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Research Article

Electrochemical Surface Treatment of Ni–Cu Alloy in a Deep Eutectic Solvent to form High Performance Electrocatalysts for Hydrogen Production

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Abstract

Anodic electrochemical treatment of nickel-copper alloy (45 wt.% Ni) was conducted in a deep eutectic solvent, ethaline (a eutectic mixture of choline chloride and ethylene glycol). The electrochemical behavior of the Ni–Cu alloy was investigated by means of linear voltammetry technique. Anodic treatment of nickel-copper alloy in ethaline was stated to enhance the electrocatalytic activity towards hydrogen evolution reaction in alkaline water electrolysis. The results obtained can be used to develop new electrocatalysts for hydrogen synthesis in hydrogen energy.

Introduction

One of the most important tasks of modern science and technology is the development of new high-efficiency electrocatalysts for the synthesis of hydrogen, which is the main energy source in hydrogen energy [1]. Among the many potential types of electrode materials suitable for use in water electrolysis, nickel-copper alloy combines high mechanical and corrosion resistance and relatively low cost (compared to precious metals) with a relatively low overvoltage of hydrogen in aqueous solutions [2,3]. To increase the electrocatalytic activity of the Ni-Cu alloy, it is advisable to treat the surface of this alloy anodically, which would provide selective etching of one of the components (copper) and the formation of a highly active porous layer enriched in nickel. However, anodic selective etching of nickel-copper alloy in "ordinary" aqueous solutions is inefficient because it leads to passivation of the alloy. In this context, it is attractive to use a new type of ionic liquids for anode treatment: Deep Eutectic Solvents (DES) [4], in which the metal components of the alloy are able to dissolve anodically without the formation of passive layers on the surface. In this work, we studied the process of anodic dissolution of the nickel-copper alloy (50%:50%, wt.) in a DES called ethaline. Ethaline is a eutectic mixture of choline chloride and ethylene glycol in the molar ratio of 1:2, respectively.

Materials and Methods

Nickel-copper alloy containing 45 wt.% of Ni and 55 wt.% of Cu was used in this study. Ethaline was prepared as a eutectic mixture of choline chloride and ethylene glycol in the above molar ratio [4]. All other procedures are described in detail elsewhere [5]. Let us note that the electrocatalytic activity of the electrochemically treated Ni-Cu alloy was investigated by linear voltammetry technique using a 1 M NaOH aqueous solution at the temperature of 298 K.

Results and Discussion

Voltammetry studies of the anodic dissolution of the Ni-Cu alloy in ethaline showed that two peaks of the anode current are observed on the polarization curve (at 0.1 V and 0.5 V relative to the silver reference electrode, respectively). With a further increase in anodic polarization (more than 0.5 V) the occurrence of a passive state is observed. Comparison of the obtained experimental data with the literature [6] suggests that the first of these peaks corresponds to the dissolution of copper, and the second is associated with the joint dissolution of nickel and copper. Passivation in this electrolyte is not due to the formation of oxide films, but the formation on the surface of the electrode layer of insoluble compounds (salts) of copper and nickel (the so-called "salt passivation").

Polarization curves were obtained to characterize the kinetics of cathodic hydrogen evolution in 1 M aqueous NaOH solution on nickel-copper alloy samples before and after their anodic activation in ethaline at the above-mentioned potentials of dissolution peaks (Figure 1). It was established that after the anodic treatment of the alloy at the potential of the second peak on the anode curve (0.5 V), a shift of the polarization curve of hydrogen evolution towards more positive potentials is observed (about 80–100 mV). This effect is associated both with the development of the true surface area (due to the formation of a porous structure) and with the growth of electrocatalytic activity (due to the enrichment of the surface layer with active catalytic sites). Polarization curves of hydrogen evolution reaction in 1 M NaOH water solution on nickel-copper alloy before electrochemical treatment (1) and after anodic treatment in ethaline at different anode potentials: (1) 0.1 V, (2) 0.5 V, (3) 1.35 V, and (4) 1.7 V.

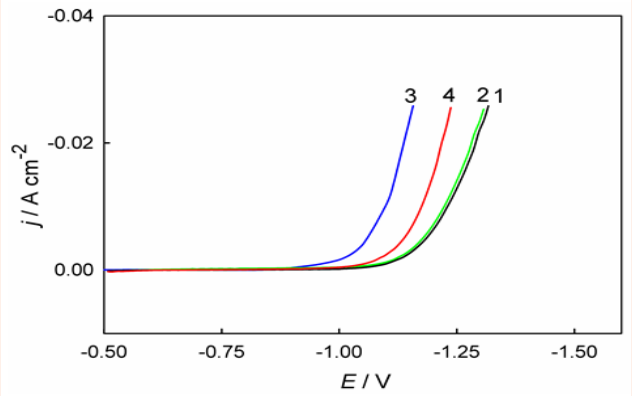

Figure 1: Polarization curves.

Conclusion

Thus, the use of electrolyte based on DES (ethaline) for anodic treatment of nickel-copper alloy allows influencing the composition and morphology of the surface layer, and, consequently, increasing the electrocatalytic activity towards the reaction of hydrogen evolution. This can be used to develop new high-performance and relatively cheap electrocatalysts for green hydrogen energy.

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