JOURNAL OF APPLIED ELECTROCHEMISTRY **14** (1984) 417–423

# Effect of halides on the corrosion behaviour of nickel in molten (Na, K)$NO_3$

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Received 26 May 1983, revised 8 August 1983

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The effect of alkali halides on the corrosion behaviour of nickel in (Na, K)$NO_3$ eutectic has been investigated at a temperature of 400° C. Initial addition of the halide ($Cl^-$, $Br^-$ or $I^-$) increases the steady-state potential to more noble values than for the pure melt. Further addition decreases the potential according to the equation $E = a - b\log C$. Gravimetric measurements show that the corrosion of nickel increases in the presence of $Cl^-$ and $Br^-$ and decreases in the case of $I^-$. The anodic polarization increases in the presence of $Cl^-$ and $Br^-$ and decreases when $I^-$ is added to the melt. These results are discussed, in the light of previous work, on the basis of the interaction of these halides with the nitrate melt to give the corresponding halogen or their catalytic effect on the dissociation of nitrate to give excess amounts of $O^{2-}$ ions. The liberated iodine may form a physically adsorbed layer on the nickel surface, offering some protection to the metal. In this respect $Cl^-$ and $Br^-$ behave as acidic additives and $I^-$ behaves as a base.

The presence of fluoride in the melt considerably increases the rate of nickel corrosion. The weight-gain increases linearly with log $C$. A small addition of fluoride shifts the steady-state potential towards more noble values. Further addition shifts it towards more negative values. These effects may be attributed to the small size of fluoride and its high reactivity. Fluoride can penetrate the oxide layer, and form insoluble nickel fluoride.

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## 1. Introduction

Experimental results for the oxidation of nickel in (Na, K)$NO_3$ eutectic at different temperatures presented previously [1], indicate that oxidation proceeds in a parabolic fashion to the formation of a passivating oxide film consisting mainly of NiO.

In this study the effect of different concentrations of $Cl^-$, $Br^-$, $I^-$ and $F^-$ ions on the corrosion behaviour of nickel in a nitrate melt has been examined. The variation of weight-gain, steady-state potential and anodic polarization of nickel with the concentration of these anions has been investigated at 400° C.

## 2. Experimental details

The experimental set-up, the preparation of the $NaNO_3$–$KNO_3$ eutectic (50 : 50/mol : mol; m.p. 225° C) and the preparation of the nickel electrodes and specimens for potential and gravimetric measurements respectively have been described previously [1, 2]. Fresh electrodes or specimens were used in each experiment, with 100.0 g of eutectic. The potentials were measured relative to a Ag/Ag(I), (Na, K)$NO_3$ reference electrode [1, 2], using a Pye Unicam potentiometer. Constant currents were obtained from a mains-operated constant current device.

## 3. Results

### 3.1. *Steady-state potential measurements under open-circuit conditions*

The variation of the nickel electrode potential under open-circuit conditions in (Na, K)$NO_3$ eutectic containing increasing additions of $Cl^-$, $Br^-$, $I^-$ and $F^-$ ions at a temperature of 400° C was followed as a function of time until steady-state values were reached.

In Figs. 1–3 curves are given representing the variation of the potential of the nickel electrode in the presence of chloride, bromide and iodide

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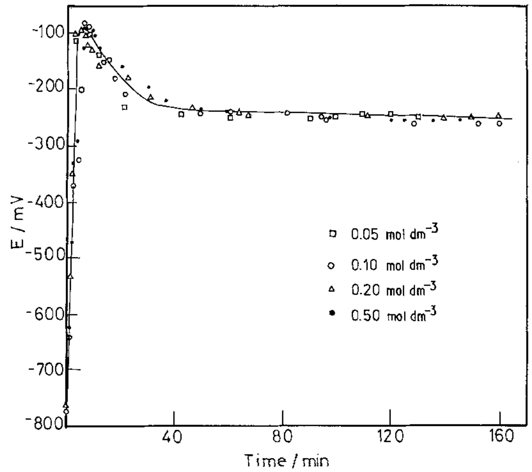

Fig. 1. Potential–time curves of the nickel electrode in (Na, K)$NO_3$ melt at 400° C in the presence of chloride ions.

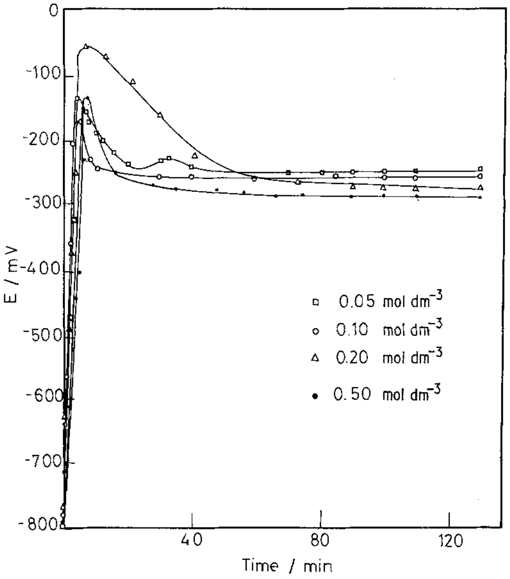

Fig. 2. Potential–time curves of the nickel electrode in (Na, K)$NO_3$ melt at 400° C in the presence of bromide ions.

additions at a temperature of 400° C. The steady-state potentials were attained after a period ranging from 100–200 min, depending on the type and concentration of the additive used. The potential shifts in the positive direction immediately after immersion of the electrode into the melt and the curves show a maximum before attaining the steady potential.

Fig. 4 represents the variation of the steady-state potential of the nickel electrode with the logarithm of the molal concentration of different halides ($Cl^-$, $Br^-$ and $I^-$) at 400° C. The plots show that the first addition of the halide shifts the steady potential to more noble values than that obtained in the pure melt at this temperature [1] (≃ 320 mV). Further additions of the halide decrease the steady potential to more negative values according to the equation: $E = a - b \log C$, in a manner depending on the nature of the halide.

Fig. 5 shows the potential vs time curves of the nickel electrode in the nitrate melt at 400° C in the presence of different additions of NaF. In these experiments, the potential was found to fluctuate before attaining the steady-state values. These values were obtained after a reaction period ranging from 90–310 min, depending on the con-

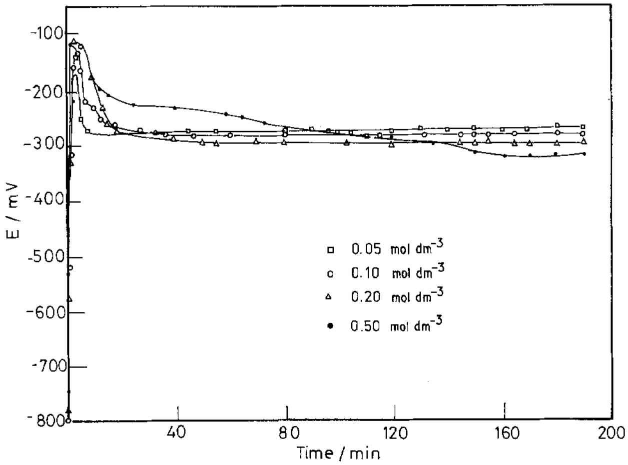

Fig. 3. Potential–time curves of the nickel electrode in (Na, K)$NO_3$ melt at 400° C in the presence of iodide ions.

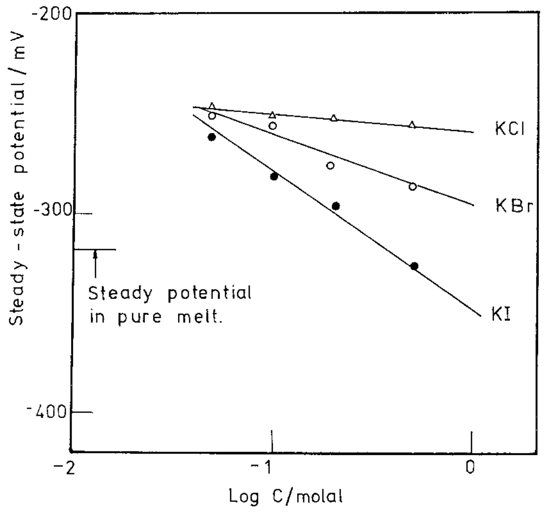

Fig. 4. Variation of steady-state potential of the nickel electrode with log $C$ of $Cl^-$, $Br^-$ and $I^-$ in (Na, K)$NO_3$ melt at 400° C.

centration of fluoride added. The variation of the steady-state potential with the logarithm of the molal concentration of NaF is shown in Fig. 6. Small additions of NaF shift the steady potential to more noble values than that obtained in the pure melt at the same temperature. Further additions give rise to a decrease in potential to more negative values.

### 3.2. *Weight-gain measurements*

The effect of the halide ions on the corrosion behaviour of nickel in $NaNO_3$–$KNO_3$ eutectic has been studied at a temperature of 400° C. The lines of Fig. 7 represent the variation of weight of the nickel specimens with the logarithm of molal concentration of the halide additions. In all experiments the weight-gain of the specimens was measured after an exposure time of 8 h.

As seen from Fig. 7 the $F^-$, $Cl^-$ and $Br^-$ additions promote the corrosion of nickel and the extent of corrosion acceleration depends on the nature and concentration of these additives. At all examined concentrations the weight-gain in the case of NaF varies at a higher rate than that for $Cl^-$ or $Br^-$. The lower curve (line) of Fig. 7 shows the retarding effect of iodide additions.

Within the concentration range studied the variation of the weight-gain ($\Delta W$) of nickel specimens in the nitrate eutectic with the molal concentration ($C$) of examined additives can be represented by the linear relation

$$\Delta W = a \pm b \log C \qquad (1)$$

Visual observation of the specimens at the end of experiments showed that in the presence of $F^-$, the scale formed is continuous, adherent and has a violet colour.

### 3.3. *Anodic polarization measurements*

The variation of the anodic polarization of the nickel electrode in $NaNO_3$–$KNO_3$ eutectic, containing increasing additions of NaCl, NaBr and NaI at a temperature of 400° C was followed as a function of current density.

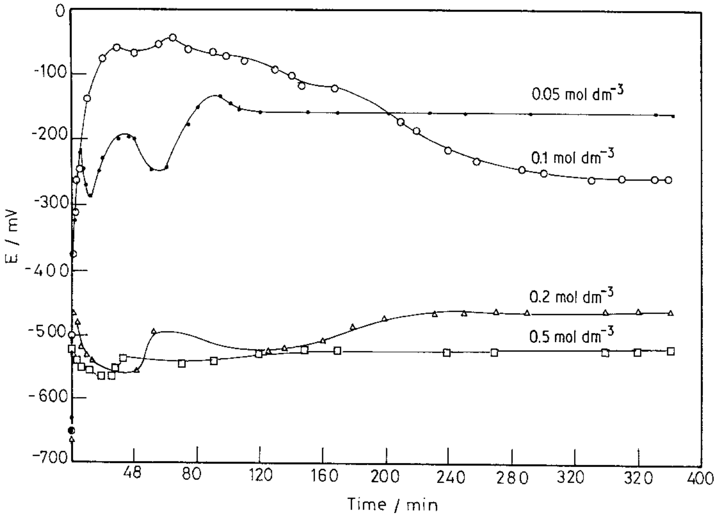

Fig. 5. Potential–time curves of the nickel electrode in (Na, K)$NO_3$ melt at 400° C in the presence of fluoride ions.

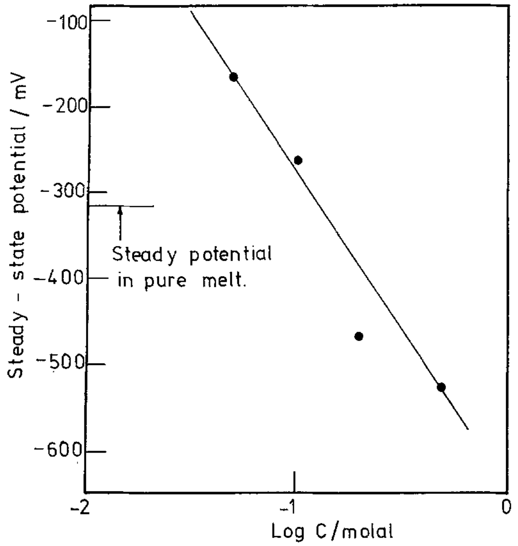

Fig. 6. Variation of steady-state potential of the nickel electrode with log $C$ of fluoride ion in (Na, K)$NO_3$ melt at 400° C.

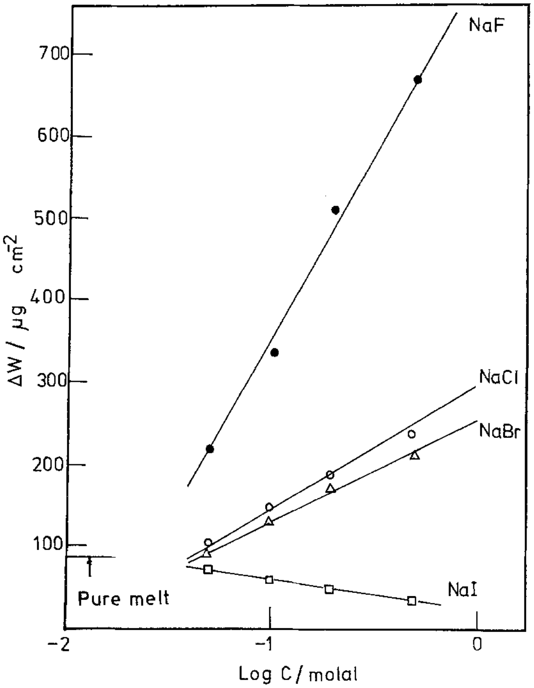

Fig. 7. Variation of the weight-gain of nickel with halide concentration in (Na, K)$NO_3$ melt at 400° C.

Semilogarithmic plots of the galvanostatic behaviour of the nickel electrode in (Na, K)$NO_3$ eutectic in the presence of increasing additions of NaCl, NaBr and NaI are given in Figs. 8–10, respectively. These results show clearly that the anodic polarization of the nickel electrode increases in the presence of $Cl^-$ or $Br^-$ additions and decreases in the case of $I^-$. The extent of the anodic passivation increase or decrease depends on the concentration of the additive in the melt.

## 4. Discussion

The results of this study showed that the potential shifted in the positive direction immediately after immersion of the nickel electrode into the melt. This positive shift of the potential may indicate a tendency for the nickel electrode to undergo spontaneous passivation in these melts. The results showed also that small additions of the halide ions ($Cl^-$, $Br^-$ and $I^-$) in (Na, K)$NO_3$ melts shifted the steady-state potential to more noble values than those obtained in the pure melt. A further increase in the concentration was accompanied by a decrease in electrode potential towards more negative values. Also the addition of increasing amounts of $Cl^-$, $Br^-$ and $I^-$ gave rise to an increase in weight-gain and anodic polarization of nickel in the case of the former ions and a decrease in the presence of the latter.

It is suggested that in the present system there are two opposing processes competing on the nickel surface. The oxide ion helps in repairing or building a passivating film of mainly NiO, while the aggressive halide ions attack the weak areas in the film. The resultant behaviour depends on the relative concentration of the two species. This system resembles the behaviour of nickel in passivating media (alkaline solutions) containing halide ions (aggressive ions). The behaviour of nickel in such a mixture of passivating and aggressive ions has been repeatedly tested in the literature [3–15]. Most of the reported views attribute the accelerating effect of halide ions on the corrosion of nickel in these passivating media to a competing adsorption of the halide and oxygen or hydroxyl ions on the metal surface. The exchange of halide ions with the adsorbed oxygen ions hinders the passivation of nickel and facilitates the corrosion of the metal [6, 12].

It is now widely accepted that halides destroy the existing passivity and hinder the passivation of many metals. $Cl^-$ ions are most reactive [13],

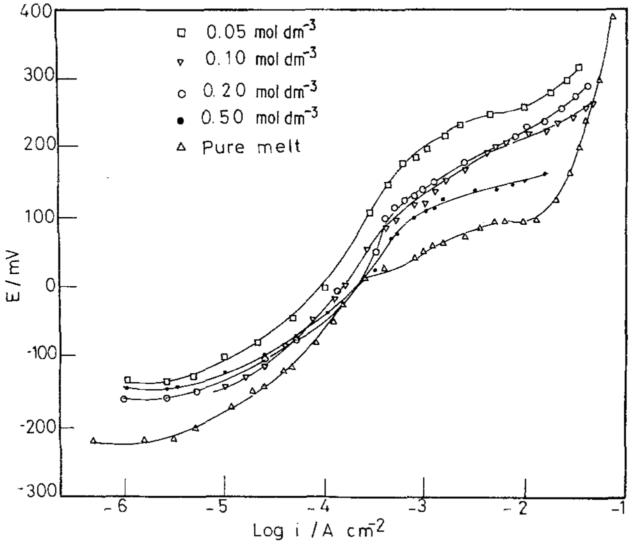

Fig. 8. Semilogarithmic plots of anodic polarization of nickel in (Na, K)$NO_3$ melt in the presence of NaCl at 400° C.

$Br^-$ and $I^-$ ions are less effective and owing to their increased deformability which leads to the formation of surface compounds, they may inhibit the acid corrosion of some metals [15]. $Cl_2$ acts as a corrosion activator, the position of $Br_2$ among the halogens enables it to act as a corrosion inhibitor as well as an activator [16]. While inhibition increases with the increase of atomic number, activation increases in the opposite direction, this means that $I_2$ can act as a corrosion inhibitor.

The chemical interaction of the halide ions with fused alkali nitrates has been investigated by different authors [14–20]. It has been reported that halide ions are oxidized by these melts to the corresponding halogens by the reactions

$$NO_3^- \rightleftharpoons NO_2^+ + O^{2-} \qquad (2)$$

$$NO_2^+ + X^- \rightleftharpoons \tfrac{1}{2}X_2 + NO_2 \qquad (3)$$

This oxidation interaction at constant temperature occurs at a rate depending on the nature of the halide ions. It was found that the rate of this oxidation process increases generally in the order $Cl^- < Br^- < I^-$. This oxidation process increases the amount of $O^{2-}$ in the melt.

The potential determining reaction in pure nitrate melt was suggested [21] as being

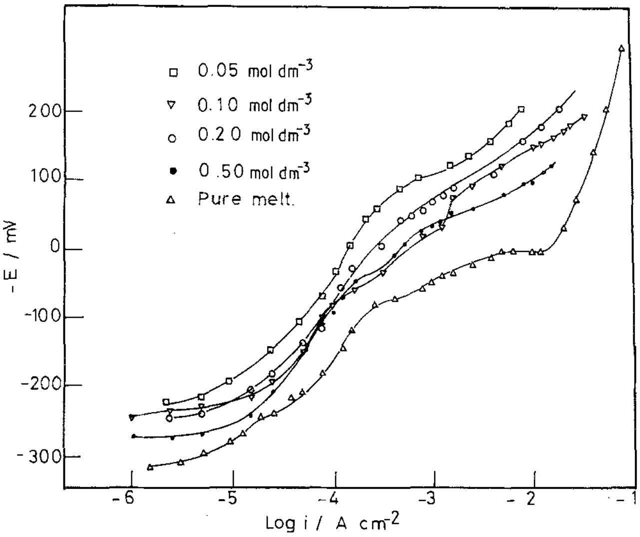

Fig. 9. Semilogarithmic plots of anodic polarization in (Na, K)$NO_3$ melt in the presence of NaBr at 400° C.

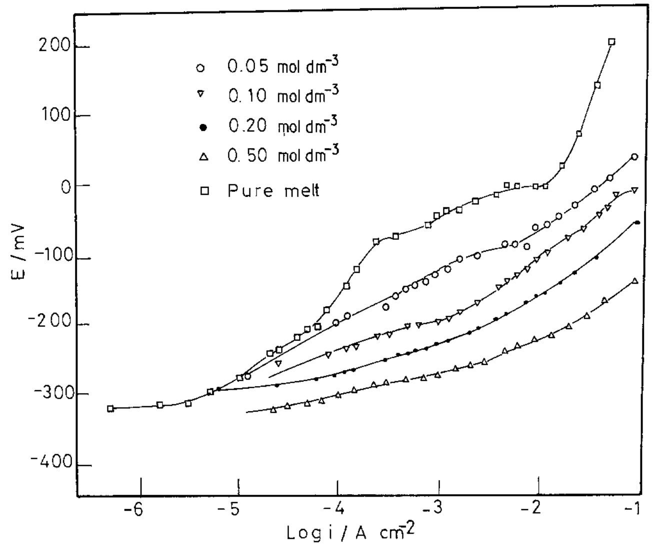

Fig. 10. Semilogarithmic plots of the anodic polarization of nickel in (Na, K)$NO_3$ melt in the presence of NaI at 400° C.

$$2NO_3^- \rightleftharpoons N_2O_5 + O^{2-} \quad (4)$$

The equilibrium of this reaction is expected to lie mainly to the left. Ions like iodide and bromide are assumed to catalyse this reaction and shift the equilibrium to the right. This catalytic effect seems to be related to the size of the halogen ion, decreasing in the direction $I^- \rightarrow Br^- \rightarrow Cl^-$, the last ion having practically no catalytic effect [21]. This catalytic effect increases $[O^{2-}]$ in the melt and consequently shifts the electrode potential to more negative values in a similar manner to basic additives.

The oxidation of iodide ions in the nitrate melt by the above-mentioned reactions gives rise to the formation of iodine [17–20] which acts as a corrosion inhibitor. The liberated iodine can form on the nickel surface as a physically adsorbed barrier (layer), offering some protection to the metal from corrosion by the melt. Also the addition of increasing amounts of iodide to the melt causes an increase of $[O^{2-}]$ in the melt [21]. These effects decrease the steady-state of the electrode potential (towards more negative values), weight-gain and anodic polarization in a similar manner as the basic additives [1, 2]. These predictions are in good agreement with the results shown in Figs. 4, 7 and 10.

The rate of nickel corrosion increases when chloride is added to the melt in increasing amounts. This effect may be attributed to the high accelerating effect of chloride on the corrosion of metals [13]. In comparison with other halides ($Br^-$ and $I^-$), chloride has a lower affinity to oxidation in the nitrate melt forming chlorine [17–20]. Also it has a negligible catalytic effect on the dissociation of nitrate to form oxide ions [21]. Even chlorine, if present, will act as a corrosion activator. The $[O^{2-}]$ in the electrical double layer decreases as a result of competing adsorption of $Cl^-$ and $O^{2-}$ ions on the metal surface. All these factors increase the weight-gain and anodic polarization in a manner agreeing with the effect of acidic additives on the corrosion behaviour of nickel in nitrate melts [1, 2].

The position of $Br_2$ among the halogens enables it to act as a corrosion inhibitor as well as an activator. For this reason the $Br^-$ additions in the (Na, K)$NO_3$ melt increase the corrosion rate to a smaller extent than in the case of $Cl^-$ additions. In galvanostatic measurements $Br^-$ affected the anodic polarization of the nickel electrode in a similar way to chloride ions.

The results obtained in Figs. 5–7 show that the fluoride additions markedly increase the corrosion rate of nickel in the nitrate melt. The initial addition of fluoride increases the steady-state potential to more noble values than for the pure melt. Further additions decrease the potential towards more negative values. Also the results of weight-gain measurements show that it is markedly high in comparison with that obtained in the presence of other halides.

In comparison with the other halides the fluoride has notably different behaviour. It has a very small ionic size, high electronegativity and reactivity. These properties suggest the possibility of penetration into the passive layer and attack of the base metal forming insoluble nickel fluoride. This effect increases the corrosion behaviour of nickel in the presence of $F^-$ in (Na, K)$NO_3$ melts. This prediction is in good agreement with results shown in Figs. 6 and 7.

## References

[1] R. M. S. Baraka, MSc Thesis, Cairo University (1983).
[2] A. Baraka and R. M. S. Baraka, *J. Appl. Electrochem.* **14** (1984) 305.
[3] F. Förster and F. Krüger, *Z. Elektrochem.* **33** (1927) 406.
[4] D. R. Turner, *J. Electrochem. Soc.* **98** (1951) 434.
[5] G. Trümpler and H. Meyer, *Helv. Chim. Acta* **35** (1952) 1304.
[6] G. Trümpler and W. Saxer, *ibid.* **36** (1953) 1630.
[7] *Idem, ibid.* **39** (1956) 1733.
[8] W. Machu and A. Ragheb, *Werkstoff. Korros. Mannheim* **4** (1953) 429.
[9] *Idem, ibid.* **5** (1954) 217.
[10] R. Landsberg and M. Hollnagel, *Z. Elektrochem.* **58** (1954) 680.
[11] *Idem, ibid.* **60** (1956) 1098.
[12] K. Schwabe and G. Dietz, *ibid.* **62** (1958) 751.
[13] R. Piontelli and G. Serravalle, *ibid.* **62** (1958) 759.
[14] I. A. Ammar and S. Darwish, *Electrochim. Acta* **13** (1968) 781.
[15] I. A. Ammar, S. Darwish and S. Raid, *ibid.* **13** (1968) 1875.
[16] I. A. Ammar, S. Darwish and W. Khalil, *ibid.* **12** (1967) 657.
[17] G. A. Sacchetts, G. G. Bombi and M. Fiorani, *J. Electroanal. Chem.* **20** (1969) 89.
[18] G. G. Bombi, G. A. Sacchetts and G. A. Mazzocchin, *ibid.* **24** (1970) 23.
[19] Yr. K. Delimarskii and G. B. Shilina, *Electrochim. Acta* **10** (1965) 973.
[20] H. S. Swofford and J. H. Propp, *Anal. Chem.* **37** (1965) 974.
[21] A. M. Shams El-Din and A. A. A. Gerges, 'Electrochemistry' (edited by A. Freind and F. Gutmann) Pergamon Press, Oxford (1964) p. 562.