THE PHOTOVOLTAIC PROPERTIES OF A LITHIATED TiO_2 ELECTRODE

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Titanium electrodes coated by TiO_2 (anatas) were prepared by decomposition of peroxotitanic compounds. Their photoelectric behavior in 1M $LiClO_4$/PC (propylene carbonate) was investigated. The photoeffect was emphasized by the process of electrolytic incorporation and removal of lithium. The effective threshold energy was 1.5 to 1.6 eV, thus indicating donor dissociation being the basic photochemical process.

The photoelectrochemical properties of TiO_2 have been studied many times in aqueous solutions since Honda and Fujishima had introduced the question of photoelectric decomposition of water[1]. TiO_2 is a semiconductor with a high gap close to 3 eV (refs[2-4]). Photovoltaic processes on TiO_2 have been studied in aqueous solutions mostly. In our recent studies, we investigated the process of cathodic incorporation of lithium into rutile-like electrodes in an aprotic electrolyte ($LiClO_4$ in PC)[5]. This process should be accompanied by the change in electronic structure of host TiO_2 and its semiconductor properties should be changed. This was the aim of this study.

EXPERIMENTAL

The electrodes were prepared in a way usual for the preparation of RuO_2 anodes by thermal decomposition of titanium peroxoacid on a titanium foil at elevated temperature. The anatas structure was found to prevail in the layer. The solution of 1M-$LiClO_4$ in anhydrous propylene carbonate was used; all potentials refer to the potential of Li/Li^+ reference electrode in the same electrolyte. Electrode impedance in audio range was measured and analysed in usual way.

First, the behavior of a fresh electrode was studied in the range of potential over 3.0 V. Then, the electrode was saturated by lithium (for 24 h at 1.7 V) and then lithium was removed by an anodic oxidation for another 24 h at 3.2 V.

Polychromatic light of a halogen lamp was used for the illumination of the electrode. The approximate method described previously[6] was used for the estimation of the threshold energy of the photovoltaic effect. Its value follows from the influence of light source temperature on the integral photoeffect. The light pulses were used to avoid thermal effects of the light absorption.

RESULTS

The current response to the pulse of light consisted of two components. Firstly, the photovoltaic current appeared immediatelly after opening the shutter, which allowed light to impact on the electrode. On the fresh electrode, which has not been lithiated yet, it decayed very fast and its measurement was therefore rather difficult. At potential below 3.0 V, it has not been observed at all. After the electrode had been lithiated and then lithium had been removed from the electrode, the photoeffect was rather stable during the whole period of irradiation (approximately 2 – 3 s). Its sign was that of the photovoltaic current of a n-type semiconductor electrode. On the contrary, the thermal response of the system was slow, it increased in time according to a quasi-exponential relation and it reached a steady state after several seconds or more. Its sign was to that of the photovoltaic one.

Attempts were done to estimate the threshold energy of the photoeffect. However, a very low value (0.8 to 0.9 eV) was found for the electrode before lithiation and only 1.5 to 1.7 eV for the lithiated one.

These results are summarized in Table I, together with the photocurrent at highest intensity of irradiation obtained at lamp temperature 2 870 K (in μA).

The electrode admittance was of a rather complex behavior, as this is always in the case of solid electrodes having highly developed surface. In general, the admittance was interpreted as a resistance R in series with a constant-phase element which had a phase shift from 70 to 80% of $\pi/2$. Its absolute value was supposed to be equal approximately to $Y_0\,\omega^{0.75}$. These values are also given in Table I. An attempt was made to draw the Mott–Schottky plot from these data. The relative surface area $\sigma = 100$, geometric surface area 2.4 $cm^2\,g^{-1}$ and relative permittivity $\varepsilon = 80$ were considered.

TABLE I

The effective threshold energy ΔU and photocurrent I (arbitrary but constant conditions) for a TiO_2 electrode at various potentials E (vs Li/Li^+ in PC). R_s and Y_0 are series resistance and the module of admittance at $\omega = 1\ s^{-1}$. Upper part: fresh electrode, lower part: electrode after electrochemical lithiation and delithiation

E, V	ΔU, eV	I, μA	R_s, Ω	Y_0, mS $Hz^{1/2}$
3.177	0.82 ± 0.05	2.03	15.5	0.000151
3.385	0.76 ± 0.08	2.52	15.9	0.000102
3.510	0.86 ± 0.04	4.10	14.6	0.000717
3.678	0.76 ± 0.03	4.51	17.0	0.000462
4.203	0.99 ± 0.04	6.94	12.1	0.000075
3.311	1.03 ± 0.07	1.77	44.0	0.0000691
3.750	1.41 ± 0.08	2.17	28.1	0.0000599
3.914	1.22 ± 0.09	2.65	30.0	0.0000585
4.310	1.30 ± 0.07	4.20	25.2	0.0000387

In this way, the donor concentrations $n = 2 . 10^{22}$ and $2 . 10^{23}$ electrons in 1 m^3 of TiO_2 were estimated very roughly.

The flat-band potential E_{fb} was 3.05 V before the process of lithiation and delithiation and 3.0 V after it.

DISCUSSION

Results of both the photoeffect and admittance measurements subject to severe estimations and should be considered as qualitative only. However, some conclusion can be drawn from them:

1) The electrode prepared by the thermal decomposition of titanium peroxide compounds is a very poor photovoltaic material. This material contains rather high amount of donors and its photoeffect dies out within one second.

2) If the electrode has been saturated by lithium and then the lithium has been removed, the photovoltaic properties are improved. The photovoltaic effect is much more stable and its observation is easier. However, it is rather due to the stability in time than to the magnitude of the effect, as its absolute magnitude is lower in the latter case.

3) The lithiation and subsequent delithiation increases the amount of donors by one order of magnitude. The donors are now of much higher dissociation energy and their level is sunk deeper into the forbidden zone. This is accompanied by the increase of effective threshold energy as well as by the lower output of photoeffect.

4) On the basis of points *1*) to *3*), we may assume, that the photovoltaic effect in this material originates by the photodissociation of donor levels and not by the ionisation of electrons from valence band.

5) Two following explanations of the donor nature are most probable. They are the deficiency of oxygen ions and the presence of lithium particles in interstitial positions.

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