The role of glycine in the iron-phosphorous alloy electrodeposition

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A B S T R A C T

The influence of glycine on the iron phosphorous alloy electrodeposition was investigated by electrochemical quartz microbalance (EQMB), in-situ external reflection FTIR spectroscopy, and electrochemical impedance spectroscopy (EIS) measurements. An increase of glycine concentration leads to a decrease of the iron-phosphorous alloy electrodeposition rate and an increase of hydrogen evolution. Strong adsorption of glycine species, such as H2(gly)+, H(gly)+ or/and Fe(gly)2+, have been observed during the hydrogen evolution and the Fe-P deposition reaction. Due to the concurrent hydrogen evolution the pH attains higher values at the interface than in the electrolyte bulk (pH2.5). The formation of adsorbed Fe(gly)+ and of the chelate complex Fe(gly)2+ in solution avoids the precipitation of Fe(OH)2 in the pH range between 2.5 and ca. 7 at the interface. The phosphorous content of the iron phosphorous alloy deposit increases with the glycine concentration. This is due to a lower deposition rate of iron caused by the adsorption of Fe(gly)+, while the hypophosphate reduction rate to phosphorous increases.

1. Introduction

The addition of additives to electrochemical baths can strongly influence the electrodeposition of metal alloy coatings. Additives may modify the deposition mechanism, the morphology, microstructure, and physicochemical properties of the alloys. Recently, there has been enhanced interest in glycine as additive [1–5], such as in the plating of Fe [6], and of Ni-Mn alloys where the influence surface morphology and grain size was reported [7]. In the later system, the minimization of the grain size is important for nanocrystalline soft magnetic materials as well as for the increase of the corrosion resistance.

Glycine is a bidentate ligand that can coordinate via its amino and carboxyl groups forming homonuclear, binuclear and heteronuclear complexes with metal ions. A study of the formation of Fe ion complexes showed that the cationic form of glycine (NH2CH2COOH)+ is present together with the zwitterion (NH2CH2COO)2− for pH < 4.0. At pH > 4.0, it exists as the zwitterion, and at pH > 9.0, as the anion (NH2CH2COO)− [1].

The Fe-P coatings become interesting in metallic foam and battery anode deposition [8–10], in magnetic [11–14] and corrosion inhibition applications [15–17]. Moreover, high strength, hardness, relatively high electrical resistivity, and advantageous mechanical properties may be achieved [10].

Glycine is known as a buffer in order to stabilize baths (e.g. avoid Fe(OH)2 precipitation) due to its zwitterion form in the pH range of ca. 5–8 (pK≈ 2.3, pK≈ 9.6) [18,19]. It can also promote hydrogen evolution and thus lead to an increase of the phosphorous content in the coatings [20]. The formation and participation of Fe hydroxide species due to the pH increase caused by the concurrent hydrogen evolution during the Fe-Mo-P electrodeposition was repeatedly investigated.

The behaviour of glycine on gold electrodes was studied by in-situ IR spectroscopy [4,5,21]. It was shown that, during cobalt electrodeposition, the pH has a drastic influence on the glycine deprotonation and the formation of Co glycine complexes [4,5,21].

The detailed mechanism of Fe-P electrodeposition has received limited attention. In the present study, a mechanistic investigation of the influence of glycine on the Fe-P electrodeposition is presented applying in-situ techniques such as the Electrochemical Quartz Microbalance (EQMB), in-situ external reflection FTIR spectroscopy, and Electrochemical Impedance Spectroscopy (EIS).
2. Experimental

The electrolyte for the Fe-P electrodeposition consisted of 0.7 M FeSO₄·7H₂O, 0.06 M Na₂HPO₄·2H₂O, and NH₂CH₂CO₂H (glycine). The concentration of glycine was varied (0.10, 0.21, 0.32, 0.43, with a surface area of 2.25 cm²) were used as working electrodes for the deposition mechanism. Analytical grade chemicals and deionized water were used. The working pH range was chosen from 1 to 3 in order to prevent too strong hydrogen evolution or precipitation of Fe(OH). It was optimized at 2.5 by the addition of sulphuric acid. All measurements were carried out at room temperature.

Thermodynamic calculations for the chemical speciation diagrams were performed by a software (Medusa-Hydra chemical equilibrium software).

The Electrochemical Quartz Microbalance (EQMB) measurements were performed with a dedicated three-electrode cell with QMB working electrode (potentiostat: Autolab, PGSTAT equipped with an EQCM module). The gold surface was cleaned by cycling in 0.1 M H₂SO₄ solution. Frequency measurements were performed with a 6 MHz, AF-cut quartz crystal coated with a 100 nm thick gold layer (exposed area 0.394 cm²). A gold coil was used as a counter electrode and an Ag/AgCl/3 M KCl electrode as reference electrode (-0.21 V vs. standard hydrogen electrode, SHE) [22]. For better data evaluation, the potentials (U) are presented versus the SHE.

In-situ external reflection FTIR spectroscopy was performed with a FTIR spectrometer (Bruker Vertex 70). An external liquid-nitrogen cooled LN-MCT detector was employed. The beam delivery optics was positioned on an aluminium breadboard in a CO₂ and water-free air-flushed compartment. A conventional three-electrode setup (potentiostat: Electrochemical Workstation, CH-Instruments 760C) with a platinum wire as counter electrode and an Ag/AgCl/3 M KCl electrode as reference electrode (+0.21 V vs. SHE) were used. The working electrode was mounted on a glass tube precisely positioned relative to the ZnSe window by a micrometer head with a resolution of 1 μm [23]. The spectra were measured under p-polarization. The sampling time for each spec-trum was 25 s.

EIS measurements were carried out in a three-electrode cell (0.1 L) without stirring using an impedance spectroscopy setup (Autolab, PGST302 N combined with a R3A32 M module; Vilnius University). Brass (1 cm²) was used as a non-costly working electrode because only cathodic potentials were applied. Brass plates with a surface area of 2.25 cm² were used as working electrodes for the galvanostatic electrodeposition of Fe-P coatings. It was ultrasonically cleaned in 0.1 M sulphuric acid (5 min) before measurements. The reference electrode was Ag/AgCl 3 M KCl (+0.21 V vs. SHE).

The surfaces were characterised with a scanning electron microscope (Hitachi FEG-SEM S4800) and with EDX for elemental analysis.

3. Results and discussion

3.1. Fe-P glycine solution equilibria

Glycine, NH₂-CH₂-COOH or H(gly), is an amino acid and can exist as a zwitterion, NH₃⁺-CH₂-COO⁻ or H(gly)²⁺, subject to the following chemical equilibria (with logarithms of the stability constants (log K, ionic strength 1.0) in the iron-glycine system (data from Ref. [24]):

\[
\text{H(gly)²⁺} + H^+ = \text{H₂(gly)⁺} \quad (\log K = 12.1) \quad (1)
\]

\[
\text{H(gly)²⁺} + 2H^+ = \text{H}^{+} + \text{(gly)}^- \quad (\log K = 9.7). \quad (2)
\]

Eq. (1) corresponds to the carboxyl group protonation of the zwitterion H(gly)⁺ resulting in NH₃⁺-CH₂-COO⁻ or H₂(gly)⁺, and Eq. (2) corresponds to the amino group deprotonation leading to NH₂-CH₂-COO⁻ or (gly)⁻. This glycinate ion, (gly)⁻, is able to form five-member chelate rings with Fe²⁺ ions. Three complex species formed with Fe²⁺ predominate in solution depending on pH:

\[
\text{Fe}^{2+} + (\text{gly})^- \rightleftharpoons \text{Fe(gly)⁺}^- \quad (\log K = 4.31) \quad (3)
\]

\[
\text{Fe(gly)⁺}^- + (\text{gly})^- \rightleftharpoons \text{Fe(gly)₂}^- \quad (\log K = 8.32) \quad (4)
\]

\[
\text{Fe(gly)₂}^- + (\text{gly})^- \rightleftharpoons \text{Fe(gly)₃}^- \quad (\log K = 9.79). \quad (5)
\]

The increase of pH promotes the iron glycinate coordination, as seen in the chemical species distribution (Fig. 1). These calculated results suggest the existence of iron glycinate complexes only beyond pH 4. This is greater than the pH of 2.5 chosen in all presented experiments. However, it has to be considered that hydrogen evolution parallel to the metal deposition will increase the pH so that all the mentioned Fe glycinate complex species may play a role (Fig. 1a). Interestingly, the calculations suggest a dominance of Fe-hydroxide species over the glycinites at elevated pH. That may compete with the interfacial role of the glycine species stable at pH 2.5, which are H₃(gly)⁺ and H₂(gly).

Considering the complexing activity of sulphate species besides glycinate one has to consider the formation of a solvated [FeH₂SO₄]aq⁻ associate at pH values less than 3 (Fig. 1b) which range is irrelevant in the present experiments:

\[
\text{Fe}^{2+} + H^+ + SO₄^{2-} \rightleftharpoons [\text{FeH}_2\text{SO}_4]^-_{\text{aq}} \quad (\log K = 3.07). \quad (6)
\]

At moderate acidity, the formation of the ion pair [FeSO₄]aq can be calculated (Fig. 1b):

\[
\text{Fe}^{2+} + \text{SO}_4^{2-} \rightleftharpoons [\text{FeSO}_4]_{\text{aq}} \quad (\log K = 2.25). \quad (7)
\]

A further increase in pH leads to the formation of iron hydroxo-complexes [25]:

\[
\text{Fe}^{2+} + \text{H}_2\text{O} \leftrightarrow [\text{FeOH}]^-_{\text{aq}} + \text{H}^+ \quad (\log K = -7.93) \quad (8)
\]

\[
\text{Fe}^{2+} + 2\text{H}_2\text{O} \leftrightarrow [\text{Fe(OH)}_2]_{\text{aq}}, + \text{H}^+ \quad (\log K = -18.94). \quad (9)
\]

[FeOH]⁻aq can only be formed to a significant extent when glycinate is absent (Eq. (8)).

3.2. Potentiodynamic investigations

The characterization of the cathodic reduction reaction of Fe²⁺ in the Fe-P electrolyte was investigated by cyclic voltammograms (CV) in combination with electrochemical quartz crystal micro-balance (EQMB) measurements. Fig. 2 shows the voltammetric response in the Fe-P electrolyte containing 0.21 M glycine at pH 2.5. The cathodic reversal potential, Uc, was varied. The potential scans started at the respective OCP (open circuit potential) around +0.3 V in negative direction. Two cathodic waves were observed which will be discussed based on data in Fig. 3. The anodic current peaks correspond to the oxidative stripping of Fe-P electrodeposited at Uc < −0.74 V where Fe-P formation begins. Actually, a reversal potential Uc of −0.74 V up to ca. −0.3 V resulted in no Fe-P deposition and, therefore, no anodic stripping peak.

Measured frequency changes, Δf, were related to interfacial mass changes by the Sauerbrey equation:
Fig. 1. Species distribution vs. pH. (a) glycine species; (b) Fe$^{2+}$ species. Fe-P glycine electrolyte: 0.7 M FeSO$_4$; 0.06 M NaH$_2$PO$_2$; H$_2$O; 0.6 M glycine.

\[ \Delta f = \frac{2f_0^2}{A \sqrt{\rho_0 \rho_q}} \Delta m \]  

(10)

where $f_0$ is the nominal resonant frequency of the crystal, \( \Delta m \) is the mass change, \( A \) is the area of the gold electrode exposed to the electrolyte, \( \rho_0 \) is the density of quartz and \( \rho_q \) is the shear modulus of quartz. Eq. (10) can be reduced to

\[ \Delta f = -G f \Delta m \]  

(11)

where \( G \) is the sensitivity coefficient of the quartz crystal balance (\( G = 0.0815 \) Hz/ng/cm$^2$ for a 6 MHz crystal).

The EQMB measurement allowed to quantify the charge and mass of the electrodeposition of the Fe-P phase and the total charge of the hydrogen evolution on the bare and Fe-P-covered gold electrode (Fig. 3). Hydrogen evolution on naked gold sets in at \( U < -0.40 \) V indicated by a negative current wave, a charge increase, \( q_{\text{H}(Au)} \), and constant frequency/mass (vertical dashed line at \( H^+ / H_2 \)). At \( U = -0.75 \) V (vertical dashed line at Fe$^{2+}$/Fe) a frequency change indicates a mass increase due to Fe-P deposition both for the negative and the positive scan. The measured charge change however, is correlated to both this deposition reaction and the hydrogen evolution on the Fe-P surface, \( q_{\text{H}(Fe-P)} \). On the reverse scan, at ca. \(-0.75 \) V, the deposition stops indicated by a constant frequency trace, while hydrogen still is evolved represented by a charge increase, \( q_{\text{H}(Fe-P)} \). The further anodic scan shows the stripping of most of the Fe-P phase by an anodic charge change, \( q_{\text{Fe-P}} \), and a frequency increase. The charge difference at potentials more positive than about \(+0.1 \) V, \( q_{\text{Fe-P}}^\text{tot} \), represents the hydrogen evolution charge on both bare gold and the Fe-P surface because the Fe-P layer has been stripped after the anodic potential scan.

The charge of the hydrogen evolution during the deposition on Fe-P layer, \( q_{\text{H}(Fe-P)} \), is:

\[ q_{\text{H}(Fe-P)} - q_{\text{H}(Au)} = q_{\text{Fe-P}}^\text{tot} \]  

(12)

The extent of the Fe-P deposition given by the frequency change, \( \Delta f_{\text{Fe-P}} \), corresponding to a respective mass change (comp. Fig. 3), and the anodic stripping charge density of the Fe-P deposit, \( \Delta q_{\text{Fe-P}} \) (comp. Fig. 3), decreases strongly with the glycine concentration (Fig. 4). This coincides with an increase of the hydrogen evolution on bare gold and on the Fe-P film, i.e. \( \Delta q_{\text{H}(Au)} \) and \( \Delta q_{\text{H}(Fe-P)} \). That means that the current efficiency of the Fe-P deposition drops with the glycine concentration [26].

The hydrogen evolution charge density, \( \Delta q_{\text{H}(Au)} \) and \( \Delta q_{\text{H}(Fe-P)} \), increases with the glycine concentration because various species act as proton donors so that the pH value in immediate proximity to the electrode surface attains pH values higher than 2.5. Starting out with a pH 2.5, the concentration of the totally protonated entity, H$_2$(gly)$^+$, and the zwitterion, H(gly)$^{\pm}$, is about equal (Fig. 1). Both these species, H$_2$(gly)$^+$ and the H(gly)$^{\pm}$, can accelerate the hydrogen evolution rate due to their deprotonation at increasing pH [4,27]. It should be mentioned that the dependence \( \Delta q_{\text{H}(Fe-P)} \) on the glycine concentration is higher than that of \( \Delta q_{\text{H}(Au)} \). This may be correlated to the higher catalytic activity of the Fe-P substrate.

The lowering of the Fe-P deposition rate can be correlated with the above described steady state of high pH near the surface due to the vigorous proton reduction. In this situation, the proton of H(gly)$^{\pm}$ is exchanged by an Fe$^{2+}$ ion forming a complex Fe(gly)$^+$ (Fig. 1), which exhibits a much lower iron reduction/deposition rate according to

\[ \text{Fe(gly)}^+ + 2e^- = \text{Fe} + (\text{gly})^- \]  

(13)
Fig. 3. Electrochemical quartz microbalance data of the Fe-P deposition (third potential cycle). 0.7 M FeSO₄; 0.06 M NaH₂PO₂·H₂O; 0.21 M glycine.
3.3. In-situ FTIR measurements

The electrode interface was investigated at various electrode potentials by in-situ FTIR spectroscopy in the present study. Previous in-situ FTIR spectroscopy investigations have demonstrated that glycine adsorbs on gold at \(U > 0.4 \text{ V} \) in perchlorate by ATR [21] and in phosphate media by both ATR and external reflection [29]. This potential range is positive of the point of zero charge (pzc) at about \(+0.15 \text{ V} \) [30]. The range negative of the pzc was studied with a cobalt glycine electrolyte by external reflection, where the electrode directly was in mechanical contact with the IR-transparent window [4]. Therefore, electrolytes were trapped in between resulting diffusing decoupling within the experimental microscale [31] always resulting in widely uncontrollable ionic concentrations.

This before-mentioned procedure is in contrast to the presently applied technique with a controllable gap between window and electrode [23]. In-situ FTIR absorption spectra of an Fe-P glycine electrolyte recorded from \(-0.13 \text{ V} \) to \(-0.83 \text{ V} \) at pH 2.5 are shown in (Fig. 5). An intensive broad band between 3200 cm\(^{-1}\) and 2900 cm\(^{-1}\) corresponds to C-H and NH\(_2\) stretching modes of the glycine species. When the applied potential is \(U < -0.4 \text{ V} \), this positive band increases reflecting the adsorption of glycine. A weak shoulder in the O-H stretch vibration region between 3600 cm\(^{-1}\) and 3400 cm\(^{-1}\) increase with more negative potentials either.

The bands at 1500, 1446, 1412, 1331 cm\(^{-1}\) and also at 1602 cm\(^{-1}\) (Table 1, Fig. 6) are correlated with the chemical functions of glycine. Their increase at \(U < -0.4 \text{ V} \) indicates the adsorption of glycine species in the hydrogen evolution region. Once the deposition Fe-P sets in around \(-0.7 \text{ V} \), these signals show a lower slope indicating a lower potential dependence of the glycine adsorption. These findings suggest that glycine species such as H\(_2\)(gly\(^+\)) or Fe(gly\(^+\)) \(_2\) are adsorbed during the iron phosphorous alloy deposition process.

The band around 1100 cm\(^{-1}\) may correlate with sulphate as negative going peak [4], or/and with adsorbed phosphate [29](Fig. 6) The band around 1645 cm\(^{-1}\) corresponds to water infrared absorption (H\(_2\)O) exhibits a decrease when shifting the potential from the pzc towards \(-0.3 \text{ V} \). This may be correlated to the exchange of solvated SO\(_4^2-\) anions by solvated Fe\(^{2+}\) ions. Thus, the amount of water molecules decreases because Fe\(^{2+}\) ions can accommodate less solvation molecules (ionic radius 0.210 nm) than the larger SO\(_4^2-\) anions (ionic radius 0.381 nm) [32]. Once protons are reduced and glycine adsorbed at \(U < -0.7 \text{ V} \), an increased band around 1645 cm\(^{-1}\) suggests the accumulation of water solvent molecules at the surface. The depletion of H\(_2\)(gly\(^+\)) as a consequence of the hydrogen evolution reaction may be evidenced by the negative band at 1740 cm\(^{-1}\) which can be related to \(\nu\) C=O stretching and \(\nu\) COH bending, i.e., the vibrational modes of protonated carbonyl [4,33].

Bare gold is a poor catalytic surface for the hydrogen evolution from a water-solvated proton which can be thermodynamically be expected negative of \(U < -0.16 \text{ V} \) (pH 2.5). This reaction only occurs at \(U < -0.30 \text{ V} \) where glycine adsorption occurs. This suggests that the protonated glycine species H\(_2\)(gly\(^+\)) \(_{ads}\) adsorbed at the negatively charged electrode surface provides a catalytically advantageous surface species. This complex can be reduced according to

\[2\text{H}_2\text{(gly)}^+ + e^- = \text{H}_2 + 2\text{gly}^-\]  \hspace{1cm} (17)

3.4. Electrochemical impedance spectroscopy measurements

Electrochemical impedance spectroscopy was performed as a function of potential in the range from \(-0.4 \text{ V} \) where hydrogen evolution and glycine adsorption started and \(-0.8 \text{ V} \) where Fe-P electrodeposition was just initiated (i.e. \(-0.75 \text{ V} \), comp. Fig. 3). The Nyquist plot in the absence of glycine (Fig. 7) exhibits an intricate mechanism. Even the electrodeposition of pure iron from a sulphate solutions involves at least six intermediate stages comprising three stages with adsorbed species [34]. In the absence...
of glycine, the Nyquist result shows inductive loops (Fig. 7) at potentials where Fe-P deposition took place ($U \leq -0.67$ V) in publication. These results can successfully be interpreted by an equivalent electric circuit (EEC) shown at the Nyquist plot in Fig. 7. R1 is a series resistance mainly due to the solution. CPE1 is a constant phase element (CPE) representing the interfacial capacity. R2 is the charge transfer resistance. The partial circuit consisting of the resistance R3 and the inductance L1 model the influence of intermediates on charge transfer. Fitting of the experimental results by this equivalent circuit yielded the respective element values (Table 2). The effective values of the double layer capacitance ($C_{eff}$) were calculated according to Ref. [36].

$$C_{eff} = Y \left( f^{max} \right)^{-1}$$  

Table 1: Vibrational frequencies of adsorbed glycine.

| $v$/cm$^{-1}$ | Assignment                                      | Reference |
|--------------|------------------------------------------------|-----------|
| 3600–3400    | O-H stretching                                  | [21,31]   |
| 3825–3200    | CH$_2$ + NH$_2$ stretching                      | [21,31,32]|
| 1602         | asym. str. COO$^-\;+$ bend NH$_3^+$            | [4,21,28,31,32]|
| 1500         | bend NH$_2$                                     | [4,21,32] |
| 1446         | bend CH$_2$                                     | [31]      |
| 1412         | sym. str. COO$^-\;+$ bend NH$_2$                | [4,21,28,32]|
| 1331         | wagging NH$_3^+\;+$ bend CH$_2$                 | [4,21,28,31,32]|

Fig. 5. In-situ FTIR investigation of Fe-P glycine electrolyte in the range of 2600–3600 cm$^{-1}$. Applied potential from $-0.13$ to $-0.83$ V vs. SHE. 0.7 M FeSO$_4$; 0.06 M NaH$_2$PO$_2$ - H$_2$O; 0.21 M glycine.

Fig. 6. In-situ FTIR investigation of Fe-P glycine electrolyte in range of 1000–1800 cm$^{-1}$. Applied potential from $-0.13$ to $-0.83$ V vs. SHE. 0.7 M FeSO$_4$; 0.06 M NaH$_2$PO$_2$ - H$_2$O; 0.21 M glycine.
where \( f_{\text{max}} \) represent the frequency at which the imaginary part of the impedance \( Z_{00} \). \( Y \) is a parameter and \( n \) is the exponent of the constant phase element, respectively.

The constant phase element CPE1 is most probably determined by a distribution of active surface sites and by an inhomogeneity of the dielectric constant due to the variation in chemical composition of the Fe-P layer involving a number of intermediate adsorption stages [34, 37]. The inductive behaviour at low frequencies during Fe-P deposition \( (U = -0.7 \text{ and } -0.8 \text{ V}) \) was caused by differences of the intermediate adsorption rate and its subsequent reduction. When the number of intermediate adsorption steps increases, the impedance spectrum becomes more complicated [38].

\[ C_{\text{eff}} \text{ at } U = -0.4 \text{ V is comparably high (Table 2). It probably not only represents the double layer capacity (typically 10–40 } \mu \text{Fcm}^{-2} \text{), but also is affected by the strong adsorption of intermediate Fe(II) compounds like e.g. } \text{FeOH}^{+}. \text{ At more negative potentials, hydrogen evolution and a faster Fe-P deposition reaction facilitate the reduction of intermediates, so that } C_{\text{eff}} \text{ attains more typical values for a double layer capacity. In parallel, the charge transfer resistance } R_2 \text{ decreases.} \]

In the presence of glycine (Fig. 8), the Nyquist plots show only two semicircles without any induction loops. The impedance spectra obtained at \( U = -0.4 \text{ V, where only hydrogen is evolved, the electrode process is modelled by the EEC in Fig. 8a. It contains a circuit representing the adsorption of glycine with resistance } R_3 \text{ and the adsorption capacitance } \text{CPE2; } R_2 \text{ is again the faradaic} \]

| Potential/V | R1/\Omega \text{cm}^2 | CPE1/\text{Fcm}^{-1} \text{cm}^2 | C_{\text{eff}}/\text{mFcm}^{-2} | n | R2/\Omega \text{cm}^2 | R3/\Omega \text{cm}^2 | L1/\text{Hcm}^2 |
|-------------|-------------------|-----------------|-----------------|---|----------------|----------------|----------|
| -0.4        | 17.2              | 0.0091          | 7235.3          | 0.74 | 46.9          | 9.1           | 22.0     |
| -0.7        | 17.4              | 0.00085         | 296.8           | 0.75 | 25.7          | 8.0           | 35.0     |
| -0.8        | 16.8              | 0.0012          | 103.8           | 0.77 | 4.8           | 1.7           | 0.3      |

Fig. 7. Electrochemical impedance spectra (Nyquist plot). 0.7 M FeSO\(_4\); 0.06 M NaH\(_2\)PO\(_2\) \cdot H\(_2\)O; no glycine. Experimental data fitted to the indicated equivalent electric circuit. Electrode potentials (vs. SHE) indicated.

Table 2
Equivalent circuit parameters. Glycine-free solution (comp. Fig. 7).

Fig. 8. Electrochemical impedance spectra (Nyquist plot). 0.7 M FeSO\(_4\); 0.06 M NaH\(_2\)PO\(_2\) \cdot H\(_2\)O; glycine concentrations indicated. Experimental data fitted to the indicated equivalent electric circuits. Electrode potentials vs. SHE (a) \(-0.4 \text{ V, (b) } -0.8 \text{ V.} \)
Table 3
Equivalent circuit parameters. Various glycine concentrations (comp. Fig. 8).

| c[H(gly)]/M | Potential/V | R1/Ωcm² | CPE1/Fe²⁺⁻¹ cm⁻² | C_m/μFcm⁻² | n | R2/Ωcm² | CPE2/Fe²⁺⁻¹ cm⁻² | C_m/μFcm⁻² | n | R3/Ωcm² |
|------------|------------|---------|-------------------|------------|---|---------|-------------------|------------|---|---------|
| 0.11       | -0.4       | 13.6    | 0.002             | 65.8       | 0.54 | 57.5    | 0.0078            | 7699.8     | 0.69 | 66.6    |
| 0.64       | -0.8       | 14.2    | 0.000012          | 10.2       | 0.83 | 6.8     | 0.069             | 72530.2    | 1.02 | 3.5     |

The increase of the glycine concentration decreased the charge transfer resistance (R2) and decreased intermediates (R3 and CPE2). The increase of the glycine concentration also decreased the adsorption impedance (circuit CPE2 and R3; Table 3), i.e. glycine adsorption facilitates the electrodeposition of Fe-P alloy.

3.5. Composition and morphology of Fe-P coatings

Analysis of the EDX data (Fig. 9) showed a dependency of the glycine concentration on the phosphorous content of the deposits obtained with various current densities (10, 20, 25, 30 mA/cm²) applying the same charge (thickness ~10–12 μm). Glycine addition results in almost an order of magnitude increase in P content. Further glycine additions exhibit a moderate and steady P content increase.

The increasing glycine concentration leads to an increase of the Fe(gly)⁺⁺ species which causes a lower deposition rate of iron so that the hypophosphite reduction rate can increase:

\[
\text{H}_3\text{PO}_2 + \text{H}^+ + \text{e}^- \rightarrow \text{H}_3\text{PO}_3^- + \text{H}_2\text{O} \quad (U = -0.508 \text{V}) \tag{19}
\]

and the phosphorous content in the deposit can increase. Even when dissolved oxygen in the electrolyte may lead to \( \text{H}_3\text{PO}_3 \), it may be re-reduced to \( \text{H}_2\text{PO}_2 \) almost at the same potential:

\[
\text{H}_2\text{PO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{PO}_2 + \text{H}_2\text{O} \quad (U = -0.499 \text{V}). \tag{20}
\]

The morphology of the deposits changes from microcrystalline (Fig. 10a) to nanocrystalline (Fig. 10b) upon addition of glycine [35,39]. XRD studies of Fe-P coatings showed the appearance of the broad bands at P concentrations higher than 13 at.% indicating amorphous morphologies [15,40]. According, to these studies the amorphous coatings can be deposited with glycine concentrations >0.2 M (comp. Fig. 9).

Fig. 9. Dependence of phosphorus content in Fe-P alloys on the glycine H(gly) concentration in the electrolyte at various current densities.

Fig. 10. SEM morphology of deposited Fe-P coatings electrodeposited (a) without glycine H(gly) and (b) with 0.21 M H(gly). Current density 30 mA/cm², 60 °C. P content: (a) 4 at.%; (b) 13 at.% (comp. Fig. 9).
Fe\(^{2+}\)\(_{aq}\) + 2H\(_2\)PO\(_2\)\(^\cdot\) → Fe\([H_2\text{HPO}_2]^{3-}\)\(_{ads}\) (21)
or the species Fe(gly)\(^1\)\(_{ads}\) adsorbed on the negatively charged electrode surface which can be reduced to Fe according to Eq. (13).

4. Conclusions

A mechanistic investigation of the influence of glycine on the Fe-P electrodeposition was presented applying the Electrochemical Quartz Microbalance (EQMB), in-situ external reflection FTIR spectroscopy, and the Electrochemical Impedance Spectroscopy (EIS).

Hydrogen evolution sets in at potentials (vs. SHE) negative of ca. −0.40 V and Fe-P deposition at ca. −0.75 V. Due to a limited current efficiency of the Fe-P deposition, hydrogen evolution causes a pH increase near to the electrode surface. Therefore, the existence of adsorbed H\(_2\)\(^{(gly)}\)\(^{ads}\), H\(_2\)\(^{(gly)}\)\(^{ads}\) and the chelate complex Fe(gly)\(^3\) in solution is suggested.

The extent of the Fe-P electrodeposition determined by charge and mass evaluations decreases strongly with the glycine concentration accompanied by an increase of hydrogen evolution. That means that the current efficiency of the Fe-P deposition drops with the glycine concentration. The hydrogen evolution rate is higher on Fe-P than on Au because the catalytic activity of Au is lower.

In-situ FTIR investigation showed an increase of glycine adsorption in the potential range of hydrogen evolution. This adsorption increase is retarded once Fe-P is deposited at potentials more negative than ca. −0.7 V. This is supported by EIS measurements.

The phosphorous content of the Fe-P deposit increases with the glycine concentration because the formation of the adsorbed Fe(gly)\(^{ads}\) species retards the deposition rate of iron relative to the hypophosphite reduction rate resulting in phosphorus.

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