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Electrode Band Structure and Interface States in Photoelectrochemical Cells

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Efficient utilization of solar energy by means of photoelectrolysis requires an electrode material that is not only stable but also has an electron affinity that is small enough to give sufficient band bending. In addition, satisfactory material must have an energy gap that is well matched to the solar spectrum. The energy gaps of both TiO_2 and SrTiO_3 , which have values of 3.0 and 3.2 eV, respectively, are considerably too large to satisfy this latter requirement.

Furthermore no better single chemical compound has been found. This suggests trying a combination of compounds for electrodes. We will describe our program to develop electrodes, with the desired electrochemical properties, by such an approach. In particular, we will discuss composite structures and solid solutions. This is an ongoing program and what will be presented are mainly the concepts with only a few preliminary results.

Composite Electrodes

Beginning with composite electrodes the simplest scheme here is to coat the surface of a small gap semiconductor that is well matched to the solar spectrum but which is electrochemically unstable with a thin film of a wide gap, electrochemically stable semiconductor. To demonstrate the feasibility of using such a composite electrode, the film must be thin enough - of the order of 50-100 Å or less - so that at least some of the photogenerated carriers in the small bandgap material can tunnel through to the electrolyte. Furthermore the film must not have any cracks or pinholes since these would

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allow the electrolyte to penetrate through to the small bandgap material and cause dissolution. The formation of such a thin defect-free film by conventional techniques is very difficult and although many attempts have been reported, success has not been achieved (1,2).

We are investigating a slightly more complex type of composite electrode, in which the small bandgap semiconductor is protected by a much thicker, two-phase film such as shown in Figure 1. Here the low bandgap substrate material is CdSe, which has an $\epsilon_g = 1.7$ eV, and the large bandgap material is SrTiO₃. In this arrangement the protective coating, which is of the order of 500Å thick, consists of small grains of CdSe (~ 50Å in size) in a matrix of SrTiO₃. During photoelectrolysis, the hole-electron pairs are generated in the CdSe and separated by the depletion field. The holes move to the substrate-film interface and then tunnel through SrTiO₃ to the nearest grain of CdSe. After a few jumps between grains, the holes reach the electrolyte. This film should be effective in protecting this substrate provided the grains are isolated from each other. In this case the grains that are initially in contact with the electrolyte will be dissolved away until a continuous protective surface of SrTiO₃ is left in contact with the electrolyte.

Figure 2 is a schematic energy band diagram of this composite electrode indicating how the minority carriers from the bulk CdSe valence band tunnel through the SrTiO₃ to CdSe grains via surface states. The easy passage of minority carriers through the interface to the electrolyte requires that the valence band edge of CdSe overlap the surface states in the bandgap of the SrTiO₃. For free passage of the majority carriers between the two semiconductors, their electron affinities should be equal so that the potential barrier at the interfaces between them is negligible. These conditions are fairly well met in the CdSe-SrTiO₃ system.

In connection with this system a number of questions arise. First of all, because of interaction and scattering effects, the optical absorption of the two-phase film could be significantly greater than that of the individual components. In this case it would be necessary to shine the light onto the back surface of the substrate and the substrate would have to be very thin, of the order of the diffusion length; secondly, even if the carriers are excited through the protective layer and within the depletion region of the substrate, how efficiently would they transfer to the electrolyte? What would the nature of the states at the interfaces be and how efficiently would charge transfer between the grains to the electrolyte. What would the tunneling efficiency be and would carrier scattering be a problem? Thirdly, would the film fabrication process cause work damage to the substrate?

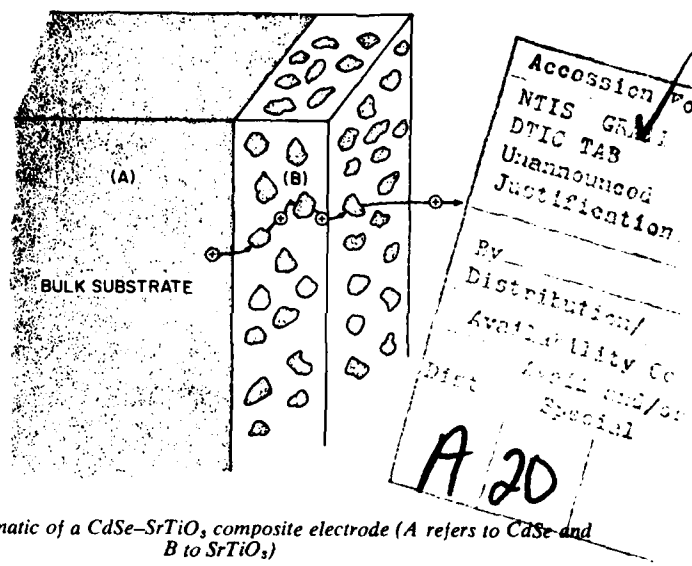


Figure 1. Schematic of a CdSe-SrTiO₃ composite electrode (A refers to CdSe and B to SrTiO₃)

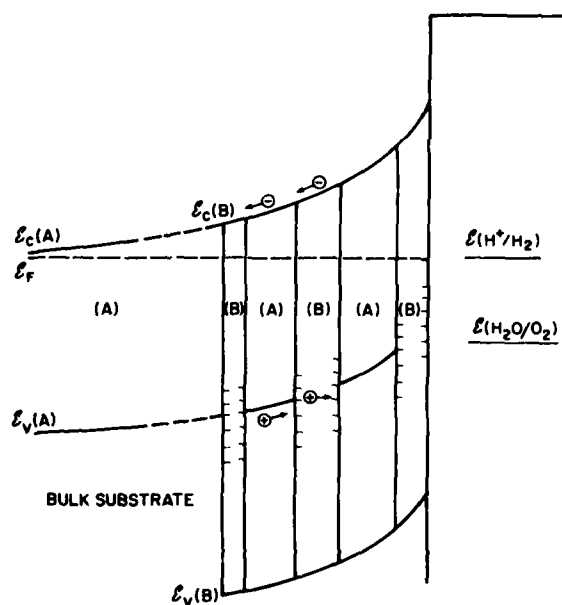


Figure 2. Energy band diagram of the CdSe-SrTiO₃ composite electrodes (A refers to CdSe and B to SrTiO₃)

Finally how would one make such a film? One way is shown in Figure 3. What is shown here schematically is an rf sputtering system. The substrate is mounted on a rotating disc and a microprocessor-controlled unit is used to produce sequential sputtering of two different targets, one for each component, with provisions for adjusting the proportions of the two components in the film to any desired value. Annealing or some other treatment after the sputtering may be necessary to insure that the SrTiO_3 forms a continuous matrix with the CdSe embedded in it.

Alloys

Another approach to the electrode problem is that of alloying either TiO_2 or SrTiO_3 with analogous compounds to form solid solutions which could have lower bandgaps and still retain the other desirable properties.

Alloying is widely used for adjusting the bandgaps in solid solutions of such semiconductors as Ge and Si, and GaAs and GaP, where the outer electrons occupy s and p orbitals. In these broadband materials an adequate description of the electronic states is provided by the band theory approximation; as a result alloying shifts the energy gap approximately linearly with composition although there are some cases in which an intermediate composition can have either a maximum or a minimum bandgap.

Transition metals such as Ti, however, have outer d electrons which exhibit a strong tendency to be localized and the simple one-electron band model is frequently not applicable to transition-metal compounds. Consequently these compounds and their solid solutions are generally not so well understood, although some experimental data and theoretical work on them exists. For these alloys not only can you get bandgap changes, but you can also introduce separate bands of levels due to the individual constituents of the alloy, and these can be partially responsible for lower energy transitions. For example, in the case of metallic alloys of Ni with Cu, one finds not just a single set of d band states, but two sets of states, one corresponding to Ni d states and the other to Cu states (3).

It is well known that the valence and conduction bands of TiO_2 are derived mainly from the oxygen 2 p states and titanium 3 d states, respectively, (4) as shown in Figure 4(a). Less is known of the compounds which are completely miscible with TiO_2 , namely TaO_2 , WO_2 , NbO_2 , VO_2 and MoO_2 . The first three of these compounds are semiconductors with a band structure similar to TiO_2 and energy gaps close to 3 eV. VO_2 on the other hand, is a semiconductor below 65°C where it undergoes a semiconductor-to-metal transition. Its bandgap of 0.7 eV separates two-subbands both derived from vanadium d-states as shown in Figure 4(b). X-ray photoemission data indicate that

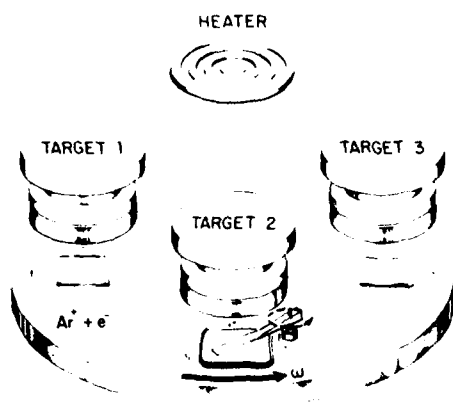


Figure 3. Simultaneous RF sputtering module

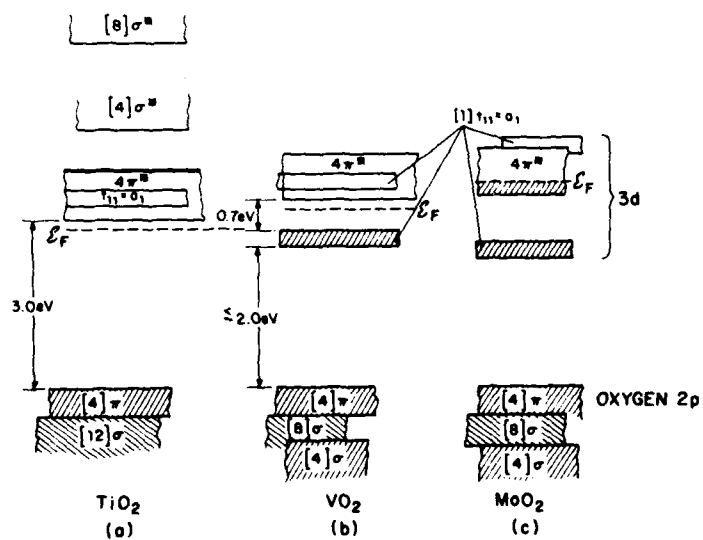


Figure 4. Energy band diagrams (after Ref. 4) for TiO_2 , VO_2 , and MoO_3

the gap in VO_2 analogous to the p-to-d gap in TiO_2 is less than 2 eV. Therefore one might expect that solid solutions containing a limited concentration of VO_2 will have the same basic band structure as TiO_2 but with a smaller bandgap. Even less is known about MoO_2 , except that it is a semimetal; its theoretical energy band diagram, as proposed by Goodenough, is shown in Fig. 4(c).

Another interesting system is based on alloys of SrTiO_3 with other ABO_3 compounds of the perovskite structure and is suggested by the work of Tributsch and co-workers, who have found stable photogalvanic action by using optical excitation between nonbonding d orbitals of transition metal dichalcogenides such as MoSe_2 (5,6,7,8). The same mechanism explains the photoelectrochemical stability of Fe_2O_3 (9,10,11,12) and YFeO_3 (13). However, a bias voltage must be applied to obtain photoelectrolysis with electrodes of the latter compounds, since their electron affinities are too high. SrTiO_3 - LaFeO_3 solid solutions appear interesting because we feel that such alloys could exhibit substantial solar absorption due to transitions between the Fe^{3+} d-levels of LaFeO_3 while retaining a large proportion of the favorable band bending of SrTiO_3 . In terms of the energy diagrams of Figure 4 SrTiO_3 would be represented by (a) and LaFeO_3 by (b) where the d-to-d gap is now ~ 2 eV. The preparation and characterization of perovskite based solid solutions, including a 50/50 LaFeO_3 - SrTiO_3 alloy, has been reported very recently by Rauh et al (14). For the latter compound, these researchers observed photoresponse at photon energies in the 2 eV range, but with very low photocurrents.

Experiments

Preliminary experiments with the composite electrodes indicate that optical scattering does not appear to be a problem; the action spectra of the composite films are similar to those of the bare substrate electrodes. The current-voltage curves, such as shown at the bottom of Figure 5 for a 50/50 composition of CdSe and SrTiO_3 , indicate that carrier scattering is a problem. Under illumination, the initial composite electrodes display very low photocurrents ($\sim 10^{-3}$ of the substrate material) and a linear dependence of current on electrode potential under both cathodic and anodic conditions, with no saturation effect in the anodic direction. Such behavior is suggestive of a barrier in which the carrier flow is diffusion limited, which would be the case if collisions at the CdSe - SrTiO_3 grain boundaries were significant (15). Annealing the electrode in an Ar atmosphere to $\sim 800^\circ\text{C}$ and then slowly cooling increases the photoresponse by one order of magnitude

but how much improvement will ultimately be obtained is not yet known.

Most of the TiO_2 and SrTiO_3 alloys were made by firing mixtures of powders of the appropriate oxides. Stoichiometric mixtures of the starting materials, which had a purity of at least 99.995% as obtained from Johnson Matthey Chemicals Limited, are finely ground and sintered in air at $\sim 1100^\circ\text{C}$ for about 12 hours. The materials are then pressed into discs, about 1 cm in diameter and 1 mm thick, and then reduced, depending on the alloy and composition, at temperatures between 1000°C and 1400°C and times ranging from 3 to 12 hours in an atmosphere of either forming gas or Ar in order to obtain conductivities which range between 10^{-1} and 10^{-3} mho/cm. Although we have fabricated solid solutions of TiO_2 with TaO_2 , NbO_2 , VO_2 and MoO_2 , the discussion here will be limited to the Nb alloys. In the case of SrTiO_3 , only results of alloys between this semiconductor and LaFeO_3 will be given.

Figure 6 shows the variation of integrated photocurrent versus photon energy for several electrodes of Nb composition, namely for 5, 10 and 20% NbO_2 in TiO_2 . Also shown for comparison is the result for a TiO_2 electrode which was reduced so as to be conducting. In these measurements the electrodes, which are all n-type, were held at a potential of +1.0 V rel to SCE. A 150 W Xe lamp in combination with low-energy-pass color filters was used to obtain these action spectra. Such a technique, while only yielding approximate action spectra, is useful in cases where the photoresponse is low. It will be noted that all the electrodes have maximum response in the UV but that the Ti-Nb electrodes have a response which extends below 3 eV into the visible region. Unalloyed TiO_2 also showed some response into the visible, but it was two orders of magnitude lower than for the alloys. Starting with the dashed curves, an increase in the low energy photoresponse is obtained as the composition is increased from 5 to 10% Nb and a small decrease as the composition is further increased to 20%. The decrease in the latter alloy is no doubt due to the fact that it is a two-phase material as identified by x-ray diffraction patterns. At the high energy end of the spectrum, on the other hand, a decrease in photoresponse is found in going from TiO_2 to increasing amounts of Nb. This tends to suggest that the same mechanism which produces the low energy sensitization also causes the lowered high energy response in agreement with the observations of Maruska and Ghosh for doped TiO_2 electrodes (16). This is not completely true, however, as the solid curve labelled (B) on this plot indicates. This curve is the action spectrum of the original 5% Nb sample labelled (A) taken after it was reoxidized in air at 1000°C for 10 minutes and then, reduced again. This heat treatment has improved not only the low energy end of the spectrum but also the high energy

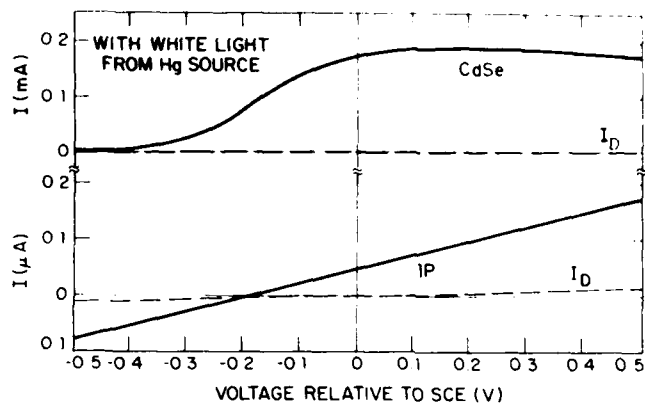


Figure 5. Comparison between I - V curves of a single-crystal, bare CdSe electrode (top) and a composite electrode (bottom) with light (—) and in the dark (---) (pH = 4.7)

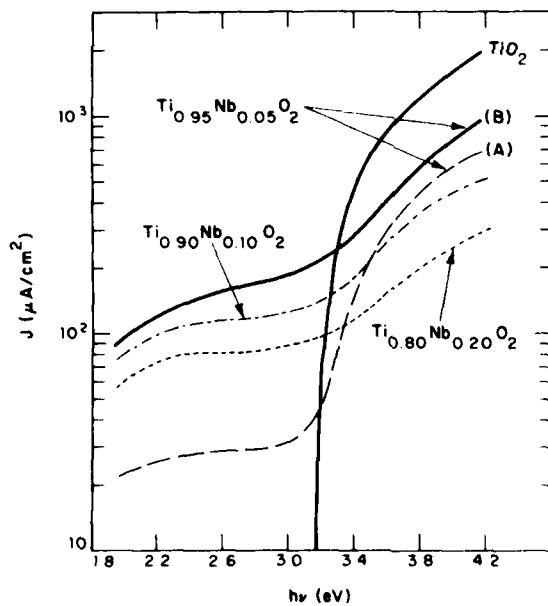


Figure 6. Integrated photocurrent vs. photon energy obtained with a 150-W Xe lamp in combination with low-energy-pass color filters. Electrodes are biased at +1.0 V relative to SCE (pH = 10). See text for difference between (A) and (B)

end. The result suggests the need for more detailed and careful characterizations (both physical and chemical) of the basic material properties in order to optimize the photoresponse.

Figure 7 is a comparison of the responsivity (that is, the variation of the normalized photocurrent with photon energy), of the 5% Nb alloyed sample (labelled (B) in Figure 6), of TiO_2 single crystal and of a NbO_2 powder disc electrode. The peak response of the alloy in the ultraviolet is one order of magnitude down from that of TiO_2 ; the alloy also has a response in the visible which, however, is several orders down from that in the UV.

The sintered NbO_2 electrode response peaks in the UV but has a tail in response which extends into the visible. The photoresponse in the UV is fast which suggests that this response arises from electronic transitions between the valence and conduction bands, and gives a value for the energy gap of NbO_2 of about 3.3 eV. The visible photoresponse on the other hand is slower and probably arises from states within the bandgap. The response of the $\text{Ti}_{0.95}\text{Nb}_{0.05}\text{O}_2$ alloy is almost a replica of the NbO_2 response but with an apparent shift of the energy gap to lower energies (~ 2.7 eV) and also a higher responsivity. This represents a shift of the energy bands rather than a tailing of the TiO_2 response which takes place with doping (16). Interestingly, this extrapolation suggests that the alloy might have a bandgap which is less than that of the two starting materials. Such effects have been observed in wide band semiconductors, e.g., the ZnSe-ZnTe system (17). The fact that the structure in the alloy action spectrum is similar to that of pure reduced NbO_2 implies that similar states exist in the alloy as in the reduced NbO_2 and that the low energy response in the alloy is not due mainly to strains arising from inhomogeneity or alloying. Conductivity versus temperature plots indicate that relatively shallow energy levels below the conduction band are introduced by the reduction process. Thus these states are bulk and not surface states.

Figure 8 compares the responsivities of a pure LaFeO_3 powder disc, single-crystal SrTiO_3 and 20% LaFeO_3 in SrTiO_3 . Curve A, the responsivity of the alloy, indicates response both in the visible as well as in the UV. Recently other methods of electrode fabrication have been reported with relatively high efficiencies; for example, Augustynski *et al* (18) have prepared thin films of TiO_2 doped with metals such as Al and Be on Ti substrates by a spraying technique. Another fabrication technique which is quite simple in principle is to fire oxide mixtures on Ti metal in the method recently described by Guruswamy and Bockris (19) who studied $\text{LaCrO}_3\text{-TiO}_2$ electrodes. Here again a very thin film of material is formed and a significant photoresponse is obtained. Fabrication technique is

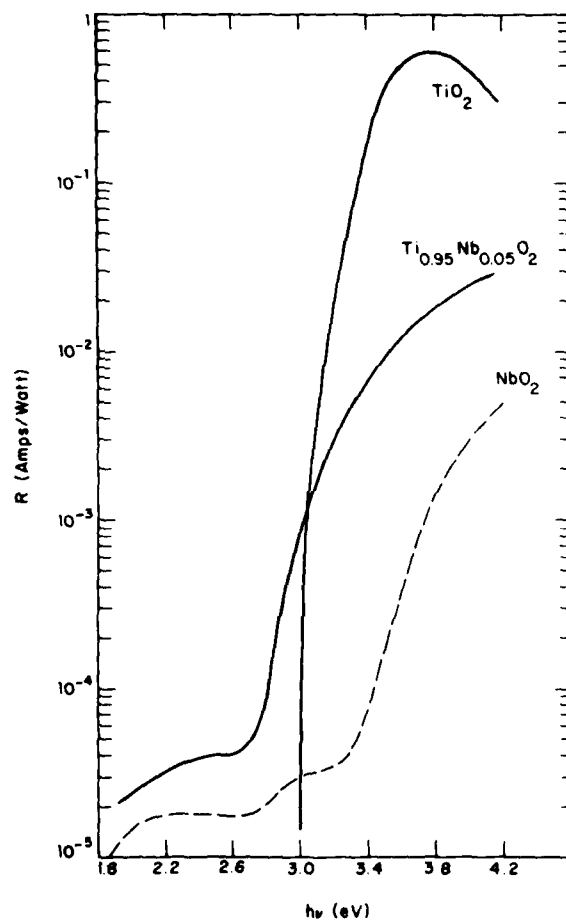


Figure 7. Comparison between responsivities of single-crystal n-TiO_2 , pressed-disc n-NbO_2 , and pressed-disc $\text{n-Ti}_{0.95}\text{Nb}_{0.05}\text{O}_2$. Electrodes are biased at $+1.0$ V relative to SCE ($\text{pH} = 10$).

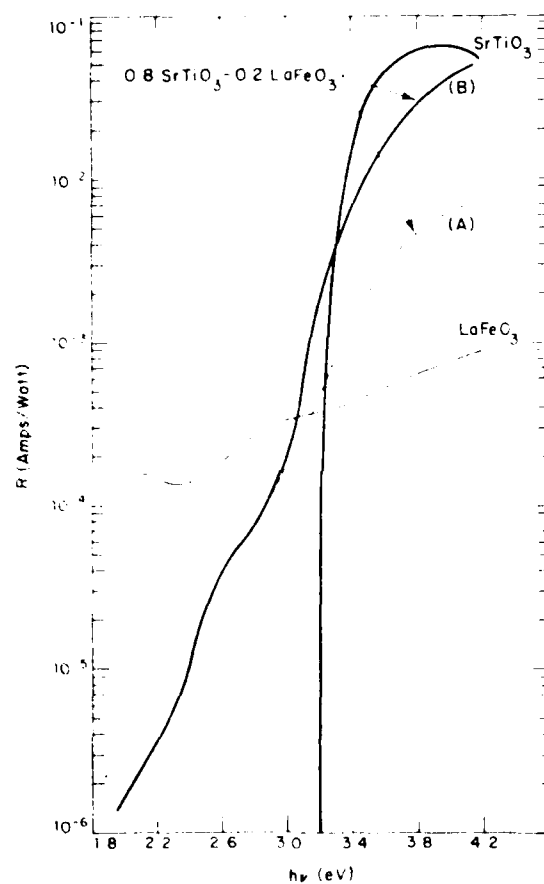


Figure 8. Comparison between responsivities of single-crystal $n\text{-SrTiO}_3$, pressed-disc $p\text{-LaFeO}_3$, and $n\text{-0.8 SrTiO}_3\text{-0.2 LaFeO}_3$. SrTiO_3 and the alloys are biased at $+1.0\text{ V}$ relative to SCE while $p\text{-LaFeO}_3$ is biased at -0.7 V relative to SCE (pH = 10). See text for difference between (A) and (B).

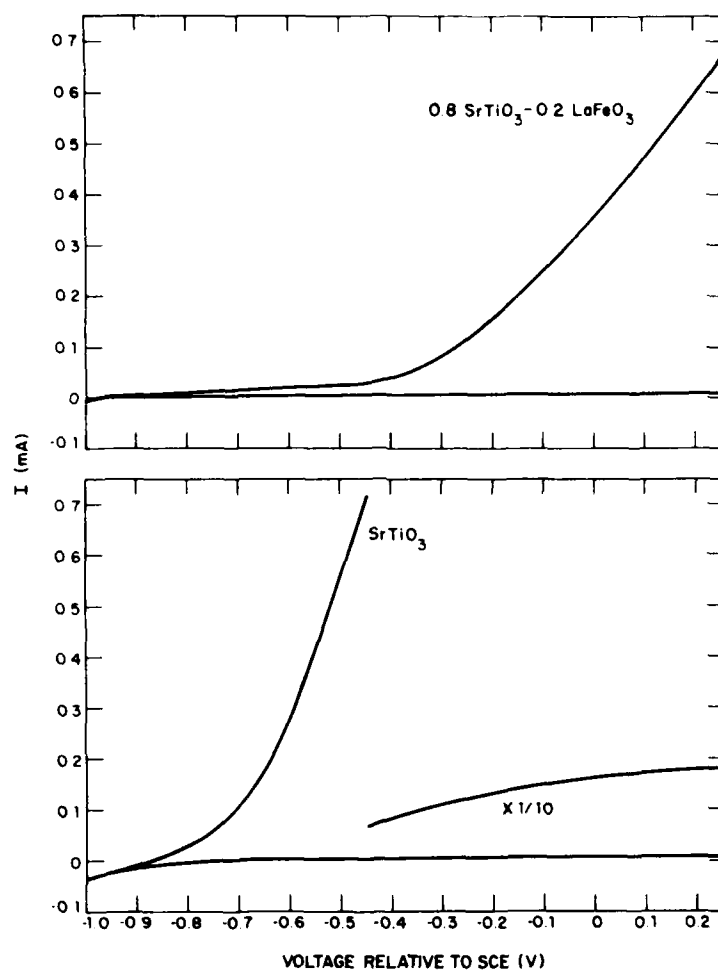


Figure 9. Comparison between I - V curves of $0.8 \text{ SrTiO}_3\text{-}0.2 \text{ LaFeO}_3$ film and single-crystal SrTiO_3 ($\text{pH} = 10$)

thus very important in determining photoresponse, especially for alloys.

Curve (B) of Figure 3 gives the photoresponse for a thin electrode prepared essentially by the method of Guruswamy and Bockris. It will be noted that although both electrodes (A) and (B) have the same visible photoresponse, which is intermediate between that of the two end materials but very low, the film, electrode (B), has a much higher response from the UV into the visible. If these alloys are to prove useful, their low energy response needs to be raised, perhaps by a combination of improved fabrication techniques and identification of the optimum alloy concentration.

Figure 9 compares the I-V curves of electrodes formed from the $\text{SrTiO}_3\text{-LaFeO}_3$ alloy film and the single-crystal SrTiO_3 at $\text{pH} = 10$. It will be observed that (with a 150 W Xe lamp) the onset of photocurrent for the alloy is at ~ -0.95 V relative to the SCE just as negative as for SrTiO_3 . However, with a little bias the SrTiO_3 electrode gives a much larger photocurrent, indicating much less hole-electron recombination.

In summary, we have described the main concepts of two components of our program, one on composite materials and the other on alloys. The experiments on composite materials are still not advanced enough to tell how effective such materials will be as electrodes. The results on the alloys show some promise, and point to the need for a more basic materials approach in order to obtain improved electrodes. This work was supported by the Solar Energy Research Institute.

Abstract

Presently available semiconducting electrodes suitable for the photoelectrolysis of water are inefficient because their action spectra are not well matched to the solar spectrum. In terms of band structure, the energy gaps of the usual stable semiconducting electrodes are too large. Semiconductors with smaller energy gaps, on the other hand, are usually not photoelectrochemically stable; furthermore, they have electron affinities which are too large. One solution to these contradictory requirements, the use of layer type compounds with d-energy bands, has been recently investigated Tributsch and co-workers. Another possible solution is the use of composite electrodes. In such electrodes, interface states become particularly significant. Not only are the states at the electrode-electrolyte interface important, but also those at interfaces between elements of the composite electrode. In this talk we will discuss the electronic properties of several kinds of composite electrodes in terms of energy band structure and interface states, as well as their fabrication and operation in photoelectrochemical cells. This work was supported by the Solar Energy Research Institute.

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