semiconductor would seem to be immaterial. A further study of such semiconductors would appear desirable, however [28].

(f) Thin films ($<400 \text{ \AA}$) of a metal such as gold on CdS have been suggested to suppress the photocorrosion. This is equivalent to the presence of an Au/CdS Schottky barrier in series with the Au/electrolyte interface. If the gold film is thick, it prevents photoabsorption by CdS; if thin, it contains pores, etc., and leads to corrosion of CdS.

(g) A novel and exciting approach to photoelectrochemical synthesis is through the so-called "wireless" electrochemistry. Here, colloidal microspheres containing both anodic and cathodic sites are suspended in an electrolyte and illuminated, with the production of, *e.g.*, H_2 and O_2 in an aqueous solution. Such microsphere cells use bifunctional catalysts (*e.g.*, platinum for the hydrogen evolution and RuO_2 for the oxygen evolution) adsorbed on colloidal microspheres of TiO_2 containing a sensitizer ($\text{Ru}(\text{bipy})_3^{2+}$) and an electron relay such as methyl viologen. The detailed mechanisms of these photoinduced electrochemical water cleavages are complex and will not be dealt with here. These systems look promising although the long-term stability has not yet been established. They would be expected to suffer from the same drawbacks as other systems containing dyes and sensitizers described above. Also, separation of the H_2 and O_2 is an additional problem in these configurations [27].

(h) Anodic oxide films formed on gold have been shown to exhibit photocurrents in the potential range 1.5 - 1.8 V (*vs.* reversible hydrogen electrode). Above 1.8 V, only u.v. response is observed, however. Possible problems here are the difficulty of maintaining the electrode potential in the 1.5 - 1.8 range in practical systems; also, the photocurrents observed are in the nanoampere range only and of little practical significance.

(i) Several other schemes either for stabilizing electrodes (*e.g.*, CdS anodes with sulphide ions) or of setting-up complex systems for photo-

electrolysis of water have been described by Heller [29] who claims to have achieved up to 12% efficiency for sunlight assisted electrolysis of water for a system (e.g., *p*-InP(Ru)/1M HCl/Pt) which involves a *Photocathode*.

The field of photoelectrochemistry has opened up significant new frontiers of the electrochemistry of semiconductors [1] and provided new understanding of the complex interactions of photochemical, electrochemical, and solid state properties of materials. It is a vigorously active arena of a very large activity in materials science where properties of solid-liquid interfaces are examined in relation to their interactions with light, electricity, and chemical reactions [24 - 32]. The future promises much productive activity built upon the recent work summarized above, and involving new and fruitful approaches of an interdisciplinary nature. The field is pregnant with many exciting possibilities although it is yet premature to predict the paths of the likely progress.

6. Living beings as electrochemical power sources

It has been shown that the biochemical energy conversion in animals implies an electrochemical mechanism of direct energy conversion [33]; the salient facts supporting this viewpoint are given in Table 2. In some recent work [34], analogies based on the principles of electrochemical fuel cells have been used to develop ideas on proticity and protonmotive reactions in biology. One may thus conclude that living beings, including humans, are electrochemical power sources. Further development of this line of thinking, and the awareness of electrochemical mechanisms in biological energy processes, is expected in the years to come as the divisions between the traditional disciplines dissolve more rapidly, and as electrochemistry is conceded its rightful hegemony as an all-pervasive fundamental science.

TABLE 2

Electrochemical energy conversion in human beings

Power equivalent of daily food consumption by a human being, assuming 100% efficiency of heat to mechanical energy	140 W
Carnot efficiency (with 10 K temp. difference inside the body) is 3%; power equivalent is	5 W
Constant power needed to operate human circulatory system is estimated to be	10 W
High efficiency of energy conversion in humans implies an electrochemical mechanism, as also suggested by some mechanistic studies	

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