Photoresponse of p-Fe_2O_3 for Water Electrolysis Under Solar Simulated Light Illumination

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Introduction. The field of photoelectrolysis of water by semiconductors has seen several advances over the past 30 years, but the greatest need is still the ability to produce a stable and low cost semiconductor with a low bandgap; therefore, being able to absorb a large amounts of the solar spectrum. However, most of today's stable semi-conductors absorb almost exclusively in the ultraviolet radiation range. The low-cost semiconductor with the most potential to be stable and also can absorb visible light is the iron oxide (e.g., α-Fe_2O_3). Iron (III) oxide has a bandgap of 2.0 to 2.1 eV, therefore absorbing solar radiation from 600 to 295 nm. The n-Fe_2O_3 (with no added metal dopant) has been extensively studied (1-6) with reported photoconversion efficiencies of up to 2% for water-splitting (1;6). However, studies on p-type doping of iron oxide are rare (7-9). An efficient p-Fe_2O_3 semiconductor can be coupled with an n-Fe_2O_3, which is replaced with the platinum metal in the present work (see **Fig. 1**). Theoretically, the coupled system will need less external bias potential than is required to split water. In this study, we focus on spray pyrolytic synthesis of p-Fe_2O_3. Magnesium has been the most studied p-type dopant for Fe_2O_3. Also, calcium and titanium were used for p-type doping in prior studies (10). Other dopants that will be included in this present work will be manganese, copper, cobalt, nickel, tin, zirconium and zinc.

Results and Discussion. Several parameters were optimized for the synthesis of iron oxide by spray pyrolysis method. These parameters include carrier gas pressure, sprayer configuration to the glass substrate, spray solution ($FeCl_3$) concentration, glass substrate temperature, sprayer distance to glass substrate, spray time and its intervals, and the spray solvent. The spray solvent was found to be most important for time management during the synthesis of efficient iron oxide semiconductors. The solvent ethanol helped to synthesize iron oxide in half the time it took with pentanol; however, pentanol generated slightly higher efficient iron oxide semiconductors. Figure 1 shows the schematic diagram of photoelectrochemical cell (PEC) and the chemical reactions taking place in solution under bias potential during illumination with a solar simulated light source (i.e., xenon arc lamp). Figure 2 shows the photocurrent for an optimized n-Fe_2O_3 semiconductor, as well as the photocurrent for a magnesium-doped Fe_2O_3 sample. For the p-type run (-0.4 to -0.7 volts), the n-Fe_2O_3 thin film shows no photo-effect, whereas Mg-doped Fe_2O_3 shows a clear p-type behavior. The magnesium doping has not been fully optimized yet, because we were broadly looking at all alternative p-type dopants at this point. So far, no viable alternatives to magnesium have been found. Dopants tested include manganese, copper, and calcium. Calcium doped iron oxide exhibited n-type behavior contrary to results reported earlier (10). Other p-type metal dopants that can be used for iron oxide are titanium, nickel, tin, zinc, and zirconium. Figure 3 shows bandgap measurements for the Mg-doped Fe_2O_3 sample. The bandgap energy of 1.99 eV agrees with literature values (6).

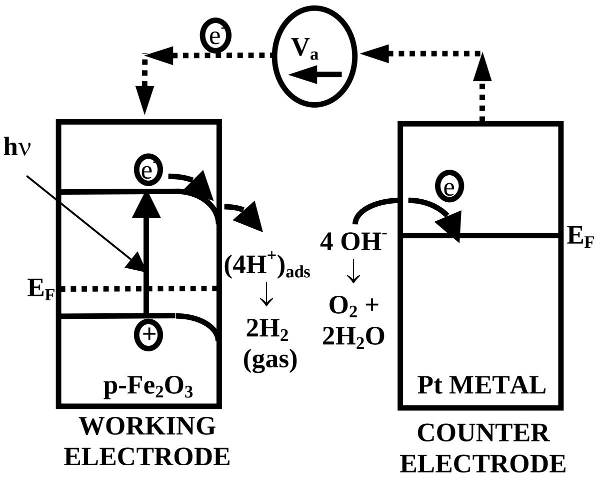

Figure 1. Schematic diagram of the semiconductor system of p-Fe_2O_3 with a platinum metal counter electrode.

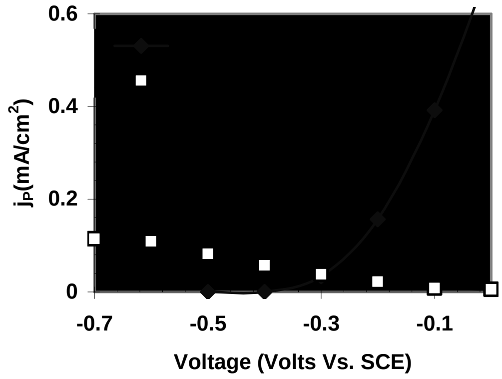

Figure 2. Plot of photocurrent density versus applied voltage for n-type Fe_2O_3 and a magnesium (p-type) doped Fe_2O_3 semiconductors.

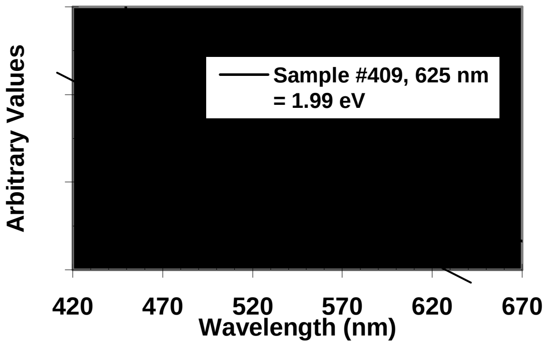

Figure 3. UV/Vis plot of a magnesium doped Fe_2O_3 sample. The intersection of the flat region with the x plane gives the bandgap wavelength for the semiconductor. The converted electron volts for the semiconductor is shown in the plot.

References.

1. Khan, S.U.M. and J. Akikusa, *J. Phys. Chem. B.* 1999. p. 7184-7189.
2. Majumder, S.A. and S.U.M. Khan, *Int. J. Hydrogen Energy*. 1994. p. 881-7.
3. Khan, S.U.M. and Z.Y. Zhou, *J. Electroanal. Chem.* 1993. p. 407-20.
4. Qian, X., *et al.*, *J. Nanopart. Res.* 2000. p. 191-198.
5. Kim, I.-K., *et al.*, *Proc. Int. Conf. Prop. Appl. Dielectr. Mater., 5th*. 1997. p. 581-584.
6. Akikusa, J., *Ph.D. Dissertation, Duquesne U.* 1996. p. 233 pp.
7. Somorjai, G.A. and C.H. Leygraf, *U.S. Patent*. 1985: United States. p. 35-47.
8. Leygraf, C., M. Hendewerk, and G.A. Somorjai, *J. Phys. Chem.* 1982. p. 4484-5.
9. Leygraf, C., M. Hendewerk, and G. Somorjai, *J. Solid State Chem.* 1983. p. 357-67.
10. Shinar, R. and J. H. Kennedy, *Solar Energy Mat.* 1982, p. 323-335.