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Water Photoelectrolysis Using Nickel Titanate and Niobate as Photoanodes

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Nickel titanate ($NiTiO_3$) and nickel niobate ($NiNb_2O_6$), both with a cationic valence and conduction band, were examined for their photoelectrochemical properties. Applied as photoanode in a photoelectrochemical cell for water electrolysis, reduced pellets of these oxides show a photoresponse when irradiated in the optical band gap. The corresponding absorption is due to $Ni^{2+} \rightarrow Ti^{4+}$ and $Ni^{2+} \rightarrow Nb^{5+}$ charge-transfer transitions, respectively. These are situated at lower energy than the $O^{2-} \rightarrow Ti^{4+}$ and $O^{2-} \rightarrow Nb^{5+}$ charge-transfer transitions. The flatband potentials of both compounds were determined from photocurrent versus applied potential measurements. During reduction both compounds showed superficial decomposition. The effect of this decomposition on the photocurrents is discussed.

Introduction

One of the key problems in the field of photoelectrolysis of water is to find the most suitable photoelectrode material. So far extensive studies have been carried out on n-type semiconductors (*1*), but unfortunately either the material corrodes under illumination, or it does not respond to visible light irradiation.

Sensitization by dye films (*2*) or by doping with transition metal ions (*3*) has been shown to be successful, but nevertheless, there are some disadvantages to these approaches. Problems with dyes are the efficiency and the decomposition (most of them are easily oxidized) (*2*), while in the case of doping, the introduced transition metal ion cannot form an electronic subband, since it is part of one of the sublattices of the host lattice (*4*).

To overcome the latter difficulty Goodenough *et al.* (*4*) proposed to use a mixed metal oxide with each band associated with a different cation. In this way it may be possible to introduce a cationic valence band in the too large band gap between the cationic conduction band and the anionic valence band already present.

Following our previous paper (*5*), in which we discussed research on this possibility, we report here on the photoelectrochemical properties of two compounds, viz., $NiTiO_3$ and $NiNb_2O_6$. Both have proved to be good examples of the mixed metal oxides mentioned above.

As we have argued before (*5*), the crystal structure of the oxides to be selected must contain two different metal ions each occupying one sublattice. The sublattices should consist of transition metal ions whose anion polyhedra make contact, so that band

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formation can occur. The compound $NiNb_2O_6$, which has columbite structure, fulfills this requirement (*5*). The compound $NiTiO_3$ has ilmenite structure. This structure can be considered as an ordered corundum structure with Ni^{2+} and Ti^{4+} ions in alternating layers along the *c* axis of the unit cell. Both cations are octahedrally coordinated by oxygen. The octahedra within each layer share edges, so that the possibility of band formation is present. In connection with the photoelectrochemical application we make similar assumptions as we did for $NiNb_2O_6$ (*5*), viz., the cationic valence band consists of nickel $3d^8$ levels and the conduction band consists of titanium $3d$ levels.

Experimental

The compounds $NiTiO_3$ and $NiNb_2O_6$ were prepared by usual ceramic techniques. The $NiTiO_3$ samples were doped with 1% of niobium. The samples were checked by X-ray powder analysis. The powders were pelletized at 50 kg/cm² and sintered in nitrogen at 1350°C for several hours. The density ratio of the pellets, obtained in this way, was around 0.8 for $NiNb_2O_6$ and around 0.9 for $NiTiO_3$. After the sintering procedure, the pellets were polished and reduced by firing at 850°C in a nitrogen atmosphere containing 5% H_2. Under these conditions the reduction was varied from 2 to 16 hr. In this way we succeeded in lowering the 4-point resistivity of the pellets to 100 Ωcm. The photoelectrochemical measurements were carried out in 1 *M* sodium acetate. The same experimental setup was used as described previously (*6*). All potentials were with respect to SCE; the measurements were made potentiostatically. The counterelectrode consisted of platinized Pt. The surface area of the semiconductor disks was typically about 1 cm². The photocurrents were measured using a 150-W Xe lamp with stabilized power and a high-intensity Bausch and Lomb monochromator (200–800 nm). The surfaces of the photoanodes were examined for their structure and composition with a Cambridge stereo Scan 150 electron microscope, equipped with an energy disperse elementary analysis apparatus (Link Systems, U.K.).

Results

In our previous paper (*5*) we reported qualitatively on the photoresponse of $NiNb_2O_6$ with columbite structure. Figure 1 shows the net photocurrents as a function of the wavelength of the irradiated light for three electrodes, each reduced during a certain time. We made a correction for the variation of the lamp intensity with wavelength by normalizing on the number of photons at 470 nm. The measurements were carried out with zero bias voltage (vs SCE). The resistivity of the electrode reduced for 2 hr was 17 kΩcm. Although the minimum value of 100 Ωcm was already attained after a reduction of 4 hr, the photoresponse still in-

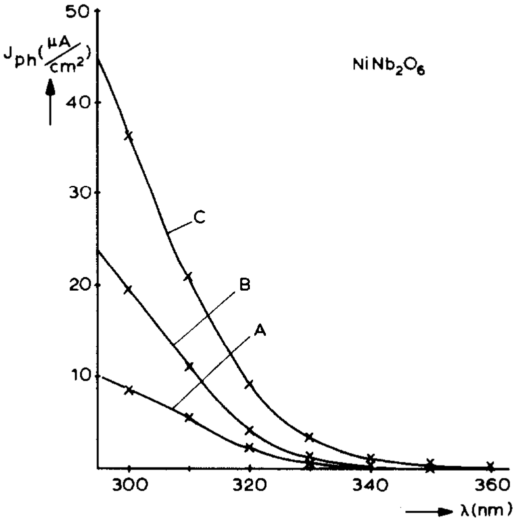

FIG. 1. The net photocurrent density as a function of the wavelength of the irradiated light for $NiNb_2O_6$ electrodes. A: Reduction during 2 hr; B: reduction during 4 hr; C: reduction during 6 hr.

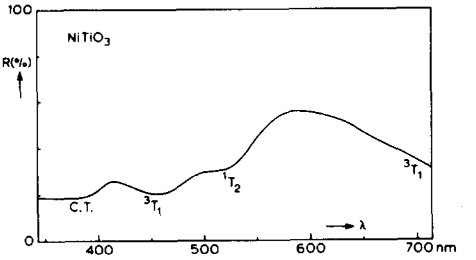

FIG. 2. Diffuse reflection spectrum of NiTiO$_3$. The crystal-field absorption transitions are given by their final states. C. T. indicates the optical band gap (charge-transfer).

creased with the reduction time up to 6 hr. Samples reduced for longer than 6 hr gave negligible photocurrents.

The diffuse reflection spectrum of NiTiO$_3$ (Fig. 2) is similar to that of NiNb$_2$O$_6$ (5) as far as the crystal-field transitions on the Ni^{2+} ion are concerned. However, the optical absorption edge is situated at about 400 nm (compare NiNb$_2$O$_6$ 350 nm). The dependence of the photoresponse on the wavelength of the incident radiation is presented in Fig. 3 for three different electrodes, reduced during different times. Correction for the variation of the lamp intensity with wavelength has been made in a similar way. No bias voltage was applied. The resistivity of these samples varied from 10 kΩcm (reduction during 2 hr) to 50 Ωcm (reduction during 16 hr). In contrast with the NiNb$_2$O$_6$ samples we did not observe an abrupt decrease of photoresponse with increasing reduction time. Samples reduced for 16 hr still gave rise to measurable photocurrents. It follows from Fig. 3 that for NiTiO$_3$ electrodes the optimum photoresponse is already obtained after a reduction period of 2 hr.

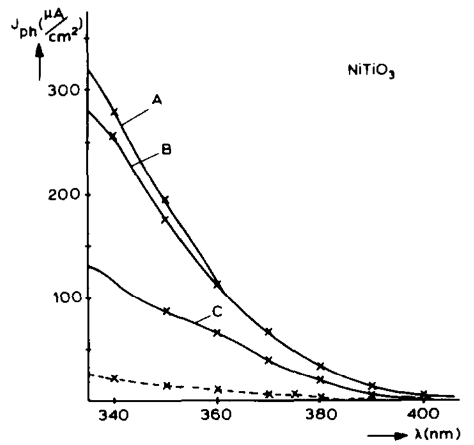

FIG. 3. The net photocurrent density as a function of the wavelength of the irradiated light for NiTiO$_3$ (1% Nb) electrodes. A: Reduction during 2 hr; B: reduction during 6 hr; C: reduction during 16 hr. The dotted line represents the photocurrent density for an undoped NiTiO$_3$ electrode.

For the niobium-doped NiTiO$_3$ electrodes an increase of photoresponse was observed during the first 3 days. After that time the photocurrents remained stable during the time of the measurements (7 to 8 days). The undoped samples showed no increase in photoresponse, but started to decrease after 1 day; after 3 days the photocurrents were only one-tenth of those of the doped samples (see Fig. 3). Although the decrease in photoresponse of the NiNb$_2$O$_6$ samples was not as drastic as with the undoped NiTiO$_3$ samples, the photocurrents did not remain stable for a period of several days.

We determined the flatband potentials of NiNb$_2$O$_6$ and NiTiO$_3$ by plotting the square of the photocurrent versus applied potential (Fig. 4). Negative values of -0.1 and -0.3 V versus SCE (pH = 7.5) were found, respectively. The shape of the photocurrent versus applied potential curves did not depend on the reduction time.

X-ray analysis of the reduced NiTiO$_3$ pellets showed a partial decomposition of the compound into nickel metal and rutile. This decomposition increased with increasing reduction time. Further examination proved that this decomposition took place only at the surface of the pellet. Scanning electron micrographs revealed the development of small grains (~0.5 μm) on the surface of the reduced samples. For samples

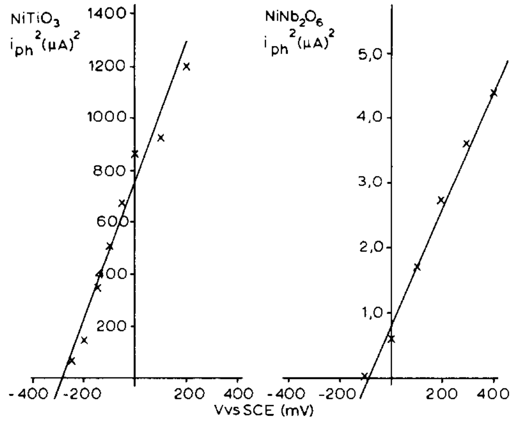

FIG. 4. The square of the photocurrents versus applied potential for $NiTiO_3$ and $NiNb_2O_6$ in 1 *M* sodium acetate (pH = 7.5). The incident monochromatic light had a wavelength of 340 and 300 nm, respectively.

which were reduced during 2 hr only the beginning of this granular structure could be discovered. With increasing reduction time, however, the amount of grains increased rapidly. We did not observe this kind of granularity on the surface of unreduced samples. Using elementary analysis the assumption was confirmed that these grains consist of nickel.

For reduced $NiNb_2O_6$ pellets a similar superficial decomposition was observed. X-Ray analysis clearly showed the presence of nickel metal and niobium pentoxide on the surface of the electrode. Only one $NiNb_2O_6$ pellet was examined by the scanning electron microscope. Although this sample was reduced for 2 hr only, the whole surface was covered with nickel grains. The size of these nickel grains was twice as large as those on the surface of the $NiTiO_3$ electrodes.

Discussion

In our previous paper we discussed the diffuse reflection spectrum of $NiNb_2O_6$ (*5*). For $NiTiO_3$ (Fig. 2) similar assignments can be made. The optical band gap is now situated at 3.1 eV and is ascribed to a $Ni^{2+} \rightarrow Ti^{4+}$ charge-transfer transition. The charge-transfer $O^{2-} \rightarrow Ti^{4+}$ in the ilmenite structure is situated around 4.5 eV as we found from the diffuse reflection spectrum of $MgTiO_3$. From this we conclude that the narrow nickel $3d^8$ band is situated between the $2p$ valence band of oxygen and the conduction band (in this case made up from $3d$ orbitals of titanium). Only the charge-transfer transitions give rise to photocurrents as demonstrated in Fig. 1.

If we correct the values determined for the flatband potentials for pH, we get −0.7 V vs SCE for $NiTiO_3$ at pH = 14. This is to be compared with the observation by Ginley and Butler (*7*), who found +0.1 V for $FeTiO_3$ with disordered structure and −0.6 V for $FeTiO_3$ with ordered, ilmenite structure. For $NiNb_2O_6$ the corresponding value is −0.5 V. This can be compared with results by Koenitzer *et al.* (*8*) for $FeNbO_4$, because the crystal structures of $NiNb_2O_6$ (columbite) and $FeNbO_4$ (wolframite) are very much alike. Both are superstructures of the α-PbO_2 structure. Koenitzer *et al.* (*8*) estimated the flatband potential of $FeNbO_4$ to be between −0.2 and +0.1 V vs SCE. From this we may conclude that both nickel compounds discussed in the present paper have a more favorable flatband potential for the photoelectrolysis of water than the iron compounds. The corresponding value for TiO_2 is −0.9 V (*9*), so that especially $NiTiO_3$ has its flatband potential not much lower. Using a method to predict flatband potentials (*9*) we derived $V_{fb} \approx -0.8$ V for TiO_2, $NiTiO_3$ and $FeTiO_3$. This shows that this prediction works and illustrates simultaneously its approximative character.

Doping with niobium did not lower the resistivity of the $NiTiO_3$ samples; nevertheless, the stability of the electrodes was improved considerably. This confirms earlier reports on this subject by Kogan and Vakulenko (*10*). The photocurrents measured with $NiTiO_3$ electrodes which were not doped with niobium were much lower than those measured with doped samples (see Fig. 3). This feature was also found by the authors mentioned above. Although we tried to improve the stability of $NiNb_2O_6$ in an analogous way, viz., by doping with tungsten, this was not successful. A reason for this might be the energy difference between the donor level and the conduction band in both compounds. The W^{6+} ion seems to be situated at a lower level under the conduction band and acts, therefore, as a trap (*11*).

Because introduction of a substitutional dopant did not lower the resistivity, we reduced the samples under the described conditions. In addition to the fact that the compounds became more conductive, another effect was introduced by this treatment. $NiTiO_3$, as well as $NiNb_2O_6$, samples showed a superficial decomposition after the reduction. This had a significant effect on the photoelectrochemical properties of the electrode (see Figs. 1 and 3). It cannot be excluded that the metallic nickel particles formed on the surface of the electrodes have a catalytic activity on the generation of oxygen. This has to be investigated further.

In our opinion the more important result of this study is that high concentrations of transition metal ions may sensitize titanates for water photoelectrolysis. The compounds $MgNb_2O_6$, as well as $MgTiO_3$, have their band gap far into the ultraviolet (both 4.5 eV (*12, 13*)). By replacing magnesium by nickel it is possible to shift this edge considerably to the visible region without losing acceptable photoelectrochemical properties. This shows that the introduction of a narrow cationic conduction band in the broad band gaps of $MgNb_2O_6$ and $MgTiO_3$ decreases the optical band gap, whereas the hole created in the narrow conduction band after irradiation is mobile. This mobility is related to the structure of the sublattice of the nickel octahedra. The lower photocurrents of $NiNb_2O_6$ relative to $NiTiO_3$ may partly be related to the fact that the hole mobility in $NiNb_2O_6$ extends along the nickel chains in the wolframite structure, whereas that in $NiTiO_3$ extends over the plane of nickel octahedra. One defect is enough to break the chain, which is not the case for mobility in a plane. However, other factors may also be responsible for the different photocurrents. It is interesting, nevertheless, to note that the trirutile phase of $NiNb_2O_6$ which contains chains with composition -Ni-Nb-Nb- does not yield photocurrents at all (*5*). The good stability of $NiTiO_3$ electrodes may be connected with the fact that the created holes are in a narrow transition metal band and not in the oxygen valence bands. This has been discussed by Tributsch (*14*) for transition metal disulfides.

This method of sensitization by transition metal ions differs from previous work in which titanates were doped with a small amount of Ni^{2+}. The latter approach is illustrated by work in this laboratory (*15*), where $SrTiO_3$ was doped with $Sr_3NiNb_2O_9$, and by Campet *et al.* (*16*), where TiO_2 was doped with Ni^{2+} and Nb^{5+}. Upon irradiation a hole is created on the Ni^{2+} ion and an electron in the conduction band. Due to the low nickel concentration a bias is necessary to draw the hole to the surface (*11*). In the present materials this is no longer necessary due to the presence of the nickel $3d^8$ subband.

On the other hand neither $NiTiO_3$ nor $NiNb_2O_6$ show an intense charge-transfer transition in the visible region. This transition may be shifted to lower energies by applying other transition metal ions (*13*). For $CoTiO_3$ and $CoNb_2O_6$ we did not observe photocurrents. This may be due to a high activation energy of the hole formed (Co^{3+} low spin (*5*)). For $FeTiO_3$, however, photocurrents have been observed under visible light irradiation (*7*). We continue our research along these lines.

After completion of this report a paper was published by Salvador *et al.* (*17*) reporting similar photocurrent wavelength curves for $NiTiO_3$ as those here. Since samples were prepared in different ways, this shows that $NiTiO_3$ acts indeed as a semiconducting anode in water photoelectrolysis. The spectral interpretation in our work is different, mainly due to the fact that we based our work on data for $MgTiO_3$ which were not used by Salvador *et al.*

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