A.c.impedance study of electrochemical hydrogenation of Ni/Y structures

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INTRODUCTION

Electrochemical hydrogenation of metals like Y, Hf, Gd and alloys of Mg with Mn, Fe, Ni, etc has been extensively studied in a hope to produce Smart Optical Windows (SOW), devices which change their reflectivity as a function of a hydrogenation degree of active material [1,2] Presently efforts are concentrated in finding the combinations of proton-containing electrolytes[3] and active metals/alloys[4] to ensure better contrast, higher longevity and reliability of the SOW.

The purpose of this work is to study in details the kinetics of hydrogen incorporation into bi-layer structures Ni(20 nm)/Y(100nm) in electrochemical cathodic reaction performed in 1M KOH. Here Ni serves as a protector of Y (active metal) against corrosion.

Figure 1(a) illustrates the kinetics of incorporation of hydrogen into the Ni/Y sample and corresponding in-situ change of its reflectivity. Numbers of the curves in Fig1.b correspond to the stages marked by arrows in Fig.1,a.

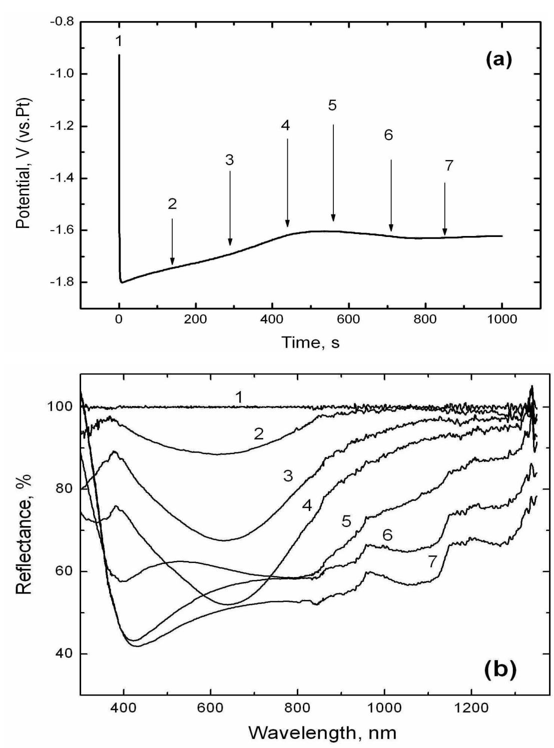

Figure 1. Polarization kinetics for hydrogenation of Ni/Y sample at - 100 $\mu A/cm^2$ (a) and corresponding changes of its reflectivity (b).

Application of positive potential to this structure partially restores the high reflectivity state and cycling of potential between negative (hydrogenation) and positive (de-hydrogenation) values results in cyclic changes of reflectivity. Differently to the case of the structures Pd/Y (very often used in gas and liquid hydrogenation) this structure sustains hundreds of cycles without breaking the device down. Here, however, we will concentrate on the electrical behavior of Ni/Y sample, particularly, on its a.c.electrical impedance. Measurements were performed using Solartron 1260 FRA and Z-Plot 2.1 software. We have acquired a series of Bode plots of hydrogenated Ni/Y sample by taking measures in the points shown in Figure 1,a. Figure 2 shows Bode plots of successive hydrogenation stages with numbers corresponding to the stages shown in Fig.1.

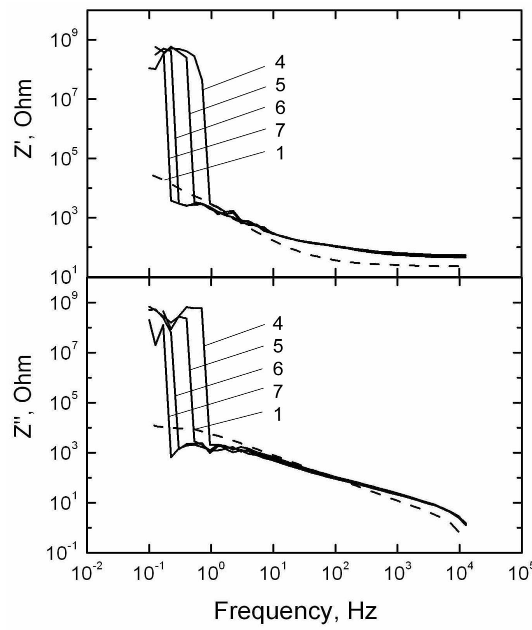

Fig.2. Bode plots for Ni/Y composite films during their hydrogenation in 1M KOH.

One can notice giant increase (5 orders of magnitude) of both imaginary and real parts of the impedance when the frequency is decreasing to 1-0.1 Hz. The effect can not be ascribed to some artifacts of measurement system, as the critical frequency at which this change is observed is gradually shifted towards lover values while the process of hydrogen incorporation is advancing.

The observed jump of the impedance is of dynamic nature – while repeating the same measurements, it disappears. A-priori this effect can be ascribed to nothing but to the redistribution of hydrogen ions in the hydrogenated material. Still, the fact that at low frequencies the sample behaves as a perfect dielectric at first run of the measurements needs proper explanation.

Other feature of impedance measurements worth pointing out is an initial decrease of both active and reactive resistance of Ni/Y sample when the outer Ni layer is hydrogenated. It is just opposite to what we might expect provided that the hydrogen incorporation should cause transformation of metal into semiconductor.

We present the phenomenological model of the hydrogenation process which assumes consecutive hydrogenation of Ni and Y layers by inward migration of hydrogen ions and their post-treatment redistribution inside the hydrogenated material. Kinetics of changes of resistance of each layer during the hydrogenation process is studied employing equivalent circuit modeling.

Acknowledgements. The work has been financed by the R&D project MAT 2001-3203 financed by the Interministerial Commission of Science and Technology of Spain.

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