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Transition metal phosphide semiconductors for their possible use in photoelectrochemical cells and solar chargeable battery (Saur Viddyut Kosh V)

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The principle of a solar chargeable battery and the necessity for development of new materials for such a battery are discussed in this paper. A survey of the literature is made for the phosphides of those metals which are cheap and chemically stable in acid and/or alkali. For the first time the phosphides of cobalt, iron, moybdenum, nickel, vanadium and tungsten are considered as suitable materials for use as photoelectrodes in such cells. The preparation and characterization for the band gap, empirical formula, band diagram and photoresponse of these semiconducting materials are discussed in this paper.

1. Introduction

When the semiconductor (n-type) electrode in a photoelectrochemical (PEC) cell comes into contact with a suitable redox electrolyte whose Fermi level is more negative than the Fermi level of the semiconductor, a depletion region is formed at the semiconductor–electrolyte interface. On illuminating the junction with photons of energy greater than the band gap of the semiconductor, photogenerated electron–hole pairs are separated in the space charge region such that the minority carriers (i.e. hole for n-type) concentrate at the surface of the semiconductor, and the electrons (the majority carrier) migrate towards the bulk of the semiconductor [1]. If the Fermi level of the redox electrolyte in contact with the semiconductor is less negative than the valence band edge of the n-type semiconductor, the photogenerated hole at the surface of the semiconductor can oxidize the reduced species of the electrolyte. On short circuiting the back of the semiconductor electrode via the external circuit with the counter electrode of the cell, the electrons can reduce the oxidized species of the electrolyte. If the semiconductor electrode and the counter electrode are separated by a suitable membrane and two different types of redox electrolytes are used in each half cell, then it is possible to oxidize one set of redox electrolytes in one half cell and reduce the other set of redox electrolytes in the other half cell. The dark potential of the cell would depend upon the redox potentials of the two redox electrolytes of the two half cells. Here solar energy is being used to perform these reactions to charge the cell. The ampere-hour of such a charged cell would depend upon the concentration of the electrolytes present in each half cell of the battery.

The charging of the storage battery can be done either by using one semiconductor electrode (anode) and a counter inert electrode (cathode) or alternatively by using one semiconductor (n-type) as anode and another p-type semiconductor as cathode. In the latter form both electrodes are illuminated. The dark current, however, cannot be drawn through the semiconductor electrode efficiently, because of the junction formation at the electrolyte–electrode interface. Therefore, the half cell containing a semiconductor electrode should also have an additional inert electrode, through which dark current could be drawn. When one semiconductor electrode is used, then the system becomes a three electrode system (Fig. 1) and when two semiconductors are used, the system will have four electrodes (Fig. 2). This type of storage cell resembles the photoelectrochemical solar cell, but is different from the photogalvanic cell [2] and the layer-type semiconductor based storage cell [3]. In order to differentiate this battery from these types of cells, we use the name Saur (the solar) Viddyut (electricity) Kosh (battery). Though few solar chargeable cells have been reported in the literature [4–10] (Table I), the ampere-hour storage has been very poor. In order to make such an economically viable chargeable battery, the following improvements are necessary.

1.1. Choice of semiconductor materials

The semiconductor material which is used either in the PEC or in the solar chargeable battery should have the band gap between 1.0 and 1.9 eV to utilize the major energy portion of the solar spectrum. In addition to the band gap requirement, the positions of the conduction band and valence band edges of the semiconductor with respect to the redox potential of the electrolyte are also important factors (as discussed above) to be considered in selecting a suitable material for this purpose [14]. Finally, the semiconductor should not be chemically, electrochemically and photoelectrochemically decomposed in the solution. There are many good review articles available which deal with these aspects of the semiconductor [11–13].

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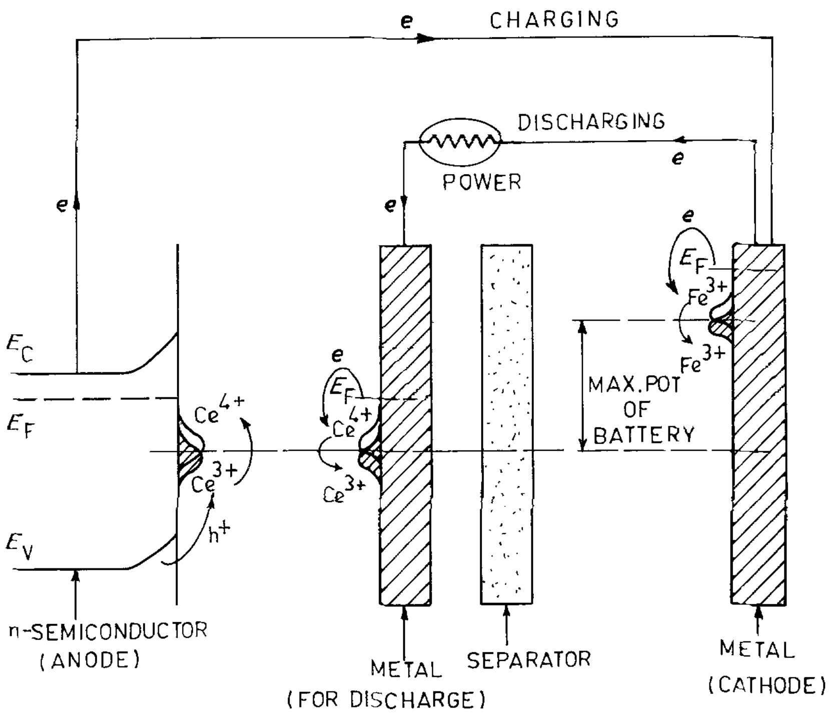

Figure 1 Three electrode storage system.

It is, however, observed from the available literature that most of the low band gap semiconductors do not meet the requirements of stability for more than a few days. Therefore, there is a need either to modify the existing low band gap materials so that they could be resistant to corrosion or synthesize new types of semiconductors to meet these demands.

1.2. Choice of electrolytes

The constitutent of the redox couple should not become oxidized or reduced by the solvent or by the dissolved oxygen in solvent. The selection of pH of the solution is also important for the stabiity of the semiconductor electrode. For example, α-Fe_2O_3 cannot be used in an acidic pH. The potential of the fully charged cell depends upon the redox potentials of the electrolytes and the ampere-hour storage depends on the concentration of the electrolyte. The Fermi levels of redox electrolytes and band edge positions of the semiconductor should match as shown in Figs 1 and 2.

1.3. Choice of separators

The selection of the separator is difficult, because the separator must be able to prevent the mixing of cations of the two compartments, but at the same time it must be able to maintain the neutrality of the two compartments by allowing either protons or anions to diffuse into the respective half cell. A membrane must be developed to meet these requirements, to avoid increasing the internal resistivity of the cell.

It would therefore be advisable completely to eliminate the separator by selecting the electrolyte such that one of its constitutents precipitates out or is deposited over the electrode (e.g. lead acid battery).

From these three factors, we have decided to concentrate on the preparation of new types of phosphide semiconductors and to study their characteristics to find their suitability for the solar chargeable battery.

2. Literature survey

Many papers are appearing on oxides, chalcogenides, a few phosphides and mixed oxides which have

TABLE I Reported papers on solar chargeable battery

Type of cell	Power input (cm^2)	Photo potential (V)	Photo current (mA)	Area exposed (cm^2)	Reference
p-WSe_2, Pt/(Methyl viologen)$^{2+}$, I^- ‖ (Methyl viologen)$^{2+}$, I^-/n-WSe_2, Pt	100 mW	0.50	0.13	1	[4]
Cd–Se/S^{2-}, S ‖ S^{2-}, S/C*	AM1 sun light	0.29	4.10	1	[5]
CdSe/S^{2-}, S ‖ S^{2-}, S/C*	AM1 sun light	1.00	10.00	1	[6]
$MoSe_2$/Br^-, Br_2/I^-, I_2/Pt	200 mW	0.49	4.00	1	[7]
GaAs/Se^{2-}, Se_2^{2-}/Cd	100 mW	0.50	8.00	1	[7]
CdSe/S^{2-}, S_n^{2-}/Se^{2-}/Se_2^{2-}/Pt	100 mW	0.40	8.00	1	[7]
CdSe/S_2^{2-}/S_n^{2-}/Cd	100 mW	0.40	10.00	1	[7]
TiO_2/HNO_3 ‖ Ag^+, Pt	1.9 × 10^{17} photon	0.28	1.00	3	[8]
$BaTiO_3$, Pt/Ce^{3+}, Ce^{4+} ‖ Fe^{2+}, Fe^{3+}/Pt	AM2 sun light	0.60	0.12	1	[9]
Pb_3O_4, Pt/Fe^{3+}, Fe^{2+} ‖ IO_3^-, I^-/Pt	60 mW	0.09	0.41	1	[10]

*Where C is aqueous paint of high surface area carbon, cobalt(II) acetate, teflon suspension on to steel gause.

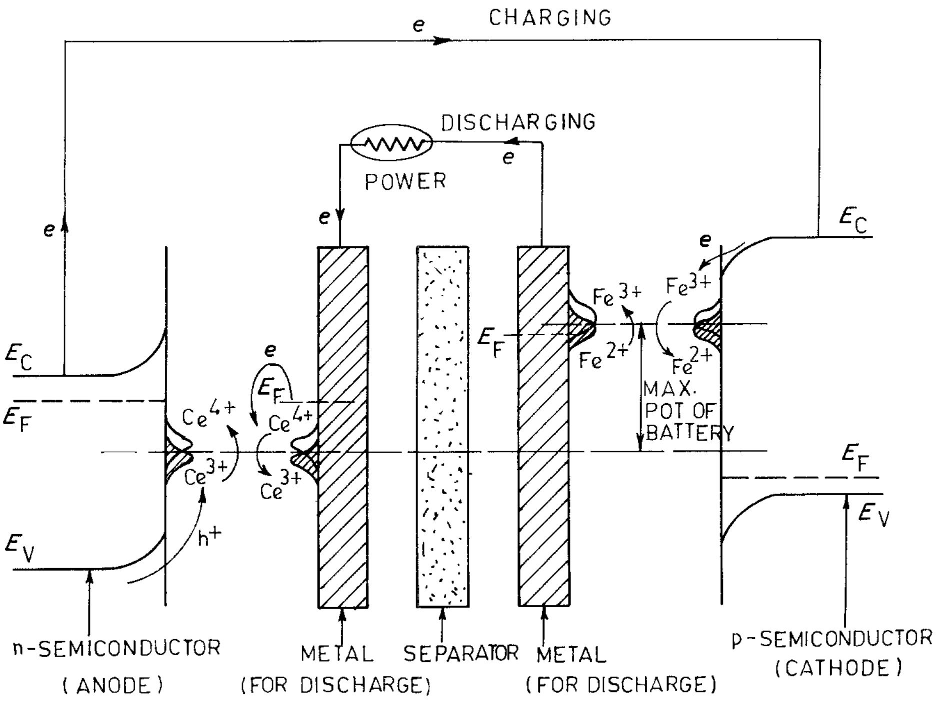

Figure 2 Four electrode storage system.

been used as electrodes in PEC cells. However, there seems to be no logical ground for selecting these materials except for the fact that they are easily available. It is therefore necessary to carry out a thorough survey on various classes of compounds like arsenates, tungstates, titanates and phosphides, on the basis of their solubility and the availabiity of the material. A short list of compounds must be made on this basis to explore their use in the PEC cell. Unfortunately, no such attempt has been made so far. In the present paper, we have tried to list all possible phosphides which should be studied for their use in a PEC cell.

2.1. Phosphide semiconductors

Those phosphides which are metallic or have low and medium band gaps are collectively given in Table II [16–31]. Recently, B_6P is reported to be a high band gap (E_g = 3.35 eV) semiconductor [15].

Some phosphides like InP [32, 33], GaP [34], $In_{2/3}PSe_3$ [30] and $GaAs_{1-x}P_x$ [29] have been extensively used as an electrode in PEC cells. Baugman and Ginley [28] have also suggested that BP might be a prospective semiconductor electrode for the photoelectrochemical cell. But all these compounds have been found to be unstable in protic solvents for long periods. For InP and GaP [12], aprotic solvents, metallic coating or application of a thin layer of high band gap semiconductor over the surface of the material have been suggested to improve the stability. Since the choice and stability of redox electrolytes in aprotic solvents is limited and the coating of metallic or large band gap semiconductor over the surface of InP or GaP prevents direct contact between the electrolyte and the semiconductor, an efficient stable PEC cell either with GaP or with InP has not yet come out. Therefore, we start our survey on phosphides of other elements with the hope of finding a suitable phosphide material for this purpose.

2.2. Stability of phosphides in protic solvents

The phosphides of alkali and alkaline earth metals are soluble in water giving phosphine gas [35, 36]. Hence the phosphides of groups IA and IIA are not suitable for the PEC cell. Similarly, the phosphides of the

TABLE II Metallic and semiconducting phosphides

Metallic phosphides		Very low band gap phosphides			Medium band gap phosphides		
Material	Reference	Material	band gap (eV)	Reference	Material	band gap (eV)	Reference
CrP_4	[16]	CoP_2	–	[22]	AlP	2.50	[27]
FeP	[17]	CoP_3	0.45	[23]	BP	2.20	[28]
Fe_2P	[18]	FeP_2	0.37	[24]	$CdGeP_2$	1.80	[27]
MnP	[19]	MnP_4	0.14	[25]	$CdSiP_2$	2.20	[27]
MoP_4	[21]	NiP_2	0.50	[26]	$CdSnP_2$	1.50	[27]
TiP	[19]	PdP_2	0.60	[26]	GaP	2.24	[27]
TiP_2	[20]	PtP_2	0.60	[26]	$GaAs_{0.85}P_{0.15}$	1.44	[29]
VP_2	[20]				InP	1.27	[27]
VP_4	[16]				$In_{2/3}PSe_3$	1.55	[30]
α-WP_2	[20]				Zn_3P_2	1.32	[31]
WP_4	[21]				$ZnGeP_2$	2.20	[27]
ZrP_2	[20]				$ZnSiP_2$	2.30	[27]
					$ZnSnP_2$	2.10	[27]

TABLE IIIa Basic materials and container for hydrogen reduction

Final compound to be prepared	Basic materials			Container
	Metal form (powder)	Amount of metal form (g)	Volume of *o*-phorphoric acid (ml)	
Cobalt phosphide	Co	5	20	Graphite
Chromium phosphide	Cr	5	20	Graphite
Iron phosphide	Fe	5	20	Graphite
Manganese phosphide	$MnCO_3$	5	20	Graphite
Molybdenum phosphide	MoO_3	5	20	Graphite
Nickel phosphide	Ni	5	20	Graphite
Titanium phosphide	Ti	5	20	Graphite
Vanadium phosphide	V_2O_5	5	20	Graphite
Tungsten phosphide	W	5	20	Quartz
Zirconium phosphide	$Zr(NO_3)_4$	5	20	Quartz and Platinum

elements of group IIIA and the phosphides of costly metals like palladium, platinum and gold have been discarded from our survey, because they would make the cost of the PEC cell very high. Apart from these phosphides, there are about sixty phosphide materials which are inexpensive and stable in the protic solvents (water and/or acid and/or alkali). Since most of the phosphides of cobalt, chromium, iron, manganese, molybdenum, nickel, titanium, vanadium, tungsten and zirconium are expected to be stable in protic solvents, the phosphides of these metals are selected for detailed studies.

2.3. Methods for the preparation of phosphides available in the literature

Although more than eight methods have been reported in the literature for the preparation of phosphides [37–45], many researchers have preferred the elemental combination and the phosphoric acid methods for the preparation of most of the phosphides. The elemental combination method needs a very high inert atmospheric pressure (up to 3 GPa) [46]. In the present work, attempts are made to prepare the phosphides of the ten metals listed in Section 2.2 by firing a mixture of metal, or metal oxide, or metal nitrate or metal carbonate and phosphoric acid. The detailed procedure is discussed below.

3. Experimental details

3.1. Preparation of metal phosphides

A known weight (5 g) of metal or its oxide or salt was slurried with ortho-phosphoric acid (20 ml). The slurry was slowly dried in air at 500° C for about 20 h. The almost dried material was fired in a furnace at a suitable high temperature for several hours in argon atmosphere. For the preparation of tungsten or zirconium phosphide a tubular furnace and quartz container were used whereas for the preparation of other phosphides, a muffle furnace and graphite container were used. The latter phosphides were prepared in normal air.The powder thus prepared was made into a pellet. The resistance of the pellet was found to be very high and therefore, it was hydrogen reduced at a suitable temperature for a definite period to get a high conducting pellet. All these conpounds, on hydrogen reduction, showed increase in conductivity except chromium, manganese, titanium and zirconium. Therefore no further work was carried out with these four phosphides. The detailed conditions of preparation for each metal phosphide are given in Tables IIIa, b and c.

This method of preparation was found to be more satisfactory than direct combination of elements because we were not sure of the correct metal/phosphorus ratio to give a semiconducting grade phosphide. In this method, phosphorus is present with metal in very large excess and phosphorus is gradually removed from the sample as phosphine gas by hydrogen reduction until we get high conducting semiconducting grade metal phosphides. Due to lack of time, we have not been successful with chromium, manganese, titanium and zirconium, which will be considered in further studies. The other six phosphides were characterized for their band gap, empirical formula, energy level diagram and their photoresponse in a PEC cell.

TABLE IIIb Firing temperature, time, atmosphere and colour before hydrogen reduction

Final compound to be prepared	Temperature at which fired (° C)	Time of firing (h)	Atmosphere at which fired	Colour before hydrogen reduction
Cobalt phosphide	960	12	Air	Dark grey
Chromium phosphide	960	12	Air	Dull green
Iron phosphide	960	12	Air	Grey
Manganese phosphide	960	12	Air	White
Molybdenum phosphide	960	12	Air	Dark green
Nickel phosphide	960	12	Air	Greenish yellow
Titanium phosphide	960	12	Air	White
Vanadium phosphide	960	12	Air	Green
Tungsten phosphide	1060	4.5	Ar	Grey
Zirconium phosphide	1000	2	Ar	White

TABLE IIIc Temperature and time of hydrogen reduction

Final compound to be prepared	Temperature (° C)	Time (h)	Colour after hydrogen reduction
Cobalt phosphide	800	2	Greyish black
Chromium phosphide	800 and 900*	8 and 3/4	Greenish grey
Iron phosphide	800 and 900*	6 and 3	Deep black
Manganese phosphide	800 and 900*	2 and 11	White
Molybdenum phosphide	800	8	Deep black
Nickel phosphide	900	2	Black
Titanium phosphide	800 and 900*	7 and 7.5	White
Vanadium phosphide	975 and 1075*	6 and 4.25	Deep black
Tungsten phosphide	500 and 800*	20 and 4	Grey
Zirconium phosphide	925	4	White

*The time and temperature at which it was fired first and then subsequently fired at higher temperature for corresponding time.

4. Results and discussion

4.1. X-ray diffraction studies

The *d*-values from the X-ray diffraction (XRD) data with copper target of these six hydrogen reduced phosphides (i.e. cobalt, iron, molybdenum, nickel, vanadium and tungsten-phosphides) were compared with the reported *d*-values [47] of oxides, phosphates and phosphides of these six metals. All the prominent peaks do not match with the reported values except for molybdenum phosphide and nickel phosphide which almost match with the reported prominent peaks of MoP_2 and Ni_2P. The *d*-values of these six compounds are given in Table IV in decreasing order of intensity (the reported values for MoP_2 and Ni_2P are given in parenthesis). However, due to the mismatching of *d*-values for corresponding metal, oxide, phosphate or phosphide with the observed XRD values, it is suggested that these materials must be phosphides with a composition not reported earlier. Studies of the structure of these phosphides are currently taking place. The XRD also suggests that all these phosphides are crystalline in nature with sharp *d*-values.

4.2. EDAX observations

The six compounds which are given in Table IIIc, namely Co–P, Fe–P, Mo–P, Ni–P, V–P and W–P were analysed by using EDAX (energy dispersive analysis of X-rays) to find out the relative atomic weight percentages. These atomic weight percentages and calculated empirical formulae are collectively given in Table V. The electron affinity values (i.e. bottom of the conduction band) for all the six phosphide semiconductors are calculated by using the Butler and Ginley method [48] and are given in Table V. Based on the band gap and the position of conduction band calculated by the Butler–Ginley method, the valence band position for all the six compounds are calculated and the band diagrams are given for all the six compounds in Fig. 5. In order to test the validity of the Butler–Ginley method for compounds whose empirical formula only is available, we calculated the electron affinity of α-$Fe_2O_3$by making formulae like $FeO_{1.5}$, Fe_4O_6. The electron affinity for all these empirical formulae was the same as that calculated by using the molecular formula. Therefore, from our calculations although we do not know the exact formula of the phosphides, we can take the empirical formula to calculate the band positions of these phosphides.

TABLE IV *d*-values (nm) in decreasing order of intensity using Cu-target

Co–P *d*-value (nm)	Fe–P *d*-value (nm)	Mo–P *d*-value (nm)	Ni–P *d*-value (nm)	V–P *d*-value (nm)	W–P *d*-value (nm)
0.309 72	0.301 53	0.21 300 (0.216)	0.225 21 (0.221)	0.33731	0.383 06
0.246 61	0.307 63	0.403 68 (0.371)	0.206 51 (0.203)	0.355 87	0.347 67
0.350 36	0.311 84	0.284 64 (0.259)	0.194 73 (0.192)		0.376 66
0.202 99	0.268 04		0.171 43		0.332 37
0.329 95	0.162 47		0.169 08		
0.439 22			0.127 99		
0.268 04			0.110 88		
0.214 93					
0.173 84					
0.295 68					

4.3. Ultraviolet/visible and near infrared reflectance spectra

The band gap values of α-Fe_2O_3, Pb_3O_4, SnS and SnSe [10, 49] determined by this method were in good agreement with the reported band gap values and hence this method was followed for finding out the band gap of the phosphide materials. The UV/visible reflectance spectra were taken for the six compounds, namely Co–P, Fe–P, Mo–P, Ni–P, V–P and W–P in a 200 to 900 nm region and they all showed no absorbance. The reflectance spectra were taken for these six compounds in the region of 1000 to 2100 nm (near IR), and these spectra showed absorbance. Since the nature of spectra of all the six compounds in the region of 1000 to 2200 nm is the same, only one spectrum (i.e. the spectrum of W–P) is shown in Fig. 3.

From these spectra, the band gaps of all the six compounds were found by plotting the differential transmittance as a function of wavelength, ($dT/d\lambda$) against λ (transmittance, T, obtained from the reflectance spectra). The differential transmittance with respect to wavelength plot of tungsten phosphide is shown in Fig. 4. The equivalent energy for a particular wavelength at which the maximum absorption takes place is taken as the band gap of the compound. The band gap values of these six compounds are given in Table VI.

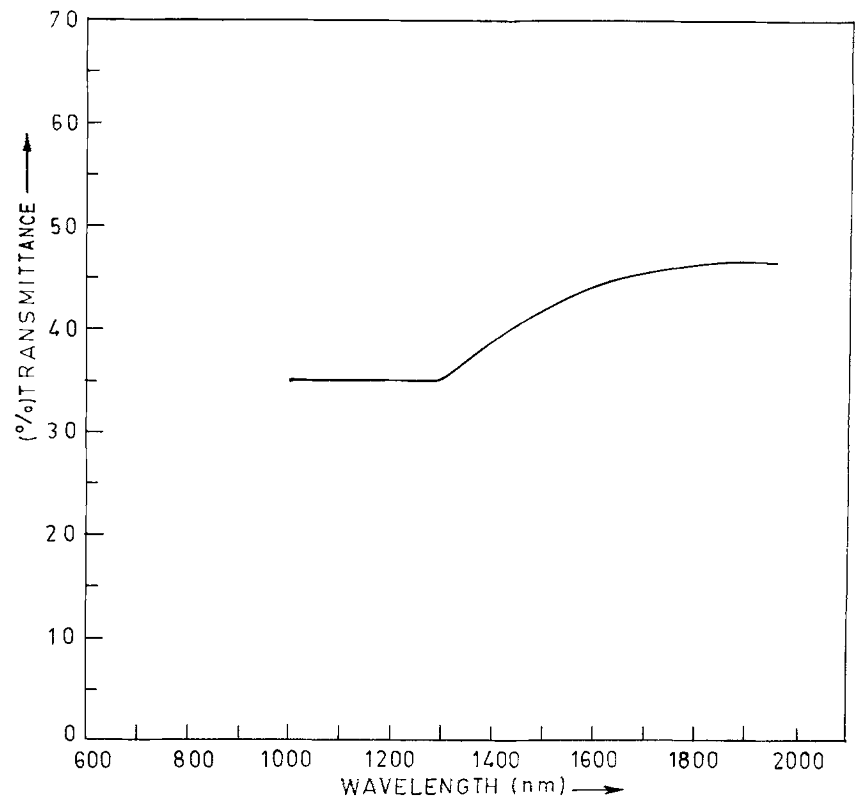

Figure 3 Reflectance spectrum of W–P.

4.4. Photocurrent measurements

Metal phosphide semiconductor/Ce^{3+}, Ce^{4+}/Pt was designed to measure the photocurrent of all the six phosphide-electrolyte-junction solar cells. In all the cases, silver was used as an ohmic contact, platinum (1 cm^2) as counter electrode and Ce^{3+}/Ce^{4+} (0.01 M) in 0.1 M H_2SO_4 as an electrolyte. The electrodes were exposed for 30 sec through a water filter, with 60 mW power, by using a tungsten halogen lamp (250 W). The dark open-circuit potential and the photocurrent, for all six phosphide semiconductors in the PEC cells of the above type, are given in Table VI. The high dark open-circuit potential may be due to the rough surface of the electrodes (used without etching) [50]. The photocurrent can be further increased by modifying the material and selecting a better electrolyte.

5. Conclusions

The survey on phosphides was very difficult, because little literature is available. Since we wanted to explore stable phosphides of cheap metals, it was possible for us to restrict the survey to chromium, manganese, titanium, zirconium, cobalt, iron, molybdenum, nickel, vanadium and tungsten. Since the band gaps of all possible stable binary phosphides of these metals are not available in the literature, it was difficult to select any particular phosphide of these elements. Therefore, it was decided to prepare those metal phosphides having maximum phosphorus content with each metal (Table IIIa) and gradually remove the phosphorus atom from the higher phosphides by hydrogen reduction to get a composition giving the required band gap. Phosphides of chromium, manganese, titanium and zirconium could not be studied in detail because it was found difficult to reduce the higher phosphides to the lower phosphides. Nevertheless, we were successful with cobalt, iron, molybdenum, nickel, vanadium and tungsten whose results are given in Tables IV, V and VI. The band gap reported in Fig. 5 does appear lower than 1.0 eV, but has been decreased from a higher band gap of about 3.0 eV. Thus, by more accurate control of hydrogen reduction one may be able to obtain these phosphides having a band gap in the region of 1.0 to 1.8 eV. Work is in progress in this direction.

The selection of decomposition temperature for converting phosphate to phosphide, and temperature for hydrogen reduction to get the required phosphide was also very difficult. The conditions were arrived at after many trial experiments (Table IIIb and c). Most

TABLE V Relative atomic weight percentage of elements, electron affinities and empirical formulae of the six metal phosphides

Material	Atomic weight percentage of metal	Atomic weight percentage of phosphorus	Empirical formula	Electron affinity (eV)
Cobalt phosphide	18.516[Co]	81.483	$CoP_{8.35}$	5.02 and 5.13
Iron phosphide	84.514[Fe]	15.485	$FeP_{0.33}$	3.97
Molybdenum phosphide	62.592[Mo]	37.401	$MoP_{1.9}$	4.54 and 4.69
Nickel phosphide	82.088[Ni]	17.912	$NiP_{0.41}$	4.29 and 4.40
Vanadium phosphide	98.403[V]	1.597	$VP_{0.03}$	3.27
Tungsten phosphide	51.484[W]	48.515	$WP_{5.58}$	4.94

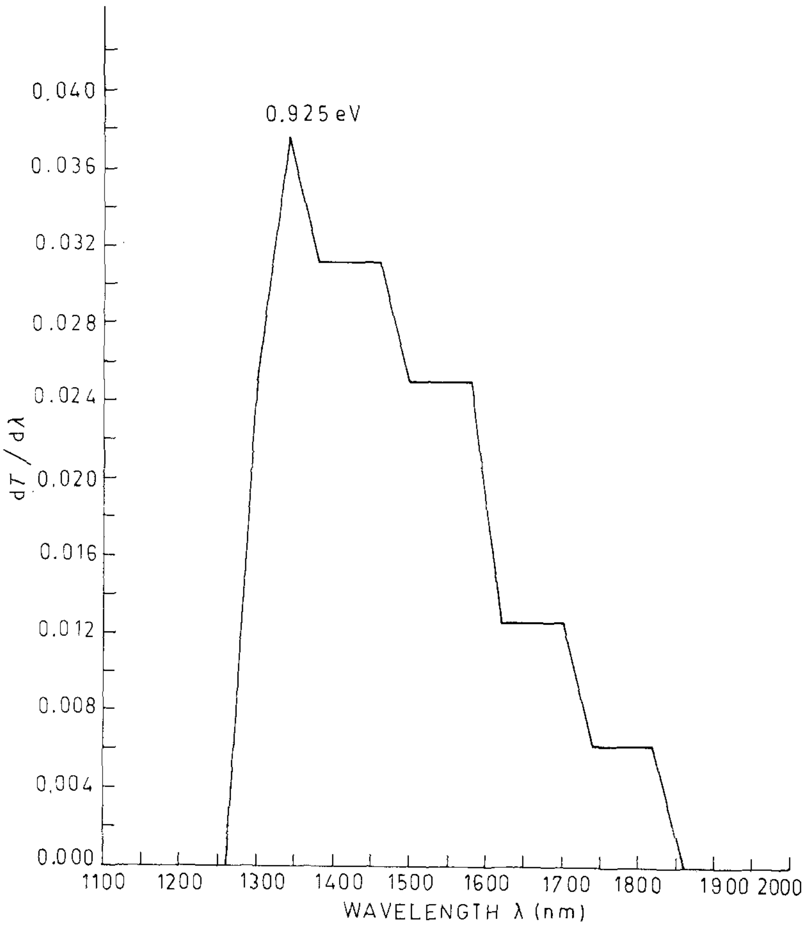

Figure 4 The differential transmittance with respect to wavelength for W–P.

of these phosphides are not reported, therefore we could not match XRD values with any published results. However, they did not match with XRD values of reported oxides, phosphates, phosphides or pure metals suggesting these compounds to be new phosphides. However, structural studies of these phosphides must be thoroughly investigated. Nevertheless, based on EDAX results and optical reflectance results, their band positions have been calculated (Fig. 5).

The theoretical band positions of these phosphides (Fig. 5) suggest that vanadium phosphide is likely to give negative flat band potential with respect to NHE (normal hydrogen electrode) whereas all the other phosphides would give a positive flat band potential with the exception of iron phosphide which can give both types of flat band potential. Therefore, in order to get the highest open-circuit potential (V_{oc}) in a solar chargeable battery one can use four electrode systems (Fig. 2) where one electrode could be made of vanadium phosphide (n-type) and the other could be either tungsten phosphide (p-type) or cobalt phosphide (p-type). Iron and nickel phosphides could also be interesting compounds to study because their respective n- and p-type materials could give V_{oc} as much as 1 V (i.e. in a four electrode system). The photoresponse values in the PEC cell (Table VI) cannot be taken as the best values, because the Ce^{3+}/Ce^{4+} electrolyte need not be the best electrolyte for all these phosphides. Nevertheless, this experiment suggests that all these phosphide materials are photosensitive and can be used in wet photovoltaic cells.

The structures of these compounds have to be studied in detail before any definite conclusion can be drawn. Presently, the metal phosphorus ratio has only been studied by EDAX. It is also necessary to realize that for the development of an economically viable solar battery no other phosphide materials except the phosphides of cobalt, iron, molybdenum, nickel, vanadium and tungsten should be tried. Although InP and GaP have given high efficiencies, neither of these materials is stable in electrolyte for long periods and both are too expensive to be used in an economically viable wet photovoltaic cell.

TABLE VI Photocurrent and band gap values

Materials	Dark open-circuit potential (V)	Band gap (eV)	Photocurrent ($mA\,cm^{-2}$)
Cobalt phosphide	1.03	0.885 and 0.666	0.223
Iron phosphide	0.77	0.860	0.919
Molybdenum phosphide	0.98	0.968 and 0.666	0.748
Nickel phosphide	0.59	0.885 and 0.652	1.768
Vanadium phosphide	0.66	0.784	1.256
Tungsten phosphide	1.11	0.925	0.215

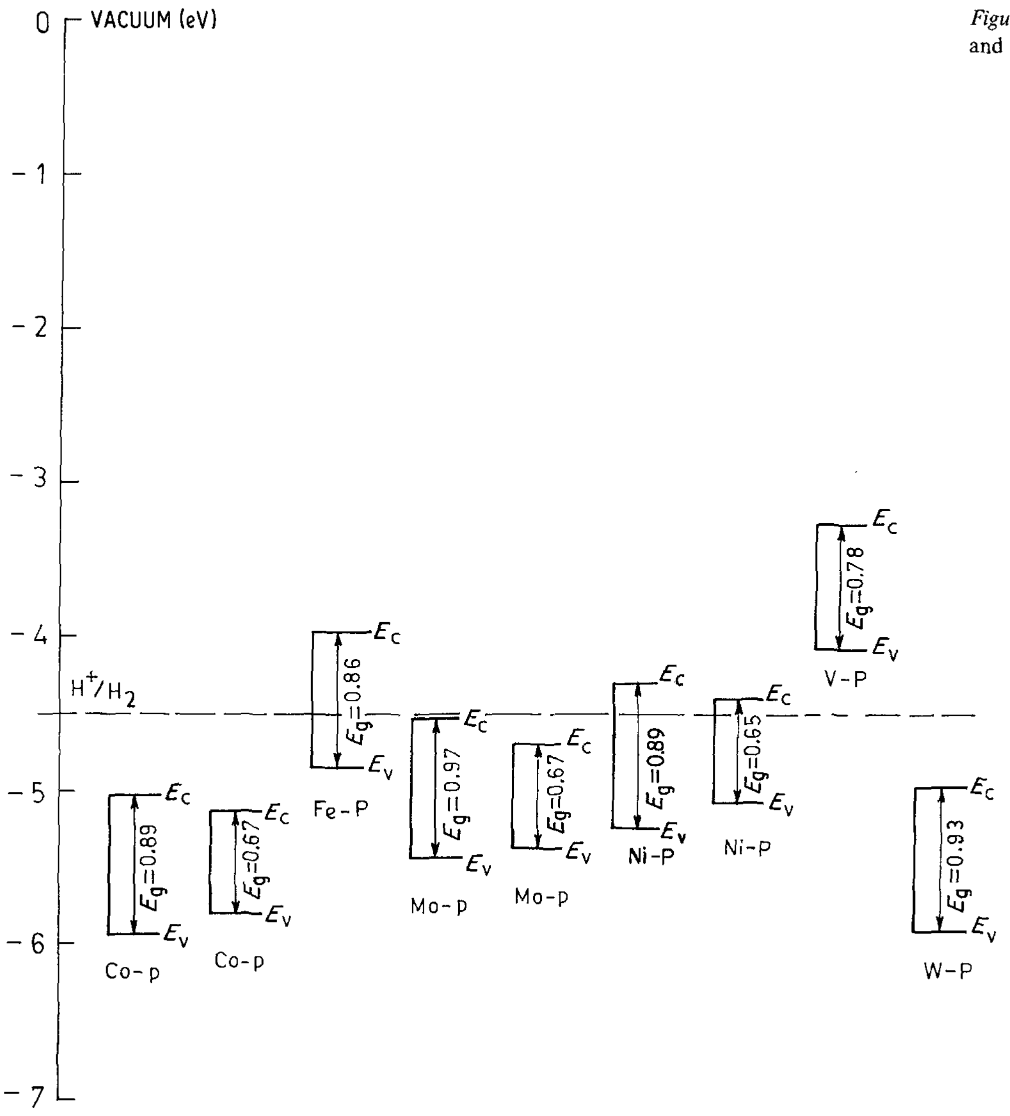

Figure 5 Positions of conduction and valence band edges.

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