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Electrodeposition of Nickel on Carbon felt

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Abstract

In this work the study of nickel deposition on to carbon felt from chloride and sulphate electrolytes at pH 3, using electrochemical impedance spectroscopy, is presented. Results compare favourably to previous studies with the mechanism of nickel deposition dependent on the concentration and applied potential. All impedance spectra are characterised by the presence of a semicircle feature at high frequencies and by complex inductance features at low frequencies. For impedance studies performed in sulphate and chloride electrolytes, at potentials not corresponding to nickel deposition, an ion effect is observed. This effect is attributed to the formation of adsorbed pre-deposition intermediates; H_{ads} in sulphate and chloride electrolytes and $Ni(Cl)_{ads}$ only in chloride electrolytes.

Keywords: Electrochemical impedance spectroscopy; Nickel; Electrodeposition; Carbon felt

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1. Introduction

Efficient recovery of metal ions from industrial waste is both industrial and financially important. This is especially true of nickel-bearing waste where both the quantity of nickel produced and the high resale price make recovery a commercially viable option. Examples of electrochemical methods of retrieving metal ions from solution using carbon felts or fibres as high-area electrodes can be found in the literature [1–3]. In this context, the study of nickel deposition on carbon felt, resulting in an understanding of the deposition mechanism, would be an important factor in maximising the efficiency of any recovery process.

The mechanism of Ni deposition has been demonstrated to depend on a number of factors, such as pH, concentration, electrode material and bath additives. Proud and Müller [4] studied the deposition of nickel on vitreous carbon and proposed the formation of $Ni(OH)^+$ over $NiCl^+$ in chloride electrolytes at low Ni concentrations. Fleischmann and Saraby-Reintjes [5], suggest that deposition from a Watts type bath proceeds via the chloride intermediate with no evidence of $Ni(OH)^+$.

The formation of two nickel phases containing included hydrogen (H_{inc}), during electrodeposition has been reported [5,6]. These are known as α and β-nickel, both being alloys of Ni and H with different Ni/H ratios in the deposited structure. α-Nickel has a ratio of 0.03 and obeys the laws of nucleation and growth. β-Nickel has a ratio of between 0.6 and 1.0 and is its growth is dependent on the migration of protons to the electrode surface. Formation of β-nickel is accelerated at low pH and higher negative potentials.

Electrochemical impedance spectroscopy (EIS) is a useful technique to study nickel deposition due to the existence of previous studies with mechanistic models elucidated using the technique [4,7–9], making interpretation easier. In this way the study of nickel deposition using cyclic voltammetry and impedance spectroscopy is presented with a view to understanding the mechanistic processes involved.

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2. Experimental

2.1. Electrodes

In all cases the working electrode was a carbon felt disc ($\phi = 1$ cm, porosity > 90%) manufactured by Donac Co. Ltd. from polyacrylnitrile (PAN) precursors. The counter electrodes were two platinum foils of area 1 cm^2 each.

2.2. Reagents and solutions

The following reagents were obtained from Fluka (purity 99.99%) and used without further purification—$NiSO_4{\cdot}6H_2O$, $NiCl_2{\cdot}6H_2O$ and H_3BO_3. The salts Na_2SO_4 (98%) and NaCl (>99.5%) were obtained from Avocado and Merck, respectively and used without further purification. Solutions of 50.0, 10.0 and 5.0 mmol/dm^3 $NiCl_2{\cdot}6H_2O$ or $NiSO_4{\cdot}6H_2O$ were prepared by dissolving the appropriate salt in a previously prepared stock solution containing boric acid (8.1 mmol/dm^3 H_3BO_3). Sodium chloride (NaCl) or sodium sulphate (Na_2SO_4) was added to the solutions to maintain the anion concentration at 1.0 and 0.5 mmol/dm^3, respectively. Chloride and sulphate solutions were acidified to pH 3 using HCl or H_2SO_4, respectively.

3. Procedure and equipment

In sulphate solutions the voltammetry and impedance measurements were referred the mercury sulphate electrode (MSE), and to the saturated calomel electrode (SCE) in chloride electrolytes. However, in the figures all potentials are referred to the SCE to aid clarity.

All electrochemical measurements (CV and EIS) were controlled using an EG & G/PAR potentiostat (model 273A) and performed in the potential range of +0.6 to –1.250 V versus SCE. All CVs were performed at 10 mV/s and recorded using XY Recorder (Allen Datagraph). Impedance measurements were performed using a frequency response analyser (Solartron S11250) linked to the potentiostat. The amplitude of the alternated signal was 5 mV in the frequency range of 10^5–10^{-3} Hz.

4. Results and discussion

4.1. Cyclic Voltammetry

In Fig. 1 the cyclic voltammogram of carbon felt in 50 mmol/dm^3 $NiCl_2$, at pH 3, repeated for two sweeps is shown. A cathodic current, commencing at ≈ -0.3 V, is observed when the potential is swept negatively. The cathodic current gives way to nickel deposition at −0.78 V. The subsequent nickel-stripping peak is seen at −0.155 V. A current loop, typical of a nucleation process, can be seen between −0.78 and −0.90 V. The repeat sweep shows a decrease in the amount of nickel deposited and stripped. This phenomenon might be due to the build-up of H_2 in the inner areas of the carbon felt or to the presence of adsorbed species at the electrode surface, as will be discussed at a later stage in this paper.

In sulphate solutions at pH 3 deposition of nickel is observed to proceed at lower overpotentials than for the equivalent chloride systems, (Fig. 2). As in chloride systems a cathodic current is observed and nickel deposition can be seen to commence at −0.40 V. The stripping peak can be seen at +0.145 V. Repetitive cycling results in a decrease in the stripping peak, which is also shifted anodically (Fig. 2). After 11 cycles the voltammetric response reaches a steady state. The reasons for the peak decrease may be related to the formation of different nickel phases, as will be described at a later point.

The formation of two phases of nickel (α- and β-nickel) is observed when the potential is swept to increasingly cathodic potentials for both chloride and sulfate systems. In Fig. 3 the deposition of nickel from 50 mmol/dm^3 $NiCl_2$ is observed when the potential is swept to −0.90 V showing a single stripping peak at −0.156 V. When the potential is

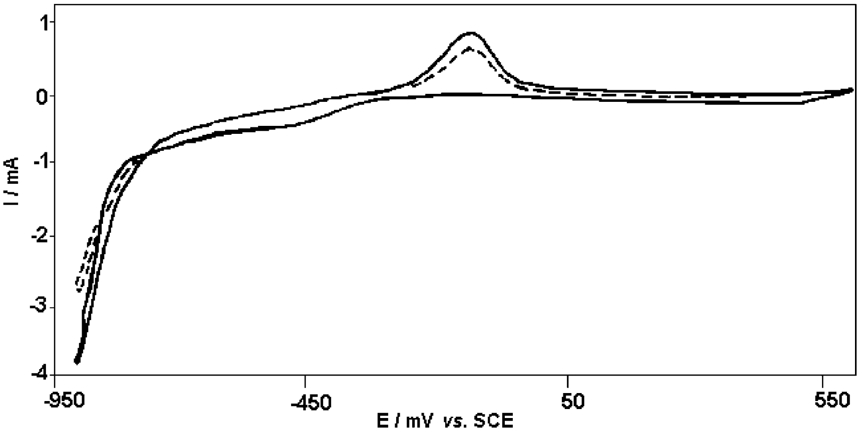

Fig. 1. CV of carbon felt disc (ϕ = 1 cm) in 50 mmol/dm^3 $NiCl_2$ at pH 3: (solid line) 1st sweep; (dashed line) 2nd sweep; v = 10 mV/s.

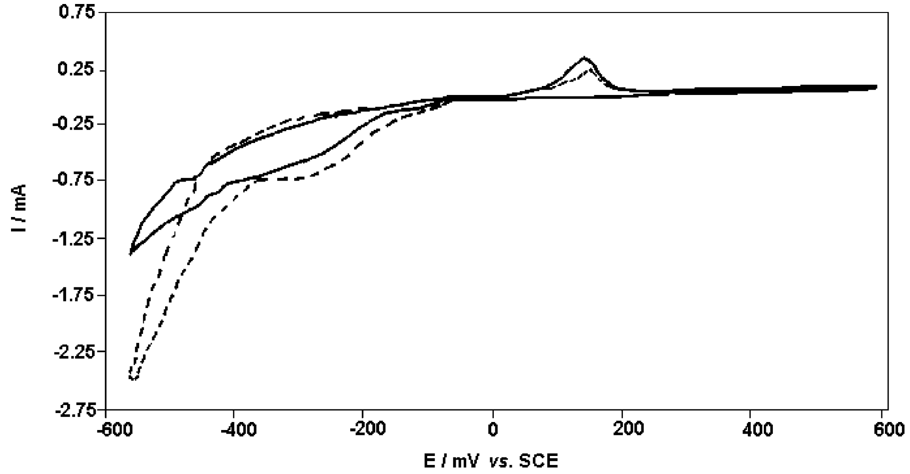

Fig. 2. CV of carbon felt disc (ϕ = 1 cm) in 50 mmol/dm^3 $NiSO_4$ at pH 3: (solid line) 1st sweep; (dashed line) 11th sweep (after reaching steady state); v = 10 mV/s.

swept to a more cathodic potential at −1.00 V, a second stripping peak is observed at −0.215 V, with each of the two peaks representing a different nickel/hydrogen alloy [5,6]. In addition, the stripping peak observed at –0.156 V (for a limit potential of –0.90 V) shifts anodically to −0.145 V (Fig. 3). The peaks at −0.145 and −0.215 V can be attributed to the stripping of α-and β-nickel, respectively [5,6]. The fact that there is a peak shift as the cathodic limit potential is increased, indicates that phase separation of α- and β-nickel occurs at more negative potentials. Subsequently this would indicate that the stripping peaks observed in Figs. 1 and 2 are formed by combination of α- and β-nickel with separation of phases only being seen at more negative potentials. Such a picture of mixed deposition in the initial stages of nickel deposition would be in agreement with previous studies by Fleischmann and Saraby-Reintjes [5].

The effect of decreasing the concentration is manifested in chloride and sulfate systems by an increase in the overpotential required to deposit nickel. In Fig. 4 the voltammogram of nickel deposition from 5 mmol/dm^3 $NiCl_2$ at pH 3 is shown. The cathodic current is present and the nickel-stripping peak is shifted anodically to −0.210 V and is much broader and less well defined. The current loop behaviour observed in 50 mmol/dm^3 is not seen. Repeated sweeps demonstrate that the stripping peak does not diminish as seen previously. In the cathodic region of Fig. 4, a decrease in the current response with repeated cycling can be observed. It is possible that this decrease is related to the formation of intermediates involved in H_2 formation or to adsorbed Ni intermediates, both of which block the electrode surface (see later in paper).

In the literature, various authors [4,7–9] suggest that nickel deposition occurs via the initial formation an adsorbed Ni(I) intermediate. $Ni(OH)_{ads}$ and $NiCl_{ads}$ have been proposed. The formation of species of this nature has been reported to occur at more anodic potentials than nickel

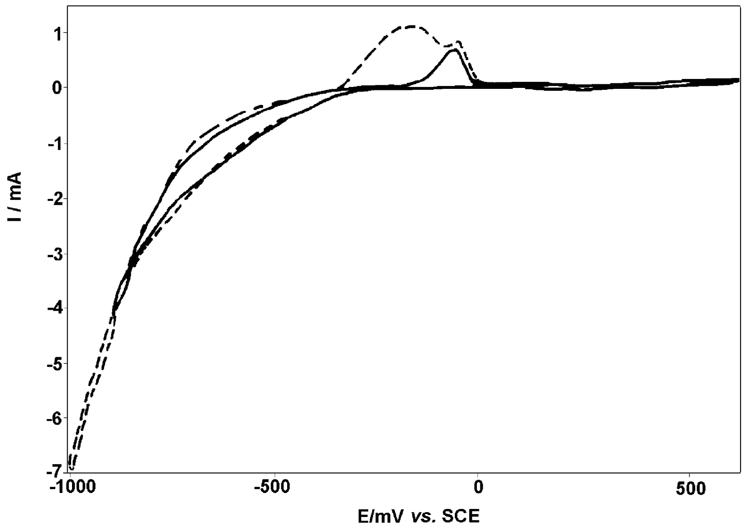

Fig. 3. CV of carbon felt disc (ϕ = 1 cm) in 50 mmol/dm^3 $NiCl_2$ at pH 3. Cathodic limit: −0.9 V (solid line); −1.0 V (dashed line); v = 10 mV/s.

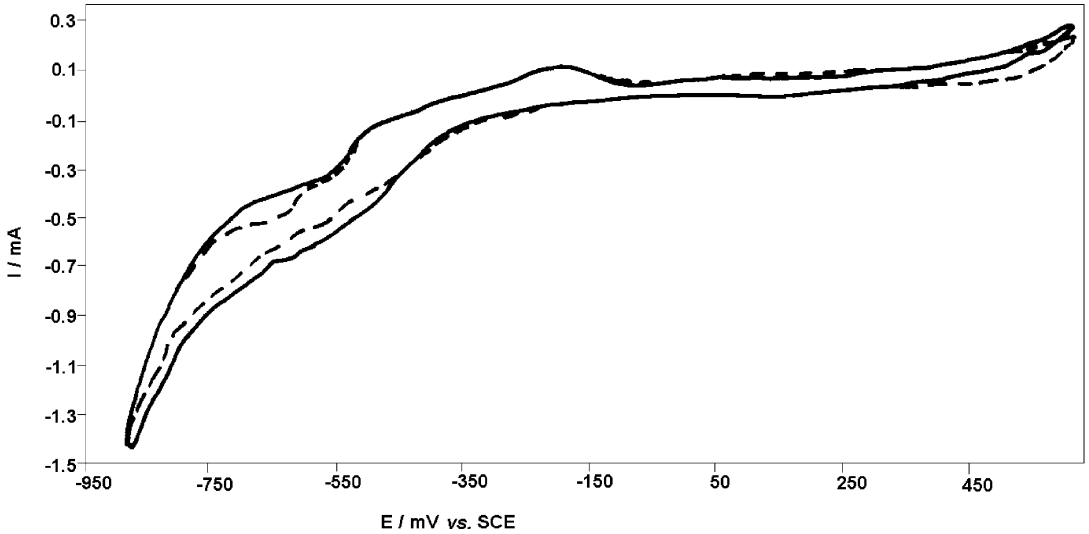

Fig. 4. CV of carbon felt disc (ϕ = 1 cm) in 5 mmol/dm^3 $NiCl_2$ at pH 3: (solid line) 1st sweep; (dashed line) 2nd sweep; v = 10 mV/s.

deposition itself [4]. With this in mind, it can be suggested that the cathodic current observed prior to Ni deposition (Fig. 1) is due to the formation of such an intermediate at the electrode surface. As the feature is observed in both systems, the intermediate formed would most probably be the $Ni(OH)_{ads}$ species.

In chloride media, continued cycling shows that the Ni stripping peak diminishes until reaching a steady state, but does not disappear completely. The diminishing of the peak current could be due to a number of factors. For example, the formation of H_{ads} and H_2 gas in the inner pores of the carbon felt is a possible reason for this passivation, However, H_2 evolution was not observed. The formation of $NiCl_{ads}$ has been suggested by Chassaing et al. [7] as a passivating factor in nickel deposition from chloride electrolytes. Secondly, in this study the phenomenon is only observed in chloride electrolytes. The formation of a passivating $NiCl_{ads}$ intermediate is suggested to be the cause of the inhibition of nickel deposition here. As stated the deposition and stripping of nickel does not disappear completely with repeated sweeps. It was found [7] that the presence of boric acid in chloride electrolytes broke or inhibited the passivation of the electrode surface at higher overpotentials. Hoare [10] found that boric acid acted as a catalyst in nickel deposition. It is probable that the small quantity of boric acid present in the electrolyte prevents the complete passivation of the electrode towards nickel deposition. In sulphate solutions there is no analogous effect probably due to the weaker sulphate ion not interacting in the system to the same extent as the chloride ion [4].

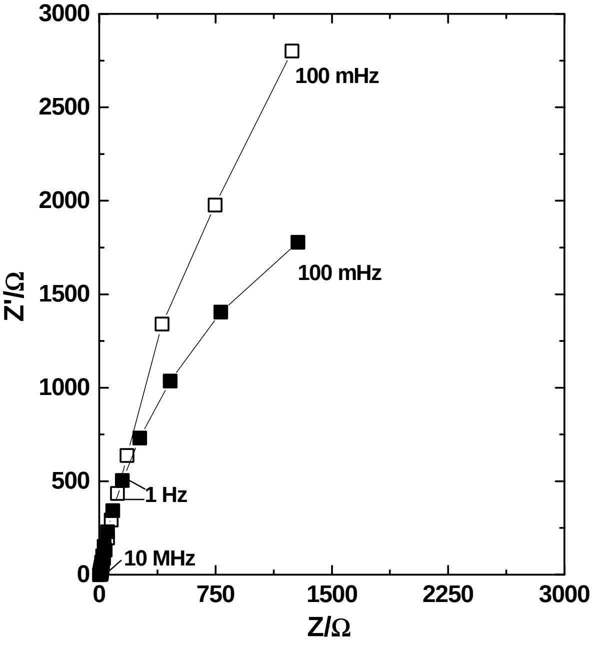

Fig. 5. Impedance plots of carbon felt disc (ϕ = 1 cm) in 50 mmol/dm^3 $NiCl_2$ (full square) and 50 mmol/dm^3 $NiSO_4$ (open square) at −0.2 V vs. SCE.

For sulphate electrolytes the effect of repeated sweeps is clearly demonstrated as the 11th sweep is diminished and clearly shifted anodically (Fig. 2). A substantial quantity of hydrogen gas was observed to form over this time, but the peak does not diminish at the same rate as in chloride systems, this again supports the hypothesis of a passivating $NiCl_{ads}$ species in chloride electrolytes. At pH 3 nickel deposition is accompanied by high-levels of hydrogen evolution [6]. It is reported by Proud et al. [6] that the formation of a β-nickel enhances the formation of H_2 and this in turn promotes the production of α-nickel. The production of α-nickel is manifested in Fig. 2 by the peak shift or in effect phase separation of the two nickel forms, i.e. over repeated sweeps the H_2, incorporated in the β-nickel phase, evolves and leaves only α-nickel resulting in an anodic peak shift.

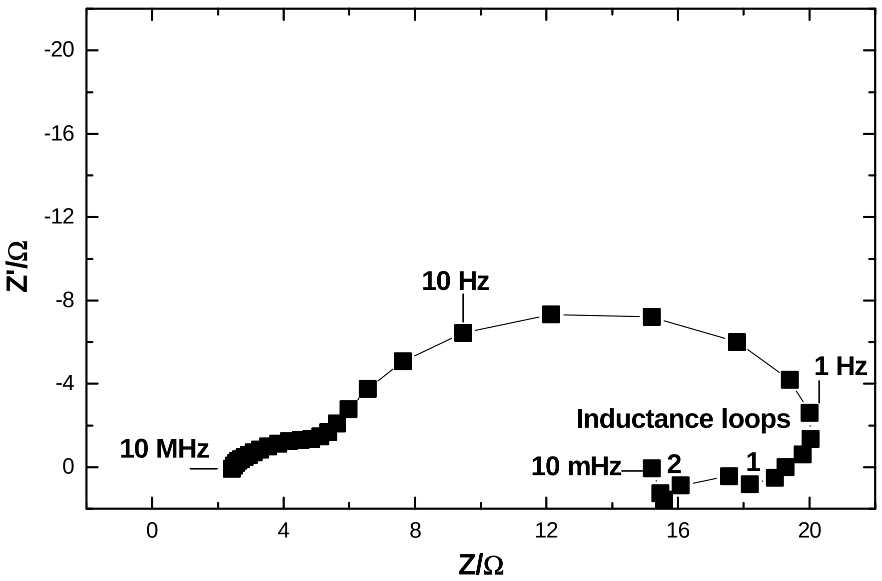

Fig. 6. Impedance plots of carbon felt (ϕ = 1 cm) in 50 mmol/dm^3 NiCl$_2$ at −0.8 V vs. SCE.

4.2. Impedance studies

The overpotential for the deposition of nickel on carbon felt was observed to be concentration dependent. The non-faradaic region (were no electron transfer takes place) varied from −0.78 V in 50 mM NiCl$_2$ and −0.40 V in 50 mM NiSO$_4$ to more negative potentials for lower Ni(II) concentrations. In all impedance spectra the presence of a high frequency semicircle feature, typical of porous electrodes, is observed.

An interesting feature of the impedance spectra taken in both electrolytes is their non-linearity in regions of potentials where nickel deposition does not occur (Fig. 5). At potentials prior to Ni deposition, an ion effect can be seen in both electrolytes. From Fig. 4 it can be observed that the spectra obtained in chloride solutions are less linear than those obtained in sulphate media. This behaviour was also observed by Proud and Müller [4] using vitreous carbon as the electrode material. Proud and Müller attributed the non-linear behaviour to the adsorption of Ni(OH)$^+$ in both chloride and sulphate electrolytes [4]. The accentuated nature of the non-linearity in chloride electrolytes indicates the additional adsorption of NiCl$_{ads}$ [4].

In chloride electrolytes at potentials corresponding to the deposition of nickel two low frequency inductive features can be seen (Fig. 6). The presence of two inductive features is in agreement with observations made by Chassaing et al. [7] during impedance studies of nickel deposition on brass or nickel electrodes. Proud and Müller [4] only observed one inductive feature in chloride electrolytes on vitreous carbon. In chloride solutions the first of the inductive loops is ascribed to the slow desorption of an anionic species and the second to the presence of H$_{ads}$ on the electrode surface [7]. It was found that the first feature was not dependent on the chloride concentration and as a result the adsorbed species was thought to be a chloride containing complex [7] (e.g. NiCl$_{ads}$), Eqs. (1) and (2).

$$\mathrm{Ni}X^{+} + \mathrm{e}^{-} \leftrightarrow \mathrm{Ni}X_{\mathrm{ads}} \quad (1)$$

$$\mathrm{Ni}X_{\mathrm{ads}} + \mathrm{e}^{-} \leftrightarrow \mathrm{Ni} + X^{-} \quad (2)$$

where X^- is HO$^-$ or Cl$^-$. Proud and Müller [4] suggested that the predominant species at the low concentrations was Ni(OH)$_{ads}$. However, Chassaing et al. [7] and Epelboin et al. [8] found no evidence of a hydroxylated nickel intermediate. It is also difficult to imagine that a Ni(OH)$^+$ species at pH 3 would be long-lived. In this way the inductance feature is probably not attributable to desorption of HO$^-$.

The second inductive feature is ascribed to strongly bonded H$_{ads}$ on the electrode surface and is observed to disappear at more negative potentials (Fig. 7) being replaced by a capacitive feature. The variation of coverage by H$_{ads}$ induces the capacitive loop.

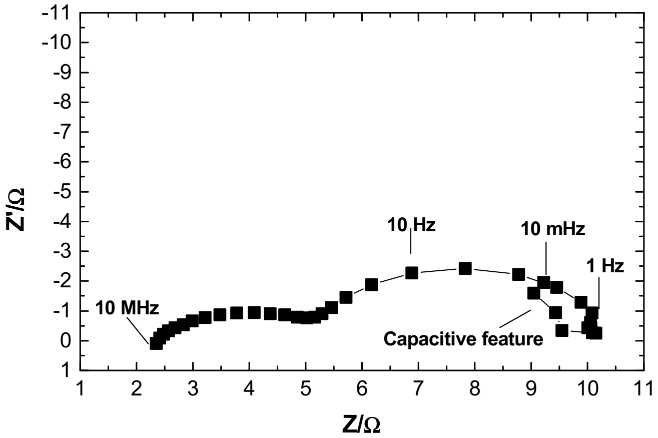

Fig. 7. Impedance plots of carbon felt (ϕ = 1 cm) in mmol/dm^3 NiCl$_2$ at –1.0 V vs. SCE.

In sulphate solutions only one low frequency inductive feature is observed. This phenomenon was observed [4] to depend on the pH of the solution and is ascribed to H_{ads} on the electrode surface. This feature is seen to give way to a capacitive loop due to the variation of electrode coverage, as seen in chloride systems previously.

5. Conclusions

The study of the deposition of nickel from sulphate and chloride electrolytes on carbon felt presents similar results to those previously shown in the literature. Cyclic voltammetry and impedance results suggest that a number of intermediate complexes and adsorbed hydrogen, H_{ads}, are involved. The behaviour in chloride electrolytes is characterised by a rapid decrease in the peak associated with Ni-stripping. In sulphate electrolytes the Ni-stripping peak also decreases, but to a lesser degree than in chloride systems. Considering the literature, the more accentuated decrease is probably due to the additional formation of a passivating $NiCl_{ads}$ intermediate.

In both electrolytes, the impedance spectra are characterised by the presence of a semicircle feature at high frequencies and by complex inductance features at low frequencies. For impedance studies performed in sulphate and chloride electrolytes, at potentials not corresponding to nickel deposition, an ion effect is observed, which is attributed to the formation of adsorbed pre-deposition intermediates.

Both electrolytes present an inductance feature at low frequencies and at low potentials. At higher potentials, in the region of the hydrogen evolution reaction, this inductance feature gives way to a capacitance feature. This phenomenon is attributable to the formation of H_{ads} (inductance) and its subsequent conversion to H_2 (capacitance). In chloride electrolytes an additional inductance feature is observed that can be attributed to the formation of a passivating $NiCl_{ads}$ intermediate, agreeing with the conclusions drawn from cyclic voltammetry.

5.1. Mechanism

A global mechanism can be suggested when considering the literature in conjunction with the present results:

$$\mathrm{Ni}^{2+} + X^- \leftrightarrow \mathrm{Ni}X^+ \quad (3)$$

$$\mathrm{Ni}X^+ + \mathrm{e}^- \leftrightarrow \mathrm{Ni}X_{\mathrm{ads}} \quad (1)$$

$$\mathrm{Ni}X_{\mathrm{ads}} + \mathrm{e}^- \leftrightarrow \mathrm{Ni} + X^- \quad (2)$$

In the case of $X^- = \mathrm{HO}^-$ the reaction in steps 1 and 2 would be very fast and no inductance feature is seen at low frequencies. However, for $X^- = \mathrm{Cl}^-$ the discharge is much slower and results in the inductance feature described.

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