CHAPTER 10

One approach for the design of semiconductor materials for photo-electrochemical applications

Today, it appears that the feasibility of photo-electro-chemical splitting of water is hampered by the correct choice of the semiconductor material that can be employed as photo-anode even though as many as 400 semiconductors have been examined with a variety of variations in each of them. This situation has arisen probably due to the fact that the system chosen has to perform both surface catalytic function for two important reactions namely hydrogen and oxygen evolution reaction and at same time should be capable of interacting with the photon field without undergoing degradation, yet possess the band edges so as to be thermodynamically capable of decomposing water yet possess reasonable value of the band gap (certainly greater than 1.23 eV (decomposition potential of water) preferably in the visible range(to be able to utilize most part of the solar radiation) yet possessing high absorption coefficient for photons. In addition, the system has to perform in an electrochemical cell mode, the electrode material should be able to withstand the inherent electrical field at the electrode/electrolyte interface and also may have to couple with both the photon and surface field necessary for the reaction. In the case of oxide semiconductors, the valence band is mostly contributed by the 2p orbitals of oxygen and hence the top of the valence band in most of the oxide systems are more or less at the same level and that is between -7.5 and -8.0 eV from the vacuum level. This level may be favourable thermodynamically for the oxygen evolution reaction from the decomposition of water. However, the substitution at the anionic sites will alter the position of the valence band and according to the nature of the substitution like Nitrogen, sulphur and other heteroatoms, the net free energy [1] for oxygen evolution reaction will be altered and possibly the oxygen evolution rate also. Similarly, the substitution at the cationic position will have effect on the bottom of the conduction band and hence on the capacity to reduce H+ ions and evolve hydrogen. When these two states that is the top of valence band and bottom of the conduction band is shifted either way, the value of the band gap is automatically altered and this has been vigorously attempted and it is called the band gap engineering of materials. Since band edge positions have to be known, the empirical method adopted in Butler Ginley scheme is usually employed and the values are compiled at various sources [2]. Among the available semiconductors, the ones based on oxides and sulphides have been examined extensively and however none of them have yielded the desired efficiency for the water splitting. A recent screening study [3] considered nearly 19000 materials generated with 53 different elements, different anions like O, N, S, F, Cl and different crystal classes like perovskites, rutile and spinels. The essence of their results is given in Fig.1. It is seen from this figure that systems which have band gap value greater than 1.23 (thermodynamic reversible value for water splitting) and 3 eV are the systems of concern for water splitting application. Among the 20 candidates shown in Fig.2, the possible successful candidates are AgNbO3, $LaTiO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $LaTaON_2$ Another function of the photoelectrochemical material is the catalytic effect for both hydrogen and oxygen evolution. The essential steps in the oxygen evolution reaction can be written as follows:

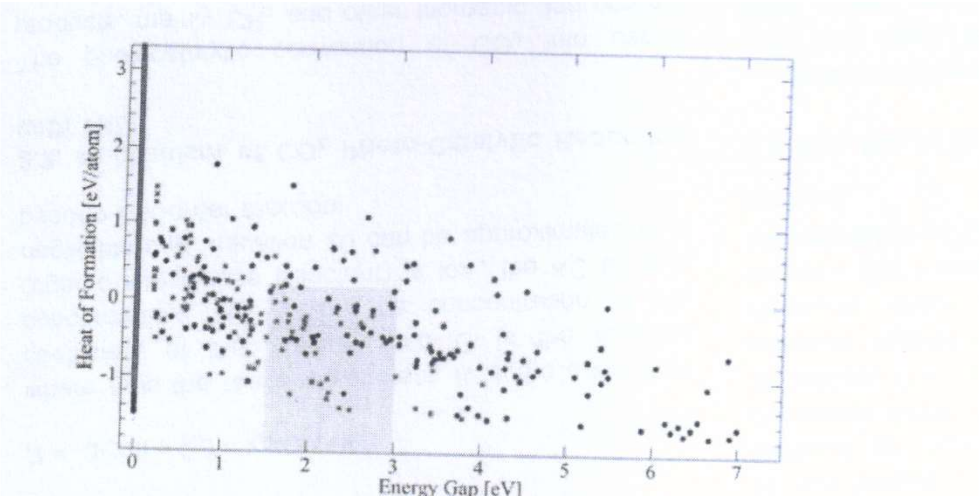

Figure 1: Stability of various semiconductors versus band gap value - Reproduced from I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci 5, 5814 (2012).

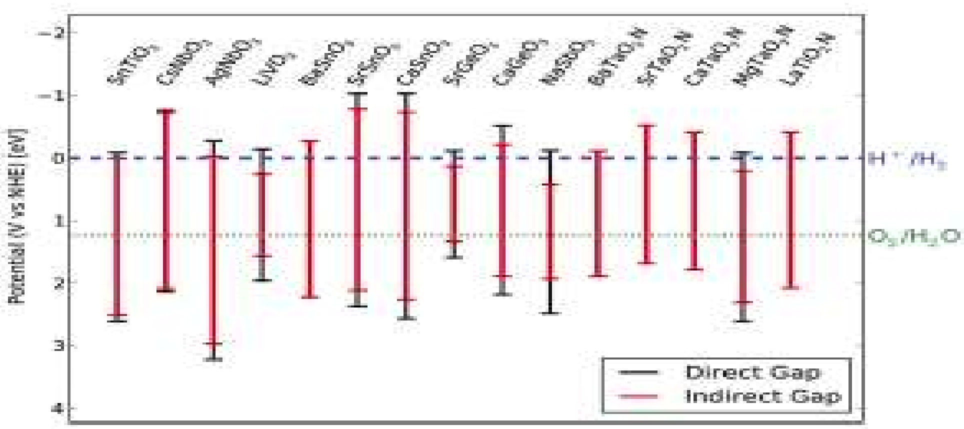

Figure 2: Some of the possible successful candidate materials; Black line direct band gap and red line indirect band gap the materials left to right are: $NaSbO_3$, $SrGeO_3$, $CaGeO_3$, $BaSnO_3$, $SrSnO_3$, $CaSnO_3$, $LiVO_3$, $CsNbO_3$, $AgNbO_3$, $SrTiO_3$, $LaTaO_2N$, $BaTaO_2N$, $SrTaO_2N$, $CaTaO_2N$, $MgTaO_2N$, $LaTaON_2$, $YTaON_2$, $BaGaO_2F$, $PbGaO_2F$, $BaInO_2F$

H2O + * → OH* + H+ + e

OH* → O* + H+ + e

O* + H2O → *OOH + H+ + e

OOH → * + O2 + H+ + e

In this reaction sequence, the step three appears to have considerable overpotential and possibly limiting this reaction. This aspect has been discussed in the paper by Noreskov et al []. The reaction sequence for hydrogen evolution involves the following steps: +

2H+ +2e → H* + H++ e

H* + H+ + e → * + H2 (g)

The projection for suitable material for this reaction has also been considered in literature and have been published by Noreskov et al []. Another possibility considered in literature for selection of materials for Photo-electrochemical cells and the concept is pictorially represented in Fig.3. There have been predictions in literature for the search of materials for PEC applications. One such prediction is shown pictorially in Fig.4. There are some predictions on the possible candidates for tandem cells they are basically either perovskite oxides or oxynitrides. However there are some limitations on the choice of materials, these include, high band gap materials and the valence band level must lie in such position so that it promotes oxygen evolution and the holes formed must be mobile enough to effect this reaction. In this presentation we have restricted to some of the predictions in literature for obvious reasons. The interested readers can look to the original literature references given.

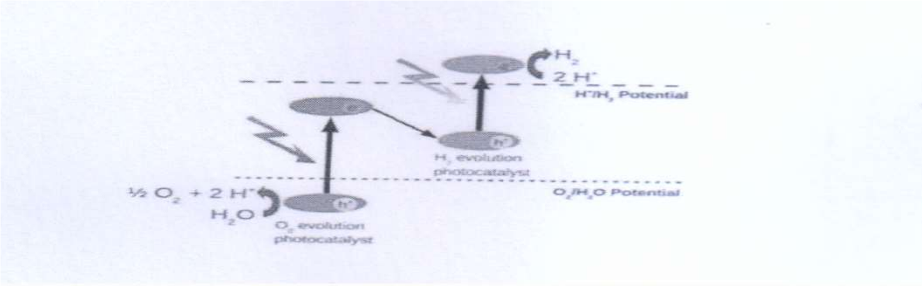

Figure 3: Pictorial representation of a tandem cell for photoelectrochemical applications

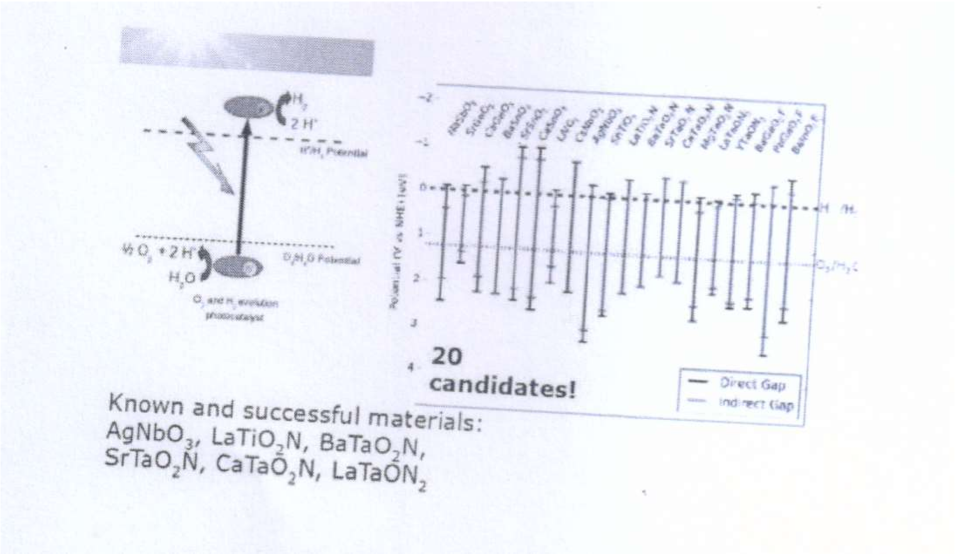

Figure 4: Pictorial representation for the selection of materials on the basis of H_2 and O_2 evolution.

References

1.I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energ Environ Sci 5, 5814 (2012).

2. https://cmr.fysik.dtu.dk 3.J.K. Nrskov, T. Bligaard, A. Logadottir, J.R. Kitchin, J. Chen, S. Pandelov, and U. Stimming, J. Electrochem. Soc. 152, J23 (2005).(hydrogen evolution)

4.J.K. Nrskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. Kitchin, T. Bligaard, and H. Jonsson, J. Phys. Chem. B 108, 17886 (2004).(oxygen evolution)

5.I.E. Castelli, T. Olsen, S. Datta, D.D. Landis, S. Dahl, K.S. Thygesen, and K.W. Jacobsen, Energy Environ Sci 5, 5814 (2012).

6. B.Viswanathan and M Aulice Scibioh, Photoelectrochemistry – Principles and applications, Narosa publishing House