Galvanostatically Deposited PtNi Thin-Films as Electrocatalysts for the Hydrogen Evolution Reaction

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The synthesis of hybrid platinum materials is fundamental to enable alkaline water electrolysis for cost-effective H₂ generation. In this work, we have used a galvanostatic method to co-deposit PtNi films onto polycrystalline gold. The surface concentrations of Ni (Γₙ) and Pt (Γₚ) were calculated from electrochemical measurements; the Γₚ/Γₙ ratio and electrocatalytic activity of these materials towards hydrogen evolution reaction (HER) in 1 M KOH show a strong dependence on the current density pulse applied during the electrodeposition. Analysis of the Tafel parameters hints that, on these deposits, HER proceeds through a Volmer-Heyrovsky mechanism. The galvanostatically deposited PtNi layers present a high current output per Pt gram, 3199 A g⁻¹, which is significantly larger compared to other PtNi-based materials obtained by more extended and more complex synthesis methods.

Introduction

The need to phase out fossil fuels to minimize global warming has led to the search for alternative energy carriers and energy storage systems. Among them, molecular hydrogen stands out as an abundant and carbon neutral. Although water splitting is a cleaner method for H₂ production, [3,4] current density pulse applied during the electrodeposition. In alkaline media, HER involves two stages: first, the dissociation of water or Volmer step [Eq. (1)]:

\[
\text{H}_2\text{O} + e^- \leftrightarrow \text{H}_2 \text{ad} + \text{OH}^- \quad \text{Volmer}
\]  

followed by the recombination of adsorbed hydrogen atoms, H₂ad which occurs via the Heyrovsky or the Tafel step [Eq. (2 and 3)]:

\[
\text{H}_2\text{O} + \text{H}_2\text{ad} + e^- \leftrightarrow \text{H}_2 + \text{OH}^- \quad \text{Heyrovsky}
\]

\[
2\text{H}_2\text{ad} \leftrightarrow \text{H}_2 \quad \text{Tafel}
\]

Noble metals like Pt owe their high catalytic activity for HER to their affinity for hydrogen adsorption and to facilitate H₂ production. [5] In alkaline media, HER involves two stages: first, the dissociation of water or Volmer step [Eq. (1)]:

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Most of these materials are generally synthesized by solvothermal methods that involve many steps and can take several hours. In contrast, electrochemical deposition is a fast and straightforward method that allows high control over the deposits’ morphology. Our group has led to the search for alternative energy carriers and energy storage systems. Among them, molecular hydrogen stands out as an abundant and carbon neutral. Although water splitting is a cleaner method for H₂ production, [3,4] current density pulse applied during the electrodeposition. Analysis of the Tafel parameters hints that, on these deposits, HER proceeds through a Volmer-Heyrovsky mechanism. The galvanostatically deposited PtNi layers present a high current output per Pt gram, 3199 A g⁻¹, which is significantly larger compared to other PtNi-based materials obtained by more extended and more complex synthesis methods.

Water splitting comprises two half-reactions: the oxygen evolution reaction (OER) at the anode and the hydrogen evolution reaction (HER) at the cathode. The leading electrolysers for low-temperature water splitting are proton exchange membrane (PEM) and alkaline; in both cases, Pt, a scarce and expensive metal, has the highest electrocatalytic activity for HER, among the pure metals. HER kinetics is significantly faster in acidic media than in alkaline media, making PEM electrolysers efficient but expensive devices. However, alkaline electrolysers present higher durability and, because alkaline media enables the use of non-noble metals as catalysts, lower prizes. [5] In alkaline media, HER involves two stages: first, the dissociation of water or Volmer step [Eq. (1)]:

\[
\text{H}_2\text{O} + e^- \leftrightarrow \text{H}_2 \text{ad} + \text{OH}^- \quad \text{Volmer}
\]

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\]

\[
2\text{H}_2\text{ad} \leftrightarrow \text{H}_2 \quad \text{Tafel}
\]

Materials that combine Pt and Ni in different compositions have exhibited an excellent catalytic activity for HER, such as Pt–Ni nanowires[10] Ni(OH)₂-modified Pt electrodes,[20] PtNi nanoparticles,[14,21,22] PtNi nanodendrites,[23] and PtNi-O nanostructures.[24] Most of these materials are generally synthesized by solvothermal methods that involve many steps and can take several hours. [14,15,24] In contrast, electrochemical deposition is a fast and straightforward method that allows high control over the deposits’ morphology. Our group has led to the search for alternative energy carriers and energy storage systems. Among them, molecular hydrogen stands out as an abundant and carbon neutral. Although water splitting is a cleaner method for H₂ production, [3,4] current density pulse applied during the electrodeposition. Analysis of the Tafel parameters hints that, on these deposits, HER proceeds through a Volmer-Heyrovsky mechanism. The galvanostatically deposited PtNi layers present a high current output per Pt gram, 3199 A g⁻¹, which is significantly larger compared to other PtNi-based materials obtained by more extended and more complex synthesis methods.

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Supporting information for this article is available on the WWW under https://doi.org/10.1002/open.202100241

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ChemistryOpen 2022, 11, e202100241 (1 of 7) © 2022 The Authors. Published by Wiley-VCH GmbH
previously used single-pulse galvanostatic electrodeposition to 
generate Ni thin-layers on a Au electrode; the Ni deposits 
hibit high catalytic activity for methanol electro-oxidation.\(^\text{[25]}\) 
The same methodology can be used to obtain NiMo deposits 
with HER activity in acidic media.\(^\text{[26]}\) Herein we report a 
-systematic study on the influence of the applied current 
density on the PtNi deposit’s activity and surface composition for HER 
in alkaline media.

## Results and Discussion

### PNi Electrodeposition

Subjecting the working electrode to constant current results in 
a fast polarization until a potential value at which the charge 
transfer demand can be satisfied by a redox reaction is reached.
For an outer-sphere electrochemical reaction, once this 
 happens, the polarization slows down until diffusion of the electro-
active species becomes insufficient to maintain the current, 
which prompts a polarization towards a more negative 
potential. Sand’s equation gives an estimate of the character-
stics of a diffusion-controlled process (Eq. (4)):

\[
\tau^{1/2} = \frac{nF(Dc^*)^{1/2}c^*}{2j}
\]

(4)

where \(n\) is the number of transferred electrons, \(F\) is the Faraday 
constant, \(j\) is the applied current density, \(D\) is the diffusion 
coefficient, and \(c^*\) the bulk concentration of the electroactive 
species, respectively.\(^\text{[28]}\)

This behavior is not observed when reducing the electro-
active species results in a new phase, like in electrodeposition.
First, the electrode polarizes, passing through a minimum 
potential value; during this stage, the nuclei of the elec-
deposited phase are formed. Then, the potential recovers to 
the bulk concentration of the electroactive species, 
respectively.\(^\text{[28]}\)

Increasing \(j_{dep}\) shifts the electrode’s potential towards more 
negative values and shortens the duration of the time domains,
as can be seen in Figure 1b. Region IV can only be observed at 
current density values higher than 4 mA cm\(^{-2}\).

Lin-Cai et al.\(^\text{[33]}\) studied Pt electrodeposition from \([PtCl_4]^{2-}\) by 
cyclic voltammetry on gold and glassy carbon from a 10 mM 
\([PtCl_4]^{2-} + 50 \text{ mM NiSO}_4 + 500 \text{ mM NaCl, pH} = 2.0\). They observed a wave positive to the 
Pt(II)/Pt peak around \(-0.40 \text{ V versus RHE}\); this feature was not 
observed for Pt electrodeposition on glassy carbon. The authors 
suggest that this wave corresponds to an initial Pt monolayer’s 
formation before the onset of bulk Pt electrodeposition. Liu et al.\(^\text{[34]}\) 
observed a similar wave between \(-0.49 \text{ V and} -0.24 \text{ V versus RHE}\) during the electrodeposition of Pt on gold 
by linear sweep voltammetry.

Electrochemical quartz crystal microbalance (EQCM) 
measurements performed during the electrodeposition showed 
that this wave is concomitant to a mass increment, suggesting that 
it is caused by Pt deposition. This pre-wave is located within 
Region I’s potential window while Region II coincides with the 
location main Pt deposition peaks observed during cyclic 
voltammetry. No nucleation minima were observed in regions I 
and II; however, the potentials reached in region II favor Pt 
electrodeposition. The galvanostatic deposition of Pt was 
carried out on glassy carbon and on a 50 nm thick vapor 
deposited Au sputtered on a Si wafer. Using a plating solution 
of 1.5 mM \(K_2[PtCl_4]\) and \(\text{pH} = 2.0\), and a \(j_{dep}\) of 4.0 mA cm\(^{-2}\), 
the resulting curves show that deposition on glassy carbon requires 
larger polarization compared to Au (see Figure S1). Further-
more, while both potential transients exhibit the expected deposition minima, in the Au/Si electrode is less evident. The difference between the minimum potential reached during the nucleation stage and the stabilization potential for this electrode is 124 mV, while for the glassy carbon electrode is 200 mV. The galvanostatic deposition proceeds at low overpotentials suggesting the high affinity of Pt for Au, which leads to barely noticeable deposition minimum, as observed for PtNi electrodeposition.

Region III starts well below the Nernst potential for Ni\(^{2+}\) reduction, which suggests that this is the active process in this region. As can be observed in Figure 1b inset, the shape of the potential transient in region II changes as the \(I_{\text{dep}}\) is increased, revealing the characteristic nucleation minimum.\(^{[29,30]}\) It has been reported that water reduction (reaction 9) occurs simultaneously to Ni\(^{2+}\) reduction and may play a role in \(I_{\text{dep}}\); thus, it is plausible that it also takes place in region III. Finally, region IV can be assigned mainly to water reduction, which may proceed once proton reduction is finished.

Figure 1c shows the voltammograms of a PtNi deposit generated at 8 mA cm\(^{-2}\) in 1 M KOH. Peaks \(I_{\text{a}}\) and \(I_{\text{bc}}\) correspond to the formation and reduction of NiOOH according to Equation (9);\(^{[38,39]}\) thus confirming the presence of Ni on the deposit:

\[
\text{Ni(OH)}_2 + \text{OH}^- \rightarrow \text{NiOOH} + e^-
\] (9)

Figure 1d presents the voltammograms obtained in 50 mM H\(_2\)SO\(_4\) before (dashed line) and after (solid line) the electrodeposition experiment. Peak \(I_{\text{bc}}\) corresponds to the reduction of a gold oxide monolayer formed during the anodic scan. After the electrodeposition stage, the gold features are no longer observed and are replaced by those of Pt, that is, an earlier onset of oxide formation and oxygen evolution, a more cathodic reduction peak \(I_{\text{ib}}\), and the characteristic hydrogen adsorption and desorption peaks \(I_{\text{ha}}\), \(I_{\text{ad}}\), \(I_{\text{ib}}\), and \(I_{\text{bc}}\). Peak \(I_{\text{bc}}\) is still visible, although diminished, after the electrodeposition, indicating that a small fraction of the gold’s surface is still exposed. For all applied currents, the presence of Ni and Pt was electrochemically confirmed.

SEM inspection of a deposit generated using an 8.0 mA cm\(^{-2}\) pulse (Figure 2a) shows no evidence of distinguishable particle formation indicating a layered deposit. Energy-dispersive X-ray (EDX) mapping analysis revealed Ni’s presence on the whole electrode surface (Figure 2b and 2c). Pt content on the deposit could not be determined by this method due to the proximity between the Pt and Au signals.

The surface composition of the PtNi deposits can be estimated from the electrochemical data in the voltammograms. The surface concentration of Ni (\(\Gamma_{\text{Ni}}\)) can be extracted from the area under the peak \(I_{\text{bc}}\) \(Q\) (Figure 1c) with the following formula (Eq. 10):

\[
\Gamma_{\text{Ni}} = \frac{Q}{nF A_{\text{geo}}} \quad \text{[mol/cm]} \quad (10)
\]

The available Pt surface area can be computed using Equation (11):

\[
\text{ECSA} = \frac{Q_{\text{red}}}{Q_{\text{Pt}}} \quad (11)
\]

where \(Q_{\text{red}}\) is the average charge of the adsorption (\(I_{\text{ha}}\), \(I_{\text{ib}}\)) and desorption (\(I_{\text{ad}}\), \(I_{\text{bc}}\)) peaks, and \(Q_{\text{Pt}}\) is the charge associated with the formation or desorption of a H\(_2\) monolayer per square centimeter \((210 \times 10^{-6} \text{ C cm}^{-2})\). Considering that the surface atom density for Pt is \(1.31 \times 10^{15} \text{ cm}^{-2}\);\(^{[27]}\) the active Pt surface concentration can be estimated by [Eq. (12)]:

\[
\Gamma_{\text{Pt}} = \frac{A_{\text{Pt}} \rho}{N_A A_{\text{geo}}} \quad \text{[mol/cm]} \quad (12)
\]

where \(A_{\text{Pt}}\) is the Pt surface area, \(\rho\) is the surface atom density, and \(N_A\) is Avogadro’s number. Table 1 shows that for all the applied deposition current pulses, the surface concentration of Pt is more than an order of magnitude larger than Ni. Deposition at \(I_{\text{dep}} = 8.0 \times 10^{-3} \text{ A cm}^{-2}\) was performed on an Au/Si electrode. This sample was subjected to an XPS depth profiling test. The results, shown in Figure S2, suggest that the deposit is richer in Pt than in Ni, agreeing with the electrochemical estimations.

| Table 1. Surface composition of the PtNi deposits for all cathodic current densities studied was determined from electrochemical measurements. |
| --- | --- | --- |
| \(I_{\text{dep}}\) | \(\Gamma_{\text{Ni}}/10^{-5}\) \text{[mol/cm]²} | \(\Gamma_{\text{Pt}}/10^{-4}\) \text{[mol/cm]²} |
| 2.0 \times 10^{-3} | 0.06 | 4.52 |
| 4.0 \times 10^{-3} | 0.69 | 6.15 |
| 6.0 \times 10^{-3} | 0.41 | 6.85 |
| 8.0 \times 10^{-3} | 0.39 | 7.72 |
| 10.0 \times 10^{-3} | 0.89 | 6.25 |

The experimental $\tau$ for Pt averaged from three measurements, and the theoretical values are tabulated in Table 2. These transition times were estimated under the assumption that Pt electrodeposition occurs during regions I and II. There is a good agreement between the theoretical and experimental $\tau_{\text{Ni}}$ (see Table 2); the latter were calculated using a diffusion coefficient of $2.2 \times 10^{-6}$ cm$^2$ s$^{-1}$ and $j$ normalized to the Au ECSA. This suggests that for Pt deposition, the roughness of the Au electrode plays an important role in defining the diffusion field, even at a time scale of hundreds of milliseconds, and that this process is limited by diffusion.

The experimental $\tau_{\text{Ni}}$ shown in Table S1 (Supporting Information), were estimated assuming that Ni deposition occurs during region III; values for the 2 and 4 mA cm$^{-2}$ pulses could not be determined since these experiments did not last long enough to observe the end of region III. For the remaining pulses, $\tau_{\text{Ni}}$ shows a large variation between repetitions. The theoretical transition times were computed assuming a diffusion coefficient of $4 \times 10^{-6}$ cm$^2$ s$^{-1}$ and normalizing the applied current to geometric area since the transition times are long enough to disregard roughness effects on the diffusion field.

In all cases, the experimental $\tau_{\text{Ni}}$ is significantly longer than the theoretical prediction. This behavior could be attributed to hydrogen evolution from the reduction of protons, which takes place in the same potential range of Ni deposition; Figure S3a shows how decreasing the pH from 6 to 2 expands the transition time for Ni deposition, most likely because reactions 7 and 8 occur simultaneously. Increasing the pH of the PtNi plating solution leads to a significant increase in the NiOOH formation of a 0.25 nm thick monolayer, which is terminated after the first second of electrodeposition by the adsorption of H. A similar self-termination process was observed by Liu et al.\textsuperscript{[34]} for Ni electrodeposition on Au by potential pulses negative to the hydrogen evolution onset, the roughness of the Au electrode plays an important role in defining the diffusion field, even at a time scale of hundreds of milliseconds, and that this process is limited by diffusion.

Liu et al.\textsuperscript{[34]} reported that for the electrodeposition of Pt thin-films on gold under potentiostatic control, in which a polarization of $-0.159$ V versus RHE led to the formation of a 33 nm thick layer after 500 s, while a $-0.559$ V versus RHE results on the formation of a 0.25 nm thick monolayer, which is terminated after the first second of electrodeposition by the adsorption of H. A similar self-termination process was observed by Wang et al.\textsuperscript{[40]} for Ni electrodeposition on Au by potential pulses negative to the hydrogen evolution onset, the formation of Ni(OH)$_2$ due to a local pH rise inhibits further deposition resulting in a thin Ni layer. Applying a potential pulse of $-1.259$ V versus RHE would result in the formation of a 1 to 2 nm thick Ni layer, depending on the Ni$^{2+}$ concentration of the plating bath. Recently Salinas-Quezada et al.\textsuperscript{[35]} showed that galvanostatic electrodeposition on Ni on Au also leads to the formation of Ni thin-layers.

XPS depth profile analysis of the PtNi deposits formed on the Au/Si samples suggests that the PtNi deposits have a 20 nm thickness. The SEM images of these samples are shown in Figures S4a and S4b. Since the applied charge is the same, and SEM images of both deposits are similar, it can be inferred that a similar thin layer is formed on the Au disk electrodes. Self-termination favors the formation of thin films; however, this cannot be confirmed from the chronopotentiometric data since the reduction of protons does not allow to pinpoint the end of Ni deposition. It is unlikely that Pt self-termination occurred during the PtNi deposition experiments since the experimental transition times are relatively close to the ones predicted by Sand’s equation, indicating that the deposition was diffusion limited. However, due to the negative potentials reached during the experiments, the deposited Pt could have been blocked by adsorbed hydrogen, preventing Ni deposition on it, which

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**Table 2.** Comparison between the $\tau_{\text{Ni}}$ values obtained experimentally, and those predicted by Sand’s equation (eqn.4) for all cathodic current densities studied.

| $J_{\text{app}}$ (A cm$^{-2}$) | Exp. $\tau_{\text{Ni}}$ (ms) | Theor. $\tau_{\text{Ni}}$ (ms) |
|-----------------------------|-----------------------------|-----------------------------|
| $2.0 \times 10^{-3}$        | $312 \pm 103$               | $362$                       |
| $4.0 \times 10^{-3}$        | $98 \pm 12$                 | $90$                        |
| $6.0 \times 10^{-3}$        | $46 \pm 14$                 | $40$                        |
| $8.0 \times 10^{-3}$        | $29 \pm 4$                  | $23$                        |
| $10.0 \times 10^{-3}$       | $19 \pm 1$                  | $14$                        |

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Figure 3. a) Polarization curves in 1 M KOH at 5 mA cm$^{-2}$ of gPtNi/Au materials generated at different currents. Pt deposited at 8 mA cm$^{-2}$ is included b) dependences of $\eta$ on $J_{\text{app}}$ and $J$ on the applied deposition current densities. Pt$_{x}$Ni$_{(1-x)}$ proportions are calculated from the ratios of the areas $J_{\text{app}}$; $\Gamma_{\text{Ni}}$ c) Tafel slopes of the materials deposited at different current densities.
would account for the high Pt surface concentration; however, contributions of surface segregation cannot be discarded.

The SEM, EDX mapping, and electrochemical characterizations suggest that galvanostatic electrodeposition on gold leads to the formation of thin-films PtNi, with both species present on the deposit’s surface.

**HER Electrocatalysis**

The linear sweep voltammograms (LSV) of the galvanostatically deposited PtNi materials (G-PtNi/Au) generated at different \( j_{\text{dep}} \) values are shown in Figure 3a. The LSV curves current was normalized to the electrode’s geometric area, and their electrocatalytic performance was evaluated by the overpotential required to reach 10 mA cm\(^{-2} \), \( \eta_{10} \). The material deposited at 8 mA cm\(^{-2} \) exhibits the lowest overpotential, 64 mV, while the highest overpotential value was 77 mV, which corresponds to the 2 mA cm\(^{-2} \) deposit. For comparison, the black line corresponds to a Pt deposit generated at 8 mA cm\(^{-2} \) in an electrochemical bath containing a similar composition to the PtNi one (1.5 mM K\(_2\)PtCl\(_4\) : 500 mM NaCl \( \phi_{\text{H}} = 2.0 \)). The inferior catalytic activity makes it evident that, despite the high Pt surface concentration of the PtNi deposits, the presence of Ni has an impact on their performance.

Figure 3b shows the dependence of the averaged observed overpotential at 10 mA cm\(^{-2} \) (\( \eta_{10} \)), on the ratio the \( \Gamma_{\text{Pt}}:\Gamma_{\text{Ni}} \) ratio, the \( j_{\text{dep}} \) values are written next to the corresponding points.

The value of the current density \( j_{\text{dep}} \) seems to have an important effect on the \( \Gamma_{\text{Pt}}:\Gamma_{\text{Ni}} \) ratio, with pulses of 2, 4, and 10 mA cm\(^{-2} \) generation deposits with ratios smaller than 10, while pulses of 6 and 8 mA cm\(^{-2} \) generate deposits with ratios higher than 13. The latter pulses are the ones that exhibit the lowest overpotential, which suggests that the Pt \( \Gamma_{\text{Pt}}:\Gamma_{\text{Ni}} \) ratio has high importance on the catalytic activity of the deposits, and that values between 6 and 8 mA cm\(^{-2} \) yield deposits with a \( \Gamma_{\text{Pt}}:\Gamma_{\text{Ni}} \) ratio that significantly enhances the activity of the materials for HER.

For all the LSV data, the Tafel plots exhibit two regions (see Figure 3c), one from 0 to –50 mV and another one from –90 to –116 mV. The Tafel slopes of both regions are presented in Table 3; values are around 35 mV dec\(^{-1} \) for the first slope and 100 mV dec\(^{-1} \) for the second and are almost independent of \( j_{\text{dep}} \) suggesting that the hydrogen evolution process follows the same pathway on all the PtNi deposits produced. This behavior is similar to the one reported by Shinagawa et al\(^{[24]} \) for simulations in which Heyrovský’s reaction was the limiting step, the resulting Tafel plots exhibited two slopes: 40 mV dec\(^{-1} \) at low overpotentials and \( \text{H}_2 \) coverage, and 120 mV dec\(^{-1} \) at high overpotentials and \( \text{H}_2 \) coverage; thus, it is probable that this is the dominant mechanism for HER on the G-PtNi/Au deposits.

As can be seen in Table 4, the material with the best catalytic properties in this work has a \( \eta_{10} \) value comparable to the hcp Pt–Ni nano-multipods reported by Cao et al\(^{[41]} \); however, it is 25 mV higher than the lowest values reported by Xie et al\(^{[21]} \) and Zhao et al\(^{[24]} \).

The mass current density, \( j_{\text{m}} \), at an overpotential of 38 mV was also used as an efficiency criterion. To obtain this value, the current was normalized to the Pt mass of the galvanostatically generated deposits, which was estimated using Faraday’s law (Eq. (13)):

\[
g_{\text{Pt}} = \frac{j_{\text{dep}} \tau_{\text{Pt}} m}{nF} \tag{13}
\]

where \( g_{\text{Pt}} \) is the Pt mass in grams, \( j_{\text{dep}} \) is the applied deposition current, \( \tau_{\text{Pt}} \) is the Pt deposition time (taken from Table 2), and \( m \) is the atomic mass of Pt. For comparison’s sake, an extreme scenario was considered in which Pt deposition proceeded at 100% efficiency during the two seconds the chronopotentiometry experiment lasted. The \( j_{\text{m}} \) at a 38 mV overpotential of this case is labeled “Pt max” in Table 3. Under this efficiency criterion, the catalytic activity of the PtNi deposited at 8.0 mA cm\(^{-2} \) is far superior to the material that exhibits lower \( \eta_{10} \) values. Even in this extreme scenario, the activity of the G-

### Table 3. Tafel slopes of G-PtNi/Au generated at different \( j_{\text{dep}} \) values.

| Head \( j_{\text{dep}} \) \( [\text{mA} \text{cm}^{-2}] \) | First Tafel Slope \( [\text{mV} \text{dec}^{-1}] \) | Second Tafel Slope \( [\text{mV} \text{dec}^{-1}] \) |
|---------------------------------|-----------------|------------------|
| 2.0 \( \times \) 10\(^{-1} \) | 35.0 \pm 1.4 | 98.8 \pm 1.1 |
| 4.0 \( \times \) 10\(^{-1} \) | 34.3 \pm 0.3 | 68.5 \pm 0.7 |
| 6.0 \( \times \) 10\(^{-1} \) | 34.7 \pm 0.2 | 95.4 \pm 1.0 |
| 8.0 \( \times \) 10\(^{-1} \) | 35.1 \pm 0.4 | 97.9 \pm 1.1 |
| 10.0 \( \times \) 10\(^{-1} \) | 38.9 \pm 0.3 | 100.6 \pm 1.2 |

### Table 4. Comparison of the galvanostatically deposited G-PtNi/Au with other PtNi material with high HER activity.

| Material | \( \eta_{10} \) [mV] | \( j_{m} \) at \( \eta = 38 \) [mVAg\(_{\text{Pt}}^{-1}\)] | Tafel slope \( [\text{mVdec}^{-1}] \) | Ref. |
|----------|-----------------|-----------------|-----------------|-----|
| G-PtNi/Au | 63 | 3485 | 35.1 \pm 0.4 | This work |
| 8.0 mA cm\(^{-2} \) | 51 (Pt max) | | | |
| PtNi–Ni Na/C/C\(^{[22]} \) | 38 | 144 | 57.0 | [21] |
| Pt/C\(^{[22]} \) | 51 | 34.4 | 42.0 | [23] |
| PtNi NDs\(^{[22]} \) | 45 | 6.48 | 52.0 | [24] |
| hcp Pt–Ni nano-multipods\(^{[22]} \) | 65 | 1080 | 74.0 | [42] |
| PtNi NWs/C\(^{[22]} \) | 50 | 320 | N.A. | [10] |
| Pt@2D–Ni(OH)\(_{2}\)\(^{[22]} \) | 186 | 858 | 72.0 | [43] |
| PtNi–O\(_{2}\)\(^{[22]} \) | 38.9 | 1740 | 78.8 | [24] |
| Pt\(_{3}2\)Ni@Ti\(_{2}\)C\(_{3}\)\(^{[22]} \) | 55.6 | 39.5 | 39.5 | [44] |

Electrolyte concentration: KOH [a] 1 M [b] 0.5 M [c] 0.1 M
PtNi/Au is higher than that for Pt/C. A comparison of the Tafel slopes also positions the G-PtNi/Au as the material with high catalytic activity. This shows that galvanostatic electrodeposition can be used to synthesize PtNi materials with high catalytic activity towards HER and low Pt loading. Additionally, the synthesis is simpler than the ones used in other works; it only comprises two steps (electrochemical cleaning of the substrate and electrodeposition) and can be finished in a fraction of the time required for other methods.

The high catalytic activity of the G-PtNi/Au deposits can first be attributed to the presence of Ni and Pt on their surface, which allows a tandem operation in which Ni cleaves the HO–H bond and the recombination step occurs on the Pt surface. The thickness deposits may also be playing an important role in their performance. Kibler showed that the number of Pd layers on Pd/Au(111) catalyst had an important impact on its catalytic activity for HER in acidic media.

It is important to stress the importance of galvanostatic control as the electrodeposition technique since it allows the working electrode to follow complex potential transients, conventional potential control techniques.

Conclusion

Galvanostatic electrodeposition was used to synthesize thin PtNi films onto gold electrodes. Thanks to this method, it was possible to obtain materials with a small Tafel slope, large $j_{\text{pa}}$ binder free, and with a synthesis time considerably shorter than other methods reported in the literature. The addition of small quantities of Ni was enough to significantly increase the activity of Pt. The magnitude of the deposition current density had a strong effect on $\gamma_{10}$ value, with the best catalyst being the one synthesized at 8.0 mA cm$^{-2}$. Tafel analysis suggests that HER on these materials follows a Volmer–Heyrovsky mechanism, regardless of the deposition current density.

Experimental Section

All glassware was cleaned by soaking it in 1 M KOH for 24 h and rinsing it with deionized water from an EASYpure II purification system (18.2 MΩ·cm). All the electrolytes were prepared with deionized water, H$_2$SO$_4$ (Fermont, ppb trace impurities), NiCl$_2$ (CTR Scientific), K$_2$[PtCl$_6$] (Sigma-Aldrich 98%), NaCl (CTR Scientific 99.9%), KOH (Sigma-Aldrich 90%) were used without additional purification. The electrolytes were saturated with N$_2$ before their use.

The working electrode was a gold disk with a 0.5 mm diameter fabricated by embedding a gold wire in epoxy resin, leaving a circular cross-section exposed with a geometrical area of 2.0 × 10$^{-2}$ cm$^2$. All the experiments were performed using a three-electrode single-compartment arrangement with a Pt coil as a counter electrode. The electrochemical cleaning and electrodeposition steps were done in a cylindrical glass cell; a cylindrical Teflon cell was used for the HER measurements and all experiments in which the electrolyte was 1 M KOH. The electrochemical cleaning and electrodeposition stages were performed with a Hg | H$_2$SO$_4$ sat. K$_2$SO$_4$ reference electrode (MMSE) [0.640 V vs. NHE] and the HER stage with a Ag | AgCl sat. KCl [0.222 V vs. NHE] reference electrode. The disk electrode was polished with alumina slurries of progressively smaller particle sizes (1, 0.3, and 0.1 μm) until a mirror finish was achieved. Subsequently, it was sonicated in acetone, isopropanol, methanol, and deionized water. The electrodes were then electrochemically cleaned in 50 mM H$_2$SO$_4$ (Fermont, ppb trace impurities) by repetitive cycling between −0.70 V and 1.06 V versus MMSE (−0.06 V and 1.70 V vs. RHE) at 0.10 V s$^{-1}$ until a stable voltammogram was obtained. Finally, a single cycle was run at 0.05 V s$^{-1}$ to compute the working electrode’s electroactive surface area (ECSA). In this case, the charge under the cathodic peak is divided by $Q_e$ (equation 11), which is the charge associated with the reduction of a gold oxide monolayer per square centimeter (390 × 10$^{-4}$ C cm$^{-2}$). The average surface area after 30 measurements was 6.7 ± 1.8 × 10$^{-5}$ cm$^2$, which translates into a roughness factor between 3 and 4.

Electrodeposition of PtNi. After electrochemically cleaning the working electrode, the electrolyte was replaced for the plating bath, a solution containing 50 mM NiCl$_2$ + 1.5 mM K$_2$[PtCl$_6$] + 500 mM NaCl, the pH 2.0 (adjusted with a 0.5 M H$_2$SO$_4$ solution), and bubbled with N$_2$ for 10 minutes. A galvanostatic pulse was applied through the working electrode; first, the electrode is held at the open-circuit voltage for 10 seconds as a stabilizing step, followed by a two-second deposition pulse. The magnitude of the latter was varied to study its effect on the electrocatalytic activity of the deposit. Since the current is an extensive property, the applied current density, $j_{\text{app}}$, was chosen as the control variable. The experimentally applied current was computed by multiplying the selected $j_{\text{app}}$ value by the ECSA previously determined.

Electrocatalytic Activity for HER. The electrocatalytic performance of the as-prepared deposits was tested in a 1 M KOH solution. The electrocatalyst was first cycled 30 times at 0.05 V s$^{-1}$ from 0 to −1.10 V versus Ag | AgCl as a conditioning step. Then, a 0.005 V s$^{-1}$ potential scan from −0.40 to −1.10 V versus Ag | AgCl was performed.

The presence of Ni in the deposit was confirmed by cyclic voltammetry by the oxidation and reduction processes observed between −0.60 and 0.55 V versus Ag | AgCl at 0.05 V s$^{-1}$ in 1 M KOH. Following this, the electrode was cycled in 50 mM H$_2$SO$_4$ between −0.70 V to 1.06 V versus MMSE at 0.05 V s$^{-1}$, to confirm Pt deposition through the adsorption of hydrogen on its surface.

A PtNi deposit was generated by applying an 8.0 mA cm$^{-2}$ pulse for two seconds. This deposit was examined by scanning electron microscopy (SEM) (Nova NanoSEM 200, FEI, Japan) equipped with EDX analysis (INCA X-Sight, OXFORD instruments, England) to confirm the formation of the PtNi deposit.

Acknowledgments

The authors express their gratitude to the School of Engineering and Sciences of Tecnologico de Monterrey for the postdoctoral fellowship granted to D.A.C.Y. and for the financial support received for the development of this research through the Research Chair of Photonics and Quantum Systems.

Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords: alkaline hydrogen evolution reaction · electrocatalysis · galvanostatic electrodeposition · platinum-nickel · water electrolysis

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