ENHANCED MASS TRANSPORT IN ELECTROGALVANIZING SYSTEMS BY HYDROGEN EVOLUTION

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Abstract—The effect of hydrogen evolution on mass transport during electrogalvanizing was evaluated for a vertical electrode by using a electrochemical tracer. The potentiodynamically measured limiting current of a cadmium tracer was compared with those obtained by the codeposition method at various current densities. The effects of pH on the hydrogen evolution and the mass transfer rate during electrogalvanizing were also determined. The Sherwood number was calculated and compared with that predicted by natural convection. It has been found that the mass transport was mainly enhanced by natural convection at current densities less than 25 mA cm^{-2} and by simultaneous hydrogen evolution at relatively higher current densities.

NOMENCLATURE

- $C_{\rm b}$ concentration in the bulk (M)
- C_i^{b} concentration at the electrode/electrolyte interface (M)
- \underline{D} diffusion coefficient (cm² s⁻¹)
- F Faraday constant (96500 coul eq^{-1})
- g acceleration of gravity (980 cm s⁻²)
- Gr Grashof number
- *i* current density $(mA cm^{-2})$
- $i_{\rm L}$ limiting current density (mA cm⁻²)
- k diffusion mass transfer coefficient (cm s⁻¹)
- $k_{\rm M}$ diffusion mass transfer coefficient of the primary ion (cm s⁻¹)
- $k_{\rm T}$ diffusion mass transfer coefficient of the tracer ion (cm s⁻¹)
- L characteristic length of the electrode (cm)
- n change of oxidation state
- Sc Schmidt number
- Sh Sherwood number, predicted for combined diffusion and natural convection
- Sh' Sherwood number experimentally determined
- t transference number
- δ diffusion layer thickness (cm)
- ρ average density across the diffusion layer (g cm⁻³)
- $\rho_{\rm b}$ density of the bulk electrolyte (g cm⁻³)
- ρ_i density of the electrolyte at electrode/electrolyte interface $(g \text{ cm}^{-3})$
- average kinematic viscosity across the diffusion layer (cm² s⁻¹)

1. INTRODUCTION

Mass transport is an important aspect in electrodeposition. Interest in high mass transport has recently increased in non-ferrous extractive and coating technology due to the trend toward higher current density processing. Not only is the mass transport of the primary metal ion important, but those of certain impurities can also affect the properties of the deposits obtained. Low level concentrations of particulates, organics and inorganics often influence polarization behavior, nucleation and growth, particularly when these are mass transport controlled. Thus there is a need to characterize the combined engineering and electrochemical design parameters to assist in controlling electrocrystallization[1].

Continuous electrogalvanizing of steel sheet at high current density is receiving considerable attention at present due to interest in producing corrosion resistant materials for automotive applications. Unfortunately, unlike the mass transport governed by gas evolution[2, 3] or natural convection[4] which have been studied extensively, there is little fundamental technical data available on that of a zinc sulfate electrolyte using various process parameters. One objective of this research was to determine what correlation might exist for this specific zinc deposition system where natural convection and hydrogen evolution are both active, particularly with changing pH and current density.

It is difficult to directly measure the zinc limiting current due to the increasing surface roughness and codepositing hydrogen when plating close to the limiting current density. A tracer technique[5], however, can be used which allows *in situ* measurement of the mass transfer conditions. The tracer must have a more noble potential than the primary species and must deposit at its limiting current density throughout the deposition cycle. The limiting current density of the tracer is obtained either by chemical analysis[5, 6] or anodic stripping[7] of the deposits. Subsequently, the mass transfer coefficient of the tracer can be calculated by

$$i = nFk(C_b - C_j)/(1 - t).$$
 (1)

Equation (1) is valid for binary electrolyte of a reacting cation and the transport coefficient can be neglected in cases with sufficient supporting electrolyte. The latter situation is the case whenever the calculations were made using the Cd tracer ion. Similar calculations were made in order to estimate the interfacial Zn^{+2} concentration using Equation (1), but it must be recognized that these data are only approximations and the trend for the change in concentration is more pertinent than the actual numerical values themselves. For more accurate values, a more rigorous treatment is required. Then the diffusion mass transfer coefficient of the primary species $(Zn^{+2}$ in this case) can be calculated by equation

$$k_{\rm M} = k_{\rm T} (D_{\rm M}/D_{\rm T})^m \tag{2}$$

where m = 3/4 for natural convection in a laminar regime, and 2/3 for other flow regimes.

Other mass transfer related properties, such as the limiting current density and diffusion layer thickness can also be estimated by use of Equation (1) and

$$\delta = D/k. \tag{3}$$

When the tracer is codeposited with Zn, the $2nSO_4$ concentration at the cathode is significantly reduced. Natural convection due to differences in electrolyte density is expected and mass transport is enhanced. Wilke *et al.*[4] correlated the Sherwood number to the Grashoff and Schmidt numbers for a laminar natural convection condition by the semi-empirical equation

$$Sh = 0.66 \, (Gr \cdot Sc)^{1/4} \tag{4}$$

where

$$Gr = gL^3(\rho_b - \rho_i)/\rho v^2 \tag{5}$$

$$Sc = v/D.$$
 (6)

The experimentally determined Sherwood number, Sh', can be calculated[4] by

$$Sh' = L/\delta$$
 (7)

and compared with the predicted Sherwood number.

In this study, the limiting current density of a Cd tracer was potentiodynamically measured in ZnSO₄ electrolytes. The limiting current was directly observed from a cyclic voltammogram[8, 9], allowing a quick evaluation of the mass transfer properties to be made. In addition, negligible natural convection occurred by using this technique since the concentration of the tracer was sufficiently low to prevent density changes of the electrolyte at the electrode surface. The limiting mass transport of the tracer during Zn, tracer and hydrogen codeposition was obtained by chemical analysis of the deposits similar to the technique used by Ettel et al. [5]. The results were compared with those determined by the potentiodynamic method. Thus the enhancement of mass transfer due to natural convection or simultaneous gas evolution during the codeposition of the tracer and Zn can be evaluated.

Since some hydrogen is evolved during electrogalvanizing, electrolytes at different pH's were used in order to see the effect of simultaneous gas evolution on the mass transport. The effect of current density on mass transport enhancement by natural convection and possible hydrogen evolution was also investigated.

2. EXPERIMENTAL

The experimental set-up consisted of vertical electrodes in a 400 ml beaker fitted with a plastic cover. The potentiodynamic measurements were made using a Pt gauze counter electrode and a saturated Hg/Hg_2SO_4 reference electrode (+0.656 volts vs she). The working electrode was a 0.75 cm × 11 cm Cd strip polised with 600 grit SiC polishing paper and covered with electroplaters' tape to expose a working area of

about 1 cm² (0.75 cm × 1.34 cm). Electrolytes containing 1.53 M ZnSO₄ (100 gl⁻¹ Zn⁺²) and 0.89 mM CdSO₄ (100 mgl⁻¹ Cd⁺²) at pH 2.5 and pH 5 were sparged by N₂ gas before each test. During the tests, the electrolyte was not agitated but kept under a N₂ atmosphere. All tests were performed at ambient temperature. The potential scanning range was from -1.25-1.35 volts vs Hg/Hg₂SO₄ reference electrode and the scan rate was 2 mV s⁻¹. In this potential range, only the Cd was deposited and its limiting current density was directly determined from the limiting current plateau observed in the cyclic voltammogram. To prove the validity of this potentiodynamically measured value, Cd deposited on different electrodes for 30 min was also chemically analysed. The electrodes included: (1) low carbon steel degreased with trichloroethylene, and electro-cleaned cathodically and then anodically for 1 min in 600 gl⁻¹ H_2SO_4 at 400 mA cm⁻², (2) Zn polished by 600 grit SiC paper, and (3) low carbon steel electrocleaned and pre-coated with Zn at 100 mA cm⁻² for 2.5 min in electrolyte at pH 2.5 or pH 5. The electrolyte was exposed to air. The potential of deposition was controlled in the Cd limiting current plateau region. Cadmium was also cemented spontaneously onto the Zn-coated steel electrode without any external power source. The Cd deposits were then dissolved in 2.5 N HNO₃ and analysed by atomic absorption (AA) spectroscopy. The limiting current densities of Cd were calculated from the analysed amount of Cd in the deposits by Faraday's law.

For codeposition of Cd and Zn, a low carbon steel cathode, as described earlier, was used. Pure Zn, with approximately 2 cm^2 area, was used as the anode and placed about 3 cm from the steel cathode. Electrolytes containing 1.53 M ZnSO₄ and 0.89 mM CdSO₄ with pH values of 5, 2.5, 1.5 and 0.6 (1.53 M or 150 gl⁻¹ H_2SO_4) were used. The deposition time varied with current density, which was in the range from 25 to 300 mA cm^{-2} , in order to give 15 coulombs and a theoretical thickness of about 7 μ m. Depositions at lower current densities $(2-10 \text{ mA cm}^{-2})$ were also carried out for electrolyte at pH 5 and a deposition time of 25 min. The deposits were dissolved, analysed by AA, and the limiting current densities of Cd were calculated as described earlier. For deposition in electrolyte containing 1.53 M H₂SO₄, the current efficiency for Zn deposition at 100 to 1500 mA cm⁻² was determined by AA analysis. The H_2 current efficiency was found by difference, then the H₂ evolution rate was calculated by Faraday's law.

3. RESULTS AND DISCUSSION

The potentiodynamically measured limiting current density of Cd decreased with time. A relatively constant current density, about 0.01 mA cm⁻² for electrolytes at pH 2.5 and 5, was observed after a steady state was reached. Similar values were obtained by AA analysis of the 30 min deposits of Cd on a steel electrode, Zn electrode, Zn-coated steel electrode or by cementation of Cd on a steel electrode pre-coated with Zn in electrolyte at pH 2.5. However, when the steel electrode was pre-coated with Zn in the pH 5 electrolyte, the limiting current of Cd obtained by cementation or

electrodeposition was about 75% higher than that measured potentiodynamically. This increase of the limiting current of Cd may be due to the increase of surface roughness of the Zn coating when compared with that deposited in electrolyte at pH 2.5.

The limiting current densities of the Cd tracer, obtained from. Zn-Cd codeposition followed by AA analysis, are plotted vs the codeposition current densities as shown in Fig. 1. The potentiodynamically measured $i_{L, Cd^{+2}}$ was also included in the same figure as the point at zero codeposition current density. The limiting mass transport of Cd was enhanced by a factor of 2.5-36 in the codeposition current density range investigated, when compared with the value potentiodynamically obtained in the absence of Zn deposition. The mass transport increased with Zn current density as expected, since the concentration gradient across the diffusion layer would be larger at higher current density, thus increasing the natural convection caused by the difference in electrolyte density. Simultaneous hydrogen evolution also enhanced the mass transport. Similar values of $i_{L,Cd+2}$ were obtained for deposits plated at 25 mA cm⁻² in electrolytes with different pH values, which indicated that the effect of hydrogen evolution on the mass transport was not significant at this low current density. For deposition at higher current densities, however, the mass transfer rate increased with the increasing acid content in the electrolyte, probably because of increasing hydrogen evolution even though simultaneous vigorous evolution of hydrogen bubbles was observed only for electrolyte containing 1.53 M H₂SO₄. In general, the reproducibility of the data was good, except for up to 15% error for the highly acidic electrolyte. Since hydrogen evolution is very sensitive to the substrate, a slight variation in the pretreatment of the substrate can result in a significant difference in the partial currents obtained.

Dendrites on the edges of the deposits were noticed when the current density exceeded about 175, 200 and



Fig. 1. The effect of current density and pH on the diffusion limiting current density of Cd tracer. Electrolytes contain 1.53 M ZnSO₄ with: \Box , 1.53 M H₂SO₄; ∇ , pH 1.5; o, pH 2.5; Δ , pH 5.

300 mA cm⁻² for the electrolyte at pH 5, pH 2.5 and pH 1.5, respectively. Deposits obtained in electrolyte containing 1.53 M H₂SO₄ were smooth for the current density range studied. Figure 2 shows the tendency toward roughness for a deposit obtained in an electrolyte at higher pH with slower mass transfer rate, probably due to less hydrogen evolution. The deposit was made at a relatively high current density, 300 mA cm^{-2} , and on a circular exposed area to avoid the dendrite formation on the edges. The micrographs were taken at the same location on the two cathodes, allowing a direct comparison. The difference in morphology was more pronounced at the edges than in the center. In general, a rough and dendritic deposit is expected when the plating current density exceeds a certain fraction of the limiting current density [10]. In other words, the roughening of the deposit could be eliminated by increasing the mass transfer if the cause is a low limiting current density. As indicated by the mass transfer results shown in Fig. 1 and the calculated $i_{\rm L, Zn^{+2}}$, the deposit was made at about 40% of the $i_{L,Zn+2}$ in electrolyte containing 150 gl⁻¹ H₂SO₄ but at about 60% of the $i_{L,Zn+2}$ in electrolyte at pH 2.5. Thus the micrographs shown in Fig. 2 are in agreement with the trend of increasing mass transfer rate in a more acidic electrolyte, probably due to more hydrogen evolution. However, other electrolyte properties such as viscosity, pH, conductivity, etc., could also influence the morphology of the deposits due to effects such as different mechanism of hydrogen bubbling and the current density distribution.

The theoretical increase in mass transport by natural convection was calculated following Wilke's approach[4], using Equations (4), (5) and (6), and compared with the measured values. Some results of calculations are shown in Tables 1 and 2 for selected electrolyte at pH 5 and electrolyte containing 1.53 M H_2SO_4 , respectively. In the tables, the *i* is the plating current density of Zn-Cd codeposition and the $i_{L, Cd^{+2}}$'s are those shown in Fig. 1. The same $D_{Zn^{+2}}$ (3.8 $\times 10^{-6} \text{ cm}^2 \text{s}^{-1}[11])$ $D_{Cd^{+2}}(3.1 \times 10^{-6})$ and cm²s⁻¹[12]) were used for all electrolytes for approximation since literature values are not available. C_i , the concentration of Zn^{+2} at the electrode/electrolyte interface, is calculated by using Equation (1). The $t_{\mathbb{Z}n^{+2}}$ values were taken as 0.22[13] and 0.07[12]for electrolyte at pH 5 and electrolyte containing 1.53 M H₂SO₄, respectively. The ρ_b , ρ_i , and ρ are calculated from the measured density (1.46 g cm^{-3}) of 210 gl⁻¹ ZnSO₄ stock solution and literature values for densities of concentrated H2SO4 and water. The Sh' is calculated using Equation (7), with L = 1.34 cm.

The Sh and Sh' numbers were plotted against $Gr \cdot Sc$ on a log-log scale as shown in Fig. 3. The solid line predicted by $Sh = 0.66 (Gr \cdot Sc)^{1/4}$ represents the theoretical value which indicates the mass transfer rate enhanced by laminar natural convection only. The Sh' number is the measured value which indicates the real mass transfer rate during the electroplating. It is clear that the measured mass transfer rate is larger than that predicted except for the lower current density region (2 to 25 mA cm⁻²) for electrolyte at pH 5. In this region, the measured Sh' did not deviate much from Wilke's correlation, which indicated that the mass transfer was mainly enhanced by natural convection in the lower current density region. However, the data appeared to



Fig. 2. Zn deposits obtained at 300 mA cm⁻² for 2.5 min in electrolytes containing 1.53 M ZnSO₄ with (a) 1.53 M H₂SO₄, (b) pH 2.5.

ZnSO ₄ electrolyte at pH 5											
$i(\mathrm{mAcm^{-2}})$	2	5	10	25	100	200	300				
C _i (M)	1.49	1.44	1.38	1.25	0.88	0.68	0.45				
$C_{i}(g^{1-1})$	97.1	94.2	90.4	81.4	57.6	44.4	29.4				
$\rho_i(gcm^{-3})$	1.211	1.205	1.197	1.177	1.125	1.095	1.062				
$\rho_{\rm b} - \rho_{\rm i}(\rm gcm^{-3})$	0.007	0.013	0.021	0.041	0.093	0.123	0.156				
$\rho(\mathrm{gcm^{-3}})$	1.215	1.212	1.208	1.198	1.172	1.157	1.140				
$v \times 10^2 (cm^2 s^{-1})$	1.99	1.97	1.95	1.89	1.74	1.67	1.59				
Sc	5237	5184	5132	4974	4579	4395	4184				
$Gr \times 10^{-5}$	0.343	0.652	1.078	2.259	6.180	8.988	12.76				
$Sh = 0.66 (Gr \cdot Sc)^{1/4}$	76	89	101	121	152	165	178				
$\delta_{Zn^{+2}} \times 10^3$ (cm)	21.1	16.7	13.9	10.7	6.12	4.01	3.39				
Sh	64	80	96	125	219	334	395				

Table 1. Calculation of Sc, Gr, Sh and Sh' numbers for different plating current densities in 1.53 MZnSO4 electrolyte at pH 5

Table 2. Calculation of Sc, Gr, Sh and Sh' numbers for different plating current densities in 1.53 M ZnSO₄ and 1.53 M H₂SO₄ Electrolyte

$i(mA cm^{-2})$	50	100	150	200	250	300
C _i (M)	1.12	1.06	0.99	0.96	0.95	0.94
$C_{i}(gl^{-1})$	73.4	69.5	64.6	63.0	62.0	61.2
$\rho_i (g \mathrm{cm}^{-3})$	1.229	1.221	1.210	1.206	1.204	1.202
$\rho_{\rm h} - \rho_{\rm i} (\rm g \rm cm^{-3})$	0.059	0.067	0.078	0.082	0.084	0.086
ρ (g cm ⁻³)	1.259	1.255	1.249	1.247	1.246	1.245
$v \times 10^2 (cm^2 s^{-1})$	2.062	2.035	2,000	1.991	1.985	1.980
Sc	5426	5355	5263	5239	5224	5210
$Gr \times 10^{-5}$	2.599	3.039	3.681	3.912	4.034	4.155
$Sh = 0.66 (Gr \cdot Sc)^{1/4}$	128	133	138	140	141	142
$\delta_{7n+1} \times 10^3$ (cm)	6.40	3.68	2.85	2.23	1.84	1.56
sh	209	364	470	601	728	859



Fig. 3. Comparison of the predicted Sh number with the measured Sh' number for electrolytes containing 1.53 M ZnSO₄ with: ▲, 1.53 M H₂SO₄;●, pH 5.

fit more closely to the equation, $Sh = 0.116 (Gr \cdot Sc)^{1/3}$ (shown as the dotted line), which was reported in the literature[14,15,16] as the form $Sh = a(Gr \cdot Sc)^{1/3}$ for turbulent natural convection. The reported value for the constant *a* was from 0.15–0.19 for different systems. Even though hydrogen evolution was not visually detected in electrolyte at pH 5, the measured current efficiency of Zn indicated that there were still some hydrogen codeposited and might cause a turbulent natural convection.

The difference between Sh' and Sh for the relatively high plating current density region for pH 5 electrolyte is probably due to hydrogen evolution, thus indicating that the mass transport is no longer in the natural convection regime. Surface roughness for deposits made in pH 5 electrolyte, could also account for some of the difference, as mentioned earlier. The maximum predicted Sh number using Equation (4) under the diffusion limiting conditions for Zn is 203 for electrolyte at pH 5 using values, $C_i = 0 \text{ gl}^{-1}$, $\rho_b - \rho_i$ $= 0.22 \text{ g cm}^{-3}$, $\rho = 1.108 \text{ g cm}^{-3}$, $v = 1.39 \times 10^{-2}$ cm²s⁻¹, and $D = 3.8 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$. However, the measured Sh' was already 219 at a current density of 100 mA cm⁻². This again indicated that the mass transport was enhanced not by natural convection alone.

The contribution to the enhancement of mass transport by natural convection is much smaller than that by the simultaneous hydrogen evolution for relatively high current density and highly acidic electrolyte. As shown in Fig. 3, the Sh' number was much larger than the predicted Sh number and almost independent of the Gr number as the current density increased in electrolyte containing 1.53 M H_2SO_4 , indicating that the mass transport was mainly enhanced by hydrogen evolution. These results have shown that simultaneous hydrogen evolution during Zn deposition is very effective in reducing the diffusion layer thickness even when no other agitation is provided.

The hydrogen evolution rate in electrolyte containing $150 \text{ gl}^{-1} \text{ H}_2\text{SO}_4$ was calculated based on the current efficiency of Zn, which was in the range from 91-71% for current densities from $100-1500 \text{ mA cm}^{-2}$. Relatively high plating current density and electrolyte containing high acid content were used so that the effect of natural convection was relatively small. A calculated δ of Zn^{+2} vs hydrogen evolution rate and hydrogen current density plot is shown in Fig. 4. Due to the increasing hydrogen evolution rate accompanying the increasing plating current density, the δ was significantly reduced. The slope of the plot is -0.57 and comparable with other reported results[2], being from -0.25-0.87, in which hydrogen evolution was the only cathodic reaction. The range of δ is slightly smaller than those listed in the literature [2, 17]. The difference could be due to the combined effect of natural convection and gas evolution during electrogalvanizing compared with a sole hydrogen gas evolution reaction. Difference in cell design and electrode orientation could also contribute some of the difference in the δ value.

4. CONCLUSIONS

The limiting current density of a Cd tracer on a vertical electrode in a stationary $ZnSO_4$ electrolyte (pH 2.5 and 5) containing 0.89 mM CdSO₄ was determined to be 0.01 mA cm⁻² by the potentiodynamic measurement. Enhancement of mass transport of the Cd tracer was observed when Cd was codeposited with Zn. The enhancement increased with plating current density and acid concentration in the electrolytes due to natural convection and simultaneous hydrogen evolution.

The measured Sherwood numbers were larger than those predicted by natural convection at current densities greater than 25 mA cm^{-2} . The difference was due to simultaneous hydrogen evolution, which was a dominant factor for enhancement of mass transfer in an electrolyte containing $1.53 \text{ M H}_2\text{SO}_4$, particularly for relatively high plating current densities.



Fig. 4. Effect of hydrogen evolution rate on δ during deposition of Zn in electrolyte containing 1.53 M ZnSO₄ and 1.53 M H₂SO₄. Current densities (mA cm⁻²): Δ , 100; o, 150; \Box , 200; ∇ , 250; \blacktriangle , 300, \oplus , 400; \blacksquare , 500; \blacktriangledown , 750; \times , 1000; +, 1250; \diamondsuit , 1500.

Simultaneous hydrogen evolution during electrogalvanizing reduces the diffusion layer thickness, which was found to be slightly smaller than values reported in the literature or studies on hydrogen evolution only, indicating that the difference was due to the combined effect of natural convection and hydrogen evolution. The tracer technique has been shown to be very useful in characterizing systems where both gas evolution and metal deposition are occurring over a range of current densities.

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REFERENCES

- T. J. O'Keefe and J. W. Evans, eds, Electrochemistry Research Needs for Mineral and Primary Materials Processing, NSF/USBM Workshop, Rolla, MO (1983).
- P. J. Sides, Tutorial Lectures in Electrochemical Engineering and Technology—II (edited by R. Alkire and D. Chin), Vol. 79, pp. 226–232. A.I.Ch.E., New York (1983).
- F. Ajersch, D. Mathieu and D. L. Piron, Can. Metall. Q. 24, 53 (1985).

- 4. C. R. Wilke, C. W. Tobias and Morris Eisenberg, Chem. Engng Progr. 49, 663 (1953).
- V. A. Ettel, B. V. Tilak and A. S. Gendron, J. electrochem. Soc. 121, 867 (1974).
- A. Weymeersch, R. Winand and L. Renard, Plating Surf. Finish. 68, 56 (1981).
- A. V. Cooke, J. P. Chilton and D. J. Fray, Energy Reduction Techniques in Metal Electrochemical Process (edited by R. G. Bautista and R. J. Wesely), pp. 111-141. TMS, Warrendale, PA (1985).
- T. J. O'Keefe, J. S. Cuzmar and S. F. Chen, J. electrochem. Soc. 134, 547 (1987).
- T. J. O'Keefe, S. F. Chen, J. S. Cuzmar and V. A. Ettel, Hydrometallurgical Reactor Design and Kinetics (edited by Bautista et al.), pp. 359-371. TMS, Warrendale, PA (1986).
- A. R. Fajardo, R. Winand, A. Weymeersch and L. Renard, AESF Fifth Continuous Strip Plating Symposium, pp. S1-S28, Orlando, FL (1987).
- 11. E. W. Washburn, International Critical Tables, p. 65. McGraw-Hill, New York, (1929).
- 12. S. F. Chen, Ph.D. Diss., University of Missouri, Rolla, MO (1986).
- 13. R. Parsons, Handbook of Electrochemical Constants, p. 88. Butterworths Scientific, London (1959).
- 14. A. A. Wragg, Electrochim. Acta 13, 2159 (1968).
- 15. E. J. Fenech and C. W. Tobias, *Electrochim. Acta* 3, 233 (1960).
- 16. N. Ibl, Electrochim. Acta 24, 1105 (1979).
- L. J. J. Janssen and L. G. Hoogland, *Electrochim. Acta* 18, 543 (1973).