FEATURES OF CHRONOAMPEROMETRIC STUDIES OF WATER SORBENT MATERIALS

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The present study examines the constant potential discharge method at −0.6 V (CPD) for three different hydrogen absorbing materials: nano-Ni-C synthesized from polystyrene and metal salts using the pyrolysis method; Ni-Raney obtained through leaching, and La₃MgNi₁₄ alloy are prepared by sintering and prolonged heat treatment. Each of the samples corresponds to distinct time domains (according to the theory of the method under consideration), indicating different mechanisms diffusion and hydrogen diffusion coefficients.

**Keywords:** MH electrode, constant potential discharge; hydrogen diffusion coefficient

Materials of metal hydride electrodes, such as AB₃ or AB₅ (where A represents a rare earth metal, including magnesium, and B denotes a transition group element), must possess not only a high charge capacity, cyclic stability, corrosion resistance, and rapid activation but also high values of the atomic hydrogen diffusion coefficient. Various physicochemical methods are employed to assess the diffusion coefficients of hydrogen in metals, alloys, and composites, including nuclear magnetic resonance, quasielastic neutron scattering, EIS spectroscopy, and various electrochemical techniques: cyclic voltammetry or chronoamperometric discharge method at a constant potential [1, 2]. Chronoamperometry is a widely used method in electrochemistry, partly due to its relative ease of execution and analysis, as well as its high sensitivity.

The purpose of this study was to determine the apparent diffusion coefficient during alkaline electrochemical cycling in a 6 M KOH solution for different hydrogen sorption materials, namely Ni-Raney, nano-Ni-C [3] and La₃MgNi₁₄ alloy using the constant potential discharge method.

The research was conducted following the methodology detailed in works [4-6]. Prior to each study involving a constant potential (V=const), powder composite electrodes composed of active hydrogen sorption material and Ni carbonyl powder were fully charged with a current of 100 mA/g and subsequently discharged at a constant potential of −0.60 V (Ag/AgCl). The discharge curves for the studied electrodes at a constant potential exhibited three distinct time domains:

1) at the beginning of discharge (t < 1/4 hour), the current rapidly decreases and is controlled by charge transfer characteristic of the Ni-C electrode.
(II) located within the range \((1/4 < t < 1 \, \text{hour})\), where diffusion gradually becomes dominant and discharge can be under mixed control of charge transfer with diffusion observed for Ni-Raney (III) long-term discharge \((t > 1 \, \text{h})\) is characteristic of intermetallic compounds (for example, \(\text{La}_3\text{MgNi}_{14}\)) in which hydrogen diffusion is the limiting step, which is characterized by a slow and linear change of \(\log (i)\) with time \(t\). In [4], it was established that the diffusion current changes according to the following equation:

\[
\log i = \log \left( \frac{6FD_H(C_0 - C_S)}{d \cdot r^2} \right) - \frac{\pi^2}{2.303} \frac{D_H}{r^2} t
\]

where \(C_0\) and \(C_S\) are the concentrations of atomic hydrogen within the particle volume and on its surface, respectively \([\text{mol} \cdot \text{cm}^{-3}]\), \(F\) is the Faraday constant \((96487 \, \text{C/mol})\), \(d\) is the density of the active material \([\text{g} \cdot \text{cm}^{-3}]\), and \(D_H\) is the effective (apparent) diffusion coefficient of hydrogen atoms \([\text{cm}^2 \cdot \text{s}^{-1}]\) within this material. \(r\) [cm] represents the particle size, which decreases cyclically due to lattice expansion/contraction.

From Eq. (2), the ratio of the hydrogen diffusion coefficient to the square of the average grain size of the alloy \((D_H/r^2)\) is determined from the slope \((d\log i/dt)\) of the linear region (III) of the discharge curves at a constant potential [5].

\[
\left( \frac{d \log i}{dt} \right) = -4.29 \frac{D_H}{r^2}
\]

According to Eq. (2), the hydrogen diffusion coefficient was calculated in the Ni-Raney, nano-Ni-C and intermetallic alloy \(\text{La}_3\text{MgNi}_{14}\). The obtained values of the hydrogen diffusion coefficient were \(8.8 \cdot 10^{-13}\), \(1.1 \cdot 10^{-12}\) and \(6.7 \cdot 10^{-11}\) cm\(^2\)·s\(^{-1}\), respectively. These values were analyzed from the point of view of the probable influence of various factors (particle size, crystallite size, hydrogen affinity of the hydrogen-absorbing material, etc.).

6. Dymek M., Nowak M., Jurczyk M. and Bala H. Electrochemical behavior of a nanostructured La\(_{1.25}\)Gd\(_{0.25}\)Mg\(_{0.5}\)Ni\(_5\) hydrogen storage material modified with magnetron sputtered nickel // J. Electrochem. Soc. – 2019. – 166. – P. A1393–A1399.