# Mechanism of Zinc Electrodeposition in a Chloride Solution

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Impedance spectroscopic measurements of sheet steel under electrogalvanizing in an acidic solution of zinc chloride as a function of pH, grain-refining additive, current density and SEM morphological observations of the electrogalvanized surfaces, have revealed the electrodeposition mechanism better than other methods. The electrogalvanizing is simply under the mixed control of charge transfer and diffusion. The hydrogen ion acts to inhibit the charge transfer slightly and to stimulate water decomposition. The grain- refining organic additive appears to be adsorbed effectively on the galvanizing surface and to deactivate growing kink sites of electrocrystallites at low current density, resulting in nucleation- controlled deposits and considerable inhibition of electrodeposition. With increasing current density, the electrodeposition becomes controlled gradually under the influence of the diffusion of zinc ion.

Electrodeposition of zinc and its alloys has been of great interest because of expanding demand for electrogalvanized and zinc-alloy electroplated sheet steels for automobile and appliance exterior panels, in addition to the increasing employment of zinc in electrochemical areas such as generators. The electrodeposition has been researched electrochemically and metallurgically to lead to industrially advanced plating processes and to improved functions of the electroplated surface.

Electrochemical studies of electrode reactions have been performed mostly by steady state and various transient polarization methods and by a-c impedance techniques. The analysis and interpretation of impedance data of an electrochemical interface, generated simply, for example, by *in-situ* perturbation of the interface with a small-amplitude sinusoidal signal over its wide frequency range of  $10^{-4}$  Hz to  $10^{4}$  Hz, typically, have provided more kinetic and mechanistic data on the interface reactions than other polarization methods. As a result of intensive application of this impedance technique to the studies of electroplating systems since the early 70s by



Fig. 1—Schematic of an electrochemical and impedance measuring apparatus for an electrogalvanizing cell.

the easy availability of wide-range frequency response analyzers, comprehensive and detailed mechanisms of the electrodeposition of zinc,<sup>1-6</sup> nickel<sup>6-8</sup> and silver<sup>9,10</sup> have been extensively investigated, mostly by Wiart<sup>1-8,10</sup> and his coworkers.

Specifically, electrodeposition processes of zinc have been well accounted for by the Wiart model of multi-step ordinary or autocatalytic discharge reactions involving adsorption of intermediate species (hydrogen adatom H<sub>ads</sub>, zinc monovalent adion  $Zn^{+}_{ads}$ , active kink site  $Zn^{*}$ , and effectively adsorbed additive  $Y_{ads}$ , if added), coupled with diffusion processes of reactants and additives to the plating interface and of intermediates on the interface. Current and impedance expressions for the overall deposition reaction were derived as a function of rate constants of partial discharge reactions, surface concentrations of adsorbed intermediates, solute concentration in the electrolyte, effective adsorption parameters of additives and diffusion data of reactants, additives and intermediates. Multiple steady states of the current as a function of cathodic overpotential were proved to appear and the complex plane impedance spectrum could show multiple inductive and capacitive loops by the corresponding intermediate coverages on the deposition surface, proving the existence and roles of the intermediates in the deposition processes. These results were in good agreement with experimental results obtained in an acid sulfate solution, a Leclanché cell electrolyte and an alkaline zincate solution. Morphological characteristics of deposits, important to their metallurgical properties, were explained by the nucleation and growth processes of the electrocrystallization, which were modified by the deposition parameters and the presence of an additive. Morphologies of deposits have been correlated with, and interpreted in terms of, impedances of the electrodeposition interface.

Electrochemical impedance analyses of electrogalvanizing and zinc-alloy electroplating on steel in a solution of concentrated zinc chloride at elevated temperature over a wide range of current densities have rarely been published. Resulting industrial processes and products have been extensively applied, however, to protection against corrosion of highquality sheet steels that have been severely deformed, welded and coated in high-quality painting processes. It has been necessary to understand better morphological changes of the electrogalvanized layer by the galvanizing parameters and additives in terms of nucleation- and growth-controlled depositions and electrochemical impedances of the galvanizing surface to modify microstructures of the layer and to develop effective additives.

### Experimental Procedure

The electrolyte was a concentrated zinc chloride solution prepared with high-purity reagents and distilled and demineralized water: 1.5 M ZnCl, and 4.7 M KCl; pH adjusted to 2.0



Fig. 2—Cathodic galvanodynamic polarization curves of an electrogalvanizing interface in quiescent pH 2 chloride solution at 60 %C as a function of additive concentration.

and 4.0 with HCl. A commercially available polyethyleneoxide-base additive was added at concentrations of 0.00, 0.25, 0.50 and 1.00 mL/L. The electrolyte was quiescent and maintained at 60 °C for all electrochemical tests. The amount of the electrolyte for a test was 800 mL.

A three-electrode method was employed for all the electrochemical measurements and controls, as shown in Fig. 1. The counter-electrode (CE: anode) was a plate of 99.9-percent zinc. The working electrode (WE: electrogalvanizing surface) was a sheet of very-low-carbon steel degreased in an alkaline solution and then ultrasonically in acetone and alcohol to remove trace amounts of rolling lubricant just before the test. The surface  $(1.0 \text{ cm}^2)$  of the WE was exposed to the quiescent electrolyte, using a PTFE specimen holder. The potential of the WE was measured and controlled against a saturated calomel electrode (SCE) as reference electrode (RE), which was maintained at room temperature and joined with the electrolyte at 60 °C, using a Luggin capillary probe with its tip positioned to the center of the WE surface to minimize contamination of the RE.

Electrochemical measurements were performed using a commercially available electrochemical interface,<sup>a</sup> a frequency response analyzer<sup>b</sup> for impedance measurement, and a personal computer for experimental control and data logging and processing, as diagrammed in Fig. 1. Cathodic galvanodynamic polarization curves of the WE were determined from the open-circuit condition to the limiting (*i.e.*, greatly hydrogen-evolving) current density at the scan rate of 1.0 mA/sec after the WE was stabilized at the open-circuit condition in the electrolyte for 10 min, to obtain a brief overall electrogalvanizing polarization behavior.

Impedance data of the WE were measured at galvanostatic conditions of 5, 10, 50, 100 and 180 mA/cm<sup>2</sup> by superposing a small amplitude (one tenth of the galvanostatic current) sinusoidal current after the WE was electrogalvanized for five min at a galvanostatic test condition. Frequency of the a-c signal was swept downward from 10 kHz through  $10^{-1}$  Hz by decreasing the frequency 0.63 times stepwise (5 measurements per decade). Application time of the signal was maintained at the minimum value, so the total frequency-sweeping time at a galvanostatic condition was about 16 min. A new



Fig. 3—Cathodic galvanodynamic polarization curves of an electrogalvanizing interface in quiescent pH 4 chloride solution at 60 %C as a function of additive concentration.

WE specimen and a new electrolyte were used for each measurement of a galvanodynamic polarization curve and each measurement of an impedance spectrum. The counter and reference electrodes were rinsed thoroughly with the test electrolyte before the test.

Surface morphologies of the WE electrogalvanized for the total 22 min in the measurement of an impedance spectrum were examined using a scanning electron microscope (SEM) to observe the influence of electrogalvanizing conditions on microstructures of the deposits.

#### Results and Discussion

Figures 2 and 3 reveal galvanodynamic polarization curves of the electrogalvanizing interface in the pH 2 and pH 4 zinc chloride solutions at 60 °C as a function of the additive concentration. First, all the polarization curves are smooth and show gradually accelerated increase of potential with the increase of applied current up to the limiting values-apparently charge transfer control at low current density and diffusion control at high current density. No noticeable S-shaped, current-potential relationship is observed in these polarizations. The limiting current densities for electrogalvanizing in the pH 2 and pH 4 solutions are about 200 and  $220 \text{ mA/cm}^2$ , respectively, in the absence of the additive, and they increase to slightly higher values in the presence of the additive. The hydrogen ion tends to stimulate water decomposition, while the additive inhibits water decomposition. A tendency that the more the amount of additive, the higher the cathodic polarization, indicating an inhibitive effect of the additive during electrogalvanizing, is generally observed in the pH 2 solution. This relationship disappears, however, at  $80 \text{ mA/cm}^2$  and more in the pH 4 solution.

Figures 4 and 5 delineate complex plane impedance diagrams of the interface being electrogalvanized in the additive-free pH 2 and pH 4 zinc chloride solutions, as a function of the current density, and depicts morphologies of the electrogalvanized surface under the conditions of Fig. 4 for 22 min, showing irregular and rough deposits leading to dendritic growth with increasing current density.

The impedance data in Fig. 4 show two capacitive loops only, so no negative polarization resistance appears in a spectrum. The capacitive loops appear to be depressed slightly to the real axis from a semicircular shape. The high-frequency capacitive loop is thought to correspond to an imped-

<sup>&</sup>lt;sup>a</sup> Solartron Model 1286

<sup>&</sup>lt;sup>b</sup> Solartron 1250



Fig. 4—Impedance diagrams of an electrogalvanizing interface in a pH 2 chloride solution without an additive as a function of current density;  $\bullet$  100 Hz,  $\star$  1 Hz,  $\blacksquare$  0.01 Hz.

ance feature by the double-layer capacitance ( $C_{dl}$ ) in parallel with the charge-transfer resistance ( $R_{cl}$ ) as in the impedance analyses of all other electroplating.<sup>1-10</sup> The value of  $R_{cl}$ , simply the length of the real axis of the high frequency relaxation to a first approximation, decreases from 1.30 to 0.33 ohm-cm<sup>2</sup> with the increasing current density 5.0 up to 50 mA/cm<sup>2</sup>, then remains nearly constant with further increase of current density, similar to ohmic resistance. The value of  $C_{dl}$ , can be obtained from the capacitance expression for a parallel circuit:

$$C_{dl} = 1/(2\pi f_m R_t)$$

where  $f_m$  is the proper or characteristic frequency for the capacitive relaxation and may be taken as approximately the frequency at the highest imaginary value<sup>11</sup> of the high-frequency capacitive loop in Fig. 4. The calculated value of  $C_{dl}$  ranges from 19.4 F/cm<sup>2</sup> at 5 mA/cm<sup>2</sup> to 48.2 F/cm<sup>2</sup> at

Table 1				
Extracted Values of Charge Transfer Resistance				
and Double Layer Capacitance				
of the Electrogalvanizing Interface				
in an Additive-free Solution*				
<b>C.D.</b> (mA/cm <sup>2</sup> )	$\mathbf{R}_{t}$ (ohm-cm <sup>2</sup> )	f <sub>m</sub> (Hz)	$C_{dl}$ (F/cm <sup>2</sup> )	
5.0	1.30	6,300	19.4	
50.0	0.33	10,000	48.2	
50.0	0.33	10,000	48.2	



Fig. 5—Impedance diagrams of an electrogalvanizing interface in a pH 4 chloride solution without an additive as a function of current density.

50 mA/cm<sup>2</sup> and more, as summarized in Table 1. These values are nearly in the same range of other electroplating systems.<sup>1-10</sup> The difference in the values of  $C_{dl}$ , at the low and high current densities in this study seems partly to result from the actually larger area at high current densities for the given apparent area of  $1.0 \text{ cm}^2$  if the value of  $C_{dl}$  for a true area of  $1.0 \text{ cm}^2$ is assumed to be roughly constant in the polarization range for the electrogalvanizing. This large-area effect at high current density means more porous morphologies, as shown by the numerous and microcrystalline facets in Fig. 6. On the other hand, an impedance spectrum for the parallel circuit of  $R_t$  and  $C_{dl}$  on a porous electrochemical interface has been proved to exhibit a depression from a semicircular shape,<sup>11-13</sup> so this fact seems to account for depression of the high-frequency capacitive loops of impedance diagrams in Figs. 4 and 5.

The proper frequency for the lowfrequency capacitive loop in an impedance spectrum in Fig. 4 is in the range of 1.0 Hz to 0.01 Hz and close to 0.1 Hz. Considering the thickness of the Nernst diffusion layer () to be in the range of 0.1 mm, the following calculation, may be made, where  $t_m$  is

the time constant (about 0.1 Hz) of the low-frequency relaxation:

$$\delta^2 / t_m = \delta^2 2\pi f_m = 6.28 \text{ x } 10^{-5} \text{ cm}^2 / \text{sec} = D$$

This is reasonably in the range of magnitude of the diffusion coefficients of a simple ion like  $Zn^{+2}$  in water at 60 °C. From this relaxation analysis, the low-frequency capacitive loops in the impedance diagrams in Fig. 4 seem to reflect diffusion impedances of the electrogalvanizing reactions. The difference of this diffusion impedance spectrum from the general semi-infinite diffusion impedance spectrum characterized by a 45-degree slope on a complex plane plot may be due to the effect of partly finite diffusion<sup>14</sup> on the porous surface.<sup>11-13</sup> The presence of the charge-transfer and diffusion impedances in the electrogalvanizing at all the current densities in Fig. 4 implies more clearly than in Fig. 2 that the electro-

	Table 2				
Extracted Values of Charge Transfer Resistance					
and Double Layer Capacitance					
of the Electrogalvanizing Interface					
in an Additive-containing Solution*					
<b>C.D.</b> (mA/cm <sup>2</sup> )	<b>R</b> <sub>t</sub> (ohm-cm <sup>2</sup> )	$\mathbf{f}_{\mathbf{m}}$ (Hz)	$C_{dl}$ (F/cm <sup>2</sup> )		
5.0	4.89	630	51.5		
100.0	0.464	6,300	54.4		
* From Fig. 7					

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\* from Fig. 4



Fig. 6—SEM micrographs of an electrogalvanized surface in a pH 2 chloride solution without an additive at current densities: (a) 5.0; (b) 50; (c) 100; and (d) 180 mA/cm<sup>2</sup>, for 22 min.

galvanizing is under mixed control simultaneously at nearly all the current densities in this quiescent solution. Relative size of the diffusion impedance, compared with the charge transfer impedance in an impedance spectrum, increases with increasing current density, as shown in Figs. 4 and 5, indicating gradual diffusion-limited electrogalvanizing with increasing current density, as in Fig. 2.

Comparing Figs. 4 and 5, the decrease of the charge transfer resistance from  $1.28 \text{ to } 0.25 \text{ ohm-cm}^2$  with increased current density from 5 to  $180 \text{ mA/cm}^2$  in the pH 4 solution is revealed by the analyses of the high-frequency capacitive loops. These values of R<sub>t</sub> are slightly smaller than those in the pH 2 solution, as in Table 1, indicating that hydrogen ions act as an inhibitor of the charge transfer at the electrogalvanizing interface. Additionally, the diffusion impedance in the pH 4 solution.

Figure 7 shows complex plane impedance diagrams of an interface being electrogalvanized in the pH 2 zinc chloride solution containing a small amount (0.25 mL/L) of the additive as a function of the current density. Figure 8 depicts morphologies of the electrogalvanized surface under the conditions of Fig. 7 for 22 min, showing transition from fine granular and nucleation-controlled deposition to coarse (not dendritic) and growth-controlled deposition with increasing current. No negative polarization resistance has been observed in the present impedance spectrum measurements. Presence of the additive changes significantly the impedance features from the spectrum composed of the two capacitive loops, as in Figs. 4 and 5, to that of the high-frequency capacitive, medium-frequency inductive and low-frequency inductive loops at low current density. The low-frequency inductive loop is reduced, however, and transformed to the low-frequency capacitive loop accompanying the reduced high-frequency capacitive loop and the highly diminished medium-frequency inductive loop as current density increases. The magnitude of this low-frequency capacitive loop increases with increasing current density.

The high-frequency capacitive loop in the impedance spectrum may develop by relaxation of the double-layer capacitance in parallel with the charge-transfer resistance at the interface. The values of  $R_t$  and  $C_{dl}$  for this loop, typically at low and high current densities (5.0 and 100 A/cm<sup>2</sup>), were



analyzed by the same method as in Fig. 4 and are listed in Table 2. The charge transfer resistance decreases with increasing current density, as in chargetransfer-controlled reactions. Values of  $R_{t}$ , however, are larger than those in the additive-free solution (Figs. 4 and 5), indicating the chargetransfer-inhibiting effect of the additive. The larger value of C<sub>dl</sub>, at low current density, compared with that in the additivefree solution (Fig. 4), may suggest microscopically larger area of

Fig. 7—Impedance diagrams of an electrogalvanizing interface in a pH 2 chloride solution containing 0.25 mL/L of the additive as a function of current density:  $\bullet$  100 Hz,  $\star$  1 Hz,  $\blacksquare$  0.01 Hz.

the electrogalvanizing interface in the additive-containing solution, resulting from grain refinement, as shown in Fig. 8a (compare with Fig. 6a).

The medium-frequency inductive loop may be associated with the relaxations<sup>1-6</sup> of the electrogalvanizing interface, covered with intermediates by adsorption:  $H_{ads}$ ,  $Zn^{+}_{ads}$ ,  $Zn^{*}$  and  $Y_{ads}$ . This loop seems to be very closely related with the grain refinement by the additive. The relaxation time con-



Fig. 8—SEM micrographs of an electrogalvanized surface in a pH 2 chloride solution containing 0.25 mL/L of the additive at current densities: (a) 5.0, (b) 50, (c) 100 and (d) 180 mA/cm<sup>2</sup>, for 22 min.

stant for adsorption of most large organic substances, such as the present additive, on an electrode is known to be larger than that for diffusion. The present inductive loops, having time constants around 1.0 Hz (Fig. 7), appear smaller than those for diffusion (at around 0.1 Hz for a simple ion, as in Fig. 4). This occurrence appears to be a result of nucleation and growth processes<sup>2.6</sup> by generating active kink sites (Zn\*) rather than adsorption of other intermediates<sup>5</sup> that were not noticeable in the electrogalvanizing without an additive, as in Figs. 4 and 5.

The low-frequ֮cy inductive loop, having a proper frequency lower than  $10^{-1}$  Hz, as shown in Fig. 7, appears to occur by the effective adsorption process of the additive because of its longer relaxation time constant, similar to those in Refs. 2 and 6. The effectively adsorbed additive (Y<sub>ads</sub>) has been known to accelerate deactivation of the growth kink sites by poisonings, resulting in grain refinement by nucleation-controlled deposition at low current densities (5 and 10 mA/cm<sup>2</sup>). The diminution of this loop with increasing current density, however, may reflect the following: Effective adsorption of the additive decreases gradually, then nearly disappears with increasing current density, so that the poisoning of growth sites decreases, resulting in grain growth at high current densities (100 and 180 mA/cm<sup>2</sup>).

Finally, the low-frequency capacitive loop is likely to occur in the electrolyte by zinc ion diffusion toward the galvanizing interface, as interpreted in Figs. 4-6, with increasing current density. Morphologies of the electrogalvanized surface in the presence of the additive at high current densities (Fig. 8c and 8d) show well-developed crystalline layers and facets, but smaller than those formed in the absence of the additive (Fig. 6c and 6d). These differences may be thought to stem from the renewal of more active-growth sites<sup>2,3</sup> because of the presence of the additive, as indicated by the medium-frequency inductive impedances in Fig. 7, although small at the high current densities of 100 and 180 mA/cm<sup>2</sup>.

## Findings

Galvanodynamic polarization, impedance spectroscopic and morphological observations of an electrogalvanizing interface in a quiescent acidic zinc chloride solution have successfully revealed detailed galvanizing features occurring at the interface. The electrogalvanizing is simply under the mixed control of charge transfer and diffusion and not under any noticeable autocatalytic discharge. The hydrogen ions stimulate water decomposition and inhibit charge transfer slightly. The grain-refining organic additive appears to be adsorbed effectively on the galvanizing interface and to deactivate growing kink sites of electrocrystallites at low current density, resulting in nucleation-controlled deposits, but less adsorption at high current density leads to growth-controlled deposits by diffusion. The impedance method is a powerful technique in understanding detailed reactions at the electroplating interface, in determining morphologies of the plated layer, and is a useful technique in developing additives.

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