PHOTOELECTROCHEMICAL PROPERTIES OF TITANIUM NIOBATE $(TiNb_2O_7)$
AND TITANIUM TANTALATE $(TiTa_2O_7)$

L.G.J. DE HAART, H.J. BOESSENKOOL and G. BLASSE

Solid State Department, Physics Laboratory, Utrecht University,
P.O. Box 80.000, 3508 TA Utrecht (The Netherlands)

ABSTRACT

The diffuse reflection spectra and the photoelectrochemical properties of $TiNb_2O_7$ and $TiTa_2O_7$ are reported. Both compounds show an optical absorption edge near 3.0 eV. $TiNb_2O_7$ can be used as photoanode in a photoelectrochemical cell. The onset potential of the photocurrent is about −0.9 V vs SCE in 1M NaOH. $TiTa_2O_7$ appears to be unstable in this electrolyte.

INTRODUCTION

One class of materials investigated so far as photoanode material for the photoassisted electrolysis of water consists of semiconducting oxides of closed-shell transition-metal ions; e.g. the simple oxides TiO_2 [1], ZrO_2 [2], Nb_2O_5 [2], Ta_2O_5 [2], WO_3 [3] and various titanates, niobates and tantalates [4]. In these compounds the valence band is constituted mainly of the oxygen 2p levels. The empty d levels of the transition-metal ions constitute the conduction band. The low electronegativities of the closed-shell transition-metal ions confer to these compounds a small electron affinity and, consequently, a low (negative) flat-band potential (V_{fb}) [5]. It was shown recently by Bin-Daar *et al.* [6] that the position of the conduction band edge of the titanate $SrTiO_3$ can be fine-tuned to the required electron affinity by using as dopant Zr^{4+}, which has an even lower electronegativity than Ti^{4+}. Replacing 25% of the Ti^{4+} ions by Zr^{4+} ions causes the flat-band potential to shift 0.15 V more negatively [ref.6]. When the forementioned materials are used as photoanodes, only a small or even no external bias is needed for the photoassisted electrolysis of water.

In relation to solar energy conversion, a disadvantage of these materials is the high value of the bandgap ($E_g > 3$ eV). This implies that these can only absorb U.V. radiation. Titanates such as TiO_2 and $SrTiO_3$ can be sensitized for visible irradiation by doping with other transition-metal ions, e.g. Cr^{3+} [7,8], but there is some disadvantage to this approach. These transition-metal ions form localized levels in the forbidden bandgap, leading to a low hole mobility. Consequently, a high bias is required to obtain a significant photoresponse in the visible region [8].

In this paper we report on the optical and photoelectrochemical properties of titanium niobate, $TiNb_2O_7$, and titanium tantalate, $TiTa_2O_7$. The crystal structures of $TiNb_2O_7$ [9,10] and $TiTa_2O_7$ [11] are isotypic. The structure contains fragments of the simple rhenium trioxide structure in the form of blocks of corner-sharing MeO_6 octahedra. In $TiNb_2O_7$ and $TiTa_2O_7$ these blocks contain 9 MeO_6 octahedra (3 x 3) and form a linear column along the b-axis of the unit cell. Perpendicular to the b-axis the columns are bound by crystallographic shear planes. Across the shear planes the MeO_6 octahedra share edges [10,11].

It has usually been assumed that the different cations occupy the octahedral sites in a completely random way. However, Von Dreele and Cheetham [10], and later Gasperin [13], have shown that the smaller and lower-charged Ti^{4+} ion has a preference for the octahedra at the corners and edges of the blocks (i.e. those octahedra which lie along the shear planes and share, therefore, one or two edges with other octahedra). Although there is no complete order in the cation distribution over the octahedra, band formation by both cations remains possible. The crystal structure shows an analogy with both the perowskite and the rutile structure, so that interesting properties are not excluded.

EXPERIMENTAL

Samples were prepared by the usual ceramic techniques using high purity starting materials. Firing was performed at 1200 °C in air for $TiNb_2O_7$ and at 1400 °C in oxygen for $TiTa_2O_7$. Samples were checked by X-ray powder diffraction. Diffuse reflection spectra were recorded at room temperature on a Perkin-Elmer EPS-3T spectrophotometer.

The powders were cold-pressed at 100 kg/cm^2 and subsequently sintered at 1300 °C ($TiNb_2O_7$) and at 1400 °C ($TiTa_2O_7$) in an oxygen atmosphere. The density ratio of the pellets thus obtained was more than 90%. The pellets were made n-type conducting by reduction in a N_2/H_2 (3 : 1) atmosphere for 3 h at 800 °C.

The cell arrangement and electrochemical measurement procedures have been described previously [8]. Electrode potentials are referred to the saturated Calomel electrode (SCE). All photoelectrochemical measurements were performed in 1M NaOH.

RESULTS AND DISCUSSION

In Fig. 1 the diffuse reflection spectra of $TiNb_2O_7$ and $TiTa_2O_7$ are presented. By extrapolating the steep slope in the curves to the long-wavelength side, values of the bandgap E_g can be estimated from these spectra. For both compounds this results in a value of 3.0 eV, which is the same value as was found for TiO_2 [14]. The optical absorption edge is situated at the same energy for both compounds. This suggests that it is due to the same optical transition, which can only be the $O^{2-} \rightarrow Ti^{4+}$ charge-transfer (C.T.) transition [15]. The $O^{2-} \rightarrow Me^{5+}$ C.T. transitions are expected at higher energy and should differ from each other, since in the case of Nb^{5+} the lowest empty level is the 4d level, whereas for Ta^{5+} this is the 5d level [15].

In Fig. 2 the photocurrent density spectra for $TiNb_2O_7$ and $TiTa_2O_7$ are presented. The observed photocurrent density for the tantalate electrode is much lower than for the niobate electrode. This can be accounted for by the higher resistivity of the tantalate electrode, which is about 35 times higher than the resistivity of the niobate electrode. Prolonged reduction of the tantalate pellet did not lower the resistivity. Another factor could be the instability of $TiTa_2O_7$ in 1M NaOH. After prolonged operating in the photoelectrochemical cell, pits were observed on the surface of the electrode. The pits might be due to (photo)corrosion. The $TiNb_2O_7$ electrode was stable during long-term cell operation. For both materials the onset wavelength is about 400 nm. This is in good agreement with the values of E_g deduced from the diffuse reflection spectra.
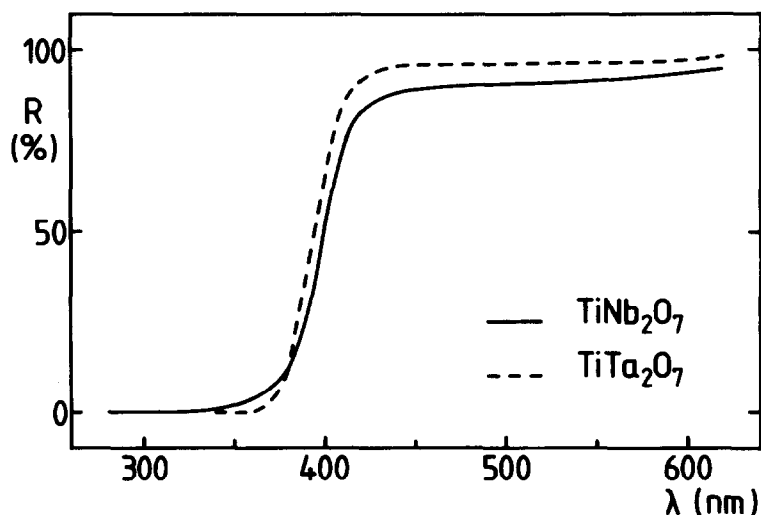

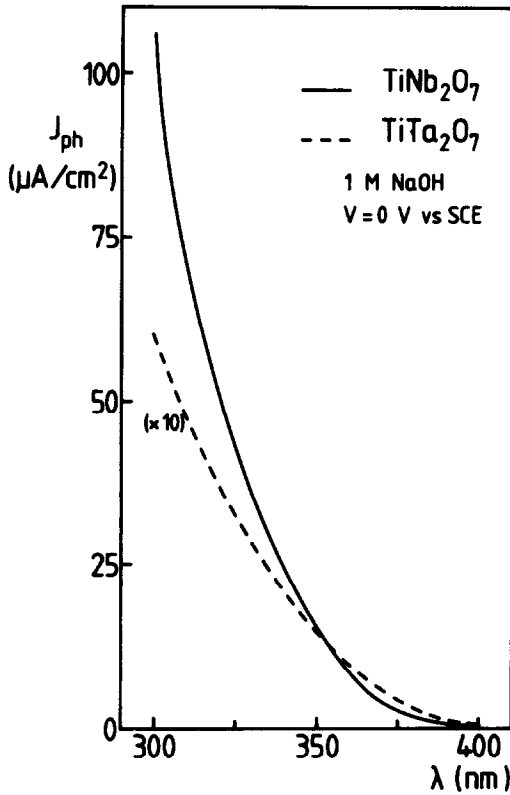Fig. 1. Diffuse reflection spectra of $TiNb_2O_7$ and of $TiTa_2O_7$.

Fig. 2. Variation of the photocurrent density with irradiation wavelength for TiNb$_2$O$_7$ and for TiTa$_2$O$_7$.

In Fig. 3 the photocurrent density is shown as a function of the potential of the TiNb$_2$O$_7$ electrode. We were not able to measure the potential dependence of the photocurrent density for the TiTa$_2$O$_7$ electrode, due to the instability of this electrode and the low value of the photocurrent. The onset potential of the photocurrent for TiNb$_2$O$_7$ is at about −0.9 V vs SCE. The photocurrent rises rapidly with increasing potential and reaches a saturation region at a potential of +0.2 V vs SCE. The photocurrent density/voltage curve observed for TiO$_2$ [16] shows a similar dependence. However, the photocurrent of the latter increases more steeply with increasing potential, so that saturation is reached at a lower potential. This indicates that in the case of TiNb$_2$O$_7$, recombination processes predominate at low potentials. This effect is even more pronounced in the photocurrent density/voltage curve observed for MgTiO$_3$ [17].
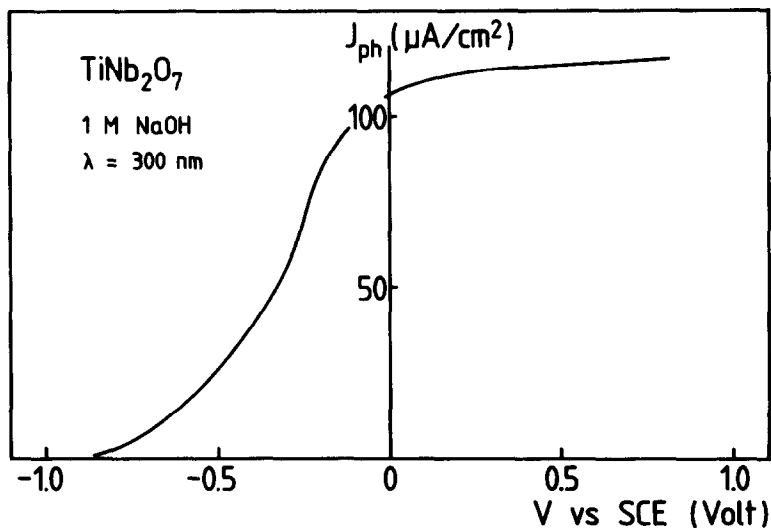
Fig. 3. Variation of the photocurrent density with applied potential (vs SCE) for TiNb$_2$O$_7$.

Due to the disordered nature of the Ti^{4+} and Nb^{5+} (Ta^{5+}) ions, there will be a departure from a perfect periodic potential, so that the bottom of the conduction band and the top of the valence band do not any longer exist as sharp levels: the band edges undulate spatially because of the compositional inhomogeneity [18]. The slow increase of the photocurrent density in the action spectra (see Fig. 2) is related to this phenomenon.

CONCLUSION

We have shown that TiNb$_2$O$_7$ can be used as a photoanode in a photoelectrochemical cell. However, similar to all other stable oxides of closed-shell transition-metal ions investigated so far, the bandgap is too high for efficient solar energy conversion.

REFERENCES

1 A. Fujishima and K. Honda, Nature, 238 (1972) 37.
  M.S. Wrighton, D.S. Ginley, P.T. Wolczanski, A.B. Ellis, D.L. Morse and A. Linz, Proc. Nat. Acad. Sci. USA, 72 (1975) 1518.
  K.L. Hardee and A.J. Bard, J. Electrochem. Soc. 122 (1975) 739.

2 P. Clechet, J.R. Martin, R. Olier and C. Vallouy, C.R. Acad. Sci. Paris, C282 (1976) 887.

3 M.A. Butler, R.D. Nasby and R.K. Quinn, Solid State Comm. 19 (1976) 1011.
  W. Gissler and R. Memming, J. Electrochem. Soc. 124 (1977) 1710.

4 H.H. Kung, H.S. Jarrett, A.W. Sleight and A. Ferretti, J. Appl. Phys. 48 (1977) 2463.
  K. Rajeshwar, P. Singh and M. DuBow, Electrochim. Acta, 23 (1978) 1117.

5 M.A. Butler and D.S. Ginley, J. Electrochem. Soc. 125 (1978) 228.

6 G. Bin-Daar, M.P. Dare-Edwards, J.B. Goodenough and A. Hamnett, J. Chem. Soc., Farady Trans.1, 79 (1983) 1199.

7 H.P. Maruska and A.K. Ghosh, Solar Energy Mat. 1 (1979) 237.
  Y. Matsumoto, J. Kurimoto, T. Shimizu and E. Sato, J. Electrochem. Soc. 128 (1981) 1040.

8 R.U.E. 't Lam, L.G.J. de Haart, A.W. Wiersma, G. Blasse, A.H.A. Tinnemans and A. Mackor, Mat. Res. Bull. 16 (1981) 1593.

9 A.D. Wadsley, Acta Cryst. 14 (1961) 660.

10 R.B. Van Dreele and A.K. Cheetham, Proc. Roy. Soc. Lond. A338 (1974) 311.

11 W. Mertin, R. Gruehn and H. Schäfer, J. Solid State Chem. 1 (1970) 425.

12 J.G. Allpress, J. Solid State Chem. 1 (1969) 66.

13 M. Gasperin, J. Solid State Chem. 53 (1984) 144.

14 L.G.J. de Haart, A.J. de Vries and G. Blasse, J. Solid State Chem., in press.

15 G. Blasse, Structure and Bonding, Vol. 42, Springer Verlag, Berlin, 1980, p.1

16 H.P. Maruska and A.K. Ghosh, Solar Energy, 20 (1978) 443.

17 L.G.J. de Haart, A.J. de Vries and G. Blasse, Mat. Res. Bull. 19 (1984) 817.

18 G.B. Inglis and F. Williams, Phys. Rev. B11 (1975) 2200.