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MATERIALS FOR *SAUR VIDDYUT KOSH* (SOLAR CHARGEABLE BATTERY)*

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The principle of solar chargeable battery (*Saur Viddyut Kosh*) is discussed. The area of research required for development is briefly touched upon. A detailed survey of materials used for developing a photoelectrode is given. Main emphasis is given on new phosphide, chalcogenide and oxide semiconductors. A survey on solar chargeable battery is also made.

Key Words: *Saur Viddyut Kosh*; **Solar Chargeable Battery; Photoelectrode; Phosphide, Chalcogenide and Oxide Semiconductors**

INTRODUCTION

THE development of any civilization depends upon the available energy resources and in particular, the present civilization is largely dependent upon its fossil fuels like coal, oil, gas, natural uranium and thorium (for India). Scientists have been working round the clock to utilise these fossil materials judiciously to extend the availability of the fossil fuels to the human civilization for the longest possible period. Extinction of such fossil sources is not too far away. The Arab world's threat to shut oil wells in 1972, made us realize what would happen if oil wells were emptied. To overcome the energy problem, new forms of energy are being visualised specially those which are renewable i.e., energy produced at a rate equivalent to the rate of consumption.

Scientists of Ancient India knew how to use solar energy[1] and the product derived out of solar energy to meet their energy demand. Scientists of today have realised that the existence of Man on this planet depends mainly upon his ingenuity to convert solar energy into a useful form of energy. Honda and Fujishima[2] proved electrolysis of water by solar energy by extending the concept of photovoltaic solar cell to a wet type solar cell (known as photoelectrochemical cell). This cell converts solar energy into electricity or into a chemical form, from which energy could be extracted easily when and where required.[3–20]

A photoelectrochemical solar cell[7,8] is a special kind of galvanic cell where anode or cathode or both are made of semiconductors. When the semiconductor electrode, dipped into a suitable redox electrolyte, is illuminated with light source of photon energy greater than the band gap of the semiconductor (due to reasons discussed below), photon's energy is converted into electrical energy.

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It is necessary to understand the role of semiconductor-electrolyte system to produce electrical energy from photon. A semiconductor has a conduction band which is normally empty of electron and a valence band normally filled with electrons. The maximum energy required to transfer an electron from the highest energy level of valence band (top level) to the bottom level of conduction band is known as the band gap of the semiconductor. The highest valence band's electrons of an extrinsic type semiconductor (*n*-type), however, require very little energy to push them into the conduction band because the Fermi level is about 0.1-0.2eV below the conduction band. Because of this factor, extrinsic semiconductor becomes a conductor at room temperature. The electrons pushed into the conduction band have the tendency to fall back to the valence band unless there is some force to prevent such process. This opposing force is generated by the help of redox electrolyte in contact with the semiconductor. In order to explain the role of redox electrolyte, it is important to realize that like semiconductor, electrolytes (e.g., Fe^{2+}/Fe^{3+}, Ce^{3+}/Ce^{4+}, etc. also have oxidation levels (equivalent to conduction band) and reduction levels (equivalent to valence band).

The energy necessary to transfer an electron from the reduced species (reduction level) to the oxidised species (oxidation level) is analogous to the band gap of a semiconductor, while redox potential is the potential required to transfer an electron from redox species to the reference level (which is hydrogen scale, NHE), in electrochemistry or zero vacuum level in semiconductor physics or vice-versa. The two reference levels are related as given in eq. 1 :—

$$E_{\text{vac·level}} = (E_{\text{NHE}} — 4.5 \text{ eV}). \qquad \ldots(1)$$

The electron transfer reaction with redox electrolyte is complicated, because the hydration energy for reduced and oxidised species may not be the same. The difference in energy states of the reduced and oxidised levels can be written as,

$$E_{ox}{}^{+}\lambda_{red} = E_{red}{}^{-}\lambda_{ox} = -E_{F_{redox}}, \qquad \ldots(2)$$

where E_{red} is ionization energy for the reduced species (i.e. reduction level) E_{ox} is the electron affinity of the oxidised species (i.e. oxidation level). λ_{ox} and λ_{red} are the polarization or reorientation energy of oxidised and reduced species respectively. The E_{ox} and E_{red} are not discrete, but are broadened into a thermal distribution of states due to (*i*) thermal fluctuations (*ii*) interaction with solvent and (*iii*) interaction with directly bonded ligands. These distributions are shown in Fig. 1, and their distribution is based on Frank-condon principle.

When a semiconductor comes in contact with a redox electrolyte, the nature of charge transfer at the interface of semiconductor redox electrolyte would depend upon the nature of level of redox electrolyte overlapping with nature of level of semiconductor. For example, valence band can be acceptor of holes or donor of electrons. It will thus donate electrons to electrolyte, if E_{ox} level overlap with E_v (Fig. 2*d*). Similarly, the conduction band can accept electrons if E_{red} level overlaps with E_c (Fig. 2*c*). No effective charge transfer can thus occur if there is no such

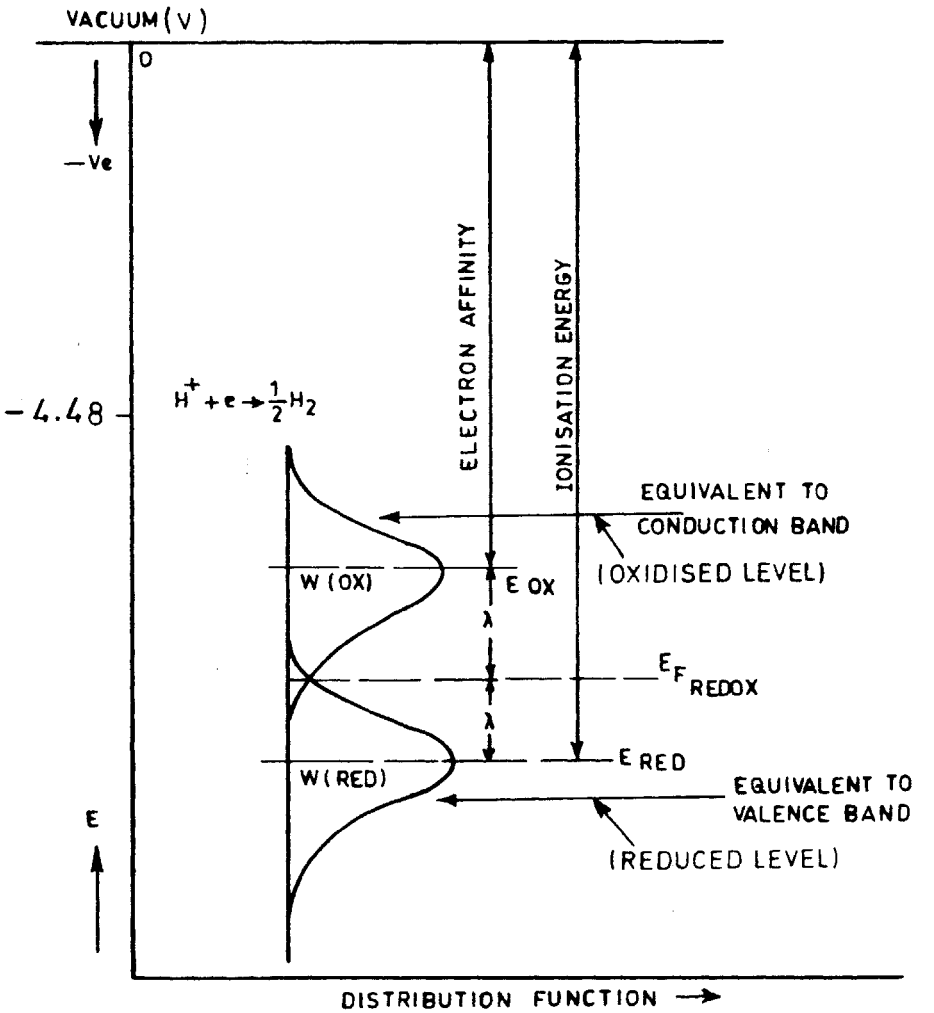

FIG 1 Redox energy level and their distribution function (W).

overlaps of two sets of energy levels. Likewise semiconductor can donate its electron to the electrolyte when E_c overlaps with E_{ox} level (Fig. 2*a*) and E_v can accept electrons if E_v ovelaps with E_{red} level (Fig. 2*b*).

When a *p*-type semiconductor like $\alpha = Fe_2O_3$ doped with nickel (Fig. 3*a*) is brought under a contact with electrolyte (Fig. 3*b*), whose E_{red} nearly overlaps with the valence band, transfer of electrons from the redox electrolyte would occur towards the valence band. This causes the valence band to be populated with energetic electrons (migrated from redox electrolyte) resulting in upward bending of bands as shown in Fig. 3*c*. The charge transfer reaction makes the surface of the semiconductor positively charged (i.e. populated with holes) and inner side of the semiconductor negatively charged (i.e. populated with electrons). Normally, the charge

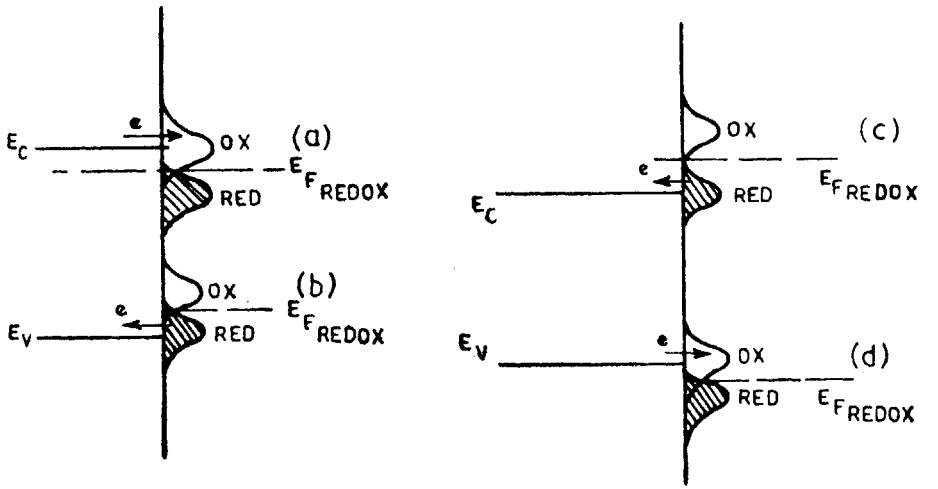

FIG 2 Electron transfer with redox electrolyte
(*a*) Oxidation level overlapping with E_C
(*b*) Reduction level overlapping with E_V
(*c*) Reduction level overlapping with E_C
(*d*) Oxidation level overlapping with E_V

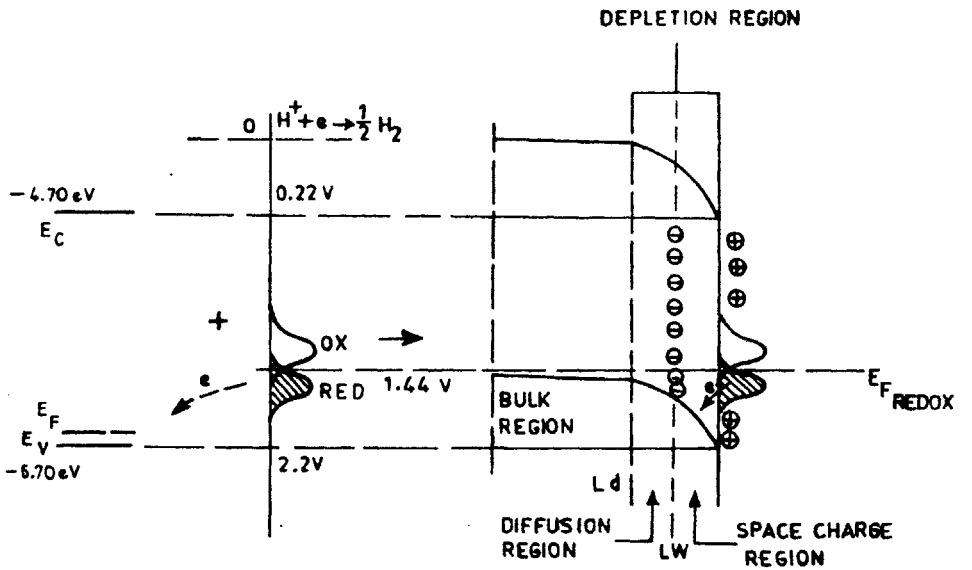

FIG 3 Energy positions of α-Fe_2O_3 with a redox electrolyte of $E_{F_{REDOX}} = 1.44V$, NHE (Ce^{+3}, Ce^{+4}).

distribution due to this electron transfer within the semiconductor does not occur in one plane (i.e. in plane parallel to the surface); however, for the purpose of understanding and mathematical calculations it is assumed that the electrons which have migrated from the electrolyte to the semiconductor are situated in one plane at a

distance of about 3000Å from the surface (Fig. 3*c* L_w). The region between this plane and the surface of the semiconductor is known as space charge region. In order to complete the story of charge transfer process, there is also a diffusion region (Fig. 3*b*, L_d) where the concentration of electrons is lower than the space charge region, but greater than the equilibrium concentration of electrons in the semiconductor and a bulk region where the concentration of electrons remains nearly equilibrium. The depletion type junction is at the interface (Fig. 3*c*). The difference in the valence band of semiconductor and the E_{red} of electrolyte approximately equals the contact potential (ϕ_0). More precisely, one uses the term Fermi level of the semiconductor rather than E_c and E_v and the Fermi level gives an idea of maximum energy the carrier in the semiconductor has achieved either because of doping and/or due to the thermal excitation. For *p*-type, the Fermi level is near E_v and for *n*-type semiconductor it is near E_c. The difference in E_c (or E_v) with the Fermi level, E_F, depends largely on the amount of doping. Normally, it is about 0.1–0.2eV different from E_c (or E_v) as the case may be. For extrinsic semiconductor, thus Fermi level gives an idea of majority carriers, which is electron for *n*-type and hole for *p*-type. Similarly, instead of using E_{ox} or E_{red}, for redox electrolyte, one uses E_F redox which is given by eq. 2. Thus the difference of E_F (semiconductor) and $E_{F\ redox}$ is equal to the contact potential. However, sometime this contact potential is different to the experimentally determined value due to the pinning of Fermi level.[22]

If the junction near the *p*-type semiconductor-electrolyte interface is radiated from the electrolyte's surface with photon of energy greater than the band gap of the semiconductor, electrons from the valence band would be excited to conduction band. The electron (minority carrier) of the conduction band will find itself at the surface of the semiconductor due to direction of the field present in the space charge region (Fig. 4). The photogenerated hole (majority carrier) would migrate towards the bulk. The electrolytes present near the surface, can accept the photogenerated electrons provided the E_{ox} level of the electrolyte is below the conduction band of the semiconductor (Fig. 4). This electron would reduce the electrolyte present in contact with the ssmiconductor. The hole will move from the bulk *via* the external circuit to the counter electrode dipped in the same electrolyte where the hole can oxidise the electrolyte. One can get power from this system if, in the external circuit, a resistance is connected in series. This type of cell is known as photoelectrochemical cell. Alternatively, if two electrodes of the cell separated by a suitable membrane[23] containing two different types of redox electrolytes present in two compartment (Fig. 4), and the semiconductor is radiated with the photon of energy greater than the band gap, the photogenerated minority carrier would reduce the electrolyte at *p*-type semiconductor provided E_{ox_1} is below E_c and oxidation of other redox electrolyte would occur at the counter electrode, provided E_{red_2} is above E_F of counter electrode. In the absence of any resistance in the external circuit, the photon energy is converted to chemical energy equivalent to the difference in the redox potentials of two redox electrolytes (i.e., E_{ox_1}–E_{red_2}). The photoreactions occuring at the two electrodes can be written as follows :

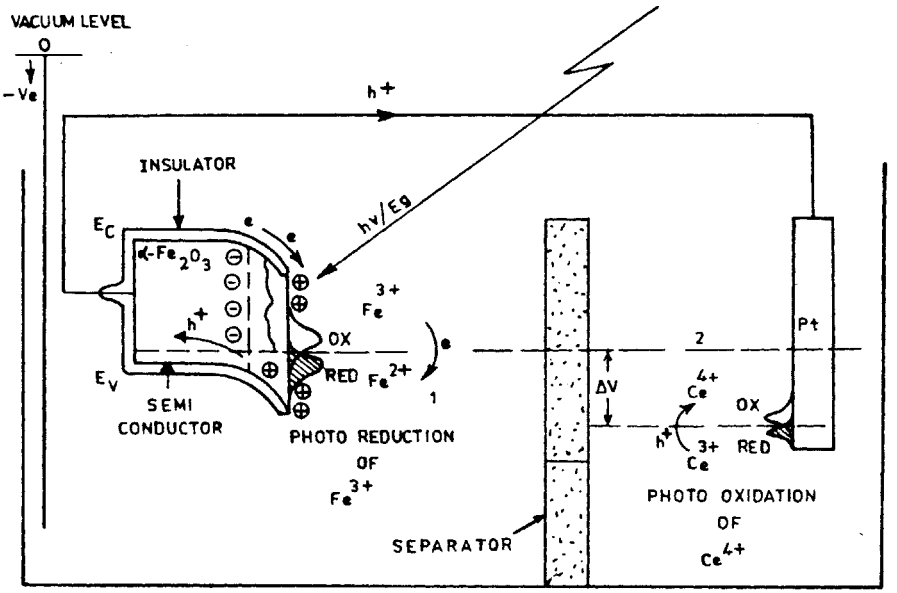

FIG 4 *Saur Viddyut Kosh* (solar chargeable battery).

$$p\text{-semiconductor} + h\nu \rightarrow e^- + h^+ \; (h\nu > E_g)$$

$$e^- + h^+ \xrightarrow[\text{space charge region}]{\text{due to field in the}} e^-_{surf} + h^+_{bulk}$$

$e^-_{surf} + Fe^{3+} \longrightarrow Fe^{2+}$ (e.g. electrolyte present near the Semiconductor electrode provided $E_{ox} < E_v$, Fig. 4)

h^+_{bulk} (semiconductor) $\longrightarrow h^+_{counter\ electrode}$

$h^+_{counter\ electrode} + Ce^{3+} \longrightarrow Ce^{4+}$ (e.g. electrolytes present near the counter electrode provided $E_{red} > E_{Fsemi}$, Fig. 4)

net photo reaction is

$$Fe^{3+} + Ce^{3+} \underset{-\Delta V}{\overset{h}{\rightleftharpoons}} Ce^{4+} + Fe^{2+} \qquad \text{.....(3)}$$

The ΔV in this case is the difference in the redox potential of Fe^{3+}/Fe^{2+} and Ce^{4+}/Ce^{3+} which is 0.62V. Thus photon's energy is converted to generate ΔV potential in the cell.

In the absence of photon and under short circuit condition there would be a tendency by the cell, to reverse the reaction by releasing an energy equivalent to 0.62V (i.e. ΔV). If the external circuit is connected in series with a resistance in dark

mode, it will produce power. Thus we have produced a battery[21] which can be charged by photon energy and discharged in absence of light to get power. However, due to formation of barrier at the junction of semiconductor-electrolyte interface (Fig. 4), there would be a tendency to oppose the dark reaction due to the nature of barrier formed at the surface (depletion region). It is therefore, necessary to use a third inert electrode in the compartment No. 1 to allow the flow of electron from compartment 1 to compartment 2 to carry out following dark reactions :—

A. At the inert electrode of compartment 1

$$Fe^{2+} \longrightarrow Fe^{3+} + e$$

B. At inert electrode of compartment 2

$$Ce^{4+} + e \longrightarrow Ce^{3+}$$

Net reaction being—

$$Fe^{2+} + Ce^{4+} \longrightarrow Fe^{3+} + Ce^{3+} \qquad \text{.....(4)}$$

—could again be the reactants for photo-reaction process.[3]

The dark reaction (discharging) would occur between these two inert electrodes, while charging would be done with semiconductor and the counter electrode (Fig. 5). Such a battery is known as the three-electrode system.

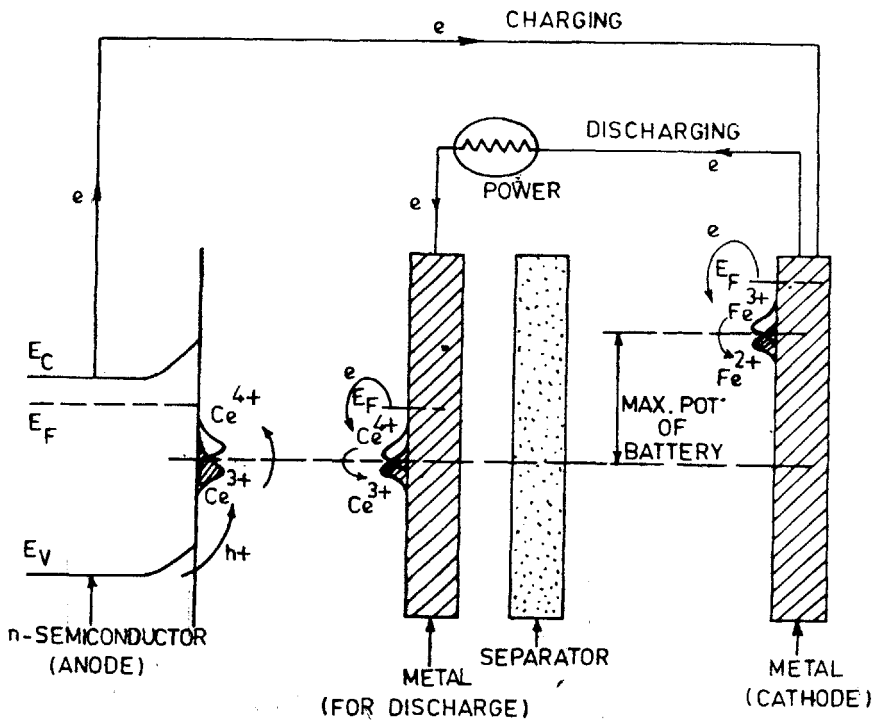

FIG 5 Three electrode storage system.

In order to complete the story of storage battery, it is also possible to replace the counter electrode of compartment 2 with a semiconductor. This semiconductor will have to be *n*–type (because in compartment 1, *p*–type has been used) and its energy level should match as shown in Fig. 6. Under this condition one additional inert electrode will have to be used in compartment 2, so that dark current could be drawn between the two inert electrodes of compartments 1 and 2. Charging of the battery could be done by illuminating two semiconductors of two compartments simultaneously. At *p*–type electrode photo-reduction of electrolyte will occur and at *n*–type, photo-oxidation of electrolyte will occur. The additional semiconductor in compartment 2 is not necessary and it only increases the photon energy conversion efficiency.

If such types of batteries are to be charged with solar radiations, the band gap of semiconductors should be slightly smaller than the photon energy of solar radiations which has the maximum intensity at *AM*–1 (i.e. the intensity of solar radiations measured at sea level with sun perpendicular to the sea level). Considering the theoretical efficiency of semiconductor and spectrum of solar radiation at *AM*–1, the best band gap is found to be between 1.0–1.8eV with an expected theoretical efficiency of about 30 per cent. Therefore, a battery which is to be charged by solar radiation should have semiconductors of band gap in the region of 1.0-1.8eV. A battery of type given in Fig. 5 and operating with solar energy has been named by our group as *Saur* (the Solar) *Viddyut* (electricity) *Kosh* (Battery), in honour of

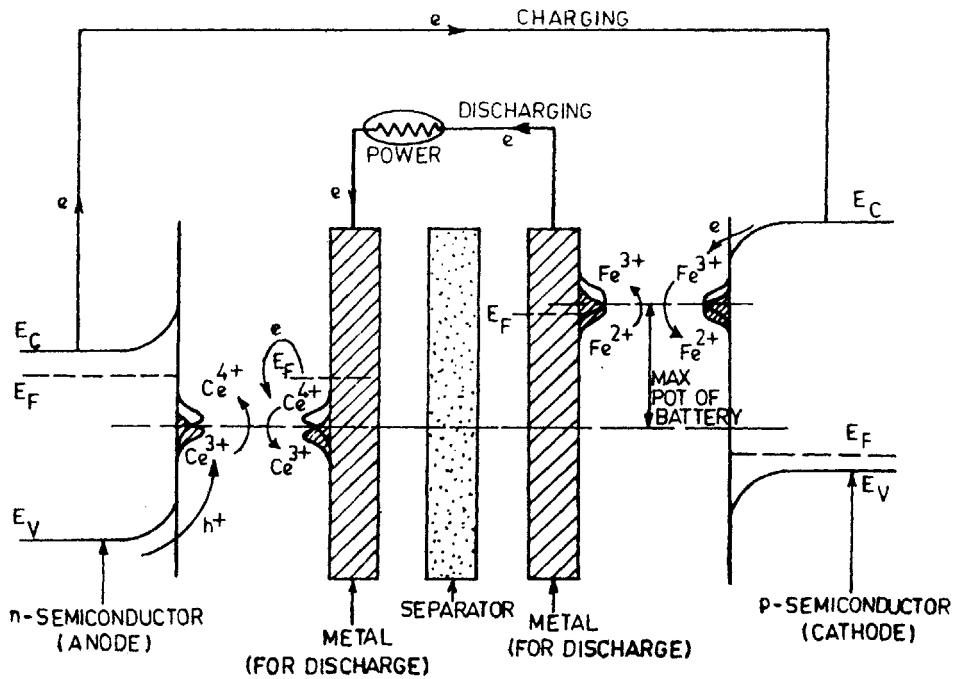

FIG 6 Four electrode storage system.

Maharshi Bhardwaj who had given a description of a system to generate power from solar energy.

The economical viability of solar chargeable battery depends upon the following factors :

1. The efficiency at which the battery is charged by solar energy depends upon the efficiency of converting solar energy into chemical reaction at the interface of the semiconductor-electrolyte. Thus, the photopotential and photocurrent are two important factors responsible for this efficiency.
2. The efficiency of battery depends upon the current density the battery can retain, the dark potential, the time for which it can retain its charge, and the number of charging/discharging cycles the battery can perform.

The most important issue facing these developments is the development of materials which could efficiently convert solar energy into chemical energy without the semiconductor being chemically and photochemically corroded. Therefore, in the present review, effort is made to review the materials like oxide, chalcogenide and phosphide which have been used to develop photoelectrochemical cell or which could be used for such cell. However, in order to appreciate the photochemical stability it is necessary to learn as to under which condition one could predict the semiconductor to be stable photoelectrochemically. At the end of this review, a list to solar chargeable battery already developed are given in tabular form.

PHOTO-CORROSION

The most serious obstacle in the technical use of low band gap semiconductors in contact with aqueous electrolytes is their susceptibility to photodecomposition.[24-26] When the semiconductor electrolyte interface is exposed to photons, the minority carriers (electrons in *p*–type and hole in *n*–type) have two possible ways to react : one with the electrolytes present at the interface or with the host material (i.e. with the semiconductor). If these carriers react with the host material, the semiconductor is said to be unstable against photogenerated minority carriers. This can happen in two ways : (*i*) cathodic decomposition by conduction band electrons (i.e. *p*–type) and (*ii*) anodic decomposition by valence band holes (i.e. with *n*–type).

The overall energy of corrosion involving holes or electrons are evaluated in such a way that they can be illustrated on the band diagram. Gerischer[27] has formulated the expressions for a binary system, MX and has considered two reactions :

$$MX + (\tfrac{1}{2})\, ZH_2 + \text{Solv} \rightarrow M + ZH^{+}_{\text{solv}} + X^{Z-}_{\text{solv}} \qquad \text{(cathodic reaction)}$$

$$MX + ZH^{+}_{\text{solv}} + ZY^{-}_{\text{solv}} \rightarrow M^{Z+}_{\text{solv}} + (\tfrac{1}{2})\, ZH_2 + ZY^{-}_{\text{solv}} + X$$

(anodic reaction)

This method has been used to calculate the n^Edec (cathodic decomposition potential) and p^Edec (anodic decomposition potential) of many compounds to

predict the stability of semiconductor against photocorrosion. *n*-type semiconductor would be anodically stable if p^Edec is below the valence band-edge of the semiconductor. Similarly. *p*-semiconductor would be cathodically stable if n^Edec is above the conduction band-edge of the semiconductor.

In order to take advantage of these calculations, especially for new materials, it is also equally important to theoretically calculate the conduction and valence band-edge positions of a semiconductor. The electron affinity values (i.e. bottom of the conduction band) for oxides, chalcogenides or phosphide semiconductors can be calculated by using Butler and Ginley method.[28] Based upon the bandgap and electron affinity, the valence band position can be calculated. This method can be used for a compound whose chemical formula or empirical formula is known, because both give same result.[3]

Materials for *Saur Viddyut Kosh* (Solar Chargeable Battery)

We shall now discuss the different classes of materials studied by different schools and summary of results obtained with these materials are shown in respective tables under various classes of materials. However, no effort is made to make any reference for materials having bandgap greater than 2.8eV, for the reasons discussed earlier.

Chalcogenides

The survey of the chalcogenides which have been studied by different scientists are given in Table I. It appears from this table that chalcogenides of cadmium though has a given efficiency of 10.2 per cent, there is a problem of reproducibility of results. It is thus important to understand why the films prepared by different techniques by different authors give photo efficiency ranging from 0.03–10.2 per cent. There is also a need to find out a system in which it could be stable for at least 1–2 years.

PtS_2, $RuSe_2$[104–107] *p*-GaSe (2eV) and *n*,*p*-InSe (1.3eV) have also been recently studied.[108–110] Chalcogenides of group III-V are also anisotropic, sandwich layer of *X-M-M-X* being reported to give photoresponse with low dark current in aqueous H_2SO_4 solution.[111] But these three materials though have low bandgap (2.1eV) they show very low efficiency of 4.5×10^{-4}. [112] Recently, a large number of papers have also appeared to understand the electrochemical properties of Mo and W-chalcogenides so that one could understand the reasons for getting variation in the efficiency. Details of observations made with these materials are shown in Table II.

From the survey of materials studied and published by scientists, it appears that tungsten chalcogenide might be the best material for PEC cell. However, this material is not stable for a longer period. There also appears to have inconsistency in the results of different laboratories giving different photo conversion efficiency for same chalcogenides under more or less similar conditions. Thus, there is a need to understand the surface-interface phenomena[182,183] of the materials as discussed in

TABLE I

Chalcogenide semiconductors

Material	Eg (eV)	Electrolyte System	Flat band Potential (*V vs SCE*)	Effi-ciency	Electrode form	Quantum efficiency	Voc (V)	Stability	Counter electrode	Refer-ence
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
n-CdS	2.4	NaOH, S, Na_2S NaOH, Na_2Te NaOH, $Na_2(SCH_2COO)$ S KCl, $K_4Fe(CN)_6$, $K_3Fe(CN)_6$ NaI, I_2 in OH_3CN	−0.8 to −1.4	0.05 to 9.5	Single crystal thin film poly cryst.	8–70	0.4–1.0	Stable in alkaline S/S^{-2} so-lution	C, SnO_2 Pt,	24,40-65,67, 68
n-CdSe	1.7	NaOH, Na_2S, S NaOH, Na_2Se NaOH, Na_2Te NaOH, Na_2S, S, Se NaOH, $Na_2(SCH_2COO)$ S, Se $Fe(CN)^{3-/4-}$ El_4NBFY in CH_3O_4 KOH, Na_2S, S_n	−0.9 to −1.45	0.5 to 9.2	,,	20–50	0.4–0.77	Stable in NaOH, S,S^{2-}	Pt, C	24,38, 40,42, 45,56-65,67, 71–74, 5.
		$Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, $pH > 8$	0.74	12.4				Stable		
		Cesium polysulphides, S, $CuSo_4$		12.7						
n-CdTe	1.4	NaOH, Na_2Se NaOH, Na_2Te K_2Se, Se, KOH	−1.45 to −1.50	9.2–10.0	,,	51–65	0.70	Stable in K_2S,S,KOH	C, Pt	52,67, 68,71
n-$CuInS_2$		NaOH-Na_2S-S	—	3.5–4.3	Single crystal	—	—	—	—	85,93
		polysulphide	—	0.9	Single crystal	—	—	—	—	—
n-$Re_6Se_8Cl_2$ 1.42		I_3^-, I^-, H_2SO_4	—	—	Single crystal	—	0.49	Stabilised with I_3^-/I^-	—	95
n-$CdIn_2Se_4$		KOH-S-Na_2S	—	—	Single crystal	—	—		—	94

(*Continued*)

TABLE I (*Continued*)

Material	Eg (eV)	Electrolyte System	Flat band Potential (*V vs SCE*)	Effi-ciency	Electrode form	Quantum efficiency	Voc (V)	Stability	Counter electrode	Refe-rence
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)
$CuIn_5S_8$		Sulphide, Polysulphide	—	—	—	—	—	Highly stable	—	103
n-WS_2	1.3	halide solution	—	6.5	—	—	—	Stabilised in halide solution	—	92
p-WS_2		$CH_3CN/(n\text{-}Bu_4N)ClO_4$	0.8	—	—	—	—	—	—	66
n-MoS_2	1.7	Et_3N, halide ion in CH_3CN NaI, I_2(aq) Fe^{2+}, Fe^{3+}	—	.002–4	,,	1–53	0.03 to 5.0	Stable in Fe^{2+}, Fe^{3+}	C, Pt	69–71, 75–77
n-$MoSe_2$	1.4	I/I_2 Fe^{2+}, Fe^{3+} (Et_4N) $X/2$ in CH_3CN X = halogen KI, I_2 HBr, Br_2, $pH=0$	+.05 – +.44	0.02–9	Single crystal Polycry-stalline film		0.09 to 0.55	Stable in I_2, I^- and Fe^{+2}, Fe^{+3}	Pt	78-87, 75,24
n-WSe_2	1.57	$Fe(CN)^{3+/4+}$ NaI, I_3^-, $pH=1$ NaI, I_3, Na_2SO_4, H_2SO_4, $pH=0$	−0.45	14	Single crystal		0.71	Stable in $Fe(CN)_6^{3-/4-}$	Pt	70,88, 89
p-WSe_2	1.35–1.57	$Fe^{2+/3+}$, H_2SO_4	0.8	2			0.51			81,90
n-Bi_2S_3		NaOH-Na_2S-S		0.14-4.7	Polycryst-alline film (doping na-ture impro-ves effici-ency)	—	0.08 to 0.18			53,91

TABLE II

Material	Observations	Ref.
n-MoS_2	1. Charge transfer is favoured with surface ∥C more than with surface ⊥C.	96
	2. Cleavage steps and dislocations enhanced the photocorrosion of these material.	97
$MoSe_2$	1. Due to the presence of indirect band gap the observed efficiency is lower than expected theoretical value.	96
	2. The pinning of Fermi level is observed to affect the efficiency.	75
	3. Highest output power is observed at low temperature (< 15 °C).	98
	4. Stable and efficient cells are demonstrated in polyiodide electrolyte.	99,100
WSe	1. High efficiency is observed with polyiodide couple.	101
	2. Co-existence of n and p in the same crystal surface leads to carrier recombination.	102
	3. Fermi level pinning observed.	22

Table II so that the cause of different results obtained by different authors could be understood. The stability of material has to be increased perhaps by modification of surface of the material. Therefore, time has come to probe into these factors, rather than carrying out experiment to produce materials with another technique without increasing the reported efficiency of the material. It is disheartening to read papers explaining a new technique of preparation with efficiency ten times lower than the maximum efficiency already achieved by other authors and not making any effort to study the reason of getting lower efficiency. A valid question also comes to the mind, as to what is the justification for omitting the study of PEC properties withl arge number of chalcogenides of other elements of periodic table, and concentrating only on elements like Hg, Bi, Cd, In, Ga, Mo, and W. It is quite possible that there might be some other chalcogenides, possessing the requisite properties to make an efficient PEC cell. Therefore, there is a need to screen all possible chalcogenides which could be tried for PEC cell. The criteria for such screening should naturally be as follows :—

(i) Material should have band gap in the region of 1.0–2.6eV so that solar energy could be used for excitation effectively.

(ii) Technique of preparation of material should be simple and material should be cheap.

(iii) The materials should be chemically and photochemically stable in aqueous solution (either acid or alkaline solution).

Based on these three factors, we have carried out a survey of chalcogenides of all unstudied elements of periodic table and elements which conforms to the above three properties listed in Table III. Amongst all unstudied elements of periodic table it is observed that chalcogenides of As, Sn, Hg and Sb are the only suitable materials meeting the above three requirements.

TABLE III

New chalcogenides

Compound	Band gap (eV)	Method of preparation	Structure	E_c (eV)	Solvent in which soluble
As_2Se_3	1.6	By direct combination of elements at high temperature	rhombohedral, black crystal	4.61	Alkali
As_2Te_3	1.0	,,	monoclinic	4.81	—
Bi_2S_3	1.3	By passing H_2S through a solution of Bismuth trioxide	rhombotic group powder	4.6	HNO_3
HgS	2.0	By the action of alkali sulphide on mercuric salts	Hexagonal, brownish black crystals	4.69	Aquaregia
$SnSe_2$	1.2	By melting tin and selenium at 650 °C in vacuum	dark brown crystals	4.7	Strong HKO_2
SnSe	1.2	By melting tin and selenium in exact proportions at bright red hot temperature	rhombic, steel group	4.48	Alkali
SnS	1.08	By passing H_2S to an acidic solution of stannous chloride	rhombic, brown crystal	4.67	Conc. HCl
Sb_2S_3	1.7	By direct combination of elements with feeble incandescence	rhombic, yellowish red	4.78	In H_2SO_4
ZnSe	2.67	By direct reaction of zinc salt with Potassium selenide	Hexagonal, Pale red	3.92	Acids
ZnTe	2.26	By direct combination of element at high temperature.	Cubic, red crystal.	3.94	Alkali

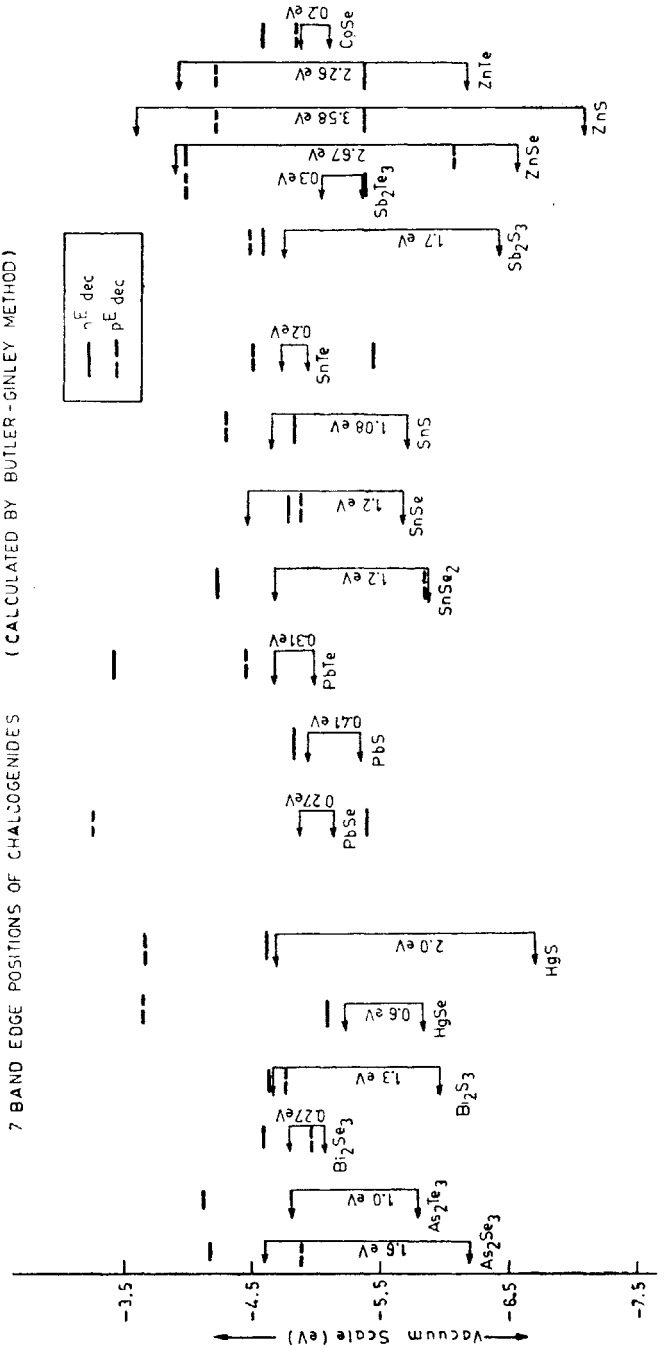
7 BAND EDGE POSITIONS OF CHALCOGENIDES (CALCULATED BY BUTLER-GINLEY METHOD)
n^E dec
p^E dec
Vacuum Scale (eV)
-3.5
-4.5
-5.5
-6.5
-7.5
As_2Se_3 1.8 eV
As_2Te_3 1.0 eV
Bi_2Se_3 0.27eV
Bi_2S_3 1.3 eV
HgSe 0.6 eV
HgS 2.0 eV
PbSe 0.27eV
PbS 0.41 eV
PbTe 0.31eV
$SnSe_2$ 1.2 eV
SnSe 1.2 eV
SnS 1.08 eV
SnTe 0.2eV
Sb_2S_3 1.7 eV
Sb_2Te_3 0.3eV
ZnSe 2.67 eV
ZnS 3.58 eV
ZnTe 2.26 eV
CoSe 0.2 eV

FIG 7

Since most of these materials are unstudied, it is important to predict their stability theoretically and also establish their band diagram. Therefore, anodic and cathodic photocorrosion potentials and the band diagram of these chalcogenides have been calculated[4] and are shown in Fig. 7.

Based on these calculations it is observed that As_2Se_3 (1.6eV), As_2Te_3 (1.0eV), Bi_2S_3 (1.3eV), HgS (2.0eV), $SnSe_2$ (1.2eV), and Sb_2S_3 (1.7eV) are cathodically stable, i.e. their cathodic decomposition potentials are less negative to their conduction band-edge value. But none of these materials are found to be anodically stable i.e. the anodic decomposition potentials are less negative to the valence band-edge of these materials. Other materials like zinc chalcogenides being high bandgap and Bi_2Se_3, PbSe, PbS, PbTe, SnTe, Sb_2Te_3 and CoSe being low bandgap materials are unsuitable for PEC cell but the former materials may find their application in PEC cell if their bandgap is reduced by making a mixed chalcogenides $MX_x\ X_{1-x}$, where X may be S or Se and Y may be Te because it has been observed that the bandgap of chalcogenides can be controlled by adding the controlled amount of Te or mixing telluride with other metal chalcogenides.[114] The bandgap can be changed from 0 to 2.5eV by mixing of HgTe with CdTe.

The chalcogenides of unstudied element suggest the necessity to study the electrochemical and photoeletrochemical properties of $AsSe_3$, As_2Te_3, Bi_2S_3, HgS, $SnSe_2$ and Sb_2S_3, so that one may be able to decide the worthiness of these materials for PEC or solar chargeable cells.

Phosphide Semiconductors

The survey of literature on phosphide semiconductors reveals that except InP, GaP, Zn_3P_2, ZnP_2, CuP_2, CdP_2, no other phosphides have been studied for PEC cell (Table IV). A question again comes to mind as to why phosphides of other elements of periodic table have not been tried for PEC cells? We, therefore, undertook

Table IV

Compound	Eg (eV)	Electrode form	Electrolyte	Efficiency	Voc (volts)	Isc ($mAcm^{-2}$)	Ref.
n-InP	1.26	single crystal	NaOH | $Fe(CN)_6^{-4/-3}$ NaoH-Na_2Te VCl_2-VCl_5 HCl	18.6	Stable for 10 hrs		155 188
P-InP		single crystal	,,	0.4–11.5	0.66	25	156
n-GaP	2.25	single crystal	—	—	—	—	142
P-GaP		single crystal	Na_2SO_4 *p*H 2.5	—	—	—	157–
P-ZnP_2	1.4	single crystal					161
CdP_2	2.0						162
Zn_3P_2	1.32	alkalinie EDTA		6.1			163
P-α-ZnP_2	2.1	alkaline *p*H = 13		12.0			162,
		V_{fb} = 0.7 V (SCE)					163, 190

to carryout a survey of phosphide materials of all unstudied elements of periodic table meeting the three requirements described earlier. It is observed that the phosphides of alkali and alkaline earth metals are soluble in water giving phosphine gas[115,116] and thus are not suitable for PEC cells. Phosphides of elements of Gr IIIA and phosphide of metals like Pt, Pd, Au are also not suitable for an economically cheap PEC cell. Therefore, the phosphides of unstudied elements which could be useful for PEC cell, are of elements of Co, Cr, Fe, Mn, Mo, Ti, V, W and Zr because phosphide of these elements are expected to be chemically more stable in aqueous solution. The bandgaps of some of these phosphides are given in Table V. The reported metallic and semiconducting phosphides are given in Table VI.

TABLE V

Bandgaps of some phosphides

Metallic Phosphides and Bandgap < 0.6		Medium Bandgap Phosphides		
Material	Ref	Material	Eg	Ref
CrP_4	164	AlP	2.50	174
MoP_4	165	BP	2.2	176
VP_4	164	$CdGeP_2$	1.8	174
CoP_2	166	$Cd\ SnP_2$	1.5	174
PdP_2	167	$Ga\ As_{.85}\ P_{.15}$	1.44	113
FeP	168	$In_{2/3}PSe_2$	1.55	171
TiP	169	$ZnGeP_2$	2.20	174
α-WP_2	170	$ZnSiP_2$	2.20	174
FeP_2	171	$ZnSnP_2$	2.10	174
PtP_2	167			
FeP	172			
TiP	170			
WP_4	165			
MnP	173			
VP_2	170			
ZrP_2	170			
NiP_2	167			

TABLE VI

Properties of new transition metal phosphides

Material	Empirical Formula	Eg (eV)	Photocurrent Isc (mA/cm^{-2})	Electron Affinity (eV)
Cobalt phosphide	$CoP_{8\cdot38}$	0.89	0.223	5.02
		0.67		5.13
Iron phosphide	$FeP_{0\cdot33}$	0.86	0.919	3.97
Molybdenum phosphide	$MoP_{1\cdot9}$	0.97	0.75	4.54
		0.67		4.69
Nickel phosphide	$NiP_{0\cdot41}$	0.89	1.77	4.29
		0.65		4.40
Vanadium phosphide	$VP_{0\cdot03}$	0.78	1.26	3.27
Tungsten phosphide	$WP_{6\cdot56}$	9.93	0.25	4.94

In the absence of available literature on the bandgap of various possible phosphide of these selected elements we decided to prepare the phosphides by a direct combination of metal with phosphoric acid, such that concentration of phosphoric acid is kept in very large excess to metal present in the reaction vessel.[3] The slurry of metal/phosphoric acid is then heated at different temperatures for different duration of time until all phosphate is converted into phosphide. The dry powder is reduced in hydrogen atmosphere for various duration at different temperatures, until a phoshide is obtained with a bandgap of around 1.0eV because it is reported that the bandgap can be increased with increase in P content in $GaAs_{1-x}P_x$ $(O < x < 1)$

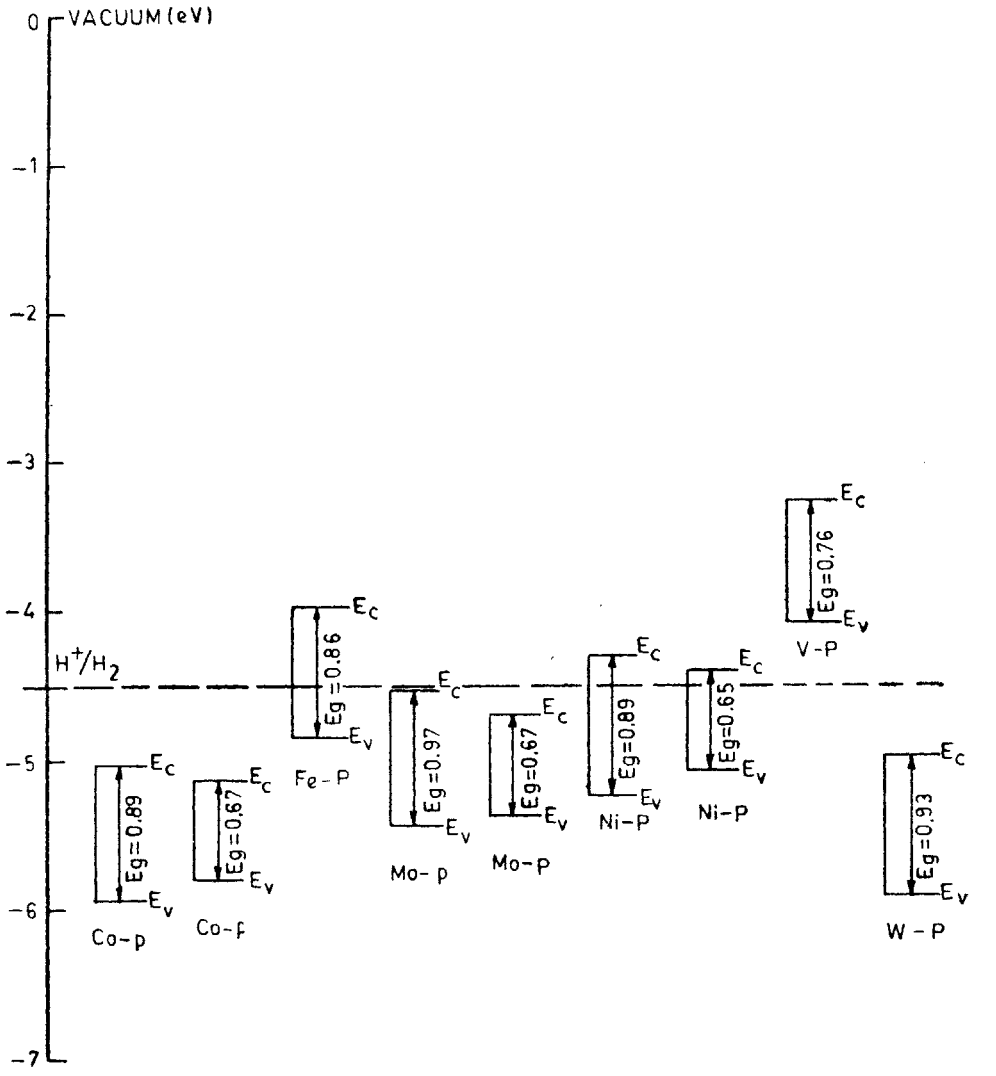

FIG 8 Positions of conduction and valence band-edges.

from 1.44 ($x = 0$) to 2.25 ($x = 1$)[117]. The materials obtained at each of the above treatments were analysed to determine the structure and the bandgap. All materials which could be produced to a composition giving bandgap around 1.0eV were studied for their photoresponse. The emperical formula of these new materials were determined by EDAX. The conduction and valence band-edges were calculated by Butler-Ginley method.

It was observed that phosphides of Cr, Mn, Ti and Zr could not be prepared of bandgap around 1.0eV by this method. However, these elements may give lower bandgap by reducing them at temperature higher than 1200 °C. Due to non-availability of high temperature set-up, we could not reduce at temperature greater than 1200 °C. Results of these observations are given in Table VI and the band diagram of these new phosphide materials are shown in Fig. 8.

It is obvious from Table VI that we should make in depth study of phosphides of Co, Fe, Mo, Ni, V and W with a hope that one of them might prove its worth for PEC cell. Our group is actively working on these new phosphide materials. However, amongst published literature, phosphides of In and ZnP_2 seem to be promising materials.

OXIDE SEMICONDUCTORS

Some of the properties of the oxide semiconductors of bandgap below 2.8eV reported in the literature are shown in Table VII. Amongst the narrow bandgap oxide semiconductors, Fe_2O_3, Pb_3O_4, $PbFe_{12}O_{19}$, $PbTi_{1\cdot5}W_{0\cdot5}O_{6\cdot5}$, $LuRhO_3$ and $CdIn_2O_4$ are few oxides which are found to be stable in electrolytic solution. However, α–Fe_2O_3 and Pb_3O_4 may be economically viable materials to be explored. The theoretical efficiency of these compounds is expected to be around 20 per cent whereas in laboratory one has been able to get efficiency of about 1 per cent. Therefore, there is a need to understand the reasons for getting low efficiency and effort should be made to achieve the expected efficiency. Both these materials (α–Fe_2O_3 and Pb_3O_4) are stable in alkaline solution.[30,34] There is also a need to make a systematic survey of all oxides of cheap metals having band gap in the region of 1.0–1.8eV. Similarly, there is a need to make a systematic study on mixed oxides like titanates, molybdates and arsenates on lines as made for chalcogenides and phosphides.

MISCELLANEOUS TYPES OF MATERIALS

Materials other than those discussed earlier and which are being studied for PEC cell includes GaAs, Si etc. are given in Table VIII. Amongst these compounds GaAs and $CuInS_2$ seem to show some promise for their use in a PEC cell. However, none of these is stable for longer duration in the electrolyte.

SOLAR CHARGEABLE BATTERY

Scientists have been trying to fabricate a solar chargeable battery by using a variety of materials and redox electrolytes. The batteries which have been published are

TABLE VII

Oxide semiconductors

Material	Eg (eV)	Flat band potential (V *vs* SCE)	Efficiency %	Nature of electrode	Stability	Ref.
Fe_2O_3 $\{E_c\ 4.71, E_v\ 5.88\}$	1.7–2.2	−0.67	0.9	Single crystal	in $pH > 8$	29,30
WO_3	2.8	−0.20	—	Single crystal	Stable Unstable under illumination	189 29,31
CdO	2.1	−0.20	—	Polycrystalline	Unstable	32
V_2O_5	2.75	+0.45	—	Polycrystalline	Unstable	33
Bi_2O_3	2.8	−0.32	—	Polycrystalline	Unstable	33
PbO	2.8	−0.54	—	Polycrystalline	Unstable	33
n-Pb_3O_4	2.1	−0.31	0.09	Polycrystalline	—	34
p-CuO	1.7	+0.06	—	Polycrystalline	Unstable	34
	1.35 (Li doped)	+0.55	—	Polycrystalline	Unstable	35
$FeTiO_3$ $\{E_c\ 4.3, E_v\ 5.72\}$	2.16	+ 0.10	—	Single crystal	—	39,140
$FeTiO_3$	2.58	−0.60	—	Single crystal	—	36
Fe_2TiO_5	2.18	+0.50	—	Single crystal	—	37,36
$YFeO_3$	2.60	−0.46	—	Single crystal	Stable	36,37
$Hg_2Ta_2O_7$	1.80	+ 0.20	—	Polycrystalline	Unstable (*n*-type)	32
$Hg_2Nb_2O_7$	1.80	+0.30	—	Polycrystalline	Unstable (*n*-type)	32
$PbFe_{12}O_{19}$	2.30	+0.20	—	Single crystal	Stable	32
$PbTi_{1.5}W_{0.5}O_{6.5}$	2.4	−0.40	—	Polycrystalline	Stable in acid	32
$SrTiO_3$	—	—	2.0	Polycrystalline	—	150
$CdFe_2O_4$	2.3	−0.10	—	Polycrystalline	—	32
$LuRhO_3$	2.20	+0.34	—	Single crystal	Stable-hole mobility = 2.5 cm^2/V sec Electron mobility = 1 cm^2/V sec	38,35 118
$CdSnO_4$	2.12	±0.1	—	Single crystal	Unstable	39
$CdIn_2O_4$	2.23	+0.7 ± 0.1	—	Single crystal	Stable	39
p-$GeFe_2O_4$	2.30	—	—	Single crystal Hall mobility = 2 cm^2/V sec	—	175

TABLE VIII

Material	Eg (eV)	Electrolyte	Efficiency	Voc (Volts)	Isc ($mA\ cm^{-2}$)	Electrode	Ref.
n-GaAs	1.4	$Fe^{2+/3+}$	12	1.09	0.89	Si-doped	38,89,
		I^-, I_4^-	with $Fe^{2+/3+}$	0.72	11.67	Wafers	119–131,
		S^{2-}, S_n^{2-}	3.3				136,137
		$Fe(CN)^{-3/4-}$					
		$Fe^{2+/3+}$, EDTA					
		KOH, Te^{2-}, mTe^{2-}	1.5	0.47	8.33		
n-Si	1.1	$FeCp_2$,	1.2–5.8	0.3	—	Single crystal	132–135,
		n-Bu_4N, ClO_4					138,139,
		in ethanol					141–145
		($FeCp_2$ = ferroceone)					
		I^-/I_3^-, $FeCl_2/FeCl_3$					
P-GaAs	1.4	I^-, I_3^- pH = O	0.5–1.3	0.2	30	Single crystal	89,146–
		KCl, VCl_2/VCl	0.6	0.3			149
		Eu^{3+}					
P-Si	1.1	VCl_3—VCl_3, HCl	0.06–11.5	0.66	25	Single crystal	151–154
							16
$GaAs_{0.72}P_{0.28}$	—	Non aqueous	13	1.01	15.7	—	113
		electrolyte					

TABLE IX

Solar chargeable batteries

Photo-electrode	Storage voltage (V)	Electrolyte redox species	$I_{photocharge}$ (mA/cm²)	Storage electrode	Photo voltage (V)	Counter electrode	$I_{discharge}$ (mA/cm²)	Ref.
CdSe	—	$S^{2-}/Sn^{=}$	—	Ag_2S	—	Pt	—	177
CdSe	—	,,	—	,,	—	C	—	178
$MoSe_2$		$Br^-/Br_2/I^-/I_3$	200	Pt	0.49	Pt	20.6	86
		$HBr/Br_2/Nafion/HI/I_2$ $pH = 3.5$		$HI/I_2/Pt$				179
GaAs	0.50	$Se^{2-}/Se_2^{=}$	100	Cd	0.50	Pt	14.6	179
CdSe	0.40	$S^{=}/Sn^{=}/Se^{=}/Sn^{=}$	100	Pt	0.40	Pt	0.75	179
CdS CdSe		$S^{=}/Sn^{=}$		$Co/Co(on)_2$ Sb/Sb_2O_3		Pt		180
$BaTiO_3$		Fe^{2+}/Fe^{3+}		Ce^{++}, Ce^{3+}		Pt		181
n-Pb_3O_4		Fe^{2+}, Fe^{3+}		IO_3^-, I^-		Pt		183
n-WSe_2 or *n*-MSe_2		I^-, I_3^-		$AQ(AQH_2)$ (Sodium 9–10 anthra (hydro) quinone 2,6 disulphonate)	1.0	C		185 184
n-WSe_2		I^-, I_3^-		*n*-InP/$S^{=}$, $Sn^{=}$		Cd		184
n-CdSe		$Se^{=}/Se$		*p*-CdTe/Cd^{++}				186
P-InP		$C_{44}H_{28}N_2Fe^{3+}$	20	Nafion/$Ru^{2+}(bpy)_3$	1.3	*n*-CdS Zn		187 21

shown in Table IX. But none of these has been found economical and therefore, the research is required to find a suitable non-corrosive photoelectrode and storage redox electrolytes. One can use storage electrodes like Ag/AgCl, Cd/CdS, Ag/Ag_2S, where one does not need any separator. However, research is required to confirm their effectiveness in the battery.

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