Optical switching of y-hybride thin film electrodes: a remarkable electrochromic phenomenon

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Optical Switching of Y-Hydride Thin Film Electrodes

A Remarkable Electrochromic Phenomenon

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ABSTRACT

The optical appearance of yttrium thin film electrodes can be electrochemically switched from mirrorlike to highly transparent by making use of the hydride-forming properties of Y. A strong alkaline solution is a suitable electrolytic environment for obtaining stable electrochromic electrodes. The presence of a thin Pd layer covering the Y electrode is essential in providing a sufficiently high electrocatalytic activity for the electrochemical charge-transfer reaction. Hydrogen is irreversibly bound in Y-dihydride and reversibly bound in Y-trihydride. The optical changes are reversible and are induced within a narrow hydrogen concentration range, making this typical electrode material interesting for application in a new type of electrochromic devices.

Introduction

It has long been recognized that metal-to-semiconductor and vice versa transitions can be induced by making use of the hydride-forming properties of rare-earth metals.1 The pronounced reversible changes in electrical conductivity, which are often accompanied by crystallographic phase transitions, are induced by changing the hydrogen content in the crystal lattice and have been attributed to changes of the electronic structure of the material. Recently, Huberts et al. reported that, in Y films, this dramatic change in electrical conductivity is accompanied by a remarkable optical effect.5 By changing the hydrogen concentration within the solid by gas-phase loading, they showed that the optical appearance changes from mirrorlike for the dihydride composition to highly transparent for the trihydride compound.6 A Pd top coating was reported to be essential for loading and unloading the Y films with hydrogen gas outside the ultrahigh-vacuum (UHV) deposition chamber.7 These coatings act as protective layers, preventing oxidation and/or poisoning of the underlying Y films in air. Furthermore, they act as catalytic layers, providing the dissociative adsorption and associative desorption of hydrogen molecules at a sufficiently high rate. This reaction can be represented by

\[ \text{H}_2 \rightarrow 2\text{H}_\text{ads} \quad [1] \]

Subsequently, the adsorbed hydrogen atoms (H_{ads}) can be transported into the solid by solid-state diffusion, which results in absorbed hydrogen (H_{abs}).

\[ \text{H}_\text{ads} \rightarrow \text{H}_\text{abs} \quad [2] \]

The Pd top coating has an additional advantage in that it forms a hydride itself and can act as a transporting medium of hydrogen toward the underlying Y film. Depending on the hydrogen concentration within the solid, two phase transitions reportedly occur in the case of Y. By changing the H/Y ratio from 0 to 3, hexagonal Y is converted subsequently into cubic Y-dihydride and hexagonal Y-trihydride.8 The complex hexagonal structure of the trihydride form has been determined just recently.9 An alternative way of hydrogen loading is via electrolytic reduction of a proton donating species, such as water. This electrochemical charge-transfer reaction occurs at the solid/electrolyte interface and can be represented by

\[ \text{H}_2\text{O} + e^- \rightarrow \text{H}_\text{ads} + \text{OH}^- \quad [3] \]

It has been shown that the kinetics of this reaction depends strongly on the nature of the electrode surface.10 Strikingly, the kinetics of this charge-transfer reaction were found to be very fast at Pd.11 Once the adsorbed hydrogen atoms are formed at the electrode surface they can be absorbed by the Pd and, subsequently, by the Y electrode. Evidently, this latter process is identical to that occurring in the gas phase as represented by Eq. 2.

To investigate whether reversible optical switching of Y films can be accomplished by electrochemical means, both galvanostatic and potentiostatic measurements are conducted. The electrochromic properties are investigated simultaneously by measuring the electrode transparency. In addition, cyclovoltammetric measurements are performed.

References


* Electrochemical Society Active Member.
to examine the hydride formation and decomposition reactions in more detail.

**Experimental**

The Pd-coated Y films were produced by conventional evaporation techniques (10⁻⁷ mbar vacuum level) on round (2 cm diam) polished quartz substrates. The Y thickness was varied between 200 and 500 nm and that of Pd between 0 and 20 nm. The layer thickness was accurately controlled through quartz microbalance measurements during the evaporation process. In addition, the amount of deposited Y was checked afterward by chemical analysis (inductively coupled plasma emission spectroscopy; accuracy 3%) and was in agreement with the microbalance measurements. Eleceldes were made by contacting the surface with a lead using a conducting adhesive (E-solder conductive adhesives No. 3021 from IMI). The contacts were shielded from the electrolyte by a chemically inert isolating lacquer. The electrode surface area was determined by optical microscopy prior to the electrochemical measurements.

The electrodes were tested in a conventional three-electrode configuration, i.e., in an open rectangular cuvette, using a Pt counterelectrode and a Hg/HgO/6 M KOH reference electrode. All potentials in this work are given with respect to this Hg/HgO electrode. All electrochemical measurements were performed with a POS 73 potentiometer scan from Wenking. The optical transmission of the films was investigated in situ by illuminating the electrodes from the back of the sample and detecting the light intensity at the front, using a white light source (Schott lamp KL, 1500) in combination with a photodetector (EG&G). The ionic properties reported here have been investigated by measuring the integrated light intensity passing through the electrode during electrochemical operation and are presented on a linear scale in arbitrary units. However, they have also been investigated spectroscopically and are presented on a linear scale in arbitrary units.

The optical properties reported here have been determined from the measured enthalpy of formation of the dihydride, \( \Delta H = -228 \text{ kJ/mol H}_2 \), and entropy of formation, \( \Delta S = -130.8 \text{ J/K mol H}_2 \), by means of the van 't Hoff relation.⁸

The result of a galvanostatic (constant reduction current of 1 mA) charging experiment is shown in Fig. 2. The electrode potential is plotted as \(-E\) for comparison with the corresponding pressure-composition isotherms. Three regions can be distinguished in the electrode potential transient curve a: (i) a more or less constant plateau at

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**Results and Discussion**

A most important requirement for the Y electrodes is their chemical stability in the electrolyte. It is well known that Y and other rare-earth metals are extremely base metals, with very negative electrolyte redox potentials.⁹ A proper selection of the electrolyte composition is therefore essential. On the basis of the Pourbaix diagram it is expected that Y dissolves into acidic solutions easily. This has been confirmed experimentally. Alkaline solutions are more promising in this respect, as hydroxides are expected to be formed at the electrode surface which may act as passivating layers. To provide a sufficiently stable electrochemical environment in which the Y dissolution rate is low, and the ionic conductivity between the Y working electrode and counter electrode is high, a concentrated alkaline solution of 6 M KOH has been selected to perform all electrochemical experiments.

Soon after immersing a freshly prepared Pd coated (5 nm) Y thin film (500 nm) electrode in the alkaline electrolyte the open-circuit potential \( E_{oc} \) stabilizes close to 0.0 V. This open-circuit potential is determined by the electrochemical nature of the electrode surface in contact with the electrolyte. In the present case, \( E_{oc} \) is determined by the presence of both Pd and Y at the electrode surface and by hydrogen and oxygen dissolved in the aqueous electrolyte. The thin Pd top layers do not form a fully closed coating. An example of the surface morphology for a 5 nm Pd-coated Y film is shown in Fig. 1. Although the contribution of the various electrochemical systems to \( E_{oc} \) cannot be established completely it seems likely, as is argued below, that the hydrogen content stored in the Y films is mainly responsible for the established open-circuit potential. In this respect it has been reported that the as-produced Y films already contain a significant amount of hydrogen.³

The absorption/desorption properties of hydride-forming metals/compounds are generally characterized by pressure-composition isotherms. There is a direct relationship between the equilibrium pressure \( p_{H_2} \) for absorption and desorption of hydrogen gas and the equilibrium potential \( E_{oc} \) of a hydride-forming electrode, according to the Nernst equation

\[
E_{oc} = -\frac{RT}{nF} \ln p_{H_2} - 0.926 \quad \text{[V vs. Hg/HgO]} \tag{4}
\]

where \( R \) is the gas constant, \( T \) the temperature, \( F \) the Faraday constant, and \( n \) the number of electrons involved in the hydrogen evolution reaction. According to Eq. 4 a pressure \( p_{H_2} \) of 1 bar corresponds to \(-0.926 \text{ V vs. Hg/HgO}\) at room temperature and every decade change in hydrogen pressure induces \( E_{oc} \) to vary by approximately 30 mV. An open-circuit potential of 0.0 V corresponds therefore to an extremely low hydrogen pressure of approximately \( 10^{-32} \) bar. This value is in good agreement with \( 10^{-32} \) bar determined from the measured enthalpy of formation of the dihydride, \( \Delta H = -228 \text{ kJ/mol H}_2 \), and entropy of formation, \( \Delta S = -130.8 \text{ J/K mol H}_2 \), by means of the van 't Hoff relation.⁶

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**Figure 1.** SEM micrograph, revealing the surface morphology of a Pd-coated (5 nm) Y thin film (500 nm) electrode after the electrochemically induced absorption/desorption experiments in a 6 M KOH alkaline solution.
The simultaneous measured optical signal is represented by curve b of Fig. 2 and reveals that the Y electrode remains optically closed, i.e., very low transmission intensities are measured up to high hydrogen contents. After a prompt charging, the electrode starts to become transparent (transmission intensity increases sharply). This process is completed within several minutes. When optical switching is defined to take place within a region where the transparency changes between 10 and 90%, it is clear that switching occurs within a narrow composition range at relatively high hydrogen content, i.e., between YH₆ and YH₁₀ (see upper axis in Fig. 2). Although the determination of the film thickness was accurate, the exact hydrogen contents are still subject to some uncertainties as both the oxide layer thickness formed in the electrolyte, and the amount of hydrogen desorbed into the electrolyte are not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is highly unreliable as part of the supplied charge is not known exactly. Evidently, the highest H-content of YH₈ is high.
The origin of the hydride loss, occurring during the previous open-circuit period (Fig. 3) has still to be discussed. Two processes may be responsible for this unstable behavior. In the first place, hydrogen may be released from the electrode in the form of gas. This chemical association reaction occurs at the electrode surface according to

$$\text{YH}_2 \rightarrow \text{YH}_x + y/2\text{H}_2$$  \[5\]

The produced hydrogen gas may be released in the form of gas bubbles or dissolve directly into the electrolyte. However, during the open-circuit conditions of the present experiment, no hydrogen gas evolution has been observed. Alternatively, the hydride may be consumed by an electrochemical process. Such an electroless process occurs at the open-circuit potential and can be represented by two separate electrochemical reactions. The first step is possibly initiated by the reduction of oxygen, which is known to dissolve easily into alkaline solutions

$$\text{O}_2 + 2\text{H}_2\text{O} + 4e^- \rightarrow 4 \text{OH}^-$$  \[6\]

The electrons to be consumed by the oxygen reduction reaction can be delivered by the YH hydride, which itself is oxidized according to

$$\text{YH}_x + y\text{OH}^- \rightarrow \text{YH}_{x-y} + y\text{H}_2\text{O} + ye^-$$  \[7\]

This reaction sequence is well known to occur in rechargeable nickel-metal hydride batteries and is responsible for keeping the oxygen pressure inside sealed batteries low. On the basis of the amount of reversibly stored hydride and the time needed to fully discharge the Y-trihydride, an O \(_2\) reduction current of the order of 15 \(\mu\)A can be calculated, which is in fair agreement with the expected reduction currents of a few microampere per square centimeter in alkaline solutions.

Since the kinetics of the hydride oxidation reaction is much better than that for the oxygen reduction reaction \(6, E_0\) can be assumed during the complete discharge process, i.e., \(E_{\alpha} \approx E_0\). Although the development of the hydrogen concentrations within the solid is not known exactly, a good indication of the desorption pressure of the isotherm can be obtained from the open-circuit potential curve a of Fig. 3. Assuming the presence of oxygen to be responsible for the unstable character of the Y-trihydride, it is evident that this problem can be solved by excluding oxygen from the electrochemical cell. In that case it is evident that electrochemical measurements are a strong tool for determining absorption/desorption isotherms for hydride-forming materials. This is especially useful when extremely low plateau pressures are involved that are generally inaccessible by conventional gas-phase methods.

Galvanostatic discharging of a fully charged Y-electrode with a relatively low current (0.2 mA) again shows the two-stage dehydriding process (Fig. 5). This not only holds for the development of the potential (curve a) but is even more pronounced for the optical transparency (curve b). Discharging was interrupted at 0 V. The potential recovery after this discharging process is followed during the subsequent 30 min and reveals some remarkable features (see Fig. 6). Initially, the electrode potential (curve a) is quickly changing toward more negative potentials followed by a slower increase to the same end potential of 0 V observed before, while the optical signal (curve b) is not influenced at all. A potential for this complex behavior may be as follows. Assuming that at the end of the discharge process, diffusion of H atoms within the electrode becomes rate-limiting, a sharp hydrogen concentration gradient is established at the electrode surface and the potential increases significantly once the hydrogen surface concentration has become very low. This concentration gradient is followed after current interruption, resulting in a higher surface concentration and, consequently, in a decreasing electrode potential. Meanwhile, due to the presence of dissolved oxygen near the electrode the hydride is slowly oxidized under electrolytic conditions, according to Eq. 6 and 7. As a result, the open-circuit potential rises again to the value expected for the stable dihydride.

The electrode properties have been investigated further by dynamic current-potential measurements. An example of such a plot is shown in Fig. 7a. Starting from 0 V, with Y-dihydride, the electrode potential is scanned toward more negative values with a low scan rate of 0.1 mV/s to ensure quasi steady-state conditions. The low reduction current flowing in this negative potential region must again be attributed to oxygen reduction. The cathodic current density starts to rise at −0.6 V and a single hydride-formation peak is found with its maximum at −0.85 V vs. Hg/HgO. Clearly, the electrode becomes transparent in the potential region where the reduction current starts to decrease again, i.e., where the main part of the hydride-formation process has been completed (Fig. 7b). This is in agreement with the earlier described observations that optical switching takes place in a high but narrow concentration range (see Fig. 4). Reversing the scanning direction leads to oxidation of the previously formed hydrides. In contrast to the hydride-formation reaction, two separate stages can be distinguished in the oxidation process, which are clearly accompanied by distinctive optical changes. During the first oxidation stage ∼ −0.8 V, only a
The decomposition reaction induces the occurrence of this has a large impact on the electrode transparency. The minor part has been attained, the electrode potential was made more by the oxygen transformation reaction. Once steady state period, the cathodic current decreases to a low steady-state value, generally a low reduction current, generated due to previous charging procedure the electrode is in the dihydride state at 0 V.

Fig. 7. Current-potential curves (a) and corresponding transmittance signal (b) of a Pd-coated (5 nm) Y (500 nm) electrode measured in 6 M KOH with a scan rate of 0.1 mV/s. Due to previous charging procedure the electrode is in the dihydride state at 0 V.

Fig. 8. Potentiostatically measured steady-state transmission signal of a Pd-coated (5 nm) Y (500 nm) electrode during hydriding (○) and dehydriding (●). The calculated hydrogen equilibrium pressure, corresponding to the steady-state electrode potential (E), is also indicated.

The electrochemical behavior. The optical properties are characterized by a clear hysteresis in this potential range. The main part of the hydrides is oxidized at more positive potentials. In contrast to the first decomposition stage, this second oxidation step has a much smaller impact on the optical electrode properties. It has been reported that, in the case of Y, the hydride formation/decomposition reaction induces the occurrence of crystallographic phase transformations. The present results suggest that phase transformation may also be important for the electrochemical behavior.

To investigate whether the hysteresis effects described above are related to kinetic limitations, potentiostatic experiments have been performed. Starting again with a Y electrode in the dihydride state, the electrode potential was initially switched to −0.2 V. During the equilibration period, the cathodic current decreases to a low steady-state value, generally a low reduction current, generated by the oxygen transformation reaction. Once steady state has been attained, the electrode potential was made more positive in successive steps of 100 mV. The equilibration time was strongly dependent on the applied electrode potential. The optical steady-state signal is shown in Fig. 8 as a function of the applied electrode potential. Since only equilibrium conditions are considered in this experiment, the electrode potentials can again be converted, according to Eq. 4, into equilibrium hydrogen pressures. This pressure equivalent is plotted in Fig. 8. Preceding the complete optical switching in the potential range of −0.9 to −1.0 V, a small intensity depression is always found at −0.8 V, making the electrode even less transparent than at more positive potentials. This unexpected suppression, which can be recognized after a more detailed inspection of the transient curves shown in Fig. 4, has been found in the gas-phase loading experiments. This blackening effect has been attributed to the disappearance of the transparency of the dihydride. This interesting phenomenon is described in more detail in a future paper. Furthermore, the electrode transparency still changes significantly at negative potentials, i.e., at high hydrogen partial pressures. Strikingly, on the reversed scan a small but stable intensity plateau is again visible, indicating that the oxidation reaction is a two-step process.

Figure 8 shows that optical switching can be accomplished by stepping the electrode potential from positive potentials to, for example, −1.0 V and vice versa. Limiting the potential range has the advantage that severe hydrogen evolution can be avoided at negative potentials and the basic material stability, becoming important at more positive potentials, can be controlled. Figure 9 shows the development of the electrode transparency after application of such potential steps. As the Pd layer thickness is expected to have a positive influence on the switching speed, the results of a 500 nm Y electrode covered with a 20 nm Pd top-coating are presented in Fig. 9. Starting with an equilibrated electrode in the dihydride form at 0 V, the electrode voltage was switched to −1.0 V. During this process the reduction current is sharply decaying. The electrode transparency is represented by curve a. It takes a few minutes to switch the electrode from mirrorlike for the dihydride composition to transparent for the trihydride. The reverse process is much faster, of the order of seconds as curve b reveals. The second stage of the dehydriding process, as already discussed in relation to, e.g., Fig. 7, takes a much longer time, as is indicated by the t = x level in Fig. 9. The time scale difference between the absorption and desorption processes is likely related to the large differences in established overpotentials. The optical electrode appearance changes at relatively high hydrogen partial pressures (see, e.g., Fig. 8), i.e., at negative potentials, which implies that the overpotential at −1.0 V becomes very low during the absorption process, whereas the overpotential is close to 1 V during the reversed process at 0 V.
Another factor which may contribute to this time scale difference may be related to the fact that the optical appearance is strongly dependent on the characteristics across the electrode thickness. For example, in hydride formation the entire electrode thickness contributes to the overall electrode transparency properties, whereas in the case of hydride decomposition only a thin surface layer may be responsible for optically closing the entire electrode.

Conclusions

Reversible hydrogen loading and, consequently, reversible optical switching of Pd-coated Y electrodes can be accomplished by electrochemical means. Chemically stable electrodes are obtained when electrochemical charging and discharging is carried out in a strong alkaline (6 M KOH) solution. A distinction can be made between irreversibly bound hydrogen, which is denoted as Y-dihydride and reversibly bound hydrogen, formed at higher hydrogen content. Reversible optical switching takes place in a narrow hydrogen concentration range at relatively high hydrogen content, i.e., in the range of YH₂ and YH₂⁺ at relatively high hydrogen partial pressures. The rate of optical switching is history dependent: switching from a transparent to mirrorlike appearance can be accomplished within a few seconds, whereas the reverse process takes much more time, of the order of minutes, which is argued to be related to the applied overpotential. This indicates that the rate of the electrochemical surface reaction plays an important role.

The reversible hydride-formation was a single-step process, whereas both the electrochemical and optical results point to a two-step decomposition reaction. The transparent form of the Y-hydride is unstable under open-circuit conditions. The loss of the reversible part of the stored hydrogen under these conditions has been attributed to an electroless reaction of oxygen dissolved in the electrolyte and the hydride. The chemical stability is poor when the Y electrodes are exposed to highly energetic light, suggesting that the higher hydride forms, which are assigned to have n-type semiconducting properties, are photoanodically converted into the oxidic form of the Y electrode.

The results described here are dealing with the electrochromic characteristics of YH₂. However, it seems likely that other rare-earth type hydride-forming electrodes, including the group III transition metals, may reveal a similar optical effect. A preliminary study confirmed that such typical electrochromic behavior can be electrochemically induced in other Pd-coated rare-earth thin film electrodes. These and other results are presented in detail in a separate paper.²

Acknowledgments

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Fig. 9. Optical transient behavior of a Pd-coated (20 nm) Y (500 nm) electrode under potentiostatic control. The optical changes induced by absorption (at –1.0 V) and desorption (0 V) are represented by curves a and b, respectively. Note the difference in time scales.

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