FORMATION OF LaNi₅ FILM ON NI SUBSTRATE 
BY ELECTROLYSIS IN MOLTEN CHLORIDE 
AND ITS HYDROGEN ABSORPTION PROPERTY

M.OKIDO*, R.ICHINO** and R.TAMURA***

* Center for Integrated Research in Science and Engineering, Nagoya University
** Department of Materials Science and Engineering, School of Engineering,
   Nagoya University
*** Graduate student, School of Engineering, Nagoya University
   Furo-cho, Chikusa-ku, Nagoya, 464-01, Japan

Lanthanum - nickel alloy films can be formed on a nickel substrate by electrolysis 
in eutectic KCl - LiCl molten salts with both 1.5 mol% La₂O₃ and 18 mol% 
NH₄Cl or in eutectic KCl - NaCl molten salts with 10 mol% LaCl₃7H₂O. An 
alloy film of 30 μm thickness was obtained by this electrolysis at 923 K for 1 
hour. The composition of the alloy films depends on the temperature, consisting 
of LaNi₃, La₂Ni₇ and LaNi₅ at less than 923 K and LaNi₅ at more than 923 K. 
The vickers hardness of the alloy films obtained by this method was less than 
that of the commercial LaNi₅ ingot specimen. The alloy films show better 
hydrogen absorption behavior in the early stage, better charge - discharge 
behavior and less pulverization compared to the LaNi₅ ingot.

INTRODUCTION

Nickel - Hydrogen absorbing alloy batteries, with an electromotive force the same as 
Ni - Cd batteries, have higher energy density by 1.5 - 2 times than the latter battery. Moreover, 
since the reaction product is only water, Nickel - Hydrogen absorption alloy batteries are 
excellent in terms of low environmental impact.

A LaNi₅ alloy is used as an active material for a negative electrode in Nickel - hydrogen
batteries. The degradation due to the brittleness of expansion with hydrogen absorption, however, decays the battery properties. Recently, partial substitution of Al, Co or Mn for Ni is found to have good charge - discharge properties and to inhibit this degradation (1),(2).

Though LaNi$_5$ source can be commercially mass-produced in a high frequency-induced furnace because of high melting points of La and Ni, lanthanum is rare and noble mineral resource and refining of La metal is too expensive. Substitution of other elements for La is carried out in practice. Misch metal, cheaper than La, is used instead of La for good cost performance. On the other hand, it is considered that the use of thin film reduces the amount of LaNi$_5$ needed, and the material diffusion in films occurs better.

Electrolysis, electroplating and electrodeposition are usual methods in surface modification technique for metallic materials. As the temperature for electrolysis in molten salts is much higher than that in aqueous solutions, the deposited metal can be sometimes alloyed with the substrate. The capability for forming alloys depends on the affinity between metals and the temperature. In this paper, La - Ni alloy phases were formed onto Ni sheets under controlled cathodic currents in molten salts. Formed films were tested for their hydrogen absorption property, charge - discharge behavior, hardness, structure and the effect of the condition of electrolysis.

**EXPERIMENTAL**

Two electrolysis in molten salts were prepared. One was eutectic KCl - NaCl molten salts with 10 mol% LaCl$_3$7H$_2$O, denoted as bath (a). The other was eutectic KCl - LiCl molten salts with both 1.5 mol% La$_2$O$_3$ and 18 mol% NH$_4$Cl, bath (b). All chemicals were commercial high purity. The latter bath was heated for 4 hours at 623 K after pre-drying for 24 hours at 353 K, in order to form a LaCl$_3$ as in the following reaction(3);

$$\text{La}_2\text{O}_3 + 6 \text{NH}_4\text{Cl} \rightarrow 2 \text{LaCl}_3 + 6 \text{NH}_3 + 3 \text{H}_2\text{O}$$ [1]

The electrolysis is carried out after preheating at 1073 K for 1 hour to remove moisture in the molten salts. Cathodic polarization curves are measured for the Ni electrode in the molten salts. The counter electrode is a carbon rod, and a reference electrode is an Ag...
electrode in equimolar NaCl - KCl with 0.1 M AgCl in a mullite tube.

In electrolysis, a Ni sheet in the size of 15 mm square with a thickness of 0.1 mm is used as a cathode electrode. Before La electrolysis, every Ni cathode is preheated in the molten salts for 30 min. to remove the stress in the Ni electrode. Pre-electrolysis is performed by using another Ni cathode at -1.5 V for 20 min. to remove contaminations and water from the molten salts. Then, lanthanum is deposited in the potential region between -1.2 V and -2.0 V with a total charge of 32 C. Lanthanum - Nickel alloy films were electrolyzed at 0.1 Acm⁻² in bath (a) at 923 K - 1073 K for 400 s to estimate the effect of temperature on the films. Every electrolysis was carried out under argon atmosphere. Deposits were analyzed by X-ray diffraction (XRD), EPMA, SEM observation and a microvickers hardness test.

Hydrogen absorption into alloys during charge, and hydrogen desorption during discharge, were evaluated in 30 % KOH solution at 298 K for comparison with commercial LaNi₅ ingot. They were performed under galvanostatic condition with cathodic and anodic current densities of 10 mAcm⁻².

Hydrogen gas evolved on the cathode was collected in a buret. Absorbed hydrogen, equal to the charging electricity, Q_c (C), was calculated by the following equations.

\[ \text{M} + \text{mH}_2\text{O} + \text{me}^- \rightarrow \text{M} + \text{mH}_{(ad)} + \text{mOH}^- \rightarrow \text{MH}_{m-n(\text{int})} + \frac{n}{2} \text{H}_2 + \text{mOH}^- \quad [2] \]

\[ Q_c = zF(m-n) = \frac{it-2FPV}{RT} \quad [3] \]

M:LaNi₅, Q_c:amount of absorbed hydrogen, z:valence, F:Faraday constant, i:current, t:time, P:pressure, V:volume of hydrogen collected in the buret, R:gas constant, T:temperature

Charge - discharge characteristics in alkaline solution were evaluated, in the unit of coulomb by calculating the ratio, Q_c / Q_d, where Q_d (C) corresponds to the amount of desorbed hydrogen during discharging.

**RESULTS AND DISCUSSIONS**
Formation of LaNi₅

The cathodic polarization curves for a nickel electrode in molten salts of bath (a) with 10 mol% LaCl₃·7H₂O, bath (b) with 1.5 mol% La₂O₃ and 18 mol% NH₄Cl and (c) without La ions at 973 K are shown in Fig. 1. In the molten salts with La ions, cathodic current peaks appear in the potential region from -1.7 V to -2.0 V. These peaks correspond to the deposition of La. In XRD results on the Ni surface electrolyzed at -2.0 V in bath (b), LaNi₅ was detected on the surface. The plateau at potentials between -1.7 V and -2.0 V in bath (b) results from the diffusion limitations of La ion because of the lower concentration of La ions, 3 mol%, versus bath (a), 10 mol%.

Figure 2 shows an alloy phase of La and Ni in the cross section of the nickel film cathode with a thickness of 100 μm, electrolyzed with a current density of 0.02 Acnr² for 1 hour in bath (b). This film thickness is less dependent on the temperature and duration of electrolysis and is approximately constant at 25-30 μm below 923 K. The EPMA line analysis of La and Ni shows the constant content of La and Ni in the alloy layer, corresponding to LaNi₅. The alloy film formed at 773 K is LaNi₅ from XRD results. The result that the Ni content in alloy films electrolyzed at 923 K is richer than that at 773 K is caused by the temperature dependence of the diffusion rate in the solid alloy film. Figure 2(3) shows the result of EPMA for a deposit which was electrolyzed at 923 K for 1 hour and then cooled rapidly from 923 K to 473 K in the rapid Ar gas flow. Lanthanum content in the surface region is higher than that in the layer. This behavior shows that La diffusion takes place at the beginning of electrolysis and continues until low temperatures during cooling after electrolysis. However, in the case of rapid cooling, since La diffusion cannot have occurred sufficiently, La content in the surface region is high. Moreover, the difference in formation between LaNi₅ and LaNi₃ can also be caused by the difference between the liquid state and the solid state. Since the melting point of LaNi₅ is lower than that of LaNi₃, from the La-Ni binary phase diagram (3), LaNi₃ can be removed and depart from electrode surface at high temperature while LaNi₅ remains on the electrode surface at high temperature.

Figure 3 shows XRD analysis for La-Ni alloy films electrolyzed in bath (a) at different temperatures for 400 s. All diffractograms show LaNi₅, Ni and LaOCl diffraction peaks. LaOCl is due to the oxidation products from LaCl₃ with H₂O and/or O₂ during drying the molten salts, and it may be included in films during electrolysis and/or may be produced from LaCl₃ with H₂O and O₂ in Ar gas during cooling in the cell after electrolysis.
Lanthanum and nickel contents in films formed in bath (a) at 923 K - 1073 K are shown in Fig. 4. The La contents are approximately constant and the profiles of La in films are similar to Fig. 2. Lanthanum contents on the surface evaluated by EDX were 28 at%, 20 at%, 18 at% and 12 at%, respectively. Lanthanum content in the film electrolyzed at 1073 K was less than the stoichiometric value of 16.7 at% in LaNi$_5$. Since LaNi$_3$ formed at 773 K and LaNi$_5$ formed at 923 K, as shown in Fig. 2, mutual diffusion velocities of La and Ni are slow at low temperature, it seems that the excess La over LaNi$_5$ exists on the surface at the temperature less than 1023 K.

Current efficiencies calculated from weight gain, using the alloy thickness, for the alloys electrolyzed at 923 K, 973 K, 1023 K and 1073 K in bath (a) were 10.3, 38.5, 9.7 and 4.3, respectively. The low values of current efficiency are mainly contribute to La remelting into the molten salts in the style of La - Ni alloy. The melting point of La - Ni alloy containing Ni between 10 at% and 40 at% is about 900 K (4), which is lower than electrolysis temperature. Moreover, La$_2$Ni$_3$, La$_2$Ni$_4$O and La$_2$O$_3$ were detected by XRD in the molten salts after electrolysis. This evidence shows that La remelts into the molten salts. Therefore the thickness of alloy films is less, and the current efficiencies are low.

Surface morphology of alloy films formed at 923 K, 973 K, 1023 K and 1073 K for 400 s in bath (a) were shown in Fig. 5. Maximum grain size formed at 1073 K was about 8 μm and the grain size reduced with decreasing in electrolytic temperature. Therefore, the grain size depends on cooling history and grains grew during cooling in cell. Deposits formed at higher temperature than 1023 K showed brightness. On the other hand, deposits at lower temperature showed dark and non-bright feature because of fine grains.

**Hydrogen absorption property**

Cathodic charge for reduction of hydrogen ion at a current density of 10 mA cm$^{-2}$ in 30 % KOH solution was compared for Ni sheets electrolyzed in bath (a), LaNi$_5$ ingot and raw Ni sheet without any activation pretreatment. The result is shown in Fig. 6. The solid lines, noted 0 % charge, corresponds to the case where all cathodic current is used for hydrogen gas evolution. The dotted line, noted 100 % charge, corresponds to the absorption of hydrogen into the electrode without any gas evolution, in other words, the current efficiency for forming a hydride alloy is 100 %.
The amount of absorbed hydrogen for alloy films deposited at 923 K and 1073 K shows constant values of 2 C and 0.8 C, respectively. This shows saturation with absorbed hydrogen in these films because they are thinner than any other films. Alloy films deposited at 973 K and 1023 K show better absorption properties, nearly 100% charged, until a cathodic electricity of 3 C compared to LaNi₅ ingot. Because the alloy films have finer grains, hydrogen is more easily able to absorb into alloy films than into LaNi₅. The lines of charge efficiency deviates from the 100% charge line at over 3 C, because the films become saturated with absorbed hydrogen.

The amount of absorbed hydrogen in LaNi₅ electrolyzed at 923 K in bath (a) was evaluated from the saturated charge electricity of hydrogen, Qₑ, i.e. approximately 2.2 C in Fig. 6. If the volume of the alloy phase is assumed to be 2.0x10⁻⁴ cm⁻³, it is found that the atomic ratio of hydrogen to LaNi₅ is 5.80, i.e. LaNi₅H₅.₈₀. In the same way, that for films electrolyzed at 923 K in bath (b) is 5.76, i.e. LaNi₅H₅.₇₆. The theoretical value of the ratio of hydrogen is 6, i.e. LaNi₅H₆. Therefore, the Ni-La films formed by this electrolysis in molten salts can absorb much hydrogen and there are almost no differences in the ratio of hydrogen between bath (a) or bath (b).

Figure 7 shows the result of discharging tests, performed in 30% KOH solution at 298 K after charging for 30 min. All potential curves show a shoulder, and the potential increases rapidly until each shoulder. As each charged alloy electrode begins to discharge at the potential of the shoulder, the lower this potential is, the more easily hydrogen discharges. Dehydrogenation takes place in the plateau region after each shoulder, and the width of the plateau region depends on the amount of charged electricity, in other words, the film thickness. Hereby, alloy films produced by this molten salts technique have good charge-discharge properties in comparison with LaNi₅ ingot. The discharged electricity for LaNi₅ electrolyzed at 973 K was approximately 3 C, which was half of the charged electricity since this sample was charged with 6 C.

Charge-discharge characteristics in cycle test

Figure 8 shows the dependence of the ratio for the hydrogen discharge to the hydrogen charge on cycling test in alkaline solution. This test was performed under the condition of cathodic current density of 10 mAcm⁻² for 200 s, charging, and remaining still in the solution
for 10 min., before the anodic current density of 10 mA cm⁻², discharging. The time for anodic discharge is determined by reaching the potential of -0.6 V. Nickel hydroxide may form over this potential, and the discharge is regarded to have ended. All alloy films, except that deposited at 1073 K, shows effective discharge properties at approximately 10 cycles, i.e. discharged electricity is as same as charged electricity. The charge - discharge ratio for alloys electrolyzed at 923 K and 973 K rapidly decreases after 20 and 10 cycles, respectively. This ratio for films electrolyzed at 1023 K is more than 0.8 after 10 cycles, and for films electrolyzed at 1073 K, it has a constant value of 0.2. This low value for the latter may come from the film thickness. On the other hand, the commercial LaNi₅ ingot shows slight cycle dependency and remains at about 0.2 after 20 cycles. Consequently, alloy films prepared by this method, especially electrolyzed at 1023 K, show better charge - discharge characteristics than commercial LaNi₅ ingot. Some powders with dark gray color were observed at the bottom of cell for all films and the LaNi₅ ingot after cycle tests. The amount of powder decreased and powder was fine and roundish with increasing in electrolyzing temperature. As for the LaNi₅ ingot, powders with brightness and large powders were observed.

The surface morphology for the film electrolyzed at 1023 K after cycle testing and for the LaNi₅ ingot before and after cycle testing are shown in Fig. 9. The morphology for alloy film after cycle testing is similar to that before cycle test in Fig. 5(3). The white angular colored part is Ni and the part which looks like lichen is Ni(OH)₂. As for the other films using different temperatures, similar behavior was shown. In the case of LaNi₅ ingot, the morphology shows a fibrous structure with certain orientation after some grains parted from surface and fell down onto the bottom of the cell.

The hardness for alloy films measured by microvickers hardness tester was about 300 Hv and that for LaNi₅ ingot was about 650 Hv. This hardness of LaNi₅ ingot causes much of the powdering in cycle testing.

There were large cracks in the LaNi₅ ingot and small ones with network in electrodeposited alloy films in Fig. 9. The cracks, which were generated during charge - discharge cycles, caused grains to break and separate into parts. This behavior made the stress of grains relaxed and small and net work crevasse released it better than large one. Hereby, powdering of the alloy surface was inhibited. Hence charge - discharge characteristics of films were better than LaNi₅ ingot.
CONCLUSIONS

Lanthanum - Nickel alloy film phase can be formed on Ni thin films by electrolysis in chloride molten salts baths containing La ion. The LaNi$_5$ film was formed over 923 K. The current efficiency for electrolysis was mainly 10 %, maximum is 38.5 % at 973 K in this study because of melting of La and La - Ni alloy into the molten salts. The LaNi$_5$ films show less powdering, good hydrogen absorption and charge - discharge characteristics in alkaline solution compared to LaNi$_5$ ingot.

REFERENCES

1. M.Latroche, A.Percheron-Guegan, Y.Chabre, J.Bouet, J.Pannetier and E.Ressouche, J. Alloys and Compounds, 231, 537(1995).
2. H.Kaiya and T.Ookawa, J. Alloys and Compounds, 231, 598(1995).
3. Y.Y.Pan and P.Nash, in Binary Alloy Phase Diagrams 3, T.B.Massalski, Editor-in-chief, p.2406, ASM International, Metal Park(1990).
4. C.Guang-sen, M.Okido and T.Oki, J. Appl. Electrochem., 20, 77(1990).
Fig. 1 Cathodic polarization curves for reduction of $\text{La}^{3+}$ on Ni electrode at 973K. 1 in bath (a), 2 in bath (b) and 3 without $\text{LaCl}_3$.

Fig. 2 EPMA line analysis of La-Ni alloy layers electrodeposited in bath (b) at (1)723 K, (2) and (3) 923 K. (1) and (2) slow cooling in the furnace, (3) rapid cooling by Ar gas after electrolysis.
Fig. 3: X-ray diffraction patterns of La-Ni alloy electrodeposited in bath (a) at (1) 923 K, (2) 973 K, (3) 1023 K and (4) 1073 K.

O LaNi5  • Ni  △ LaOCl
Fig. 4  EPMA line analysis of La-Ni alloy layers electrodeposited in bath (a) at (1) 923 K, (2) 973 K, (3) 1023 K and (4) 1073 K.
Fig. 5  SEM photographs of La-Ni alloy surface electrodeposited in bath (a) at (1) 923 K, (2) 973 K, (3) 1023 K and (4) 1073 K.
Fig. 6 Charge performance of LaNi₅ ingot, Ni sheet and LaNi₅ electrodeposited in bath (a) at various temperature in 30 wt% KOH solution at 298 K.

Fig. 7 Discharge performance of LaNi₅ ingot and LaNi₅ electrodeposited at various temperature in bath (a), after charging.

Fig. 8 Change in discharged electricity/charged electricity with cycle number on LaNi₅ ingot and LaNi₅ electrolyzed in bath (a) at various temperature.

- ○923K, □973K, ◇1023K, △1073K and ●LaNi₅ ingot
Fig. 9 SEM photographs on LaNi$_5$ surface after cycle tests; (1) LaNi$_5$ electrodeposited at 973K in bath (a) and (2)LaNi$_5$-ingot. (3) is LaNi$_5$ ingot before cycle tests.