A New Type of Solid State Solar Cell Based on Fe_2O_3, SiC and Crystal Growth Inhibitors

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Abstract

A new type of solid state solar cell is produced by using Fe_2O_3 (working electrode) and SiC as a hole collector (counter electrode). Two molten salts, 1-ethyl-3-methylimidazolium chloride (EMICl) and 1-butyl-3-methylimidazolium iodide (BMII) were used as crystal growth inhibitors with a SiC film. It was found that BMI1 shows about 10 times higher efficiency compared to an EMICl-based SiC film solar cell.

Keywords: Fe_2O_3; SiC; Solid state solar cell; Molten salt.

1. Introduction

The field of photovoltaics is of major importance among renewable energy sources, because solar energy is largely abundant, surpassing our present global annual energy needs by a factor of 10,000 [1]. The field of photovoltaics is exclusively dominated by conventional inorganic semiconductor technologies like silicon or thin film solar cells until a very promising and low-cost alternative dye-sensitized photoelectrochemical solar cell is introduced by O'Regan and Grätzel [2]. An impressive 10% light to-electricity conversion efficiency has been obtained for such photovoltaic devices with organic solvent-based electrolyte [3]. However, the presence of liquid electrolytes in such modules may result in some practical limitations of sealing and long-term operation [4]. Therefore, liquid electrolyte is replaced by a p-type semiconductor forming a new version of solar cell called a dye-sensitized solid state solar cell (DSSSC).

   The working principle of DSSSC is based on ultrafast electron-injection from a photoexcited dye into the conduction band of an oxide semiconductor and subsequent dye

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regeneration and hole transportation to the counter electrode (hole collector). Several potential problems arise from this new DSSSC, which are summarized schematically in Fig. 1 [5, 6]. In order to reach high external photo-to-electron efficiencies each of the sequential electron transfer steps shown in Fig. 1 needs to proceed with a quantum efficiency close to unity.

As the capture of TiO_2 conduction-band electrons by dye radical cations competes with dye regeneration, the latter has to be at least one order of magnitude faster than the recombination process. Once the hole is transferred to the hole conductor and the electron is located inside the TiO_2 phase, recombination might still occur via the sensitized interface, so the lifetimes of the carriers have to be substantially longer than the time they require to reach the contacting electrodes. As an alternative of the dye sensitized TiO_2, visible light-responsive semiconductor metal oxides such as iron oxide (Fe_2O_3) can be used to avoid the regeneration problem of dye molecules. Fe_2O_3 is cheap and has a small band gap energy of 2.0 eV [7] which enables it to absorb the photons of the solar spectrum. Recently, Somekawa et al. reported the laser-deposited Fe_2O_3 thin film for a new type of solar cell [8].
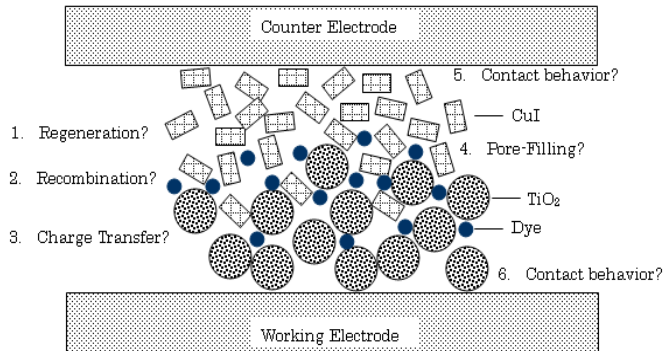

Fig. 1.   Schematic illustration of potential problems arising in a dye-sensitized solid state solar cell.

In order to support high photocurrents the charge transport capacities of the two interpenetrating networks (i.e., n-type and p-type semiconductor materials) need to be sufficiently high so as not to limit the cell efficiency, due to their high ohmic resistances. These properties will mainly be governed by material properties such as charge mobility and charge carrier concentration. A further important requisite for a functioning solar cell is to find suitable contact and window materials, which show an appropriate contact behavior to both TiO_2 and the holes conductor. The hole mobility in the hole collector is quite an important parameter for the performance of DSSSC as the hole diffusion length depends on the mobility. DSSSCs have comparatively high electron-hole recombination rates [5]. Thus, making the diffusion length larger or comparable to the thickness of the n-type nanocrystalline film becomes a necessary requirement. The drawback of using

crystalline semiconductors as the hole collector has been the rapid crystal growth (during deposition from a solution or by electrolysis) that interferes with the filling of the pores of the nanocrystalline n-type semiconductor (e.g., TiO_2) matrix. Formation of crystals larger than the pore dimensions leaves a good portion of pores unfilled. Even more severe is the problem of entrapping gases and the solvent in the voids between larger crystals [6].

So far, CuI has been used extensively as a hole collector. But CuI-based DSSSCs do not remain stable, that is, both the short-circuit photocurrent (Isc) and the open-circuit voltage (Voc) undergo rapid decay. The cause of instability seems to be loosening of the contact between the dyed TiO_2 surface and CuI crystal [9]. Silicon carbide (SiC) is also an interesting p-type semiconductor material with application to electronic and optoelectronic devices due to its excellent thermal stability and wide-band gap energy. Moreover, SiC is especially attractive for high-temperature, high power, high-frequency and high-radiation operating devices, since its saturated electron drift velocity, breakdown electric field, thermal conductivity and tolerance to ionizing radiation are significantly superior to those of Si and GaAs [10].

In this report we show the application of SiC as a hole collector followed by the effect of two different crystal growth inhibitor for SiC. Moreover, we replaced the conventional dye sensitized TiO_2 film with an Fe_2O_3 film.

2. Experimental

Fe_2O_3, SiC and ethanol were purchased from Wako (Japan), 1-ethyl-3-methylimidazolium chloride (EMICl) and 1-butyl-3-methylimidazolium iodide (BMII) were purchased from Tokyo Chemical co., Japan and used without further purification. All films were prepared on indium-tin-oxide (ITO, Aldrich) coated glass which has a resistance of 8-12 ohm. In a beaker 0.12 g of Fe_2O_3 (Wako) was mixed with 100 ml of ethanol, followed by sonication for 5 min. For the films of different thicknesses, different amounts of the Fe_2O_3 were dropped on an ITO glass put on a hot plate heated at 120 °C. The films were then calcinated at 500 °C under air atmosphere for 1 h. 30 mg of SiC was smashed in a mortar, followed by addition of EMICl and BMII in desire amounts. After addition of ethanol the mixture was sonicated for 5 min. Different amounts of SiC with a crystal growth inhibitor were dropped on the Fe_2O_3 film and ITO glass put on a hot plate heated at 120 °C. The above two films were clipped in a way that the Fe_2O_3 and SiC layers are sandwiched between two ITO glass supports. The UV-vis absorption spectrum was measured by a UV spectrophotometer (Shimadzu Corporation, MPS-2000). The *I-V* curves were analyzed by an *I-V* curve analyzer (Peccell, PECK2400-N). The incident photon-to-photocurrent conversion efficiency (IPCE) was measured with a solar cell evaluation system (EKOPRP1-SAO-001). A Xenon lamp (Inotex 300-W LX300F) was used as a light source. Crystal structure identification was made by X-ray diffraction (XRD) using a PANalytical Advance X-ray diffractometer with CuKα radiation. The films were analyzed by field-emission scanning electron microscope (FE-SEM, Hitachi, S-4100H).

3. Results and Discussion

The SEM image of Fe_2O_3 in Fig. 2(a) shows that the size of Fe_2O_3 particles ranges from 70 to 90 nm. From the XRD pattern of Fe_2O_3 film in Fig 3, it is found that the structure of the Fe_2O_3 crystal is unchanged on calcinations.

The SEM images of SiC films (Fig. 2(b, c)) before and after the addition of molten salts show that the particle size ranges from 130 to 150 nm. The general functions of the molten salts are; (1) to inhibit the crystallization of the p-type semiconductor particle (here is SiC) and (2) to work as an ion conducting surfactant. It was found from the SEM images of SiC that both of the molten salts are unable to inhibit the rapid crystal growth of SiC.

We assume in this experiment that only the later function of molten salt is active to increase the efficiency of the solar cell i.e., molten salts work as an ion conducting surfactant during the regeneration of holes in the semiconductor particles. Different amounts of crystal growth inhibitors were added to SiC. It is seen from Fig. 4 that EMICl and BMII give the highest efficiency at contents of 134 mol% and 78 mol% of those added to SiC, respectively. Here it should be noted that BMII shows 10 times higher efficiency than that of EMICl.

The ion conducting capacity of molten salts depends on its melting point, viscosity and properties of anion attached with the main cationic part (here is methylimidazolium). It was found that BMII is in a liquid state at room temperature whereas the melting point of EMICl is 84 °C. It is reported that the crystal growth inhibitors having lower melting point show higher efficiency [11]. Moreover, the molten salts having lower viscosity show higher ion conducting efficiency [12]. But, for efficient ion conductivity the molten salts should be in a liquid state at room temperature and should show a minimum viscosity. At room temperature EMICl can not show any viscosity due to its higher melting point. But BMII in a liquid state at room temperature shows some viscosity. Thus, BMII has higher ion conducting capacity and can enhance the efficiency of solar cell by regeneration of electron-hole pair in the semiconductor particle.
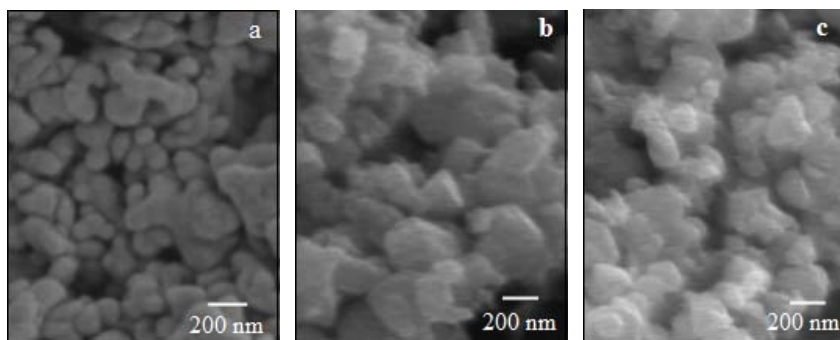

Fig. 2. SEM pictures of (a) Fe_2O_3 film and SiC films (b) before (c) after addition of molten salts.
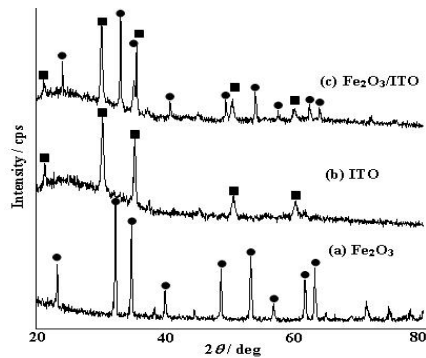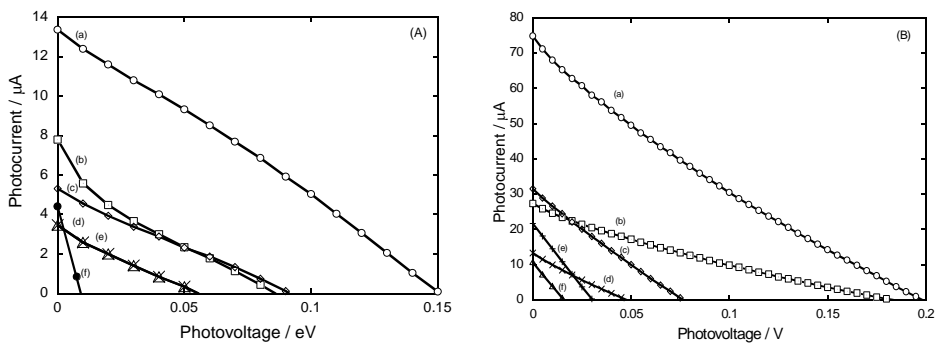
Fig. 3. XRD pattern of Fe$_2$O$_3$ film.

Fig. 4. Dependence of I-V curves on the content (mol%) of (A) EMICl and (B) BMII added to SiC. In Fig A: (a) 134 (b) 120 (c) 147 (d) 27 (e) 67 and (f) 201 mol%. In Fig B: (a) 78 (b) 97 (c) 58 (d) 39 (e) 116 and (f) 136 mol%.

It was reported by Suzuki *et al.* [13] that the electrochemical activity of semiconductor oxide depends on the size, the surface area and the resistance of the films. The sheet resistance of an electrode has an effect on the internal resistance of a solar cell and consequently, influences the fill factor of the cell and its conversion efficiency. For the optimization of solar cell efficiency the thickness of the Fe$_2$O$_3$ and SiC films was adjusted by dispersing different amount of Fe$_2$O$_3$ and SiC colloidal solution on the ITO glass. It is seen that the photocurrent increases with increasing thickness of the Fe$_2$O$_3$ films. This is due to an increase in the amount of adsorbed light with increasing of film thickness. An increasing thickness would lead to increasing loss of injected electrons due to recombination in the electron transfer process in Fe$_2$O$_3$ nanoparticles and increasing series resistance of the cell, resulting in a decrease in photovoltage [14]. It was found that Fe$_2$O$_3$ and SiC at thicknesses of 10 μm and 9 μm, respectively, give the highest efficiency with the BMII crystal growth inhibitor (Fig. 5).
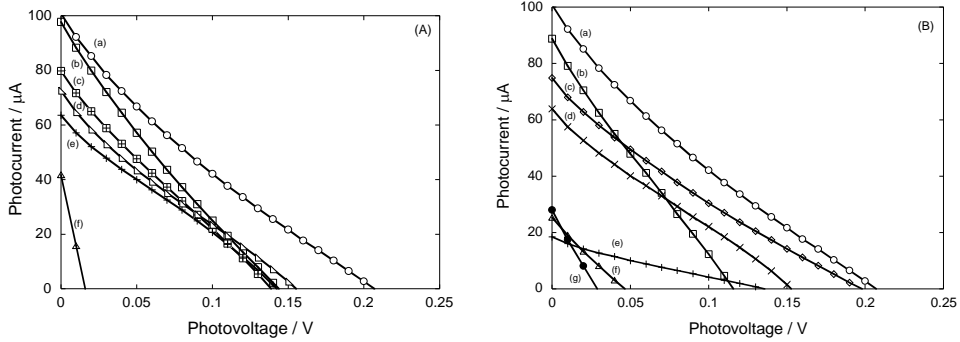
Fig. 5.   Dependence of I-V curves on the content (ml) of suspension of (A) Fe_2O_3 and (B) SiC. In Fig A: (a) 10 (b) 8 (c) 12 (d) 15 (e) 20 and (f) 5 μm. In Fig. B: (a) 9 (b) 8 (c) 10 (d) 7 (e) 20 (f) 15 and (g) 6 μm.
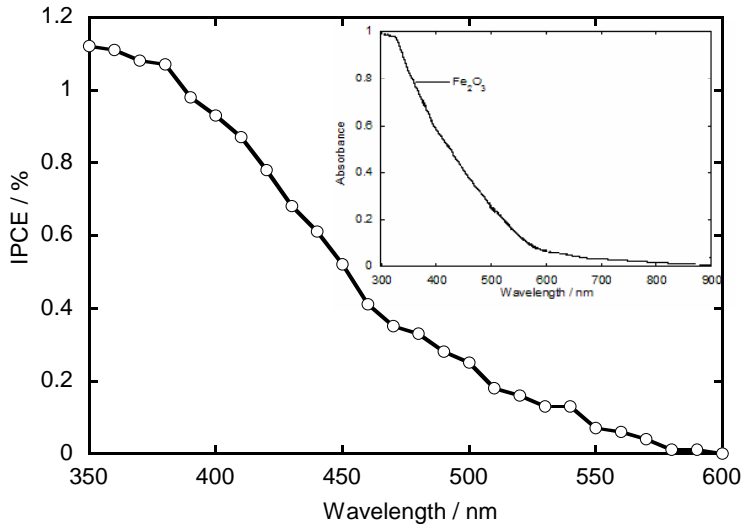

Fig. 6.   IPCE curve and UV-visible spectrum (inset) of Fe_2O_3 film.

The IPCE curve of the solid state solar cell is shown in Fig. 6. Also, the UV-visible spectrum for the Fe_2O_3 film is shown in Fig. 6 (inset). We can see that the film has the absorption edges in the visible range at around 580 nm. However, it shows the strong absorption also in the UV range. It is seen that the photon-to-current conversion occurs due to the light absorption by Fe_2O_3 film. This solar cell can convert visible light in the region from 350 to 400 nm to photocurrent. The maximum IPCE reached 1.1% at 350 nm which is very low compared to dye-sensitized solar cell. The inability of molten salts to

inhibit the crystallization of SiC may be one of the reasons of low efficiency of the solar cell.

However, further research is required to increase the IPCE and efficiency of the Fe_2O_3-film solar cells. Comprehensive studies are underway in our laboratory.

4.   Conclusion

From the above results it can be concluded that SiC films are applicable in the solid state solar cell based on the Fe_2O_3 film. Addition of crystal growth inhibitors to SiC gives higher efficiency than that of SiC alone. The thickness of Fe_2O_3 and SiC films has considerable effect on the efficiency of solid state solar cells. BMII shows 10 times higher efficiency than EMICl as the crystal growth inhibitor.

Acknowledgements

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