Degradation mechanisms of Pt counter electrodes for dye sensitized solar cells

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ABSTRACT

This work investigates the stability of platinum (Pt) electrodes prepared by electrodeposition and thermal decomposition of hexachloroplatinic acid (H_2PtCl_6) solutions. To this aim, the electrodes were stored in an electrolyte solution (0.5 M KI, 0.05 M I_2 in 90%/10% PC/EG) or in air, within a closed vessel, for up to 70 days. A drop of up to 40% in the current density for triiodide reduction was caused by storage in the electrolyte solution and of about 15%–20% when the electrodes were stored in air. Electrolyte storage was found to cause a 40% increase in the activation energy of both kinds of electrodes. XPS measurements have shown that the main degradation mechanism in the case of electrolyte storage is the dissolution of Pt from the substrate. Regeneration of the electrodes by heat or acid treatment was not possible. The observed electrode degradation is expected to appear in dye sensitized solar cells using this kind of counter electrodes and thus affect their long term stability.

1. Introduction

Dye sensitized solar cells (DSSCs hereafter) offer a promising solution to the production of solar electricity. Compared to other PV technologies, DSSCs have certain advantages: They can be produced by relatively low cost processes and materials under ambient conditions. They are suitable for low power density applications; they can work under diffuse and low light conditions without significant performance reduction. Furthermore, the angle of incidence of the incoming light has a minimal effect on their efficiency. DSSCs can be developed on flexible substrates and can be made semi-transparent for use in energy producing windows. Depending on the dye used, they can have different colors, or even patterns (such as company logos, etc). Moreover DSSC can be integrated to many devices other than photovoltaics, such as energy storable solar cells [1], photoelectrochromic windows [2,3], water splitting solar cells [4] and many others. However, further improvement of their efficiency (which is currently around 11% [5]) and stability is required in order to become commercially viable.

A typical DSSC is based on a nano-structured semiconductor film such as TiO_2 with large internal surface area. Dye molecules, adsorbed on the semiconductor surface, are used to "sensitize" it, extending its light absorption range in the visible and infrared

spectrum. Incident light is absorbed by the dye molecules and electrons are injected into the conduction band of the semiconductor. The electrons are collected by transparent conductive electrodes (ITO or FTO). Through the external circuit of the cell, electrons are transferred to a platinized counter electrode. An electrolyte (liquid, gel or solid) containing a redox couple such as iodide/triiodide intervenes between the working and counter electrode. Triiodide is reduced to iodide on the counter electrode surface (Eq. (1)).

$$I_3^- + 2e^- \overset{(Pt)}{\Rightarrow} 3I^- \tag{1}$$

The operation cycle of the DSSC is completed with the reduction of the oxidized dye molecules by the resulting iodide ions (Eq. (2)).

$$2S^+ + 3I^- \Rightarrow 2S^o + I_3^- \tag{2}$$

In order to catalyze the triiodide reduction at the counter electrode (reaction Eq. (1)), an ultra-thin platinum film is deposited on its surface. Even a small amount of Pt (5–10 $\mu g/cm^2$) is sufficient to keep the overvoltage for triiodide reduction low for exchange current densities up to 20 mA/cm^2 [6]. Large catalytically active area, good catalytic activity and mechanical stability are prerequisites for an efficient counter electrode. Different techniques have been used for the preparation of platinum films such as thermal decomposition of a hexachloroplatinic salt in isopropanol [6], electrodeposition [7,8], sputtering [7,9,10], spraying [9], vapor deposition [11], screen printing [12], self assembly

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[13,14]. Platinum nanoparticles have also been prepared by other methods [12,15,16].

The use of Pt in photoelectrochemical cells in combination with electrolytes containing an iodide/triiodide redox couple has been applied before the breakthrough in DSSCs [17]. Pt films are considered to be stable because Pt is a noble metal, however there are reports showing that the properties of platinum films can change in the presence of the iodide/triiodide redox couple [6,18]. Two main factors are considered responsible for the degradation of platinum counter electrodes: The change of their electrocatalytic properties (such as the valence state of platinum) and dissolution from the substrate. Adsorption of iodine (I_2) and iodide (I^-) but not triiodide (I_3^-) on platinum electrodes has been observed since the early 60's. [19,20] Hauch A. and Georg A. [21] found that the charge transfer resistance of platinum electrodes was increased from 2 to 100 Ω/cm^2 when the platinum electrodes were stored in air for some months (not specified by the authors), due to the influence of atmospheric gases. Wang et al. [22] used x-ray photoelectron spectroscopy analysis to examine the stability of platinum electrodes. They found that the valence state of platinum was altered from 0 to +2 and +4, during the thermal sealing process of the cells and an amount of inactive iodine was adsorbed on the surface of the film, in the presence of air. Degradation of the Pt electrode by the iodine redox electrolyte at 80 °C changed the concentration of the electrolyte according to Hara et al. [23].

Dissolution of platinum films and formation of PtI_4 was observed by Olsen et al. for vapor deposited films [11], Papageorgiou et al. [6], Koo et al. [24] and Kay and Grätzel [25]. Dissolution of platinum under continuous cycles has been also reported recently by Xiaoguang Mei et al. [26].

Degradation of the catalytic activity of the counter electrode has a profound influence on the cell performance, causing the charge transfer resistance to increase as a result of the incomplete reduction of triiodide, thus reducing the short circuit current and the fill factor [9]. Dissolution of a small amount of Pt and adsorption on the TiO_2 film or on the underlying conducting substrate would enhance the recombination of electrons from the conduction band of the TiO_2 with the triiodide ions in the electrolyte (dark current). This would increase the series resistance [13] and would reduce the open circuit voltage and the fill factor [21,27,28].

In this work we present a systematic experimental study of the degradation mechanisms of platinum counter electrodes, prepared by two different techniques, namely thermal decomposition and electrodeposition. The electrodes were stored in air or were immersed in an electrolyte for several days in order to simulate the DSSC working conditions. The electrolyte used for storing the electrodes was chosen to have the standard synthesis used for dye sensitized solar cells, e.g., 0.5 M KI, 0.005 M I_2 in propylene carbonate/ethylene glycol (90%/10%) [29]. In this manner it was possible to examine the change in the properties of the counter electrodes under prolonged contact not only with air, as in [21], but with the electrolyte as well. Cyclic voltammetry and x-ray photoelectron spectroscopy were used in order to study the effects of air and electrolyte storage on the properties of counter electrodes.

2. Experimental

2.1. Preparation of the platinum films

Platinum films were deposited on conductive glass substrates (SnO_2:F coated glass with sheet resistance of 16.7 Ω/sq and 80% transmittance in the visible). The substrates were first cleaned with a soft detergent. Then they were cleaned ultrasonically in acetone and rinsed with ethanol and deionized water. Calcination at 120 °C for 15 min completed the cleaning procedure.

Platinum films were prepared by two different methods, by electrodeposition (E samples) and by thermal decomposition (T samples) of a hexachloroplatinic acid solution (H_2PtCl_6). In order to prepare films by electrodeposition a potentiostat–galvanostat (AMEL, model 2053), a function generator (AMEL, model 586) and noise reducer (AMEL NR 2000) were used. An aqueous solution of 0.002 M H_2PtCl_6 and a three electrode configuration was used with a SnO_2:F coated glass serving as the working electrode, an Ag/AgCl electrode as reference and a Pt wire as the counter electrode. The electrodeposition process was carried out at a constant current of 0.5 mA/cm^2 for different time intervals. More than one electrodeposition cycles were used to obtain higher electrode coverage.

In the case of thermal decomposition one drop of an H_2PtCl_6 solution in isopropanol (0.005 M) was spread on the substrate. In order to increase the homogeneity of the resulting films, the glass substrates were heated at 70 °C before deposition. Annealing in 380 °C for 15 min [6] followed, with a constant rate of 15 °C/min during the temperature rise.

2.2. Characterization of the platinum films

Scanning electron microscopy (SEM) images were taken using a JEOL 6300 microscope, in order to characterize the structure of the films.

Cyclic voltammetry was used in order to evaluate the electrocatalytic activity of the counter electrodes for the triiodide reduction [30]. The composition of the electrolyte, used for the cyclic voltammetry experiments, was 10 mM KI, 1 mM I_2 and 0.1 M $LiClO_4$ in a mixture of 90%/10% propylene carbonate/ethylene glycol. Lithium perchlorate ($LiClO_4$) was used as a supporting electrolyte in order to minimize the contribution of migration to the mass transfer of the electroactive species in the electrolyte, and thus making it possible to observe the characteristic peaks for the triiodide oxidation/reduction [8,31]. The same three electrode setup was used as for the electrodeposition and the sweep rate was 10 mV/s. Diffusion coefficients and activation energies were calculated from cyclic voltammetry experiments.

The photoemission experiments were carried out in an ultra-high-vacuum system, which consists of a fast entry specimen assembly, a sample preparation and an analysis chamber with a base pressure $< 5 \times 10^{-10}$ mbar. The system is equipped with a hemispherical electron energy analyzer (SPECS LH-10) and a dual anode which produced the AlK_α and MgK_α x-ray lines. The unmonchromatized MgK_α (1253.6 eV) line was used for the present XPS measurements. The analyzer was working at constant pass energy (Ep=97 eV) giving a full width at half maximum of the main Pt4f XPS peak of 1.7 eV. The XPS core level spectra were analyzed using a fitting routine, which can decompose each spectrum into individual mixed Gaussian–Lorentzian peaks after a Shirley background subtraction. Regarding the measurement errors, for the XPS core level peaks we estimate that for a good signal to noise ratio, errors in peak positions are of about ± 0.05 eV.

2.3. Soaking of the platinum films in the electrolyte

The platinum films were immersed in a standard electrolyte consisting of 0.5 M KI, 0.05 M I_2 in a mixture of 90%/10% propylene carbonate/ethylene glycol and stored in the dark. When the films were removed from the electrolyte for the cyclic voltammetry measurement they were rinsed gently with deionized water, to remove the excess electrolyte.