STUDY ON ELECTROWINNING OF SOLID LANTHANUM-NICKEL ALLOYS IN LiCl-KCl EUTECTIC MELT

G.S. Picard, Y.E. Mottot and B.L. Trémillon

Laboratoire d'Electrochimie Analytique et Appliquée
associé au CNRS (LA 216)
Ecole Nationale Supérieure de Chimie de Paris
11, rue P. et M. Curie – 75231 – Paris Cedex 05 – France

ABSTRACT

The variation of the e.m.f. of the cell La/La$^{3+}$ in LiCl-KCl eut/La$_x$Ni was measured over the whole composition range of lanthanum-nickel alloys, at a temperature of 450°C. The alloys were formed by intermetallic diffusion from either chemical deposits of nickel or lanthanum, or electrochemical deposits of lanthanum on nickel. Seven intermediate alloys LaNi$_5$, La$_2$Ni$_7$, LaNi$_2$, LaNi$_3$, La$_2$Ni$_5$, LaNi and LaNi$_2$ were observed. Moreover, our results suggest the existence of metastable compounds. Coulometric titration technique for a composition range from pure lanthanum to LaNi alloy confirmed these results. The determination of the composition dependence of the chemical diffusion coefficient for that composition range is included. The Gibbs free energies of formation of the La-Ni alloys have been deduced from these measurements.

INTRODUCTION

Some rare earth-transition metal alloys have the ability to absorb and desorb hydrogen reversibly. At room temperature, and for a pressure range of 1-10 atm, the absorbing capacity reaches a maximum at a composition close to ReM$_5$ (1) (Re = Rare earth; M = 2d Metal); in particular, the compound LaNi$_5$ absorbs hydrogen up to a density of nearly twice that of liquid hydrogen (up to 6 x 10$^{22}$ atoms per cm$^3$). Thus, the hydride LaNi$_5$H$_{12}$ is of considerable interest for hydrogen storage purposes and for fuel technology (2).

As the rare earth metal cannot be readily obtained, the melting processes (direct fusion of rare earth and 2d metals mixed together in convenient proportions) are of little interest for large-scale production. The present procedure is a metallothermic reduction (3) which can be applied to the production of alloys with relatively fine particle size; the rare earth oxide is reduced by calcium in the presence of the 2d metal powder or metal oxide, at high temperature (over 1000°C). This process is a simple and low-cost method for the production of alloys, but is subject to various drawbacks:
calcium is an expensive reactant, and the alloys have high oxygen contents and a heterogeneous microstructure.

An electrolytic process was described in 1968 by Morrice et al. (4). According to it, a liquid alloy is obtained by electrodeposition of the rare earth metal on a 2d metal cathode, by electrolysis of Re₂O₃ dissolved in a molten fluoride mixture at about 900°C. This process may be easily controlled and monitored, but is yet more expensive than the former. The composition of the alloy, determined by the temperature, is close to ReM₂. Therefore, it must be melted again with additional 2d metal to reach the convenient composition (ReM₅, for instance).

The use of a molten chloride electrolyte instead of the fluoride + oxide mixture leads to a less expensive process at a rather low working temperature (400-500°C), with less difficulty for material selection and cell design.

We intended to obtain fundamental data which would help us to define clearly the practicability of such a process in the case of La-Ni alloys.

We have first studied the behavior of lanthanum and its ions in LiCl-KCl eutectic at 400-500°C, and then attempted to obtain the La-Ni alloys by electrodeposition of solid lanthanum on a nickel cathode at 450°C. We have determined the thermodynamic parameters of the alloys so produced, as well as the kinetic parameters of the lanthanum diffusion in the nickel electrode.

EXPERIMENTAL PART

Equipment and Procedure

Apparatus.

The cell consisted of a 150 ml pyrex crucible placed in an insulated pyrex body (Bercauverre) already described (5).

A gaseous atmosphere of fixed composition or vacuum could be imposed on the cell. High vacuum was obtained by means of an ALCATEL 1004 AC vacuum pump. The temperature was maintained constant within 2°C by means of a furnace and a programmable device described elsewhere (6). Temperature was measured with a chromel-alumel thermocouple inside a closed pyrex tube submerged in the melt. It was recorded with a SEFRAM Servofram recorder connected to a high impedance AOIP millivoltmeter.

E.m.f. measurements were carried out by means of a high impedance TACUSSEL Minisis 6000 voltmeter connected to a SEFRAM model Servofram recorder. A TACUSSEL PRT 10
potentiostat was used as a coulometer by means of a calibrated resistance (4.7Ω). This potentiostat was controlled by a periodical triangular signal generator TASCUSSEL model GSTP 3.

Melts.

Lithium chloride and potassium chloride were PROLABO (R.P. normapur quality) products. The procedure for the preparation and purification of the eutectic mixture has been previously described (7). Lanthanum chloride (LaCl₃, 7H₂O) was supplied by Rhône-Poulenc. It was dehydrated using a procedure similar to that described by Johnson and MacKenzie (8). The hydrous salt was placed on a sintered glass (porosity 0) assembly in a pyrex vessel. The chloride was heated under vacuum for two hours at 180°C, then ground and placed at 250°C under an hydrogen chloride atmosphere for one hour and a half. The salt was then weighed and transfered into the eutectic mixture.

The dehydrated salt dissolved in water yielded a clear solution; it may be considered as pure lanthanum chloride (less than 5% oxychloride detected by analysis). The possible oxychloride was removed by hydrogen chloride bubbling through the melt for one hour.

Electrodes.

a). The working electrodes (cathodes) used were the following: (i) Ø 1 mm nickel wire (Johnson-Matthey), grade 1), (ii) Ø 1 mm tungsten wire (Sochibo, Koch-light, 99.9%), (iii) Ø 1 mm lanthanum wire (Johnson Matthey, grade 1, delivered in a vacuum sealed tube) set up in an inert atmosphere, (iv) electrode constituted of a glassy carbon (Le Carbone Lorraine) rod : quality V 25 of 3 mm diameter, material which is non-oxidizable but forms interaction compounds with lithium (9).

b). The auxiliary electrode (anode) was glassy carbon (3 mm diameter, le Carbone Lorraine, quality V 25) in a pyrex compartment connected to a sintered pyrex capsule (porosity 4).

c). The reference electrode was made from a silver wire (1 mm diameter) dipped in a pyrex glass tube containing silver chloride 0.65 mol.kg⁻¹ dissolved in LiCl-KCl eutectic. All potentials measured with this reference electrode are given versus the chlorine reference (Cl₂(l atm)/Cl⁻) whose potential is 1.060 V versus our experimental reference electrode.

Preliminary determinations.

1. Voltammetric curves.

The reduction of Ni²⁺ on a glassy carbon electrode has been studied by cyclic voltammetry at 450°C. Fig. 1 shows a
voltammogram obtained (curve 1). The reaction on the electrode is a reversible deposit of metallic nickel under diffusion controlled conditions. The peak potential value $E_p$ does not depend on the voltage sweep rates, nor does the ratio $i_p/v^{1/2}$ ($i_p = \text{peak current}$; $v = \text{sweep rate}$). The peak current $i_p$ (Amperes) obeys the formula (10):

$$i_p = 0.61 \left( zF \right)^{3/2} \left( RT \right)^{-1/2} AD^{1/2} \left[ \text{Ni}^{2+} \right] v^{1/2}$$

where $z$ is the number of electrons ($z = 2$ for $\text{Ni}^{2+}$), $R$ the gas constant, $F$ the Faraday, $T$ the temperature (K), $A$ the area of the electrode ($7.07 \times 10^{-2}$ cm$^2$), $D$ the diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$), $\left[ \text{Ni}^{2+} \right]$ the concentration of $\text{Ni}^{2+}$ ions ($\text{mol.cm}^{-3}$) and $v$ the voltage sweep rate ($\text{V.s}^{-1}$). The concentrations in mol.cm$^{-3}$ are calculated by considering the density of the bath as equal to 1.65 g.cm$^{-3}$ (11). The diffusion coefficient of nickel ion was determined to be $D_{\text{Ni}} = 2.12 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$ which is in good agreement with the values given by several authors (12-14).

On a glassy carbon electrode the reduction of lithium ions appears at a potential of -2.3 V versus the chlorine reference electrode. Therefore it is impossible to use this electrode to study the lanthanum system. We have made La deposits on a tungsten electrode ($0.15$ cm$^2$) and on a nickel electrode ($0.13$ cm$^2$).

Typical voltammograms are shown in Fig. 1. The deposition on the tungsten electrode may be considered as reversible. Relation analogous to (1) was therefore used to determine the diffusion coefficient of lanthanum ion. Our value, $D_{\text{La}} = 8.76 \times 10^{-6} \text{cm}^2 \text{s}^{-1}$, is slightly lower than the one determined by Smirnov et al. ($D_{\text{La}} = 1.28 \times 10^{-5} \text{cm}^2 \text{s}^{-1}$) (15).

The voltammograms obtained on a nickel electrode show several current peaks for potential values located between the peak potential of lanthanum ion on the tungsten electrode and the peak potential of nickel ion on the glassy carbon electrode. Those peaks are characteristic of the formation of intermetallic compounds between nickel and lanthanum. La-Ni alloys can therefore be obtained by a deposit of lanthanum on nickel at 450°C.

2. Standard potentials of the electrochemical systems $\text{La}^{3+}/\text{La}$ and $\text{Ni}^{2+}/\text{Ni}$.

In order to determine the standard potential of $\text{Ni}^{2+}/\text{Ni}$, a nickel deposit was formed on a planar glassy carbon electrode and the equilibrium potential of this electrode, dipped into a mixture of LiCl-KCl eutectic and NiCl$_2$, was measured for several concentrations of nickel chloride, at various temperatures (Table 1). The observed slope is in accordance with a two electron-exchange per nickel ion. The standard potential measured at 450°C ($E = -1.084$ V versus the chlorine reference electrode) is higher by 15 mV than the
value determined by Liu et al. (16) \( E_a = -1.1 \text{ V} \); these authors measured directly the potential of a nickel wire dipped into LiCl-KCl eutectic.

In a similar manner, the equilibrium potential of a lanthanum electrode (1 mm diameter wire) in presence of dissolved \( \text{LaCl}_3 \) at various concentrations was measured.

This potential became stabilized in a few minutes (potential variation less than 1 mV/10 min). After each measurement the electrode was removed from the bath, and replaced by a new one, before the next measurement for a new concentration of lanthanum chloride. The Nernst relation:

\[
E_{\text{La}} = E^\circ (\text{La}^{3+}/\text{La}) + \frac{2.3RT}{3F} \log \text{La}^{3+}
\]

followed for temperatures 400, 450, and 510°C, and Table 1 indicates the corresponding values of \( E^\circ (\text{La}^{3+}/\text{La}) \). The standard potential as a function of temperature is given (in V versus the chlorine reference electrode) by:

\[
E^\circ (\text{La}^{3+}/\text{La}) = -3.474 + 4.3 \times 10^{-4} \ T
\]

\((T = \text{temperature in Kelvin})\). This result agrees well with the value given by Lesourd and Plambeck at 450°C (17):

\[
E^\circ (\text{La}^{3+}/\text{La}) = -3.159 \text{ V}
\]

Study of the lanthanum-nickel alloys formation.

Two sorts of experiments based on intermetallic diffusion were carried out. The first one corresponds to a chemical deposition of nickel on a lanthanum electrode, and the second one to an electrochemical deposition of lanthanum on a nickel electrode. In both sorts of experiments we have measured the variation of the potential of the electrode just after the metallic deposition. This potential is expressed in the following as the e.m.f. of the cell:

\[
\text{La/La}^{3+} \text{ in LiCl-KCl eut./La Ni}
\]

by using the value of \( E(\text{La}^{3+}/\text{La}) \) previously determined. This procedure makes easier the analysis of the results.

1. Experiments with chemical deposition.

Chemical deposits of nickel on a lanthanum electrode have been achieved under an argon atmosphere from an electrolytic bath containing lanthanum trichloride ([\( \text{La}^{3+} \)] = 0.24 mol.kg\(^{-1}\)) and nickel chloride ([\( \text{Ni}^{2+} \)] = 0.18 mol.kg\(^{-1}\)). Nickel cations react spontaneously with metallic lanthanum according to the following general reaction:

\[
(2/3 + y) \text{La} + \text{Ni}^{2+} \rightarrow 2/3 \text{La}^{3+} + \text{La} \text{Ni}_y
\]

A lanthanum-nickel alloy is therefore produced on the surface of the electrode, and we measured the variation of the potential of this
electrode as a function of time. A typical chronopotentiogram obtained during this sort of experiment is given in Fig. 2. We can observe, before the complete corrosion of the electrode, two plateaus whose potentials are indicated in Table 2.

2. Experiments with electrochemical deposition.

Electrochemical deposits, either at a controlled potential or at a controlled current, of lanthanum on a nickel electrode result in the formation of alloys in the whole range of composition (from pure lanthanum to almost pure nickel).

- Deposits realized at a controlled potential.

The discharge curve 1 of Fig. 3 was obtained under an argon atmosphere after a lanthanum deposit realized at \( E = -3.230 \text{ V} (\varepsilon = -0.070 \text{ V}) \) during 100 s. We can observe 9 plateaus before reaching the rest-potential of nickel in the melt. The potential of some plateaus varies (up to 50 mV) with the duration of the electrochemical deposition, especially for the plateau h (Fig. 3).

In such experiments, only \( 1.5 \times 10^{-6} \) mole of lanthanum was deposited on the nickel electrode. So, oxide (or hydroxide) anions can interfere because the equilibrium concentration of \( O^{2-} \) is about \( 10^{-5} \) mol.kg\(^{-1} \) after purification of the eutectic melt (18, 19). Therefore we have carried out numerous experiments under a low HCl pressure which permits to reach a \( pO^{2-} \) value close to 8, for which no lanthanum oxychloride is formed (20). In the course of these experiments, HCl oxidized the lanthanum very slowly and the duration of the relaxation has practically been the same as the one observed for experiments performed under an argon atmosphere.

The curve 2 of Fig. 3 was obtained after deposition of lanthanum at \( E = -3.230 \text{ V} (\varepsilon = -0.070 \text{ V}) \) during 100 s. We observe 9 plateaus of potential corresponding to the formation of La-Ni alloys by diffusion of La inside the nickel electrode, and one more relative to the rest-potential of nickel in melt (\( \varepsilon = 1.860 \pm 0.05 \text{ V} \)). We remark that the plateaus are very close to those obtained under argon. The most noticeable differences correspond (i) to the existence of a plateau at \( \varepsilon = 0.088 \text{ V} \), (ii) to the disappearance of the two plateaus a' and e' (observed on the curve 1), and (iii) to the shift of the potential of the 8th plateau (h).

In the case of lanthanum deposition at \( E = -3.330 \text{ V} (\varepsilon = -0.170 \text{ V}) \), the discharge curve 3 of Fig. 3 made clear the appearance of two supplementary plateaus (i and j), the others being similar to those of the preceding experiment achieved at \( E = -3.230 \text{ V} \).

In order to determine the influence of the preelectrolyze potential upon the nature of the alloys formed, we obtained lanthanum deposits at potentials whose values varied between \( E = -3.100 \text{ V} (\varepsilon = 0.060 \text{ V}) \) and \( -2.700 \text{ V} (\varepsilon = 0.460 \text{ V}) \). For
E = -3.100 V (curve 4, Fig. 3), only the last three plateaus \((f,g,h)\) are observed. For \(-3.05 \text{ V} < E < -2.95 \text{ V}\) (curves 5 to 7), only the plateaus \(g\) and \(h\), corresponding to the two nickel rich alloys, appear (for \(g\), the more reductive is the preelectrolysis potential, the larger is the plateau). When we preelectrolyze at \(E > -2.700 \text{ V}\) \((\varepsilon > 0.460 \text{ V})\) no alloy formation is observed (curve 9), and we reach the rest-potential of nickel directly.

- Deposits realized at a controlled current.

The preceding experiments only give the variation of the e.m.f. \(\varepsilon\) as a function of time, but do not allow us to establish experimentally the relation between the e.m.f. and the composition of the alloys formed. We therefore made coulometric titrations using the method called "Electrochemical Galvanostatic Intermittent Titration Technique" or GITT, developed by Weppner et al. (21-24). Very small amounts of lanthanum are deposited by means of pulses at a controlled current, and after each pulse, the equilibrium potential is measured at the end of the relaxation time. Thus, it was possible to know the exact composition of the alloy relative to the e.m.f. \(\varepsilon\) measured.

In these experiments, the cathode used was a 0.1 cm diameter nickel wire, dipped by 0.7 cm in the bath. The value of the coulometric current \(I_c\) was 20 mA. With each pulse of current (duration \(\tau = 60 \text{ s}\)), the variation in alloy composition is given by the formula:

\[
\Delta y = \frac{I_c \tau}{2F} \cdot \frac{M_{Ni}}{m_{Ni}}
\]

where \(z\) is the number of electrons exchanged, \(F\) the Faraday constant, \(M_{Ni}\) the molecular weight of nickel, and \(m_{Ni}\) the weight of nickel in the alloy. With our experimental conditions \(\Delta y\) is \(5 \times 10^{-2}\). After each pulse, therefore, it is possible to calculate the theoretical composition of the alloy, assuming total interdiffusion. The duration of relaxation (between two pulses of current) was 1000 s, which appeared sufficient to reach equilibrium. In our experiments we applied the coulometric signal 200 times, in order to reach a final composition corresponding to LaNi.

Fig. 4a shows a typical curve which was experimentally obtained under an HCl atmosphere and which gives the relation between the e.m.f. \(\varepsilon\) and the alloy composition. This curve has the same general from as the curves shown in Fig. 3. The equilibrium potential of the nickel-richest part of the curve has a value near that of plateau \(h\) of curve 1 in Fig. 3. It occurs after a shift of potential at a composition close to \(\text{LaNi}_{10}\).

**INTERPRETATION OF THE RESULTS AND CONCLUSION**

Lanthanum-nickel intermetallic compounds.

Fig. 5 gives the phase diagram of the lanthanum-nickel system which was determined by Bushow and Van Mal (25).
This diagram shows the existence of seven lanthanum-nickel alloys of definite compositions. Moreover, all these alloys are solid at our working temperature (450°C) because the La₃Ni alloy, which has the lower melting point, melts at 485°C. So after having coated a nickel electrode with lanthanum, this last metal diffuses inside nickel and the surface composition varies from pure lanthanum to an alloy very rich in nickel (the supporting metal).

Theoretical variation of the e.m.f. e as a function of the surface composition of the working electrode (lanthanum-nickel alloy).

The e.m.f. e(y) corresponding to a chemical composition of the alloy (formed at the surface of the electrode) is related to the activity of lanthanum, by the expression:

\[ e(y) = -\frac{RT}{3F} \ln a(\text{La}) \quad (2) \]

where \( a(\text{La}) \) is the activity of the rare earth in the alloy (taking the pure lanthanum as the standard state). When the electrode surface is composed of a mixture of alloys of definite compositions \( \text{La}_y\text{Ni} \) and \( \text{La}_{y+2}\text{Ni} \), the activity of the lanthanum is fixed by the equilibrium:

\[ \text{La}_y\text{Ni} + (y_2 - y_1)\text{La} \ \rightarrow \ \text{La}_{y+2}\text{Ni} \quad (3) \]

and so the e.m.f. e has a constant value during the complete transformation of the definite alloy \( \text{La}_y\text{Ni} \) into the definite alloy \( \text{La}_{y+2}\text{Ni} \). For the exact composition of a definite alloy, \( \text{La}_y\text{Ni} \) for example, we observe a sudden variation of e from the value of the two phase plateau corresponding to the mixture of \( \text{La}_y\text{Ni} \) and \( \text{La}_{y+2}\text{Ni} \), to the value of the two phase plateau of \( \text{La}_{y+2}\text{Ni} \) and \( \text{La}_y\text{Ni} \) mixture. Such sharp variations, however, are not observed when solid solutions exist; in that case the e.m.f. varies slowly from one two phase plateau to another. So, the plateaus observed in an e.m.f. - composition diagram are related to the two plateau areas in the phase diagram (Fig. 5 and 6).

Analysis of experimental curves.

The e.m.f. corresponding to the two phase plateaus observed with our experimental conditions, are listed in Table 2. The values obtained from the chemical deposits of nickel on a lanthanum wire (Fig. 2), can be assigned to the lanthanum-rich alloys \( \text{La}_3\text{Ni} \) and \( \text{LaNi} \) mentioned in the phase-diagram of Fig. 5. The measurements achieved under a low HCl partial pressure, and after an electrochemical deposition of lanthanum on a nickel electrode at a controlled potential of -3.230 V (curve 2; Fig. 3) are the most reliable because the experimental conditions minimize the possibility of a codeposition of lithium and of the influence of dissolved O²⁻ ions. The plateaus a, b, c, d, e, f, g, may be clearly related to the successive two phase domains obtained with the lanthanum and its seven alloys with nickel (Table 2). The plateaus d' and h also observed for
\( e = 0.110 \) V and \( \varepsilon = 0.648 \) seem to be due to metastable phases: the plateau \( d' \) observed in curve 2 (Fig. 3) does not appear in curve 3, and the plateau \( h \) corresponds to different values of \( e \) in curve 2 and curve 3. The plateaus \( i \) and \( j \) (curve 3, Fig. 3) may be assigned to lanthanum–lithium alloys. In fact, no nickel–lithium alloys can be formed because no plateau appears after an electrochemical deposit of lithium alone on a nickel electrode, the potential varying from that of lithium to that of nickel in the bath (26) (Experiment performed with no lanthanum chloride in the bath). Besides, the analysis of the obtained deposits (X rays, backscattered electrons) does not indicate the presence of lithium.

The plateau \( e' \) which appears in curve 1 (Fig. 3) may be due to the influence of oxide ion. It is not observed in curves obtained under an HCl atmosphere, and the analysis of the compound formed indicates the presence of lanthanum oxychloride.

The preceding assignment of the plateaus is confirmed by our results by the GITT method giving the relation between the e.m.f. \( \varepsilon \) and the compositions of the alloys (Fig. 4a).

Our values agree very well with those calculated from values of Rezukhina and Kutsev (27) obtained at higher temperatures in molten fluorides (Table 2). These authors didn't study the alloys whose composition is included between LaNi and pure lanthanum.

Our results allow us to calculate the Gibbs free energies of formation of the lanthanum–nickel alloys at 450°C. The Gibbs free energy of formation \( \Delta G^\circ \) of an alloy of composition \( \text{La}_{y_1}\text{Ni} \) is related to that of a \( \text{La}_{y_2}\text{Ni} \) alloy by the relation:

\[
\Delta G^\circ (\text{La}_{y_1}\text{Ni}) = -3F \int_{y_1}^{y_2} \varepsilon(y) \, dy + \Delta G^\circ (\text{La}_{y_1}\text{Ni})
\] (4)

The values obtained are collected in Table 3 and are corroborated by values derived from literature data (27, 28) as shown in Table 3.

The kinetic parameters of metallic interdiffusion, the chemical diffusion coefficient \( D \), may be obtained from results of the GITT method as it was described by Weppner and Huggins (21–23). The chemical diffusion coefficient \( D \) expresses the variation of the concentration of one species at the surface of the electrode, according to Fick's second law:

\[
\frac{\partial C_{\text{La}}}{\partial t} = \tilde{D} \frac{\partial^2 C_{\text{La}}}{\partial x^2}
\] (5)

where \( t \) is the time, \( C_{\text{La}} \) the local concentration of lanthanum, and \( x \) the distance into the solid form the electrode/electrolyte interface. A solution of equation (5) gives the concentration \( C_{\text{La}} \) of lanthanum at the surface of the working electrode as a function of time for small total currents i.e. \( \tau \ll r^2/D \) (\( \tau \) = duration of the current pulse; \( r \) = radius of the electrode) (24):
\[ C_{\text{La}}(t) - C_{\text{La}}(0) = 2 \int_0^t I \sqrt{z F A \sqrt{\tau}} D^{-1} \]  \hspace{1cm} (6)

with \( C_{\text{La}}(t) \) and \( C_{\text{La}}(0) \) being respectively the surface concentration of lanthanum at time \( t \) and at the origin of time, \( I \) the current for the coulometry and \( A \) the area of the interface electrolyte/electrode.

Equation (6) may be related to the variation \( \Delta \xi \) of the cell voltage during the current pulse (neglecting the IR drop) and to the variation \( \Delta \xi \) of the equilibrium potential between two successive relaxations (assuming that \( \Delta \xi \) is small and that the variation of \( \xi \) is linear as a function of \( t \) during the coulometric pulse, which is verified for our experimental conditions):

\[ D = \frac{4}{\pi^2} \frac{(V)^2}{A} \left( \frac{\Delta \xi}{\Delta \xi_c} \right)^2 \]  \hspace{1cm} (7)

\((V \text{ is the volume of the electrode). With our experimental conditions} \ (r = 60 \text{ s, } V = 6.10^{-3} \text{ cm}^3)\), the relation (7) becomes:

\[ D = 1.33.10^{-5} \left( \frac{\Delta \xi}{\Delta \xi_c} \right)^2 \]

The maximum values of the chemical diffusion coefficient reported in Fig. 4b correspond to sudden variations of the concentration of lanthanum at the surface of the electrode, i.e for single phase components. Related to Fig. 4a, this curve gives the composition of the definite alloys observed. The values of the coefficient vary from \( 1.8.10^{-6} \text{cm}^2 \text{s}^{-1} \) for the LaNi\(_5\) phase to \( 1.33.10^{-7} \text{cm}^2 \text{s}^{-1} \) for the La\(_2\)Ni\(_7\).

**Conclusion**

In this study we have determined the Gibbs free energies of the seven lanthanum-nickel alloys. It was found that the presence of oxide ions must be carefully avoided, and that metastable phases might be formed, especially for a composition close to LaNi\(_{10}\). Further investigations are needed to better understand the phenomena that occur. At the present time experiments are carried out as a function of temperature in order to obtain the temperature dependence of the thermodynamic parameters of La-Ni alloys.

**ACKNOWLEDGMENTS**

This research was supported by Rhône-Poulenc S.A. and by the French Ministry of Research and Technology under contract n\(^\circ\) 81.F.0487. Y.E.M. thanks R.P.S.A. for a doctoral grant.

**REFERENCES**

1. R.A. Guidotti, G.B. Atkinson and M.M. Wong, J. Less Common Metals, 52, 13 (1977).
2. D.P. Gregory "The Rare Earths in Modern Science and Technology", G.J. Mc Carthy Ed, Plenum Press, N.Y. (1978), p. 1.
3. C. Herget and H.G. Domazer, Goldschmidt Informiert, 35, 4 (1975).
4. E. Morrice, E.S. Shedd and T.A. Henrie, Direct Electrolysis of Rare Earth Oxides to Metals and Alloys in Fluoride Melts, U.S. Bureau of Mines, R.I. 7146, 1968.
5. F. Séon, G. Picard and B. Trémillon, J. Electroanal. Chem., 138, 315 (1982).
6. R. Combes, J. Vedel and B. Trémillon, Electrochim. Acta. 20, 19 (1975).
7. G. Picard, F. Séon and B. Trémillon, J. Electroanal. Chem., 102, 65 (1979).
8. K.E. Johnson and J.R. Mackenzie, J. Inorg. Nucl. Chem., 32, 43 (1970).
9. J.R. Selman, "Electrochemistry of Lithium Carbide", ANL-75-46, 33 (1975).
10. G. Ting, Ph. D. Thesis, University of Tennessee (1973).
11. E.R. Van Artsdalen and I.S. Jaffe, J. Phys. Chem., 59, 118 (1955).
12. W.K. Behl, J. Electrochem. Soc., 118, 889 (1971).
13. J. Bouteillon and M.J. Barbier, J. Electroanal. Chem., 56, 399 (1974).
14. E. Schmidt, Electrochim. Acta, 8, 23 (1963).
15. M.V. Smirnov, Yu.N. Krasnov, V.E. Komarov and V.N. Alekseev, Tr. Inst. Elektrokhim. Akad. Nauk. SSSR., Ural'sk filial, N° 9, 59 (1966).
16. C.H. Liu, A.J. Zielen and D.M. Gruen, J. Electrochem. Soc., 120, 67 (1973).
17. J.B. Lesourd and J.A. Plambeck, can. J. Chem., 47, 3387 (1969).
18. F. Séon, Doct. Etat Thesis, Paris 1981.
19. B. Trémillon and G. Picard, "Proc. 1st Internat. Symposium on Molten Salt Chemistry and Technology", Kyoto (1983) p. 93.
20. G. Picard, Y. Mottot, C. Duval and B. Trémillon, to be published.
21. W. Weppner and R.A. Huggins, "Proceedings on the Symposium on Electrode Materials and Process for Energy Conversion and Storage", The Electrochemical Society, 833 (1977).
22. W. Weppner and R.A. Huggins, J. Electrochem. Soc., 124, 1569 (1977).
23. W. Weppner and R.A. Huggins, J. Electrochem. Soc., 125, 7 (1978).
24. G.J. Wen, B.A. Boukamp, R.A. Huggins and W. Weppner, J. Electrochem. Soc., 126, 2258 (1979).
25. K.H. J. Buschow and H.H. Van Mal, J. Less. Common Metals, 29, 203 (1972).

26. Y. Mottot, unpublished results.

27. T.N. Rezukhina and S.V. Kutsev, Zh. Fiz. Khim., 56, 1 (1982).

28. C. Chatillon-Colinet, H. Diaz, J.C. Mathieu, A. Percheron-Guegan and J.C. Achard, Ann. Chim., 8, 657 (1979).
| Temperature T/°C | Lanthanum \[2.3 \text{ RT}/2^\circ\text{F. mV standard}] | Theory | Nickel \[2.3 \text{ RT}/2^\circ\text{F. mV standard}] | Exp. | Theory |
|-----------------|---------------------------------|--------|---------------------------------|--------|--------|
| 400             | 45 46                            | -3.185 |                                 |         |        |
| 435             |                                 |         |                                 | 77 74  | -1.083 |
| 450             | 45 49                            | -3.164 | 80 74  | -1.084 |
| 500             |                                 | 81 80  | -1.086 |
| 510             | 54 53                            | -3.137 |                                 |

Table 1: Verification of the Nernst relation for the La\(^{3+}\)/La and Ni\(^{2+}\)/Ni electrochemical systems in LiCl-KCl eutectic.

| lanthanum deposit on a nickel cathode | N\(_2\) deposit on a La electrode | Alloys in molten fluoride | observations |
|--------------------------------------|---------------------------------|---------------------------|---------------|
| plateau i                            | curve(1)                         | curve(2)                  | curve(3)      | REZUKHINA et al. |
|                                      | Fig. 3                           | Fig. 3                    | Fig. 2        | (17)            |
|                                      | -0.056                           | -0.030                    | 0             | La-Li alloys    |
|                                      |                                  |                           | 0             | La on a Ni wire |
|                                      |                                  |                           | 0             | La/La\(_2\)Ni alloys |
|                                      | 0.015                            |                           |               | alloys+oxychlorides |
|                                      | 0.042                            | 0.042                     | 0.041         | La\(_2\)Ni/LaNi alloys |
|                                      | 0.070                            | 0.072                     | 0.071         | La\(_2\)Ni/La\(_2\)Ni alloys |
|                                      | 0.088                            | 0.085                     | 0.094         | La\(_2\)Ni\(_3\)/LaNi\(_2\) alloys |
|                                      | 0.109                            | 0.110                     |               | metastable phase |
|                                      | 0.131                            | 0.136                     | 0.137         | LaNi\(_2\)/LaNi\(_3\) alloys |
|                                      | 0.153                            |                           |               | oxychloride influence |
|                                      | 0.215                            | 0.206                     | 0.204         | LaNi\(_2\)/La\(_2\)Ni\(_3\)/ LaNi\(_2\) alloys |
|                                      | 0.425                            | 0.478                     | 0.471         | LaNi\(_2\)/Ni alloys |
|                                      | 0.608                            | 0.648                     | 0.700         | Metastable phase |
|                                      | 1.860                            | 1.860                     | 1.865         | N\(_2\) wire electrode potential |

Table 2: Relation between experimental e.m.f. (see text) and lanthanum-nickel phases. (T = 450°C).
Table 3: Gibbs free energies of formation of the La-Ni alloys.
Figure 1: Voltammograms of La$^{3+}$ and Ni$^{2+}$ ions in LiCl-KCl eutectic melt at 450°C.
   (1) Ni$^{2+}$ ($4.82 \times 10^{-2}$ mol kg$^{-1}$) on glassy carbon electrode.
   (2) La$^{3+}$ ($4.2 \times 10^{-2}$ mol kg$^{-1}$) on tungsten electrode.
   (3) La$^{3+}$ ($4.2 \times 10^{-2}$ mol kg$^{-1}$) on nickel electrode.

Figure 2: e.m.f. variation (see text) as a function of time observed when a lanthanum electrode is dipped into LiCl-KCl eutectic melt containing Ni$^{2+}$ ($0.18$ mol kg$^{-1}$) at $T = 450^\circ C$. 

599
Figure 3: e.m.f. variation (see text) as a function of time after coating a nickel electrode with a thin layer of lanthanum by electrolysis at a controlled potential of: (1) -3.23 V under argon; (2) -3.23 V (3) -3.33 V, (4) -3.1 V, (5) -3.05 V, (6) -3 V, (7) -2.95 V, (8) -2.9 V and (9) -2.7 V under a slight HCl pressure.
Figure 4: Coulometric titration curve for La-Ni system at 450°C:
a) e.m.f. – composition diagram, b) dependence of the chemical diffusion coefficient with composition.
Figure 5: Phase diagram of the La-Ni system from Buschow and Van Mal (25).

Figure 6: e.m.f. - composition diagram for La-Ni system at 450°C.