MASTER

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PHOTOELECTROCHEMISTRY AT IRON OXIDE ELECTRODES

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This year research has been devoted extensively to the role dopants play in the photoelectrochemistry of iron oxide. Although it was reported in our early publications (1,2) that photoresponsive Fe_2O_3 (n-type) could be synthesized by using titanium (IV) as a dopant it was not realized until last year that our nominally pure Fe_2O_3 contained silicon (IV) as an impurity which gave it photoelectrochemical properties. The effects of silicon-doped Fe_2O_3 have been reported in our recent publications (3,4,5).

The fact that Fe_2O_3 could be made photoresponsive by doping with Ti and Si led us to investigate other group IV elements as dopants. It was found that doping $\alpha\text{-Fe}_2\text{O}_3$ with group IVA elements is superior to doping with TiO_2 . The photocurrent at 0 V vs. SCE is negligible at TiO_2 -doped electrodes but quite high at 0.1-2 a/o SiO_2 -doped electrodes, 0.01-0.05 a/o GeO_2 - and SnO_2 -doped electrodes and 0.1-1 a/o PbO_2 -doped electrodes. All of these electrodes appear to be stable under long periods of illumination.

To date we have found no clear correlation between dopant type and level with photoactivity of the electrodes. It seems that in order to understand more deeply the phenomena occurring at these electrodes surface analysis studies will need to be carried out. This is presently underway with the help of Professor Somorjai at the University of California, Berkeley. These studies are particularly important in the case of PbO_2 because sintering should lead to decomposition, and the final state of lead is not known. A lower oxidation state would be anticipated, but the results are similar to the other dopants existing in the plus four oxidation state. It is possible that PbO_2 is converted to a plumbate during sintering leading to the photoactivity observed.

Chemical reactions which take place at illuminated Fe_2O_3 electrodes have also been studied this year. Oxidation of iodide and bromide at 1 a/o TiO_2 -doped and 0.1 a/o SiO_2 -doped $\alpha\text{-Fe}_2\text{O}_3$ electrodes in competition with oxygen production was investigated in the pH range 9-13 in aqueous media. At high pH values the rate-determining step for iodide oxidation involved mass transport from the bulk of the solution to the electrode surface. Adsorption of I^- and/or I_3^- plays a significant role in the competition reactions and may depend on the doping level of the electrode. Some of the results have been reported (3,4,5).

Photocurrents at $\alpha\text{-Fe}_2\text{O}_3$ in NaOH solution were enhanced if the electrode had been previously soaked in a KI solution at pH 9. It appears that in this weakly basic solution iodide ion competes effectively with OH^- for surface sites. The adsorbed iodide

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modifies the surface to increase its photoactivity. Washing the electrode with water and immersing it in water for 48 hr had no effect, and the photocurrents remained relatively high. On the other hand, heating the electrode to $\sim 130^{\circ}\text{C}$ for about 1 hr reduced the photocurrents back to their original values. The dark currents remained the same after all treatments. These results have also been reported (4,5).

Another approach taken this year was to enhance the photoelectrochemical properties of $\alpha\text{-Fe}_2\text{O}_3$ by doping with another transition metal oxide, namely Cr_2O_3 . The reasons for choosing Cr_2O_3 are that (1) both $\alpha\text{-Fe}_2\text{O}_3$ and Cr_2O_3 are in the corundum structure and form single phase solid solutions across the composition diagram and (2) Cr_2O_3 has a lower bandgap (1.68 eV) than Fe_2O_3 but cannot be used by itself because it is unstable towards anodic conditions. The hope is that Cr_2O_3 -doped $\alpha\text{-Fe}_2\text{O}_3$ would exhibit a lower bandgap (and thereby a wider spectral response) than $\alpha\text{-Fe}_2\text{O}_3$ and still maintain the stability of $\alpha\text{-Fe}_2\text{O}_3$. Samples of $\alpha\text{-Fe}_2\text{O}_3$ doped with 5, 15, and 25 a/o Cr were prepared and studied as photoanodes. Satisfactory electrodes have been prepared although the sintering time and temperature must be increased. This was anticipated since Cr_2O_3 has a much higher melting point than Fe_2O_3 . Also on the negative side, the resistivity increased with increasing Cr content, and the dark current at $>0.6\text{V}$ vs SCE bias potential also increased. However, the objectives were reached in that $(\eta h\nu)^{1/2}$ vs $h\nu$ showed that the bandgap (intercept on X-axis) decreased as the chromium content increased. Iron oxide containing no Cr (0.1 a/o Si-doped $\alpha\text{-Fe}_2\text{O}_3$) showed a bandgap of 2.15 eV while 25 a/o Cr-doped $\alpha\text{-Fe}_2\text{O}_3$ showed a bandgap of 2.00 eV. The effect was small but in line with single crystal studies carried out by Wold and co-workers. It should be noted that a change of 0.2 eV in this energy region would have a dramatic increase in photocurrent efficiency.

References

1. J. H. Kennedy and K. W. Frese, Jr., J. Electrochem. Soc., 125, 709 (1978).
2. J. H. Kennedy and K. W. Frese, Jr., J. Electrochem. Soc., 125, 723 (1978).
3. J. H. Kennedy, R. Shinar, and J. P. Ziegler, J. Electrochem. Soc., 127, 2307 (1980).
4. J. H. Kennedy, R. Shinar, and J. P. Ziegler, Proceedings, 4th DOE Solar Photochemistry Research Conference, June, 1980.
5. J. H. Kennedy, R. Shinar, and J. P. Ziegler, Proceedings, 3rd International Conference on Photochemical Conversion and Storage of Solar Energy, August, 1980.