

# Electrocatalytic properties of electrodeposited Ni–15Mo cathodes for the HER in acid solutions: Synergistic electronic effect

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## Abstract

The electrocatalytic evolution of H<sub>2</sub> in acid solution on well-adhering layers of Ni and Ni–Mo alloy (15 at.% Mo) electrodeposited from a citrate bath onto a glassy carbon disc has been investigated. The kinetic parameters and the rate constants of the forward and backward reactions of Volmer, Heyrovsky and Tafel steps for the hydrogen evolution reaction (HER) were deduced from the linear polarization and electrochemical impedance spectroscopy (EIS) measurements. The high apparent catalytic activity was interpreted with a porous structure of the Ni–15Mo deposits having an enlarged number of active sites.

The main factor influencing outstandingly high electrocatalytic activity of the Ni–15Mo electrodes as a cathode material in terms of HER in acid media has been explained by the synergistic electronic effects. The synergy was interpreted with theoretical predictions based on the complex band structure calculations and magnetic properties of Ni–Mo which suggest a pronounced density of states in d orbitals at the Fermi level obtained by alloying Ni with the threshold content of paramagnetic Mo.

The enhanced catalytic activity of the Ni–15Mo catalyst in comparison with the Ni catalyst in an acid solution was discussed within the framework of a bifunctional Volmer–Heyrovsky mechanism in which the simple cooperative functioning of the alloy components is mediated via a rapid intra-(inter) H-adatoms diffusion. Ni-sites act as an H-source for Mo-sites where the ion-atom recombination (and H<sub>2</sub> desorption) takes place. As a results, the ion-atom recombination reaction rate increases in comparison to pure Ni.

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## 1. Introduction

Ni-based alloys display a high electrocatalytic activity for hydrogen evolution in alkaline media [1–8], while little attention has been paid to this phenomenon in acidic media [9–12], in spite of the good prospects of stabilization towards corrosion by the addition of elements such as Cu, Cr, P, Nb and W [12].

The growing interest in commercial application of solid polymer electrolyte membrane (PEM)-type generators has stimulated the study of Ni-based materials as cheaper alternatives to Pt and Ir electrodes to lower investment costs. It has been estab-

lished that alloying Ni with Mo enhances the electrocatalytic activity of bare nickel [1,9,10,13]. A few theoretical statements have been used to predict the electrocatalytic properties of the *hypo-hyper-d* alloys and their intermetallics [14–16]. A simple mechanism for the increasing hydrogen evolution reaction activity of the *hypo-hyper-d* alloys based on the Brewer–Engel valence-bond theory is frequently cited in literature [14,15]. A somewhat different view results from the tight-binding linear muffin-tin-orbital atomic sphere approximation method [17,18] in combination with magnetization measurements [19–23], that has been successfully applied to rare earth and transition metals and, in particular, to some alloys of special interest for the HER [17]. A more sophisticated mathematical refinement, based upon modern physical approaches providing more reliable estimates, has revealed a more complex mechanism than that predicted by the Brewer–Engel theory. This indicates that the increase in electrochemical activity should be ascribed to an

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### Nomenclature

<i>A</i>	electrode surface area (m <sup>2</sup> )
<i>b</i>	Tafel slope (V dec <sup>-1</sup> )
<i>c</i>	concentration (mol m <sup>-3</sup> )
<i>C</i>	capacitance (F m <sup>-2</sup> )
CPE	constant phase element
<i>D</i>	diffusion coefficient (m <sup>2</sup> s <sup>-1</sup> )
<i>E</i>	potential (V)
<i>F</i>	Faraday constant (96 485 C mol <sup>-1</sup> )
<i>j</i>	current density (A m <sup>-2</sup> )
<i>k</i>	reaction rate constant (mol m <sup>-2</sup> s <sup>-1</sup> )
<i>l</i>	pore length (m)
<i>n</i>	characteristic parameter of CPE
<i>n</i>	number of pores
<i>r</i>	radius of pores (m)
<i>R</i>	resistance (Ω m <sup>2</sup> )
<i>R</i>	gas constant (8.314 J mol <sup>-1</sup> K <sup>-1</sup> )
<i>T</i>	absolute temperature (K)
<i>v</i>	reaction rate (mol m <sup>-2</sup> s <sup>-2</sup> )
<i>z</i>	number of electrons
<i>Z</i>	impedance (Ω m <sup>2</sup> )

### Greek letters

$\eta$	overpotential (V)
$\theta$	phase angle (°)
$\rho$	electrolyte resistance (Ω m)
<i>v</i>	parameter describing the relation between the potential and concentration gradient (V)

### Subscripts

abs	absorbed
ads	adsorbed
c	cathodic
ct	charge transfer
dl	double layer
el	electrolyte
oc	open circuit
Ω	ohmic

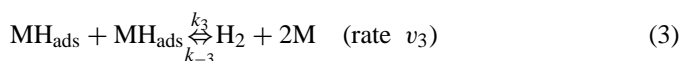
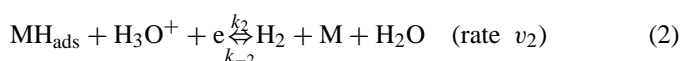
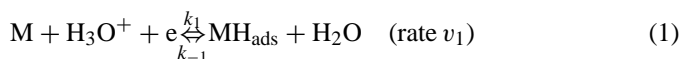
overall modification of the density of states of the host metal rather than to electron transfer.

Modification of the electronic structure of ferromagnetic Ni alloyed with paramagnetic Mo is indicated by a nonlinear decrease in magnetization with increasing Mo concentration [19]. The ferromagnetic ordering vanishes around 8 at.% (≈12 wt.%) Mo indicating that the simple picture of a linear decrease in the magnetic moment does not hold. It was found [5,9,10] that maximum electrocatalytic activity and the optimum performance of Ni–Mo(W) catalysts toward the hydrogen evolution reaction can be obtained by utilizing a threshold concentration of Mo(W) (≤15 at.%) alloyed with Ni. This result can be explained as a pronounced synergy between Ni, which has internally paired d electrons (3d<sup>8</sup>), and Mo(W), which has half-filled d orbital (4d<sup>5</sup>) and therefore can bind hydrogen atoms strongly. The activity maximum appears to be related to the point

at which the magnetic moment disappears, due to modification of the Ni electronic configuration or, in the simple picture, filling of the d orbital of Ni.

Our aim was to produce well-adhering Ni and Ni–15Mo electrodeposited layers on an inert glassy carbon substrate and to investigate their electrocatalytic activity for the HER in 0.5 M H<sub>2</sub>SO<sub>4</sub>. Choice of electrodeposition variables, such as nucleation of new grains is favoured over the growth of the existing grains [24], leads to high surfaces area electrodes. As Ni–Mo deposits cannot be obtained on a substrate into which significant hydrogen diffusion occurs [25,26], electrodeposition on an inert conducting glassy carbon (GC) substrate was considered.

For metal electrodes in acidic solution the HER occurs via the following well-known reaction steps [1]:



Steps (2) or (3) are alternative desorption steps for H<sub>2</sub> formation but each follows step (1). The distinction between (1), (2) and (3) as rate-determining steps in the HER is usually accomplished from Tafel slopes or by calculating the rate constants of the forward and backward reactions through simultaneous fitting of polarization and impedance data [1,2,27,28].

## 2. Experimental

The electrocatalytic performance of well adhering electrodeposits of Ni–15Mo and Ni on glassy carbon (GC), compare to a spectrographically pure nickel electrode were investigated for the HER in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution. Ni and Ni–15Mo films were deposited on a disk-shaped glassy carbon electrode (Sigradur-Sigri Elektrographite, GmbH, Germany) of surface area 0.28 cm<sup>2</sup>. Before electrodeposition, the GC disc was polished mechanically using 1200 grit emery paper and rinsed with deionised water in an ultrasonic bath. The surface of the GC was activated for electrodeposition by potentiostatic anodic polarization for 25 s in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution at 3.2 V versus Ag/AgCl electrode [29].

The freshly prepared GC disk was immersed in the plating solution and deposition was carried out at a constant current density of –70 mA cm<sup>-2</sup> for 1 min. The temperature of Ni plating bath (pH 3.4) was 55 °C and the plating solution composition was: 300 g dm<sup>-3</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O, 50 g dm<sup>-3</sup> NiCl<sub>2</sub>·6H<sub>2</sub>O, 40 g dm<sup>-3</sup> H<sub>3</sub>BO<sub>3</sub>, 1 g dm<sup>-3</sup> Na<sub>3</sub>C<sub>12</sub>H<sub>25</sub>SO<sub>4</sub>·2H<sub>2</sub>O (sodium lauryl sulphate). The plating solution composition for Ni–15Mo was: 79 g dm<sup>-3</sup> NiSO<sub>4</sub>·6H<sub>2</sub>O, 48 g dm<sup>-3</sup> Na<sub>2</sub>MoO<sub>4</sub>·2H<sub>2</sub>O, 88 g dm<sup>-3</sup> Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>·2H<sub>2</sub>O (tri-sodium citrate 2-hydrate), excess NH<sub>4</sub>OH, pH 10.5 [6]. A general agreement is that electrodeposition of Ni–Mo films occurs in two steps with the formation of a molybdenum–nickel oxide that is further reduced by hydrogen to a metallic molybdenum–nickel alloy. The surface morphology of the deposited layers was examined using a

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