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Dispersion deposition of metal – Particle composites and the evaluation of dispersion deposited nickel – Lanthanum nickelate electrocatalyst for hydrogen evolution

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A method for the preparation of high surface area coatings and its application towards fabrication of prospective composite electrocatalysts for hydrogen evolution is proposed. Exploratory studies with such a composite, ($Ni/LaNiO_3$), as a hydrogen electrode in alkaline solutions indicate that it is a more active electrocatalyst than sintered or electrodeposited nickel. The electrocatalytic properties were found to be a strong function of the deposition parameters as well as of the history of the oxide powder.

1. Introduction

Hydrogen evolution, apart from being the main cathode reaction during electrolysis of water, is the cathode reaction in chloralkali cells and also in several other electrochemical processes (e.g., electro-organic oxidation). Its kinetics therefore influence the performance parameters of the electrochemical process in the cell. Improved electrode activity by catalysis and increase in effective surface area are thus essential for an increase in the efficiency of cells in which hydrogen evolution is the cathodic reaction.

In the search for new materials, as well as for new applications of technologically established ones, high levels of electrocatalytic activity for hydrogen evolution have recently been reported with oxide electrodes [1–4]. The most intriguing aspect of these oxide electrodes is that they are, in principle, thermodynamically unstable in the hydrogen adsorption region [5, 6] and are thus not expected to be good cathodes for this purpose. Rare earth oxides such as cobalt and molybdenum oxides have been reported to have long lifetimes at the potentials relevant to hydrogen evolution [1, 7, 8]. Other oxides of interest include IrO_x [2, 9] and RuO_x [10–12] which have been compared to Pt and Ru in respect to their electrocatalytic activity for hydrogen evolution even in the presence of metallic impurities [11].

In this work, we present our exploratory results on the performance of composite metal (Ag, Ni)/$LaNiO_3$ as electrocatalysts for hydrogen evolution. The composite material was prepared by dispersion deposition, a relatively new process variant of electroplating. This technique is characterized by suspension of inert non-metallic particles (e.g. carbides, oxides or dry lubricants such as MoS_2, boron nitride) in the electrolyte; during plating, the suspended particles move together with the metal ions to the cathode where they are incorporated in finely dispersed form into the metal layer that is deposited on this cathode [13]. The quantity and properties of dispersion coatings depend on several parameters, including the composition and microstructure of the matrix, the type and concentration of the finely-dispersed phase as well as the cathode current density and electrolyte flow condition.

2. Experimental details

2.1. *Materials and materials preparation*

Lanthanum nickelate was prepared by a coprecipitation method starting from solutions of hydrated nickel and lanthanum nitrates [14]. Potassium hydroxide solution (1 M) was added gradually onto a continuously stirred mixture of equimolar concentrations of the nitrates. This formed precipitates of the metal hydroxide which was separated from the solution by a centrifuge technique. After washing with deionized water, the precipitate was dried and thereafter, calcined under varied conditions (e.g., at 600° C for 2 h) to form the mixed oxide, $LaNiO_3$.

Coatings of nickel as well as composite nickel/lanthanum nickelate were deposited onto smooth and sintered nickel substrates in an acid nickel plating system. The basic bath composition [15] was: $NiCl_2 \cdot 6H_2O$ ($300\,g\,L^{-1}$); H_3BO_3 ($30\,g\,L^{-1}$); $LaNiO_3$ powder ($\sim 50\,g\,L^{-1}$); and pH 3.3–3.7.

For some depositions, $LaNiO_3$ powder was replaced with nickel powder for comparison of surface area effects on electrocatalytic activity. For plating of the composite with silver matrix, the silver plating bath used was [15]: AgCl (35–$40\,g\,L^{-1}$) and KCN

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(100–125 g L^{-1}). Silver chloride was obtained by precipitation of silver nitrate solution using hydrochloric acid. The plating current density was in the range of 0.1 to 0.5 A dm^{-2}. Deposition was carried out in a two compartment cell, with a Nafion® membrane as separator, at room temperature. The finely ground lanthanum nickelate powder (with an average size of ~ 1–10 μm in diameter) was introduced into the cathodic compartment, to which an external system for catholyte circulation was attached. The ion-selective membrane served as a filter/barrier to prevent the powder from reaching the anode, thereby avoiding possible short-circuiting of the cell. The plating bath was continuously agitated by catholyte circulation during composite deposition.

All the chemicals used were of EP grade. Phase formation and compositional analysis were carried out using X-ray diffraction (XRD), scanning electron microscopy (SEM) and energy-dispersive X-ray spectrometry (EDS) techniques.

2.2. *Electrocatalytic studies*

The electrocatalytic activity of the composite material for hydrogen evolution was evaluated in 3 M and 5 M KOH solutions in a one-compartment cell at room temperature. The electrochemical cell contained a working electrode which was either the composite material, sintered nickel, or electroplated nickel; a nickel gauze counterelectrode; and a Hg/HgO reference electrode with Luggin capillary. All data were obtained galvanostatically, using a Solatron electrochemical interface model No. 1286 and a BK Precision DC power supply as the power sources.

3. Results and discussion

Figure 1 is the representative XRD pattern of the calcined powder with numbers above the diffraction peaks indicating *d*-spacing values. The powder was determined to be stoichiometric $LaNiO_3$, crystallizing with the perovskite structure. It was observed that the oxide had a high catalytic activity for decomposition of hydrogen peroxide in alkaline medium, and this activity decreased when the dried powder was calcined at a higher temperature and for longer times (e.g., at 1000° C for 10 h).

The pH of the nickel plating bath was initially 3.5, and increased to about 5.0 when $LaNiO_3$ powder was added. To prevent precipitation of nickel hydroxide during electrodeposition, the solution pH was adjusted by addition of HCl to give a value between 3.3 to 3.7, preferably 3.5. More acid pH values would cause

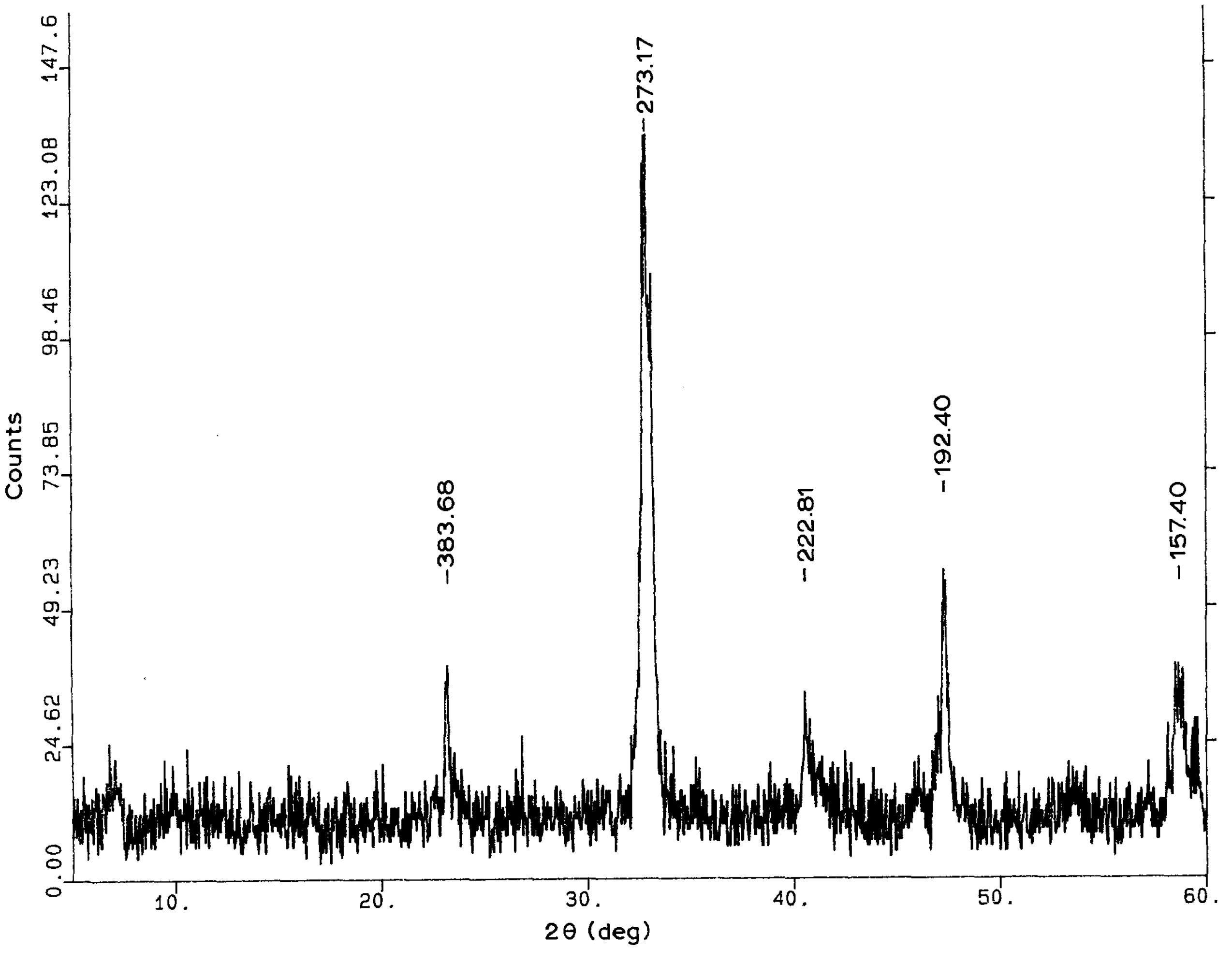

Fig. 1. Representative X-ray Diffraction pattern of a typical powder sample, obtained after calcination at 600° C for 2 h, of the mixed metal (La and Ni) hydroxide precipitates. Pattern indicates $LaNiO_3$ with a distorted perovskite structure. Numbers above peaks represent *d*-spacing values in picometres (pm).

dissolution of the lanthanum nickelate. The lanthanum nickelate content in the composite was found to vary proportionately with the plating current density, reaching a maximum at about 15 mA cm^{-2} for the current range employed in this work. As the current density was increased, however, the surface of the deposits were observed to become rougher. One possible explanation of this trend is that at very slow plating rates, the number of adsorbed particles are not sufficient to be surrounded by newly deposited metal atoms and are therefore carried away by the fluid. As the current density is gradually increased, the rate of metal ion reduction is increased and both the adsorbed particles and metal atoms are supplied at a balanced rate to the cathode surface giving rise to enhanced particle content. It is expected, however, that at very much higher plating rates, particles simply cannot be supplied at a rate comparable to the reduction of the metal ions, thereby resulting in reduced particle content. This trend in particle content/current density behaviour was also observed with electrolyte flow rate. At too slow a speed, the fluid was not fully capable of transporting the particles to the cathode surface, whereas at high flow rates, freshly adsorbed particles could not withstand the impact of strong flow and were again carried away.

These observations suggest that the extent of particle codeposition depends on a balance of the adsorption of the particles, the mechanical bonding between the particles and the surrounding metal atoms as well as the fluid momentum which tends to blow the adsorbed particles away. Hence, optimum values for both the plating current density and electrolyte flow rate are essential for incorporation of greater number of particles in finely dispersed and practically agglomeration-free form as well as enhanced electrocatalytic acitivty. During electrodeposition, it was observed that hydrogen evolution took place at the electrode surface when the plating solution containing the nickelate powder particles was stirred. No hydrogen evolution occurred if the solution was unstirred.

To illustrate the deposition technique as a potential method for preparing high surface area coatings, lanthanum nickelate powder was replaced with nickel powder during electrodeposition of nickel. Comparison of the surface morphology of electrodeposited nickel with that of composite nickel with nickel powder via their scanning electron micrographs revealed that the composite coating has a higher surface area. XRD and EDS analysis of resulting composite coatings showed that the metals and lanthanum nickelate existed as separate phases in the deposits. An illustrative EDS spectrum for silver codeposited with $LaNiO_3$ is shown in Fig. 2, where silver rather than nickel was used as the metal phase. Since silver does not exist as a component in $LaNiO_3$, and shows up in the EDS spectrum, it becomes apparent, even in the case of $Ni/LaNiO_3$, that both the metal and oxide phases exist separately in the deposits.

The electrocatalytic property of the $Ni/LaNiO_3$ composite material was assessed and compared with that of nickel from the potential against current density behaviour in alkaline solutions. Figure 3 shows a

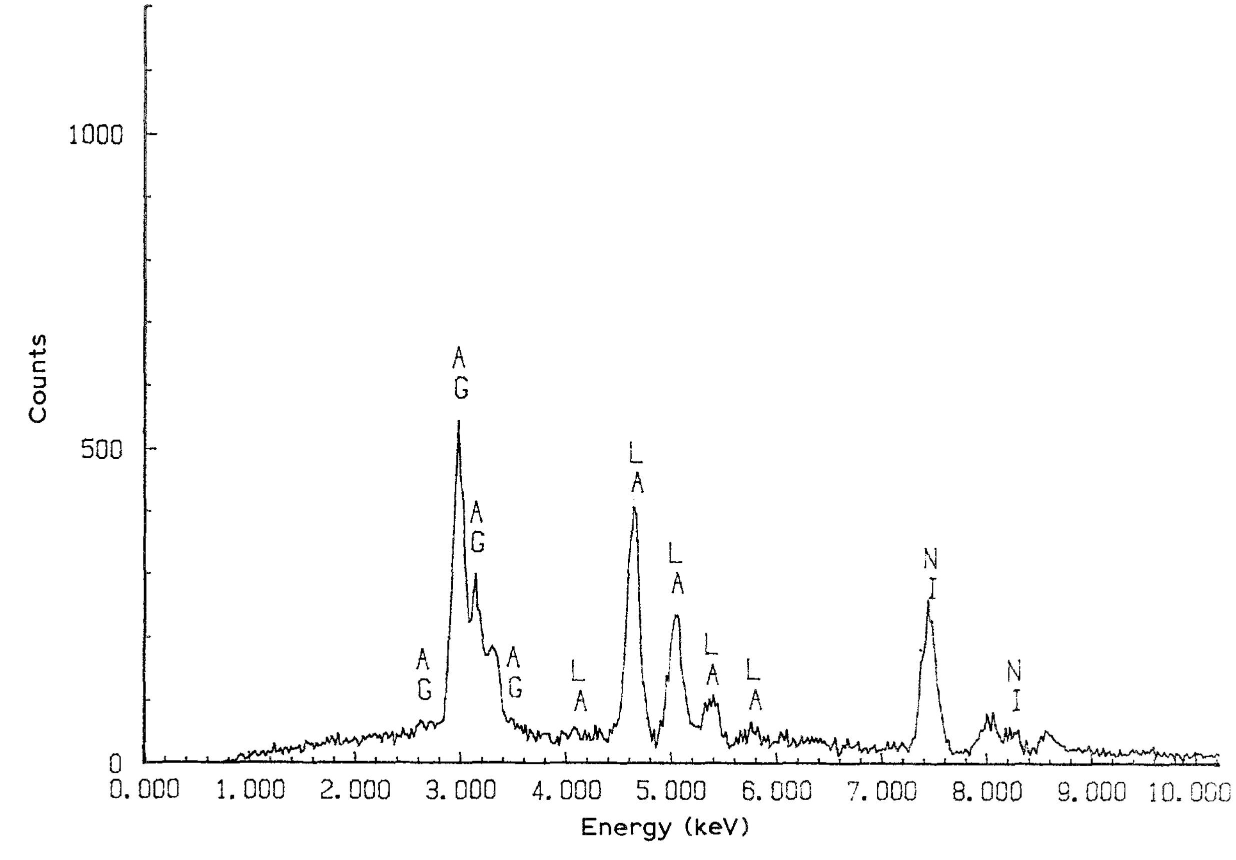

Fig. 2. A typical EDS spectrum of codeposited silver with $LaNiO_3$ particle dispersions. The presence of all three metallic components – La, Ni and Ag – is indicative of a $Ag/LaNiO_3$ composite deposit.

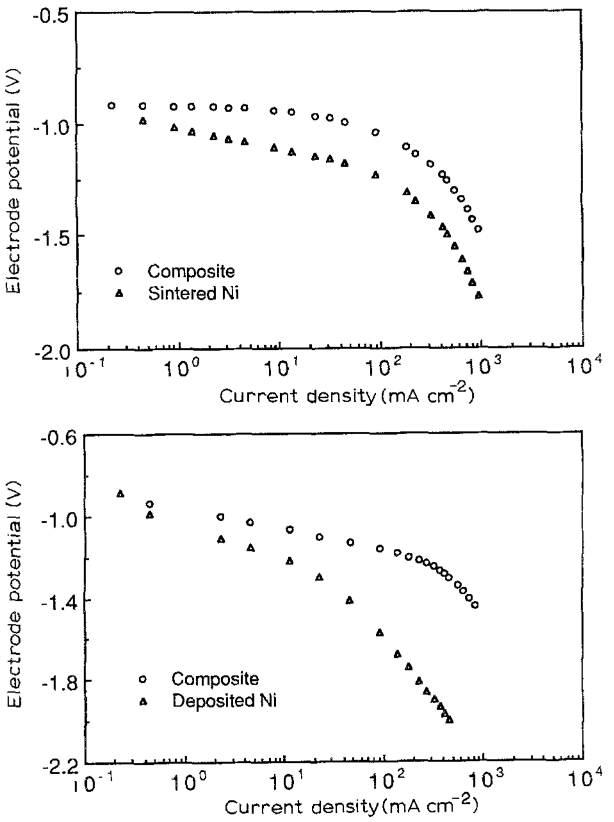

Fig. 3. Comparison of the steady state electrode potential (with respect to Hg/HgO) against current density (geometric area) plots of composite Ni/LaNiO$_3$ with those for sintered nickel (top) and electrodeposited nickel (bottom). Measurements were made after 17 h of electrolysis at 250 mA cm^{-2} in 3 M KOH solution at 25° C. Substrates were sintered and smooth nickel for the top and bottom plots, respectively.

comparison of the potential against current density (geometric area) plots for the composite material deposited on sintered nickel with those for sintered nickel alone and nickel electrodeposited on a smooth nickel substrate. These overpotential measurements were made after 17 h of electrolysis at 250 mA cm^{-2} in 3 M KOH solutions at room temperature. Sintered nickel, which is a good electrocatalyst for hydrogen evolution, was used for comparison because it has a high surface area, allowing a good comparison of activity. The effect of using higher surface area composite electrodes is thus clearly shown in Fig. 3. By comparing the plots for the composite material deposited on smooth nickel with those deposited on sintered nickel, it is apparent that there is an immediate decrease in the electrode potential from open circuit (steady state) values when current was applied to the electrode with the composite material deposited on smooth nickel. This potential decrease is, however, hardly noticeable for the case where the composite material is deposited on sintered nickel until a current density of about 50 mA cm^{-2} is attained.

We may therefore conclude, as in the case with pure sintered nickel [1], that the increased internal area available on the higher surface area composite electrodes is indeed utilized during electrolysis. There was no observable coalescence of hydrogen gas bubbles in the electrode structure, with the net result that the composite electrode functioned relatively well within the porous structure allowing entry of the electrolyte. It is not clear to us, at the present time, whether this observed performance of the composite electrode is an effect attributable solely to the increased surface area or if it is due to the electrocatalytic nature of the composite. Our experimental observation, however, show that the composite material has a higher electrocatalytic activity than sintered nickel, (see for example, Fig. 3), under the same operating conditions. This, by itself, is of great interest in finding better electrocatalysts for cathodic evolution of hydrogen. Studies on the effect, and contribution, of the increased surface area of the composite during hydrogen evolution is presently being pursued. Here, the electrocatalytic properties of Ni/LaNiO$_3$ powder composite will be compared with those of Ni/Ni powder composite, both deposited on sintered nickel. Figure 3 also shows that an overpotential difference of over 500 mV at 250 mA cm^{-2} of geometric area exist between the composite and electrodeposited nickel. The difference is over 200 mV between the composite deposit and sintered nickel.

Figure 4 compares the iR corrected plots of both the composite and sintered nickel materials. Correction was achieved by fitting the actual data, using the linear least square regression, to the general equation of the form

$$E = E_0 + b \ln i + iR$$

where $E_0 = E_r - b \ln i_0$, E_r is the reversible potential, b and i_0 the Tafel slope and exchange current density for the hydrogen evolution reaction and R the ohmic resistance between the test electrode and the reference electrode. The Tafel slope obtained for the composite material was 37 mV (decade)$^{-1}$, compared with a value of 85 mV (decade)$^{-1}$ for sintered nickel. The ohmic resistances were approximately equal in the two cells.

At very small currents approaching steady state conditions, the composite electrode potential approaches -0.91 V with respect to Hg/HgO, which is the approximate reversible potential for hydrogen evolution at

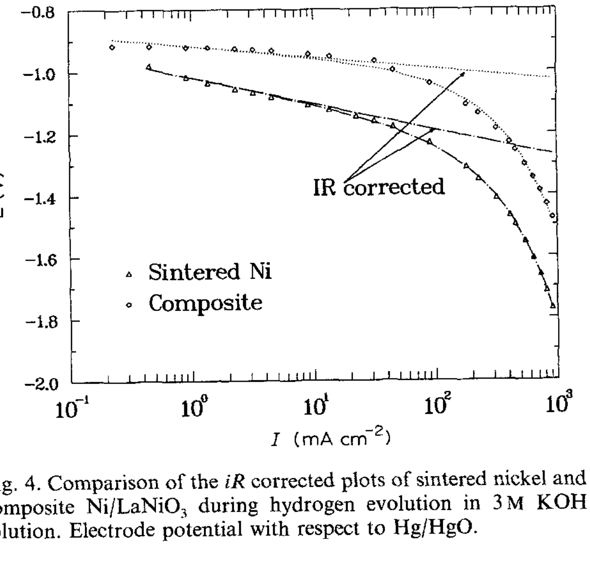

Fig. 4. Comparison of the iR corrected plots of sintered nickel and composite Ni/LaNiO$_3$ during hydrogen evolution in 3 M KOH solution. Electrode potential with respect to Hg/HgO.

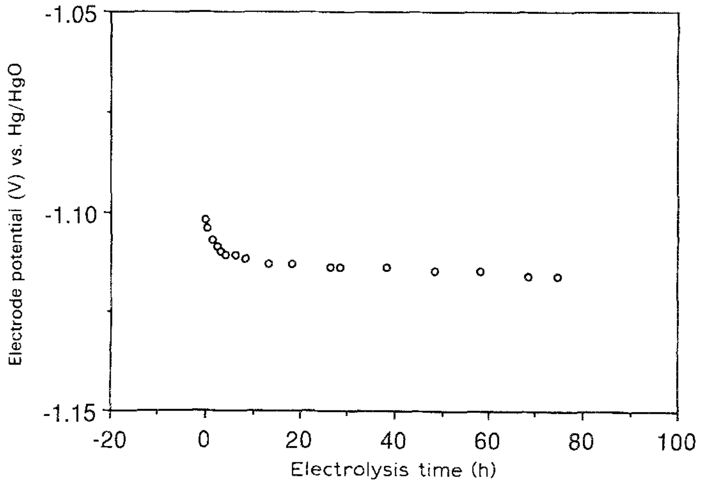

Fig. 5. Performance of composite Ni/LaNiO$_3$ catalyzed electrode (A = 2 cm^2) as a function of time (iR included). Electrode loading condition: 30 mA (15 mA cm^{-2}) for 15 min electrolysis condition 500 mA cm^{-2} in 3 M KOH at 25° C.

the prevailing hydrogen pressure and the hydroxide ion activity. Only a -10 mV variation in electrode potential of the composite material was observed upon electrolysis for 100 h at 250 mA cm^{-2}. In contrast, a change of at least -200 mV was noticed for the sintered nickel electrode.

Intermediate term electrolysis experiments were also conducted to determine the life-time stability of the composite electrodes. Preliminary results on the variation of the electrode potential of the composite electrodes as a function of time is shown in Fig. 5. The plot is shown for composite electrode deposited at 30 mA for 15 min and electrolysis at 500 mA cm^{-2} in 3 M KOH solution. The result is characterized by an abrupt initial increase in the electrode potential which is attributable to the ohmic (iR) drop between the test and reference electrodes. Thereafter, only a slow increase in the potential was observed, with a cumulative change of only 12 mV over a period of about 80 h, after which, the potential was stable. During this time, overpotential measurements were again carried out on the composite electrode incorporating lanthanum nickelate. Results are shown in Fig. 6. There is apparently no change in the electrode performance, which is a fairly good indication of electrode stability.

After the electrolysis studies, the electrode was analysed using energy-dispersive X-ray spectrometer. Figure 7 is a representative EDS spectrum of a sample composite electrode before and after three days of electrolysis in 3 M KOH solution. The negligible change in composition, coupled with non-degradation of surface morphology of the composite (as observed by SEM) and the low overpotential shown by the composite electrode during electrolysis suggests a promising hydrogen evolution electrocatalyst with long term stability in alkaline solutions.

Results obtained in 5 M KOH solutions were identical with those in 3 M KOH when the loading level of the electrode was kept the same. Thus while the effect of a change in KOH concentration is likely to be negligible at this temperature, the same is not necessarily true for the effect of loading level, as already mentioned. In fact, this effect is illustrated in Fig. 8 where it is shown that the electrode performance is a strong function of the loading level (deposition rate). The performance seems to improve with increased deposition rate, reaching a maximum at about the 15 mA cm^{-2} rate. This is further illustrated in Table 1 with the corresponding equilibrium potentials at different current densities for composite electrodes fabricated with different loading levels.

4. Conclusion

In this work, high surface area coatings of metal/particle composites have been prepared by dispersion

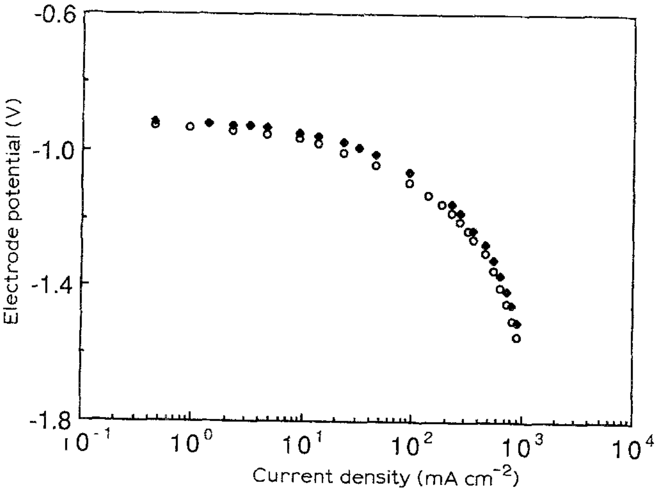

Fig. 6. Steady state potential against current density measurements on a Ni/LaNiO$_3$ composite electrocatalyzed electrode surface at two intervals during electrolysis in 3 M KOH solution at 500 mA cm^{-2}: (○) after 15 h and (◆) after 72 h. Potential referred to Hg/HgO.

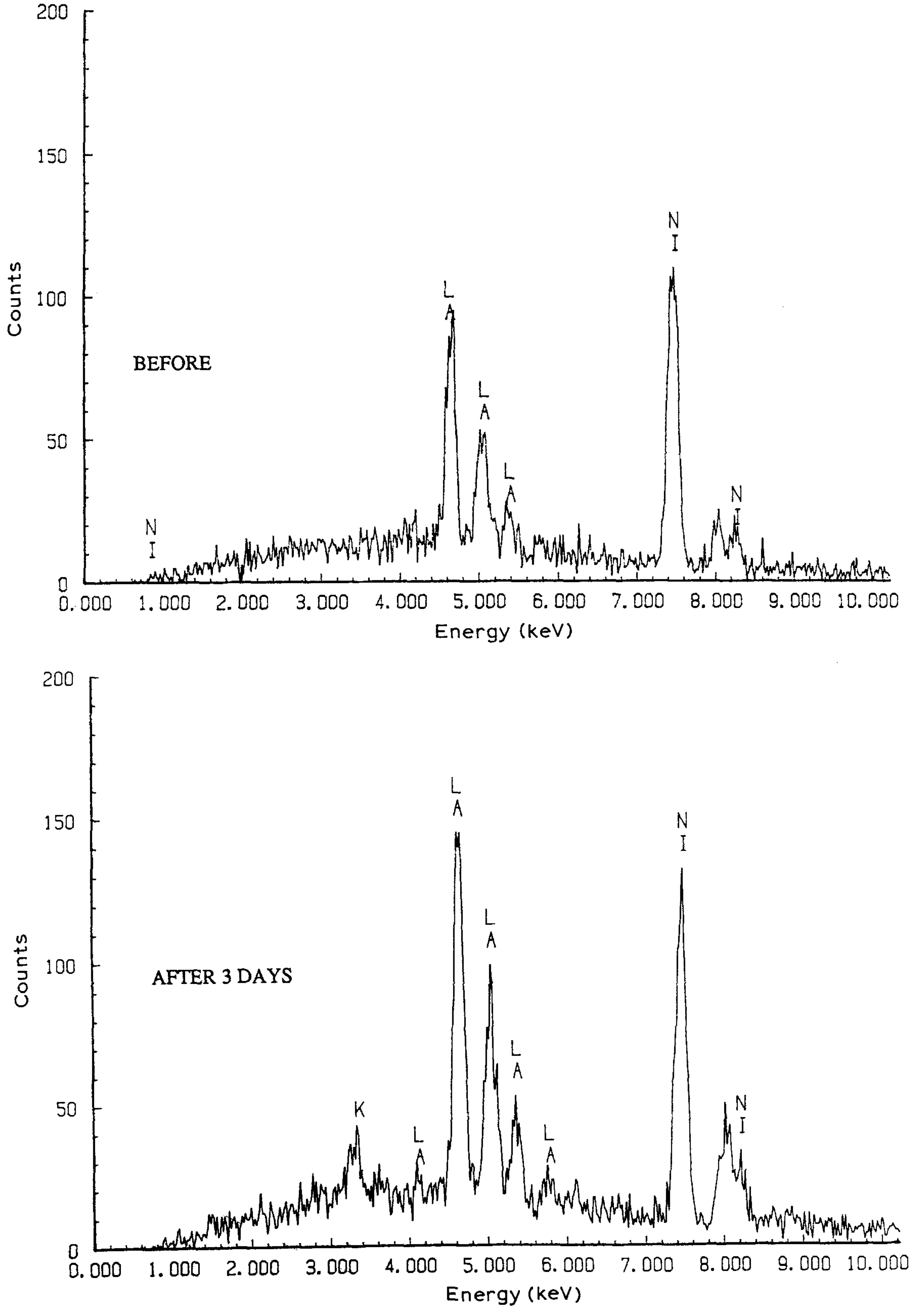

Fig. 7. EDS spectra of a sample composite electrode before (top) and after (bottom) about three days of electrolysis in 3 M KOH solution.

deposition. The particles were incorporated in the metal matrix in finely-dispersed form with perfect bonding between the dispersion and the surrounding metal atoms. During deposition, it was necessary to maintain a balance between the applied current, electrolyte agitation and the flow rate of the electrolyte in order to maintain the particles in suspension and to transport them to the active electrode surface. The technique was used to prepare composite Ni/$LaNiO_3$ electrodes for evaluation as an electrocatalyst for hydrogen evolution in alkaline solutions. This composite is a more effective electrocatalyst than sintered and electrodeposited nickel. Its electrocatalytic properties are a strong function of the deposition parameters,

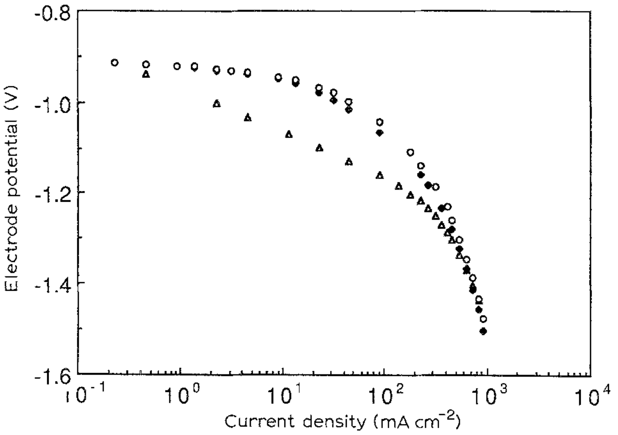

Fig. 8. Effect of loading rate/time on the electrocatalytic activity of the composite electrode during hydrogen evolution. Measurements were taken after 15 h of electrolysis in 3 M KOH at 25° C. Substrate area: 2 cm^2. Conditions: (△) 15 mA/30 min, (◆) 25 mA/18 min/B and (○) 30 mA/15 min.

Table 1. Comparison of steady state potentials at different current densities for composite Ni/LaNiO$_3$ electrodes fabricated with different deposition rates

Current density (mA cm^{-2})	*Electrode potentials* (V)*		
	15 mA/30 min	*25 mA/18 min*	*30 mA/15 min*
0.46	0.938	0.917	0.918
2.27	1.002	0.929	0.926
4.55	1.032	0.936	0.933
22.73	1.099	0.977	0.967
45.45	1.128	1.013	0.997
90.91	1.159	1.064	1.040
227.27	1.215	1.158	1.137
272.73	1.232	1.183	–
318.18	1.249	–	1.186
363.64	1.267	1.231	–
409.09	1.284	–	1.230
454.54	1.302	1.277	1.257
545.45	1.336	1.321	1.302
636.36	1.370	1.367	1.344
909.09	–	1.504	1.477

* All listed electrode potentials are negative with respect to Hg/HgO reference.

as well as of the history of the oxide powder. The material shows long term stability in strong alkaline solutions with minimal degradation. The dispersion deposition technique may suggest a method for obtaining other high surface area coatings. Further investigations on refining the procedure and evaluating other composite coatings as electrocatalysts for hydrogen evolution are in progress.

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