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Kinetics of interaction of hydrogen with thin C-Pd films

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Introduction

Nanocomposite C-Pd films with porous structure and palladium nanograins placed in/on carbon matrix are promising materials for hydrogen sensor application. It is connected with highly developed surface area of these films and highly selective hydrogen absorption properties of palladium. The sensing mechanism of C-Pd films is based on their resistance changes in the presence of hydrogen due to H_2 absorption into palladium nanograins. Interaction between hydrogen and palladium nanograins begins with adsorption of H_2 on palladium surface following homolytic dissociation of hydrogen molecules to H atoms. These hydrogen atoms diffuse into Pd nanograins and occupy the interstitial sites of the lattice, forming solid solution [1]. At higher hydrogen pressure, further incorporation of hydrogen atoms induces a phase transition from α- to β-phase and creating of palladium hydride [2]. The Pd-H system is characterized by higher resistance than metallic palladium.

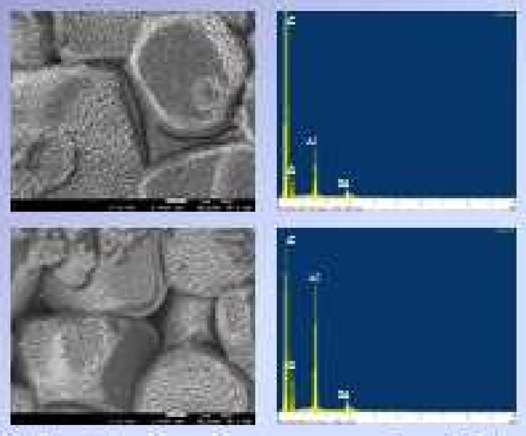
Experimental

The nanostructural C-Pd films were synthesized by Physical Vapour Deposition (PVD) method. In PVD process two separated sources containing fullerene C_{60} and palladium acetate $Pd(OAc)_2$ were used to prepare films on alundum substrate. The obtained films were characterized by Scanning Electron Microscopy (SEM) and Energy Dispersive Spectroscopy (EDS). Then sensing measurements in various hydrogen concentrations in nitrogen were performed.

Characterization of C-Pd films by SEM and EDS

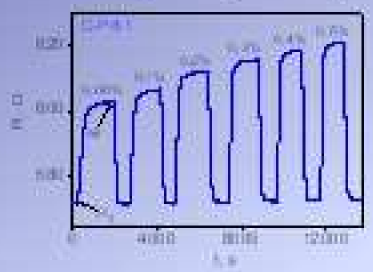
C-Pd-1

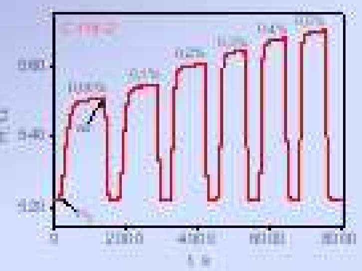
C-Pd-2



Nanocomposite C-Pd films in the form of carbonaceous grains with Pd nanograins were deposited on the Al_2O_3 substrate. Pd nanograins are invisible on the SEM pictures because of their small diameter (few nanometers). Film C-Pd-1 covers more surface of Al_2O_3 substrate than film C-Pd-2. This is particularly visible at the grain boundaries of Al_2O_3. Hence on the X-ray spectrum of sample C-Pd-1 the peak of Al is of much less intensity than the same peak on spectrum derived from the second film.

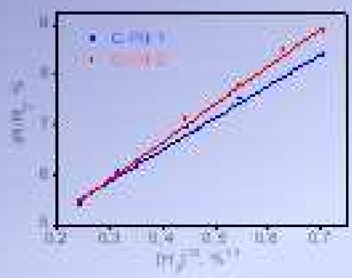
Hydrogen response of C-Pd films





The presence of hydrogen causes the increase of C-Pd films resistance while air introduction leads to the decrease of resistance to its initial value. The films' resistance increase is connected with the adsorption of H_2 and following forming of Pd-H solid solution, whereas resistance decrease is related to hydrogen desorption. Magnitude of resistance changes depends on the concentration of hydrogen in the ambient atmosphere.

Hydrogen sensitivity of C-Pd films

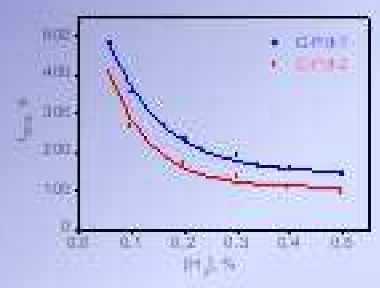


We found the linear correlation between C-Pd films sensitivity ($\Delta R/R_0$) and $[H_2]^{1/2}$. Linear character of this relation is consistent with Sievert's law [2]. Sievert's law implies that the ratio of the dissolved atomic hydrogen to palladium atoms (H/Pd) is proportional to the square root of H_2 partial pressure (p_{H_2}) and the change of this ratio leads to respective $\Delta R/R_0$ response:

$$\Delta R/R_0 \propto \frac{H}{Pd} = \frac{1}{K_s}(p_{H_2})^{1/2}$$

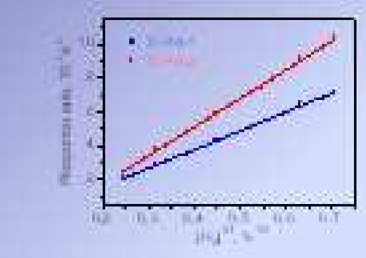
where K_s is the Sievert's constant [2].

H_2 response time of C-Pd films



The response time ($\tau_{90\%}$) decreases in the function of increasing hydrogen concentration. The sample C-Pd-2 is characterized by shorter response time than film C-Pd-1 in the whole range of examined H_2 concentrations and achieves ~90 s at 0.8% H_2.

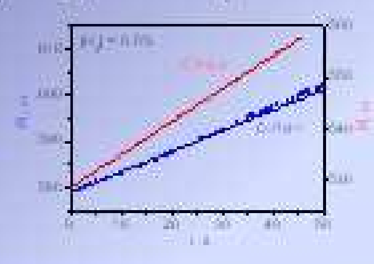
H_2 response rate of C-Pd films



The response rate of C-Pd films increases linearly in the function of $[H_2]^{1/2}$, similarly to their sensitivity. It results from the stoichiometry of the following equation describing dissociative chemisorption of hydrogen on the palladium surface:

$$0.5\,H_{2(gas)} \rightleftharpoons H_{(ads)}$$

Hydrogen absorption kinetics



Determination of the rate-limiting step of H_2 absorption can be made by a measurement of the initial response rate [3]. The obtained experimental data, showing linear relation between initial response of C-Pd film and time of exposure to H_2 atmosphere, suggests that the rate-limiting step of H_2 absorption process is not diffusion of atomic hydrogen into the bulk palladium, but dissociation of H_2 molecules on the surface of palladium nanograins.

Conclusions:

- The sensitivity of C-Pd films increases with hydrogen concentration and reaches 9% at 0.8% H_2. The response rate of C-Pd films also increases linearly with $[H_2]^{1/2}$. The linear nature of these changes is in good accordance with Sievert's law.
- The response time is shortened in the function of increasing hydrogen concentration and achieves 90 s at highest examined H_2 concentration.
- The measurement of the initial response rate suggests that the rate-limiting step of H_2 absorption process is dissociation of H_2 molecules on the surface of palladium nanograins.

References:

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2. E. Lee, J.M. Lee, J.H. Koo, W. Lee, T. Lee, Int. J. Hydrogen Energ. 35 (2010) 6984
3. C.H.F. Peden, B.D. Kay, D.W. Goodman, Surf. Sci. 175 (1986) 215

INNOVATIVE ECONOMY

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