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Cation adsorption by mesoporous titania photoanodes and its effect on the current-voltage characteristics of photoelectrochemical cells

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ABSTRACT

Current-voltage curves recorded during the study of photoelectrochemical cells functioning in the presence of aqueous electrolytes contain a characteristic anodic current feature, which may interfere in the interpretation of the results. This anodic current is observed at negative potentials and it derives from the adsorption of cations into the mesoporous structure of nanoparticulate titania photoanodes. The shape and the height of the peak depends on the size of the cation, its concentration, the thickness of the titania film and the nature of the counter ion and the corresponding pH. This anodic current is similar to the one observed in other works during ion storage and electrochromism studies with mesoporous titania. In the presence of an organic sacrificial agent, like ethanol, adsorption of cationic species is still strong but it decreases at higher organic content.

1. Introduction

Several metal oxide semiconductors have been used as photocatalysts to construct photoanode electrodes for photoelectrochemical cells employed for water splitting [1–5] or PhotoFuelCell applications [6–9]. These cells function mostly in the presence of aqueous neutral or alkaline electrolytes, for example, Na_2SO_4, or NaOH. However, mesoporous metal oxides are known to adsorb ionic species from the electrolyte solution and this may affect the current-voltage characteristics of the cells. This matter is overlooked but its effects are present and they may lead to erroneous conclusions. In order to isolate this possibility, we have studied this case for nanoparticulate titania (np-TiO_2) and present the obtained results as a function of the nature of the salt, the nature of the anions and the cations, the nc-TiO_2 film thickness, the pH, etc. We believe that this information will be useful to all researchers working with photoelectrochemical cells.

Adsorption of cations by mesoporous titania or other metal oxides has been studied mainly for purposes of electrochromism and ion storage [10–16]. However, it is limited almost exclusively to Li salts dissolved in polycarbonate. The present work deals with aqueous electrolytes and with a variety of salts and bases, which may be employed in the study of photoelectrochemical cells. To our knowledge, works dealing with such satellite phenomena in the behavior of aqueous electrolyte solar cells are very limited [17].

2. Experimental

2.1. Materials

Unless otherwise indicated, reagents were obtained from Sigma-Aldrich and were used as received. Commercial nanocrystalline titania Degussa P25 was used in all photoanode constructions and Millipore water was used in all experiments. SnO_2:F transparent conductive electrodes (FTO, Resistance 8 Ω/square) were purchased from Pilkington.

2.2. Deposition of the photocatalyst as film

The following procedures were undertaken in order to deposit photocatalyst on the photoanode electrode. Nanoparticulate titania (np-TiO_2) film was deposited in two layers, a bottom compact layer and a top open structure. The bottom layer was synthesized by the sol-gel method while the top layer was deposited by using a paste made of Degussa P25 nanoparticles. A densely packed nanocrystalline titania layer was first deposited on a FTO electrode, which was cleaned by sonication in acetone, isopropanol and ethanol: 3.5 g of the non-ionic surfactant Triton X-100 was mixed with 19 ml ethanol. Then 3.4 ml glacial acetic acid and 1.8 ml of Titanium Tetraisopropoxide were added under vigorous stirring. After a few minutes stirring, the film was

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deposited by dipping in the sol and then it was left to dry in air for a few minutes. Finally, it was calcined at 550 °C. The temperature ramp was 20 degrees/min up to 550 °C and the sample was left for about 10 min at that temperature. The final compact film, was about 350 nm thick. On the top of this compact nanostructured layer, commercial Degussa P25 was deposited. For this purpose, we used a paste, which was applied by doctor blading. The paste was prepared by using the recipe analytically described in Ref. [18]. It was finally calcined again at 550 °C. This last sequence was repeated in order to obtain a top layer of about 10 μm thick. In the case when experiments were made as a function of film thickness, the latter was modified by modifying the number of sol-gel layers or the top layers. The thickness of the films was measured by their SEM profiles. The geometrical area of the film was 1 cm^2 = 1 cm x 1 cm.

2.3. Description of the photoelectrochemical cell

The cell was home made of Plexiglas. It could accommodate the photoanode electrode described in section 2.2, a Pt foil counter electrode (1.4 × 1.4 cm^2 active surface) and a Ag/AgCl reference electrode. The distance between photoanode and counter electrode was 5 mm and the quantity of the electrolyte 10 ml. Illumination of the photoanodes was made by using an Oriel LCS-100 Solar simulator set at 100 mW.cm^{-2}. Linear and cyclic voltametry curves were traced with an Autolab potentiostat PGSTAT128 N.

3. Results and Discussion

np-TiO_2 mesoporous films have been deposited on FTO electrodes using standard procedures employed by us and by others and reported in several previous publications. A FE-SEM image of the film can be seen in Fig. 1. The size of the nanoparticles and the corresponding pore size is that expected for P25 nanoparticles, i.e. around 20–30 nm, while the BET specific surface is around 45 m^2/g [19]. The study of the behavior of a photoelectrochemical cell starts with the recording of IV curves. Fig. 2 shows typical linear plots obtained with a np-TiO_2 photoanode in the dark, a platinum foil counter electrode and a Ag/AgCl reference electrode in the presence of aqueous alkaline electrolytes of various cations. The cations were chosen to be of varying size ranging from Li^+ to NH_4^+. All curves were recorded in the dark to avoid any interference from photocurrent. All curves contained a rising part above +0.7 V vs. Ag/AgCl (i.e. about 1.6–1.7 V vs. RHE for alkaline pH), which corresponds to electrolytic water oxidation. In the range between -1.5 to -1.0 V vs. Ag/AgCl, there is an anodic peak, which apparently corresponds to adsorption of cations into the titania mesoporous structure. This adsorption is affected by the size of the cation in a rather dramatic manner. Thus it was very intense in the case of Li^+ but decreased fast in the case of Na^+ and K^+ and almost disappeared in the case of NH_4^+. Anodic peaks are reproducible for several cycles, as can be seen by the cyclic voltamograms of Fig. 3. The height of the peak increased after the first cycle but it remained practically the same after the second. In order to concretize the original assertion that this anodic peak derives from the adsorption of cations, we have also studied IV behavior of the system in the dark, as a function of cation concentration and of film thickness. The corresponding results are presented in Fig. 4. Indeed, Fig. 4a shows that anodic peak was more intense when Li^+ concentration was higher while Fig. 4b

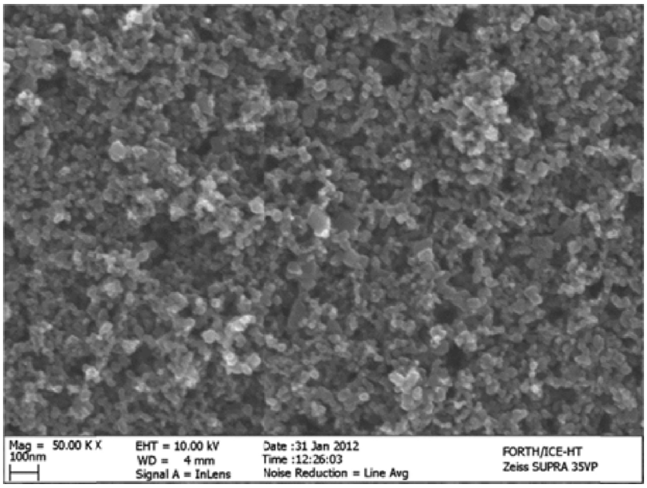

Fig. 1. FE-SEM image a np-TiO_2 film made by using commercial Degussa P25 powder. The scale bar is 100 nm.

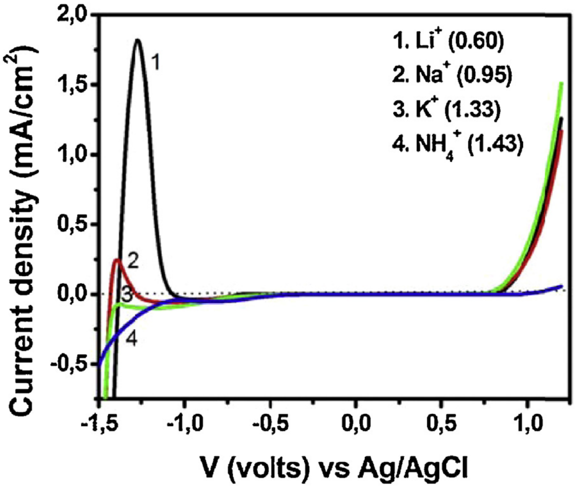

Fig. 2. Linear IV plots in the dark for an electrochemical cell comprising a np-TiO_2 photoanode, a platinum foil cathode, a Ag/AgCl reference electrode and an aqueous alkaline electrolyte containing 0.5 M XOH, where X is: (1) Li^+; (2) Na^+; (3) K^+; and (4) NH_4^+. Insert: the numbers in parentheses give the size of the ion in Angstroms.

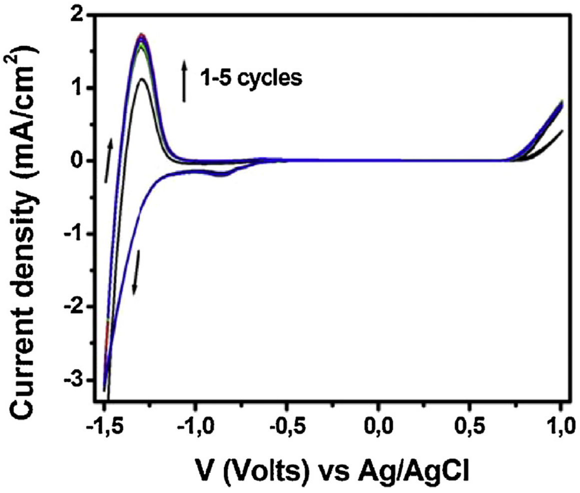

Fig. 3. Cyclic voltamograms in the dark for an electrochemical cell comprising a np-TiO_2 photoanode, a platinum foil cathode, a Ag/AgCl reference electrode and an aqueous alkaline electrolyte containing 0.2 M LiOH. Scan rate was 10 mVs^{-1}.