Electrodeposition of TiO_2 thin films promoted by anodic oxidation of dihydroxybenzene

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Recently, TiO_2 thin films find a number of important applications such as dye-sensitized solar cells (DSSCs), photocatalysts, batteries and electrochromic devices. There are several reports dealing with the preparation methods of TiO_2 thin films. For their practical use, however, it is very important to achieve reduction of cost and environmental stress upon processing. Therefore, we pay attention to electrodeposition process from an aqueous solution, which is cost effective, environmentally friendly and has an advantage to achieve facile control of the film thickness.

Electrodeposition of TiO_2 films has been achieved by anodic and cathodic electrolysis from acidic aqueous solutions containing $TiCl_3$[1)] and $TiO(SO_4)$,[2)] respectively. In both systems, however, the primarily electrodeposited films are insulating amorphous Ti(IV) hydroxides which are then converted into crystalline TiO_2 by heat treatment. Due to the electrically insulating nature of the deposited films, the films with limited thicknesses and with porous structures can only be obtained by these methods.

We have recently reported a simple method to prepare basic aqueous solution of Ti(IV) by mixing titanium tetraisoproroxide(TIP) and alkylammonium hydroxides (hereafter called TM solution).[3)] The TM solution is stable and can be stored at room temperature for a long time, but forms precipitates when pH of the solution is lowered. Hence, we have attempted anodic precipitation of Ti species from the TM solution containing redox active organic molecules such as o-, m-, and p-dihydroxybenzene which can be oxidized to generate protons at the vicinity of the electrode. These molecules also tend to form complexes with Ti(IV).

In the absence of dihydroxybenzene, the deposits formed on the anode was poorly adhesive probably due to the formation of O_2 bubbles by oxidation of water. A large increase of anodic overpotential was also noticed during the galvanostatic electrolysis because of the electrical insulation by the deposits (Figure 1). When dihydroxybenzene was added, the shift of the overpotential remained very small. Anodic electrolysis in the TM solution containing p-dihydroxybenzene yielded transparent yellow-colored thin films with good adhesion (Figure 2). The coloring of the films were found as due to complex formation between oxidized dihydroxybenzene molecules and Ti(IV). The loaded dihydroxybenzene molecules were removed from the film on firing at 450˚C for 30 min, while the film was crystallized into anatase TiO_2 (Figure 3). The SEM and AFM images of the films revealed very smooth surface and highly dense structure of the films. It is supposed that the loaded dihydroxybenzene molecules provide conductive pathways to allow formation of dense films and to achieve high thickness of the films.

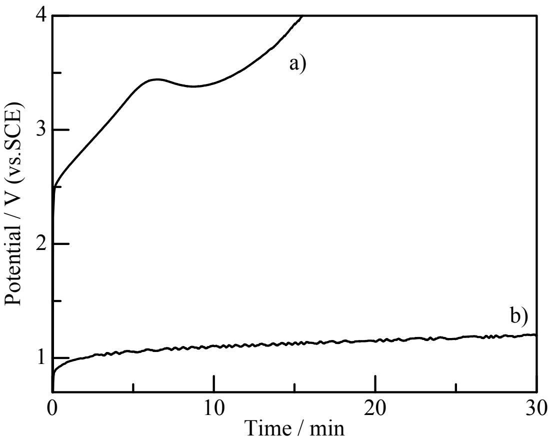

Fig. 1 Chronopotentiograms measured during galvanostatic electrolyses at 1 mA cm^{-2} in the TM solutions (0.05 M Ti(O^{i}Pr)$_4$ + 0.1 M tetramethylammonium hydroxide) without (a) and with (b) the added 0.1 M p-C_6H_4 $(OH)_2$.at 20ºC.

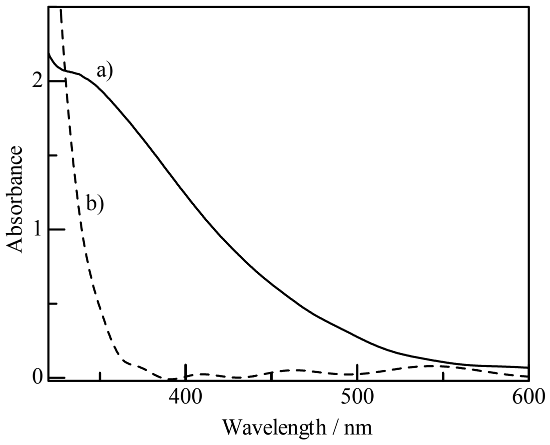

Fig. 2 Absorption spectra of the Ti(IV)/p-$C_6H_4O_2$ hybrid thin film anodically electrodeposited from the TM solution (20ºC) containing 0.1 M p-C_6H_4 $(OH)_2$.at 1mA cm^{-2} for 100 s (a) and that of the same film after heat treatment at 450˚C for 30 min under air (b).

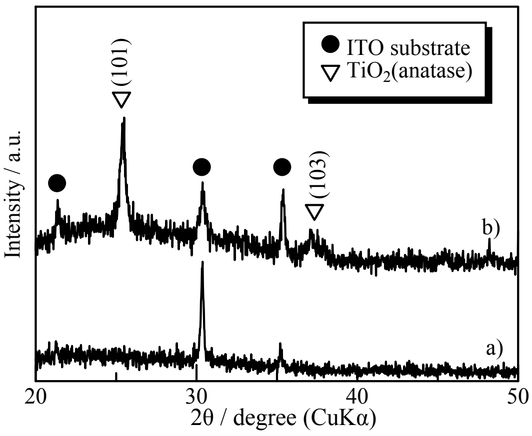

Fig. 3 X-ray diffraction patterns of the films same as those in Fig. 2.

1) L. Kavan, B. O'Regan and M. Grätzel, *J. Electroanal. Chem.,* **346**, 291 (1993).
2) C. Natarajan and G. Nogami, *J. Electrochemical. Soc.,* **143**, 5 (1996).
3) T. Ohya, T. Ban, Y. Ohya and Y. Takahashi, *Ceram. Trans,* **112**, 47 (2001).