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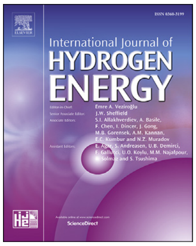

Electrodeposition and characterization of NiMoW alloy as electrode material for hydrogen evolution in alkaline water electrolysis

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The electrodeposition of ternary NiWMo alloys films from citrate ammonia-free electrolyte at room temperature was studied in an effort to evaluate the effect of applied potential on the composition limits, corrosion resistance and the electrocatalytic properties of the deposits towards the hydrogen evolution reaction (HER) in concentrated alkaline solution. The alloys were potentiostatically electrodeposited onto pure copper sheet substrates. The electrodeposits were characterized by means of field-emission scanning microscopy (FESEM) and energy dispersive X-ray analysis (EDXA). In an electrolyte where $MoO_4^{2-}/WO_4^{2-} = 1:1$, at a given deposition potential, there is more Mo than W in the deposits, indicating an advantageous induced co-deposition of Mo compared to W. The nucleation mechanism, studied according to Scharifker-Hills theoretical model, revealed an instantaneous nucleation followed by a three-dimensional growth. On the hand, increasing MoO_4^{2-}/WO_4^{2-} ratio in the electrolyte under the same deposition potential reduced both Ni and W content in the deposits. A different trend was observed in an equimolar solution, when applying more negative potentials, both Mo and W contents decreased leading to the enhancement of Ni amount. The stability in corrosive media and the catalytic performances of the coatings depended mainly on the applied overpotentials, A mechanism of induced co-deposition of molybdenum and tungsten with nickel is proposed and discussed.

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Introduction

Hydrogen production by water electrolysis is one of the most promising techniques for the global future energy needs as an entirely clean and powerful alternative to climate -altering fossil fuels processes, particularly when renewable energy sources such as solar and wind energy are used [1]. Unfortunately, compared to technologies available on the market such as the steam reforming of methane gas or partial oxidation of oil, alkaline water electrolysis is not at present cost-effective due to the high amount of electricity used in the process which restrains its large-scale utilization.

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Nomenclature

AC	Alternative current
B	Tafel slope, log2.303RT/αF
B	Charge transfer coefficient
C	Electrode capacitance
CSL	Cathodic scan limit
Edep	Deposition potential
EDS	Dispersive X-ray spectroscopy
EEC	Electrochemical Equivalent Circuit
EIS	Electrochemical impedance spectroscopy
Erev	Reversible thermodynamic potential
F	Faraday constant, 96500 °C
FESEM	Field emission scanning electron microscope
HER	hydrogen evolution reaction
I_0	Apparent exchange current density
i_c	Cathodic current density
i_{max}	Current coordinate of the peak
K	Electrochemical reaction rate constant
K_0	Rate constant at $E_{i=0}$
n	Number of electrons transferred
η_a	Anodic overpotential
η_c	Cathodic overpotential
OCP	Open circuit potential
Rct	Charge transfer resistance
Rs	Solution resistance
SCE	Saturated calomel electrode
t_{max}	Time coordinate of the peak
Zi	Imaginary part of Z
Zr	Real part of Z

In order to make water electrolysis more efficient and at affordable cost, reduction of the cell voltage is indispensable. The applied potential to drive the electrochemical cell at an applied current, *I*, includes a thermodynamic and a kinetic (dissipation) contribution due to inefficiencies in the system:

$$\Delta E_{Cell} = \Delta E_{rev} + \eta_a + |\eta_c| + IR + \Delta E_{st}$$

Where ΔE_{rev} is the reversible thermodynamic value (≈1.23 V) which depends on the nature of the electrochemical reactions, η_a and η_c the overpotentials at anode and cathode, *IR* the inter-electrode resistance, and ΔE_{st} the in time stability characteristic expressing the tendency of the actual cell voltage to increase as a consequence of the electrolyzer performance degradation [2]. It is worth mentioning that while the inter-electrode ohmic losses could be reduced by enhancing the bath conductivity and minimizing the space between the electrodes, the cathodic and anodic overpotentials depend mainly on the electrode material properties. During the last few years, significant improvements have been made in alkaline water electrolysis through the development of advanced alkaline water electrolysis systems with the so-called "zero gap cell" design (no space between anodes, diaphragms, and cathodes in the cell units) [3]. On the other hand, some research works on water vapor electrolysis have been carried out. Ganley [4] and Boll and co-workers [5] reported that increasing the operating steam electrolysis temperature and pressure up to 400 °C and ≈10 MPa or 500 °C and 400 MPa respectively, improved the reaction kinetics at the electrode surface and lowered the applied potentials to provide high current densities. However, increasing bath temperature and pressure drastically decreased the terminal potentials and strongly affected the stability of electrode materials in concentrated alkaline corrosive media. This fact motivates the extensive research efforts that have been recently focused on the improvement of the electrolysis cell performances through the devel opment of efficient and low-cost catalyst materials. According to the Brewer-Engel valence-bond theory [6,7], alloying transition metals with hypo-hyper-*d* - electronic structure, i.e., combination of metals of the left half of the transition elements in the Periodic Table having empty or half-filled vacant *d*-orbitals with metals of the right half of the series, having internally paired *d*-electrons, leads to pronounced increase in the electronic density of states and consequently to advanced synergetic effect in electrocatalysis for the hydrogen evolution reaction (HER). Alloys of nickel ([Ar] $3d^8$ $4s^2$) with tungsten, W ([Xe] $4f^{14}$ $5d^4$ $6s^2$) and/or molybdenum, Mo ([Kr] $4d^5$ $5s^1$) are among the materials fulfilling these requirements [8–11]. Moreover, the Pt-group metals are known to be the best electrocatalysts for hydrogen evolution reaction (ΔG ≈ −0.1 eV). The next ideal HER catalysts are nickel and cobalt (ΔG ≈ −0.28 eV) followed by molybdenum (ΔG ≈ −0.36 eV) and tungsten (ΔG ≈ −0.42 eV) [12]. Ni–W and Ni–Mo alloys are known to possess outstanding functional properties such as high corrosion resistance in many aggressive environments [13] and excellent electrocatalytic activity for hydrogen evolution. The electroplating process of NiMo and NiW alloys is classified as an induced alloy deposition type since tungsten and molybdenum cannot be deposited alone from their aqueous solutions, but are codeposited in the presence of nickel, forming an alloy [14]. Commonly, a complexing agent is needed to codeposit these metals, otherwise, the amount of Mo or W does not exceed 2 wt% in the alloy. Although a great number of different complexing agents have been reported in the literature, citrate has been among the most popular, particularly in the deposition of nickel alloys [15]. Sodium citrate forms stable complexes enough to bring closer the potentials of the alloy constituents and prevent deposition of hydroxides of the metals. Moreover, citrate aqueous solutions are environmentally friendly and can function as a complexing, buffering, brightening and levelling agent [16] in electroplating of metals and alloys. Several investigations have been devoted to the deposition of NiMo and NiW alloys. Sanches et al. [17] investigated the electrodeposition of the binary Ni–Mo alloys using different molar ratios of Ni:Mo, in a sodium citrate electrolyte at pH 4.0. They have found that high Ni:Mo molar ratio favors deposition of the metallic molybdenum, while deposits coated from molybdate-rich bath contained higher amount of Mo, a mixture of polyvalent molybdenum oxides or hydroxides, mainly in the form of the Mo(IV) and Mo(V)) in addition to metallic molybdenum. Krstajic et al. [9] reported that NiMo alloy deposited from a pyrophosphate-based bath onto Ni mesh exhibited better catalytic activity for hydrogen evolution in 1 M NaOH solution than pure Ni electrode. However, the stability of the film in concentrated solution (33 wt%) was very poor and the coating was scaled from the substrate after 2 h of hydrogen evolution. Xu and co-

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