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PHOTOVOLTAIC ASSISTED PHOTOELECTROCHEMICAL HYDROGEN PRODUCTION AND STORAGE OF HYDROGEN USING COMPOSITE MATERIALS

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ABSTRACT

Photovoltaic assisted photoelectrochemical hydrogen production using thin films of TiO_2 grown by reactive RF magnetron sputter technique at different substrate temperatures were investigated. Structural characterization of the thin films were carried out using powder X-ray diffractograms (XRD). Photospectroscopic studies were carried out on these thin films to determine the variation of absorption edge for films grown at different substrate temperatures. AB_2 type composite material was prepared by ball milling the arc melted alloy with microporous media. Structural characterization were carried out using powder XRD. Hydrogen storage properties of these materials were studied by pressure reduction method using high-pressure hydrogen absorption/desorption experimental facility.

Keywords: Metal hydrides; photoelectrochemical ;ball milling; composite materials

1. INTRODUCTION

Hydrogen is the ideal source of chemical energy that can be converted to electricity directly and efficiently via fuel cells with zero emissions of hazardous species such as volatile organic compounds, nitrogen oxides and carbon oxides[1,2]. Production and storage of hydrogen are very important issues to be addressed to achieve a good hydrogen economy. Important methods of hydrogen production[3] as of now are steam reforming of hydrocarbons, water electrolysis (using a variety of energy sources such as solar, geothermal, hydroelectric and nuclear energy) and biological methods (photosynthesis or fermentation processes of certain algae and bacteria produce hydrogen as one of their byproducts). Water electrolysis utilizing solar energy is an ideal method for hydrogen production due to the fact that both water and solar energy are abundant and renewable[4]. Photoelectrochemical [PEC] water electrolysis is a single step hydrogen production method, wherein light energy is directly converted to chemical energy thus eliminating inherent losses of the naive water electrolysis[5].

Hydrogen storage is another aspect which has attracted intense research. Hydrogen storage in certain alloy interstitials is a promising method due to its ease to charge, transport and recover[6]. AB_2/AB_5 (A= Rare Earth elements, Ti, Zr and B=Transition elements) type alloy materials are most ideal and suite the best[7]. Further increase in hydrogen storage capacity of these alloys can be achieved by milling these alloys with certain microporus media. This paper discuses the production of hydrogen using photovoltaic assisted photoeletrochemical technique with reactive RF magnetron sputtered TiO_2 thin film as photoanode material. Further, hydrogen storage studies have been carried on AB_2 type composite materials and are discussed.

2.EXPERIMENTAL DETAILS

Wide band gap semiconducting TiO_2 photoanodes were prepared using reactive RF magnetron sputter technique. Surgical grade glass slides were cleaned using standard cleaning procedure to remove all organic and inorganic impurities. These slides were then dried using argon gun and placed in the RF chamber. Target surface was etched out with low argon current to remove all surface oxide impurity layers. These glass slides were coated with pure Ti films for 15 min (Ti film acts as electrical contact for the semiconducting TiO_2 electrode), TiO_2 film was then coated on this Ti coated glass slides. Coating of TiO_2 was done on plain glass slides for powder XRD studies, and on quartz slides for photo spectroscopic measurements. Thin films of TiO_2 were grown at different substrate temperatures to study the effect of substrate temperature on the crystallinity of these films and their photoelectrochemical properties.
Composite materials [AB_2 alloy + microporous media] for hydrogen storage studies were prepared by arc melting the constituent elements in stiochiometric proportions to obtain the AB_2 alloy and ball milling the prepared alloy with the microporous media in inert atmosphere in the ratio 50:50. Structural characterization was carried using powder XRD. Hydrogen storage properties of these materials were studied by pressure reduction method using high pressure hydrogen absorption/desorption facility

3.RESULTS AND DISCUSSIONS

3.1 XRD results of TiO_2 thin films:

XRD results (Fig. 1) show that the films grown at substrate temperatures 100-200 $^{\circ}$C are in amorphous state. The film grown at 300 $^{\circ}$C shows the growth of crystalline phase. Hence crystalline films of TiO_2 could be obtained by growing films at higher substrate temperatures (>300 $^{\circ}$C).

3. 2. Photospectroscopic studies of the thin films:

Photospectroscopic studies of the films (Fig. 2) show that the absorption edge of the TiO_2 thin films are in the UV region. The absorption edge shifts towards the visible portion of the electromagnetic spectra for the film coated at a higher substrate temperature which can be attributed to increase in crystalline nature of the thin films.

3. 3. Photoelectrochemical studies :

The TiO_2/Ti semiconducting electrode was used as photoanode in the PEC and electrolysis of water was carried out using a U shaped photoelectrochemical cell with one arm having a quartz window so as to enable shining of the photoanode electrode with UV light (Fig. 3). 0.1M KOH solution has been used as electrolyte. External voltage 1.2V obtained from photovoltaic panels has been applied. Photocurrent is negligibly small when there is no UV light shining on crystalline TiO_2 thin film. The variation of photocurrent with time shows that the film is quite stable for almost 60 min in the alkaline electrolyte with steady hydrogen evolution (Fig. 4). The initial sharp rise of the photocurrent is due to the stabilization time required for the UV source. The slow rise of the photocurrent after the saturation can be attributed to the rise in temperature of the cell due to the heating effect of the UV lamp. Dark current and voltage after stabilization were recorded to be 0.02 mA, 1.208 V respectively, while the bright current and voltage after stabilization were found to be 0.04 mA, 1.236 V respectively.

3. 4. XRD results of composite material:

Powder XRD of microporous media, composite material, and AB_2 alloy are shown in (Fig. 5). AB_2 alloy is of single phase and crystallizes in C 14 structure. Lattice constants and unit cell volume of the alloy evaluated using a least square refinement technique are a= 5.004 Å, c= 8.174 Å, v= 177.3 $Å^3$. Powder XRD of the composite material shows two sets of Bragg's reflections each corresponding to the pure alloy and the microporous media, which reveals that there are no additional phase formation. The only effect of milling is to disperse the micro sized alloy powder over the microporous media.

3. 5. Hydrogen storage properties:

Hydrogen storage properties of the alloy and composite material have been studied by pressure reduction method using high-pressure hydrogen absorption/desorption experimental facility. Figures 6 and 7 give the hydrogen absorption isotherms of pure alloy and the hydrogen absorption isotherms of composite material respectively. Maximum hydrogen storage capacities of 1.6 wt% and 2.2wt% have been obtained for the alloy and composite material respectively. Increase in storage capacity of hydrogen in composite material can be attributed to adsorption of hydrogen by the microporus media.

4. CONCLUSION

Good crystalline thin films of TiO_2 by RF magnetron sputtering technique can be obtained by selecting proper substrate temperature. A shift in the photospectroscopic absorption edge towards the visible region of the spectra was observed as one increases the crystalline nature of the thin film. TiO_2 crystalline thin film is stable during photoelectrochemical hydrogen production for almost 60 min in 0.1M KOH electrolyte with steady hydrogen evolution. Ball milling pure alloy with microporous media does not result in any new phase as seen by the XRD results. Increased hydrogen storage capacity is seen in composite material when compared with the pure alloy.

5. ACKNOWLEDGEMENT

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FIGURES

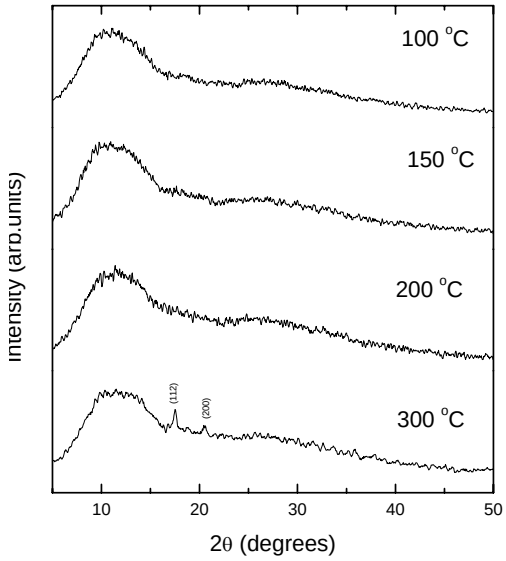

Fig.1. XRD results of the TiO_2 thin films grown at different substrate temperatures.

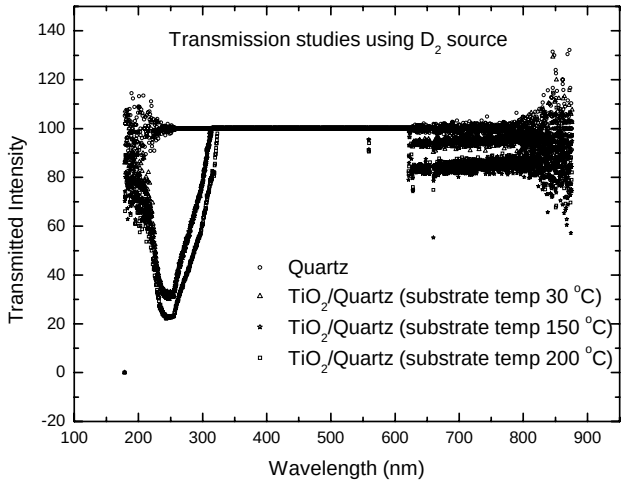

Fig.2. Photospectroscopic measurements of TiO_2 films

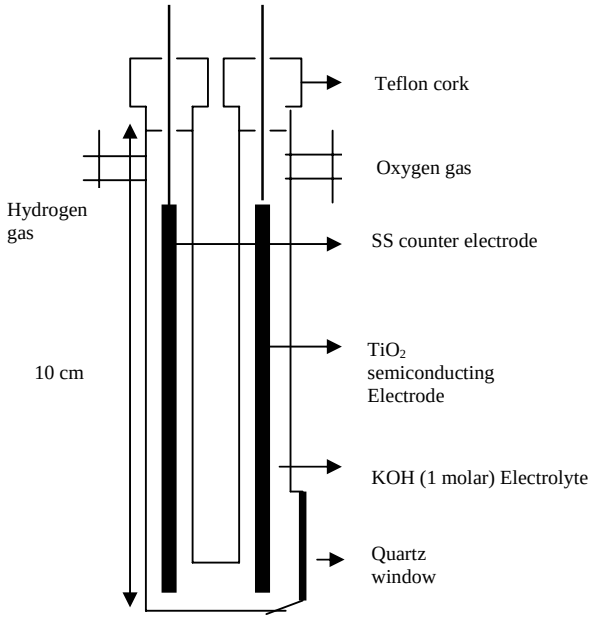

Fig. 3. Design of the Photoelectrochemical cell for hydrogen production

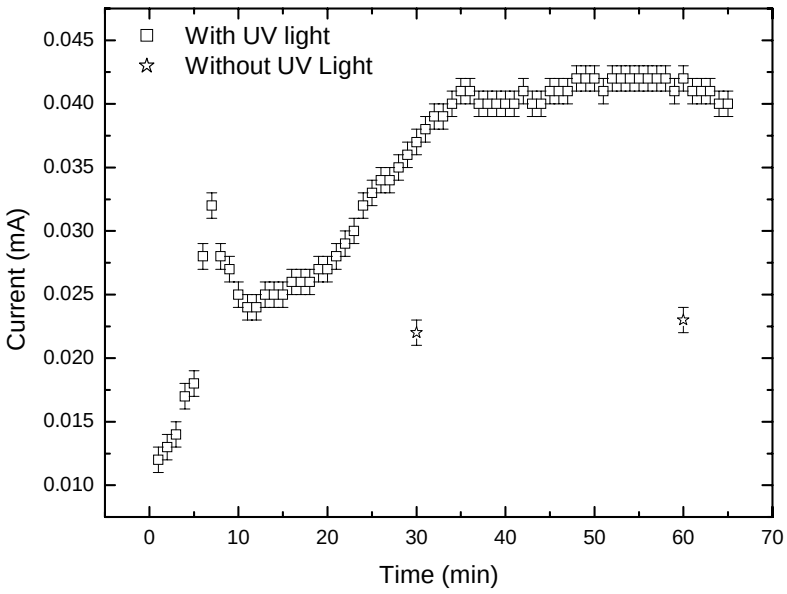

Fig.4. Photocurrent variation with time in the PEC hydrogen production

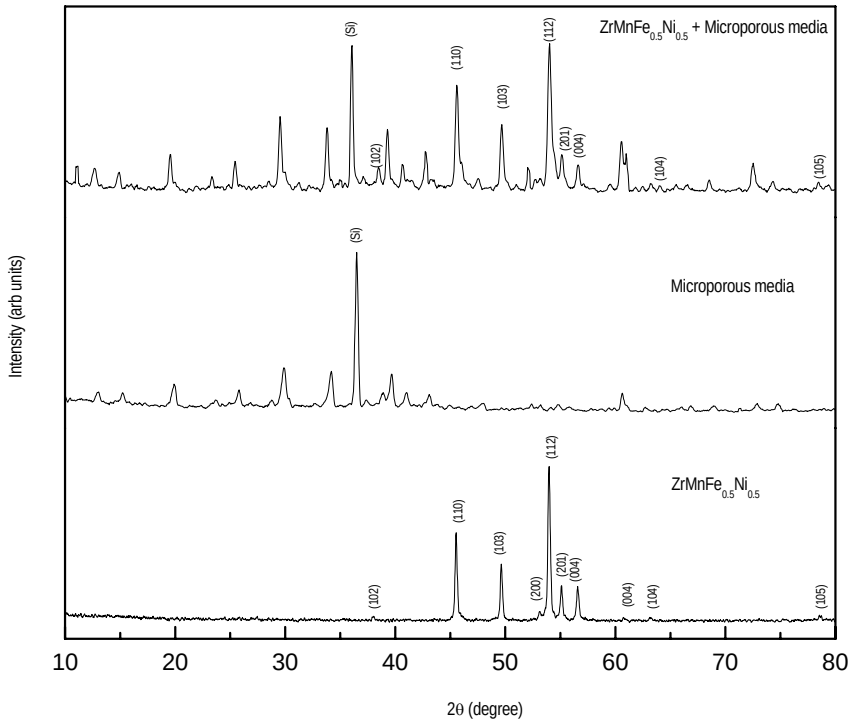

Fig.5. Powder XRD of micro porous media, AB_2 alloy and composite material

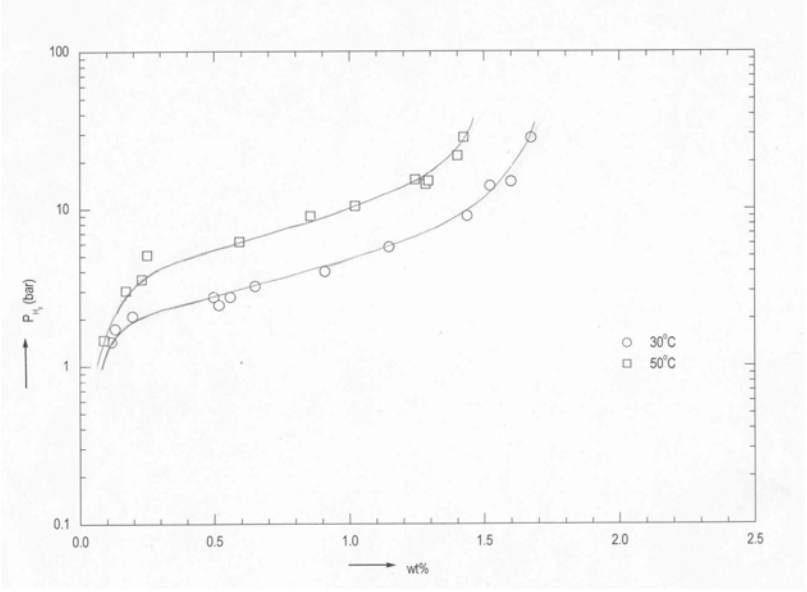

Fig.6. Hydrogen absorption isotherms of $ZrMnFe_{0.5}Ni_{0.5}$ alloy

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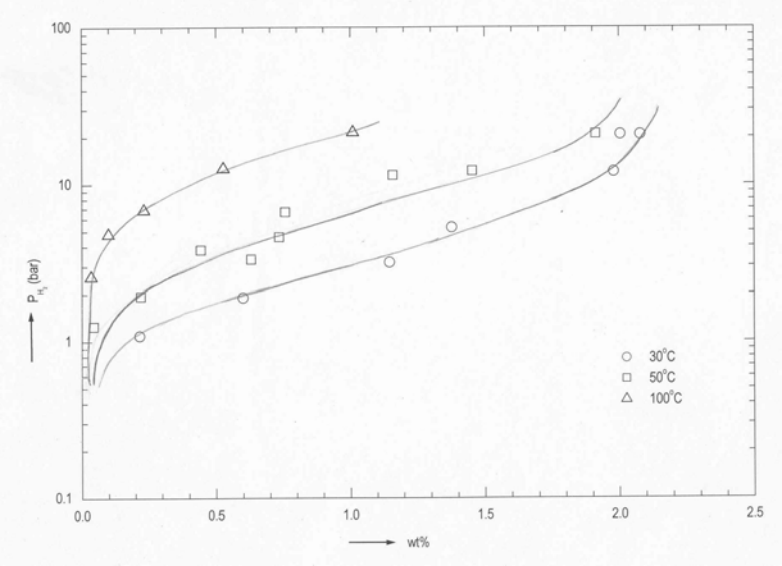

Fig.7. Hydrogen absorption isotherms of $ZrMnFe_{0.5}Ni_{0.5}$ +microporous media