# In situ activation of a Ni catalyst with Mo ion for hydrogen evolution reaction in alkaline solution

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## Article Information

## Abstract

In this study, the Ni catalyst has been activated during an hydrogen evolution reaction (HER) by adding Mo ions into the alkaline electrolyte. After dissolving different amounts of ammonium molybdate in 1M NaOH as an electrolyte, a Ni catalyst was used as the cathode for the HER. Then, a comparison between the hydrogen overpotential measured in the Ni catalyst with and without in situ activation has been made. The in situ activation shows an improvement in electrocatalytic properties of the Ni catalyst for the hydrogen evolution reaction. In the other words, the impact increase of in situ activation of Mo ions on the Ni structure shows an extremely significant impact in improving the Ni catalyst activation during in situ activation. The values of the Tafel slope for the Ni catalyst without Mo is an average of about 141 mVdec-1, while this value is about 172 mVdec-1 using in situ activation with an activator Mo ion. As well as the values of overpotential for the Ni catalyst, are an average of about 625 mVwhen using in situ activation, these values are about 482 mV at the current density of 250 mAcm-2 ($\eta$250). In this study the electrochemical data was obtained from linear sweep voltammetry (LSV), the steady state polarization Tafel curves, and electrochemical impedance spectroscopy (EIS).

## 1. Introduction

Fossil fuels are one of the main causes of global warming pollution, and climate changeis now considered as a global challenge. A promising replacement candidate for fossil fuels is hydrogen gas ($H_2$), which is a regenerable and nonpolluting fuel. Also, hydrogen is one of the most promising carriers of energy for various applications such as fuel cells. One of the methods for the production of clean hydrogen is water electrolysis which is performed via two half reactions: oxygen evolution reaction (OER) and hydrogen evolution reaction (HER). The HER method demands an efficient electrocatalyst such as platinum (Pt)-based metals, to improve the

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reaction rate and reduce the overpotential (η) for reduction of energy consumptions [1-4]. However, wide use of these reactions is not possible for industrial application because their scarcity and high cost. One guide to find an alternative electrocatalyst is a volcano plot at the equilibrium potential of the HER [5-6]. Among the non-precious metals studied using the volcano plot, Ni, as the most studied media, is the only active catalyst toward the HER that is stable in a concentrated alkaline solution [7]. Unfortunately, the electrochemical activity of Ni toward the HER is low at high current densities [8]. One method for to enhance its activity toward the HER is alloying it with other metals or non metals to increase its intrinsic activity (synergetic effect). One of the most investigated catalysts is the Ni Mo system which shows superior qualities for HER. There are many methods for preparing Ni Mo electrodes applied in catalyzing the HER such as ball milling, machine alloying, composite electrodeposition, electrodeposition and so on [9-11]. However, the preparation of multi component catalysts is a time consuming, expensive and complicated process. On the other hand, in situ activation is a simple and fast procedure for increasing HER activity in catalysts and is achieved by dissolving a substance directly into the electrolyte during the HER [12-15]. The current research work was planned on in situ activated Ni catalyst using a Mo ion in 1 M NaOH for the HER. The kinetics of the electrodeposited Ni on Cu substrate in the absence and presence of a Mo ion activator was studied by electrochemical techniques of linear sweep voltammetry (LSV), polarization Tafel curves and electrochemical impedance spectroscopy (EIS).

# 2. Experimental

## 2.1. Chemicals and material

A high pure Cu rod with a diameter of 0.5 cm was sealed in a shrinkable tube and polished with sandpaper, and then washed with deionized water and acetone. Then the Ni catalyst was prepared by

the electrodeposition method on Cu substrates from a Watts bath (1.14 M $NiSO_4$, 0.19 M $NiCl_2.6H_2O$, 0.49 M $H_3BO_3$) at j= -22 mA cm$^{-2}$ and a temperature 298 K for 30 min. The HER studies on the investigated electrodes were performed in 1 M NaOH at various concentrations of $(NH_4)_6Mo7O_{24}.4H_2O$ as in situ activator agent.

## 2.2. Measurements

All measurements of the HER studies on the investigated electrodes were performed in 1M NaOH at temperatures 298 K, in the absence and presence of various concentrations (25, 50, 75 and 100 ppm of Mo) as the in situ activator agent in 1 M NaOH solution. For the study, the electrochemical cell of the HER was a two-compartment Pyrex glass cell consisting of a large surface area Pt plate counter electrode (25 cm$^2$, Pt 99.99% ) and a Hg/HgO/1 M NaOH reference electrode. The temperature was controlled by a water jacket. All electrochemical measurements were performed with a Biologic SP-150 potentiostate/galvanostate. In order to obtain the stationary conditions necessary for polarization Tafel curves and EIS studies, the working electrodes were polarized at 100 mA for 5 h in 1M NaOH at 298 K. The reproducible Tafel curves were obtained after almost 5 cycles. The kinetic parameters, i.e. Tafel slope (b), exchange current density ($j_0$), and overpotential at the current density of 250 mA cm$^{-2}$ ($\eta_{250}$), were evaluated for the Ni catalyst in the absence and presence of various concentration of the Mo activator using the linear least square (LLS) approximation method. The EIS experiments were performed in the frequency range from 100 kHz to 100 mHz and 10 mV ac amplitude at different η from -50 to -250 mV and the data were approximated using ZView® software and the modified complex nonlinear least square (CNLS) method [16]. The scanning electron microscopy (SEM) (Tescan Vego 3) and energy dispersive X-ray spectroscopy (EDS) techniques were used to characterize the morphology of the Ni catalyst in the absence and presence of Mo ion in 1 M NaOH.

# 3. Results and discussion

## 3. 1 Characterization of catalyst

The SEM images of the Ni catalyst in the absence (a) and presence (b) of Mo ions are shown in Fig. 1. It can be observed that Mo adsorbed uniformly on the surface of the Ni catalyst as confirmed by the EDS method. Typical EDS images of the Ni catalyst, after performing HER on its surface for 1h at $\eta=250$ mV in the absence (a) and presence of 75 ppm Mo ion (b) in 1 M NaOH are shown in Fig. 2. It can be seen in these figures that in situ activation by Mo ion in alkaline solution could modify the Ni surface. It is probably an origin of the high electrocatalytic activity of a Ni catalyst toward the HER. Although the EDS experiment was performed in the presence of a higher concentration of Mo ion than 75 ppm, the results revealed that there was not any change in the investigated catalyst composition. Therefore, the Ni catalyst surface and its active sites for the HER were saturated with Mo when its concentration in alkaline solution was 75 ppm.

## 3.2. Kinetic studies

### 3.2.1. Polarization curves

The influence of the Mo ion activator on HER activity of the Ni catalyst was studied with the LSV method. Fig. 3 shows the LSV polarization curves for various concentrations of Mo ion in 1 M NaOH at 298 K and a sweep rate 2 mV s$^{-1}$. It can be seen that the increase of concentration of Mo from 25 to 75 ppm increased the HER activity of the Ni catalyst and electrocatalytic activity of Ni catalyst can be clearly observed. But at higher concentrations of Mo ions (for example: 100 ppm in Fig. 3), no significant effect on the HER electrocatalytic activity of Ni catalyst is observed. Additionally, the steady-state polarization Tafel curves of the HER were studied to evaluate the electrocatalytic activity of the Ni catalyst in the absence and presence of various concentrations of Mo ion in 1 M NaOH. A typical Tafel curve for this
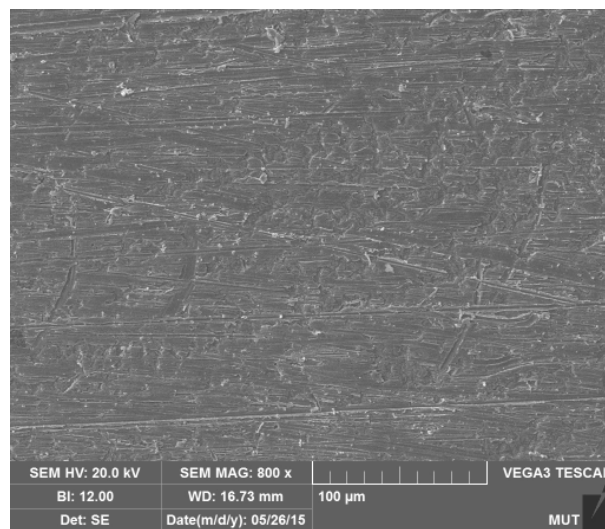


(a)
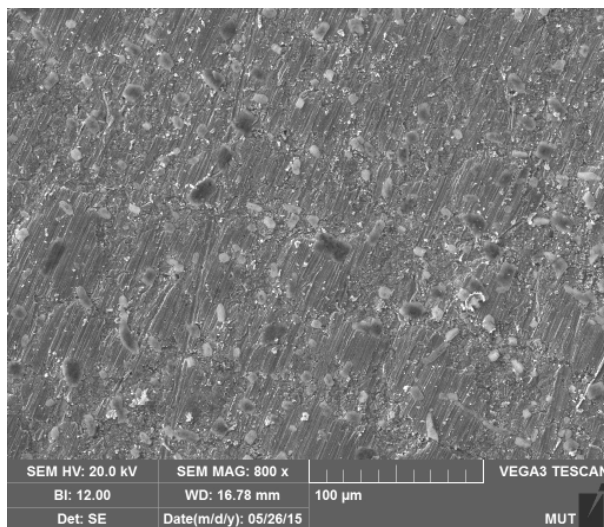


(b)

**Fig. 1. SEM images of Ni catalyst in the absence (a) and presence (b) of Mo ions in 1 M NaOH.**

study is shown in Fig. 4. The average values of the Tafel slope (b), the exchange current density (j0) and the overpotential at 250 mA cm-2 ($\eta$250) are presented in Table 1. These kinetic parameters were determined from the linear part of polarization Tafel curves at high overpotential, and j0 values were derived by extrapolation of Tafel plots to zero potential. It can be seen in Fig. 4 and Table 1 that the HER electrocatalytic activity was significantly increased in the presence of the Mo ion.
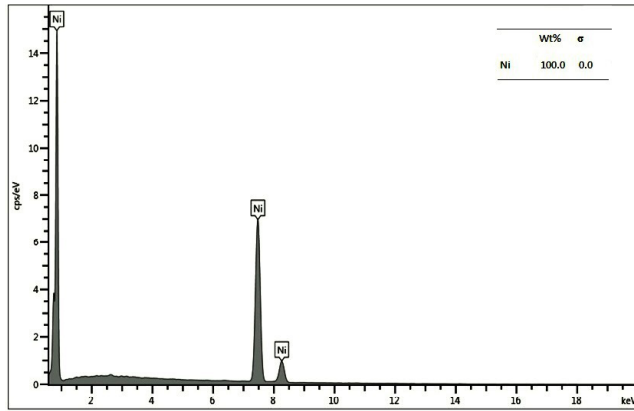
(a)
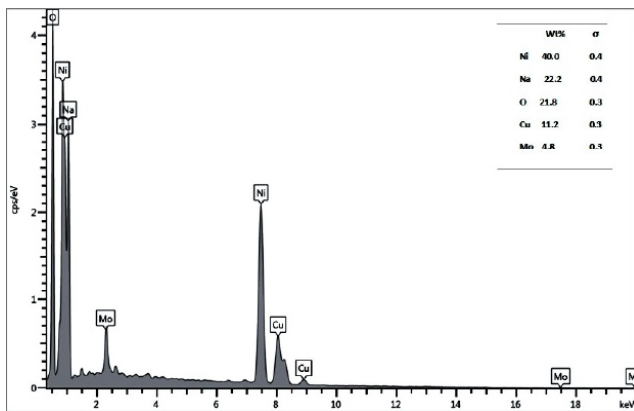


(b)

**Fig. 2. EDS images of Ni catalyst in the absence (a) and presence (b) of Mo ions in 1 M NaOH.**
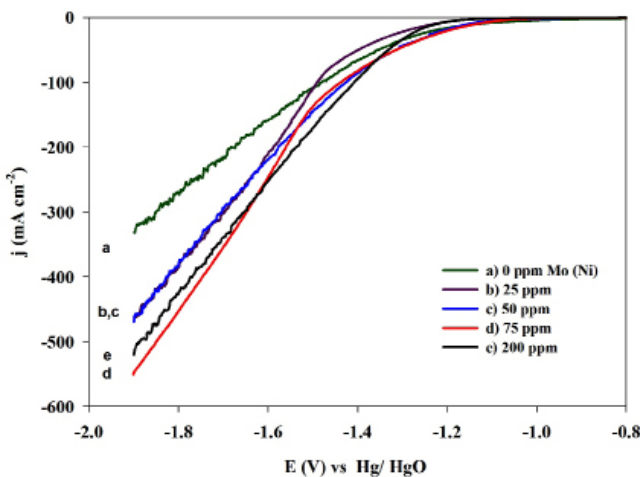


**Fig. 3. Polarization LSV curves of Ni catalyst at various concentrations of Mo ion in 1 M NaOH at 298 K.**
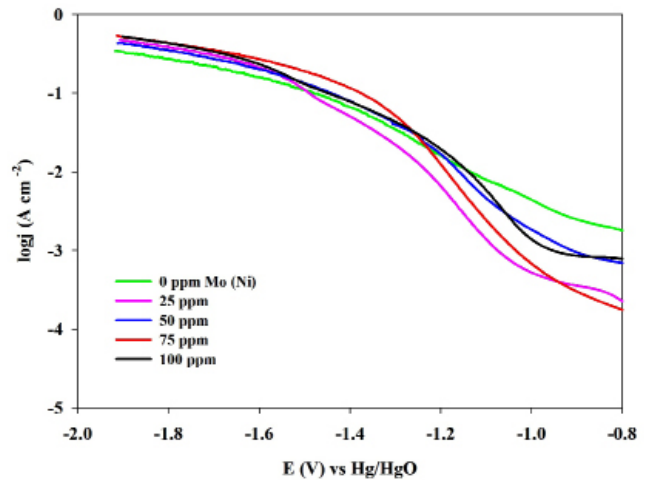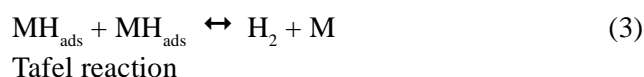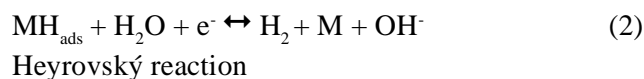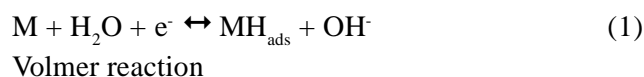


**Fig. 4. Polarization Tafel curves of Ni catalyst at various concentrations of Mo ion in 1 M NaOH at 298.**

**Table 1. HER Kinetic parameters for Ni catalyst obtained from polarization Tafel curves in 1 M NaOH at 298 K in presence of various concentrations of Mo**

| Concentration of Mo (ppm) | -b (mV dec$^{-1}$) | -j$_0$ (×10$^{-3}$ A cm$^{-2}$) | -η$_{250}$ (mV) |
|---|---|---|---|
| 0 | 141 | 0.012 | 625 |
| 25 | 178 | 0.042 | 511 |
| 50 | 170 | 0.044 | 508 |
| 75 | 172 | 0.071 | 482 |
| 100 | 177 | 0.064 | 498 |

Furthermore, the value $\eta_{250}$ decreased about 30 mV as the Mo ion concentration increased from 25 to 75 ppm. However, increasing the concentration of Mo ion higher than 75 ppm (for example: 100 ppm in Fig. 4), stopped the increase of the HER activity for the Ni catalyst. These results were in good agreement with the SEM-EDS observations (Fig. 1 and 2) and predict that Ni surface active sites for the HER were saturated with Mo ions at its concentration of 75 ppm. However, beside the similar morphology for Ni catalyst (Fig. 1) in the absence (a) and presence (b) of 75 ppm Mo ion in 1 M NaOH at 298 K, from this behavior we can conclude that the observed electrocatalytic activity is mainly originating from the synergetic effect of Ni and adsorbed Mo. Similar results were observed for electrodeposited bi metallic Ni Mo alloys [17]. A Tafel slope can be

used to interpret the mechanism of the HER on the investigated catalyst. It was thought  that the HER would performed in the alkaline solution by (1) a first electro sorption proton discharge step or Volmer reaction, and then (2) an electro desorption step or Heyrovský reaction or a chemical desorption step or (3) Tafel reaction (3) [7,18]:

$$M + H_2O + e^- \leftrightarrow MH_{ads} + OH^- \qquad (1)$$
Volmer reaction

$$MH_{ads} + H_2O + e^- \leftrightarrow H_2 + M + OH^- \qquad (2)$$
Heyrovský reaction

$$MH_{ads} + MH_{ads} \leftrightarrow H_2 + M \qquad (3)$$
Tafel reaction

The linearity of the Tafel plots at negative potentials was observed (Fig. 4) for the Ni catalyst in the absence and presence of various concentrations of Mo ion and indicated that the HER proceeds via reactions of the Volmer and Heyrovský mechanism (neglecting the Tafel reaction) [19]. Furthermore, according to classical theory, if the Volmer reaction step is a rate determining step in the HER mechanism, the resulting Tafel curve should yield a slope of around 120 mV dec$^{-1}$ at 298 K. Also, if the Heyrovský or Tafel step is a rate determining step, the measured Tafel slope would yield a value of about 40 or 30 mV dec-1, respectively. It can be seen in Table 1 that the HER electrocatalytic activity of the investigated catalyst increased in the presence of Mo, and  the b parameter for the investigated catalyst in the presence of various concentrations of Mo ranged from 170 to 178 mV dec$^{-1}$ indicating that the charge transfer reaction (Volmer step) is the rate determining step [16,20].

### 3.2.2. EIS parameters

The HER electrocatalytic performance of the Ni catalyst in the absence and presence of a Mo ion in the electrolyte was also analyzed using the EIS technique. EIS measurements were carried out in the potential range corresponding to the linear part of the Tafel curves (Fig. 4) at different overpotentials. Typical Nyquist plots of a Ni catalyst in the absence (a) and presence of 75 ppm of Mo (b) at different overpotentials are shown in Fig. 5. It can be seen that only one semi circle was found for all studied systems over the explored frequency range and all investigated overpotentials, thereby indicating that the charge transfer process was the principal reaction on the catalyst surface [21,22].
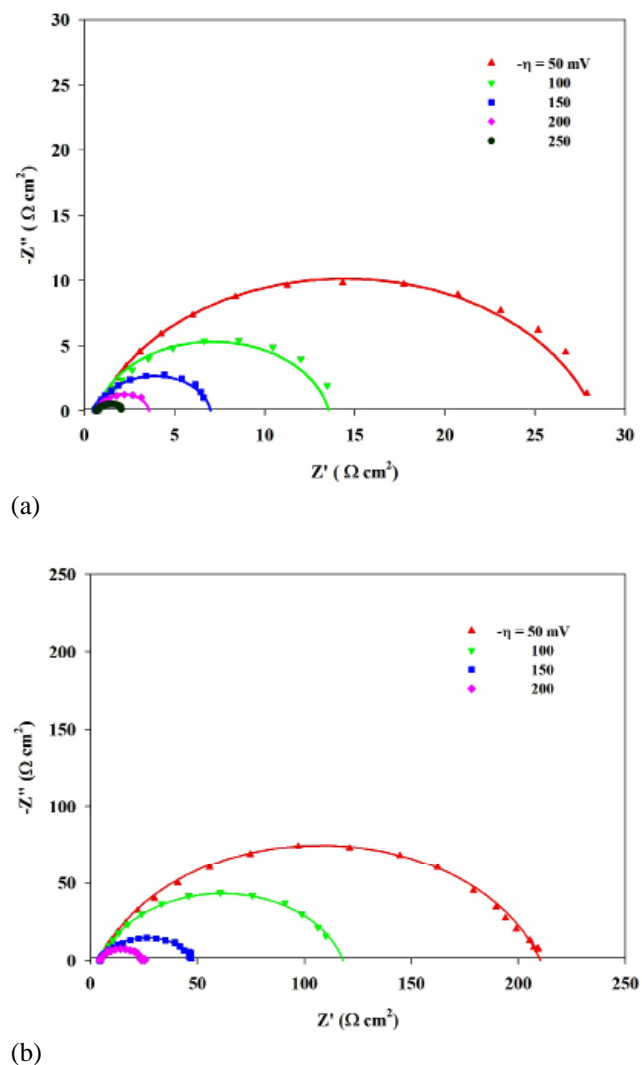


(a)



(b)

**Fig. 5. Nyquist plots for Ni catalyst in the absence (a) and presence of 75 ppm Mo (b) in 1 M NaOH at various overpotentials (η) and 298 K; Symbols indicate experimental results and solid lines approximated data obtained using one-CPE model and CNLS.**

These data were modeled using Randles electrical equivalent circuit, Fig. 6, which includes the solution resistance ($R_s$) in series with the charge transfer resistance ($R_{ct}$) of the HER, which is in parallel connection with the constant phase element (CPE) in a place of capacitance [23]. The impedance of CPE is given as [24]:

$$Z_{CPE} = 1/ [T (j\omega)^{\varphi}] \qquad (4)$$

The capacitance parameter (T) is related to the average double layer capacitance ($C_{dl}$) by the relation:

$$T = C_{dl}^{\varphi}/ (R_s^{-1} + R_{ct}^{-1})^{(1-\varphi)} \qquad (5)$$

Where $j = (-1)^{\frac{1}{2}}$, $\omega$ is the singular frequency ($\omega = 2\pi f$), dispersion parameter $\varphi$ is a parameter related to the CPE model (the value of $\varphi$ changes between zero to one, and is equal to one for a completely smooth electrode, i.e. for $\varphi = 1$, $T = C_{dl}$) and T is the capacity parameter which can be obtained by fitting of experimental impedance data using ZView software. Determination of the precise number of active sites per unit of surface area is a difficult task; [25] however, comparing values of 20 µF cm$^{-2}$, assumed for a double layer capacitance of a smooth electrode [26], and the Cdl of the objective electrode is a suitable method to approximate surface roughness:

$$R_f = C_{dl}/20 \text{ µF cm}^{-2} \qquad (6)$$

These EIS parameters are shown in Table 2. As can seen in this table, the value of Rct decreased about 7 times from 0 to 75 ppm Mo ion in the alkaline solution. Also in good agreement with the SEM results, the values of Rf are small and almost similar for all investigated systems.
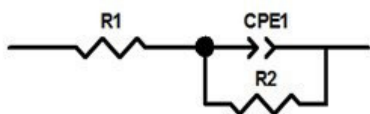
**Table 2. The HER Kinetic parameters for Ni catalyst obtained from the EIS experiments in the in 1 M NaOH at 298 K in presence of various concentrations of Mo at η = 250 mV**

| Concentration of Mo (ppm) | $R_s$ | $R_{ct}$ | $^a\varphi$ | $C_{dl}$ (mF cm$^{-2}$) | $R_f$ |
|---|---|---|---|---|---|
| 0 | 1.21 | 21.1 | 0.91 | 0.85 | 42.5 |
| 25 | 0.75 | 3.1 | 0.85 | 1.31 | 65.2 |
| 50 | 0.72 | 3.3 | 0.84 | 1.38 | 69.1 |
| 75 | 0.71 | 3.3 | 0.81 | 1.52 | 76.1 |
| 100 | 0.71 | 3.2 | 0.82 | 1.58 | 79.3 |

[a] Dispersion parameter related to CPE model

These results reveal that the HER electrocatalytic activity of the Ni catalyst was improved in the presence of a Mo ion and the source of this activity originated especially from synergetic effects. Additionally, a linear variation was observed for log ($1/R_{ct}$) as a function of η for the Ni catalyst in the absence and presence of 75 ppm of Mo ion in 1 M NaOH at 298 K with the slope 142 and 168 mV dec$^{-1}$, respectively (Fig. 7). These values are in good agreement with their respective values obtained from Tafel slopes 141 and 172 mV dec$^{-1}$, respectively, for concentrations of 0 and 75 ppm Mo ion; Fig. 4 and Table 1 and predict the Volmer–Heyrovský reaction mechanism [16,17] for a in situ activated Ni catalyst with Mo.
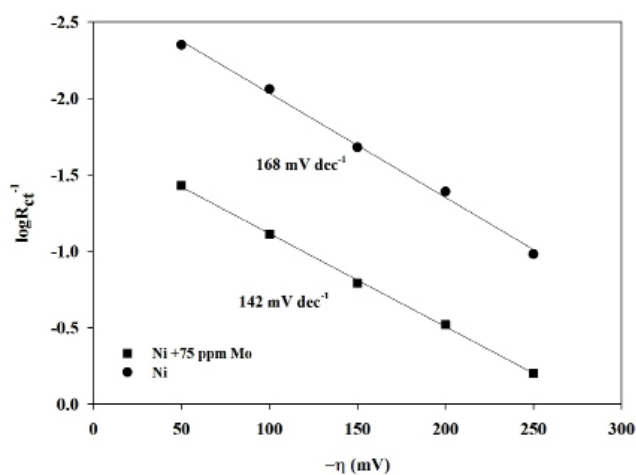


**Fig. 6. Equivalent circuit used for approximation of the EIS data: one-CPE model.**



**Fig. 7. Dependence of Cdl in various overpotential for Ni catalyst in the absence and presence of in Mo.**

All results of the electrochemical observations include LSV, polarization Tafel curves and EIS measurements and reveal that the high electrocatalytic activity of the investigated catalyst mainly originated from an increase in intrinsic activity of Ni and adsorbed Mo via in situ activation of Ni by the Mo ions activator in 1 M NaOH.

## 4. Conclusions

The electrocatalytic activity of a Ni catalyst increased significantly in the presence of a Mo ion as an in situ activator agent in 1 M NaOH. The linearity of the polarization Tafel curves at negative potentials was observed for the Ni catalyst in the absence and presence of various concentrations of Mo and revealed that the HER proceeds via reactions of the Volmer and Heyrovský mechanism with the Volmer reaction as the rate determining step. This result was in good agreement with the EIS experiments results. The highest electrocatalytic activity was observed at 75 ppm Mo in an alkaline solution. The Ni catalyst modified with an Mo activator agent was characterized by a Tafel slope: b (170 mV dec$^{-1}$), exchange current density: $j_0$ ($0.07 \times 10^{-3}$ A cm$^{-2}$), overpotential at the current density of 250 mA cm$^2$: $\eta_{250}$ (-482 mV), charge transfer resistance: $R_{ct}$ (3.3 $\Omega$ cm$^2$) and double layer capacitance: $C_{dl}$ (1.52 mFcm$^2$) at 298K.

## Acknowledgement

## 5.References

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