Influence of hydrochloric acid on response time and photoelectric performance of dye-sensitized solar cells under chopping light

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A dye-sensitized solar cell was assembled by adsorbing dye onto TiO_2 porous film, deposited on TCO glass. Photovoltage of DSSC under chopped light was studied and compared to a standard silicon cell. It was observed that DSSC has a slower response to pulsed irradiation than crystalline silicon cells. The influence of hydrochloric acid as electrolyte additive on the response time and cell performance was investigated. It was found that, by adding HCl in the electrolyte, the cell efficiency is maintained and the response time decreases significantly. If HCl exceeds a limit value, response time becomes better, but efficiency decreases strongly.

1. Introduction

Developing clean energy alternatives to fossil fuels technology has become one of the most important tasks of modern science. Direct solar energy conversion to electricity using solar cells is one of most promising of this technology. So far, crystalline silicon solar cells (Si-c cells) dominate the commercial photovoltaic market. In the past years a new kind of solar cell based on dye-sensitized nanocrystalline titanium dioxide has been developed [1-3]. The dye-sensitized mesoscopic TiO_2 solar cells have numerous advantages over silicon solar cells, such as low materials cost, ease of production and good photoelectric conversion efficiencies [4]. A dye-sensitized solar cell (DSSC) is based on a wide band gap semiconductor, usually a porous film of nanocrystalline TiO_2, which is sensitized for visible light by a monolayer of adsorbed dye, electrolyte and opposite electrode. When DSSC is irradiated by light, the electrons of dye are excited from ground state to excited state by adsorbing photons. The excited electrons are injected to the conductive band of TiO_2, and then transfer to the conducting glass through the porous TiO_2 film. Mesoscopic TiO_2 porous film plays a key role in photoelectric conversion efficiency of DSSC; so many scientists focus their researches especially for chemical and physical treatment methods to improve the surface state of TiO_2 porous film [5-7]. Electrolytes, additives and dye are also some of the critical components in DSSC and have been intensely studied [3, 8-10].

In this article, a dye-sensitized solar cell is assembled by adsorbing N719, onto TiO_2 porous film. The influence of the hydrochloric acid, as additive in electrolyte solution, with different concentrations, on the photoelectric performance and response time of DSSC is investigated by electrical measurements. It was found that, for platinum and carbon coated counter electrodes, by adding small quantities of HCl as additive in the electrolyte, the cell efficiency is maintained and the response time decreases significantly. If the quantity of HCl exceeds a limit value, response time is still excellent but photovoltage decreases strongly.

2. Experimental

In order to fabricate the solar cells, oxide semiconductor paste was prepared at first using nanocrystalline powder of TiO_2 obtained by hydrothermal method [11-13]. Quasi-spherical particles have an average size of about 12 nm. The TiO_2 powder (0,20 g) with HNO_3 1N (0,5 ml) was inserted into a shaker. Water (20 %) and two kinds of polyethylene glycol (PEG), with molecular weight 400 and 20,000 respectively, were added into the shaker in equal proportion under continuous stirring.

The obtained TiO_2 paste was deposited on a glass substrate coated with a transparent conducting oxide (TCO, F doped SnO_2 - FTO), purchased from Solaronix SA. The TCO substrate was initial cleaned using ethyl alcohol and acetone. The film was deposited using doctor-blade technique and subsequently sintered at 500ºC in air for 2 h. The dye (N719), purchased from Solaronix SA, was dissolved in dehydrated ethanol (Merck) at a concentration of 0.2 mM. Then, the dye was adsorbed onto the oxide semiconductor film surface by dipping the substrate into the dye solution for six hours at room temperature.

Two types of counter electrodes were prepared as follows. Platinum as counter electrodes (for Pt-DSSC) are prepared using thermal decomposition, at 450ºC, on 5% H_2PtCl_6 in pure ethanol on FTO glass. Carbon counter

electrode (for C-DSSC) was prepared by heating, at 400ºC, a mixture of carbon-graphite powder and polyethylene glycol (PEG, Molecular Weight 400 with PEG Molecular Weight 20000 in 1/1 ratio) on FTO using doctor-blade technique. Electrolytes were based on I^-/I_3^- (0.5M + 0.05M) in acetonitrile (AN 50 – Solaronix). The electrolyte solution, with different concentration of hydrochloric acid is inserted between the electrodes and the assembly is sealed. One is the FTO glass coated by the oxide semiconductor film (nano-TiO$_2$/TCO), other one is the Pt/TCO and C/TCO respectively.

The electrical behaviour of the obtained dye-sensitized solar cells, under the chopping light using a non-inertial light source, driven by an adjustable frequency power astable circuit, was measured and compared to a standard silicon cells. Three light source (white LED area), with the spectrum shows and compared with solar spectrum in figure 1 (measured with OceanOptics JAZ-EL200 optical fibber spectrometer), and irradiance in the order of 8-10 mWcm^{-2} (measured with PCE-SPM 1 solar radiation meter), are using in this study.
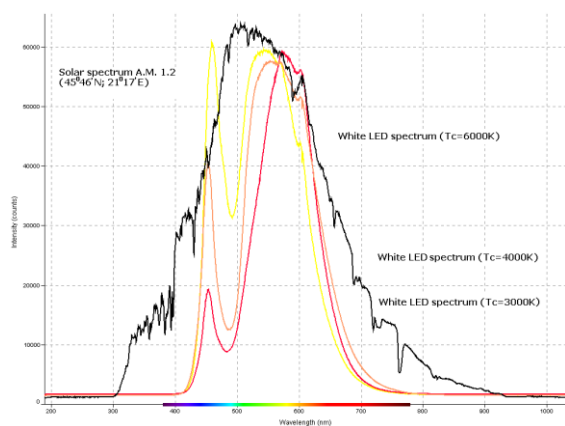

Fig. 1. Spectrum of LED light sources compared with solar spectrum.

The modulated output signal was monitored with a dual channel digital storage oscilloscope (Fluke 190C).

3. Results and discussion

Analysis of modulated signals Fig. 2 represents the modulated block shaped signal of a DSSC and a reference silicon solar cell under chopped light. Response time found for DSSC with platinum coated counter electrode (about 170 ms – Fig. 2a) is better than DSSC with carbon coated counter electrode (about 1.2 s – Fig. 2b) but much slower than crystalline silicone reference cells. However, this are sufficiently fast to ensure a constant output level during one period of the signal; witch is 900 ms for Pt-DSSC and 3.8 s for C-DSSC respectively, thus creating a blockwave.
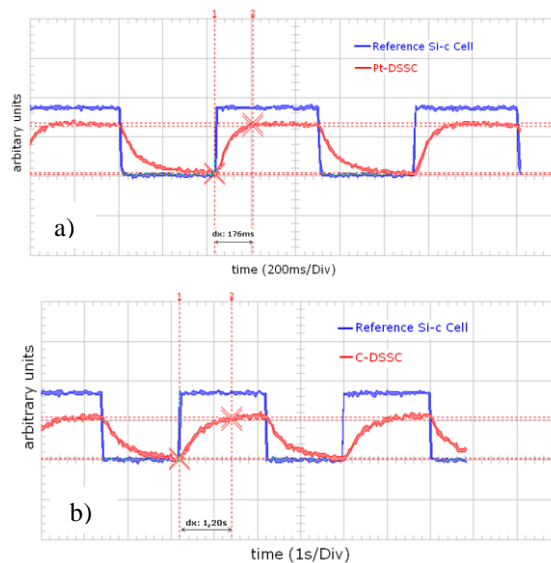

Fig. 2. Modulated signals of reference crystalline silicon cells and DSSC; a) with platinum coated counter electrode, chopper frequency 1.1 Hz; b) with carbon coated counter electrode, chopper frequency 0.26 Hz.

The behaviour of both cells changes by adding different quantities of HCl as additive in the electrolyte.

For a little concentration of HCl in the platinum coated counter electrode DSSC electrolyte, from 0 to 0.01 M, response time decreases and photovoltage increases slowly (Fig. 3, 4). With increasing concentration of HCl as additive in electrolyte, from 0.01 to 0.03 M, the response time continues to decrease but also the photovoltage decreases. If the quantity of HCl exceeds a limit value, response time gets better but cells photovoltage strongly decreases.
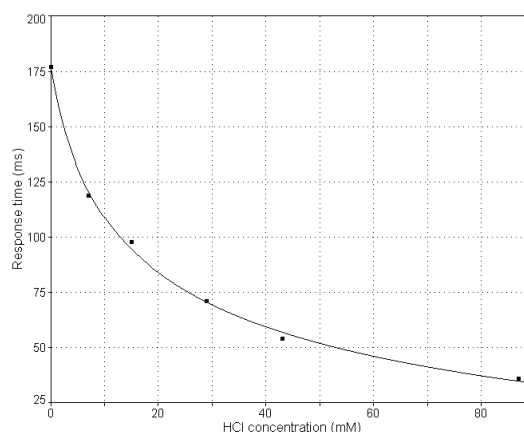

Fig. 3. Influence of HCl concentration in electrolyte on Pt-DSSC response time.
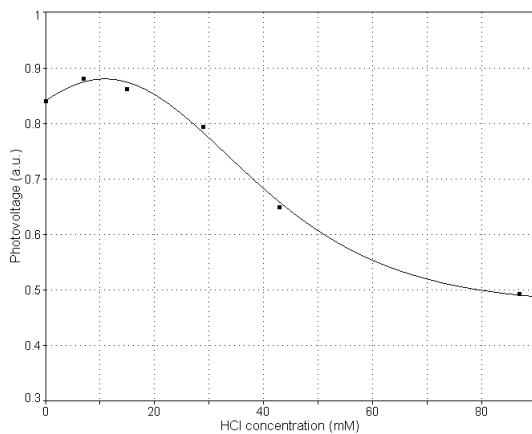
Fig. 4. Photovaltage for Pt-DSSC compared with reference silicon cells for diferent concentration of HCl in electrolyte.
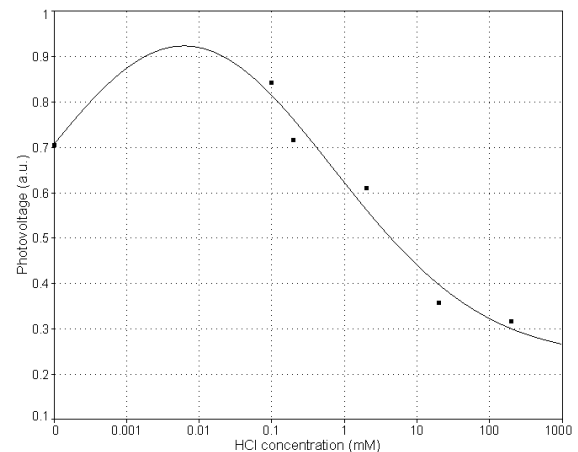

Fig. 6. Photovaltage C-DSSC compared with reference silicon cells for diferent concentration of HCl in electrolyte.

For carbon cover counter electrode DSSC, the response time and photovoltage are shown in Fig. 5 and Fig. 6. As in the previous case the response time becomes better with the increase of the hydrochloric acid concentration in the electrolyte, but no so pronounced. Also the photovoltage genereted by DSSC compared with photovoltage generated by reference silicon cell under the same ilumination slightly increases for little concentration of HCl in electrolit from 0 to 0.1 mM, still good up to 0.3 mM, then pronounced decrease.
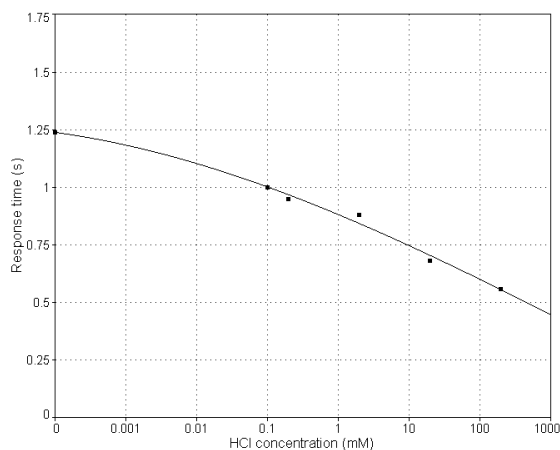

Fig. 5. Influence of HCl concentration in electrolyte on C-DSSC response time.

DSSC behaviour under chopping light can be explained when it is assumed that trapping of electrons in the mesoporous TiO_2 semiconductor is responsible for the slow response of the cells [14]. Filling of electron traps at the semiconductor surface discourage the photocurrent transients. Injected electrons can be trapped and released several times, along the TiO_2 layer, before the back contact is reached, as a results response time is high. Also the response time is influenced by the light intensity, since the time constant for trapping depends on the density of conduction band electrons. Another process which limits the response rate is the charge transport in electrolyte. Science response time did not significantly depend on the viscosity of the electrolytes, means another process is involved in DSSC response time decreasing by adding hydrochloric acid in electrolyte. The charge transport in the electrolyte is the longest process involved in DSSC working principle [15] so; better charge transport can be responsible for improving response time of dye-sensitized solar cells by adding HCl as electrolyte additive.

The photovoltage has a lightly enhancement with slightly increase of hydrochloric acid as electrolyte additive, but drops suddenly if concentration exceed) a value limit. According to the fundamental principle of DSSC, photovoltage is the potential difference between the reversible redox couple (I^-/I_3^-) in electrolyte and the Fermi level of TiO_2. Science the TiO_2 layer is the same in the experiments, we can conclude that reversible redox couple in electrolyte shifted down when the hydrochloric acid was added in small quantities as additive. Photovoltage decreases strongly when concentration of hydrochloric acid exceed) a value limit. This fact can be attributed to two things - TiO_2 electrode surface destruction and dye damage.

TiO_2 surface is negatively charged in basic medium and positively in acid medium [16]. According to [17], N719 dye adsorption on TiO_2 involving Ti-OH groups on the semiconductor surface, consuming them at the same time. Dye excess can adsorb on TiO_2 but this does not increase cell efficiency [17]. The addition of HCl increasing concentration of H_3O^+ ions in the electrolyte

solution and can induce formation of new Ti-OH bonds on the surface of TiO_2. This allows the redistribution of the dye on the oxide surface with slight increase in cell efficiency.

The electrical conductivity of the electrolyte increases with HCl concentration in the investigated range. When the concentration of H_3O^+ ions exceed the optimal value, protonation of the pyridinic nitrogen atom from the 2,2 '-bipyridyl-4, 4'-dicarboxylate ligand can occur, blocking metal ligand charge transfer.

This causes the decreases of solar cells efficiency. At high concentrations of HCl corrosion of SnO_2: F may occur. This facts increase the nanoTiO$_2$ -TCO contact resistance. In this case the ligand 2,2 '-bipyridyl-4, 4'-dicarboxylate could bind Sn^{4+} ions from electrolyte releasing ruthenium ions.

3. Conclusion

Dye-sensitized solar cells were assembled by adsorbing N719 dye onto TiO_2 porous film, deposited on TCO glass using platinum and carbon cover counter electrodes.

Under chopped light Pt-DSSC and C-DSSC have a slower response than crystalline silicon cells.

By adding hydrochloric acid as additive in the electrolyte solution, response time is significantly better for Pt-DSSC and improves for C-DSSC. Pt-DSSC and C-DSSC photovoltage increases slowly for low concentrations of HCl as electrolyte additive.

If the quantity of HCl exceeds a limit value, response time is still excellent but photovoltage decreases strongly for both types of DSSC.

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