THE APPLICATION OF NICKEL MOLYBDATE AND NICKEL VANADATES AS PHOTOANODES IN A PHOTOELECTROCHEMICAL CELL

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ABSTRACT

The application of nickel molybdate, $NiMoO_4$, and the nickel vanadates NiV_2O_6, $Ni_2V_2O_7$ and $Ni_3V_2O_8$ as photoanodes in a photoelectrochemical cell is investigated. Based on the optical and structural properties reported and discussed, NiV_2O_6 would be a good candidate, but attempts to prepare dense pellets were not successful. For $Ni_2V_2O_7$ and $Ni_3V_2O_8$ no photocurrents were observed. This is discussed in relation with the crystal structure of these compounds.

INTRODUCTION

In the field of the photoelectrochemical decomposition of water one of the key problems is to find the most suitable photoelectrode material. Either the stability of the material is a severe problem or the material does not respond to visible light irradiation, as is the case with the most popular materials TiO_2 (rutile) and $SrTiO_3$ [1]. Sensitization of the titanates with transition-metal ions has been shown to be successful [2,3], but nevertheless, there is some disadvantage to this approach. The introduced transition-metal ion cannot form an electronic subband, since it is part of one of the sublattices of the host lattice. Even when the ratio transition-metal ions to titanium ions is increased, like in titanates with the hollandite structure, this problem remains [4]. To overcome this difficulty Goodenough et al. [5] proposed using a mixed metal oxide with each band associated with a different cation, each occupying a different sublattice. This has been realized amongst others in $NiNb_2O_6$ with the columbite structure [6,7] and in $NiTiO_3$ with the ilmenite structure [7]. Between the oxygen valence band and the niobium (titanium) conduction band a narrow transition-metal band ($Ni^{2+}:3d^8$ sub-band) is situated. The hole, created in this sub-band after

irradiation, is mobile. Unfortunately the optical absorption edges of $NiNb_2O_6$ and $NiTiO_3$, which are assigned to $Ni^{2+} \rightarrow Nb^{5+}$ and $Ni^{2+} \rightarrow Ti^{4+}$ charge-transfer (C.T.) transitions, are situated at about 400 and 450 nm, respectively [7], so the sunlight conversion efficiency is still very low. In $CoTiO_3$ and $MnTiO_3$, which both also have the ilmenite structure, the optical absorption edge is shifted to longer wavelength [8], but no photocurrents were observed for excitation in the $Co^{2+} \rightarrow Ti^{4+}$ and $Mn^{2+} \rightarrow Ti^{4+}$ C.T. bands [8,9].

Rossman et al. [10] investigated the optical absorption of various complex nickel oxides, among which compounds of Ni^{2+} with the closed-shell transition-metal ions Ti^{4+}, V^{5+}, Nb^{5+}, Mo^{6+} and W^{6+}. It was shown that the more easily reduced ions such as V^{5+} and Ti^{4+} produce a charge-transfer tail, which extends well into the visible region. For NiV_2O_6 and $Ni_3V_2O_8$ these C.T. bands are observed upto around 650 and 520 nm, respectively. Intermediate tails were observed for W^{6+}, Mo^{6+} and Nb^{5+} [10].

In view of this we investigated the application of nickel vanadates and the nickel molybdate $NiMoO_4$ as photoanode. The optical absorption of the latter was not studied by the authors of ref.10. The application as photoanode of the nickel tungstate $NiWO_4$ was investigated earlier in our laboratory, but no photocurrents were observed for excitation in the C.T. band [11].

The phase-diagram of the system $NiO-V_2O_5$ shows besides the two compounds NiV_2O_6 and $Ni_3V_2O_8$ a third compound $Ni_2V_2O_7$ [12]. All these compounds have an incongruent melting point at: 720 °C (NiV_2O_6), 880 °C ($Ni_2V_2O_7$) and 1220 °C ($Ni_3V_2O_8$) [12]. All three compounds were included in this study.

The nickel molybdate $NiMoO_4$ undergoes a structural transformation at 690 °C. The high-temperature, β, form is isotypic with $\alpha-MnMoO_4$, while the low-temperature, α, form is isotypic with $\alpha-CoMoO_4$ [13]. The basic difference between the $\alpha-CoMoO_4$ and the $\alpha-MnMoO_4$ structure is the coordination of Mo^{6+}, which is tetrahedral in $\alpha-MnMoO_4$ and essentially octahedral in $\alpha-CoMoO_4$ [13].

EXPERIMENTAL

Samples were prepared by usual ceramic techniques. Firing was performed between 600 and 1200 °C in air or oxygen depending on the composition. Samples were checked by X-ray powder diffraction. Diffuse reflection spectra were recorded at room temperature on a Perkin-Elmer EPS-3T spectrophotometer.

Two methods were applied to obtain dense polycrystalline pellets of the materials. In the first method the powders were cold-pressed at 50-100 kg/cm^2 and subsequently fired for several hours in air or oxygen. In the second method a hot-press technique was used. The photoelectrochemical measurements were carried out in 1M sodium hydroxide and 1M sodium acetate. The same experimental set up was used as described in ref.[3].

RESULTS AND DISCUSSION

Nickel molybdate

The $NiMoO_4$ we obtained from the sample preparation was in every case the low-temperature α-form. As was found before [13], it was not possible to obtain the β-form at room temperature by quenching.

The diffuse reflection spectrum of α-$NiMoO_4$ is shown in Fig. 1. In the visible region the crystal-field transitions on the Ni^{2+} ion are observed. The $Ni^{2+} \rightarrow Mo^{6+}$ C.T. band starts around 450 nm. This is in line with the results of Rossman et al. [10] and makes $NiMoO_4$ tempting as a photoanode. Attempts to prepare dense pellets of the $NiMoO_4$ sample by the first method were unsuccessful. Hardly any sintering of the cold-pressed pellet was observed just below the transition temperature (690 °C). The hot-press experiments performed at a pressure of 75 kg/cm^2 and at temperatures below (650 °C) and above (975 °C) the transition temperature were unsuccessful too. So no photoelectrochemical measurements could be performed for this material.

As was mentioned before, the structure of the α-form of $NiMoO_4$ is isotypic with α-$CoMoO_4$ [14]. The $Co^{2+}(Ni^{2+})$ and Mo^{6+} ions are both octahedrally coordinated by oxygen ions. The $CoO_6{}^{10-}(NiO_6{}^{10-})$ and $MoO_6{}^{6-}$ octahedra share edges to form infinite chains parallel to the c-axis, with an ordered sequence in the occupation of the octahedra [15]. This inhibits band formation by both cations. There exists no infinite chain of edge- and corner-sharing cobalt octahedra, because there are always molybdenum octahedra in between. The same holds for the molybdenum octahedra. On structural grounds, the nickel molybdate is therefore expected to be an unsuitable choice for a photoanode.
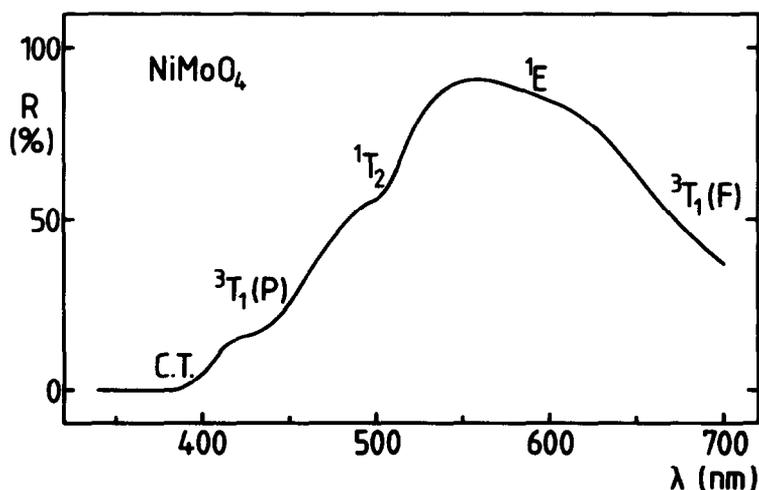

Fig. 1. Diffuse reflection spectrum of α-$NiMoO_4$. The crystal-field transitions are given by their final states. C.T. indicates the optical bandgap (charge transfer).

Nickel vanadates

   The diffuse reflection spectra of the nickel vanadates investigated are shown in
Fig. 2. The spectra of NiV_2O_6 and $Ni_3V_2O_8$ are in good agreement with those reported by
Rossman et al. [10]. The C.T. band in $Ni_2V_2O_7$ and $Ni_3V_2O_8$ starts at about 580 nm,
whereas this band covers in the case of NiV_2O_6 nearly the whole visible region. Only
in the former two compounds the crystal-field transition $^3A_2 \rightarrow {}^3T_1(F)$ on the Ni^{2+} ion
is clearly observable around 700 nm.

   As in case of the $NiMoO_4$ sample, attempts to prepare dense pellets of NiV_2O_6 were
unsuccessful. The temperature (700 °C) was too low to induce any sintering of the
powder. Hot-press experiments were performed at 75 kg/cm^2 and 650-680 °C, but also
under these conditions hardly any sintering behaviour was observed.

   For $Ni_2V_2O_7$ and $Ni_3V_2O_8$ we obtained with the first method pellets with a density
of around 80% of the theoretical value. After sintering, these pellets were fired for
30-45 minutes at 550 °C in a nitrogen atmosphere containing 2-5% H_2. In this way we
obtained a resistivity of the pellet of 20 kΩ. This value is rather high, but we had
to maintain the mild reducing conditions to prevent the formation of metallic Ni.

   The $Ni_2V_2O_7$ and $Ni_3V_2O_8$ electrodes dissolved in 1M NaOH, but were stable in 1M
sodium acetate. However, no photocurrents were observed for these materials. This can
be explained by considering the structures of these compounds. In $Ni_3V_2O_8$ the Ni^{2+}
ions are octahedrally and the V^{5+} ions tetrahedrally surrounded by oxygen ions. The
nickel octahedra share edges with each other, forming infinite zig-zag chains. The
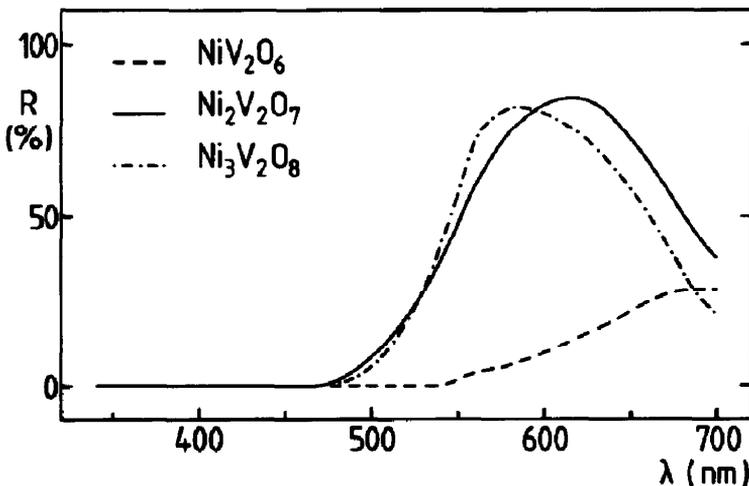vanadium tetrahedra are isolated from each other [16]. In $Ni_2V_2O_7$ the coordination of

Fig. 2. Diffuse reflection spectrum of NiV_2O_6, $Ni_2V_2O_7$ and $Ni_3V_2O_8$.

the cations with oxygen is the same. The nickel octahedra, also as a result of edge sharing, form linked chains running parallel to the c-axis. Adjacent chains are connected by edge sharing. Two vanadium tetrahedra have one oxygen in common, thus forming a $V_2O_7^{4-}$ polyhedron. These vanadium polyhedra are isolated from each other [17].

In both structures the infinite chains of edge-sharing nickel octahedra makes it possible to form a $Ni^{2+}:3d^8$ valence band. But no vanadium 3d conduction band can be formed, due to the isolated nature of the vanadium polyhedra. This means that there is no conduction path for the photoexcited electrons. So no photocurrents can be observed for these materials.

Let us return to NiV_2O_6. We assume that the structure of NiV_2O_6 is isotypic with its cobalt analogue, as is the case for $Ni_2V_2O_7$ [17] and $Ni_3V_2O_8$ [16]. In CoV_2O_6 the cobalt ions are octahedrally coordinated to oxygen. The cobalt octahedra share opposite edges, thus forming linear chains along the b-axis. The V^{5+} ions are coordinated to five oxygen ions, which form a highly distorted trigonal bipyramid. These vanadium polyhedra are nearly identical with those observed in V_2O_5. Also the packing of the vanadium polyhedra is analogous to V_2O_5. Along the b axis the vanadium polyhedra form infinite chains by edge sharing [18]. The formation of the infinite chains of both cation polyhedra in the same direction makes d-band formation by both cations possible. NiV_2O_6 would thus be a good candidate for a photoanode material, but unfortunately no photoelectrochemical measurements have been performed for this material up to now.

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