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ELECTRODE OVERVOLTAGES IN MOLTEN FLUORIDES

III. THE ANODIC BEHAVIOUR OF NICKEL ELECTRODES IN MOLTEN $KF-NiF_2$, KF-NaF-LiF, KF-NaF and KF-LiF MIXTURES

by

S. PIZZINI, R. MORLOTTI and E. RÖMER

1965

Joint Nuclear Research Center
Ispra Establishment - Italy
Materials Department
Chemistry Service

Paper presented at the San Francisco Meeting of the Electrochemical Society
San Francisco (Calif.), May 9/13, 1965

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1. INTRODUCTION

In some previous investigations, dealing with overvoltage measurements on aluminum electrodes in molten KHF_2 (1), on lead electrodes in molten PbF_2-NaF eutectic mixtures (2) and of iron electrodes in molten alkali fluorides (3) it wasshown that the contamination of the melts by oxides or water leads to the anodic passivation of the electrode.

The active-passive behaviour, however, is quite different for the different metals.

Aluminum, which is passive in oxide-containing alkali fluoride melts, behaves as a "Korrosion Deckschicht-Elektrode" (4) in KHF_2 melts and reaches passive conditions only when anodically polarized. Lead, which is "active" even when covered with a film of PbO, can be passivated under anodic polarization (see Fig. 1) and there is the experimental evidence that the passive condition is reached when a layer of Pb_3O_4 grows over the PbO layer. The same type of behaviour is observed, under certain experimental conditions, also in the case of iron electrodes in oxide containing fluoride melts, as is shown in Fig. 2, which indicates a sufficiently sharp active-passive transition. The presence of a peak, which appears when the electrode is polarized in the "active" direction, starting from a potential lying in the transpassive zone, indicates however an irreversible behaviour.

The aim of this paper is to give a critical discussion of the results of an investigation on the anodic behaviour of nickel in molten alkali fluoride mixtures.

Manuscript received on February 17, 1965.

2. EXPERIMENTAL

Overvoltage measurements have been carried out by the intensiostatic, potentiostatic and potential sweep method, as described elsewhere (1, 2, 5); transient techniques were extensively used in order to evaluate small charge transfer overvoltage contributions and ohmic drops across surface oxide layers. The tensiometric cell (see Fig. 3) consists of a nickel electrode and of an isoelectrodic reference electrode, with a Luggin capillary of about 0,1 mm. in diameter.

Boron nitride was used as insulating and shielding material.

As counter-electrode the graphite crucible was used and the electrolytic cell was arranged according to cylindrical symmetry of the current density distribution.

Cells were assembled in vacuum tight quartz containers for atmosphere control and the experiments were performed under high vacuum as well as under dry (10-50 ppm H_2O) and deoxigenated argon.

The fluoride mixtures were dried at 400-450°C under high vacuum prior to melting.

The procedure, standardized with different crucible materials for LiF by using an Omegatron type mass spectrometer (6) consists in the heating of the solid mixture under a very clean vacuum at step-wise increasing temperatures, starting from 100°C up to 400-450°C. It was demonstrated that at temperatures lower than 500°C the main component of the release gases is water whereas at higher

temperatures increasing amounts of HF has been detected, indicating the occurence of hydrolysis reactions of the type:

(1) $H_2O + AlkF \rightleftharpoons HF + AlkOH$

or

(2) $H_2O + 2\ AlkF \rightleftharpoons 2HF + Alk_2O$.

3. RESULTS

Owing to the substantial difficulty of a good $pO^=$ control, experiments were carried out in oxide free and in NiO saturated melts. It was observed that not only the saturation of the melt with NiO as well as relatively high partial pressures of water lead to the currentless passivation of the electrode but also that traces of $O^=$, resulting from the hydrolysis of residual water in the melt (7) are sufficient for the current-induced passivation of the electrode.

In molten NiF_2-KF (10-90% in moles) eutectic the reaction:

(α) ${}_{I}Ni^{2+} \rightleftharpoons {}_{II}Ni^{2+}$

is shown to occur at 800°C without exchange overvoltage up to relatively high current densities (2 A/cm^2) and the measured overvoltage appears merely due to the ohmic drop across the electrolyte. The blue colour of the melt, after contacting it with nickel metal, and the appearence of unidentified peaks in the X-rays powder spectra of the solidified mixture, probably indicates a certain solubility of Ni metal in Ni^{++} containing melts.

Apparently this process does not influence the anodic dissolution and cathodic deposition of nickel.

In oxide-free LiF-KF-NaF melt the reaction (α) occurs reversibly in a less extended c.d. range as is shown in Fig. 4. This figure shows a plot of the anodic overvoltage vs. the log of c.d., where the slope b, which equals RT/2F, indicates the diffusion controlled anodic dissolution of nickel.

The anodic polarization of both active and passive electrodes in alkali fluoride melts leads however, at a certain critical c.d. or voltage (according to the kind of experimental technique), to the oscillatory instability of the electrode voltage as well as of the cell current or directly to the reactivation of the passive electrode as is shown in the following figures.

Fig. 5 shows the set-in of the oscillatory instability of the electrode voltage of nickel electrodes in an oxide-free LiF-NaF-KF melt. On passive electrodes in molten LiF-NaF-KF and LiF-KF melts the high overvoltage peak, which is observed in this figure, was not detected and also the oscillatory behaviour of the electrode was shown to be less reproducible in frequency as that observed on initially active lectrodes.

Fig. 6 shows the corresponding instability of the cell current observed by the potentiostatic method at potentials higher than 400 mV vs. a Ni/NiO reference electrode in a NiO saturated LiF-NaF-KF melt at 550°C.

Fig. 7 shows the anodic and cathodic reactivation of a passive nickel electrode in a molten NaF-KF eutectic mixture at 800°C observed by the potential sweep method, the potential sweeps being generated at a traverse rate

of 0,1 V/min.

The dashed line shows the corresponding ε_{Ω} vs. d.c. plot obtained by the intensiostatic method in a separate experiment. The increase of layer thickness is indicated by the deviation from linearity of the experimental curve. The cathodic reduction of the surface layer takes place at a potential very close to the reference potential, whereas the anodic reactivation occurs at a potential lying between + 200 ÷ ÷ + 300 mV vs. the reference Ni/NiO electrode.

Figg. 8 and 9, which refer to the anodic polarization of nickel at 560°C in oxide free LiF-KF eutectic show the intensiostatic charging curves and the corresponding potential decay curves oscillographically recorded at current densities higher than the critical current density. The corresponding curves in NiO saturated LiF-KF melts and in NiO saturated LiF-NaF-KF melts are quite similar.

The transition times, as well as the persistency of the voltage plateau, which is observed at about + 300 mV against the reference electrode clearly depend both on the total charge passed and on the previous history of the electrode. For this reason any attempt to plot the transition times in a i vs. $\tau^{1/2}$ plot results to be unsuccessful.

4. DISCUSSION

In order to account for these experimental results let us suppose that the currentless or current-induced passivation of nickel electrode in Li^+-free and in Li^+ containing melts results from a non conductive NiO surface film.

All the possible reaction occurring at a Ni/NiO electrode, considering both the case of a stoichiometric and a non-stoichiometric oxide layer are reported in the phase-scheme of Fig. 10. In this scheme the reactions which involve exchange of electrons are described (reaction ζ) in terms of jumps of electrons between Ni^{2+} and $Ni^{2+}\oplus$, where $Ni^{2+}\oplus$ corresponds to a positive hole in the non-stoichiometric NiO_{1+x} lattice, according to the well known p-type semiconductive behaviour of the non stoichiometric nickel oxide.

In the same scheme the oxygen chemisorption reaction is indicated by the reaction:

$$(3)\quad \beta'' + \zeta + \xi : \tfrac{1}{2}\,{}_{II}O_2 + 2\,{}_{III}Ni^{2+} \longrightarrow {}_{III}O^{2-} + 2\,{}_{III}Ni^{2+}\oplus$$

and the substitutional Li^+ dissolution in the cationic sublattice is indicated by:

$$(4)\quad \pi + \sigma + \xi : \quad {}_{II}Li^{+} + {}_{III}Ni^{2+} \longrightarrow {}_{III}Li^{+}(Ni^{2+}) + {}_{III}Ni^{2+}\oplus$$

In the latter case the mass balance is satisfied by the simultaneous occurring of the reaction (ω).

If the rate of the reaction (3) and (4), both of which lead to a non-stoichiometric oxide layer, is lower than the rate of the Ni diffusion, via cation vacancies into the oxide layer, the NiO surface layer remains at its stoichiometric composition, according to the reaction:

$$(5)\quad Ni + 2\,Ni^{3+} \longrightarrow 3\,Ni^{2+}$$

which corresponds to the electroneutral coupling of the reactions:

$$(\alpha')\quad {}_{I}Ni^{2+} \longrightarrow {}_{III}Ni^{2+}$$

and

$$(\beta')\quad 2\,{}_{I}e + 2\,{}_{III}Ni^{2+}\oplus \longrightarrow 2\,{}_{III}Ni^{2+}.$$

From the point of view of the Li^+ dissolution reaction (4) the previous assumption corresponds to the non-stability of the $Ni_{1-x}Li_{2x}O$ solid solution as an oxide covering layer on nickel electrodes in Li containing melts.

There is however experimental evidence that the stoichiometry of the NiO surface layer depends on the melt composition and on the temperature.

Measurements of oxygen diffusion in NiO single crystals (8) indicate that the oxygen diffusivity in NiO is at least of several order of magnitude lower than the Ni diffusivity at every temperature.

Moreover, from the slope of the Arrhenius plot (*) of the measured d.c. resistance (from iR drops at passive Ni electrodes in Li^+ containing melts) a value of the activation energy of about 23 Kcal is obtained, as is seen in Fig. 11, which is in agreement with the data given by B.R. Heikes and W.D. Johnston (9) and by Wright and Anderson (10). The break shown in Fig. 11 at about 650°C indicates that at temperatures higher than 650°C the assumption of the stoichiometry of the NiO layer no longer holds.

Finally, the work of D.C. Hill, B. Porter and A.S. Gillespie (11) indicates that in the molten Li_2SO_4-K_2SO_4 eutectic melt the Ni/NiO electrode behaves reversibly up to about 650°C, where a break in the EMF vs. T plot is observed.

(*) which is taken as a measure of the activation energy of the electrical resistivity according to the relationship:

(6) $\rho - \rho^{o} \exp (\Delta E/RT)$

They accounted for this result by recalling a deviation from the stoichiometry of NiO at temperatures higher than 650°C due to the Li^+ dissolution in solid solution, and supposing a high solubility of the $Ni_{1-x}Li_{2x}O$ solid solution at temperatures lower than 650°C.

However, the previous considerations on the phase-scheme of fig. 10 indicate that the break in EMF vs. T or log R vs. 1/T plots depends mainly on the change in the kinetics of the Li^+ dissolution in NiO rather than on sudden change in the solubility of the solid solution.

It appears indeed that at temperatures lower than 650°C in Li^+-containing melts and at every temperature in Li^+-free melts, the anodic dissolution of nickel at passive electrodes is described by the reaction (see Fig. 10).

(7) $\alpha' + Ni^{2+}$-transfer $+ \alpha''$

at current densities or potential lower than the critical transition current or the transpassive potential, respectively. The growing of the oxide layer depends on the $O^=$ concentration of the melt, the diffusion coefficient of Ni^{++} in the NiO phase and the diffusion coefficient of $O^=$ in both solution and oxide phases. Moreover, from the curves of fig. 7 the cathodic reduction of the oxide layer:

(8) $NiO + 2e \longrightarrow Ni + O^{2-}$

or

(α'') ${}_{III}Ni^{2+} \longrightarrow {}_{I}Ni^{2+}$

is demonstrated to occur at the reversible potential with an uncertainty of few mV.

We suggest that the high overvoltage peak, observed by the anodic polarization of "active" electrodes at c.d. higher than the transition current indicates the sudden passivation of the electrode according the reaction:

(8) $Ni + O^{2-} \longrightarrow NiO + 2e$

At current densities above the transition current as well as at potentials higher than the transpassive potential we postulate the occurence of the reaction:

(β') ${}_{III}Ni^{2+} \longrightarrow {}_{III}Ni^{2+}\oplus + {}_{I}e$

which lead to an highly conductive, non-stoichiometric NiO_{1+x} layer. Reactivation directly due to the oxygen discharge reaction can be excluded, as the value of the reactivation potential in decay curves is much lower than the calculated standard potential for the oxygen discharge reaction:

(9) $O^{2-} \longrightarrow \frac{1}{2} O_2 + 2e$

which for instance equals + 820 mV at 600°C vs. a Ni/NiO reference electrode (7).

The highly reproducible values of the reactivation potential and that of the voltage plateau in the potential decay curves suggest that the reaction (β') leads to a new solid phase, as Ni_2O_3 or Ni_3O_4, which however is easily reduced to NiO, in absence of any external current, according to the reactions α' + β', as is shown in Figg. 8 and 9.

The growing of this higher nickel oxide phase, according to the reactions:

(γ') $2\,{}_{I}Ni^{3+} \longrightarrow 2\,{}_{III}Ni^{2+}\oplus$

(ω) $3\,{}_{II}O^{2-} \longrightarrow 3\,{}_{II}O^{2-}$

depends on the oxide content of the melt and indeed on the limiting current for the reaction (ω).

The low value of the limiting current for the reaction (ω) in high vacuum dried LiF-NaF-KF melts ($3 \div 9$ mA/cm^2 according the results of a previous investigation (7)) accounts for the oscillatory instability of the electrode potential, according to the cyclic occurring of the reaction:

(8) $Ni + O^{=} \longrightarrow NiO + 2e$ (passivation step)

and

(β') ${}_{III}Ni^{2+} \longrightarrow Ni^{2+}\oplus + e$ (activation step)

where reaction (8) causes the complete depletion of O^{2-} in the diffusion layer.

5. Nomenclature

$\mathcal{E}$ Electrical potential difference measured across the tensiometric cell;

$\mathcal{E}_{\Omega}$ Resistance overvoltage
Subscrits I, II, III indicate the metal, solution and oxide phase, respectively;

Me_I^{z+} corresponds to ${}_IMe - z_Ie$

$Me^{2+}\oplus$ indicates a positive hole in the cationic sublattice.

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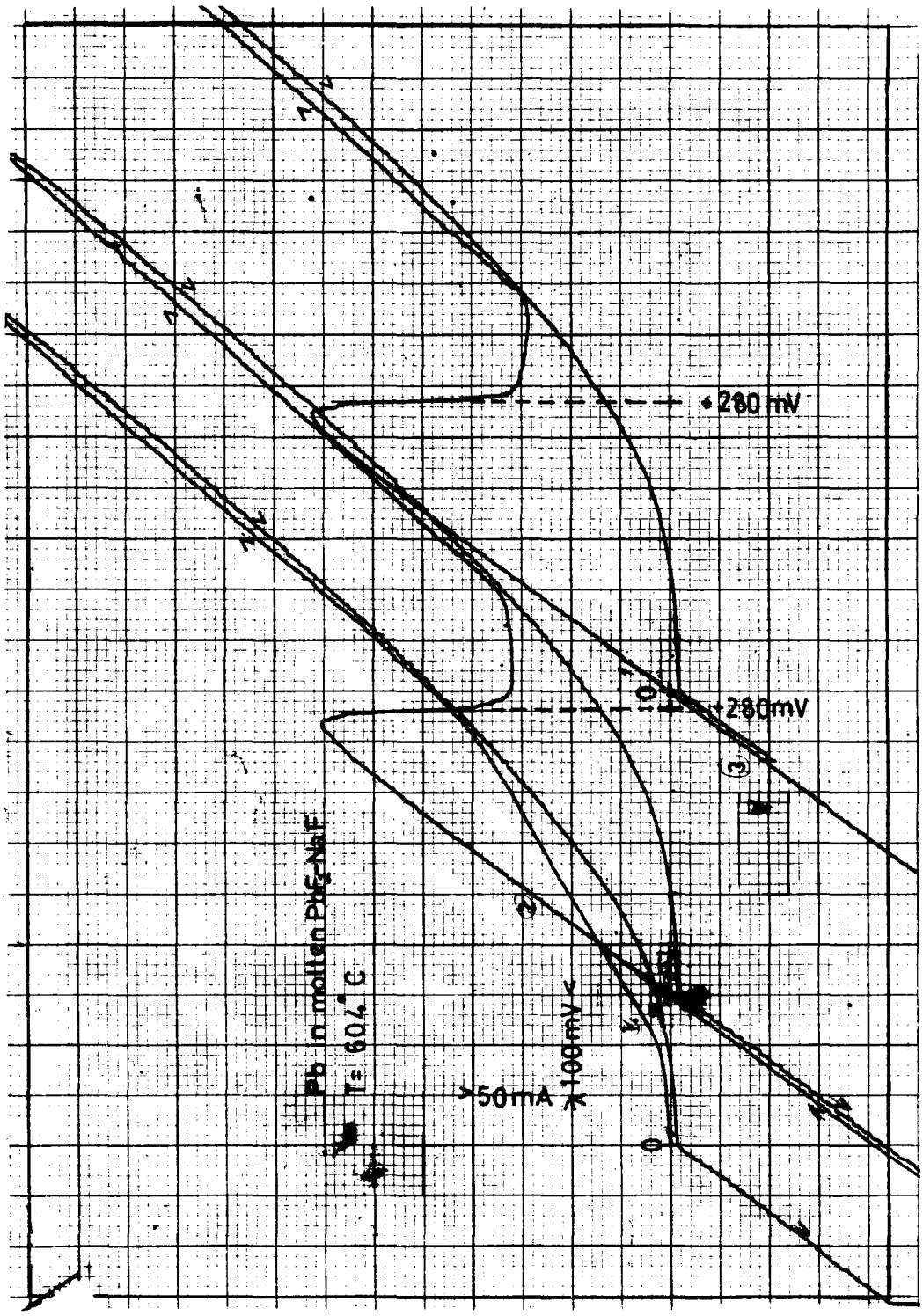


FIG. 1

i vs ε plot for the potentiodynamic anodic polarization of lead electrodes in molten PbF_2-NaF melts, contaminated with lead oxides.

Electrode area 0.85 cm^2. Traverse rate 0,1 V/min. Pb/PbO reference electrode.

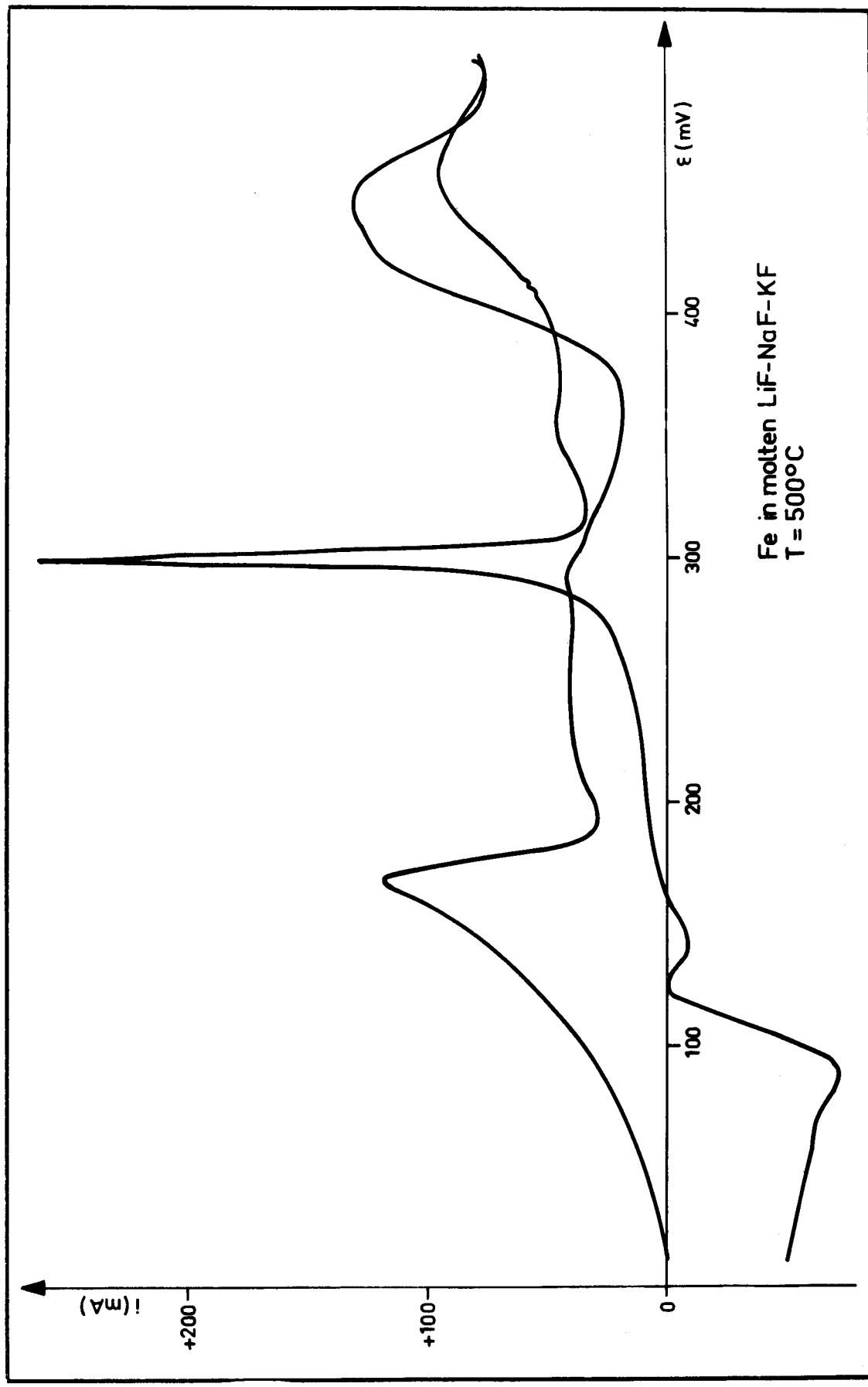
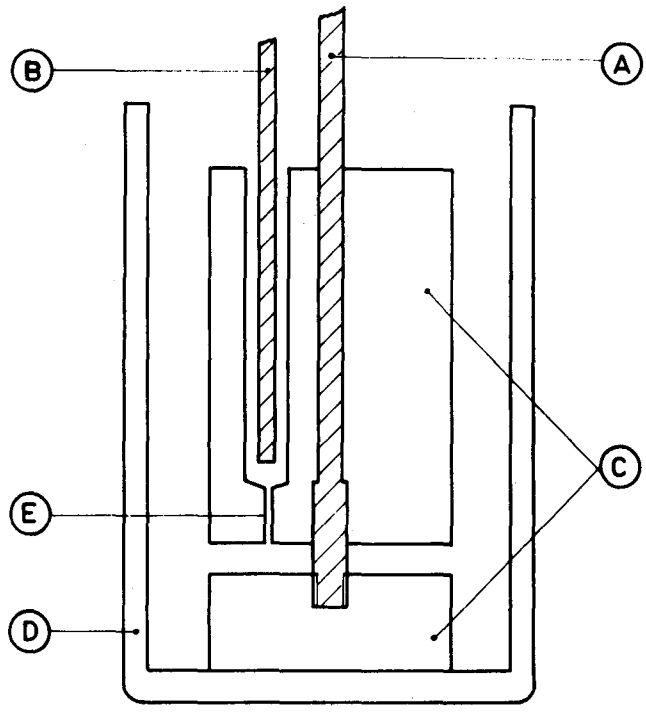


FIG. 2

i vs ε plot for the potentiodynamic anodic polarization of iron electrodes in molten KF-NaF-LiF melts, contaminated with oxides.

Traverse rate 0,1 V/min.



A . NICKEL ELECTRODE
B . NICKEL REF. ELECTRODE
C . BORON NITRIDE
D . GRAPHITE CRUCIBLE
E . CAPILLARY END OF THE
REF. ELECTRODE COMPARTMENT

CELL ASSEMBLY

FIG. 3

Cell assembly for overvoltage measurements on nickel electrodes.

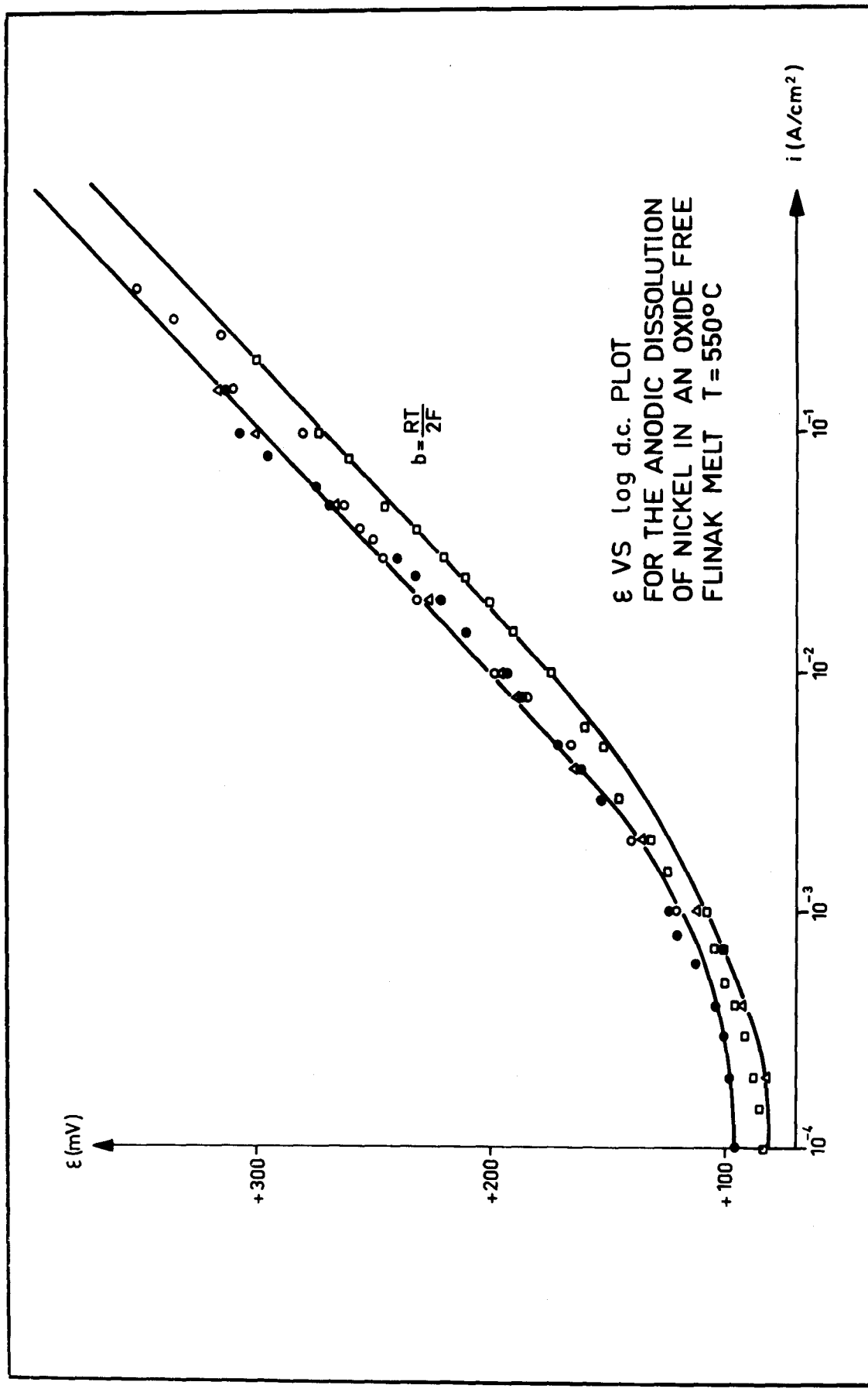


FIG. 4

ε vs log d.c. plot for the anodic dissolution of nickel in oxide-free KF-NaF-LiF melts. T = 550°C (from intensiostatic measurements)

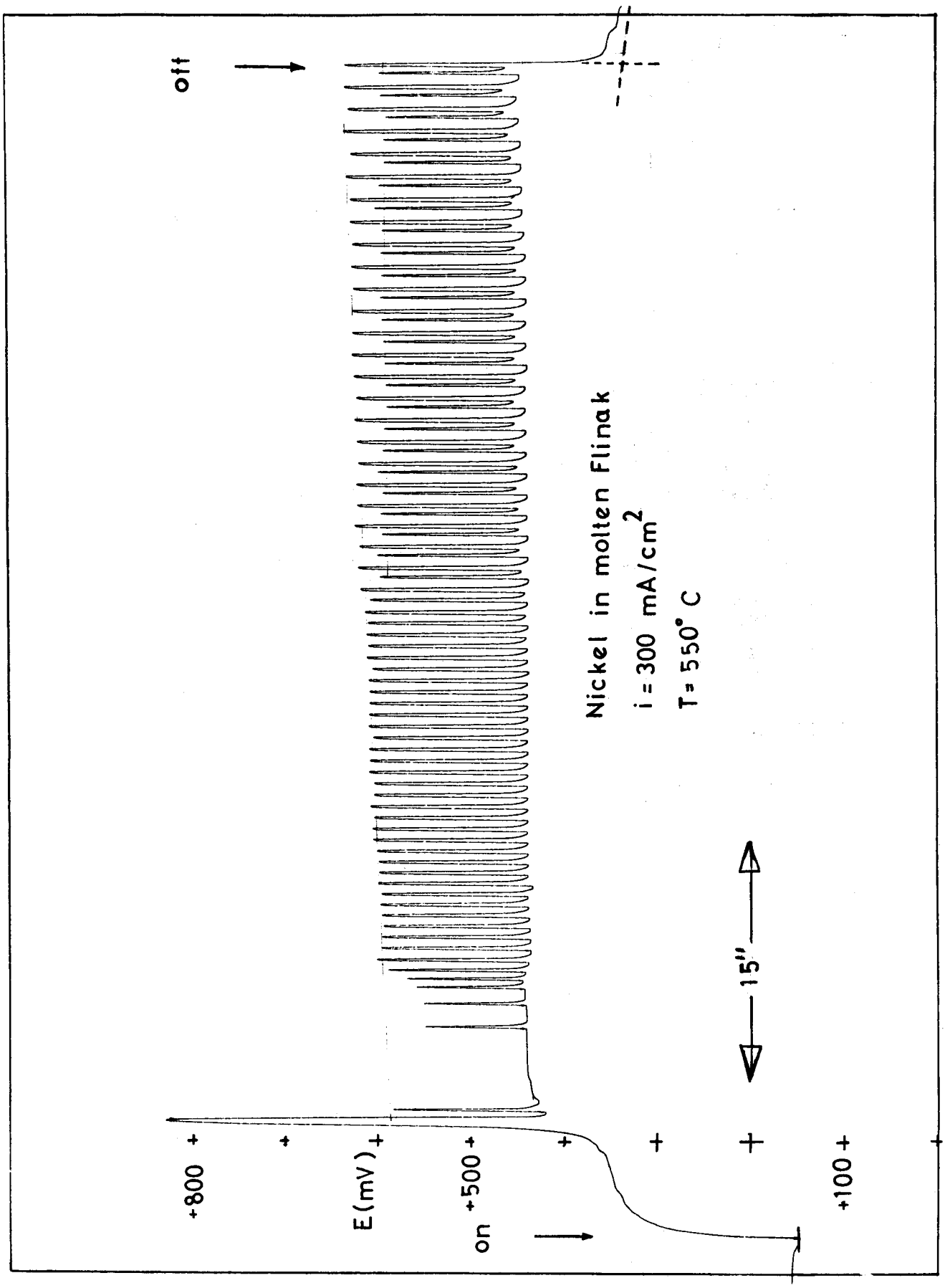


FIG. 5

Chronopotentiogram for the intensiostatic polarization of nickel electrodes in oxide-free KF-NaF-LiF melts at 550°C.

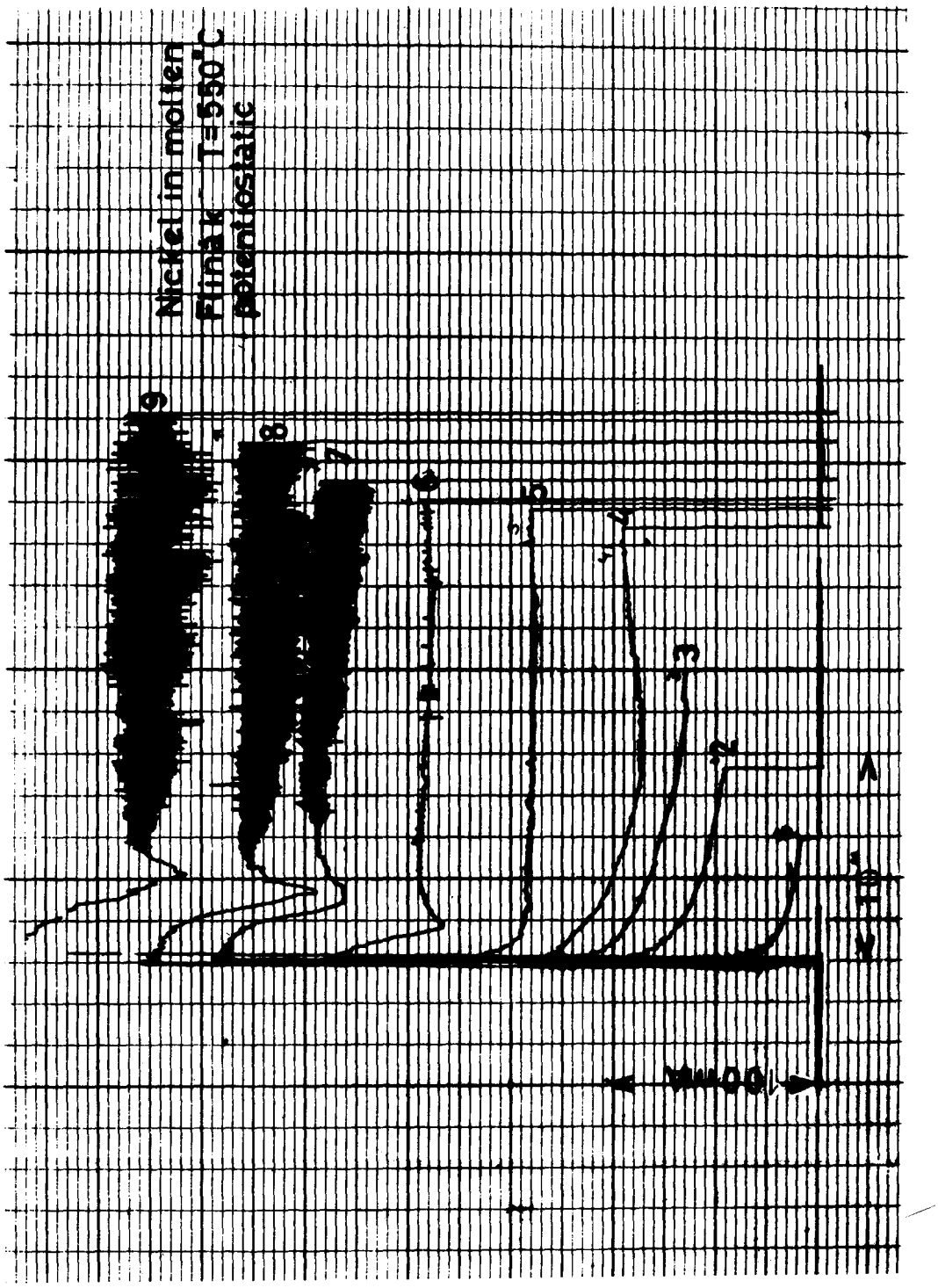
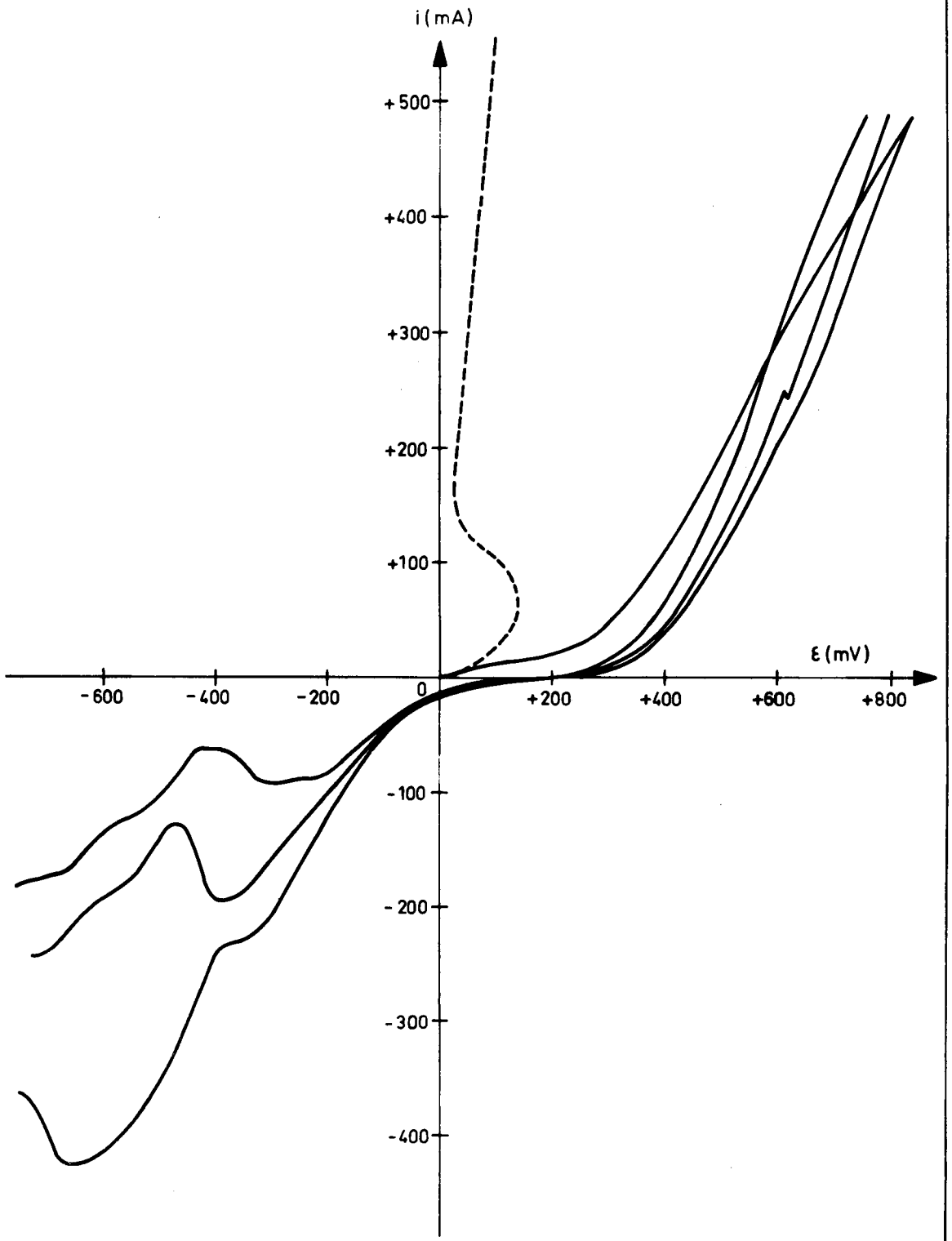


FIG. 6

i vs time plots for the potentiostatic polarization of nickel in NiO-saturated KF-NaF-LiF melts.

T = 550°C - Ni/NiO reference electrode.

1. + 100 mV	6. + 400 mV
2. + 200 mV	7. + 450 mV
3. + 250 mV	8. + 500 mV
4. + 300 mV	9. + 550 mV.
5. + 350 mV	



I VS ε CURVES (POTENTIAL SWEEP) FOR THE ANODIC DISSOLUTION AND CATHODIC DEPOSITION OF NICKEL IN MOLTEN NaF-KF T = 800° C

FIG. 7

i vs ε curves (by the potentiodynamic method) for the cathodic and anodic polarization of Ni in NaF-KF melts at 800°C.
Ni/NiO reference electrode. Traverse rate 0,1 V/min.
The dashed line (from intensiostatic measurements) reports the corresponding iR drops.

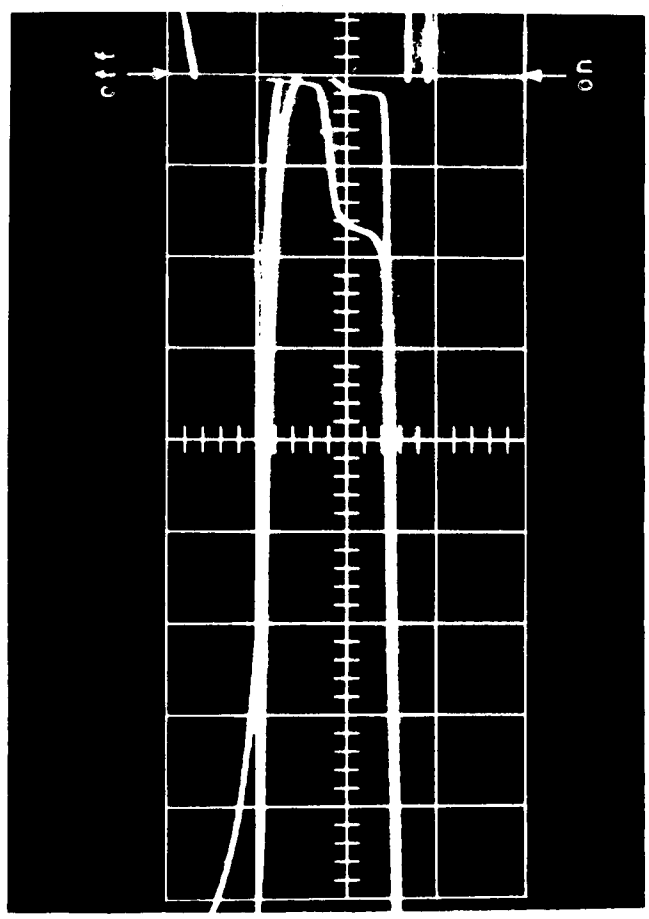


FIG. 8

Oscillogram for the anodic polarization of nickel electrodes in LiF-KF melts at 560°C. $P \sim 10^{-3}$ torr.
X axis - 50 m sec/cm Y axis - 200 mV/cm
c.d. - 900 mA/cm^2 (Ni/NiO reference electrode)

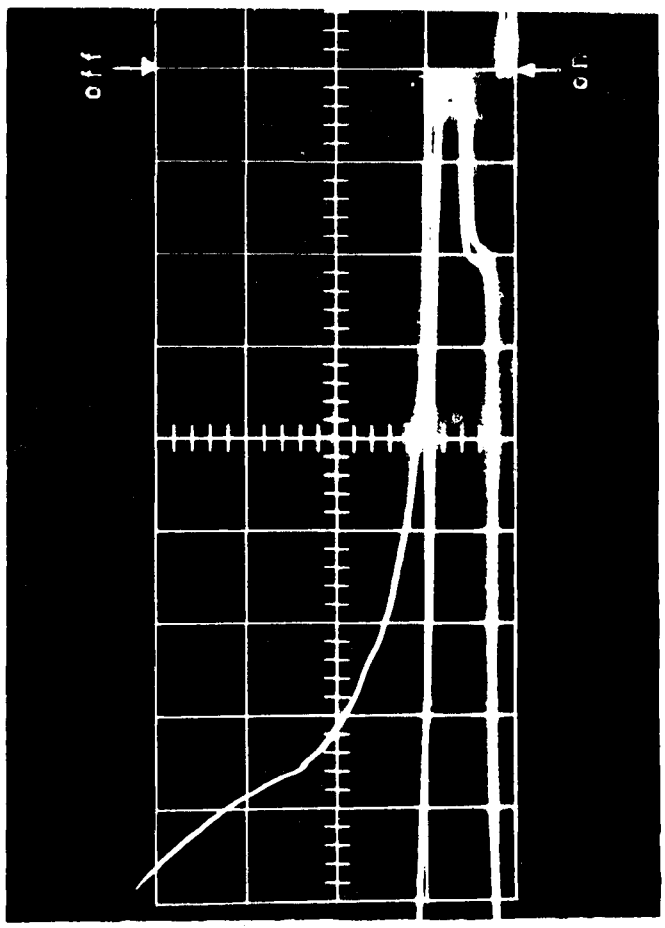


FIG. 9

Oscillogram for the anodic polarization of nickel electrodes in LiF KF melts at 560°C. P - 10^{-3} torr
X axis - 50 m sec/cm - Y axis - 500 mV/cm
c.d. - 1,1 A/cm^2 (Ni/NiO reference electrode)

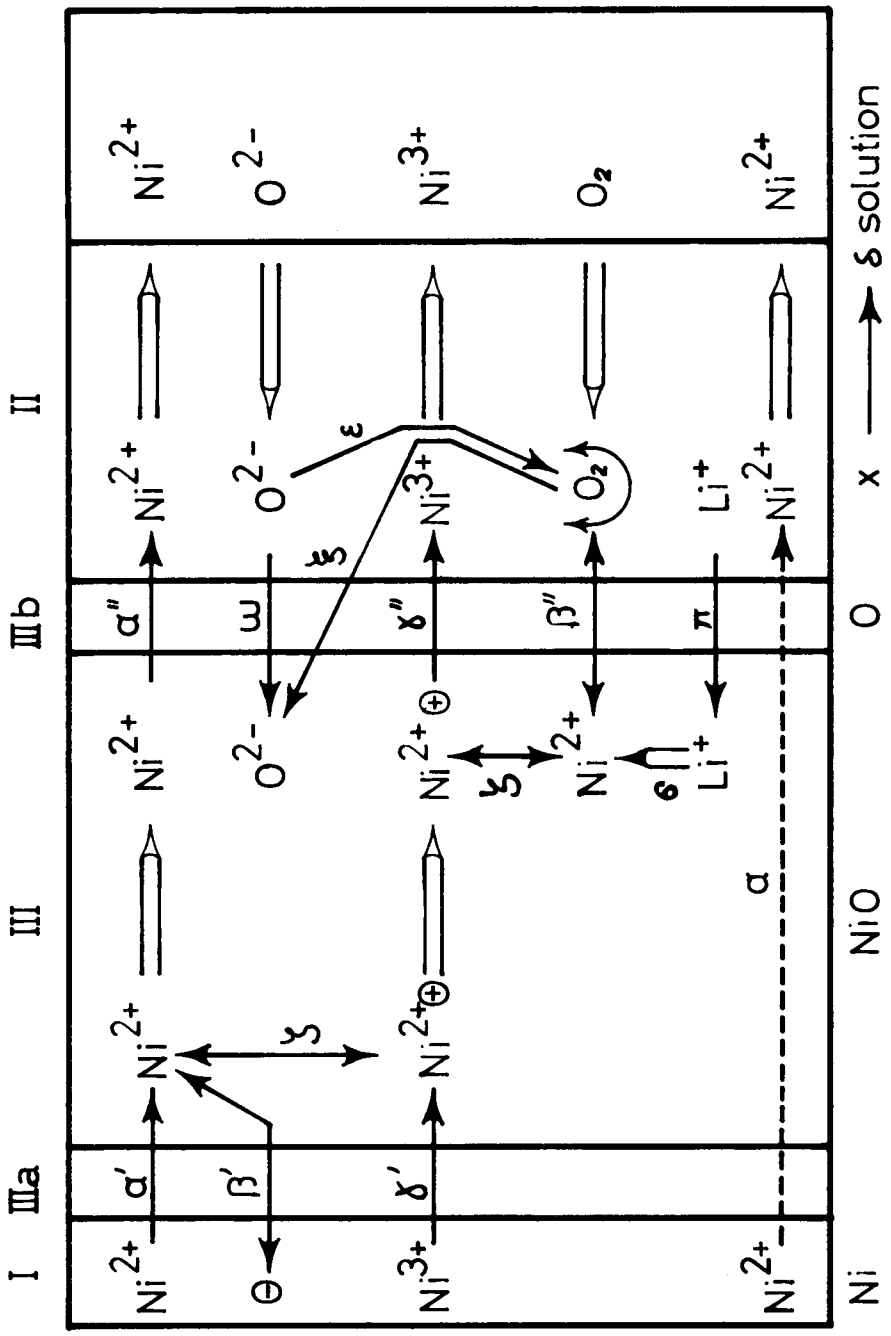


FIG. 10

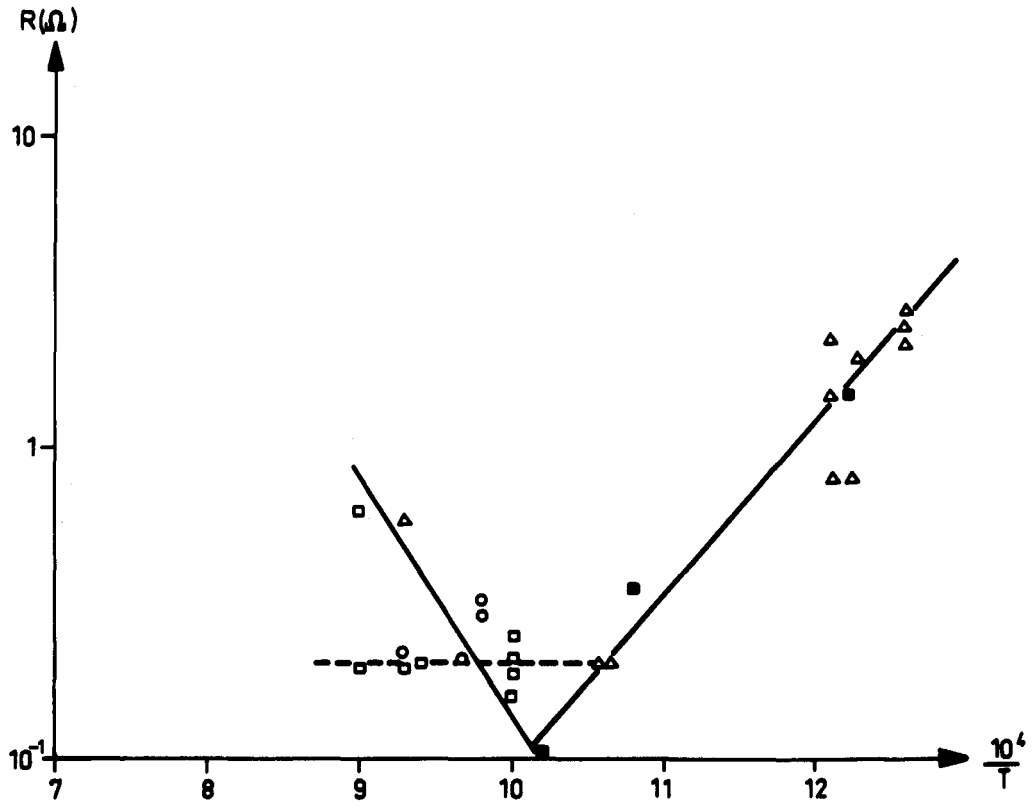
Phase-scheme for a Ni/NiO_{1+x}/electrode.

⟶ indicates a charge-transfer process at the interphaces IIIa and IIIb or in the bulk of the oxide-phase -

⇨ indicates a mass-transfer process across the bulk of a phase -

⇨ indicates the mechanism of substitutional exchange of a lattice position.

$Ni^{2+}\oplus$ indicates a positive hole in the lattice.



Log R_{exp} vs $\frac{10^4}{T}$ PLOT

FIG. 11

R vs $\frac{1}{T}$ plot from the experimental electrical resistance of surface layers on Ni electrodes in Li^+-containing melts.
Different symbols refers to different experiments under the same experimental conditions.

To disseminate knowledge is to disseminate prosperity — I mean general prosperity and not individual riches — and with prosperity disappears the greater part of the evil which is our heritage from darker times.

Alfred Nobel

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