

9th International Workshop on Electrodeposited Nanostructures

Electrochemical study and comparison of kinetics of iron-palladium alloy electrodeposition at flat electrode and in porous alumina template

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ABSTRACT

Fe-Pd alloy has attracted extensive attention recently because of its many potential applications in magnetic and hydrogen storage devices. Many studies were dedicated to study physical properties of Fe-Pd alloys [1] whereas less research was done on electrochemical process [2]. Kinetics of Fe-Pd alloy electrodeposition at flat electrode and in porous alumina template from citrate-based bath was studied. Alumina (AAO) template was sputtered on the one side with 600 nm thick conductive gold layer in order to fill pores completely. Glass was sputtered in the same batch as template and served as flat electrode. Stability of the electrolyte and co-deposition of both metals were achieved by complexing Pd with ammonia and Fe with citrate via the formation of metal complexes Fe^{3+} -citrate and $[\text{Pd}(\text{NH}_3)_4]^{2+}$ at pH 9. Cyclic voltammetry was used for determination the oxidation/reduction potentials of free metal ions and those in the complex form. Electrodeposition of Fe-Pd alloy is found to be diffusion-controlled. Diffusion coefficient, charge transfer coefficient and kinetic constant for both metallic ions in porous alumina template and at flat electrode were determined with voltammetric and chronoamperometric analysis. Diffusion and kinetics is found to be faster at flat electrode than in template. Diffusion coefficient for Fe^{3+} at flat electrode is higher ($0,7 \times 10^{-6} \text{ cm}^2/\text{s}$ obtained by voltammetric analysis and $0,4 \times 10^{-6} \text{ cm}^2/\text{s}$ by chronoamperometric analysis) than in template (voltammetric $1,2 \times 10^{-5} \text{ cm}^2/\text{s}$ and $2,0 \times 10^{-5} \text{ cm}^2/\text{s}$ by chronoamperometric analysis). This can be explained with hindered diffusion in template due to high aspect ratio of pores. Also the kinetics is found to be slower in template ($1,7 \times 10^{-5} \text{ cm/s}$) than at flat electrode ($1,8 \times 10^{-4} \text{ cm/s}$) for the first step in reduction process of Fe^{3+} to Fe^{2+} . The same trend can be observed in case of Pd electrodeposition process. Diffusion coefficient for Pd^{2+} at flat electrode is higher ($1,2 \times 10^{-5} \text{ cm}^2/\text{s}$ voltammetric analysis and $2,0 \times 10^{-5} \text{ cm}^2/\text{s}$ chronoamperometric analysis) than in template ($4,7 \times 10^{-6} \text{ cm}^2/\text{s}$ voltammetric value and $4,3 \times 10^{-6} \text{ cm}^2/\text{s}$ chronoamperometric value) and kinetics at flat electrode ($1,3 \times 10^{-4} \text{ cm/s}$) is faster than in template ($1,3 \times 10^{-5} \text{ cm/s}$).

References:

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[2] M. Rezaei, M. Ghorbani, A. Dolati, Electrochemical investigation of electrodeposited Fe–Pd alloy thin films, *Electrochimica Acta*, **56**, 483–493 (2010).