

Electrochemical ways of tapping solar energy: an appraisal†

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Abstract. In recent years, solar cell technology has advanced significantly and is nearing commercial viability. Practical solar cells that are capable of converting the solar radiation directly into electricity are now available. It is, however, imperative to couple them with appropriate power storage systems. This article is a brief review of the current status of electrochemical power systems such as storage batteries and fuel-electrolysis cell hybrids which could be successfully utilized to this end.

Keywords. Solar cell-batteries; energy storage and conversion; storage batteries; fuel-electrolysis cells.

1. Introduction

The transition from reliance on fossil fuels to long-term energy sources is an urgent technical challenge to modern civilization. One of the most engrossing prospects is that of harnessing sunlight for the production of electrical energy. Experts are fairly confident that at least part of the electricity required in the future will be supplied from solar tap. It is estimated that earth receives approximately 126 trillion horse power (94 billion kilowatts) from the sun each second. If this enormous and unlimited energy could be more fully utilized, our dependence upon fossil fuels might be drastically reduced.

Solar energy is available in several forms such as direct solar radiation, wind, wavepower, rain (in the form of hydropower), photosynthesis and ocean thermal gradients. Among these, the direct generation of electricity from solar radiation through solar cells seems quite attractive. However, due to the intermittent nature of solar radiation, efficient and economic management of the electrical energy generated from solar cells involves its storage. The storage and retrieval of electrical energy is most conveniently accomplished at present with electrochemical systems. Electrochemical systems which could be used to this end are: (i) storage batteries, (ii) fuel-electrolysis cell hybrid systems combined with hydrogen and oxygen storage, and (iii) dissolved-redox-flow accumulators.

Battery and fuel cell development has undergone intensive research and development efforts in the past two decades. The advantages of these systems are that these are modular, safe, have a fast response to load fluctuations and operate at high-enough conversion efficiencies of about 75%. On the other hand, solar cell ribbon technology seems to be nearing the stage of perfection. With these developments and continued financial help of government departments, it should be possible in the near future to convert solar energy directly into electrical energy through solar cell-batteries, store it in electrochemical cells and later retrieve it on demand in a commercially viable manner. This paper is an appraisal of such a solar-cum-electrochemical energy technology.

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2. Solar cell-batteries

The simplest device to convert solar radiation directly into electrical energy is the photovoltaic cell. A high-efficiency silicon photovoltaic cell was first demonstrated in 1954 by Chapin, Fuller and Pearson of Bell Laboratories which paved the way to modern solar cells.

Photovoltaic cells are junction devices. In a silicon photovoltaic cell, a thin *p*-type layer is formed on a *n*-type silicon layer. These *n*- and *p*-type layers form a relatively large area *p-n* junction across which there is a natural electric field. Light energy impinging upon the exposed outer layer generates electron-hole pairs and minority carriers (electrons in *p*-type layer and holes in *n*-type layer), and electrons are swept from *p* to *n*, and holes from *n* to *p*. This action produces the output voltage of the solar cell.

A solar cell-battery is a DC power source made up of several solar cells connected in series or parallel, or both to deliver useful amounts of power when illuminated by sunlight. Such heavy-duty photoelectric batteries are used in conjunction with storage batteries on space missions, as emergency power supply units and in several other places. Figure 1 shows a solar cell-battery being used to trickle charge a 12-volt storage battery. This solar cell-battery consists of a panel of thirty $\frac{1}{2}$ -volt silicon photovoltaic cells connected in series and a diode which prevents back flow of the current through the cell during darkness. In bright sunlight the unit delivers 12 volts at 0.1 ampere and has capacity of 30 watt hours per week. Figure 2 shows an early experimental automobile which is sunpowered. Here, the large solar cell panel placed atop the automobile contains 10,640 silicon photovoltaic cells. Its output converts sunlight into enough electricity to keep charged the batteries that run the car. Alternatively, the electrical power required for driving an electrolytic cell could also be derived from a suitable solar cell-battery; the hydrogen and oxygen generated by the electrolytic cell are stored and later supplied to the fuel cell units to generate electric power. Similarly, dissolved-redox-flow accumulators could also be used for electrical energy storage (see § 3).

The advantages associated with solar cells are that they yield the highest overall conversion efficiency of solar radiation to electricity, have unlimited life, are simple and easy to fabricate and have high power output/weight ratio. On the other hand, the associated disadvantages are the high capital, need for a storage device in most applications, large surface areas for high power outputs, and degradation of the cells in certain high-energy radiation fields.

In recent years, thin-film solar cells have been developed which offer considerable reduction in the material used and a substantially fewer labour per unit area of the cell constructed. The Westinghouse Electric Corporation in United States has developed the dendritic-web process to produce silicon ribbons (40 mm wide and 0.25 mm thick) which eliminates slicing, lapping and polishing processes from photovoltaic cell production (Electrical Review International). Several other industrial research and development establishments in United States, Europe and Japan are trying to develop low-cost, high-performance and long-life solar cell-batteries for terrestrial uses of the device and a significant degree of success has been claimed by Matsushita Electrical Industrial Company of Japan (Mochzuki and Murogona 1979). Research on solar cell-batteries has increased in recent years because of the expected decrease in the production cost for mass produced solar cells. The projected learning curve due to Palz

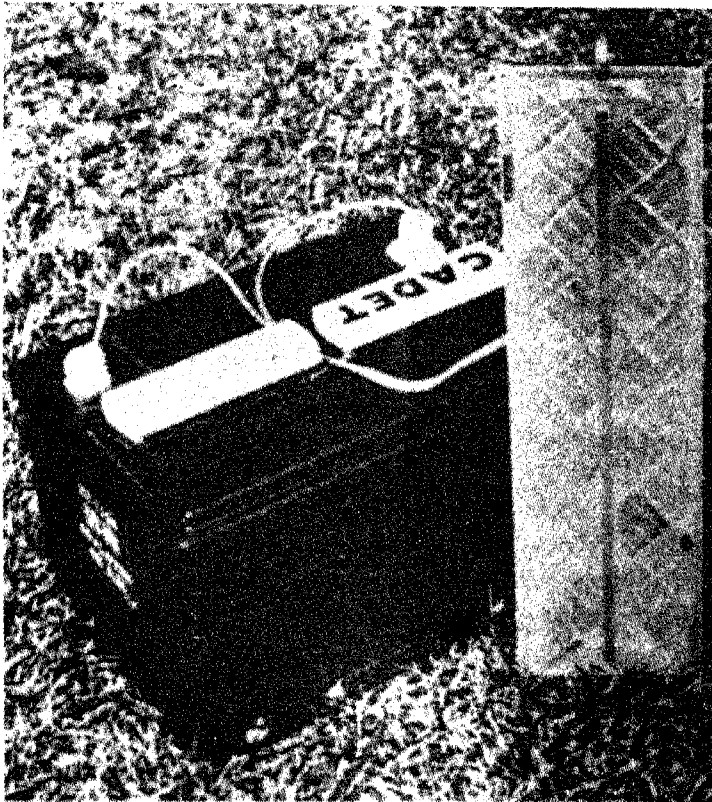


Figure 1. Solar-cell panel charging a 12-volt battery.

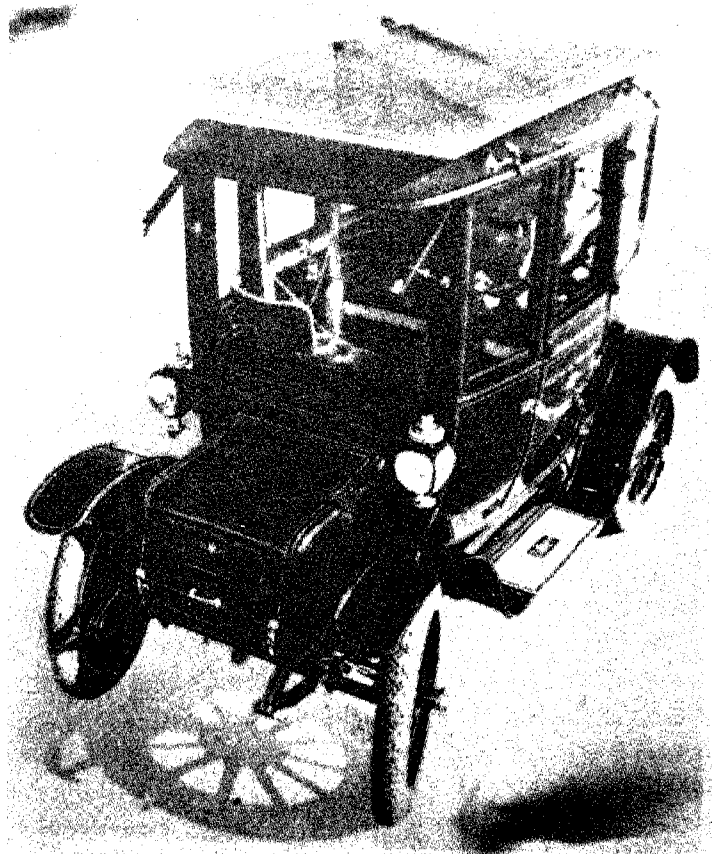


Figure 2. World's first sun-powered automobile.

(1978) for photovoltaic systems is shown in figure 3. As solar cell costs fall, greater use of solar electricity will become directly dependent on storage costs, making cheap, long-life storage batteries and fuel cells essential for power generation by this method.

3. Electrochemical energy storage and conversion

Various electrochemical systems currently considered for energy storage and conversion are indicated together with their merits and demerits in the following sections.

3.1 Storage batteries

Batteries store a fixed amount of chemical energy and secondary (rechargeable or storage) batteries can be recharged when the built-in active chemicals have been exhausted. At present several types of storage batteries are available which differ in their design, in particular, in the choice of electrodes, the electrolyte and operating temperatures. These characteristics create substantial differences in the performance, life-time and cost of the systems. In the following, scientific and technical aspects of several competitive storage battery systems are highlighted to assess their viability for projected energy storage applications.

3.1a *The lead-acid system:* Of all the commercial accumulator types currently available, only the industrial lead-acid battery seems to be an attractive prospect. It is, however, imperative that its cost be decreased and the life-time expectancy improved. There also exists the problem of limited lead resources which cannot be neglected in spite of the possibility of lead recycling. The known world lead reserves amount to

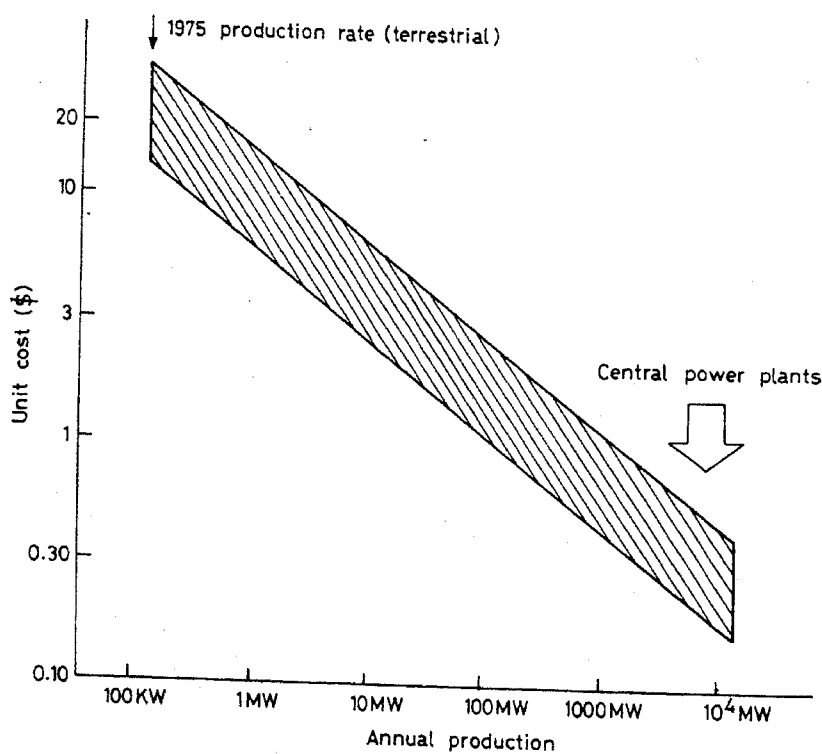


Figure 3. Projected learning curve for photovoltaic systems.

1.41×10^8 tons at an annual production rate of 4.07×10^6 tons of which approximately 40% is used in accumulator production (Reed 1975). Major non-stationary applications of lead-acid batteries are: (a) starting, lighting and ignition (SLI) for ICE systems and (b) traction for in-plant vehicles. A new application of lead-acid batteries requiring considerable storage capacities for electrical energy will obviously have a large adverse impact on the other industries requiring lead such as cable-sheaths, nuclear applications etc.

3.1b Alkaline storage batteries: Alkaline storage batteries which could be considered as candidates for storage applications are: nickel-iron, nickel-zinc and iron-air systems. Other alkaline systems such as nickel-cadmium, silver-zinc and nickel-hydrogen employ materials or construction methods that are too expensive to find applications in commercial energy storage.

Nickel-iron and nickel-zinc are major competitors to lead-acid and are being developed by a number of countries throughout the world. The major advantage of these systems is increased energy density (nickel-iron ~ 60 wh/kg and nickel-zinc ~ 70 wh/kg) compared to the present day lead-acid batteries (20–25 wh/kg).

Nickel-iron batteries are available for some 80 years and have been employed for traction applications in mine locomotives particularly in Europe. They have the advantage of a very long cycle life (typically about 3000 cycles) even under adverse conditions such as overcharge, over discharge, charge-stand, discharge-stand or poor maintenance. However, the battery system suffers from a poor peaking capability, low-cell voltage (necessitating more cells for a given battery voltage), the low-hydrogen overvoltage of the iron-electrode causing self-discharge and low-cell efficiency (typically about 50%). The present research and development efforts are mainly aimed at: (a) increasing energy density and current capability through improvements in the design of the iron electrode, (b) decreasing cost by improving materials utilization in the traditional sintered nickel electrode or by developing pasted type nickel electrodes, and (c) improving the energy efficiency. Recent developments in the Japanese and Swedish systems are fast placing this battery on par with other accumulators. At present, nickel-iron batteries are about twice as expensive as their lead-acid counterparts. Compared to the nickel-iron system, the nickel-zinc system has the advantages of greater energy density and higher energy efficiency (typically $\sim 75\%$). However, there is the serious problem of short life-times of nickel-zinc batteries resulting from dendritic growth, space charge and densification of the zinc electrode; reported cycle lives for nickel-zinc batteries cover a wide range between 20 and 500.

Iron-air rechargeable batteries which can use virtually inexhaustible raw materials (Reed 1975) and can provide long charge-discharge life under low maintenance conditions seem to be quite promising energy storage systems. Although functional iron-air batteries have been designed and tested, the system is not a front runner at the present time. The energy per unit weight is certainly satisfactory but the volumetric energy density is comparatively low as the required auxiliary systems are bulky. The overall efficiency is poor due to polarization at the air-electrode. Work on this system is continuing mainly in US, Japan and Europe (Blurton and Sammell 1979; Bursell 1981; Özefors and Carlsson 1977, 1978; Takahashi 1979). The system is in an advanced stage of its development with prototype units from pilot plants undergoing field trials.

3.1c Solid-state batteries: (a) *The high-temperature systems:* Among these systems the high-temperature solid electrolyte batteries are notable. The electrochemical strategy

underlying the development of these batteries is the minimization of irreversible losses arising from the high resistances in traditional battery systems. The reduction of internal resistances will assist in attaining high reaction rates and good transport conditions. One way to reduce these resistances in the battery systems would be to operate them at high temperatures. This necessitates the use of ceramic materials having suitably high specific conductivity for ions which can take part in electrochemical processes. The development of such materials, called solid electrolytes, has contributed to a breakthrough in electrochemical energy storage and conversion. With these systems molten states of either the electrodes or the electrolyte would be desirable to avoid interfacial contact resistances. However, in an all solid-state cell, such a problem would be inevitable.

Among the battery systems which employ this concept, sodium-sulphur cells with β -alumina as the solid electrolyte and lithium-sulphur cells with molten salt electrolytes are promising candidates. These battery systems provide attractive energy densities and high charge-discharge performances. Nevertheless, in spite of considerable expenditure incurred over the last decade, no sodium-sulphur or lithium-sulphur battery system has yet come into production and doubts prevail whether such a product would ever be feasible. At present, several potential, technical and scientific hurdles remain. These are: electrolyte optimization (conductivity/composition/strength), electrolyte breakdown, undercharge containment, safety aspects of molten sodium and lithium electrodes and separators.

(b) *The low-temperature systems:* It is desirable to develop inherently safe and low-cost solid electrolyte systems if solid-state batteries are to find commercial viability. Results of alternative battery concepts indicate that such improvements may be possible and particular interest attaches to ambient temperature organic electrolyte batteries using solid-solution insertion electrodes and all solid-state batteries involving composite electrolytes or hybrid polymer electrolytes.

Work on advanced battery materials has been continuing for the last few years and various solid electrolytes such as Nasicon ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$), Li_3N , zeolites and several others have been investigated. These batteries would avoid the intrinsic problems of aqueous-state systems such as corrosion, electrode and electrolyte containment, electrode structural changes and shedding on cycling. However, as indicated earlier, solid-state systems introduce the problems of maintaining effective interfacial contact between solids which may change during operation and have different coefficients of expansion. Such systems appear to be limited to quite low current densities. One proposed solution is to increase the surface area considerably by the application of very thin laminated paper technology wherein one side of the solid electrolyte paper is coated with the positive electrode and other side with the negative. The strip is then rolled to form the battery. Such a system under consideration at present at Mallory, USA, is the Li/Li-titanate/intercalation compound (such as TiS_2).

It appears therefore that solid-state systems are still in initial stages of development. At this stage, it is rather difficult to present a justified picture of their commercial viability and they may at most be considered as futuristic energy systems.

3.2 Fuel-electrolysis cells

A concept strongly considered for the projected energy storage and retrieval application is the fuel-electrolysis cell hybrid system. Fuel cells, which are distinguished

from the secondary batteries by their external fuel store, date back even further than the lead-acid battery. Though the first hydrogen-oxygen fuel cell was demonstrated as early as 1839 by W R Grove, most of fuel cell development has taken place in the last 30 years and the major application has been in the space industry. The fuel can be generated from electrical energy, which could be derived from a solar cell panel, by electrolysis†. The electrolysis cell operates in the direction opposite to that of a fuel cell. Akin to a storage battery, in a fuel-electrolysis cell hybrid system, the fuel tank is loaded with fuel during electrolysis and is emptied when the electrical energy is retrieved from the fuel cells.

A simple analysis (Cha 1974) shows that perhaps the most promising fuel cell system for distributed applications on a wide scale is the ambient temperature hydrogen-oxygen fuel cell using an aqueous electrolyte*. Other aqueous-electrolyte fuel cells such as ammonia-air and methanol-air have also been projected as attractive systems (Kordesch and Tomantschger 1980); the problems with these systems are the difficulties in finding materials which are electrocatalytically active at low temperatures. The regenerative hydrogen-oxygen fuel cell is particularly fascinating owing to its simple concept. In addition large volumes of hydrogen and oxygen gases can be stored in underground caverns and the technology in the field of electrolysis and hydrogen-oxygen fuel cells is quite advanced. However, the economics of operation are not yet satisfactory mainly due to the need for noble metal electrocatalysts on the electrodes. Fuel cell electrodes have undergone a virtual explosion of research and development in recent times. Beginning with the space programme of the sixties and followed by the energy related problems of the seventies, we have seen a truly substantial improvement in fuel cell electrode technology. From the pure platinum black structures of the early seventies to the carbon and graphite support catalysts of the present, the yield of power per unit weight of the catalyst has increased several fold. The controlled structure of the hydrophobic binder and catalyst on the electrode for producing a gas-liquid-solid interface has shown that electrochemical reaction rates may some day approach those of direct combustion. More and more research should be directed to the development of inexpensive electrocatalysts for electrodes based on carbon or titanium sustaining the reactions of anodic-oxidation of hydrogen and cathodic-reduction of oxygen. During the last few years, several metallic transition-metal oxides have also been employed as oxygen-evolution and oxygen-reduction electrodes (Horowitz *et al* 1979; Trasatti 1980/81). If successful, the fuel-electrolysis cell hybrids will receive wide acceptance. Indeed, the concept is highly beneficial from both, energy and environmental, viewpoints because of the high efficiency (due to the absence of thermodynamic limitations) and to the fact that the reaction products consist mainly of water.

Though preliminary work on fuel cell systems was initiated by Francis T. Bacon at Cambridge in UK, no support was offered either from the governmental agencies or British industry to raise the concept to commercial status (Bacon 1979, 1981). The result

† Photoelectrolysis is another possibility of electrolysing water through solar radiation. Photoelectrochemical cells are in initial stages of conceptual and laboratory development. The prospects for widespread application of photoelectrochemical cells in the future are meagre due to poor spectral response, high capitals, several modes of corrosion, poor electrolysis and high running costs.

* High-temperature fuel cells are also known which do not require any electrocatalyst because of thermal activation of the electrode reaction. However, these are unsuitable for distributed applications of the nature projected here.

was that work on fuel cells at Cambridge ended with the retirement of Francis T. Bacon. Research on fuel-electrolysis electrodes has just been identified as an especially significant area by a working party of the SERC energy committee of UK (1983). The United Technologies in US has been the only company continuously engaged in fuel cell research with financial help from the American gas and electric utility companies. Under the TARGET-programme (Team to Advance Research for Gas Energy Transformations) power plants with power outputs ranging between 2.5kW and 1MW have been successfully developed. A 1 MW fuel cell plant developed under this programme is shown in figure 4. At present two large scale 5 MW demonstration plants are being checked and are scheduled to start producing power in 1983—one at Consolidated Edison Company, New York (scheduled to start this spring) and the other at Tokyo Power Company. It is estimated that by 1986, the first commercial prototype unit should be available (Parkinson 1983). In Europe, attention has been mainly focussed on the development of fuel cell powered vehicles (see figure 5). The concept is based on lead-acid/hydrogen-air fuel cell hybrids with hydrogen stored as compressed gas. This is said to be an outstanding piece of work but the search for a novel and greatly improved method of hydrogen storage seems imperative for a commercial endeavour; metal hydrides are too heavy and expensive for general use. Dissolved-redox-flow (DRF) accumulators have also been considered for large energy storage (Beccu and Crepsy 1976). A single cell DRF-accumulator is shown schematically in figure 6. Various redox couples such as Ti, Cr, Fe and V have been examined in



Figure 4. 1 MW fuel cell plant built under the TARGET-Program.

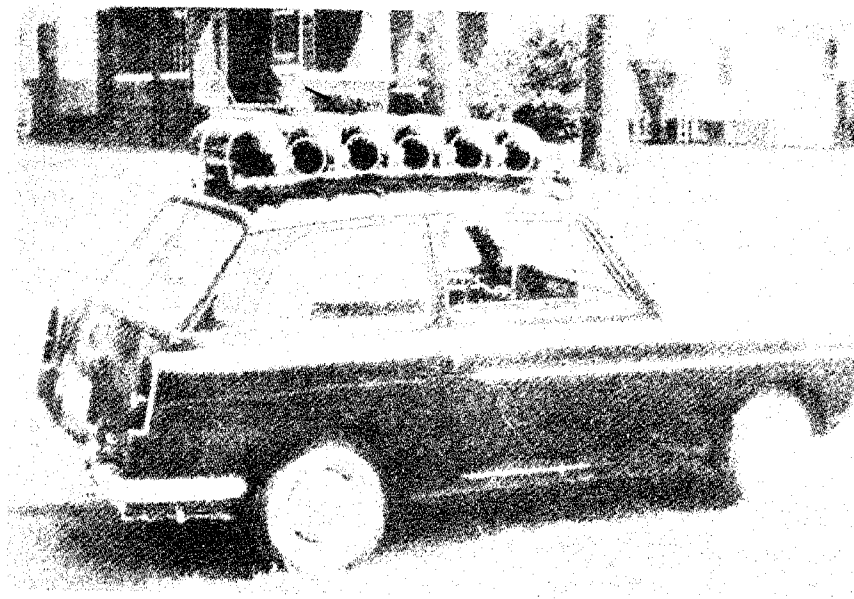


Figure 5. An automobile propelled by hydrogen-air fuel cell.

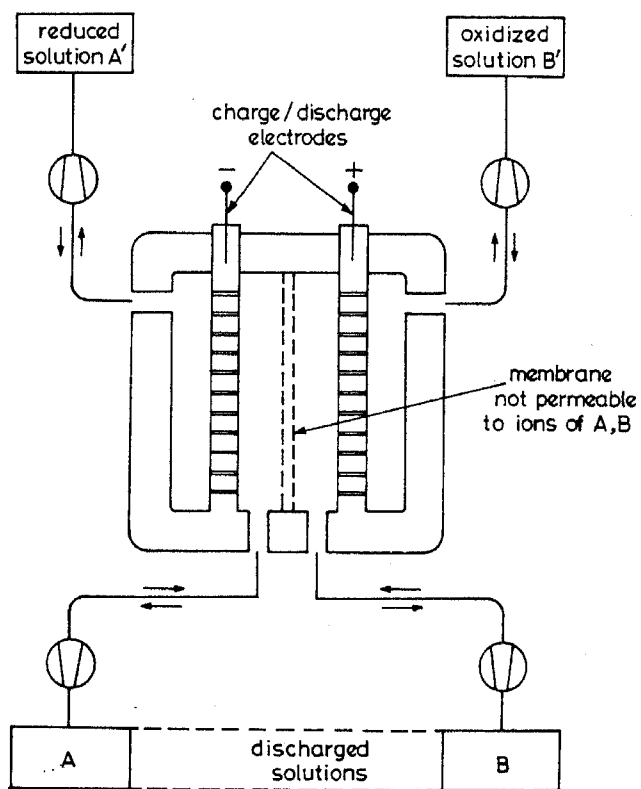


Figure 6. A single cell DRF-accumulator.

the past but often from a rather academic viewpoint that focusses on problems which are less significant for large-scale energy storage.

As it stands today, the overall viability of fuel cells is no more in doubt. They do function but problems of cost and longevity remain. However, such problems are present in all emerging energy technologies.

4. Conclusion

It appears that in the near future it will be possible to develop low-cost solar cells which can be plugged with appropriate storage batteries or fuel-electrolysis cell hybrids to store and retrieve electrical energy. This has been possible after significant engineering research and investment. However, several technical and scientific hurdles still exist; interactions between several scientific disciplines including ceramics, solid-state chemistry, electrochemistry, metallurgy and engineering seem imperative to overcome these.

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