PHOTOELECTROCHEMICAL PROPERTIES OF Zr$_x$Ti$_{1-x}$Nb$_2$O$_7$ MIXED OXIDES

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ABSTRACT

The suitability of Zr$_x$Ti$_{1-x}$Nb$_2$O$_7$ mixed oxides as photoanodes in photo-electrochemical cells is investigated. The mixed oxides are not as suitable as the end members. ZrNb$_2$O$_7$ can be expected to be a promising candidate from the point of view of stability.

INTRODUCTION

Oxides containing closed shell transition metal ions, e.g. TiO$_2$ [1], ZrO$_2$ [2], Nb$_2$O$_5$ [3], Ta$_2$O$_5$ [2], WO$_3$ [4] and various titanates [5], niobates [6] and tantalates [6] have been examined for their use as photoanode materials in photoassisted electrolysis of water. In these systems, the valence band is mainly constituted by the oxygen 2p levels, while the conduction band is formed by the empty d levels of the transition metal ions. Studies on perovskite titanate systems [7] have shown that the photoelectrochemical (PEC) properties can be associated with the (TiO$_2$) octahedra present in these compounds. Blasse and coworkers [8] from their studies on ilmenite type transition metal titanates have proposed that the PEC properties of these systems arise out of excitation from the transition metal valence band to the Ti-conduction band without involving the oxygen 2p level. Similarly, studies on Nb$_2$O$_5$ [9], Sr$_2$Nb$_2$O$_7$ and (Ba$_{0.5}$Sr$_{0.5}$)Nb$_2$O$_6$ [10] have revealed that (NbO$_6$) octahedra are the photoactive centres. Studies by Hormadaly et al. [10], Campet et al. [11], Blasse et al. [12] and Claverie et al. [13] have led to certain crystal structure-PEC property correlations. These include the following:

1) the variations in the band gap among related compounds containing TiO_6 or NbO_6 octahedra are primarily due to the structural class in which they crystallise.

2) the differences in the flat band potential (V_{fb}) of a series of related compounds are related to the nature of the A-ion.

3) the slope of the quantum efficiency vs photon energy plot is a structure sensitive parameter and is also as important as the band gap value (E_g).

Further extended studies are needed to establish the validity of these correlations as well as the formulation of any further correlations. We report in this communication the studies carried out on the solid solution series $Zr_xTi_{1-x}Nb_2O_7$ with x = 0.0, 0.025, 0.5, 0.75 and 1.0 for evaluating the suitability of these materials for PEC applications.

EXPERIMENTAL

The compounds were prepared by mixing stoichiometric quantities of ZrO_2 (AR BDH), Nb_2O_5 (AR, GLOBA) and TiO_2 (E Merck) and heating at $1300^\circ C$ for 48 hr. The formation of single phase $ZrNb_2O_7$, $TiNb_2O_7$ and $Zr_xTi_{1-x}Nb_2O_7$ (x = 0.25, 0.5 and 0.75) was confirmed by X-ray diffraction studies (Phillips PW1140) using CuK_α radiation.

The compounds were ground in an agate mortar, compacted into pellets (10 mm dia and 2-3 mm thick) with a WC lined die at 5 tons/cm^2 pressure and sintered at $1300^\circ C$ for 24 hr. All the sintered materials were found to be insulators with resistivities >10^{10} ohm cm. The samples were reduced in hydrogen at $600^\circ C$ for 3 hr after which the resistivity dropped to around 200 ohm cm. Electrodes were made from these pressed pellets after suitable chemical and mechanical polishing and ohmic contacts were made with silver paint and silver epoxy (Epo-tek H31 USA). The pellets were mounted on a glass holder and epoxy resin (Araldite) was used to insulate all the other surfaces of the electrode except the surface exposed to irradiation.

Electrochemical measurements were made in a three electrode configuration (saturated calomel reference and Pt indicator electrode) using a potentio-scan (Wenking model POS73). A 450 W Xe lamp (Carl Zeiss) was used as the light source.

RESULTS AND DISCUSSION

The X-ray diffraction data obtained for the series of mixed oxides are given in Tables I and IA. Least square fitted lattice parameters were obtained for the systems which are crystallising in monoclinic form (namely, with x = 0, 0.25, 0.5) and are given in Table II. $ZrNb_2O_7$ and

Table I. XRD data for $Zr_xTi_{1-x}Nb_2O_7$ with x = 0, 0.25 and 0.5.

hkl	$TiNb_2O_7$ d(Å)	I/I$_o$	$Zr_{0.25}Ti_{0.75}Nb_2O_7$ d(Å)	I/I$_o$	$Zr_{0.5}Ti_{0.5}Nb_2O_7$ d(Å)	I/I$_o$
00$\underline{2}$	5.1556	80	5.111	80	7.1095	10
40$\overline{1}$	5.0968	70	--	--	5.1081	40
110	3.7081	90	3.7002	80	3.7124	90
11$\overline{1}$	3.6045	10	3.6115	10	3.5617	100
00$\underline{3}$	3.4143	100	3.4205	100	3.4141	30
31$\overline{1}$	3.3389	10	3.2999	10	3.3204	20
112	2.8758	10	2.8684	10	--	--
51$\overline{1}$	2.7801	30	2.7508	30	2.7799	50
11$\overline{3}$	2.6751	20	2.6672	20	2.6749	20
004	2.5782	10	2.5743	10	2.5566	10
601	2.5152	20	2.5150	20	2.5163	10
113	2.3986	10	2.3983	10	--	--
51$\underline{1}$	2.3212	10	2.3151	20	--	--
51$\overline{4}$	2.2984	10	2.2981	10	2.3066	20
005	2.0627	50	2.0623	50	2.0623	50
020	1.9062	30	1.9028	30	1.9065	50
11,13	1.6666	40	1.6642	40	1.6788	40

Table IA. XRD data for $Zr_xTi_{1-x}Nb_2O_7$ with x = 0.75 and 1.

$Zr_{0.75}Ti_{0.25}Nb_2O_7$ d(Å)	I/I$_o$	$ZrNb_2O_7$ d(Å)	I/I$_o$
7.2016	20	--	--
5.1702	10	5.0676	5
4.7882	80	4.8610	15
3.7619	30	3.5900	45
3.5900	100	3.5270	100
3.4335	50	--	--
2.9573	95	2.9402	65
2.7985	40	2.7549	5
2.7816	30	--	--
2.6465	20	2.6180	5
2.5750	20	2.5601	10
2.0964	20	--	--
2.0526	95	2.0557	30
1.7939	30	1.7761	10
1.6865	30	1.6851	5
1.5488	10	1.5453	10
1.5038	10	1.5011	10

Table II. Solid state and photoelectrochemical properties of $Zr_xTi_{1-x}Nb_2O_7$ mixed oxides.

Properties	$Zr_xTi_{1-x}Nb_2O_7$				
	x = 0.00	x = 0.25	x = 0.50	x = 0.75	x = 1.00
Crystal System	Monoclinic	Monoclinic	Monoclinic	Not known	Not known
Crystal parameters	a = 20.256 A	a = 20.189 A	a = 20.181 A	--	--
	b = 3.621 A	b = 3.642 A	b = 3.592 A	--	--
	c = 11.661 A	c = 11.592 A	c = 11.501 A	--	--
	β = 121°02'	β = 120°56'	β = 120°48'	--	--
Band gap (eV)	3.20	3.15	3.15	3.15	3.20
Flat band potential (V)	-1.20	-1.16	-1.02	-0.97	-0.75
Stability under illumination (min)	130	120	70	30	150

$Zr_{0.75}Ti_{0.25}Nb_2O_7$ do not crystallise in monoclinic form, though single phase formation was observed in this study. The direct band gap values as deduced from UV absorption measurements are also included in Table II. The current voltage curves were measured for these substances at pH = 13 and 2 and are given in Figs. 1-5. The I-V plots obtained for $TiNb_2O_7$ agree with those reported in the literature [9b]. The values of the band gap of the semiconductors were also determined from the measurement of photocurrent as a function of wavelength of irradiation and were found to agree with those obtained from spectroscopic measurements. The values of the flat band potentials were determined (included in Table II) from the plot of the square of the photocurrent against applied voltage (-1000 to +400 mV) Fig. 6. The values of the photocurrent, photopotentials and flat band potentials were found to be smaller under acidic conditions. The stability of these materials was determined under the conditions of PAE of water by measuring the photocurrent at various time intervals at pH = 13. The results obtained are given in Fig. 7. It is seen that $ZrNb_2O_7$ appears to be comparatively more stable than other oxides used in the present study. However, the value of the flat band potential is small (-0.75 V) as compared to $TiNb_2O_7$ (-1.20 V). The solid solution compounds are less stable under illumination
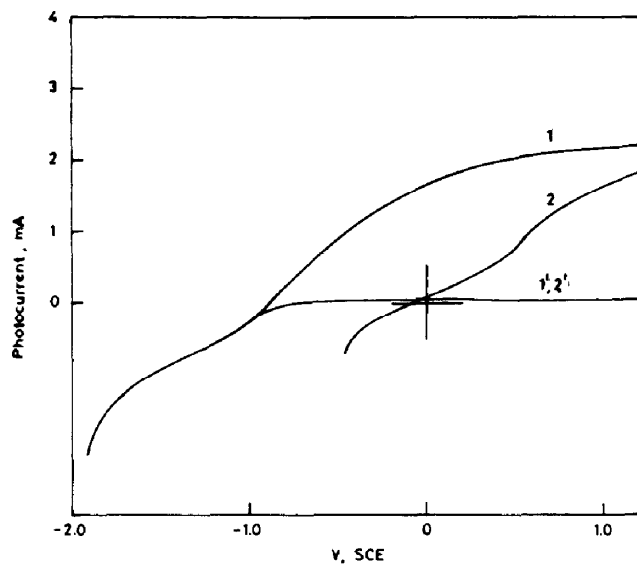
Fig. 1. Potentiostatic current voltage curves for $TiNb_2O_7$ (1,2 under illumination; 1'2' dark).
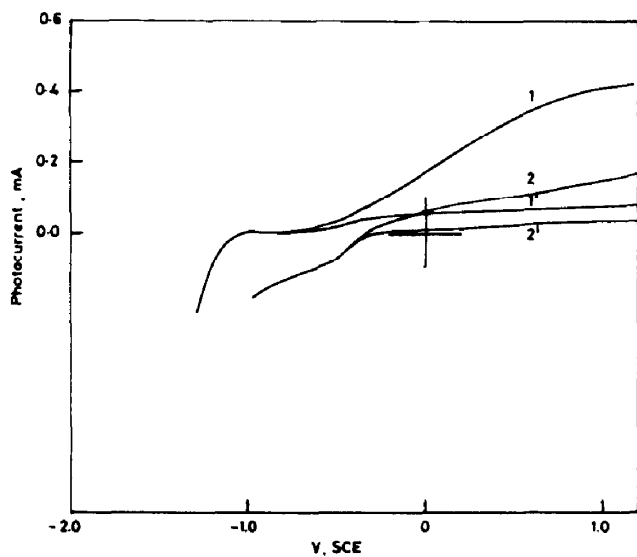

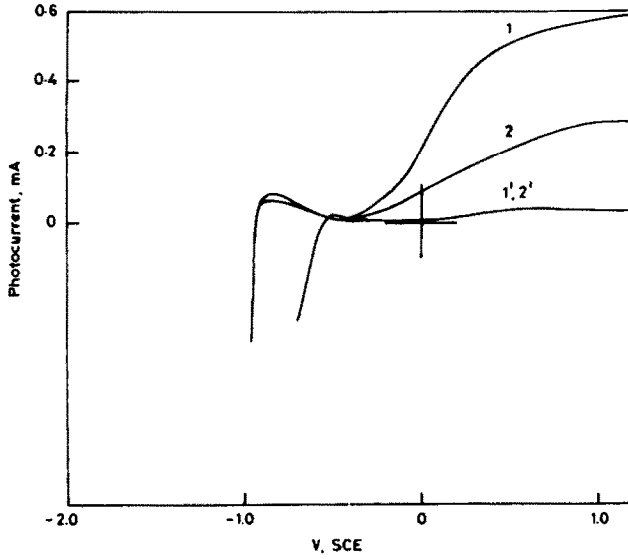Fig. 2. Potentiostatic current voltage curves for $Zr_{0.25}Ti_{0.75}Nb_2O_7$ (1,2 under illumination; 1'2' dark).

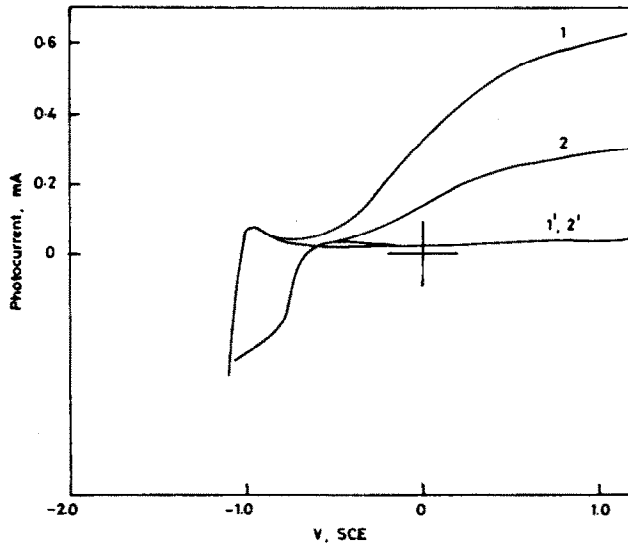Fig. 3. Potentiostatic current-voltage curves for $Zr_{0.5}Ti_{0.5}Nb_2O_7$ (1,2 under illumination; 1'2' dark).

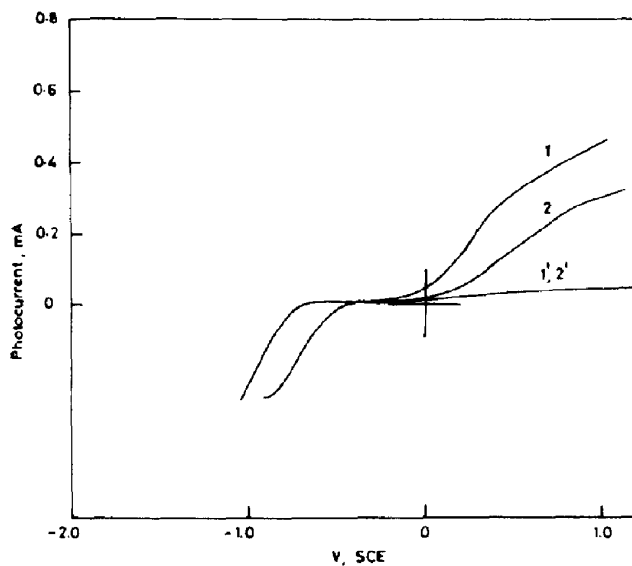Fig. 4. Potentiostatic current-voltage curves for $Zr_{0.25}Ti_{0.25}Nb_2O_7$ (1,2 under illumination; 1'2' dark).

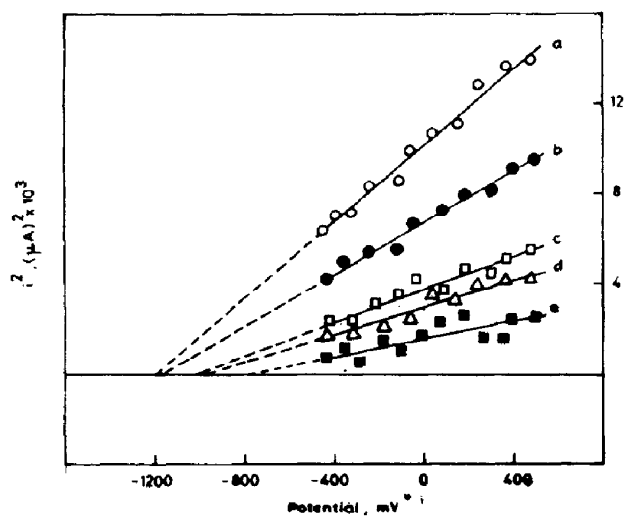Fig. 5. Potentiostatic current-voltage curves for $ZrNb_2O_7$ (1,2 under illumination; 1'2' dark).

Fig. 6. Variation of i_{photo} vs V for $Zr_xTi_{1-x}Nb_2O_7$ in 1M NaOH solution.
   a) $TiNb_2O_7$, b) $Zr_{0.25}Ti_{0.25}Nb_2O_7$, c) $Zr_{0.5}Ti_{0.5}Nb_2O_7$,
   d) $Zr_{0.25}Ti_{0.25}Nb_2O_7$, e) $ZrNb_2O_7$.

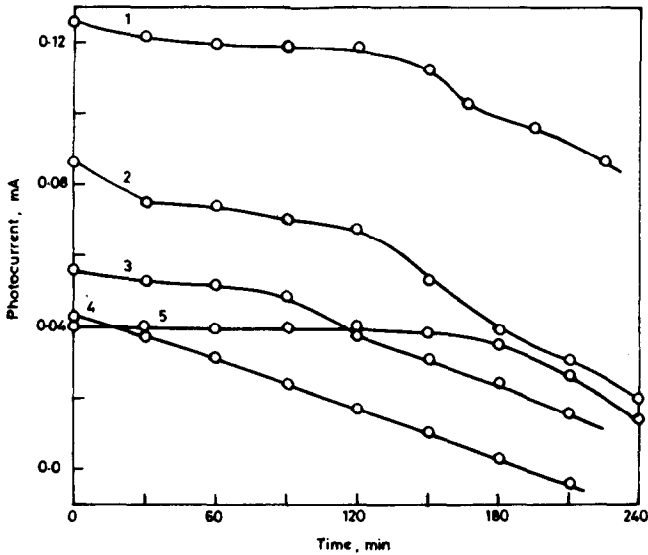Fig. 7. Photocurrent vs.time plots $Zr_xTi_{1-x}Nb_2O_7$ in 1M NaOH solution.
1) $TiNb_2O_7$, 2) $Zr_{0.25}Ti_{0.25}Nb_2O_7$, 3) $Zr_{0.5}Ti_{0.5}Nb_2O_7$,
4) $Zr_{0.25}Ti_{0.25}Nb_2O_7$, 5) $ZrNb_2O_7$.

and also the values of the flat band potentials are smaller than that observed for $TiNb_2O_7$. It may therefore be deduced that substitution of Ti by Zr is not favourable for PEC applications. However, due to its stability $ZrNb_2O_7$ appears to be a promising candidate for further investigation as a photoanode.

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