NANOSTRUCTURED TITANIA BASED PHOTOELECTRODES FOR WATER SPLITTING

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1. INTRODUCTION

The actual economy is mostly dependent on fossil fuels, which proved to be responsible for environmental damage such as air pollution, oil spills, carbon dioxide emission and for global warming. Therefore there is a move towards a hydrogen economy with a great economical potential and environmental benefits as a substitute for fossil fuels. It represents the ultimate clean fuel with water as only final product and no other emission of harmful gases to the atmosphere. The scientific efforts are directed towards finding new ways to produce hydrogen by clean technologies. Such a way seems to be the photocatalytic water splitting which during the last years become extremely studied from the view point of converting the solar energy in a clean energy from abundant water. Water splitting for hydrogen production can be accomplished by means of semiconducting oxide material. Among the semiconducting materials suitable for water splitting titanium dioxide proved to satisfy many of the requirements for such a job. Iron doped samples of TiO_2 seems to enhance the photocatalytic activity as well as the p type conductivity thus increasing the photolytic efficiency. In the present investigation we report on the results obtained on iron doped TiO_2 photoelectrodes properties obtained by a slightly modified mixed oxide technique in an effort to produce nanostructured materials with a better photoactivity.

2. OBJECTIVES

- To find a new semiconducting material to be used as photoelectrode for water splitting by photoelectrolysis;
- Titania based material seems to correspond to such a job, its bandgap being 3 eV for the rutile phase;
- Titanium dioxide was doped with iron which can enter the titanium positions into the lattice due to the compatibility of ionic radii (0.68 Å for Ti and 0.64 Å for Fe);
- The doping level of iron into TiO_2 was between 1 and 20 at %.

4. RESULTS

Figure 1 shows the XRD patterns of both starting powders and the powders mechanically mixed for 5 and 10 hours for T5 compositions. A rough estimate indicates that the initial powder consists of about 70 % anatase and 30 % rutile. The first observation is the gradual phase transformation of anatase to rutile brought about only by mechanical energy released during milling. The second observation is the decrease of the grain size, at a rate of more than 100 nm/h, in the first couple of hours of the milling process, and about 40 nm/h at the end of it (figure 2). During 10 hours of milling the average grain size decreased from 1150 nm down to about 200 nm. The evaluation of samples density for different sintering temperatures is illustrated in figure 3 where one can see that the maximum densification of about 95 % of TD is attained for 1200 oC. The structure of the as fired surface of the sintered samples is illustrated in fig. 4 for T_5 compositions. The average grain size was estimated to about 500 nm. The photoactivity of the sintered iron doped titania photoelectrodes was determined by measuring the photocurrent produced by illuminated photoelectrode. In order to achieve this we designed a photoelectrochemical cell shown schematically in figure 5. The cell consists simply of the following main elements: the working electrode (W), the platinum counterelectrode (Pt) and a saturated calomel reference electrode (SCE). All electrodes are immersed in the electrolyte solution of 1M KOH (ES) contained in a glass cell provided with a quartz window (Q_w), which allows the radiant beam to pass through it and illuminate the working electrode with an area A of about 1 cm². The cell is also separated by a porous frit (F) situated between the working electrode and the platinum electrode. In order to determine the photocurrent I_p and the applied bias V_b we recorded the voltage difference between the working electrode and the counter electrode. By having measured the photocurrent I_p it is rather easy to calculate the conversion efficiency by making use of the following relationship: $\eta = I_p(1.23-V_b)/E_SA$ where I_p is the photo current, V_b is the bias voltage applied between the working and the counterelectrode, 1.23 V is the Gibbs free energy change per electron required in the chemical reaction for water splitting, E_S is the irradiance energy of the incoming radiation at the position of the photoelectrode and A is the active illuminated area of the photoelectrode.

3. EXPERIMENTAL

The compositions investigated were titanium dioxide, TiO_2, impurified with iron oxide, Fe_2O_3, within the following range 1 to 20 at %. The compositions made were labeled as: T_1, T_5, T_{10} and T_{20}, meaning impurification levels with Fe_2O_3 of 1, 5, 10 and 20 at. % respectively. The technique used to prepare the material samples was a slightly modified mixed oxide route. The raw materials were the commercial titania powder (Merk) of 99.2 % purity with an average grain size of 1 μm and a nanostructured iron oxide, Fe_2O_3, of 99.9 % purity with an average grain size of 5 nm. The oxide mixing process was made in a high energy planetary ball mill Retsch PM400 MA type using hardened steel jars of 250 ml capacity and hardened steel balls of 10 and 15 mm diameter. Steel jars and balls were chosen in order to avoid material impurification with foreign ions but iron. We used a balls/oxides ratio of 3/1 which proved sufficient to provide nanostructured powder. The evolution of phase changes of the mixed oxides was monitored by X-ray diffraction data obtained as a function of milling time. After milling the powder was pressed into discs of about 20 mm diameter and 1 mm thickness in a steel die at pressures of about 50 MPa. Next the samples were sintered at temperatures between 1100 and 1350 oC for 5 hours afer which they were physically and photoelectrochemically characterized.
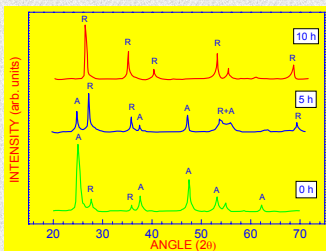

Fig. 1. X-ray patterns for iron doped TiO_2 for different milling times.

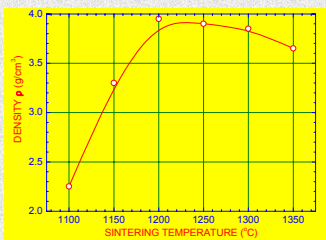Fig. 2. Average grain size of iron doped TiO_2 as a function of the milling time.

Fig. 3. Density of 5 at. % iron doped TiO_2 samples sintered at different temperatures between 1100 ℃ and 1350 ℃ for 5 hours.

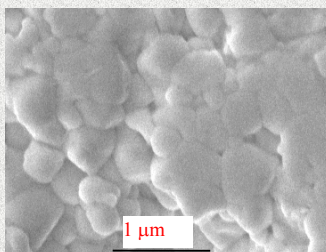
Fig. 4. The surface structure of as fired sample of 5 at. % iron doped TiO_2 sintered at 1200 ℃ for 5 hours.

Fig. 5.
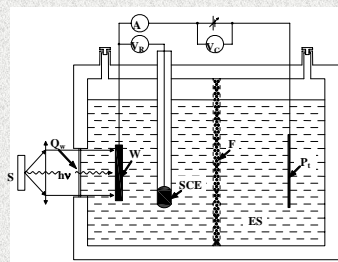The photoelectrochemical cell for determining the photocurrent of iron doped TiO_2 photoelectrodes.

Fig. 6. The photocurrent of iron doped TiO_2 photoelectrodes as a function of iron content.

Fig. 7. The photocurrent of different iron doped TiO_2 photoelectrodes as a function of the sintering temperatures.

Fig. 8. The photocurrent of different iron doped TiO_2 samples as a function of the bias voltage.

Fig. 9. The efficiency of different iron doped TiO_2 photoelectrodes as a function of the bias voltage.

Figure 6 illustrates the values of the photocurrent I_p as a function of the iron doping level. One can see that a maximum value of about 2.9 mA was obtained for a doping of 5 % at. that is for samples with compositions around $Ti_{0.95}Fe_{0.05}O_2$. Figure 7 shows the behavior of the photocurrent for different compositions as a function of the sintering temperature. All samples show a slight increase of I_p with increasing sintering temperature, and rather maximum values for about 1200 oC. The best results were obtained for T_5 composition which provides, for example, a photocurrent with up to 20 % greater than for T_{20} at the same sintering temperature. The photocurrent I_p as a function of the bias for the compositions investigated is shown in figure 8 and the corresponding efficiency η, in figure 9.

5. SUMMARY

Sintered samples of iron doped titania for photoelectrodes were prepared by the mixed oxide route, using a prolonged mixing of about 10 hours, in order to obtain nanometric sized powder with a high degree of homogenization. This technique induced a transformation from anatase to rutile during milling by the impact energy of the balls and powder. The doping level for iron into titania was within 0 and 20 at. %. Sintering of compacted samples was carried out at temperatures between 1100 ℃ and 1350 ℃, the optimum temperature being 1200 ℃. The photolytic activity of the sintered photoelectrodes was determined by means of a photoelectrolytic cell which used a 1M KOH aqueous solution as electrolyte. The best results, that is the highest photocurrent and efficiency were obtained for samples doped with 5 %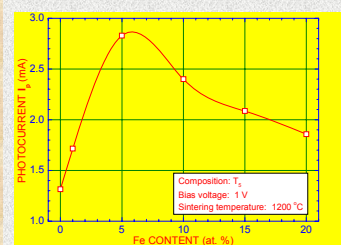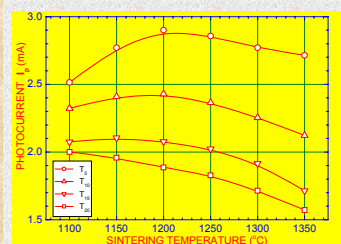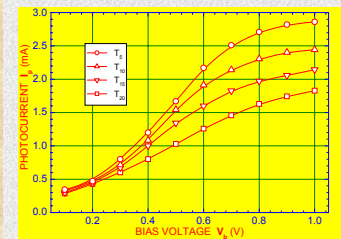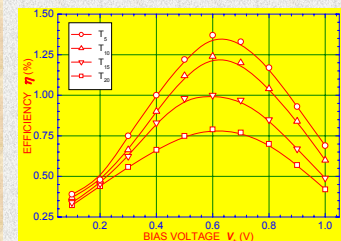 at. iron, sintered at 1200 ℃ and using a bias of 0.6 V