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Materials aspects of photoelectrochemical energy conversion

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Stabilization of the light-harvesting semiconductor electrode is a key factor in the design of a photoelectrochemical (PEC) system for solar energy conversion. Approaches to circumvent the problem of PEC corrosion of these electrodes involve four major categories of materials: (a) the electrode materials themselves; (b) protective coatings; (c) catalysts; and (d) electrolytes. Wide band-gap semiconductors are candidates for electrode materials; however, their use hinges on devising effective means of sensitizing their photoresponse to wavelengths comprising the solar spectrum. These and related aspects in the design of PEC systems are reviewed in this article. Devices both of the regenerative type as well as photoelectrolysis approaches are considered.

1. Introduction and scope

Photoelectrochemical (PEC) methods of converting sunlight into electricity and chemicals have been a fertile area of research in recent years. The many advances that have been made in the science and technology of PEC systems have been the subject of several review articles [1–17] and conference proceedings [18–21]. High conversion efficiencies have been demonstrated on a laboratory scale for a variety of systems. However, many questions remain before the scientific knowledge and technology based on these systems can be translated to routine adoption of PEC methods for utilization of solar energy. As with the solid-state photovoltaic counterparts, the majority of these questions are in an ultimate sense materials-related. It is, therefore, the purpose of this review to summarize the state-of-the-art in materials aspects of PEC systems.

The light-harvesting electrode material is a key component of PEC systems. A preliminary cost analysis on model PEC assemblies reveals that materials and cell efficiency* far outweigh other factors in the cost of the overall system (cf. Fig. 1) [22]. Of the variety of materials constituting a PEC cell module, the semiconductor substrate and associated fabrication procedures comprise a large fraction of the total materials costs [22]. Thus the ultimate question in the widespread adoption of PEC systems (or for that matter any photovoltaic system) distils to the following: can we find or fabricate a semiconductor in a form which is (a) efficient and (b) economically competitive? This article addresses the present state of knowledge on aspects related to (a). The cost factor is not addressed herein since it is the perspective of this author that such considerations are best postponed until the technical merits of a candidate system are first firmly established.

No attempt was made in this article to provide a comprehensive compilation of the numerous studies that have been made on PEC systems in general. Rather, the approach adopted is one wherein an important finding on a given material is highlighted using some typical model studies. The literature cited covers mostly the period from 1978 onwards; earlier studies have been reviewed elsewhere [2]. Also it is not the purpose of this article to review the materials requirements for optimal conversion of sunlight. Such aspects, particularly those related to the semiconductor and electrolyte, have been the subject of earlier works [23–26]. Finally, the materials aspects in

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*For a discussion of various methods of defining PEC cell efficiencies, see Rajeshwar, Singh and DuBow [2].

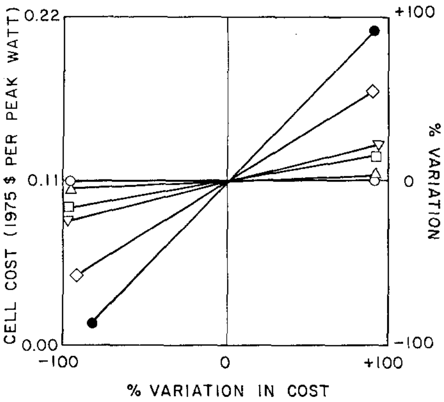

Fig. 1. Sensitivity of cell costs to selected parameters for the n-CdSe/Na_2S, S, NaOH/C PEC cell: ● – inverse efficiency; ◇ – materials; ▽ – labour; □ – equipment; △ – area; ○ – utilities (from [22]). (Published with the permission of Elsevier Sequoia.)

the closely allied area involving colloidal semiconductor suspensions (cf. [27, 28]) are not treated here *per se* except in their relevance to 'single-cell' PEC systems employing massive semiconductor electrodes.

2. Electrode materials

2.1. *Wide band-gap semiconductors*

For purposes of the following discussion, wide band-gap semiconductors are defined as those materials with an energy band-gap, $E_g > 2.5$ eV. Thus, n-TiO_2 ($E_g = \sim 3.0$ eV) and n-$SrTiO_3$ ($E_g = 3.4$ eV) qualify for inclusion in this category whereas n-CdS ($E_g = 2.4$ eV) and n- and p-Fe_2O_3 ($E_g = 2.2$ eV) do not. Wide band-gap semiconductors are of little practical use in photovoltaic and photoelectrolysis systems unless means are found to enhance their light response at higher wavelengths into the visible and IR region. Studies oriented in this direction have employed three strategies:

(a) doping of host material with 'impurity' ions such that levels (or bands) are introduced within its energy band-gap region,

(b) surface-modification of the semiconductor with a luminescent species (e.g. $Ru(bpy)_3^{2+}$, bpy = 2,2'-bipyridine) and

(c) mechanical treatment of the surface (e.g. polishing), again to induce sub band-gap states as in (a) above.

Each of these approaches is discussed in turn below.

Two doping methods have been advocated [29] to circumvent the problem with a low-lying valence band (typical of oxide semiconductors such as TiO_2) and consequent efficiency losses resulting from high O_2–H_2O overpotentials and inadequate utilization of the solar spectrum: (a) use of the same cation array to provide both valence and conduction bands and (b) use of a second cation array to provide the valence band, i.e. a mixed metal oxide with each band associated with a different cation. The first approach has been demonstrated with the perovskite, $LuRhO_3$ [30]. This material with an $E_g = 2.2$ eV, however, suffers from the handicap that its electron energy levels are not optimally placed relative to the redox levels for water oxidation and reduction.

Incorporation of two different cations in the same sublattice can give rise to either a new valence band with an energy, E_{VB}, falling in the gap region or localized trap states. A variety of transition metal ions has been introduced into TiO_2 [31–38] and $SrTiO_3$ [39–46] and the ground-states for these elements have been deduced from the positions of the d^n manifolds. A summary of the type of data available is assembled in Tables 1 and 2. Although extension of the spectral response into the visible region has not presented much of a problem for these materials the observed photocurrents as yet are nowhere near the levels required of a respectable PEC system. The results obtained by various authors, moreover, show serious conflict (cf. Table 1), a consequence, perhaps, of the varying fabrication procedures that have been employed. The poor efficiency of these candidate systems can be mostly traced to inducement of localized electron configurations in the host material and the formation of low mobility polarons (cf. Blasse, Dirksen and de Korte [47]).

Of related studies on the doping of wide band-gap oxide semiconductors, mention must be made of attempts to impart long-time stability to these materials by elimination of oxygen vacancies in the lattice via altervalent anion doping. Thus fluorine has been substituted for oxygen in TiO_2, $SrTiO_3$, SnO_2 and WO_3 [48]. The stability of *narrow band-gap* semiconductors such as n-Si is also claimed to be improved by doping of the sur-

Table 1. Representative studies on doping of n-TiO$_2$ photoanodes

Dopant	*Remarks*	*Reference*
Al, Sr, Ga, Eu, B	Wavelength response similar to undoped material. Improved stability and current–voltage characteristics observed in some cases.	[31]
Al, Cr	Spectral response extended. Improvement in quantum efficiency of carrier generation with aluminium doping.	[32]
Be	Negative shift in E_{fb} observed. Extension of spectral response minimal. Improvement in quantum efficiency and current density.	[33]
Al, V, Cu, Y, Ta, Nb, Mo, Ni, Pd	Effects similar in nature to those outlined above.	[34]
Ni, Cr, Zn, Cd	Decrease of quantum efficiency noted for all elements except cadmium. A red shift in spectral response observed.	[35]
Cr, Mn, V, Cu, Ni, Zn	Cathodic photoresponse observed from an impurity band located close to the conduction band of TiO$_2$. Enhancement of visible light response.	[36]
Ni, Nb	Enhancement of visible light response observed. Stabilization of Ni^{2+} species in TiO$_2$ lattice observed on Nb^{4+} incorporation.	[37]
Cr, Co, Ni, V, Mn	Enhancement of visible light response observed only for chromium. Incorporation of cobalt and nickel reported unsuccessful.	[38]

face layer with boron, aluminium or indium [49].

The second approach to the extension of the visible light response of wide band-gap semiconductors involves dye sensitization. Early work used ZnO and SnO$_2$ as model substrate compounds [50, 51]. More recent representative studies are summarized in Table 3. It was recognized early on that only dye layers in close proximity to the semiconductor surface were effective in sensitizing its photoresponse. This led to the rationale of covalently anchoring dye molecules, D, on the semiconductor surface [56]. However, it is pertinent to note that the efficiency of electron transfer from the excited state, D^*, into the conduction band generally has been low. A further handicap is the large reorganization energies observed for electron transfer in these systems. Notwithstanding this deleterious factor, strategies to minimize concentration quenching on dye-

Table 2. Representative studies on doping of perovskite semiconductors

Material	*Dopant*	*Remarks*	*Reference*
SrTiO$_3$	Al, V, Cr, Mn, Fe, Co, Ni	Response to visible light highest for chromium decreasing across this period of elements. No response to visible light observed for cobalt, nickel and aluminium.	[39]
SrTiO$_3$	Ni, V	Visible-light response observed. Low photocurrents.	[40]
CaTiO$_3$, SrTiO$_3$, MgTiO$_3$, CaZrO$_3$, SrZrO$_3$	Cr, Mn, Ni	Charge-transfer transitions observed for chromium and predicted for manganese and nickel.	[41]
SrTiO$_3$	Cr, Co, Pt, Rh	Visible light response attributed to impurity levels near the conduction band of SrTiO$_3$.	[42]
NiTiO$_3$	Nb	Visible light shown to induce Ni^{2+} → Ti^{4+} charge transfer transition. Ni^{3+} levels too high, however, for efficient photooxidation of water.	[43]
SrTiO$_3$	Cr with RuO$_x$ surface film	Hole trapping of Cr^{3+} minimized by presence of RuO$_x$ film.	[44]
SrTiO$_3$	Ru, V, Cr, Ce, Co, Rh	Enhancement of visible light response shown by electroluminescence experiments.	[45]
SrTiO$_3$	Zr		[46]

Table 3. Representative studies of dye sensitization of wide band-gap semiconductors

Dye/Substrate	*Remarks*	*Reference*
Rose Bengal*/ZnO	Quantum yield for electron injection, η_e, observed to be ~ 22%. Influence of halide ion supersensitizers studied.	[52]
Rose Bengal/TiO_2	$\eta_e = 4.0 \times 10^{-3}$ and is independent of pH. Photoreduction of dye observed on cathode polarization of TiO_2.	[53]
$Ru(bpy)_3^{2+*}/TiO_2$	Prolonged irradiation produces hydrolysis of outer dye lasers and decrease in photocurrent.	[54]
$Ru(pby)_3^{2+*}/TiO_2$, SnO_2	Rate of electron injection found to be faster for TiO_2 than for SnO_2. Water claimed as supersensitizer.	[55]
Rhodamine B*/SnO_2, TiO_2	No anodic photocurrent enhancement observed for modified electrode. Hydroquinone used as supersensitizer.	[56]
$Ru(bpy)_3^{2+}/TiO_2$	A cathodic photocurrent observed and a phenomenological model presented in terms of chemisorbed O_2^- species.	[57]
Eosine Y/ZnO	Electron injection studied by ESR techniques. Transient absorption for ZnO powder dispersed in gelatin studied by photoacoustic spectroscopy.	[58]
Rhodamine B/ZnO	Further evidence for electron injection from excited dye molecules presented. Radical cation formation implicated in CT mechanism.	[59]
Copper phthalocyanine/ZnO	Both anodic as well as cathodic photocurrents detected. Latter attributed to exciton generation and dissociation. Hydroquinone, *p*-quinone and O_2 used as supersensitizers.	[60]
Chlorophyll a/SnO_2	Quantum efficiencies of the order of 30% observed in some cases for electron injection.	[61]
Rhodamine B/SnO_2, TiO_2	Aspects related to fluorescence quenching by dimer formation and electron injection from monomers and dimers discussed.	[62]
Cyanine/ZnO	Characteristics of carrier injection from *J*-aggregates discussed.	[63]
Eosine Y, Phloxine B, Erythrosine, Rose Bengal, metal tetraphenylporphyrin/TiO_2, ZnO	Electron injection for xanthene dyes much faster than tetraphenyl, porphyrins. Effect of substitution on the electron injection process investigated.	[64]
Rose Bengal/Al-doped ZnO, CdS, TiO_2	An η_e value of 22% observed. Highest power conversion efficiency was ~ 2.5%.	[65]
Prussian Blue/TiO_2	Photoelectrochromic behaviour studied.	[66]

*The dyes have been covalently anchored on the semiconductor surface in these studies. In all the other cases, the molecules are simply adsorbed on the substrate.

sensitized surfaces by further immobilization of surface moieties in a polymer matrix (cf. Kaneko *et al.* [67]) seem worthy of further exploration. Understanding of heterogeneous charge transfer mechanisms at semiconductor/excited dye interfaces is an area receiving much current attention (cf. [53], 68]).

The third approach to visible light sensitization centres around creation of defects (and consequently band-gap states) in the material by appropriate surface treatment procedures. In the case of TiO_2, the visible light response induced by mechanical polishing was attributed to the existence of O: 2*p* and Ti: 3*d* (t_{2g}) sub-band gap states as a result of broken Ti–O bonds at the surface [69, 70]. Mechanical polishing has been more recently extended to sensitization of $SrTiO_3$ polycrystalline anodes [71]. The problem with this sort of approach is that defect states also act as efficient carrier traps thereby causing a decrease in quantum efficiency. The deleterious effect of surface flaws on the current–voltage characteristics of semiconductor photoelectrodes has been the subject of several studies (Tobayashi *et al.* [72]).

To summarize the present state-of-the-art on the use of wide band-gap semiconductor electrodes in PEC systems, the future of these materials will hinge to a large extent on breakthroughs in the above avenues and other new approaches to visible light sensitization.

2.2. *Narrow band-gap semiconductors*

As mentioned previously, all semiconductors with $E_g \leqslant 2.5$ eV are included in this category. It is convenient to discuss this class of materials in terms of various compound types.

2.2.1. Oxides. Perhaps the most widely studied of all narrow band-gap oxide semiconductors is Fe_2O_3. This is not surprising in view of the relatively small value of E_g for this material (E_g = 2.2 eV). An earlier report of a 'p/n diode' water photoelectrolysis system comprising p-GaP and n-Fe_2O_3 [73] was soon followed by a study on a similar system utilizing p- and n-Fe_2O_3 [74]. Acceptor doping was achieved by the introduction of silicon. The reported efficiency, however, is only 0.05% which raises questions related to intrinsic limitations [75] with this material. It has been concluded that such limitations are mostly traceable to poor surface properties rather than to bulk transport problems [75]. Interestingly enough, a surface layer of Fe_3O_4 has been implicated in the *appearance* of photocurrents in α-Fe_2O_3 [76]. An increase in sample resistivity was reported by removal of this layer [76]. A variety of dopants has been evaluated in efforts to decrease the resistivity of this material [76–78]. The use of Pt catalyst dispersed on an n-Fe_2O_3 surface also is reported to enhance photoeffects [79].

Of other oxide semiconductors in this category, mention may be made of NiO ($E_g = \sim 1.4$ eV) and CuO ($E_g = \sim 1.35$ eV). Both semiconductors are usually p-type; the former has problems with facile carrier recombination [80, 81] and the latter is photoelectrochemically unstable [82]. Relative to Fe_2O_3, these two materials do not seem promising for use in PEC systems.

2.2.2. Groups II–VI compounds. Cadmium chalcogenides (CdX where X = S, Se and Te) have received intense scrutiny in recent years [2]. The majority of these studies has been directed at the use of these materials in PEC cells of the regenerative type, although more recently photoelectrolytic (storage) systems have been demonstrated (e.g. [83–86]). Since single-crystals are of little practical interest, aside from their utility in model investigations, a variety of approaches has been adopted to fabricate CdX semiconductors in polycrystalline form. These approaches have been very recently reviewed [17]. The susceptibility of these materials to PEC corrosion remains a serious problem. Redox stabilization in aqueous electrolytes, while a viable alternative, has worked well only for polychalcogenide and $Fe(CN)_6^{4-/3-}$ couples (cf. [17, 87]). These redox electrolytes, however, suffer from major handicaps with poor visible light transmission characteristics, toxicity problems and susceptibility to photochemical degradation (see below). A more attractive approach is the use of nonaqueous electrolytes. The interfacial chemistry in these electrolytes seems to be very sensitive to surface treatment procedures, as demonstrated in recent studies on single-crystal CdTe photoelectrodes in acetonitrile [88–91].

Another class of Group II–VI compounds under investigation comprises ZnSe, ZnTe, and ZnTe–CdTe alloys [92–96]. ZnSe has been fabricated both in n- as well as p-forms although its energy band-gap is rather high ($E_g = \sim 2.7$ eV). ZnTe ($E_g = 2.3$ eV) occurs mostly as p-type material. As with their CdX counterparts, all these compounds are susceptible to PEC corrosion problems.

2.2.3. Group III–V compounds. Prominent candidates in this class of compounds are GaAs, GaP and InP. All these compounds occur in n- as well as p-types. Discussion of p-type compounds is mostly deferred to a subsequent section on catalytic surface modification.

PEC systems based on n-GaAs in general have exhibited high conversion efficiencies (e.g. [13, 97–100]). In order to render this candidate more attractive for use in practical PEC systems, efforts have been made to passivate grain-boundary recombination in epitaxially grown polycrystalline n-GaAs [17, 101, 102]. The results have proved quite encouraging. At the present state-of-the-art, this material, however, seems feasible only for use in concentrator-type solar photovoltaic devices. This is because of two factors:

(a) fabrication of thin film n-GaAs (and other Group III–V semiconductors) is still at an infant stage of development;

(b) high recombination rates of photogenerated carriers (both at the surface and in the bulk) remain an intrinsic problem with this material.

The latter, however, can be tackled with proper optimization of fabrication parameters as has been demonstrated in recent studies [99, 100].

The majority of the work with InP has centred around p-type material and its use in photoelectrolysis devices (e.g. [103]) (cf. Section 3). High efficiencies, however, have been reached in solar-to-electrical conversion PEC systems utilizing p-InP in contact with acidic VCl_3–VCl_2 electrolytes [104–106]. The use of p-type material avoids problems with oxidative corrosion of the surface. The relatively better performance of p-InP over p-GaAs in these cells is attributed to the different oxide surface chemistry of the latter [107]. Here elemental As is implicated in the creation of photocarrier killer traps in the band-gap region. There has been some discussion on interfacial chemistry at p-InP/electrolyte junctions. Work [108] on aqueous electrolyte interfaces shows no evidence of Fermi level pinning [109] whereas a constant photovoltage is observed with a wide range of couples in acetonitrile [110]. This difference in observed behaviour underscores the sensitivity of semiconductor electrode surfaces and interfacial effects to the nature of the solvent, redox couple and other variables. Attempts to offer explanations to account for the behaviour of *all* interfaces in general without taking into consideration factors unique to each system, as have been done by some authors (e.g. [111]), are flawed in this author's opinion.

Studies on GaP again are largely confined to p-type material in applications directed at driving suitable endergonic chemical reactions [112–115]. Unlike GaAs and InP, however, the relatively high E_g of this material ($E_g = 2.4$ eV) has resulted in attempts to extend the spectral response to the visible region. One such series of studies (e.g. [116, 117]) has been directed at incorporation of monolayers of metals such as gold, silver, palladium or copper on the electrode surface and consequent creation of band-gap states. (Sub-band-gap response also has been induced in GaP by H- and He-ion implantation [118] and by Ru-ion surface treatment [119].)

Similar to the cases of GaAs and InP discussed above, the presence of oxide layers has been shown to be important in the stabilization of p-GaP photocathodes [120]. Another interesting study describes construction of a PEC battery with n-GaP in contact with aqueous $Fe(CN)_6^{4-/3-}$ couple [121]. The energy gained at the photoanode is stored by nickel deposition on a platinum substrate.

2.2.4. Silicon. It is probably safe to conclude that silicon is the single most widely used semiconductor electrode material in PEC systems. As with solid-state photovoltaic systems, the high level of technology which currently exists for this material is largely responsible for its popularity. The indirect band-gap of silicon, however, necessitates the use of rather thick layers. Amorphous silicon, on the other hand, has a direct band-gap transition which is more optimally matched with the solar spectrum ($E_g = 1.4$ eV vs $E_g = 1.1$ eV for crystalline silicon). Representative results on these two types of silicon are summarized below.

The extreme susceptibility of silicon to PEC corrosion and subsequent passivation in aqueous media has led to a variety of attempts to stabilize this material. Aspects related to the use of coatings are discussed in a subsequent section. Here we review three other strategies; namely, the use of (a) derivatization, (b) nonaqueous solvents, and (c) p-type material with protective native oxide layer. The feasibility of stabilization by surface doping was mentioned previously (cf. Section 2.1.).

Photoanodic decomposition of n-Si has been suppressed by derivatization of OH groups via silylation [122, 123]. Surface-attached ferrocene electroactive centres have been used in these studies to mediate charge transfer to suitable reducing agents in solution [124]. Although long-term efficiencies have been demonstrated, solar conversion efficiencies in general have been low for these systems even with monochromatic light.

Use of nonaqueous solvents, while generally handicapped by poor mass transfer characteristics (see below), can also lead to stabilization of the n-Si surface [125]. With proper optimization of materials parameters, however, high efficiencies have been reported for a cell utilizing n-Si in MeOH with a ferrocene derivative as the redox system [126].

Similar to the approach with p-InP as described above, p-Si photocathodes have shown efficient and durable performance in acidic $V^{3+/2+}$ redox electrolytes [108]. As with p-InP, the presence of a thin protective native oxide layer is claimed to be responsible for PEC stability. Again similar to the case of InP, significant differences exist in the interfacial chemistry in these electrolytes relative to the nonaqueous electrolyte case, wherein the existence of Fermi level pinning has been claimed [127, 128].

Amorphous silicon in hydrogenated form has been the subject of recent studies [129–131]. Both aqueous [129] as well as nonaqueous solvents [130, 131] were employed in these studies. Conversion efficiencies reported in these studies are quite respectable and significantly enough, seem to approach the performance of n-Si under comparable conditions. This material will undoubtedly receive closer scrutiny in future if trends in solid-state photovoltaic technology are any indication at all of the shape of things to come.

2.2.5. Layered compounds. Transition metal dichalcogenides MX_2 have a two-dimensional structure comprising M–X–M sandwich layers. Next to Si, this class of compounds has, perhaps, received the most attention, largely because of the favourable combination of narrow energy band-gap and relative inertness to surface corrosion reactions in aqueous media. Table 4 summarizes typical results and applications of this class of materials in PEC systems. Counterbalancing the aforementioned attractive features of these systems are problems with anisotropic effects [133, 136, 169, 170] and difficulties with fabrication of these compounds in polycrystalline form (e.g. [164, 171, 172]). As is evident from Table 4, the majority of studies has been directed at MoS_2, $MoSe_2$ and the tungsten counterparts. More recently, zirconium and hafnium compounds have been examined, particularly with reference to their applicability to photointercalation strategies [173–175]. Intercalation offers a viable means of energy storage; an approach that has received considerable scrutiny in battery applications (e.g. [176]). PtS_2 and $RuSe_2$ are two other compounds whose PEC properties have been evaluated recently [177–180].

Another class of layered compounds under consideration is the Group III–VI chalcogenides (GaX and InX). Of these, p-GaSe ($E_g = 2.0$ eV and n- and p-InSe ($E_g = 1.3$ eV) have been the subject of recent studies [181–183]. As with the compounds discussed in the preceding paragraph, Group III–VI chalcogenides are also anisotropic; sandwich layers of X–M–M–X being held together by van der Waals forces. Chalcogenophosphate compounds, MPX_3, have been evaluated recently for use in PEC cells [184]. Three compounds in this series, namely, $SnPS_3$, $FePS_3$ and $NiPS_3$, were reported to yield clear photoresponse and low dark currents in aqueous H_2SO_4 solutions. $SnPS_3$ as grown by I_2 vapour transport, was found to be n-type whereas the other two compounds were p-type.

2.2.6. Ternary compounds. The cases of perovskite oxide semiconductors and alloyed Group III–V semiconductors were treated in preceding sections. We will consider ternary chalcogenides in this section along with a brief review of other ternary oxides that have been examined recently.

Ternary oxides derived from cadmium have been evaluated as candidates for photoanodes. Among the compounds are Cd_2SnO_4 (E_g = 2.12 eV), $CdIn_2O_4$ (E_g = 2.23 eV) and Cd_2GeO_4 (E_g = 3.15 eV) [185–188]. Cd_2SnO_4 is unstable on long-term operation in a PEC cell [185]. On the other hand, Cd_2GeO_4 has shown greater stability [186] although its large energy band-gap and the indirect nature of the optical transition are unfavourable characteristics. Further increases in PEC stability of this compound have been attained by partial substitution of silicon by germanium [187].

A sampling of other ternary oxides evaluated may be found in Table 5. In general, none of these compounds have as yet shown the combination of optimal electronic, optical and stability characteristics necessary to render them attractive for use in PEC systems. In most cases, favourable optical and stability characteristics are counterbalanced by unfavourable electron affinity (positive flatband potential, E_{fb}) and the consequent need for the application of external bias for photoelectrolysis reactions (cf. [2]). The use of 'ternary' oxides (e.g. Sb-doped SnO_2) as coatings for PEC electrodes, however, remains an attractive possibility. These compounds are taken up in a subsequent section.

An early report on the use of n-$CuInS_2$ in PEC cells [194] was more recently followed by a spate

Table 4. Examples of studies on photoelectrochemistry of transition metal dichalcogenides

Compound(s)	*Focus of study*	*Remarks*	*Reference*
n-MoS_2	Influence of crystal surface orientation on redox reactions	Rate of charge transfer greater by approximately one order of magnitude for $\parallel C$ surfaces than for $\perp C$ surfaces	[132]
n-$MoSe_2$, n- and p-WSe_2	Nature of optical transition, role of surface morphology, PEC H_2 evolution	Presence of an indirect band-gap implicated for lower-than-theoretical conversion efficiency	[133]
n-MoS_2, n-$MoSe_2$, n-WSe_2	Potential distribution and band-edge positions at the interface in acetonitrile	Beneficial role of inversion layers at the surface discussed	[134]
n-WSe_2, n-$MoSe_2$	Competition between PEC corrosion and hole transfer	Redox potential ordering seen to be strongly affected by specific surface interactions	[135]
n-WSe_2	Cell efficiency and surface morphology	Role of steps in carrier recombination elucidated	[136]
n-WSe_2	Cell efficiency and surface morphology	Edge sites are implicated by sub-band-gap spectral response	[137]
n-MoS_2	Potential distribution and band-edge positions at the interface in acetonitrile	Sustained photooxidation of chloride demonstrated	[138]
n-$MoSe_2$	Potential distribution and band-edge positions at the interface in acetonitrile	Fermi level pinning implicated. Efficiency for conversion of light to electricity with various solvent/halogen/halide combinations described	[139]
n-MoS_2, $MoSe_2$	Visible light driven oxidation of chloride and bromide	Sustained generation of halogens demonstrated in aqueous media	[140]
n-WSe_2	PEC cells for light-to-electricity conversion	High efficiencies demonstrated with polyiodide couple	[141]
n- and p-WSe_2	Photoelectrochemistry and photovoltaic PEC cells in aqueous solution	Light-to-electricity conversion, a rechargeable cell and photoproduction of H_2 and I_2 demonstrated	[142]
n-MoS_2, n-$MoSe_2$	Role of electron–hole recombination of photoanodes	–	[143]
n-$MoSe_2$, n-WSe_2	Effect of temperature on power output	Highest output observed at low temperatures ($< 15°$ C)	[144]
p- and n-WSe_2	Carrier-type inhomogeneity and efficiency losses	Coexistence of p- and n-domains in the same crystal leads to carrier recombination	[145]
n-$MoSe_2$, n-WSe_2	Chemical treatment of the surface	Passivation of edge sites observed by specific treatment procedures	[146]
n-WSe_2, n-$MoSe_2$	Photovoltaic PEC cells	Stable and efficient cells demonstrated in polyiodide electrolyte	[147]
n-WSe_2	Mapping of band-edges and redox chemistry in acetonitrile	Fermi level pinning observed	[148]
p-WSe_2	Photovoltaic PEC cells in nitrobenzene and acetonitrile	–	[149]
n-$MoSe_2$, n- and p-WSe_2	Redox chemistry in aqueous media	–	[150]
n-MoS_2, n-$MoSe_2$, n-WS_2	PEC oxidation of SO_2 in strong acid solution	Iodide mediated oxidation of SO_2 demonstrated	[151]
n-$MoSe_2$	Interfacial energetics in the presence of highly oxidizing redox systems	Formation of a surface inversion layer demonstrated	[152]
n-$MoSe_2$	Storage PEC cell	Halogen couples used to store solar energy	[153]
n-$MoSe_2$	Reactivity of water in acidic dissolution process	–	[154]
n-MoS_2, n-$MoSe_2$, n-WSe_2	Photocorrosion of these materials	Role of cleavage steps and dislocations studied. Enhanced reactivity observed at these sites	[155]
n-$MoSe_2$	Impedance of the n-$MoSe_2$/acetonitrile interface	Density and energy position of donor-like states at edge sites mapped	[156]
n-$MoSe_2$, n-WSe_2	Relative rates of hole transfer to selected redox probes	–	[157]

Table 4. (Continued) . . .

Compound(s)	*Focus of Study*	*Remarks*	*Reference*
n-$MoSe_2$	Redox chemistry of the polyiodide couple	Deactivation of recombination centres by adsorbed I_2 discussed	[158]
n-WSe_2, n-$MoSe_2$, n-WS_2, n-MoS_2	Photocurrent spectroscopy	–	[159]
n-$MoSe_2$, n-WSe_2	Photoelectrolysis of HBr and HI in a 'two-shot' PEC system with p-InP	Spontaneous evolution of H_2, Br_2 and I_2 with high efficiency claimed	[103]
p-WS_2	Electrochemical and PEC reduction of O_2	Mediated reduction via a naphthaquinone derivatized surface demonstrated	[160, 161]
n-WS_2	Photooxidation of halides in aqueous and nonaqueous media	–	[162]
p-WS_2	Characterization in acetonitrile	Catalytic modification is used to effect H_2 evolution	[163]
p-WSe_2	Fabrication of polycrystalline layers	–	[164]
n-WSe_2, n-$MoSe_2$	Passivation of carrier recombination sites by electrochemical polymerization	Selective polymerization at edges and steps passivates them	[165]
n-$MoTe_2$	Impedance spectroscopy in acetonitrile	–	[166]
n-$MoSe_2$	Surface stability of van der Waals surface	No reactivity of surface observed to a variety of species including I_3^-	[167]
n-$MoSe_2$, n-WSe_2	Transient photocurrent spectroscopy	–	[168]

of investigations. This renewed interest is due largely to the success achieved with ternary chalcogenides in solid-state photovoltaic devices [195, 196]. I–III–VI_2 compounds have been the focus of attention [197–202] although II–III_2–VI_4 and II_2–IV–VI_4 compounds are receiving scrutiny for PEC applications [202, 203]. All these compounds have very attractive optical properties although problems with high surface recombination rates, gradual deterioration in photoresponse and excessive dark current flow have been reported (e.g. [199, 203]). These problems, however, reflect those associated with the infancy of the art of fabricating these materials. Aside from their other favourable characteristics (cf. [204]), the most attractive feature with these materials is their amenability to fabrication in efficient polycrystalline form; a feature which has been demonstrated in recent studies on solid-state devices [195, 196]. This class of materials will undoubtedly continue to pose serious competition to silicon as the primary semiconductor candidate for photovoltaic applications. In terms of PEC applications, studies oriented towards better understanding of interfacial aspects (e.g. [205, 206]) will be necessary to resolve outstanding questions related to long-term operation (see above).

Table 5. Some ternary oxide systems evaluated for use in photoelectrolytic PEC systems

Compound	*Energy bandgap, $E_{g_{eV}}$*	*Conductivity type*	*Remarks*	*Reference*
$CdFe_2O_4$	2.3	n	Low current densities attributed to high resistance	[189]
$Hg_2Ta_2O_7$	1.8	n	–	[189]
$Hg_2Nb_2O_7$	1.8	n	Similar characteristics as above compound	[189]
$GeFe_2O_4$	$\geqslant 2.3$	p	Problem with low carrier mobility	[190]
$Sr_2Nb_2O_7$	3.86	n	–	[191]
$FeNbO_4$	2.0	n	E_{fb} is too positive	[192]
Fe_2WO_6	?	p, n	E_{fb} is too positive	[193]

2.2.7. Polymers. The emergence of conducting polymers as a new class of materials and their applicability to energy conversion devices (e.g. batteries) is intriguing from a PEC point of view. Doped polyacetylene is one such material which has been evaluated [207, 208]. While decent solar cell parameters were reported by the first group of researchers [207] for $(CH_3)_x$ films in sodium polysulphide solution, disappointing photoresponse was noted by the second group [208] for a cell based on methyl viologen as the redox species. In most organic photoconductors, the conductivity is dominated by trap-limited behaviour and the carrier-lifetimes are generally low. In view of this, the use of conducting polymers as protective coatings for narrow band-gap PEC electrodes seems to be a more attractive approach. This approach is discussed further in Section 3.2.

3. Electrode coating materials

The proclivity of most narrow band-gap semiconductors to PEC corrosion (cf. [209, 210]) necessitates some sort of coating on the electrode surface to prevent electrolyte attack. The strategy of surface derivatization was discussed in a preceding section. In a sense, the surface derivatized layer may be treated as an electrode coating with redox functionality incorporated in it. More frequently, the coating does not possess the latter characteristic; this is the case with metal films and wide band-gap semiconductor overlayers that have been employed as electrode coatings. In general, the optimal characteristics which a candidate coating material must have for PEC applications are fairly obvious: (a) high optical transparency over the solar spectrum and (b) good electrical conductivity. Chemical inertness is another useful characteristic especially since electrolytes for PEC applications span a wide range of reactivity (see below). This section will consider three major classes of coating materials, namely, metal (and metal-like) films, polymers and dyes.

3.1. *Metal films*

Depending on process parameters the extent of coverage of the semiconductor surface can be varied from catalytic amounts (much less than a monolayer) to complete coverage and fairly thick (a few hundred Å) films. We will consider the former case in Section 4 on catalyst materials for p-type films since catalytic amounts of metal will not generally afford corrosion protection for n-type semiconductor electrodes. Indeed an early report on gold overlayers on n-GaP photoanodes claimed a 'new' photovoltaic effect for 'Type B' porous films fabricated by rapid deposition [211]. This type of electrode was claimed to be effective for photoelectrolysis of water; a claim which since then has been challenged in subsequent studies [212, 213]. These studies suggest photocurrent flow in Type B electrodes as being due to photoanodic corrosion by electrolyte attack through the porous overlayer.

Metal overlayers will induce Schottky barrier formation at the metal–semiconductor interface if the electrostatic factors (work function–electron affinity differences) are satisfied (cf. [214]). In such cases, the electrolyte merely functions as a carrier collection medium and a constant photovoltage is developed at the metal–semiconductor interface regardless of the location of the solution (redox) potential. This 'heterojunction photoelectrode' concept has been illustrated for n-GaAs [215], n-GaP [211, 216] and interconnected n–p/p–n–Si junctions [217–219]. The last case differs somewhat from the other two examples in that the photovoltage is gained at the p–n junctions with the metal films merely acting as ohmic contacts. The photovoltage gained at the p–n junctions can be used to drive a suitable endergonic reaction (e.g. photoelectrolysis of HI, HBr, HCl) [220, 221]. Other reactions have been demonstrated with such electrode designs; namely photobromination of phenol, photochlorination of cyclohexene, and reduction of O_2 [222]. Use of metal overlayers on PEC electrodes necessitates the balancing of absorptive losses in the metal film *vis à vis* the maintenance of adequate film thickness to insure sufficient integrity against electrolyte attack. Degenerate oxide semiconductors can offer a potential solution to these problems.

Early work on the use of wide band-gap oxide semiconductors as protective coatings [223] combined with the success achieved with metallic films (see above) has logically led to the evaluation of materials such as heavily doped SnO_2 as a candidate for electrode overlayers [224–228]. These materials possess the dual characteristics of high optical transparency and good electronic conductivity; herein lies the main advantage in their use relative to metal films. Tin-doped indium oxide (ITO) has been used successfully with n- and p-Si electrodes in aqueous electrolyte-based PEC cells of both the regenerative as well as the photoelectrolysis type [225]. Catalytic modification of the oxide layer was found to be necessary for the latter type of cell [224]. Electrochemical deposition of transparent oxide layers with controlled catalyst loading remains an intriguing problem. The related strategy of obtaining catalyst films by such methods is being tackled with reference to RuO_2 [229].

Noble metal silicide layers have been fabricated by initial deposition of the metal on silicon substrates followed by thermal treatment [230, 231]. Monitoring of the layer potential in contact with various redox couples reveals a behaviour consistent with a PtSi–Si heterojunction model, i.e. the photovoltage is developed at the silicide–Si interface [232]. As with the ITO case discussed above, these electrodes have been used in PEC cells of photoelectrolysis and regenerative types [230, 233].

3.2. *Polymers*

Spurred by reports of electrodeposition of conducting polypyrrole films on gold and platinum electrodes [234], n-GaAs photoanodes were stabilized by photoelectrochemically generated polypyrrole films in acetonitrile [235]. These studies have been later extended to CdX and Si photoanodes [236]. Peeling of polymer from the electrode surface was found to be a problem in this study although good adhesion was reported in a subsequent examination of polycrystalline n-Si [237]. Another group reports partial stabilization with hydrogenated a-Si-photoanodes coated with polypyrrole [238]. Use of a metal underlayer [239–241], interestingly enough, seems to offer increased corrosion protection for these polypyrrole-coated electrodes. Adhesive polypyrrole coatings have been reported on silicon electrodes using a silyl–pyrrole linkage [242]. Polypyrrole-coated n-CdS photoanodes have been recently used to drive the photoelectrolysis of water [243]. In a later study by the same authors, however, the role of the polymer film in electrode stabilization was found to be minimal, essentially similar degrees of stabilization being achieved with a catalyst alone [244]. Polyaniline films have been electrodeposited on CdX, Si, GaAs and GaP electrodes [245]. While efficient charge exchange with selected redox probes was not a problem, these films have shown less-than-ideal adhesion characteristics.

Aside from their role as agents to promote adhesion, metal underlayers also can enhance the rate of charge transfer at the electrode–polymer–electrolyte interface. This rationale has been applied in a two-layer ferrocene–polypyrrole-coated n-Si based PEC cell [246]. The kinetically-fast ferrocene–ferricenium ion couple introduces a redox functionality into the polymer film; simultaneously the ferrocene layer acts as a replacement for the metal underlayer. This approach, while attractive, needs to be explored further since problems remain with resistive effects in the two-layer coating with consequent deterioration in fill-factors.

Incorporating a redox functionality in the polymer film is an attractive means of mediating charge transfer across the interface. For n-type electrodes this redox mediator has to possess a redox potential which lies positive to the corresponding species in solution [247]. If the redox functionality additionally possesses useful photochemical characteristics, interesting possibilities emerge. One such model system under consideration is polystyrene film containing pendant $Ru(bpy)_3^{2+}$ moieties [248, 249]. The first requisite of affording corrosion stability to the semiconductor has been demonstrated for this film with n-GaAs and n-CdS electrodes [248, 249]; the latter under testing conditions of high chemical reactivity (photoxidation of Cl^- and Br^-). Aspects related to the mediating role of $Ru(bpy)_3^{2+}$ moieties remain to be clarified. Charge transfer across the interface is undoubtedly facile under optimized conditions as demonstrated for the n-GaAs cell containing the $Fe^{2+/3+}$ couple [248] and the n-CdS–aqueous electrolyte interface containing corrosive Cl_2 and Br_2 [249]. Redox reactions involving radical intermediates such as the latter example require the use of a multi-electron storage catalyst (e.g. RuO_2). This catalyst can be dispersed in the polymer matrix.

Rather than covalently anchoring the redox functionality in the polymer backbone, electrostatic binding of redox ions in a charged polymer matrix (cf. [250]) can be employed. This strategy has been demonstrated for n-Si electrodes coated with poly([4,4′-bipyridinium]-1,1′-diylmethylene-1,2-phenylenemethylene) dibromide [251]. The positively-charged polymer binds an anion redox species such as the $Fe(CN)_6^{4-/3-}$ couple.

The use of redox mediator polymer films is not restricted to n-type electrodes. Poly(benzyl viologen) layers have been deposited on p-Si photocathodes to afford the photoproduction of H_2 [252]. Incorporation of platinum catalysts in these layers results in underpotential evolution of H_2 although slow decomposition of the viologen is observed in long-term irradiation experiments.

A radically different approach to polymer coatings has been adopted by recent authors [253]. Based on the beneficial influence of an intervening oxide layer in solid-state photovoltaic devices (cf. the so-called metal–insulator–semiconductor type, cf. [7]), these authors propose the use of *insulating* polymer layers [253]. Poly(methyl methacrylate) and poly(ethylene terephthalate) were adsorbed onto an n-Si electrode surface. The current densities observed are not surprisingly poor (considering the thickness of the polymer films employed) although a fair degree of stabilization seems to have been achieved.

Of other polymers that have been evaluated, mention may be made of poly(3-methyl-thiophene) and poly(3,4-dimethyl-thiophene) deposition on n-GaAs electrodes [254].

To summarize the state-of-the-art in this area, it is the author's opinion that the strategy of using polymeric coatings in PEC electrode stabilization problems is at least as competitive as the other approaches that have been attempted. Further advances in this area on new polymers, on means of improving adhesion, and on a better understanding of charge-transfer processes at the interface should offer new perspectives and allow conclusions to be drawn. In the same manner that use of new semiconductor materials as PEC electrodes has kept pace with corresponding developments in solid-state photovoltaic technology, these advances should mirror those occurring on the electrocatalysis applications of polymer-modified metal electrodes.

3.3. *Dyes*

Dyes were discussed in a preceding section on sensitization of wide band-gap semiconductors. They are being employed also for stabilization of narrow band-gap semiconductors. The majority of such studies have considered metal or metal-free phthalocyanine films as candidates [255–257]. Interestingly enough, these materials as a class are semiconductors themselves [258]. Somewhat contradictory results have been reported for the efficacy of these materials in protecting the electrode surface from PEC corrosion. While no long-term stabilization was reported for CdS, CdSe and GaP even for thick (1–1.5 μm) films, even an ~ 100 nm film has been claimed to stabilize n-Si in aqueous media [256]. Obviously, the degree of stabilization is a sensitive function of a variety of factors (e.g. light intensity, redox concentration). The stability characteristics in general seem to improve at low light fluxes [257]. One interesting aspect of these materials concerns the influence of 'redox doping' on film conductivity [257]. Evidence for iodine penetration into the phthalocyanine layer has been presented [257]. Motivated by knowledge of the electrocatalytic behaviour of phthalocyanines towards the reduction of molecular oxygen [258], a recent study describes electrochemical incorporation of iron phthalocyanine in a polypyrrole matrix [259]. In these experiments involving glassy carbon electrodes, evidence for both $2e$ and $4e$ O_2 reduction mechanisms is presented. Extension of this approach to semiconductor electrodes should provide interesting results. Direct reduction of O_2 via a $4e$ transfer obviously has important implications in fuel cell applications.

Another class of materials under investigation is tetraphenylporphyrins [260]. These materials like the phthalocyanines are p-type semiconductors [260]. The mediator role of porphyrin films in interfacial charge transfer has been discussed for p-GaP as a model substrate [260]. This particular example provides a logical bridging point to the use of catalysts on p-type semiconductors; a topic considered in the next section.

4. Catalysts

As should be obvious from the preceding discussion, most PEC storage (photoelectrolysis) systems have involved H_2 generation as one of the half-cell reactions. Unfortunately, nature's trick has been to render the kinetics of this process sluggish on all semiconductor surfaces in general. Interestingly enough, this has the consequence that cathodic electrodeposition of semiconductors becomes feasible with essentially no interference from H_2 evolution reactions (cf. [261, 262]). The mechanistic and kinetic aspects of H_2 evolution at p-type III–V semiconductors have been addressed in recent studies [263–265]. The overall mechanism seems to be similar to that at metal electrodes; namely a two-step process involving adsorbed hydrogen atoms as intermediate species. The role of noble metal catalysts then is to provide suitable sites for adsorption and catalyse the conversion of H-atoms to H_2 such that back-reactions are hindered. Considerations for optimal spacing of catalyst islands on the semiconductor surface are discussed by a previous author [16]. For optimal collection of photogenerated electrons, the island spacing has to be less than the surface diffusion length of electrons. Implicit in this argument of course is the reasonable assumption that lateral diffusion of H-atoms (initially formed on the naked semiconductor surface) followed by their subsequent combination is less facile than the catalytic route.

The use of multi-electron storage catalysts is not limited to semiconductor photocathodes. Such catalysts have been deposited on n-type wide band-gap semiconductors (e.g. TiO_2) in applications related to construction of water photoelectrolysis systems based on colloidal particles [27, 28]. The semiconductor substrate in such studies has been called a 'multi-functional' catalyst (e.g. [266]) although use of the term 'catalyst' perhaps is more appropriately applied to the metal (or metal-like compounds, e.g. RuO_2) on the semiconductor surface. Such is the definition adopted here. We now proceed to discuss the use of such catalysts on two classes of semiconductors, namely, wide band-gap materials and narrow band-gap compounds.

4.1. *Wide band-gap semiconductors*

TiO_2 is the material most widely employed (see above) although $SrTiO_3$ [267, 268] and other oxide semiconductors such as WO_3 [269] and ITO [270] have been used as substrates for metal catalyst deposition. A variety of techniques has been used to deposit the metal islands (cf. [271]). The PEC method of metal deposition (cf. [272]) uses photogenerated electrons for the metal ion reduction and photogenerated holes in an anodic reaction involving the solvent (e.g. water) or sacrificial agents (e.g. acetic acid) to set up the local cell. Active sites for photodeposition of Pd at a TiO_2 surface have been found to be flawed regions whereas water oxidation is claimed to selectively occur at defect-free portions of the crystal [273]. Factors in the selectivity of anodic and cathodic processes in the overall deposition reaction have been further analysed by the same group [274, 275]. If the photogenerated charge can be separated by suitable addition of scavenging agents, then charge collection should be possible on an inert electrode in contact with a colloidal suspension [276, 277]. An enhancement of photoanodic current flow has been observed using Cu^{2+} and Fe^{3+} as electron-scavenging agents [278]. Platinized TiO_2 is also seen to enhance photoanodic current flow in the presence of acetate ions; an observation which seems to be consistent with the intermediacy of Pt–H species. A dual function of Pt overlayers is suggested for TiO_2 electrodes by other authors [279]. An electrocatalytic mechanism is advanced for H_2 generation and O_2 reduction for very thin 0.3 nm layers whereas mediation by band-gap states created by platinization (cf. Section 2.1.) is implicated in reduction of Ce^{4+}, Fe^{3+} and O_2 for thicker layers ($>$ 10 nm). Oxidation of platinum on TiO_2 was indicated by IR absorption studies using adsorbed CO as a probe [280]. Studies of a related nature on hydrogen isotope scrambling on Pt–TiO_2 contacts reveal spillover of hydrogen and/or deuterium from platinum onto the oxide in a vacuum environment [281].

The nature of the barrier at Pt–TiO_2 or in general noble metal–n-type semiconductor junctions has elicited much discussion [282–286]. The apparently facile reduction of protons that has been observed at illuminated Pt–TiO_2 junctions can be rationalized only if there is efficient transport of electrons across the interface. The question of whether noble metals (e.g. ruthenium, rhodium, platinum) form Schottky barriers on n-TiO_2 has been addressed in a recent study [284]. While expected barrier heights for M/TiO_2 range from 0.1 eV for ruthenium to ~ 0.7 eV for platinum, facile electron transfer is rationalized by invoking a mechanism whereby H_2 evolution is claimed to reduce the barrier height to a situation approximating near-ohmic behaviour [284]. Another school of thought considers the role of noble metal as merely to increase the exchange current density (i.e. the metal functions as an electrocatalyst rather than as a barrier-inducing material) [285]. Evidence to support this model has been put forward in terms of linear overpotential vs exchange current density variations for a variety of metals [285]. Shifts in the potential of metal films on n-TiO_2 have been monitored during the course of the H_2 evolution reaction [282, 283]. While a negative shift in film potential has been correlated with catalytic behaviour in one study [282], another set of experiments by the same group on identical metals reveals a positive shift in the potential of the metal film [283]. The polarization state of the underlying n-TiO_2 substrate obviously plays a critical role in dictating the extent of electron spillover from the semiconductor to the metal. The extent of coverage of the metal on the semiconductor also seems to influence the charging behaviour of the metal film (cf. [283]). Interestingly enough, a bi-functional role of n-TiO_2 in photoassisting O_2 and H_2 evolution requires asymmetric behaviour whereby the barrier is enhanced on O_2 exposure and diminished in H_2-containing ambients. Such asymmetry has been experimentally observed [284, 287]. It is not yet clear, however, to what extent band-bending effects; clearly applicable to single-crystal substrates, play a dominant role in colloidal semiconductors, wherein the entire dimensions of the particle more often are comparable to the nominal depletion-layer width at the interface.

4.2. *Narrow band-gap semiconductors*

The nature of the barrier and function of noble metal catalysts have been studied using p-InP as a model compound [288]. Contrary to expectations from the widely varying vacuum work-functions of platinum, rhodium and ruthenium, a constant gain in onset potential for H_2 generation has been observed at p-InP photocathodes for these metals [288]. The aforementioned role of H_2 alloying in altering the metal work-function is again implicated here; the barrier height is now *increased* because of the p-type conductivity of the semiconductor substrate (cf. [214]). Another aspect of this study is the role of the hydrated oxide layer on p-InP in passivating carrier recombination. Periodic anodic pulses have been used to restore this oxide layer during operation of catalytically modified p-InP as a photocathode [289, 290].

Another approach to facilitate rapid electron transfer from the semiconductor to the catalyst is via an electron relay. Alkly viologens are known to be facile relays in this regard. The case of poly (benzylviologen) was discussed in Section 3.2. 'Uphill' photoreduction of compounds such as N,N′-dimethyl-4,4′-bipyridinium ion (PQ^{2+}) to the cation radical (i.e. $PQ^{2+} + e \rightarrow PQ^{+\cdot}$) has been accomplished thus on p-Si photocathodes to demonstrate the feasibility of this type of approach [127, 291, 292]. Taken one step further, functionalization of this redox reagent on the p-Si surface has been carried out using the trimethoxysilyl derivative in conjunction with dispersed platinum or palladium catalysts [293, 294]. Such modified electrodes are claimed to afford efficient H_2 generation with monochromatic light.

Photoelectrolysis of H_2O and hydrogen halides remains the focus of attention in most studies on PEC storage systems. Other redox reactions, however, demonstrate the versatility of PEC methods. Two such examples are photoassisted reduction of 2-*t*-butyl-9,10-anthraquinone (as a synthetic pathway to photochemical production of H_2O_2) and photoassisted reduction of SO_2 [295, 296]. The latter reaction has been carried out in nonaqueous media at p-Si, p-WS_2 and p-InP photocathodes [296]. Platinization is found to have beneficial effects, particularly for p-InP. As with the cases treated in the preceding section (cf. Section 4.1.) there seems to be some ambiguity here also in the characterization of the contact formed by platinization.

Finally, an interesting example for uphill reduction of CO_2 (clearly an issue of environmental concern) is afforded by a recent study on p-InP [297]. Photoreduction of methyl viologen to the cation radical is coupled to a formate dehydrogenase enzyme. The latter reduces CO_2 to formate ion.

To summarize the situation as regards the role of noble metal catalysts on semiconductors, the question of ohmic contact vs Schottky barrier vs electrocatalyst needs to be further clarified. These catalysts certainly offer scope for challenging experimentation aimed at elucidation of factors controlling their chameleonic behaviour.

5. Electrolytes

Desirable characteristics for redox electrolytes in PEC systems have been reviewed by a previous author [25]. While consideration of properties such as toxicity and optical transparency is undoubtedly important, a primary factor in electrolyte screening is redox kinetics. Intuitively, a fast one-electron outer-sphere redox system is eminently suited to regenerative applications. This expectation is not strictly fulfilled for a variety of efficient systems that have been reported in the literature. Two examples that spring to mind are the polychalcogenide and polyiodide redox couples. Specific interactions with the semiconductor surface undoubtedly play a role here in insuring good kinetic facility for these otherwise rather sluggish redox systems. This aspect has been emphasized in a previous study [298]. However, it is reassuring to note that fast, well-behaved couples involving ferrocene and ferrocene derivatives yield satisfactory behaviour for a variety of semiconductors (e.g. [99, 100, 126, 299]).

The case of aqueous redox systems needs little amplification at this point other than to note that the majority of systems evaluated up to now are highly coloured and quite toxic. The search for more suitable candidates obviously must continue.

Amongst nonaqueous redox systems, four major categories may be recognized; namely conventional organic solvents (e.g. acetonitrile, nitrobenzene, tetrahydrofuran); molten salt electrolytes; liquid ammonia (and ammoniates); and solid electrolytes.

5.1. *Organic aprotic solvents*

The rationale for choosing an aprotic solvent is quite simple: the free energy gain associated with solvation of corroding species is minimized thereby stabilizing the semiconductor. Counterbalancing the attractive solvation characteristics of solvents such as acetonitrile are their poor mass-transport characteristics. Use of supporting electrolytes coupled with proper attention to cell geometry (e.g. use of thin-layer cells), however, can alleviate many of these problems as has been strikingly demonstrated in recent studies [99, 100, 126].

5.2. *Molten-salt electrolytes*

One advantage in the use of molten salt electrolytes rather than nonaqueous solvents such as acetonitrile is that related to conductivity. Molten salts have significantly higher conductivity than organic solvents. This obviates the need for supporting electrolytes in the former case. Counterbalancing this favourable characteristic of molten salts is their handicap with high viscosity. Even at elevated temperatures (175° C) studies have shown that diffusion coefficients of electroactive species such as ferrocene are an order of magnitude lower than corresponding values in acetonitrile [299]. Again as in the case of organic solvents, this difficulty may be partially overcome by the use of thin-layer cell designs.

Room temperature, molten salt electrolytes comprising mixtures of organic and inorganic halides are an interesting class of solvent candidates for PEC systems. Previous studies in the author's laboratory on $AlCl_3$–n-butylpyridinium chloride (BPC) mixtures as model systems have described stabilization of n-GaAs and n-InP electrodes [301–303]. A major advantage with $AlCl_3$–BPC mixtures is the capability to vary the acid base characteristics by adjustment of the $AlCl_3$:BPC mole ratio [304]. This has the important consequence that surface energetics of the semiconductor band-edges can be tuned with respect to the redox couple [298, 301–304]. Thus, deleterious back-reactions can be suppressed with consequent improvement in interfacial charge-transfer as demonstrated for the n-GaAs–$AlCl_3$–BPC interface [304].

A further advantage with acidic haloaluminate mixtures is the stability of aromatic radical cations in these electrolytes [300, 305, 306]. This contrasts with the behaviour observed for the oxidation of aromatic hydrocarbons in solvents such as acetonitrile (cf. [307]). The enhanced stability of radical cations ($Ar^{+\cdot}$) renders the use of aromatic hydrocarbons (Ar) as redox systems attractive in thin-layer PEC cells of the regenerative type (cf. [306]). $Ar^{0/+\cdot}$ redox processes, like the ferrocene/ferricenium ion couple, are usually characterized by fast kinetics; definitely an attractive prerequisite for redox candidates in PEC applications. A variety of haloaluminate molten salt electrolytes have been screened for PEC applications [308].

Related to the approach of using molten salt electrolytes in PEC systems is that employing highly concentrated alkali halides (e.g. lithium salts). As in the case of molten-salt electrolytes, problems with high viscosities remain in the use of these redox electrolytes. These electrolytes have been used in conjunction with layer dichalcogenide electrodes to drive the photooxidation of halides [140]. Si/ITO electrodes also have been used with success in concentrated (15 M) LiCl in the author's laboratory to drive the photooxidation of Cl^- ions [224]. In a similar fashion, n-InP electrodes have been stabilized in concentrated potassium iodide electrolytes [309].

5.3. *Liquid ammonia and related solvents*

Highly reduced species are very stable in liquid NH_3; so are solvated electrons in this medium [310]. Underpotential photoemission of electrons at p-GaAs electrodes has been used to construct regenerative PEC systems of the type, p-GaAs/NH_3, e_s/Pt where e_s denotes a solvated electron [310]. The high underpotential (~ 0.9 V) relative to platinum indicates a very negative value for E_{fb} in this medium. In a subsequent study by the same authors, photoemission at p-Si electrodes also has been demonstrated at potentials considerably more positive than the reversible value [312]. The observation of photoreduction processes involving e_s at potentials well negative of the conduction band-edge of p-Si is invoked as evidence for the existence of Fermi level pinning at this interface. However, it is not clear to what extent voltage drops across the ubiquitous native oxide layer can also account for observation of photoprocesses at potentials beyond the band-edges of the semiconductor.

Unlike the case of liquid ammonia where the use of low temperatures (~ – 50° C) is necessary, ammoniate derivatives of alkali halides (e.g. $NaI + xNH_3$) can be used at room temperature. Characterization of the latter class of protonic nonaqueous solvents has been the subject of recent studies [313, 314].

5.4. *Solid electrolytes*

Solid solutions of alkali metal salts and poly (ethylene oxide) have been considered as electrolytes in high energy density battery applications [315–317]. The high series resistance of this class of materials is presently a problem in the use of these materials for PEC applications. The use of thin films (~ 100 nm) to circumvent this difficulty (see above) is hampered by cell shorting problems (cf. [317]). Perhaps a more fundamental objection to further consideration of these electrolytes for PEC applications is that associated with the usual problems with the use and fabrication of solid-state photovoltaic junctions (e.g. lattice mismatch, thermal expansion). Indeed, the many advantages claimed earlier with the use of a semiconductor/electrolyte interface for photovoltaic applications relative to solid-state devices would be lost with this approach.

6. Miscellaneous components

In all of the preceding discussion, it was assumed that a front-illuminated cell design was employed for the PEC system. An approach to cut down solution absorption and reflection losses in the cell would be to illuminate the photoelectrode through a transparent rear contact. Again, Sb-doped SnO_2 is an eminently suitable material for such applications. The main factor in the design of 'back-wall' illumination cells is the optimization of film thickness relative to the minority carrier-diffusion length. Examples of studies on back-wall cell designs may be found in [26]. Another intriguing approach to minimize absorption losses in the electrolyte is the use of fluorescent cell windows. If the window absorbs certain wavelengths that are otherwise strongly absorbed by the electrolyte and re-emits them in a region wherein the electrolyte is transparent, absorptive losses can be theoretically precluded [318]. For useful collection efficiencies, however, rather large Stokes shifts will be necessary.

Another important component of a PEC system is the counter electrode. It was assumed thus far that polarization losses at this electrode are minimal. Such need not be the case for current densities (a few mA cm^{-2}) typical of efficient regenerative devices. Platinum is the material of choice in most applications although cheaper substitutes (e.g. brass) may function equally well for selected redox systems [319].

7. Concluding remarks

The aim of this article was twofold: (a) to summarize the current state-of-the-art and (b) to preview possible developments in materials aspects of PEC systems. The items highlighted in this article include developments of significance as well as areas wherein further clarification is necessary, at least in this author's crystal ball. It is pertinent to note that proponents of PEC approaches to solar energy conversion and storage chose, early on in the evolution of this field, to emphasize the inherent simplicity in fabrication of semiconductor/electrolyte junctions. It is debatable at the current stage of development whether the same researchers can claim that junction formation would be as simple as mere immersion of a semiconductor in an electrolyte! It should be apparent from the contents of this review that fabrication of stable and efficient PEC electrodes and cell designs has reached a level of complexity approaching that of solid-state photovoltaic devices. In spite of this trend, however, PEC systems offer intriguing possibilities for solar energy utilization. Their versatility in a variety of applications ranging from photoelectrosynthesis to environment control is the primary factor to be considered in the assessment of PEC systems relative to solid-state photovoltaic devices. Herein lies the future of PEC systems in the perspective of this author.

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