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Development and characterization of new nickel coatings for application in alkaline water electrolysis

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ABSTRACT

The purpose of this paper is to report on the synthesis and characterization of different electrocatalytic materials for the hydrogen and oxygen evolution reactions (HER and OER) in alkaline water electrolysis. Ni meshes surface coated with porous nickel layers have been used as substrates for electrodes. Porous nickel coatings have been modified by amorphous NiP_x or Pt nanoparticles (to improve the cathode efficiency) and nickel–cobalt spinels (to improve the anode efficiency). The structure, roughness and composition of the active layers have been determined by SEM analysis, porosimetry, laser atomic emission spectroscopy (LAES), energy-dispersion analysis (EDA) and XRD analysis. Overpotentials for both HER and OER have been measured in 6 M KOH over the 0–1.0 A/cm² current density range. Both hydrogen and oxygen overpotentials are found significantly reduced compared to smooth nickel electrodes. The hydrogen and oxygen evolution mechanisms on these catalytic surfaces are discussed.

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Introduction

Alkaline water electrolysis (AWE) is now increasingly considered as a promising method for the large-scale production of carbon-free hydrogen and oxygen in view of power grid regulation and large scale energy storage. In spite of significant technological developments during the XXth century,

modern alkaline electrolysis cells are still limited by high energy consumption at somewhat limited operating current densities. For comparison, whereas modern proton-exchange membrane (PEM) water electrolyzers are commonly operating at 1 A/cm², with a cell voltage of approximately 1.8 V and an enthalpy efficiency of ≈80% [1–3], large-scale commercial alkaline electrolyzers are usually operating in the 0.2–0.5 A/cm² range, with a cell voltage of ca. 2 V corresponding to a cell

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efficiency of $\approx 75\%$ [4]. However, H. Vandenborre et al. [5] obtained the same high results for AWE as for PEM using platinum electrocatalyst for the hydrogen evolution reaction (HER). To become economically interesting for the large scale hydrogen production, the energy consumption of modern AWE cells should lie somewhere in the 4.2–4.8 kWh/Nm³ H₂ range, at operating current densities of 0.5–1.0 A/cm². In order to reach such level of performance the development of more efficient non-platinum electrocatalysts is still needed.

The HER has been extensively studied in the literature. The overall reaction in alkaline media is written as:



Eq. (1) is in fact a multi-step process. When metallic electrodes are used as cathodes, metal active centers (M) are involved in the reaction path. It is generally accepted that the first reaction step is a one electron discharge, so-called Volmer step (2), leading to the formation of surface-bounded hydrogen ad-atoms (MH_{ads}):



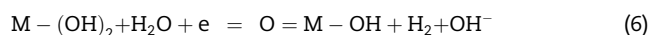
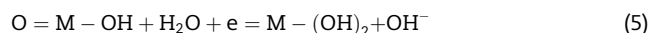
The second step is either electrochemical desorption, (so-called Heyrovsky electrochemical desorption (3)) or chemical recombination, (so-called Tafel catalytic recombination (4)). Both steps lead to the evolution of molecular hydrogen and involve the adsorbed hydrogen H_{ads}:



Thus the rate of hydrogen evolution depends on the energy of the metal–hydrogen bond. Platinum-group metals (PGM) present the highest catalytic activity with regard to the HER. They have an optimum enthalpy value for the M–H bond [6]. However, PGM-electrocatalysts are not used in the large-scale AWE because of their high cost. A lot of research has already been made and is still going on to find materials with high catalytic activity with regard to the HER [7–13]. The analysis of literature data tells that to obtain the most active material, it is first necessary to develop the electrode surface and then to modify it. It was convincingly shown recently [7] that when a pure Ni powder is used, the smaller the size of particle is and the more defective the particles are, then the greater their electrocatalytic activity is. The lowest overpotentials were obtained for Ni nano-particles of 5 nm. The problem is that active non-PGM electrodes that contain Ni and Co are prone to progressive deactivation during AWE under steady-state operating conditions.

Nowadays Raney nickel and skeletal nickel-based catalysts having a large surface area are often used in commercial AWE. These materials exhibit a high intrinsic catalytic activity and can be further improved by surface modification: addition of molybdenum [8–11], adatoms of some heavy metals [13], sulfur [11,13,16], phosphorus [11,17,18] and so on. Skeletal nickel-based catalysts are of particular interest, showing low overpotentials and Tafel slopes of 40–80 mV/dec in 6 M KOH at elevated temperatures [11,13]. Regarding the implementation of such structures, main limitations come from the complexity of technological processes and a lack of stability

because of a gradual degradation of amorphous structures [11–13]. Besides highly developed metal surfaces, some oxides of transition metals are also active towards the HER [14,15,19,20]. Oxide particles can be incorporated into surface layers or coated over metal substrates. The HER mechanism on oxides apparently differs from that on metals. Some authors consider that surface oxide or hydroxide groups are involved in the process and no chemical recombination takes place [13,20]:

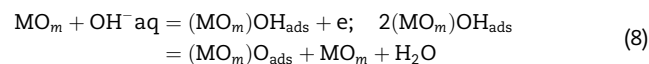


Surface deposition of appropriate transition metals, metal oxides or non-metallic species can be used not only to improve the electroactivity of the electrodes but also to enhance their durability. For example, results reported in Refs. [17,18] showed that coatings containing an optimal value of ca. 3 wt.% of phosphorus were even more active than smooth platinum electrodes and showed excellent durability as electrodes for the HER: no structural change was observed after 2000–4000 h of steady-state operation. Poisoning effects and a sharp decay in electrochemical activity have been observed with higher phosphorus contents.

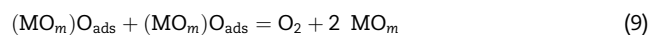
The development of catalytically active anode materials for the oxygen evolution reaction (OER) in AWE is an even more challenging task. This is due to severe operating conditions, a combination of the high anode potential in aggressive chemical environments at elevated temperatures. In alkaline media the overall OER reaction includes four electrons and can be written as:



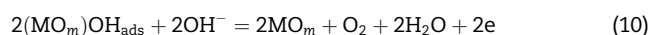
The reaction (7) is a complex multi-step process. In spite of a lot of fundamental investigations, there are still unanswered mechanistic questions; it is commonly assumed that all metals, including platinum, operating at anodic potentials, are covered with surface oxides. In Refs. [21,22], the mechanism taking place on spinels has been analysed. It was considered that the process occurred through the stage of adsorption and discharge of OH[−] ions, taking into account that the anode surface in 6 M KOH is covered with oxides and hydroxides:



The desorption of oxygen molecules may take place according to either surface recombination:



or electrochemical desorption:



Our data are somewhat in agreement with this mechanism and are discussed below.

The most active anodes are made of nickel with developed surface, for example, skeletal Ni, Ni–Co alloys, mixed oxides with spinel-type structure (NiCo₂O₄ and Co₃O₄) or perovskite

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