# 2 Developments in PEC

2.1 WORLD ENERGY OUTLOOK

It is interesting to watch the growing debate over the future of energy in global platforms. Ever soaring oil prices and increasing energy demands accelerated environmental, ecological and global climate changing problems. The challenges in energy security, environmental security, national security, and economic security can be met by addressing the energy demands in a sustainable fashion, not only through increased energy efficiency, and by introducing new methods of using the existing carbon-based fuel sources, but by haunting for new carbon-neutral energy. We are now witnessing the beginning of a global paradigm shift toward clean energy. The search for alternative energy is set. The finding of secure, clean, sustainable energy is an inevitable issue faced by the scientific, technological and policy making communities.

Alternative energy can generally be classified into two categories. The first one is to looking for substitutes to the excising petroleum - liquids such as ethanol, biodiesel, biobutanol, dimethyl ether, coal-to-liquids, tar sands, oil shale - from biomass and/or fossil feed stock. The second one is to look for alternatives to the generation of electric power and power-storage technologies - wind, solar, photovoltaics, solar thermal, tidal, biomass, fuel cells, batteries. In the decades ahead, the world will need to expand energy supplies in safe, secure, affordable and environmentally responsible ways.

What can we foresee for the next 25-30 years? The answer to this question may vary by region, based on diverse economic and demographic trends, evolution of technologies and energy policies set by governments. The growth in primary energy demand is shown in Figure 2.1. It can be seen that the global energy demand increases by one-third from 2010 to 2035, with India and China accounting for 50% of the growth. In the countries belonging to the Organization for Economic Cooperation and Development (OECD), including North America and Europe, we see that the energy usage appears to remain flat, even as these countries achieve economic growth and higher living standards. In contrast, Non-OECD energy demand will surge by close to 50%. China's

demand for energy will extend over the next two decades and then gradually flatten as its economy and population mature.
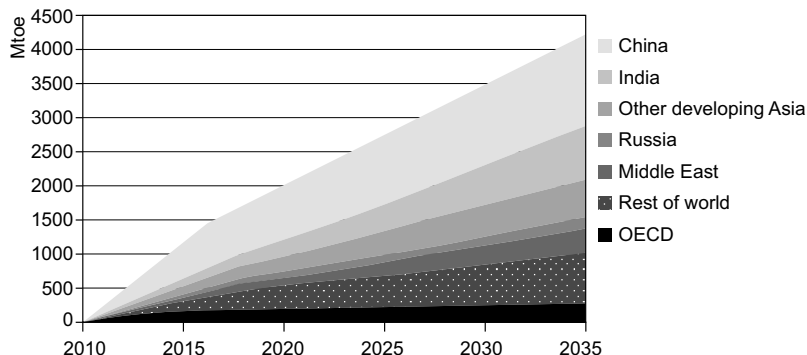
Figure 2.1   *Growth in primary energy demand [Source:World Energy Outlook 2012, by International Energy Agency].*

In order to shift concerns about oil security, changing scenario in oil net imports are set, as shown in Figure 2.2. The United States oil imports drop due to rising domestic output and improving transport efficiency; the European Union oil imports overtake those of the US around 2015; China becomes the largest importer around 2020. As new technologies and sources emerge, we witness that the energy has been used more efficiently with diverse energy supplies.
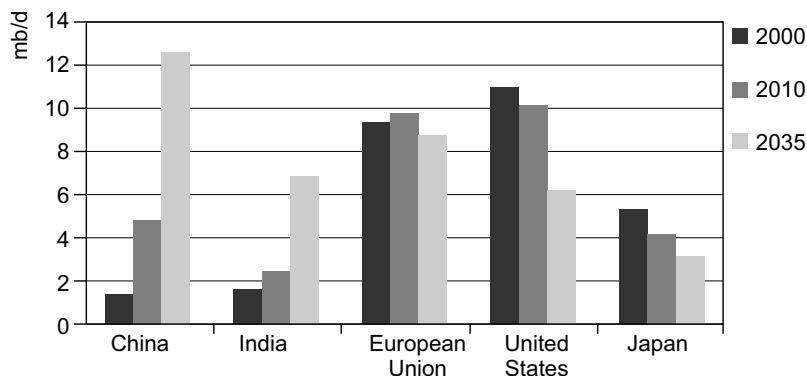
Figure 2.2   *Net imports of oil [Source:World Energy Outlook 2012, by International Energy Agency].*

Population and income growth (gross domestic product, GDP) are the two most powerful driving forces besetting energy demands. It can be evidenced from the following data (Figure 2.3). Since 1900, world population has more than quadrupled, real income has grown by a factor of 25, and primary energy consumption by a factor of 22.5. The next two decades are likely to see

continued global integration, and rapid growth of low and medium income economies. Population growth is appear to trending down, but income growth is treading up. In the past two decades, the world population has increased by 1.6 billion, and it is projected to increase by 1.4 billion in the coming 20 years. At the outset, in the global level, the fundamental relationship in energy economics remains robust, as more people with more income means that the production and consumption of energy will hike.
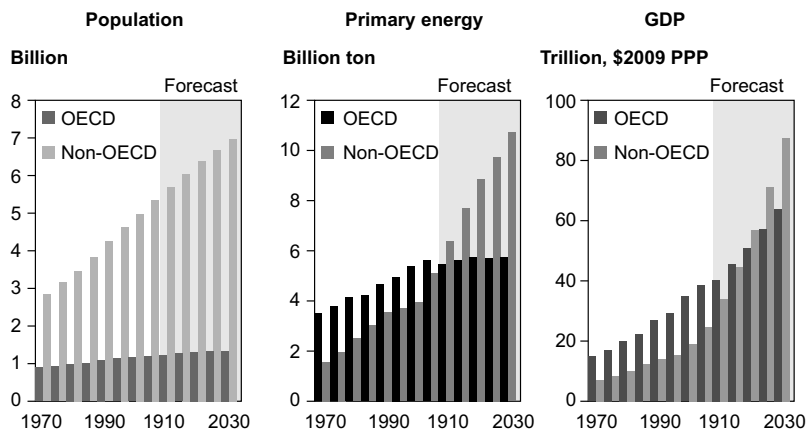

Figure 2.3   *Population, income growth and primary energy usage [Source: BP Statistical Review of World Energy, London, UK, 2011].*

The energy consumption and the fuel mix are shown in Figure 2.4. The first wave of industrialization was based almost entirely on a truly disruptive technology, the steam engine and on coal. Coal remained as a dominant fuel until after World War II. The next major transition came with electricity and the internal combustion engine, which enabled diversification away from coal. Oil replaced coal usage, in transport. While coal remains as the principal fuel in power generation, it is gradually being replaced first by natural gas and now by renewable.

Figure 2.4. (a) World commercial energy use (b) Contribution to total energy growth [Source: BP Statistical Review of World Energy, London, UK, 2011] The global energy consumption is projected to increase, in spite of substantial declines in energy intensity, at least two-fold by midcentury relative to the present, because of population and economic growth. Several sources indicate that there are ample fossil energy reserves, in some form or other, to supply this energy at tolerable cost. The World Energy Assessment Report estimates of the total reserves, and of global resource base including both conventional and non-conventional sources, based on 1998 consumption rates. We deliberately provide the decade old data, so as to provide a chance for us to examine with the present day trends with the projected data, and we find that the historical
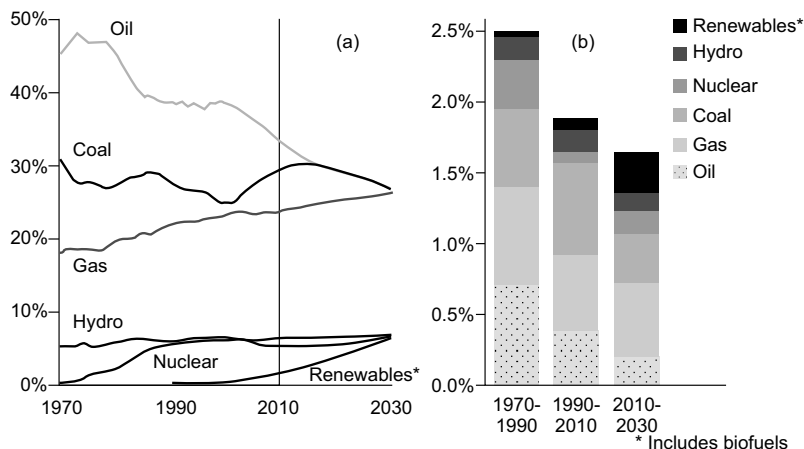
Figure 2.4   *(a) World commercial energy use (b) Contribution to total energy growth [Source: BP Statistical Review of World Energy, London, UK, 2011].*

energy data is compatible with the projected data. Accordingly, 40-80 years of proven conventional and unconventional oil reserves exist globally in our planet, and 50-150 years of oil are available if the estimated resource base is included. 60-160 years of reserves of natural gas are present, and between 207-590 years of gas resources, excluding the natural gas potentially available in the form of methane clathrates at the continental shelves, which are in the estimated resource base. A 1000-2000 years supply of coal, shales, and tar sands are in the estimated resource base. Therefore, the estimated fossil energy resources could support a 25-30 TW energy consumption rate globally for at least several centuries [1]. However, consumption of fossil energy at that rate will result in catastrophic global issues. Historical trend reveals that the mean carbon intensity i.e., the kg of C emitted to the atmosphere as CO_2 per year per W of power produced from the fuel, in the global energy mix is declining. This is because, in the past two centuries, the energy mix has shifted from being dominated by wood to coal to oil and now more to natural gas. Such a shift has produce a decrease in the average carbon intensity of the energy mix, since oil and gas have higher H/C ratios, and hence upon combustion yield more water and less CO2 per unit of heat released than the coal. The following Figure 2.5, indicate that gas and renewable win in the fuel share coverage, and the energy supply mix diversifies.

It can be seen that oil continues to suffer a long run decline, while gas steadily gains in the market share. Coal's recent gains in market share due to rapid industrialization in China and India are reserved by 2030. The diversifying fuel mix can be seen most clearly in terms of contributions to
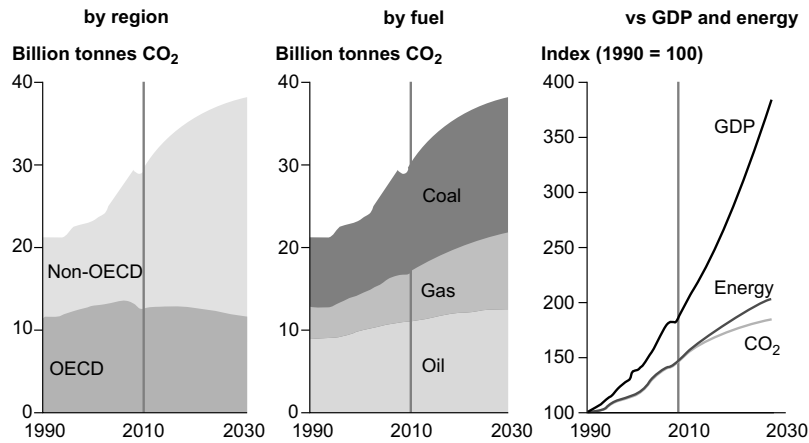
Figure 2.5   *(a) Shares of world primary energy (b) Energy sources contribution to growth [Source: BP Statistical Review of World Energy, London, UK, 2011].*

growth. Over the period 1990-2010, fossil fuels contributed 83% percent of the growth in energy; over the coming 20 years, fossil fuels contribute 64% of the growth. Piecing together, the contribution of all non-fossil fuels to growth the next 20 years (36%) is, for the first time, larger than that of any single fossil fuel. Renewables including biofuels account for 18% of the growth in energy to 2030. The rate at which renewables penetrate the global energy market is similar to the emergence of nuclear power in the 1970s and 1980s. For many centuries, CO_2 emissions are building up in the atmosphere. The CO_2 equilibrates on an approximately 10 to 30 years timescale between the atmosphere and the near surface layer of the ocean [2], which accounts for the reason why only 50% of the anthropogenic CO_2 emissions remain in the atmosphere, and the remainder partitioning into the biosphere and the oceans. Since there are no destruction mechanisms of CO_2 in the atmosphere, the long-term removal of CO_2 must occur by convection. The time required for the relevant mixing between the near surface ocean layer and the deep ocean is between 400 to several thousand years [2, 3]. Therefore, in the absence of geoengineering or active intervention, whatever environmental effects might be caused by the atmospheric CO_2 accumulation over the next five decades will persist globally for the next 500 to 2000 years or more. Though the precise future effects of such anthropogenic CO_2 emission are uncertain, the emission levels are viewed with caution in historical prospective. The data from Vostok ice core indicate that the atmospheric CO_2 concentration has been between 210 and 300ppm for the 420, 000 years [4], and a later study of Dome Concordia ice cores have extended this time line to 650, 000 years [5]. The CO_2 concentrations in the past five decades have been rising due to anthropogenic

CO_2 emissions from fossil fuel consumption, and now they are exceeding 380 ppm. Figure 2.6 depicts the global CO_2 emission from energy use.
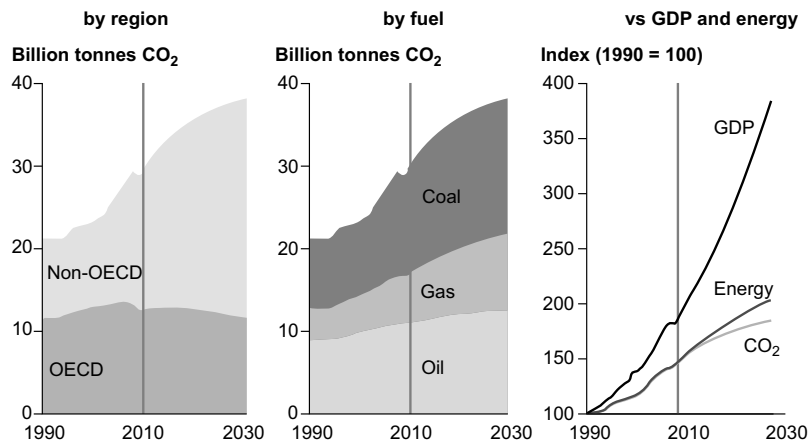
Figure 2.6   *Global CO_2 emission [Source: BP Statistical Review of World Energy, London, UK, 2011].*

Strong growth in non-OECD energy consumption, particularly of coal translates into continued growth of global CO_2 emissions. The growth of global CO_2 emissions from energy averages 1.2% per annum over the next two decades, compared to 1.9% per annum, in the years 1900-2010, leaving the emissions in 2030, 27% higher than in the present days. Even with the implementation of carbon abatement policies in the OECD, the levels of CO_2 can only be reduced to an extent of 10% in 2030. Non-OECD emissions may grow by 2.2% per annum on average, up 53% by 2030. The energy policies in non-OECD countries focus on reducing the carbon intensity of economic growth. Carbon per unit of GDP falls by 42% in 2030, and the rate of fall accelerates steadily. By 2020-30, non-OECD emissions are growing by 1.3% per annum, compared to 5.2% per annum growth over 2000-2010. Cumulatively, this trend implies some progress towards climate change goals, but enough to put the planet on a path to stabilization at 450 ppm. The only way by which we can reduce the mean carbon intensity is by adapting to carbon-free power. Three general options are available to produce such daunting amount of carbon-neutral power. Nuclear fission is one method, but it would require widespread implementation of breeder reactors. The estimated terrestrial uranium sources are sufficient to produce nearly 100 TW-per year electricity using conventional once-through uranium reactor technology. Hence, if 10 TW of power were obtained from conventional nuclear fission, the terrestrial uranium resource would be exhausted in less than a decade. Moreover, the construction of nuclear power plant would need to proceed at a very rapid rate by historical standards - 1 gigawatt electric power plant every 1.6 days for the

next 45 years. The international thermonuclear experimental reactor (ITER) - magnetic confinement fusion experiment is scheduled to demonstrate an energy breakdown point in 35 years, for a few minutes of operational time. Though the fusion might possibly provide a credible option to the amount of carbon-neutral energy production, the ITER time line is too far in the future to meet any reasonable atmospheric CO_2 concentration target in the next 5 decades. The second approach comprises the carbon capture and storage. In this approach, the CO_2 is dissolved in underground aquifers. To make this technology viable, the CO_2 must not leak at a globally averaged rate of 1% in a time scale for centuries. If not, the emitted flux will be greater than that intended to be mitigated initially. Realizable experiments at scale are needed, along with extensive modeling, monitoring, and validation, to ascertain >99% confidence that the leak rate will be low for 500-1000 years. Caution must be exercised to the fact that each reservoir is geologically different and hence the proof that one sequestration works technically at one may not be considered as a general proof to the process at a global level. The global reservoir capacity has been estimated to be equivalent to 100-150 years of carbon emissions. Therefore, sequestration could buy time, if it works technically well and is so validated within the next 2-3 decades. An additional requirement is that the energy distribution and end-use chain must be transformed to handle massive quantities of carbon-free fuels such as hydrogen or electricity on the required time-scale to mitigate carbon emissions. The third approach is to employ renewable energy. Among various renewable energy sources, the largest resource is provided by the sun. If solar energy is to become a practical alternative to fossil fuels, we must have ways to convert photons into electricity, fuel and heat.

2.2   RADIATION AS A RENEWABLE SOURCE

Naturally, the sun has always held the attention of humanity and been the subject of worship by many cultures over the millennia, such as Egyptians, Incans, Greeks, Indians, and Mayans among many others. The sun provides enormous amount of energy to our planet earth, sufficient to power the great oceanic and atmospheric currents, the cycle of evaporation and condensation that brings fresh water inland and drives rivers flow, and typhoons, tornadoes and hurricanes that so easily destroy the natural and men-made landscape. Solar energy is energy force that sustains life on earth for all plants, animals and people. It offers a compelling solution to all societies to meet their needs for clean, abundant sources of energy in the future. The source of solar energy is the nuclear interactions at the core of the sun, from in where the energy originates by the conversion of hydrogen into helium. The amount of energy from sunlight strikes the earth in one hour is 4.3 x 10^{20} J, which is greater

than all of the energy currently consumed on the planet in one year (4.1 x 10^{20} J). Earths ultimate recoverable resource of oil, estimated at 3 trillion barrels, contains 1.7 x 10^{22} J of energy, which the sun supplies to earth in 1.5 days. The staggering power that the sun continuously delivers to earth, 1.2 x 10^5 terawatts, dwarfs every other energy source, renewable or non-renewable. Sunlight is readily available, secure from geopolitical tensions, and poses no threat to our environment and our global climate systems from pollutants emissions. Although the solar energy source is inexhaustible and free, it is not the most convenient energy source because it is not constant during the day and not readily dispatched. However, there are ways to overcome these shortfalls. The vast supply of solar energy is complemented by its versatility, as depicted in Figure 2.7. Sunlight can be converted into electricity by exciting electrons in a solar cell. It can yield chemical fuel via natural photosynthesis in green plants or artificial photosynthesis in human-engineered systems. Either concentrated or unconcentrated sunlight can produce heat for direct use or further conversion to electricity. In general, solar energy utilization requires (a) solar energy capture and conversion and (b) storage.
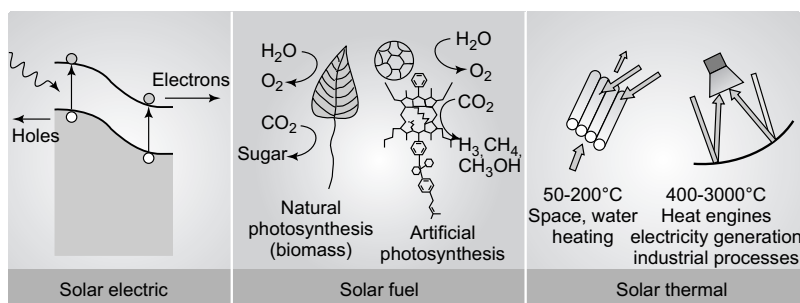
Figure 2.7   *Solar photons convert naturally into three forms of energy electricity, chemical fuel, and heat [6].*

Solar capture and conversion can be accomplished by photovoltaics (PV). The challenge here is to dramatically lowering the cost per W of delivered solar electricity. Solar cells capture photons by exciting electrons across the bandgap of a semiconductor, which creates electron-hole pair that are then charge separated, by typical p-n junctions introduced by doping. The space charge at the p-n junction interface drives electrons in one direction and holes in the other, which results in a potential difference equal to the band at the external electrodes gap as shown in the first picture in Figure 2.7. The principle and device are similar to a semiconductor diode, except that electrons and holes are introduced into the junction by photon excitation and are removed at the electrodes. Compared to fossil sources, solar energy is diffuse, and therefore material cost must be inexpensive to realize a solar-based power source. In

the absence of cost-effective storage, solar electricity can never be a primary energy source, because of diurnal variation in local insolation. In principle, storage in a battery is possible, but at present no battery is inexpensive enough, when amortized over the 30 year lifetime of a solar device, to satisfy the needed cost per W targets for the whole system. A second option is to store the electrical energy mechanically. For example, electricity could be used to drive turbines to pump water uphill. This method is relatively cheaper for storing large quantity of energy at modest charge and discharge rates, but is not well suited to being charged and discharged every 24 hours to compensate for the diurnal cycle. For instance, buffering a day/night cycle in the US energy demand by this route would require a pumping capacity equivalent to> 5, 000 Hover dams, filling and emptying reservoirs every 24 hours. Presently, the cheapest method of solar energy capture, conversion and storage is solar thermal technology, which costs about \$0.10 0.15 per kW-hr for electricity production. Advancement in this important technology will require new materials for the harvesting, as well as advancements in thermochemical cycles for solar energy. A third approach for storage is to mimic the design of nature, in which chemical bonds are cleaved and formed to produce solar fuels in an artificial photosynthesis process. Natural photosynthesis itself is inefficient, when scaled on a yearly average basis per unit area of insolation. For instance, one of the fastest growing crops, switch-grass yields energy stored in a biomass at a yearly averaged rate of ¡1 W m^{-2} [1]. Whereas the biofuels derived from existing plants could provide a notable contribution to liquid fuels for transportation. One viable proposition is to develop artificial photosynthetic process with an average efficiency significantly higher than plats or algae. The primary steps in photosynthesis involve the conversion of sunlight into a wireless current. In all cases, to form a useful fuel, O_2 must evolve and it can be released into our oxygen-rich atmosphere, and used elsewhere as an oxidizing agent for fuel consumption. The reduced fuel could either be hydrogen from water reduction, or it could be an organic species, such as methane or methanol, which is derived from the fixation of atmospheric CO_2. Recombination of the reduced fuel with the released O_2 would then regenerate the original species, completing the cycle in a carbon-neutral fashion. In natural photosynthesis, the anodic charge of the wireless current is used at the oxygen-evolving complex to oxidize water to oxygen with the concomitant release of four protons. The cathodic charge of the wireless current is captured by photosystem to reduce the protons to hydrogen, with the reduced hydrogen equivalents stored through the conversion of NADP to NADPH. Thereby, the overall primary events of photosynthesis store sunlight through the rearrangement of the chemical bonds of water, to form oxygen and natures form of hydrogen. In essence, the sun has a unique role in sustainable energy production, as it is an undisputed champion

of energy. From the materials points of view, chemistry will assume a prime role for solar energy capture, conversion and storage, because new catalysts are required for the desired chemical bond conversions.

2.3   SCOPE OF PHOTOELECTROCHEMITRY (PEC)

A number of authors have provided definitions for photoelectrochemistry (PEC). Kuwana [7] defined it as follows:

(a) Introduction of photo-excitation into the electrochemical system
(b) Creation of the excited state through the electrochemical process

Kenichi Honda [8] defined as: (a) Reaction at the electrode in excited state: (i) Excitation of the electrode (metal or semiconductor); (ii) Excitation of substances (adsorbed molecules, etc.,) at the interface between the electrode and solution; (iii) Excitation of reactive species in a solution. (b) Generation of electronically excited state by electrode reaction: (c) Combination of photochemical and electrode reactions; (d) Alternate generation of photochemical and electrode reaction: In this section, we set to discuss on introduction of photo-excitation into the electrochemical system as described above. We classify our discussion based on the following three perspectives according to the region at which the electronically excited state is formed during the photo-irradiation in the electrochemical system. The light irradiation mode can be: 1. electrode (e.g., photocatalysis, water decomposition); 2.interfacial layer (e.g., dye sensitization); 3. bulk solution (e.g., photogalvanic cell). Figure 2.8, is a schematic sketch of these three modes.
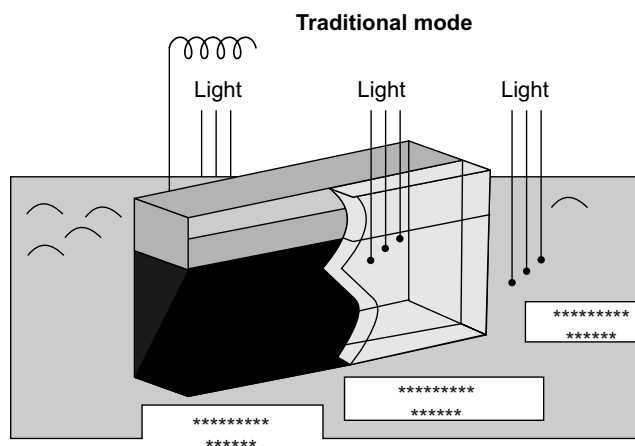
Figure 2.8   *Irradiation mode of the electrochemical system [9].*

2.3.1 Historical Sketch

Becquerl Effect   The French scientist Edmond Becquerel immersed two different metal electrodes such as platinum, gold, silver, brass and silver coated with silver halogenide on the surface into the acidic, neutral and alkaline electrolyte solutions. By exposing one of the electrodes to sunlight, he found that electric current flows through the external circuit between two electrodes. The current was very small, as the pointer in the galvanometr moved only to several degrees. At the age of 18, Becquerel reported this effect at Academy in Paris in 1839 [10]. His study was considered as the first paper in photoelectrochemistry, and this phenomenon is named as Becquerel effect. Figure 2.9, illustrates Becquerel experiment. This invention, opened up a new branch namely photoelectrochemistry in the field of electrochemistry. The era of 1950s, witnessed a tremendous escalation in the research activities of semiconductor materials, in both electrochemistry and photoelectochemistry fields in the aspects of fundamental and applied research.
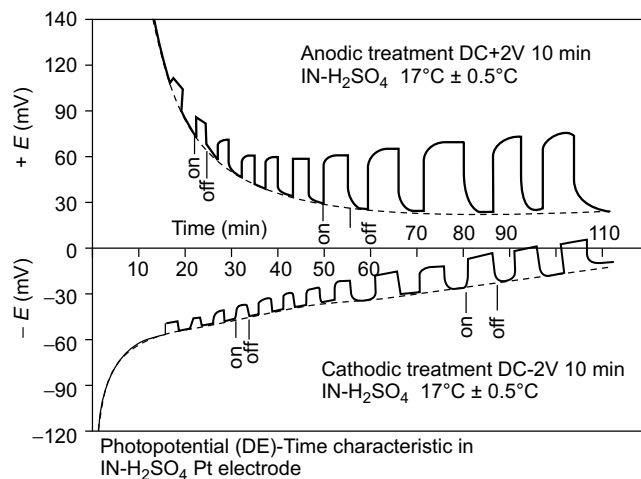
Galvanometer
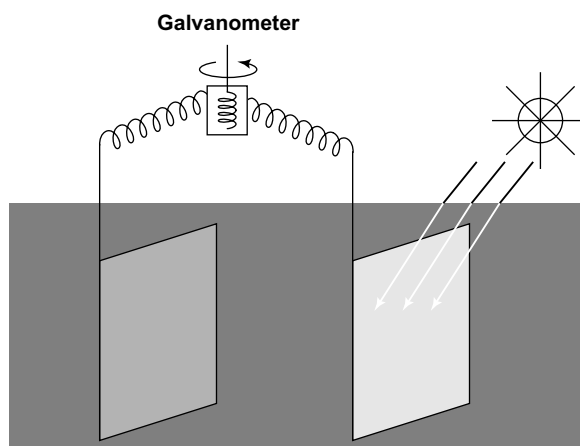
Electrode: Pt, An, Ag, Brass,
and Ag coated with AgI, AgBr, and AgCl

Solution: acid, neutral, basic

Figure 2.9   *Diagrammatic representation of Becquerels experiment (1839) [9].*

Although photoelectrochemistry continued to draw attention in 1950s through 1960s, no attempts were to reexamine Becquerels research in quantitative perspective. In 1966, Honda carried out research by immersing two smooth platinum sheet electrodes in sulfuric acid solution, irradiating one of the electrodes with high pressure mercury lamp, and measured the photovoltaic effect, as shown in Figure 2.10 [11]. Simply by tuning the light on and off, the photovoltaic changes of several 10 mV were found.

Figure 2.10 shows the Photopotential (DE)-Time characteristic in IN-H_2SO_4 Pt electrode, with an upper region for Anodic treatment DC+2V 10 min IN-H_2SO_4 17°C ± 0.5°C and lower region for Cathodic treatment DC-2V 10 min IN-H_2SO_4 17°C ± 0.5°C.

Figure 2.10   *Effect of light irradiation at platinum electrode [11].*

Excitation of the Solution   The dawn of the twentieth century witnessed a spurt of research activities on photoelectrochemical and electrochemical studies, by irradiating the electrolyte solution as depicted in Figure 2.8, and such phenomenon is named as Swensson-Becquerel effect. This is an example of photogalvanic system, involving photochemistry and electrochemistry in subsequent steps as follows.

Photochemistry: $A^* + D \rightarrow (h\nu) A + D +$ First cell
Electrochemistry: $A \rightarrow A + e$
Ground state electrochemistry: $D^+ + e \rightarrow D$ Second cell

In these systems, the products of the photochemical reaction in the first cell return to their initial states via the conventional reverse electrochemical reactions in the first and the second cells, generating current. This system stands for the conversion of light energy to electrical energy. The study of Rabinowitch using thionine and Fe^{2+} is well known [12]. In order to realize a practical application, the reactants are to be completely recycled for harvesting light energy. Examples of this kind include the studies of Goldmann [13], Baur [14], Iimori [15], Rabinowitch [16] and Eisenberg and Silvermann [17].

Excitation of Electrode   Both metal and semiconductor electrodes are generally employed, and the following diagram (Figure 2.11) depicts the photo-process in these two types of electrodes.

The discharge of photoelectrons from metal is a known physical phenomenon. In 1960s, especially in the field of polarography with droping mercury electrodes, generation of photocurrent through light irradiation on
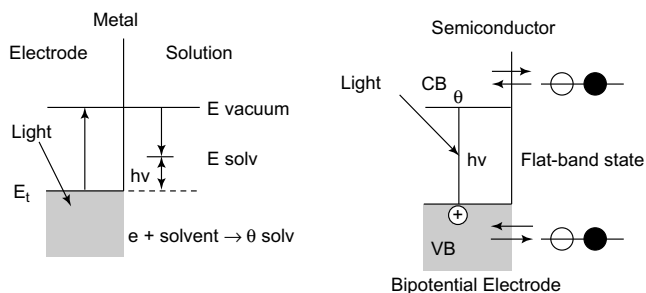
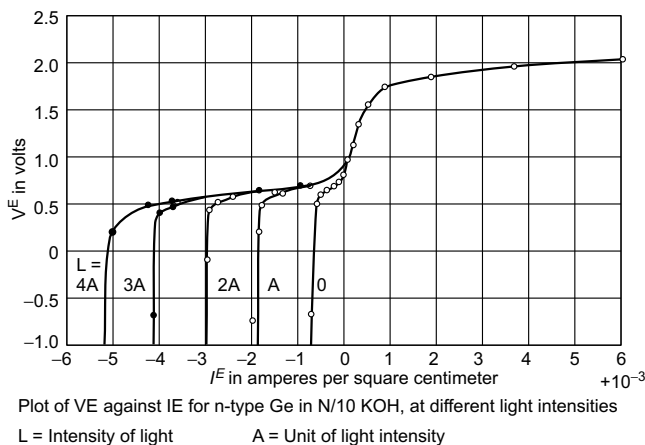**Figure 2.11**   *Excitation of electrode [9].*

electrodes in immersed in electrolyte solution started to appear. Though several theories on the mechanism are proposed, it is understood through experiments in the present days that the difference between the work function E_f of the metal electrode and the salvation energy of the electrode Esol corresponds to the photoenergy required to generate photocurrent. Examples of this kind, where metal electrodes are employed, include the studies of Berg et al., [18], Heyrovsky [19], and Brodsky and Pleskov [20] in the years 1967, 1963 and 1972 respectively.

With the advancement of knowledge of semiconductor properties, semiconductors are widely employed as electrodes in electrochemistry. Photoconduction is a notable property of semiconductors. Brattain and Garrett [21], the Nobel Prize winner of the year 1955, reported the photoreaction properties of germanium electrode, and their work is considered to be a milestone on semiconductor photoelectrochemistry and for the dawn of progress in this field. Figure 2.12 shows the photo-response characteristics with typical current-potential trace of n-Ge in their report.

During negative polarization, typical rectification can be found in the dark, though the current is increasing in proportion to irradiated light intensity, L. As shown in Figure 2.11 for the semiconductor electrodes, electrons in the conduction band and holes in the valence band generated by light absorption cause charge transfer through the interface of the chemical species in the solution at different potential levels corresponding to the band width. Research activities on the theories and dynamics of semiconductor photoelectrode reactions are continue to emerge till date and numerous reports are available.

Emergence of TiO$_2$ After the prominent research by Brattain et al [21], the focus of monocyrstalline semiconductor research in 1960s has been shifted to single crystals in the field of photoelectrochemistry, as single crystals are indispensible from scientific standpoint. Here we list such semiconductor materials in a chronological order in terms of their period of study.
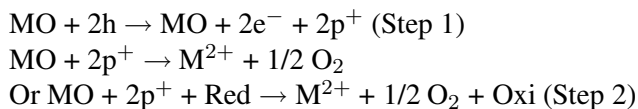
Plot of VE against IE for n-type Ge in N/10 KOH, at different light intensities

L = Intensity of light   A = Unit of light intensity

Figure 2.12   *Current (I) vs Potential (V) curve of n-Ge as a function of Intensity of Light [21].*

Semiconductor material	Year of study
N-Ge	1955
n-Si	1958
n-CdS	1960
N-,p-GaAs	1965
n-ZnO	1966
p-NiO	1966
n-Znse	1967
n-,p-GaP	1968
n-Sno$_2$	1968
n-KTaO$_3$	1968

Semiconductor materials other than Ge and Si include oxide semiconductors, chalcogenide semiconductors, III-V group semiconductor among others. Mostly they are of n- type, while few of them belong to p-type. As indicated in his article [9], Honda employed single crystals of Ge, Si, CdS, ZnO etc., for his research. In spite of their importance, single crystals are often expensive and difficult to obtain. For an n-type semiconductor, as shown in Figure 2.12, the anode photocurrent is proportional to the intensity of the light. For oxide semiconductors ($M^{2+}O^{2-}$), such a reaction can be represented as follows.

$MO + 2h \rightarrow MO + 2e^- + 2p^+$ (Step 1)
$MO + 2p^+ \rightarrow M^{2+} + 1/2\ O_2$
Or $MO + 2p^+ + Red \rightarrow M^{2+} + 1/2\ O_2 + Oxi$ (Step 2)

Step 1, indicates the dissolution reaction (etching) of the semiconductor itself. Step 2 indicates the oxidation reaction of the reductant, Red, in the electrolytic solution to Oxi induced by photo-generated holes in the electrode. This reaction represents the evolution of oxygen when water molecules become the donor. The reactions are competitive when both steps occur simultaneously. In this case, the etching of the electrode is inevitable. In the year 1969, at University of Tokyo, in the lab next to Hondas coincidently, the experiments on electrophotography using TiO_2 as the photoreceptor has been carried out. Fujishima, a co-researcher of Honda, obtained TiO_2 by following the suggestion of Prof. Iida, and used it as a photoelectrode and found that only oxidation reaction of the chemical species takes place in the solution without any etching of the electrode [22]. Then using platinum as the counter electrode, in 1972, Fujishima and Honda [23] constructed a cell as shown in Figure 2.13, irradiated the light from a high pressure mercury lamp on the TiO_2, and found that oxygen is generated on TiO_2 by the decomposition of water due to anode reaction, and hydrogen is generated by cathode reaction of the Pt electrode. At the same time, electrons flow in the arrow direction through the external circuit, achieving electrochemical photolysis of water.
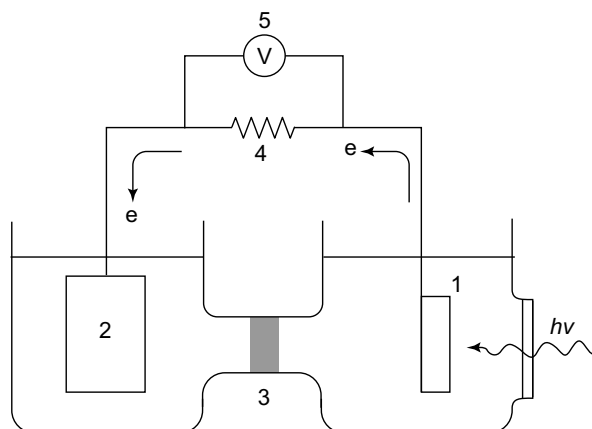

Electrochemical cell in which the TiO_2 electrode is connected with a platinum electrode The surface area of the platinum black electrode used was approximately 30 cm^2

Figure 2.13   *Cell for the decomposition of water with TiO2 Photoanode [23] A similar figure is also given in chapter 1.*

Though this study was carried out from a purely academic perspective of photoelectrochemistry, as it was a coincident with the Oil Shock in 1973, it drew prominent attention of the world and considered as a doorway to the use of solar energy. It was also greatly anticipated as a means of producing hydrogen fuel. As the cost of the single crystal of TiO_2 used in this research

was expensive than diamond, for practical application inexpensive materials are indispensable. In an attempt to reduce the cost, Honda et al [24] tried to form TiO_2, as oxide film on the surface by heating titanium metal available in the market using a heating burner. Water decomposition experiments by sunlight outdoors were made using this as a large photoanode for the first time. The results indicated that hydrogen can be generated by natural light without supplying any external energy. The view of TiO_2 photoanode formed by Ti plate and used at that time is shown in Figure 2.14.
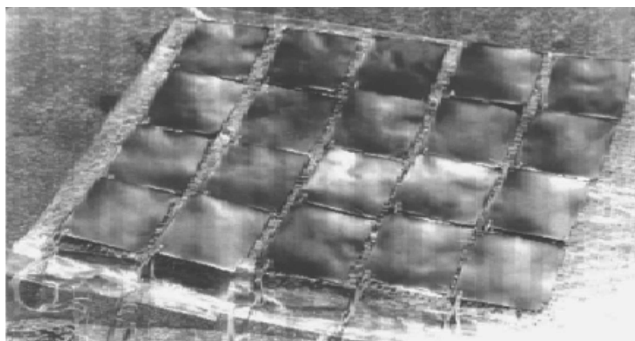
Figure 2.14   *View of TiO2 photoanode formed by heating Ti plate [9].*

In this fashion, the outstanding characteristic of TiO_2 as a photoelectrode has been attributed to its strong oxidizing power. For comparison, in Figure 2.15, we show a graphical representation of the positions of conduction band (CB) and valence band (VB) of the generally used n-type semiconductors. Lower portion of the valence band is equivalent in representing to greater oxidation ability. It shows that TiO_2 exhibits the lowest point among others. Since the report on TiO_2, several reports emerge using new semiconductor
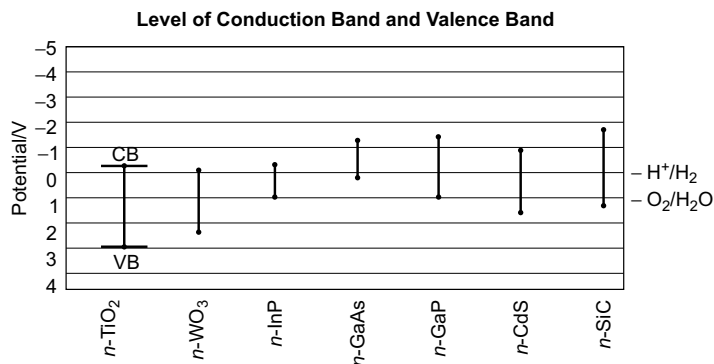
Figure 2.15   *Levels of conduction band (CB) and valence band (VB) of n-type semiconductor electrodes [9].*
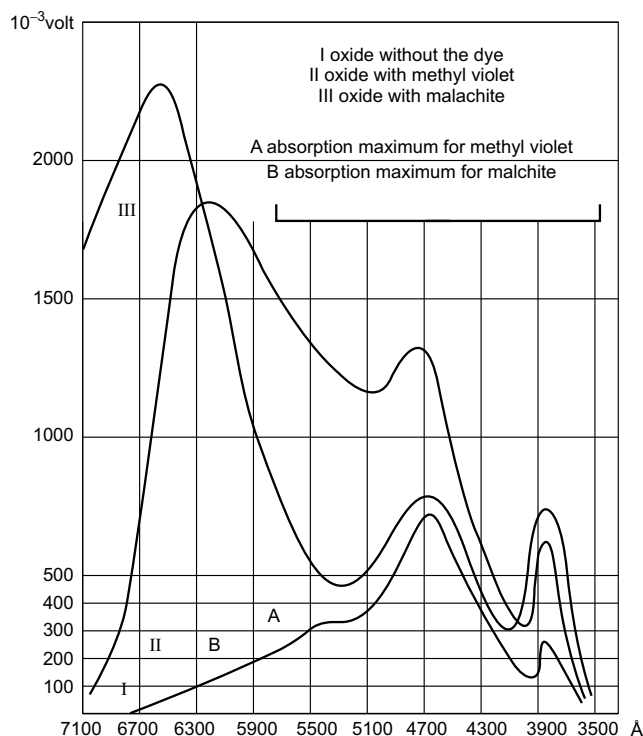
materials, hybrid semiconductors, doped systems etc., and for details one can refer to the respective literature.

Dye Sensitization of Photoelectrochemical Process Always, photoelectrochemical process takes place after semiconductor electrodes absorb light with the wavelength of the intrinsic absorption band. Most semiconductors absorb a part of sunlight spectrum. For effective utilization of sunlight, the working wavelength band of the photoelectrode reaction has to be expanded. By 1873, Vogel [25] already discovered dye sensitization employing silver halide photosensitive material. Since then, voluminous knowledge on dye sensitization has been evolved. Becquerel was truly captivated by this study, and carried out immense research in photographitic and photoelectrochemistry fields, and reported his notable research on photosensitization by chlorophyll [26]. Studies on dye sensitization in the arena of photoelectrochemistry dated back to the end of 19th century for metal electrodes. Since 1960, the year in which semiconductor electrodes made their emergence systematic studies were carried out in this direction. As a historical sketch, Figure 2.16 shows the sensitization curve by methyl violet and malachite green of copper oxide electrode [27], from the studies of Audubert in 1931. The extent of sensitization is represented by the photopotential. Realization of sensitization in longer wavelength can be seen. Remarkably, Audubert predicted in his article [27], that electrochemical photolysis of water would be realized in the future. Major studies on dye sensitization carried out using semiconductors between 1960s and 1970s are listed in chronological order as follows: ZnO [28, 29], GaP, GaAs, Cu_2O [30], p-GaP [31], TiO_2 [32], and CdS [33, 34], in the years 1968, 1969, 1971, and 1974, 1975 respectively. The dyes employed for the dye sensitizations are of general category such as xanthane. It has been indicated that most of the dyes used in these earlier studies were not satisfactory in terms of sensitization efficiency and durability. In 1991, Gratzel and his team [35] reported that the ruthenium bipyridyl complex exhibited high sensitization efficiency and durability. Subsequently, research solar cells using dye as a sensitizer has been ever expanding. In an exclusive chapter on dye sensitization in this book, we set to discuss the later advancements in detail.

2.3.2   Configurations of Photoelectrochemical Cells (PEC)

Photoelectrochemical cells convert light energy into a useful product via photo-induced chemical reactions. The product is usually electrical energy, but can also be useful chemicals such as hydrogen and oxygen, or even the degradation of hazardous wastes into harmless chemicals. A photoelectrochemical cell is defined as a cell in which the irradiation of an electrode in contact with an appropriate electrolyte produces a change in the

10^{-3}volt

I oxide without the dye
II oxide with methyl violet
III oxide with malachite

A absorption maximum for methyl violet
B absorption maximum for malchite

Figure 2.16   *Review of the photoelectrochemical dye sensitization work by Audubert[27].*

electrode potential with respect to a reference electrode (under open circuit conditions) or produces a change in the current flowing in the galvanic cell containing the electrode (under closed-circuit conditions).

Wet photovoltaic (WPV) cells (liquid junction solar cells)   These cells are composed of a semiconductor photoelectrode, either n or p type, a solution of a redox couple appropriate to the photoelectrode, and a counter electrode, usually kept in dark, which is reversible to the same redox couple. The cell generates electric power when the semiconductor photoelectrode is illuminated and there is ideally no net chemical change since the same reaction occurs in opposite directions at the two electrodes. The principles of this type of cell are depicted in Figure 2.17.

The open circuit voltage (V_{op}) of these cells depends on the energy difference between the Fermi level in the solution and the flat-band potential, and for the efficiency should exceed 0.5 V. The current I_s is generated from the electron-hole pairs photogenerated in the seminconductor reduced by recombination, concentration polarization at the dark electrode and other loss
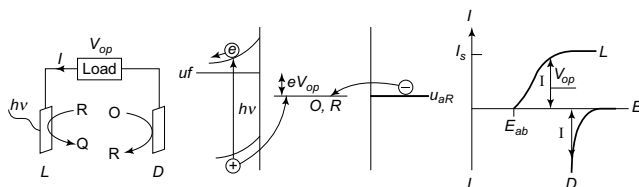
Figure 2.17   *Basis for function of a WPV cell depicting electrode reactions, band diagram and I/E curves, for n- type photocathode (L), redox couple (O, R), reversible dark electrode (D) and output voltage (V_{op})[36].*

mechanisms. If the WPV cell is to operate in sunlight, the semiconductor has to be an efficient absorber of sunlight, with a band gap around 1.5 eV. Table 2.1 summarizes the major results obtained in 1980s for WPV cells. The power conversion efficiency of some cells, were up to 15% in full sunlight, which is equivalent to that of commercially available silicon PV cells, but around half the best efficiency was realized in the laboratory for advanced solid state devices the same area in that era. Large area photoanodes of polycrystalline cadmium chalcogenides, prepared by using vacuum evaporation, electrodeposition or screen printing showed good results with power conversion efficiencies of about half to two-thirds of the efficiency exhibited by single crystal device.

Table 2.1   *Major developments in WPV cells in 1980s.*

Photoanode/redox couple	Efficiency%	Reference
n-CdSe/Se|Fe(CN)$_6{}^{3-}$/Fe(CN)$_6{}^{4-}$	12-14	37, 38
n-CdSe$_{0.65}$Te$_{0.35}$|Sn^{2-}/S^{2-}	12.7	39
n-WSe$_2$|I$_3{}^-$/I$^-$	10-13	40
	13.3	41
n-CuInSe$_2$|I$_3{}^-$/I$^-$	12	42
n-CuInSe$_2$| I$_3{}^-$ /I$^-$ (Cu$^+$, HI)	12.2	43
p-InP| V^{3+} / V^{2+}	12	44
n-GaAs| Se$_2{}^{2-}$ / Se$_2{}^{2-}$	13	45
n-GaAs (Os^{3+})| Se$_2{}^{2-}$/Se$_2{}^{2-}$	15	46
n-GaAs$_{0.6}$P$_{0.4}$ — Te$_2{}^{2-}$ / Te$_2{}^{2-}$	18 (458 nm)	47
n-Si / Ti$_2$O$_3$ — Fe (CN)$_6{}^{3-}$ / Fe (CN)$_6{}^{4-}$	14	48
n-Si / Li-MgO / Pt — Br$_2$ / Br$^-$	13	49
n-Si / MgO / Pt — Br$_2$ / Br$^-$	11	49
n-GaAs$_{0.72}$P$_{0.28}$ | Fe$^+$ /Fe in CH3CN (Fe=Ferrocene)	13	45

Fuel Producing Cells   Fuel producing cells are the most common category of photoelectrochemical cells using semiconductor electrodes. They covert the cheap, readily available material such as water into useful high energy fuel such as hydrogen. This class of cell can be classified into three basic types.

Photoelectrolysis Cells (PE Cells)   This type of cell is operated in a short circuit mode under light irradiation to produce maximum flux of fuel but no electric power. Both electrodes are immersed in the same electrolytic solution at constant pH. The principle of this type of cell is shown in Figure 2.18, for the water-splitting n-SrTiO$_3$/ 1M NaOH/Pt cell.
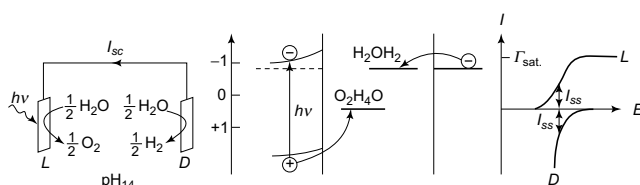

Figure 2.18   *Basis for operation at the short-circuit current Isc of an unbiased PE Cell for water splitting showing electrode reactions, band diagram and I/E curves [36].*

Photo-assisted Electrolysis Cells (PAE Cells)   The cells operate under irradiation plus an assisting bias, which serves either to drive electrolytic reactions for which the photon energy is insufficient or to increase the rate of fuel production by reducing the recombination rate of electrons and holes in the bulk semiconductor through the reduced band-bending. (a) Chemically biased PAE Cells: Chemical bias is obtained by using different electrolytes in two half cells, with the electrolytes being chosen to reduce the voltage required to cause the chemical splitting. For example, the use of 1 M NaOH and 0.5 M H$_2$SO$_4$ as electrolytes in the half cells of Fujishima and Honda [23] yields a pH difference of 14 and reduces the minimum photovoltage required for decomposition of water from 1.23 V to about 0.4 V. Production of hydrogen, of course, draws work from both the incident radiation and the electrolytes causing the acidic and alkaline pH values to converge. The operational principles of such cells are shown in Figure 2.19.

   (b) Electrically biased PAE Cells: The electrical energy input required for a given fuel output is reduced by the contribution of the incident radiation. If the cell is to have the capability of storing solar radiation in the form of the fuel produced, then the operating voltage under irradiation must be smaller than that in dark. An example of the principles of this type of cell is shown in Figure 2.20.
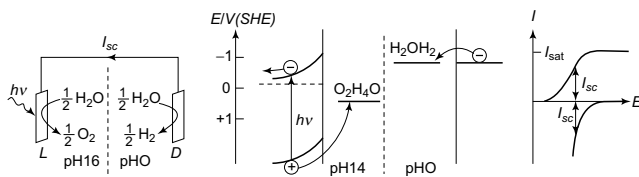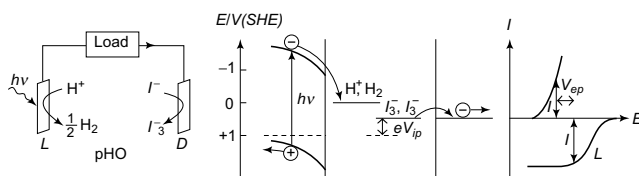
Figure 2.19 *Basis for operation of pH-based PAE cell for water splitting showing electrode reactions, band diagram and I/E curves [36].*
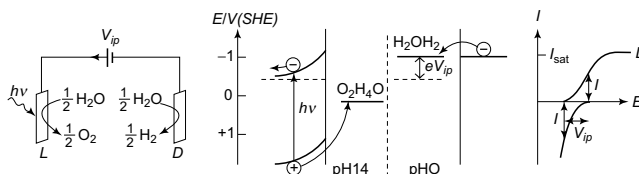
Figure 2.20 *Electrically-biased PAE cell for water splitting showing electrode reactions, band diagram, I/E curves for assisting input voltage V_{ip} [36].*

Photovoltaic electrolysis cells (PVE Cells)   These devices produce both fuel and electrical power via a low energy electrolytic reaction, as shown in Figure 2.21 for splitting of hydrogen iodide. The definition of the efficiency of the fuel producing cells, which have multiple input powers of different kinds, requires careful consideration.

Figure 2.21 *Basis for a operation of a PVE cell for water splitting showing electrode reactions, band diagram, I/E curves for assisting output voltage V_{op} [36].*

A detailed discussion is offered by Archer and Bolton [36], and their definitions are shown here. They showed that the Gibbs energy storage efficiency is the most appropriate figure-of-merit for all three types of fuel producing cell, where $\eta_G = [E_{cell} - V']I / E_0$ where, V = 0 for PE Cells, V_{ip} for electrically biased cells, and V_{op} for PVE cells; I = photocurrent density; E_0 = irradiance; E_{cell} = e m f of cell reaction. Some of the major achievements in improving the efficiencies of fuel producing cells in 1980 s are given in Table 2.2.

Photoelectrochemical storage cells (PES Cells)   PES cells can be viewed as secondary batteries which are recharged by the light absorption. The absorption

Table 2.2 *Major advances in fuel-producing cells during 1980s.*

Cell structure	Efficiency (%)	Ref.
Splitting of water PE Cells		
n, p-GaAs(RuO$_2$) | 5M H$_2$SO$_4$ | (Pt) n, p-GaAs	7.8	50
Pt | 0.5 M H$_2$SO$_4$ | p-BP	8	51
PAE Cells		
n-BaTiO$_3$ | 1M NaOH | Pt	3	52
Splitting of hydrogen halides PE Cells		
n-MoSe$_2$ | HBr, NaClO$_4$ | (Pt) p-InP	8 (633 nm)	53
n-Si / p-Si (Ir)| HBr, HBr | (Pt) n-Si /p-Si	8	54
n-Si / p-Si (Pt)| HI, HBr | Pt	8	55
N, p-GaAs (Ti / RuO$_2$)| HCl, NaCl | (Pt) n, p-GaAs	8	50
PAE Cells		
Pt (RuO$_2$)| HCl, KCl | (Ru) p-InP	12	56
n-MoSe$_2$ | HBr, NaClO$_4$ |(Pt) p-InP	11	53
PAE Cells		
p-InP (Ru) | HI, NaClO$_4$ | n-MoSe$_2$	7 (514 nm)	53

of light energy in one part of the PES cell produces photoreaction products which are stored and/or reacted in a different part of the cell, in the dark, to produce electricity, and regenerate the original state. PES cells may have just the photoelectrode and the storage electrode, but then both must operate in reverse during the discharge cycle. The cell efficiency can be improved by the addition of one or more auxiliary electrodes. In a three-electrode cell, the auxiliary is chosen to be efficient to the reverse of the photoreaction. In a four-electrode cell, the reverse of the photoreaction occurs through the auxiliary electrodes and these may be placed in a separate cell. An example of a three-electrode device is shown in Figure 2.22. This PES cell, devised by Licht et al [57], was the most efficient PES of 1980s, and generated constant current to the load by careful choice of electrode areas. Tow half-cells of a PES cells are normally separated by a semi-permeable membrane, as shown by dotted lines in Figure 2.22. The storage and auxiliary electrodes should be non-polarizing, but otherwise, their form and material is not critical. The notable works on PES cells in 1980s are listed in Table 2.3. More than 10% photo efficiencies were realizable, as compared to the overall efficiencies of crystalline silicon PV molecules of 14% feeding secondary batteries of 70% power efficiency. One of the most exciting developments in PES technology in the late 1970s was the Texas Instruments device. This was a closed loop system in which microspheres of semiconductor silicon solar cells were

embedded in a glass matrix that were used to electrolyze aqueous solutions of hydrogen bromide. The reaction products, hydrogen and tribromide in a fuel cell produced electricity and regenerated the hydrogen bromide solution. Both charge and discharge cycles operated near the reversible potential and the operational efficiency for splitting of hydrogen bromide was 8.6%. Though this was technically successful, the long-term reliability and cost-effectiveness of this system is unable to match with those of conventional PV modules plus storage battery, and the development was discontinued in 1983.
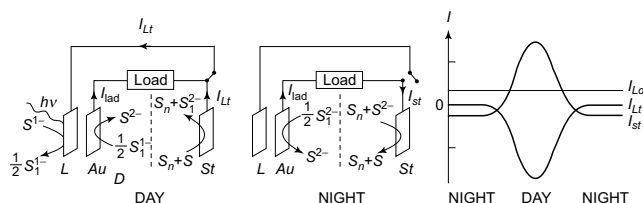
Figure 2.22 *Basis for operation of a PES cell, as designed by Licht et al [57]. The constant load current is ensured by choice of electrode areas. Electrode reaction and positive current directions are shown for day- and night-time operation. L = 0.08 cm^2 , n-CdSe$_{0.65}$Te$_{0.35}$; Au = 3 cm^2; CoS, St = 3 cm^2 Sn, SnS [36].*

Table 2.3 *Major developments in PES devices during 1980s.*

Materials	Efficiency (%)	Ref.
Single crystal photoelectrodes		
n-CdSe$_{0.65}$Te$_{0.35}$ $\mid$ Cs$_2$S$_4$, CsSH, CsOH		
CsHS, CsOH $\mid$ SnS, Sn CoS $\mid$ *	11.3	57
p-WSe$_2$ $\mid$ AQ, AQH$_2$, H$_2$SO$_4$ I$_2$,		
KI, Na$_2$SO$_4$, H$_2$SO$_4$ $\mid$ Pt AQ = anthraquinone	10 (633 nm)	58
n-WSe$_2$ or n-MoS $\mid$ KI, Na$_2$S$_4$O , H$_2$SO$_4$		
AQ, H$_2$SO$_4$ $\mid$ C	10 (633 nm)	58
n-GaP $\mid$ K$_3$Fe (CN)$_6$, K$_4$ Fe (CN)$_6$		
NiSO$_4$ $\mid$ Ni	1.9	59
Polycrystalline photoelectrodes		
n-CdSe $\mid$ S, Na$_2$S, NaOH Na$_2$		
Zn (OH)$_4$, NaOH $\mid$ Zn Ni $\mid$*	3	60
n-CdSe, Se $\mid$ CdSO$_4$ $\mid$ p-CdTe, Cd	10^{-7}	61

*The discharge electrode is shown on the left, under the charge electrode, with the auxiliary electrode on the right. The dotted line represents semi permeable membrane that separates two half cells.

In summary, photoelectrochemical reactions between the electrode materials and the electrolyte are rarely completely reversible and side reactions can occur with dissolution of the electrodes. PE cells are thus liable to degrade

over periods of time, ranging from minutes to years, depending on the materials of choice, their form and the energy densities involved.

2.4   A COMPARISON: PHOTOSYNTHESIS, PHOTOVOLTAICS, PHOTOELECTROCHEMISTRY

There are at present, three known methods of converting light into energy sources. Among these three the first one is the remarkable natures path namely Photosynthesis. Probably this may be the most preferred pathway by which nature provides energy sources for living beings on earth. The total solar energy reaching the earth surface per year is approximately $3850,000 \times 10^{18}$ joules. Possibly the energy utilized in photosynthesis can account for about 3000×10^{18} joules. Thus, it can be seen that only a tiny fraction of the total solar energy is harnessed by the plants, but still this level of energy storage is sufficient to support living systems on earth. It is clear that energy conversion by photosynthesis appears to be a possible means of providing the energy requirements of earth. There are two alternate methods of energy conversion that have been proposed and are being developed for increasing the efficiency of the processes. One of them is termed as Photovoltaics in the last 3-4 decades. A photovoltaic cell consists of two different types of solids connected at an abrupt but defined junction. This type of cell promotes the current flow in only one direction in the external circuit and thus produces electrical power. Unlike the photosynthesis, wherein solar energy is utilized to produce fuel, photovoltaics produce electricity directly. This brings us to the concept of electron versus fuel for energy conversion. There are some distinct advantages of Photovoltaics, like the device can be compact in nature and net efficiencies achievable even today is nearly the Carnot efficiency and are durable and can last nearly 20 or more years. The third possibility is the Photo-electrochemical cells. The main component of the phtoto-electrochemical cells is the photoactive electrode which is usually a semiconductor. Metals are not very effective in this operation since the energy levels are continuous (between occupied and unoccupied states) and hence excitation in these systems will lead to fast recombination and hence the net free energy change cannot be harnessed. For conventional redox reactions, one is interested in either reduction or oxidation of a substrate. For example consider that one were interested in the oxidation of Fe^{2+} ions to Fe^{3+} ions then the oxidizing agent that can carry out this oxidation is chosen from the relative potentials of the oxidizing agent with respect to the redox potential of Fe^{2+}/Fe^{3+} redox couple. The oxidizing agent chosen should have more positive potential with respect to Fe^{2+}/Fe^{3+} couple so as to affect the oxidation, while the oxidizing agent undergoes reduction spontaneously. This situation throws open a number of possible oxidizing agents from which

one of them can be easily chosen. However, in the case of water splitting one has to carry out both the redox reactions simultaneously namely, the reduction of hydrogen ions ($2H^+ + 2e^- \rightarrow H_2$) as well as ($2OH^- + 2H^+ \rightarrow H_2O + 1/2O_2$) oxygen evolution from the hydroxyl ions. The system that can promote both these reactions simultaneously is essential. Since in the case of metals the top of the valence band (measure of the oxidizing power) and bottom of the conduction band (measure of the reducing power) are almost identical they cannot be expected to promote a pair redox reactions separated by a potential of nearly 1.23 V. Another aspect is that metals liberate hydrogen preferentially and if these semiconductors can be designed to have enhanced metallic/reducing properties it may be advantageous. But this aspect is not considered in this presentation. Therefore one has to resort to systems where the top of the valence band and bottom of the conduction band are separated at least by 1.23 V in addition to the condition that the potential corresponding to the bottom of the conduction band has to be more negative with respect to $2H^+ + 2e^- \rightarrow H_2$ while the potential of the top of the valence band has to be more positive to the oxidation potential of the reaction $2OH^- + 2H^+ \rightarrow H_2O + 1/2\ O_2$. This situation is obtainable with semiconductors as well as in insulators. However insulators are not appropriate due to the high value of the band gap which demands high energy photons to create the appropriate excitons for promoting both the reactions. The available photon sources for this energy gap are expensive and again require energy intensive methods. Hence insulators cannot be employed for the purpose of water splitting reaction. Therefore, it is clear that semiconductors are alone suitable materials for the promotion of water splitting reaction. In the operation mode, the semiconductor electrode-electrolyte interface is the key factor and a complete understanding of this interface alone can lead to a successful development of highly efficient photo-electrochemical cells. In some sense, photo-electrochemical cells can be considered as a notional hybrid of photo-synthesis and photo-voltaics since these cells can generate either or both electricity and fuel. However, the development of Photo-electrochemical cells with the desired efficiency appears to be one of the major issues calling the attention of the developers. It is better to comment further between the similarities and also differences between PEC and Photosynthesis and Photovoltaics. Photosynthesis appears to provide remarkable efficiencies due to various factors. The essential points of relevance are (i) The absorption of the photon takes place in the chlorophyll dimmer or the special pair facilitated by the antenna and chlorophyll pigment. (ii) The excited electron- electron vacancy (hole) pair could normally undergo de-excitation thus releasing the optical energy as heat without producing fuel or electricity. However, in the photo-synthetic reaction centre the separation of the excited electron from

its vacancy is achieved by the presence of a series of electron acceptors that are not only strategically located in the protein but could also adjust their redox potentials like in an escalator thus positioning the acceptor states suitable for harnessing the energy. (iii) In addition, the presence of a series of electron acceptors make the electron to move from one species to another thus spatially separating the electron hole farther away thus restricting the thermodynamically feasible recombination of the excited electron and hole thus bringing in a kinetic control. This alone facilitates the use of the excited electron to perform the chemical reactions in photosynthesis and is responsible for fuel production. In the case of Photovoltaics, the free energy gradient caused by the potential energy gradient present at the junction of the two solids is the cause for the flow of electrons or electricity. In the case of photoelectrochemical cells also the driving force is the electrical field gradient that is available at the semiconductor/electrolyte interface and also the interaction of the photon field in the semiconductor adds cumulatively for this field gradient which is responsible for the vectorial transfer of electrons and also for driving the chemical reaction in the electrolyte. Hence, PEC can thus produce electricity, chemical reaction or both. However, PEC can be operated exclusively in the current mode if the reaction that takes place at the counter electrode to the semiconductor electrode (usually a metallic electrode) is simply the reverse of the anodic reaction that takes place at the semiconductor. In this mode of operation (for example the oxygen evolution and oxygen reduction were to occur at the two electrodes) then the PEC is presumed to operate similar to Photovoltaic cell as an energy conversion device. However, if the energetics of the electrons is suitable it is possible to reduce water to hydrogen at the counter electrode instead of the reduction of oxide ions and this process may be considered as fuel production produced by the use of photon energy and also the electrical field gradient. Depending on the net energetics, it is possible to produce both fuels and also electricity. In this sense the PEC appears to be unique if one were to understand and implement both the process in the same cell. It is also possible that other concurrent reactions can also take place in the PEC like corrosion and passivation processes of the semiconductor electrode can compete with the desired energy conversion process. These dissolution or degradation processes can restrict the life time of the electrodes. Secondly some trap states can be present in the materials which will lead to loss processes for the effective conversion of excited states into energy and thus contribute to the lowering of the conversion efficiency. Third parameter is the Electrode electrolyte interface which may not give rise to a large free energy gradient so that effective charge separation is achieved at the interface. This is an important component of PEC and deserves careful attention.

2.5 CONCLUDING REMARKS

A number of promising devices have emerged for the conversion of solar energy to chemical energy or electricity, based on the R & D efforts at a number of laboratories. Stable and efficient systems have been demonstrated, but economically useful and practical systems have yet to be realized. Further developments such systems will require new materials and configurations, improvements in efficiencies with polycrystalline and amorphous materials, and fundamentally a better understanding of semiconductor materials and the nature of semiconductor/electrolyte interface.

REFERENCES

1. Nathan S Lewis and Daniel G Nocera, Proceedings of National Academy of Sciences, 103 (43), 2006, 15729 15735.
2. T.M.I. Wigley, R. Richels and J. A. Edmonds, World Energy Assessment Report: Energy and the Challenge of Sustainability (United Nations, New York).
3. E. Maier-Reimer and K. Hasselmann, Climate Dyn, 2, 1987, 63-90.
4. J. R. Petit, J. Jouzel, D. Raynaud, N.I. Barkov, J-M. Barnola, I. Basile, M. Bender, J. Chappellaz, M. Davis, G. Delaygue, et al., Nature, 399, 1999, 429-436.
5. U. asiegenthaler, T.F. Stocker, E. Monnin, D. Lathi, J. Schwander, B. Stauffer, D. Raynaud, J-M. Barnola, H. Fischer, V. Masson-Delmotte, et al., Science, 310, 2005, 1313-1317.
6. G. W. Crabtree and N.S. Lewis, Physics Today, 60, 2007, 37-42.
7. T. Kuwana, Electroanalytical Chemistry, Vol. 1, Marcel Dekker Inc., New York, 1966, p. 197.
8. K. Honda, J. Chem. Soc. Jpn. Ind. Chem. Sec., 72, 1969, 63.
9. K. Honda, J. Photo Chem. Photo Biol. A, 166, 2004, 63-68.
10. E. Becquerel, Compt. Rend., 9, 1839, 58.
11. S. Kikuchi, T. Yura, K. Honda, Seisankenkyu, 18, 1966, 165.
12. E. Rabinowitch, J. Chem. Phys. 8 (1940) 551.
13. A. Golgmann, Ann. Physik 27 (1908) 449.
14. E. Baur, Z. Physik Chem. 63 (1908) 683.
15. S. Iimori, J. Tokyo Chem. Soc. 38 (1917) 507.
16. E. Rabinowitch, J. Chem. Phys. 8 (1940) 551.
17. M. Eisenberg, H.P. Silverman, Electrochim. Acta 5 (1961) 1.
18. H. Berg, H. Schweiss, E. Stutter, K. Weller, J. Electroanal. Chem. 15 (1967) 415.

19. M. Heyrovsky, R.G.W. Norrish, Nature 200 (1963) 880.

20. A.M. Brodsky, Y.V. Pleskov, Progress in Surface Science, vol. 2, part 1, Pergamon Press, 1972.

21. W.H. Brattain, C.G.B. Garrett, Bell System Tech. J. 34 (1955) 129.

22. A. Fujishima, S. Kikuchi, K. Honda, J. Chem. Soc. Jpn. Ind. Chem. Sec. 72 (1969) 108.

23. A. Fujishima, K. Honda, Nature 238 (1972) 37-38.

24. A. Fujishima, K. Kohayakawa, K. Honda, J. Electrochem. Soc. 122 (1975) 1487.

25. H. Vogel, Ber. Bunsen. Phys. Chem. 6 (1873) 1302.

26. E. Becquerel, Compt. Rend. 79 (1874) 185.

27. R. Audubert, Les piles sensibles laction de la lumire, Hermann et Cie, Paris, 1931, p. 16.

28. K. Hauffe, J. Range, Z. Naturforsch. 23B (1968) 736.

29. H. Gerischer, H. Tributsch, Ber. Bunsen. Phys. Chem. 72 (1968) 437

30. H. Tributsch, H. Gerischer, Ber. Bunsen. Phys. Chem. 73 (1969) 850.

31. R. Memming, H. Tributsch, J. Phys. Chem. 75 (1971) 562.

32. A. Fujishima, E. Hayashidani, K. Honda, Seisankenkyu 23 (1971) 363.

33. H. Gerischer, Faraday Disc. Chem. Soc. 58 (1974) 219.

34. A. Fujishima, T. Iwase, T. Watanabe, K. Honda, J. Am. Chem. Soc. 97 (1975) 4134.

35. B. ORegan, M. Grtzel, Nature 353 (1991) 737.

36. M. D. Archer and J. R, Bolton, Photoconversion of Solar Energy, Wiley Interscience, New York, 1991

37. K. W. Frese, Appl. Phys. Lett., 40 (1982) 275 - 277.

38. J. Reichman and M. A. Russak, J. Electrochem. Sot., 131 (1984) 796 798

39. S. Licht, R. Tenne, G. Dagan, G. Hodes, J. Manassen, D. Cahen, R. Triboulet, J. Rioux and C. Levy-Clement, Appl. Phys. Lett., 46 (1985) 608 - 610.

40. G. Kline, K. Kam, D. Canfield and B. A. Parkinson, Sol. Energy Mater., 4 (1981) 301 - 308.

41. R. Tenne and A. Weld, Appl. Phys. Lett., 59 (1985) 2249 2251

42. D. Cahen, Y. W. Chen, R. Noufi, R. Ahrenkiel, R. Matson, M. Tomkiewicz and W. M. Shen, Sol. Cells, 16 (1986) 529 - 548.

43. S. Menezes, H. J. Lewerenz and K. J. Bachmann, Nature (London) 305 (1983) 615 - 616.

44. A. Heller, J. Vat. Sci. Technol., 21 (1982) 559 - 561.

45. C. M. Gronet and N. S. Lewis, J. Phys. Chem., 88 (1984) 1310 - 1317.

46. B. J. Tufts, I. L. Abrahams, P. G. Santangelo, G. N. Ryba, L. S. Casagrande and N. S. Lewis, Nature (London), 326 (1986) 861 - 863.

47. W. S. Hobson and A. B. Ellis, Appl. Phys. Lett., 41 (1982) 891 - 893.

48. J. A. Switzer, J. Electrochem. Sot., 133 (1986) 722 - 728.

49. A. T. Howe and T. H. Fleisch, J. Electrochem. Sot., 134 (1987) 72 - 76.

50. J. Murphy and J. OM. Bockris, Znt. J. Hydrogen Energy, 9 (1984) 557 - 561.

51. J. Lee, A. Fujishima, K. Honda and Y. Kumashiro, Bull. Chem. Sot. Jpn., 58 (1985) 2634 - 2637.

52. J. F. Juliao, An. Simp. Bras. Electroquim. Electroanal. 3rd, 1 (1982) 341 - 347.

53. C. Levy-Clement, A. Heller, W. A. Bonner and B. A. Parkinson, J. Electroanal. Chem., 129 (1982) 4116 - 4120.

54. E. L. Johnson, Recent Progress in Photovoltaic/Electrochemical Energy System Application, in U. Landau, E. Yeager and D. Korton (eds.), Electrochemistry in Industry, Plenum, New York, 1982, p. 299 - 306.

55. Y. Nakato, M. Yoshimura, M. Hiramoto, A. Tsumura, T. Murahashi and H. Tsubomura, Bull. Chem. Sot. Jpn., 57 (1984) 355 - 360.

56. A. Heller and R. G. Vadimsky, Phys. Rev, Lett., 46 (1981) 1153 - 1156.

57. S. Licht, G. Hodes, R. Tenne and J. Manassen, Nature (London), 326 (1987) 863 - 864.

58. B. Keita and L. Nadjo, J. Electroanal Chem., 163 (1984) 171 - 188.

59. H. Yonezawa, M. Okai, M. Ishino and H. Hada, Bull. Chem. Soc. Jpn., 56 (1983) 2873 2876.

60. P. Bratin and M. Tomkiewicz, J. Electrochem. Soc., 129 (1982) 2469 - 2473.

61. H. J. Gerritson, W. Ruppel and P. Wuerfel, J. Electrochem. Soc., 131 (1984) 2037 - 2041.