

POTENTIODYNAMIC CHARACTERISTICS OF ZINC ELECTRODEPOSITION FROM CHLORIDE SOLUTION

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ABSTRACT

The major goal of this potentiodynamic study was to explore the characteristics of zinc electrodeposition from chloride ($\text{ZnCl}_2 - \text{HCl}$) media. The influence of various operating parameters such as zinc concentration in the 30 – 150 g/dm^3 range, acidity level (pH in the 1.5 – 5.5 range) and rotation speed (0 – 950 r.p.m.) were investigated at room temperature. Deposit morphologies were recorded by a digital camera during cathodic polarization. The physical quality of the electrode surface seems to be one of the important parameters not only for the deposit structure but also for the side reaction of H_2 evolution and also for the development of the polarization curves. There are three kinds of cathodic depositions occurring. It generally starts with a uniform and stable structure, followed by a sponge-like deposit and finally it turns into a dendritic growth due to concentration changes near the surface. However, electrolyte agitation can influence the deposition pattern. With increased rotation speeds (above ~ 500 r.p.m.), resulting in higher available concentrations of electro-active ions at the surface, there is not much sponge-like deposit, yet the dendrite formation at the edges could not be avoided. The strong increase in the actual specific surface area of the cathode, due to the sponge-like deposit and the dendrite formation, caused irregularities in the potential change executed by the computer controlled potentiostat. Although this instrument was designed and produced at the institute specifically for high speed measurements. By lowering the pH in the electrolytes of the lowest Zn concentrations, the side reaction of H_2 evolution soon appeared, after the limiting current of Zn deposition was reached. At higher Zn concentrations though, instead of a clear limiting current, the slope of the polarization curve persisted all across the examined potential range, indicating a continual co-deposition of H_2 together with that of Zn.

1. INTRODUCTION

Hot dip galvanizing (HDG) is one of the most common processes to protect steel objects and structures from corrosion. However, this technology may produce numerous pollutants too, causing serious environmental concern. The steps of HDG process imply the generation of different types of wastes, with the spent pickling liquor (SPL) from the pre-treatment step being the major challenge [1]. Due to European environmental protection regulations, the metal and chloride ion contents in the spent pickling liquor (SPL) must not be higher than 2 mg/dm^3 Zn, 10 mg/dm^3 Fe and 1 g/dm^3 Cl^- with an acidity in the range between 6 and 9 [2]. Even though this liquid is classified as waste, it can be also a rich source of secondary zinc. Processes of Zn recovery from various industrial wastes have been lately becoming progressively more attractive. Spent pickling liquors with different concentrations of Zn^{2+} ion are taken more and more into account. However, it is hard to define the optimum condition to recover this metal economically from this secondary source.

Zinc electrodeposition has been studied widely, also from chloride media, and the main focus was directed to the influence of iron as the dominant impurity, the effect of current density and hydrogen evolution, related to the loss of the acid content [3], [5]. Higher solubility and electrical conductivity are significant advantages of zinc electrodeposition from chloride media. However, chlorine gas may also be evolved, which is harmful and also leads to HCl loss. Certain portion of Cl_2 gas soluble in the electrolyte may corrode cathode materials, re-dissolving some metal, thus the application of diaphragms between the two electrodes to trap most of the chlorine gas has also been tested [6].

Acceptable deposition of Zn on the cathode mainly depends on the composition of the bath, in which various agents and the temperature may influence the deposition process and the structure of the final deposit. Chloride solutions offer higher rates of zinc deposition on the cathode surface compared to that of sulphate systems. However, it is hard to obtain smooth and compact deposits [7], [8]. With regard to that problem, a detailed study of zinc and HCl concentration, current density and temperature effect to deposit quality has been conducted by several researchers [4], [6], [8]. Quite surprisingly, it has been reported that fine-grained deposits were obtained with only 10 g/dm^3 Zn at current densities lower than 300 A m^{-2} , while at higher currents, dendritic and sponge-like deposits evolved. In the highest examined current densities ($\sim 1000 \text{ A/m}^2$), dense deposits occurred with a slight acidification by 0.5 g/l HCl . Further acidification (to 50 g/l HCl) shifted dendrite formation to higher current densities [10]. It was also stated that increasing zinc concentration could produce more compact deposits, but the actual current efficiencies related to these results were not specified. Further studies were directed to the effect of organic additives. Glue – as the most commonly used inhibiting agent - had little effect in the chloride electrolytes, and other additives as tetrabutylammoniumchloride (TBACl), tetraethylammoniumchloride (TEBACl) or even HCl, were neither found as efficient as in sulphate solutions [10].

Another research found that the optimum hydrogen ion concentration in chloride electrolytes with respect to deposit morphology was 0.24 mol/dm^3 at 538 Am^{-2} . The resulted deposit showed no void spaces and was better than that without no-addition of HCl [9]. In a further series of experiments, McKinnon [9] tested the effect of more electropositive impurities (e.g. Cu, Co, Ni...), which lower the hydrogen overpotential. It was found that they could sharply reduce the current efficiency of zinc deposition even at relatively small concentrations ($< 10 \text{ mg/dm}^3$). This fact may have serious consequences in the case of treating SPL, which – according to a wide survey – may contain [2] the following characteristic ranges of composition: $30 \sim 80 \text{ g/dm}^3$ Zn, $50 \sim 150 \text{ g/dm}^3$ Fe and $40 \sim 160 \text{ g/dm}^3$ HCl, with Cu and Co below 10 mg/dm^3 , but Ni and Pb often exceeding it. Therefore, it may be critically important to apply a preliminary purification step to any real solution originating from the HDG industry before zinc electrodeposition can be attempted. In this approach, it is primarily important to define the possible limiting conditions for a decent electrowinning operation. It can be based on the investigation of the cathodic processes. A suitable first approach can be the potentiodynamic technique of experimentation. As the deposit can be expected to form irregular growths of dendrites and loose crystals, the potentiostat should be capable of following the rapidly changing surface conditions by increasing the current in the required pace. For this reason, our laboratory has been engaged in developing custom made equipment especially designed for fast polarization rates and relatively high current increments.

Table 1 summarizes the suggested [9] electrolysis parameters for optimum zinc deposition with smooth appearance and practically no dendrite formation. Although these results seem very promising in avoiding the major difficulties, the application has not been proved by so far in known definite industrial processes. Also, there are some other recent publications reporting even quite contrary results and highlighting the inherent difficulties

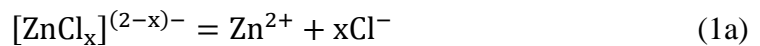
of obtaining compact deposits from chloride media, especially for Zn from HCl containing solutions [11], [12], [13].

Table 1 Practical parameters of Zn electrodeposition from chloride solutions [9]

Parameter	Value
Final cell electrolyte	15 g/dm ³ Zn
	0.12 mol/dm ³ HCl
	15 mg dm ⁻³ TBACl
Feed electrolyte	30 g/dm ⁻³ Zn
	0.12 mol/dm ³ HCl
	15 mg dm ⁻³ TBACl
Current density	323 A/m ²
Temperature	35°C
Feed rate	2.2 cm ³ /min
Air sparging rate	4750 cm ³ /min
Aluminium cathode	0.005 m ²
Time	24 hours

Another challenge in zinc electrodeposition is the energy consumption due to the competition between zinc and hydrogen ions at the electrolyte/electrode interface. Zinc deposition is expected as the dominant cathodic reaction. The occurrence of hydrogen ion reduction strongly depends also on the impurity content in the electrolyte. In the SPL, iron is the dominant impurity, which has more positive reduction potential compared to that of zinc, therefore it tends to deposit on the cathode surface [14]. Furthermore, since the overpotential of hydrogen on iron is lower (by ~ 400 mV) than on zinc[15], iron could promote the hydrogen evolution. In this case, the current efficiency will be decreased so that energy consumption becomes higher.

As reported in many studies, zinc deposition is often coupled with the evolution of hydrogen. Due to the readily formed zinc-chloro-complex species [16] [17], the metal deposition must be preceded by the dissociation of the complex structure, liberating the electro-active cation:



This mechanism has a natural inhibiting effect at the cathode, but also some bubbles are produced by hydrogen evolution at the same time:



The complex form of the dissolved zinc even in weak HCl solutions may be a reason why the ion supply to the cathode surface is hindered. This case has also been found with tin in HCl media [18]. However, the inhibiting effect of the preliminary complex dissociation may have a beneficial effect on the structure of the formed cathodic deposit. It is confirmed by the large dendrites observed to be formed from close to neutral ZnSO₄ solutions [19]. Therefore, it is to be clarified how zinc can be electrodeposited with an acceptably compact structure and a feasible current efficiency from close-to neutral HCl solution. In view of the ambiguities related to the electrodeposition of Zn from HCl media, the purpose

of this investigation is to understand the controlling factors that determine Zn deposition, in particular the effects of process parameters.

2. EXPERIMENTAL

Model solutions were prepared from analytical grade ZnCl_2 dissolved in distilled water. The variation of the Zn^{2+} concentration: 30, 60, 90, 120 and 150 g dm^{-3} was relevant to the SPL liquors. Hydrochloric acid was added to modify the pH in order to examine the H_2 evolution, deposit structure, cathodic potential and cathodic current development at different acidity levels. The pH was measured by a Thermo Orion 420 digital instrument and a combined electrode when the current was cut.

An electrolysis cell with the dimensions of $50 \times 50 \times 50 \text{ mm}$ made of glass was used as shown in Fig. 1. The saturated calomel reference electrode was connected to the surface of the cathode (work electrode) through a bridge tube ending in a Luggin-capillary tip (of $\sim 1 \text{ mm}$ diameter) and filled with the electrolyte solution. The anode (counter electrode) was made of pure zinc, in order to compensate for the loss of Zn^{2+} concentration loss caused by the repeated cycles of cathodic deposition.

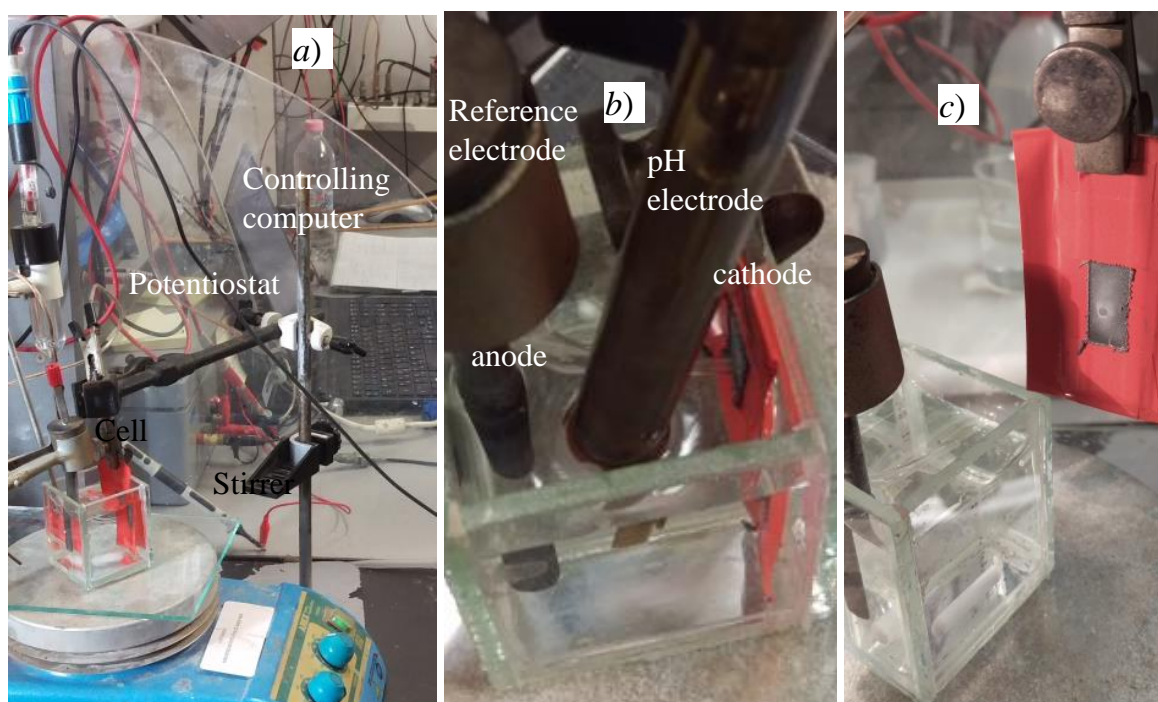


Fig. 1 The experimental set-up of the potentiodynamic studies (*a* – the test cell and the potentiostat, *b* – electrode arrangement, *c* – removed cathode).

The potentiodynamic experiments were performed with 85 cm^3 volume of the solutions. The initial cathode was made of copper plate with the active surface of 2 cm^2 and the anode was made of a pure zinc rod of 5 mm diameter. The cathode surface was polished with an 800 grit SiC paper giving a uniform surface, then washed with distilled water and acetone, finally dried before setting into the cell. All the runs were carried out at room temperature with 40 mV s^{-1} continuous polarization speed – giving the widest range of clear results - and with 10/s sampling rate. We have developed a special computer controlled potentiostat at the University of Miskolc that was capable to produce rapid polarizations, suitable for the investigation of the cathodic processes under fast changing conditions. It was controlled and the results were recorded by a special software – developed and run on the NI LabView platform. A magnetic stirrer and a rotating rod of 2 cm length at the bottom of the cell were used with rotation speeds from 50 to 950 r.p.m.

The surface structures during the potentiodynamic process were photographed through the glass wall of the cell.

3. RESULTS AND DISCUSSION

In the first series of the experiments, our aim was to identify the dominant cathodic process in different ranges of the examined parameters. Figure 2 shows the surface structures of the cathodes in potentiodynamic runs applying 60 gdm^{-3} Zn concentration and no rotation. The tip of the Luggin-capillary is also visible in the pictures. It is clearly seen that in the pH range lower than 2, the hydrogen evolution constituted most of the cathodic reaction, but as the pH was raised, zinc deposition started to take over the initial dominance. With pH values higher than 2, the initial stage of zinc deposition forms a uniform coating of zinc on the surface, followed by black spongy deposits which later propagate the growth of dendrites at the edges of the active cathode surface.

It was found that with an initial cathode already coated with zinc, the produced new layer could not be detached, although the substrate had been polished as usual. In contrast, the deposit could be easily detached from the original copper surface. It can also be seen that the appearance of the zinc deposits obtained from the electrolytes with pH lower than 2 and those from the higher pH solutions are markedly different.

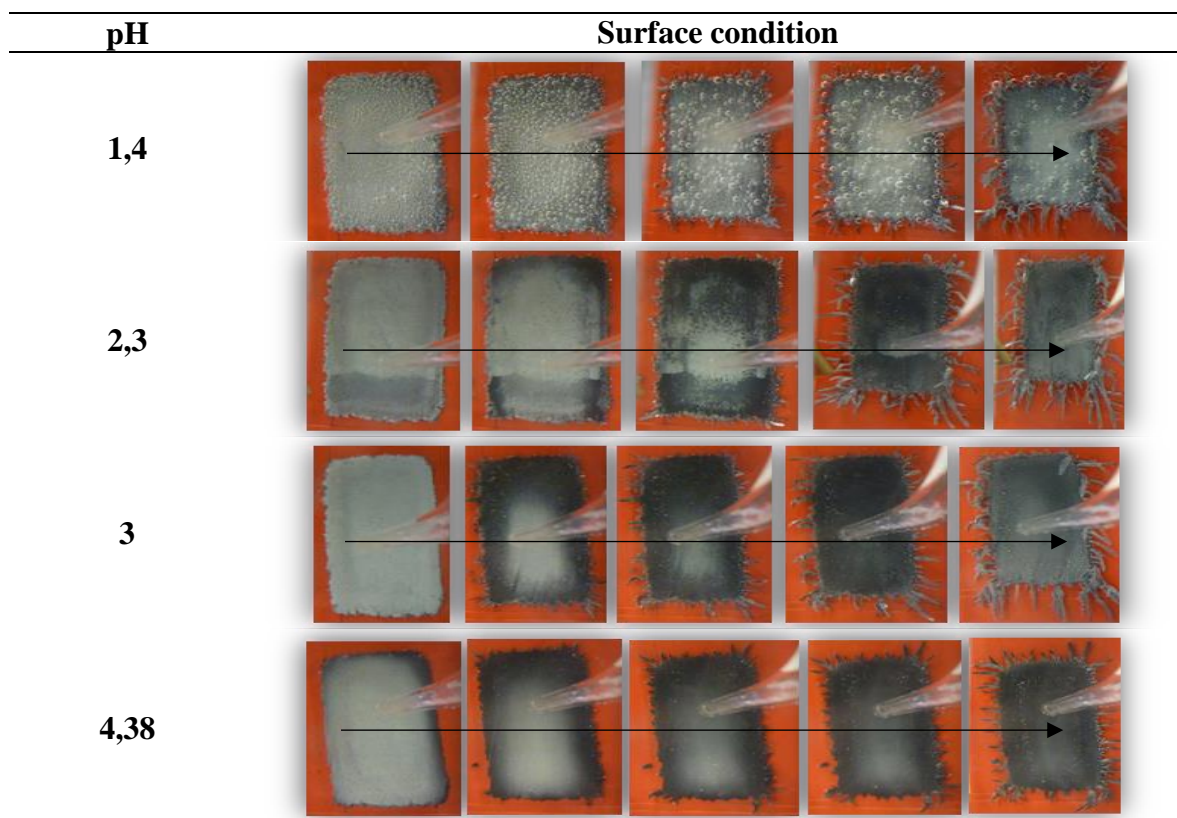


Fig. 2 The changes of the cathode surfaces during polarization at the indicated pH of the stationary solution (60 g/dm^3 Zn, 0 r.p.m).

Hydrogen evolution started right at the beginning in the lowest pH range. At first, small bubbles accumulated, which hindered the deposition of zinc. The accumulated gas bubbles may block the active surface more or less before being evolved. It may even create a virtual limiting current for H_2 evolution while zinc may continue to deposit. Figure 3 shows the polarization curve at the highest examined acidity (pH 1.4). In order to better interpret the observed phenomena, the surface images recorded during the process are fit

into the diagram. At this low pH value, there are enough electroactive H^+ ions, therefore H_2 evolution could develop easily at the cathode.

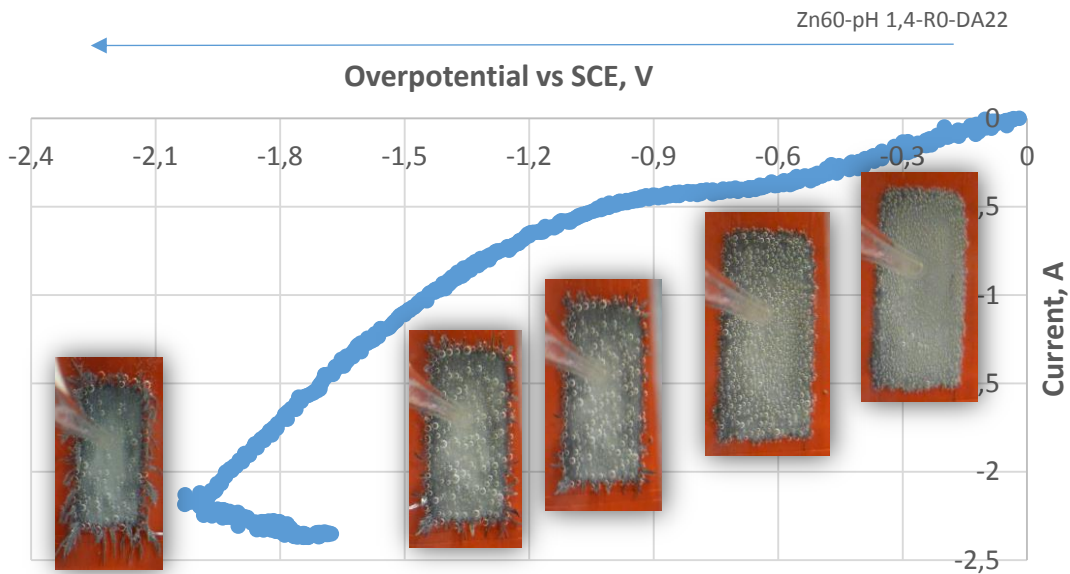


Fig 3. Potentiodynamic Zn electrodeposition at pH 1.4 ($60 \text{ g/dm}^3 \text{ Zn}$, 0 r.p.m.).

As the cathodic overvoltage is increased, as the surface is still blocked by hydrogen bubbles, the reaction at the surface tend to be mixed with zinc deposition, especially at the edges. Finally, the Zn deposition becomes dendritic, thus the effective cathode surface is greatly increased. Consequently, the potentiostat program even had to reduce the overpotential to keep the growth of the current at bay. This is reflected by the rather unusual final downturn of the polarization curve.

In contrast, increasing pH by just one unit to 2.3, hydrogen bubbles were hardly found on the surface initially. As shown in Fig.4, the appearance of the deposit changed from flat, to spongy, then to dendritic. This progressive roughening of the cathode surface with increasing current is obvious.

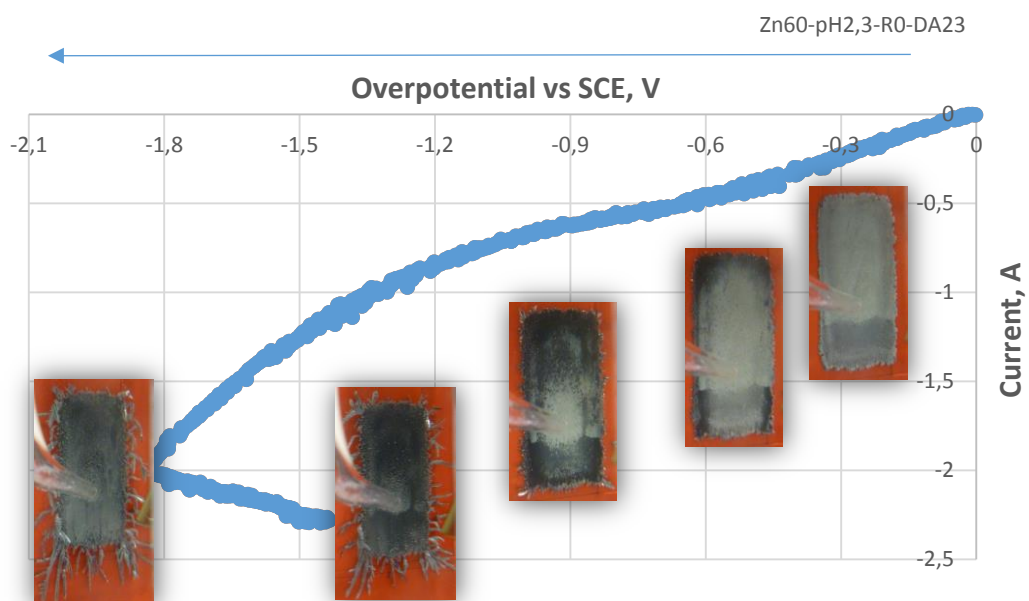


Fig 4. Potentiodynamic Zn electrodeposition at pH 2.3 ($60 \text{ g/dm}^3 \text{ Zn}$, 0 r.p.m.).

This result confirms Fischer's description on the electro-crystallization of metals under ideal and real conditions [20], stating that at low overpotentials (i.e. low current densities) growth starts with the growth of two dimensional nuclei, and continues by the propagation of the layer. Whereas, in the high overpotential and current density range, electrodeposition is characterized by continuous nucleation and growth of three dimensional nuclei. Mackinnon also argued in his study of zinc deposit structures obtain from synthetic zinc chloride electrolytes [9] that fine-grained Zn were deposited at the current densities lower than 300 A m^{-2} while at values exceeding that, dendritic and spongy deposits existed.

The roughest crystal growth – observed in many cases during the potentiodynamic experiments - may have develop when the surface concentration of zinc decreased strongly during the electrodeposition. Under this condition, the current density will be higher at the tips of the long crystals grown outward from the surface, enhancing the further growth of the long dendritic or needle crystals. At low currents the concentration is more uniform thus a smoother surface tends to develop.

The effect of zinc concentration on the potentiodynamic characteristics of zinc electrodeposition is shown in Fig 5 and 6. No well-definable difference could be observed in the growth pattern of the deposit, yet the final appearance showed to be more brightly metallic in colour with increasing Zn concentration. The curves in Fig 5 – obtained with no stirring - show that the higher the Zn concentration, the higher potential can be reached. It indicates that the dendrites start to grow later, as there is a greater concentration of electroactive Zn species near the surface. Thus the actual surface area is kept closer to the original for a longer time.

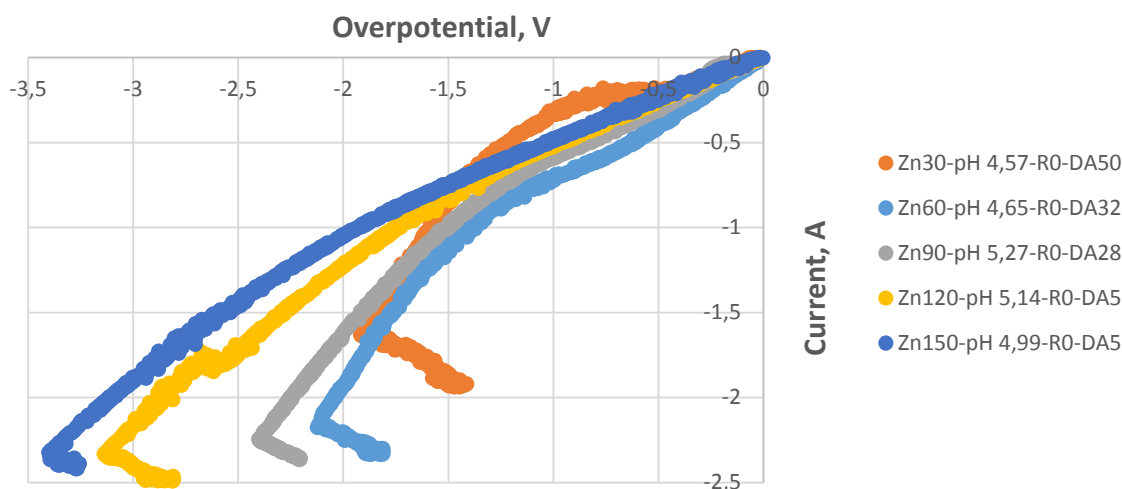


Fig 5 Cathodic polarization curves at different Zn concentrations (0 r.p.m.).

Limiting current is clearly observed with the lowest (30 g dm^{-3}) Zn concentration, in the $-0.5 \dots -1.0$ overpotential range. This was followed by the onset of the hydrogen evolution, indicated by a new and steep slope of the current curve. It lasted until $\sim -2 \text{ V}$ overpotential was reached, where the formation of Zn dendrites took over control and the by the consequently increasing actual surface area, the potential started to drop. At higher Zn concentrations, the current did not stop increasing, indicating that limiting conditions for the Zn deposition could not arise. The polarization curves showed continued rise (in the cathodic direction) but the slopes were not changing consistently with the different Zn concentrations. It is caused by the different ratios of the partial currents related to either rough/dendritic Zn deposition or the evolution of H_2 . As the slopes are lower and more constant with higher Zn concentration, it indicates that the zinc deposition may dominate rather than hydrogen evolution.

As shown by Fig. 6, agitation can strongly affect the surface structure of the growing deposit. As magnetic stirring (at a moderate speed) was introduced, the structure of the metallic deposit became more compact, and the H₂ bubbles could easily detach from the surface, as assisted by the streaming of the solution. It modifies the limiting current vaguely appearing at the lowest concentration, as well as the slopes of the polarization curves in the higher concentration range. Furthermore, the curves show no change in their slope at Zn concentrations higher than 120 g dm⁻³.

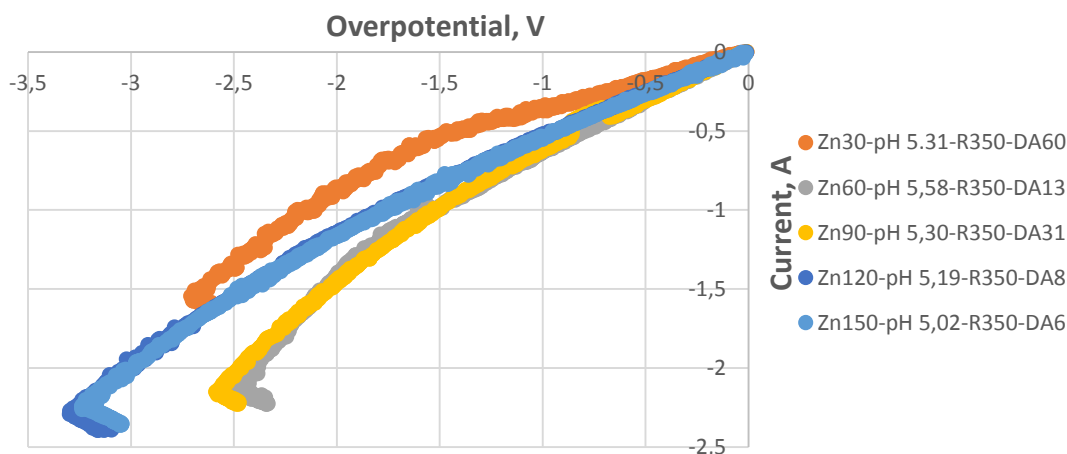


Fig 6. Cathodic polarization curves at different Zn concentrations (350 r.p.m.).

The final irregularity in the polarization curves expressing a reversed tendency in the potential while the current increases is shorter in Fig. 6. Also, the maximum currents were lower before the total voltage limit of the potentiostat was reached in the whole circuit. This is an indication of a later and reduced extent of dendrite formation resulting from the effect of the introduced stirring. If the stirring speed is further increased, the final irregularity is completely eliminated from the polarization curves and the dendrites almost disappeared from the cathode. The deposits were simply thicker at the edges and just a few and less developed dendrites appeared sporadically at the bottom edge.

4. CONCLUSION

In conclusion, the parameters such as pH, Zn concentration and the agitation intensity of the electrolyte could be shown to play important impacts on the electrodeposition of zinc from chloride media. Thus to achieve an acceptable quality of zinc deposition, these parameters must be set properly. Applying the lowest examined 30 g/dm³ Zn, increasing the pH from 1.4 to 2.3 could change the cathodic process greatly. The H₂ evolution was depressed until the potential was not increased to higher levels. As the Zn concentration was increased, the deposit became more metallic and brighter in colour, while the current could increase less rapidly, indicating less co-deposition of hydrogen. Introducing a mild agitation efficiently reduces the growth of the dendrites and the deposit tends to become compact.

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