

ELECTROCHEMICAL SCIENCE AND TECHNOLOGY

The Influence of Foreign Cations on the Electrochemical Behavior of the Nickel Hydroxide Electrode

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ABSTRACT

The influence of Co, Cd, and Zn ions on the voltammetric behavior of the nickel hydroxide electrode in binary and ternary metal hydroxide layers in 0.1M KOH and 0.08M KOH + 0.02M LiOH was investigated. The presence of Co hydroxide increases the reversibility of the Ni(II)/Ni(III) electrochemical reaction and hinders aging effects involving unstable Ni hydroxide species. The simultaneous presence of Co and Zn ions in the metal hydroxide layer has a beneficial influence for the long-term stability and efficiency of the active material. The incorporation of Cd hydroxide increases the polarization of the oxygen evolution reaction. Results are interpreted in terms of either the existence of intermediate oxidation level of the foreign cations which can be produced at potentials lower than the equilibrium potential of the Ni hydroxide electrode or the influence of the foreign metal hydroxide on the oxygen evolution reaction.

The addition of foreign metal ions to the nickel hydroxide electrode in Ni-Cd, Ni-Fe, Ni-Zn, and Ni-H batteries improves the utilization of the active material, increases the polarization of oxygen evolution reaction, and depresses the capacity loss during long charge-discharge cycles.¹⁻⁴ Research efforts were made on the beneficial effects on the charge storage reaction attained by incorporation of cobalt⁴⁻¹⁰ and lithium ions^{8,11-13} and, to some extent, zinc ions.^{4,14-17}

Recent studies on nickel hydroxide colloidal layers coprecipitated with cobalt hydroxide, formed on a platinum substrate electrode¹⁰ have shown that the presence of cobalt hydroxide increases the reversibility of the Ni(II)/Ni(III) redox reaction. This behavior was assigned to a catalytic effect of the Co(II)/Co(III) redox couple on the Ni(II)/Ni(III) electrode reaction presumably resulting from a particular structure due to foreign ion insertion into the coprecipitated metal hydroxide pseudolattice. It should be noted that the electrochemical behavior of coprecipitated nickel and zinc hydroxide thin layers formed on a platinum substrate showed up the greatest catalytic effect on the Ni(II)/Ni(III) electrode reaction when the Zn(II)/Ni(II) concentration ratio in the coprecipitated layer was about 0.2.¹⁷ The incorporation of zinc hydroxide up to 20% appeared to be the optimum concentration for simultaneously improving the efficiency of the nickel hydroxide active material, depressing the capacity loss during prolonged charge/discharge processes, and increasing the polarization of the oxygen evolution reaction (OER). These effects can be explained through the formation of nickel hydrous zincate in the metal hydroxide gel-like layer. On the other hand, the addition of a third component such as manganese ions can improve the stability, corrosion resistance, and catalytic activity for the OER of binary mixtures of nickel and iron hydroxides.¹⁸ Accordingly, the detrimental effect of iron^{19,20} on the nickel hydroxide battery electrode can be manipulated in order to produce a better electrocatalyst for the OER.

The present paper reports data on the influence of Co, Cd, and Zn incorporated in the Ni hydroxide electrode as bi-

nary and ternary metal hydroxides layers and on the influence of Li⁺ ions in the alkaline solution on the Ni(II)/Ni(III) electrochemical reactions. In the former case composite metal hydroxide layered electrodes were prepared by chemical precipitation on smooth platinum substrates. For the sake of comparison the electrochemical response of the layered structured (sandwich-type) metal hydroxide electrodes has been also investigated. The electrochemical data resulting from these types of electrodes offer the possibility of discovering new aspects of the Ni(OH)₂ + OH⁻ = NiOOH + H₂O + e⁻ redox reaction, of interest in battery electrode design.

Experimental

The experimental setup was the same as already described in previous publications.^{10,17,21} The working electrodes consisted of layers of chemically precipitated metal (nickel, cobalt, cadmium, and zinc) hydroxides on a platinum wire ("Specpure," Johnson Matthey Chemicals Ltd., 0.5 mm diam, 0.20 cm² apparent area). The latter was cleaned by immersion in a 1:1 H₂SO₄ + HNO₃ mixture for 15 min, and later repeatedly rinsed with triply distilled water. Two preparation procedures for the metal hydroxide layer (hereafter denoted as the electrode) were used depending on whether one started from a coprecipitated nickel, cobalt, cadmium, and zinc hydroxide mixture (procedure 1) or a layer structured nickel and cobalt hydroxide plus nickel and zinc hydroxide, or vice versa (procedure 2). Procedure 1 involved the coprecipitation of the metal hydroxides from *n* alternate immersions in *x*₀M NiSO₄ + *y*₀M CoSO₄ + *w*₀M CdSO₄ + *z*₀M ZnSO₄ solution (for the sake of comparison some measurements with electrodes prepared for *y* = *w* = *z* = 0 were also made) and in 0.1M KOH. Procedure 2 involved the *n*₁ alternate immersions in *x*₁M NiSO₄ + *y*₁M CoSO₄ (or *z*₁M ZnSO₄) solution and 0.1M KOH solution, followed by *n*₂ alternate immersions in *x*₂M NiSO₄ + *z*₂M ZnSO₄ (or *y*₂M CoSO₄) solution and 0.1M KOH solution (0.0005 ≤ *x*₁ ≤ 0.025; 0.0001 ≤ *y*₁ or *w*₁ or *z*₁ ≤ 0.005. The electrode preparation procedures 1 and 2 allowed us to modify the composition of the metal hydroxide layer in the 0.2 ≤ *y*/*x* = *w*/*x* = *z*/*x* ≤ 5 range, whereas procedure 2 also allowed us to vary the composition profile within the metal

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hydroxide layer. The immersion time in each solution was 5 s, and the number of alternate immersions (either n or $n_1 + n_2$) was varied from 5 up to 100. After its preparation the electrode was immediately placed in the cell and maintained at $E = 0.24$ V during 1 min before the voltammetric run. The amount of Ni(II), Co(II), and Zn(II) ions in the precipitated hydroxide layer was evaluated by atomic absorption spectrometry after dissolving the layer in nitric acid solution.

Potentials were measured against a saturated calomel electrode (SCE) connected to the cell in the usual way,¹⁰ but in the text they are referred to the normal hydrogen electrode (NHE) scale. The counterelectrode was a large area platinum sheet placed in a separate cell compartment.

Runs were made at 25 and 50°C in 0.1M KOH and in 0.08M KOH + 0.02M LiOH solutions under purified N₂ gas saturation. Both the precipitating and the electrolyte solutions were prepared from analytical grade (p.a. Merck) reagents and triply distilled water. Voltammetric measurements were performed by using either single (STPS) or repetitive (RTPS) triangular potential sweeps between fixed cathodic ($E_{s,c}$) and anodic ($E_{s,a}$) switching potentials at different scan rates (v) in the $0.001 \text{ V s}^{-1} \leq v \leq 0.1 \text{ V s}^{-1}$ range. The nickel, cobalt, cadmium, and zinc ion concentration in the metal hydroxide layer before and after different potential cycling conditions were determined by atomic absorption spectrometry (Rank Hilger Atomspek H 1550).

Results

Composed Ni hydroxide electrodes.—The voltammogram of the Pt/coprecipitated hydrous [Ni(OH)₂ + Co(OH)₂ + Zn(OH)₂] electrode in 0.1M KOH at 25°C is shown in Fig. 1 in comparison to the response of Pt/precipitated hydrous Ni(OH)₂, Pt/precipitated hydrous [Ni(OH)₂ + Co(OH)₂], and Pt/precipitated hydrous [Ni(OH)₂ + Zn(OH)₂] reference systems. The voltammograms of these electrodes depend on the amount of metal hydroxide, and on the number of repetitive potential cycles, plus the characteristics of the perturbing potential. The voltammograms of those electrodes consisting of either a hydrous Ni(OH)₂ or a coprecipitated binary metal hydroxide layer run at $v = 0.1 \text{ V s}^{-1}$ between 0.24 and 0.88 V are similar to those already described for these systems.^{10,17} For the Pt/Ni(OH)₂ electrode, during the initial charging/discharging cycles (not shown), there is a gradual shift of the main anodic and cathodic current peaks towards more positive potentials, to become stable after 60 min RTPS at ca. 0.72 and 0.64 V, respectively (Fig. 1, dot-dashed trace). The voltammograms of coprecipitated binary metal hydroxide electrodes run under comparable conditions exhibit only small shifts in the peak potentials during cycling for the Pt/coprecipitated hydrous [Ni(OH)₂ + Co(OH)₂] electrode, the

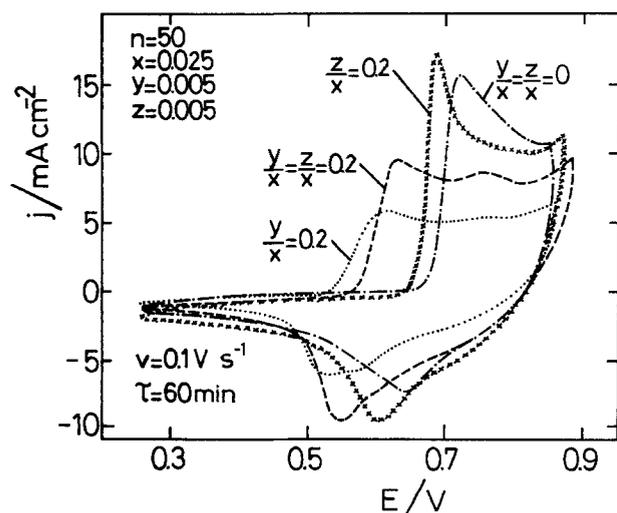


Fig. 1. Voltammograms obtained after 60 min potential cycling at $v = 0.1 \text{ V s}^{-1}$ for electrodes prepared according to procedure 1, $n = 50$; $x = 0.025$; (—) $y = z = 0$; (xxxx) $y = 0, z = 0.005$; (....) $z = 0, y = 0.005$; (-·-·-) $y = z = 0.005$. 0.1M KOH, 25°C.

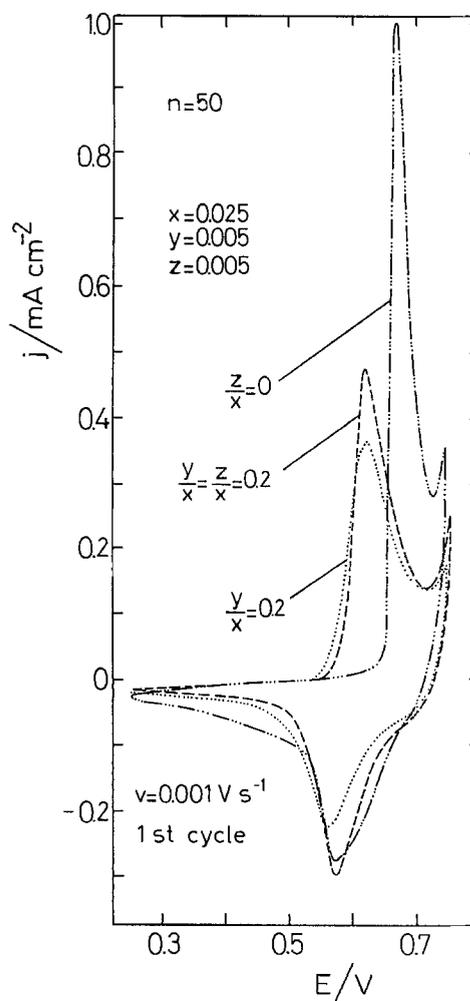


Fig. 2. STPS voltammograms at $v = 0.001 \text{ V s}^{-1}$ for electrodes prepared according to procedure 1, $n = 50$; $x = 0.025$. (—) $y = 0, z = 0.005$; (....) $z = 0, y = 0.005$; (-·-·-) $y = z = 0.005$. 0.1M KOH, 25°C.

voltammogram after 60 min RTPS shows two anodic peaks at ca. 0.61 and 0.75 V, respectively, the former being better defined than the latter, and two cathodic peaks at ca. 0.53 and 0.57 V, respectively (Fig. 1, dotted curve). Otherwise, for the Pt/coprecipitated hydrous [Ni(OH)₂ + Zn(OH)₂] electrode the voltammogram presents two well-defined peaks, one anodic at ca. 0.69 V and another cathodic at ca. 0.61 V (Fig. 1, cross symbols).

The simultaneous addition of Co(OH)₂ and Zn(OH)₂ to the active material modifies the voltammetric response of the precipitated hydrous Ni(OH)₂ electrode, by changing the position of the current peaks related to the Ni(II)/Ni(III) redox reaction although the peak potentials remain practically unaltered during the oxidation/reduction cycles (ORC). The voltammogram run with the Pt/coprecipitated hydrous [Ni(OH)₂ + Co(OH)₂ + Zn(OH)₂] electrode shows, after 60 min RTPS, two anodic peaks at ca. 0.63 and 0.76 V, respectively, and one cathodic peak at ca. 0.55 V with a shoulder at ca. 0.59 V (Fig. 1, dashed trace). Besides, the threshold potential for the Ni(II)/Ni(III) electro-oxidation reaction occurs at potentials less positive according to the following order: Pt/[Ni(OH)₂ + Co(OH)₂] > Pt/[Ni(OH)₂ + Co(OH)₂ + Zn(OH)₂] > Pt/[Ni(OH)₂ + Zn(OH)₂] > Pt/[Ni(OH)₂] (Fig. 1). It should be noticed that for the last two electrodes during the initial 10 min RTPS the corresponding threshold potentials are temporarily inverted.

The STPS voltammograms of the ternary metal hydroxide electrodes run at $v = 0.001 \text{ V s}^{-1}$ (Fig. 2) show only a single anodic current peak at ca. 0.62 V and a single cathodic current peak at ca. 0.57 V, and simultaneously ΔE_p , the potential difference between the anodic and cathodic main current peaks, decreases, so that the reversibility of the Ni(II)/Ni(III) electrochemical reaction appears to be

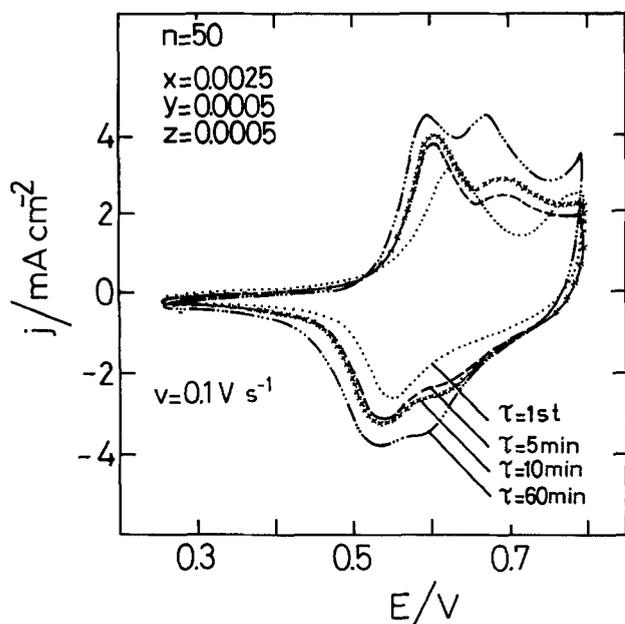


Fig. 3. RTPS voltammograms at $v = 0.1 \text{ V s}^{-1}$ obtained for a Pt/coprecipitated hydroxys $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2 + \text{Zn}(\text{OH})_2]/0.1 \text{ M KOH}$ electrode prepared according to procedure 1 for $x = 0.0025$ and $y = z = 0.0005$. The first scan and those recorded with different durations of the potential cycling are shown, 25°C .

enhanced. For the ternary metal hydroxide electrode the value of ΔE_p becomes close to 0.045 V , whereas for the binary metal hydroxide electrodes containing either $\text{Co}(\text{OH})_2$ or $\text{Zn}(\text{OH})_2$, the values of ΔE_p are 0.060 and 0.095 V , respectively.

For the ternary metal hydroxide electrode, at least under the experimental conditions covered in the present work, there is a fast increase in the overall voltammetric charge during cycling at $v = 0.1 \text{ V s}^{-1}$ (Fig. 3), attaining, after about 200 cycles, a maximum charge which remains practically constant for at least 1400 ORC [(▼) Fig. 4]. By contrast, the nickel hydroxide electrode cycling provokes a decrease in charge when the number of ORC exceeds about 100 [(Δ) Fig. 4]. In order to make this comparison more reliable the voltammetric cathodic charge obtained for the different electrodes have been included in Fig. 4 instead of the anodic one as the latter may involve some unknown contribution from the OER. For the binary metal hydroxide electrode containing $\text{Co}(\text{OH})_2$ [(●) Fig. 4], the initial rate of charge accumulation increases during the ORC as it does for the ternary metal hydroxide electrodes, but the stabi-

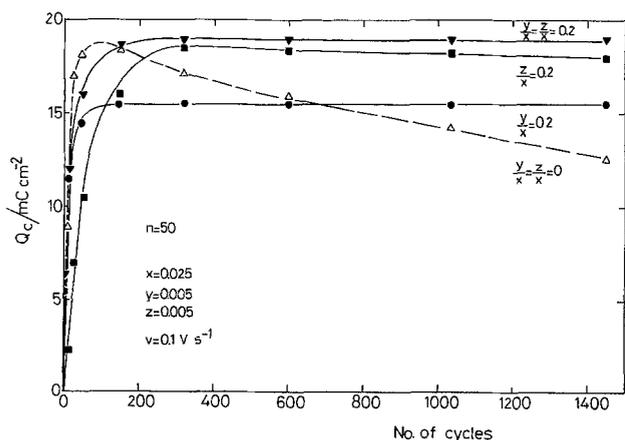


Fig. 4. Dependence of the cathodic charge on the number of cycles during RTPS at $v = 0.1 \text{ V s}^{-1}$ between $E_{s,c} = 0.24 \text{ V}$ and $E_{s,a} = 0.89 \text{ V}$ for electrodes prepared according to procedure 1, $n = 50$, $x = 0.025$. [(Δ) dashed line] $y = z = 0$; [(■) solid line] $y = 0$, $z = 0.005$; [(●) solid line] $z = 0$, $y = 0.005$; [(▼) solid line] $y = z = 0.005$. 0.1 M KOH , 25°C .

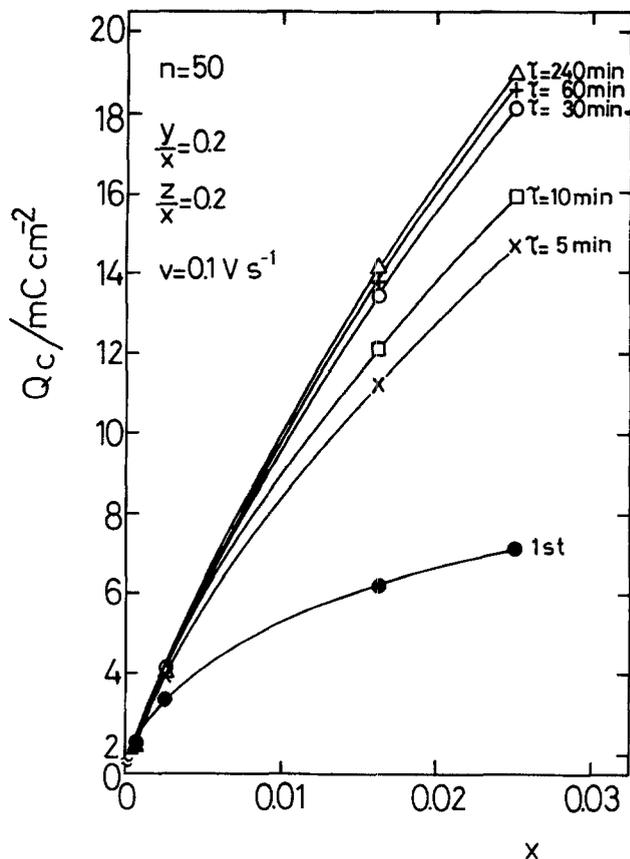


Fig. 5. Dependence of the cathodic charge on the concentration of the precipitating solutions for fixed $y/x = z/x = 0.2$ ratio at different potential cycling τ , for Pt/coprecipitated hydroxys $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2 + \text{Zn}(\text{OH})_2]/0.1 \text{ M KOH}$ prepared according to procedure 1. $n = 50$, $E_{s,c} = 0.24 \text{ V}$, $E_{s,a} = 0.89 \text{ V}$.

lized voltammetric charge resulting after about 50 ORC is in the former case about 20% smaller than for the latter. Likewise, for binary metal hydroxide electrodes containing $\text{Zn}(\text{OH})_2$ [(■) Fig. 4] the charge accumulation during the ORC becomes considerably smaller than that observed for the reference systems, although the maximum charge value which can be reached after about 300 ORC is close to that obtained for the ternary metal hydroxide electrodes. Nevertheless, during the prolonged cycling the voltammetric charge decreases slightly, although the charge loss resulting from a prolonged cycling is remarkably smaller in those electrodes containing $\text{Co}(\text{OH})_2$. Likewise, the charge accumulation effect becomes considerably greater as $\text{Zn}(\text{OH})_2$ is incorporated into the active material (Fig. 3).

The effect of the metal ion concentration used for preparing the coprecipitated ternary metal hydroxide electrodes on the voltammetric response was also investigated. This effect can be seen by comparing data shown in Fig. 1 and 4 for the Pt/coprecipitated hydroxys $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2 + \text{Zn}(\text{OH})_2]$ electrode at $v = 0.1 \text{ V s}^{-1}$, 25°C , $z = y$, and systematically varying the y/x and z/x concentration ratios. As the metal ion concentration in the precipitating solution decreases, a greater voltammetric resolution of two $\text{Ni}(\text{OH})_2$ reacting species during the ORC can be observed. The height of the anodic and the cathodic current peaks located at more positive potentials increase relatively faster than others, the cycling time to reach the stabilized voltammogram becomes longer, and the corresponding peak potentials shift negatively.

Experiments performed by keeping the optimum $y/x = z/x = 0.2$ concentration ratio¹⁷ reveal a noticeable increase in the cathodic charge as both the metal ion concentration and the number of ORC increase (Fig. 5). However, after about 60 min RTPS the voltammograms attain practically the stabilized E/j profile, and only a slight charge increase can be observed after 240 min potential cycling. A strong overlapping of the two anodic, as well as the two cathodic current contributions, results in the voltammogram for the

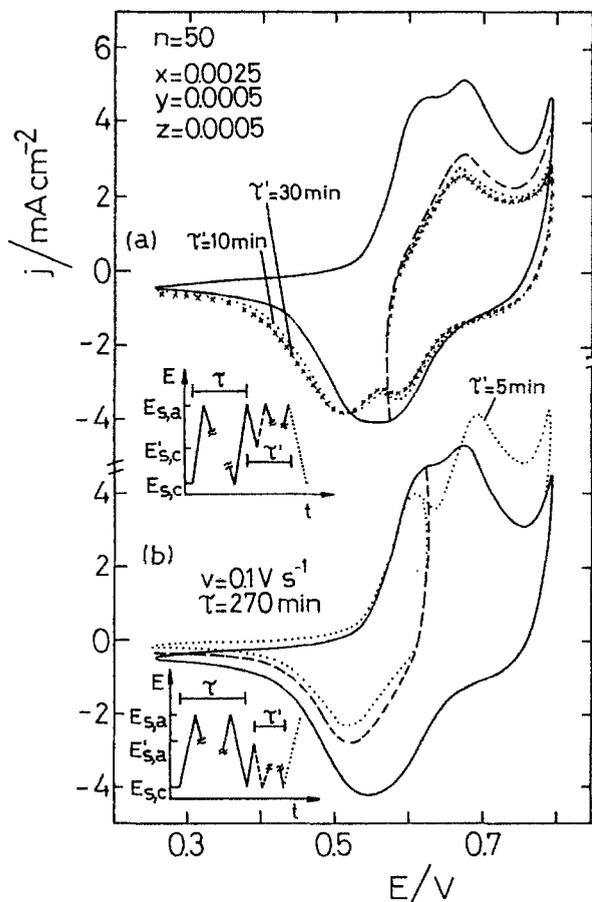


Fig. 6. Potentiodynamic E/j displays recorded at $v = 0.1 \text{ V s}^{-1}$ for Pt/coprecipitated hydroxous $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2 + \text{Zn}(\text{OH})_2]/0.1\text{M}$ KOH prepared according to procedure 1 as indicated in Fig. 4. The potential perturbation program includes 270 min RTPS between $E_{s,c}$ and $E'_{s,c} = 0.24 \text{ V}$ and $E_{s,a} = 0.79 \text{ V}$ before applying the intermediate RTPS between either $E'_{s,c} = 0.57 \text{ V}$ and $E_{s,a}$ (a) or $E_{s,c}$ and $E'_{s,a} = 0.62 \text{ V}$ (b), 25°C .

ternary metal hydroxide electrode after prolonged potential cycling time (τ).

The voltammetric changes resulting after the electrode has been subjected to an intermediate RTPS were analyzed by setting different switching potential values. Thus, when the intermediate RTPS switching potential values are 0.57 and 0.79 V (Fig. 6a) the cathodic voltammograms resulting after either $\tau' = 10 \text{ min}$ or $\tau' = 30 \text{ min}$ exhibit two ill-defined peaks whose contours appear to be slightly affected by changing τ' . Otherwise, when the switching potentials are 0.24 and 0.62 V, the anodic voltammogram after $\tau' = 5 \text{ min}$ (Fig. 6b) exhibits a net charge increase for the anodic peak located at more positive potential.

Results shown in Fig. 4-6 suggest that the $\text{Ni}(\text{OH})_2/\text{NiOOH}$ redox reaction for the ternary metal hydroxide electrode involves, at least, two oxidized as well as two reduced species, the progressive transformation from the most unstable hydroxous $\text{Ni}(\text{OH})_2$ species into the most stable one being a relatively slow process. These results differ from those obtained either for anodically grown nickel hydroxide layers on nickel electrodes under voltammetric conditions²³⁻²⁴ or for chemically precipitated hydroxous $\text{Ni}(\text{OH})_2$ layer on different conducting substrates, like platinum, gold and vitreous carbon.^{25,26} For these systems the formal rate constants for interconversion reactions of both $\text{Ni}(\text{II})$ and $\text{Ni}(\text{III})$ species, appear to be of the same magnitude.²³⁻²⁵

The amount of $\text{Ni}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Zn}(\text{II})$ ions in the precipitated hydroxide layer increases linearly with n . These results are in agreement with the observations already made for coprecipitated $[\text{Ni}(\text{II}) + \text{Co}(\text{II})]$ and $[\text{Ni}(\text{II}) + \text{Zn}(\text{II})]$ hydroxide electrodes.^{10,17}

The voltammograms run with ternary metal hydroxide layers involving a sandwich-type structure (Fig. 7) show

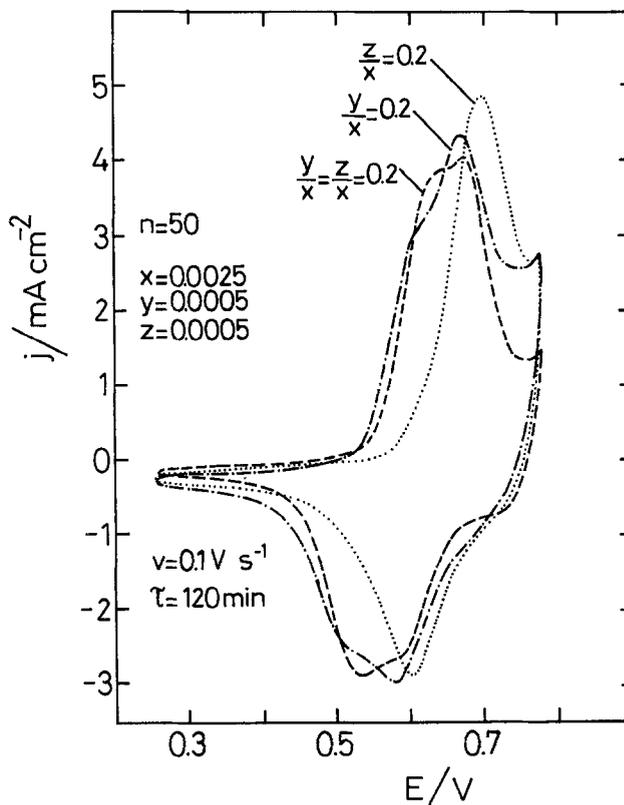


Fig. 7. Potentiodynamic E/j display recorded at $v = 0.1 \text{ V s}^{-1}$ after 120 min RTPS for electrodes prepared according to either procedure 1 for $n = 50$, $x = 0.0025$, $y = z = 0.005$ (---) or procedure 2 for $n_1 = 25$ and $x_1 = x_2 = 0.0025$ by changing the precipitation sequence. Curve 1 (....): $y_1 = 0$, $z_1 = 0.005$, $y_2 = 0.005$, $z_2 = 0$; Curve 2 (---): $y_1 = 0.005$, $z_1 = 0$, $y_2 = 0$, $z_2 = 0.005$. 0.1M KOH, 25°C .

that the influence of the foreign cations on the kinetics of the $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ reaction for thin layers of active material is about the same as that found when Co hydroxide is mostly distributed at the inner part of the layer in contact with the substrate.

Results obtained with the binary $[\text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2]$ electrode show two particular features, one concerning the $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ ORC (Fig. 8 and 9) and another one related to the polarization of the OER (Fig. 10). The voltammograms of the $\text{Ni}(\text{II})/\text{Ni}(\text{III})$ electrochemical reaction exhibit an active charge smaller than that involved in the absence of $\text{Cd}(\text{II})$, and a remarkable interconversion of the different $\text{Ni}(\text{II})$ and $\text{Ni}(\text{III})$ hydroxide species (Fig. 8 and 9) as deduced through the trend of the voltammogram to display

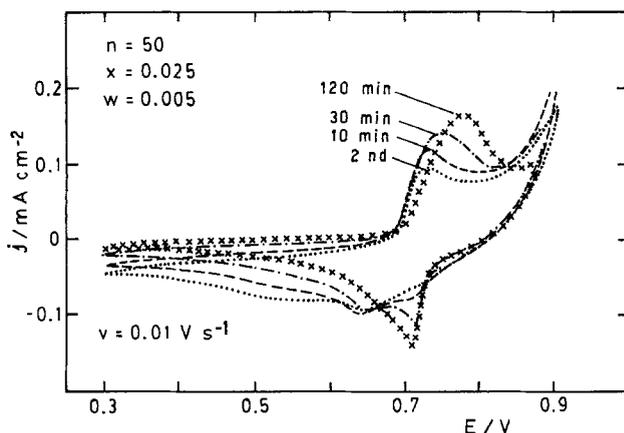


Fig. 8. Voltammograms obtained at $v = 0.01 \text{ V s}^{-1}$ for a Pt/coprecipitated hydroxous $[\text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2]/0.1\text{M}$ KOH electrode prepared according to procedure 1, $n = 50$, $x = 0.025$, and $w = 0.005$. 25°C .

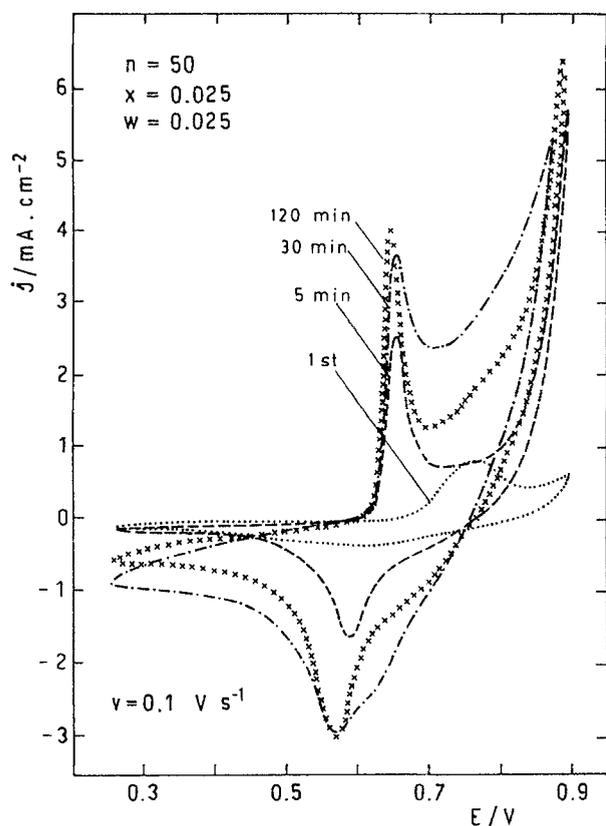


Fig. 9. Voltammograms obtained at $v = 0.01 \text{ V s}^{-1}$ for a Pt/coprecipitated hydrous $[\text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2]/0.1\text{M KOH}$ electrode prepared according to procedure 1, $n = 50$, $x = 0.025$, and $w = 0.025$. 25°C .

complex peaks which are related to different forms of Ni(II) and Ni(III) hydroxide species.^{23,25} The Tafel plots related to the OER present a clear depolarizing effect, as the slopes of the linear portions are 0.06 V/decade for $\text{Ni}(\text{OH})_2$ electrode, and 0.08 V/decade for the binary $[\text{Ni}(\text{OH})_2 + \text{Cd}(\text{OH})_2]$ electrode under the conditions indicated in Fig. 10.

The influence of Li^+ ions in the nickel and composed Ni hydroxide electrodes.—The ORC of the Ni hydroxide electrode in 0.1M KOH at 25°C (Fig. 11a) shows a gradual in-

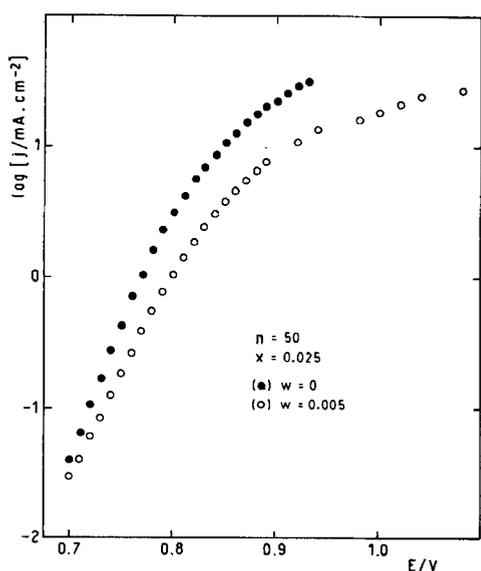


Fig. 10. Influence of cadmium addition on the oxygen evolution reaction under steady-state conditions for precipitated hydrous nickel hydroxide electrodes, $n = 50$ and $x = 0.025$. (●) $w = 0$; (○) $w = 0.005$. 25°C .

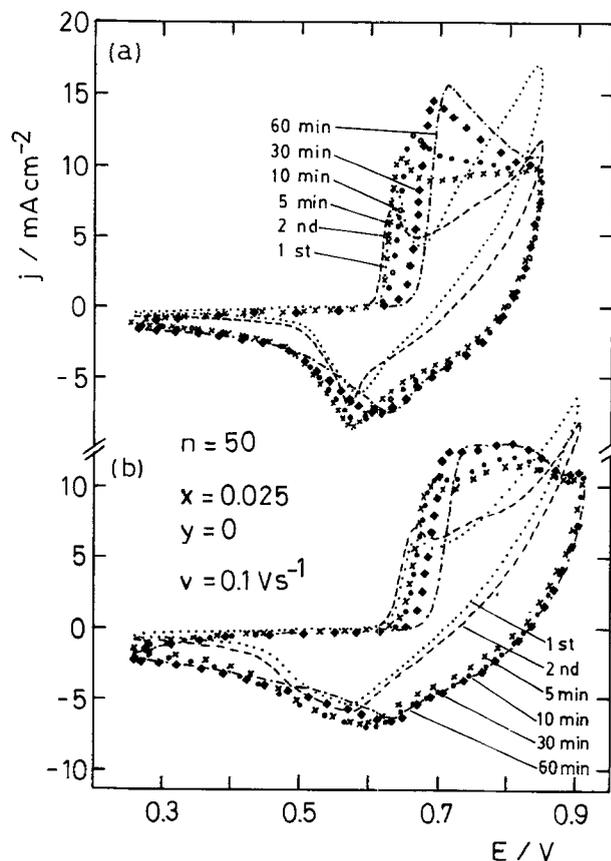


Fig. 11. RPS voltammograms obtained at $v = 0.1 \text{ V s}^{-1}$ for a Pt/ $\text{Ni}(\text{OH})_2$ electrode in 0.1M KOH (a) and in $0.08\text{M KOH} = 0.02\text{M LiOH}$ (b). $n = 50$, $x = 0.025$. 25°C .

crease in the overall charge, a positive potential shift of the Ni(II)/Ni(III) redox couples voltammetric peaks, and a decrease of the OER contribution at $E_{s,a}$. The presence of Li^+ ions in solution (Fig. 11b) has only minor effects on the preceding voltammetric description perhaps improving the efficiency of the process in the long time range (Fig. 12). It should be noted that there is a maximum in the Q_c vs. number of cycle plots which depends on the foreign cations present in the $\text{Ni}(\text{OH})_2$ electrode and Li^{2+} ions in solution.

The voltammetric ORCs made by using $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2]$ electrodes (Fig. 13) show an entire negative shift independent of Li^+ ions in the solution, but for the latter case the overall voltammetric charge is increased and the contribution of the $\beta\text{-Ni}(\text{OH})_2/\beta\text{-NiOOH}$ redox couple is considerably enhanced. The efficiency of the $[\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2]$ electrode is in this case particularly improved at 25°C (Fig. 12). In any case, after 60 min ORC, a steady voltammetric profile is reached.

The behavior of these systems at 50°C is illustrated in Fig. 14 and 15. The increase of temperature produces an increase in the rate of the different processes, as well as a negative potential shift of the entire voltammograms. The specific effects produced by the foreign cations either in the $\text{Ni}(\text{OH})_2$ layer or in the solutions remained also at 50°C .

Discussion

It is already well established that there is an influence of the electrolyte composition involving both cations and anions on the kinetics of the Ni(II)/Ni(III) redox reaction in electrochemically produced $\text{Ni}(\text{OH})_2$ and NiO layers. In alkaline solutions the presence of cations such as Li^+ , Co^{2+} , Ba^{2+} , Cd^{2+} , Pb^{2+} , and Mn^{2+} modifies the transport mode of the ionic species, and accordingly, the overall resistance operating on the electrochemical reaction either anodic or cathodic. Given that in this matter there are many controversies to be found in the literature, it is reasonable first to make a survey of the experimental facts, and later to establish some important differences and thus approach the probable mechanisms of the processes involved in a more comprehensive way.

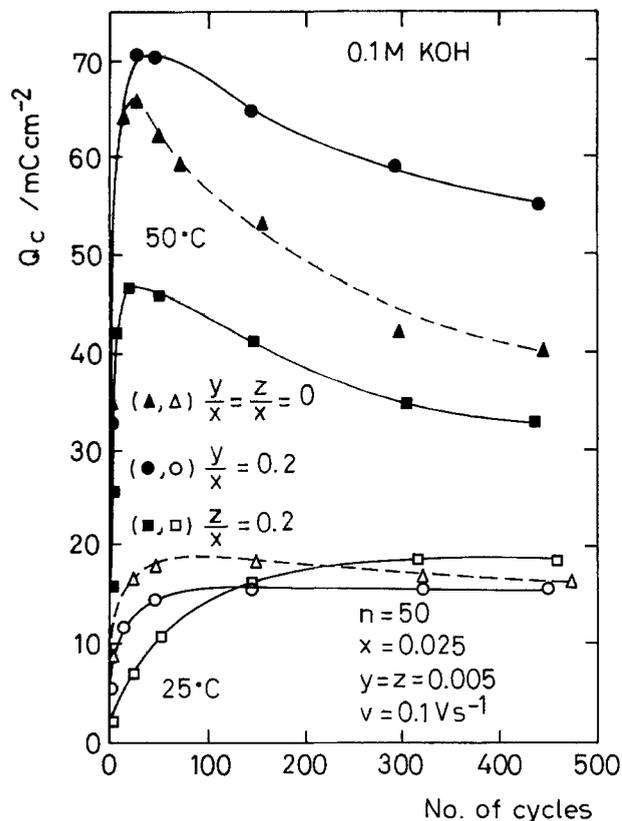


Fig. 12. Dependence of the cathodic charge on the number of cycles during RTPS at $v = 0.1 \text{ V s}^{-1}$ in $0.08\text{M KOH} + 0.02\text{M LiOH}$ for electrodes prepared according to procedure 1, $n = 50$, $x = 0.025$, ($\blacktriangle, \triangle$) $y = z = 0$; (\bullet, \circ) $y = 0.005$, $z = 0$; (\blacksquare, \square) $z = 0.005$, $y = 0$. 50°C (filled symbols); 25°C (open symbols).

1. The behavior of the nickel hydroxide electrode has been often considered as either consisting of a homogeneous and stable nickel oxide-nickel hydroxide phase^{25,27} or a nonhomogeneous layer obeying no simple stoichiometry. This is perhaps the origin of the controversy over the occurrence of the γ -phase nickel oxide.

2. Binary composite hydroxides of nickel exhibit different characteristics depending on the foreign cation. Thus, Fe and Ce hydroxides have detrimental effects on battery electrodes,⁴ whereas the presence of Co hydroxides increases the overpotential for the OER,¹⁰ although it has been reported that Co and Mn hydroxides decrease the threshold potential for the Ni(II)/Ni(III) redox reaction.⁴ Finally, Cd, Zn, and Pb hydroxides probably have a poisoning effect on the OER.

3. In binary hydroxides such as those containing Co or Zn hydroxides, the greatest influence of the foreign metal hydroxide implies a definite foreign cation/Ni ion ratio, which for those systems previously studied is close to 0.2 independently of the nature of the foreign cation.^{10,17}

These aspects of the nickel hydroxide electrode cannot be fully explained as the proper operation of this electrode is still a matter of discussion. It seems quite reasonable to stress that many structural and electrochemical differences probably exist within the same α and β phases of Ni(OH)₂ and β and γ/γ' phases of NiOOH, depending on both the preparation method and the proper history of the electrochemical interface. Hence, the definition of α , β , and γ phases actually should be taken as generic entities.²⁷ This fact is supported by the existence of short- and long-term range aging effects.²²⁻²⁵

The incomplete electroreduction of nickel hydroxides lead to a high resistivity layer of nickel hydroxide produced at the electronically conductive substrate. Coprecipitated ions may also influence the transformation between α - and β -Ni(OH)₂ phases.⁴

In the case of c-type NiO films the incorporation of Li⁺ ions in the nickel oxide leads to the same electrode behavior as with Li⁺ ions in solution, suggesting that the Li⁺ ions

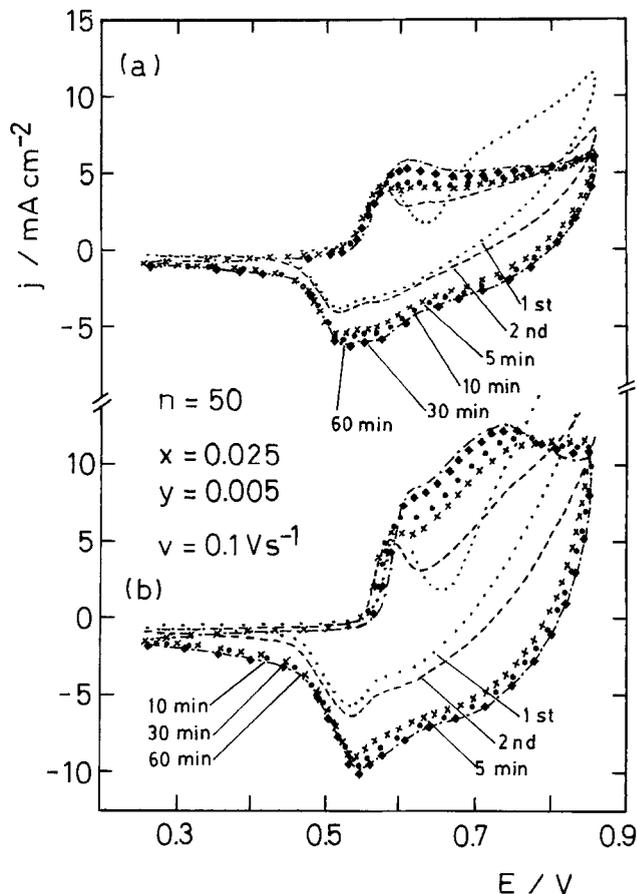


Fig. 13. RTPS voltammograms obtained at $v = 0.1 \text{ V s}^{-1}$ in 0.1M KOH (a) and in $0.08\text{M KOH} + 0.02\text{M LiOH}$ (b) solutions for a Pt/coprecipitated [Ni(OH)₂ + Co(OH)₂] electrode prepared according to procedure 1, $n = 50$, $x = 0.025$, $y = 0.005$. 25°C .

from solution are quickly incorporated in the nickel oxide film, so that the two situations produce the same end result.

The chemically precipitated Ni(OH)₂ and composed Ni(OH)₂ layers become increasingly more active in the course of the ORC. This fact indicates that the resistance of the films is initially relatively large, and during cycling the outer plane of the low resistance film moves from the solution/metal hydroxide layer plane inward toward the surface layer. Accordingly, the thickness of the low resistance film diminishes and one should accept that the composition of reactant and products of the Ni(II)/Ni(III) electrochemical reactions do not necessarily coincide with those of simple stoichiometries.

On the other hand, from the present data it is clear that for the binary composite hydroxides of nickel, the amount of material participating in the charging/discharging cycles increases from the first cycle to reach a limiting value after a certain number of ORC which depends on the composition of the metal hydroxide layer. This change in charge during the voltammetric cycling is accompanied by a change in color.^{4,19} These facts suggest that the composite layer consists of a nonhomogeneous layered structure with a water content increasing in going from the metal/hydroxide layer plane to the hydroxide layer/solution interface. It appears that during the ORC water deficient inner layers gradually become transformed into active material. Thus, the resistivity of the inner nickel hydroxide approaches that of nickel oxide and decreases to approach that of a concentrated electrolyte solution at the outer hydrous nickel hydroxide layer portion. This change of resistance depends strongly on the nature and composition of the binary composite hydroxide of nickel.

The preceding description is equivalent to admitting that the metal hydroxide layer behaves as a mixture of an ordered phase and a disordered (or amorphous) one which changes during the initial ORC. Hence, it seems rather unlikely that in the present case definite stoichiometric and

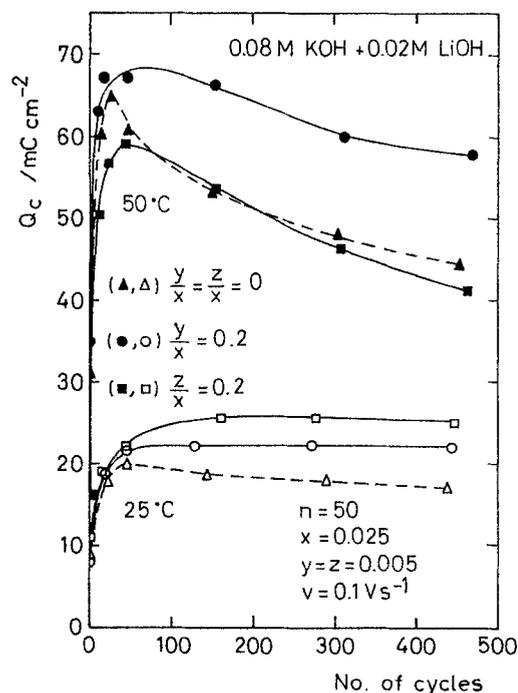


Fig. 14. Dependence of the cathodic charge on the number of cycles during RTPS at $v = 0.1 \text{ V s}^{-1}$ in 0.1 M KOH for electrodes prepared according to procedure 1, $n = 50$, $x = 0.025$, ($\blacktriangle, \triangle$) $y = z = 0$; (\bullet, \circ) $y = 0.005$, $z = 0$; (\blacksquare, \square) $z = 0.005$, $y = 0$. 50°C (filled symbols); 25°C (open symbols).

structural descriptions of the metal oxide layer be entirely valid. The resulting stoichiometries depend considerably on the electrochemical preparation routine and they approach in the long-time range (aging) the structure of a known substance. This is perhaps the case of the γ -phase Ni oxide which could be considered as one of the most stable species produced from the α - and β -phases. The corresponding phase change should imply a modification of the Ni-O bond strength influenced by the hydration shell of either incorporated or adsorbed foreign cations. Apparently no foreign cations can be detected for γ -phase Ni oxide.²⁷

The influence of foreign cations in the electrochemical response of the nickel hydroxide electrode can be understood in the following way. The active material, *i.e.*, the hydrous nickel hydroxide layer, can be described as a nearly uniform distribution of Ni^{2+} , OH^- -ions, H_2O molecules, and counterions from the solution. This model has been recently employed for simulation of various electrochemical reactions.²⁸ The distribution of all these species should be modified according to the nature and concentration of foreign cations exhibiting specific solvodynamic diameter and hydration shell characteristics. These ions which are presumably randomly distributed in the nickel hydroxide layer may interfere in the Ni(II)/Ni(III) reaction in different ways.

Foreign cations probably assist the Ni(II)/Ni(III) electrochemical reaction through the participation of intermediate oxidation levels of those cations appearing at potentials lower than the Ni(II)/Ni(III) equilibrium potential. This may be the case of $\text{Co}(\text{OH})_2$ or $\text{Mn}(\text{OH})_2$ added to the $\text{Ni}(\text{OH})_2$ layer. It has been reported that no voltammetric peak related to the Co(II)/Co(III) redox couple can be observed for the corresponding binary composed hydroxide nickel electrode.¹⁰ This type of catalytic effect on the Ni(II)/Ni(III) redox couple should involve a composed metal hydroxide layer structure in which as the optimal Ni^{2+} ion-foreign cation distance is reached, conditions favorable for Ni(II)/Ni(III) electrochemical reaction are achieved. In this case the effect of foreign cations would depend on the nature and concentration of those cations in the $\text{Ni}(\text{OH})_2$ structure, and it would involve electronic interactions as has been concluded from *in situ* Mössbauer spectroscopy.^{4,19} This explanation for the catalytic effect of foreign cations can be to some extent comparable to the role

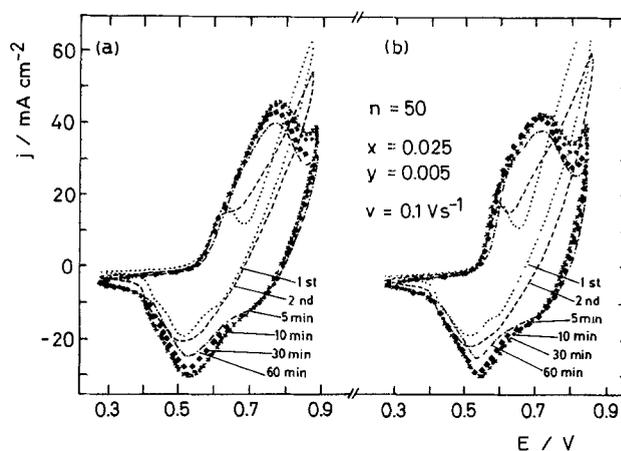


Fig. 15. RTPS voltammograms obtained at $v = 0.1 \text{ V s}^{-1}$ in 0.1 M KOH (a) and in $0.08 \text{ M KOH} + 0.02 \text{ M LiOH}$ (b) solutions for a Pt/coprecipitated $[\text{Ni}(\text{OH})_2 + \text{Co}(\text{OH})_2]$ electrode according to procedure 1, $n = 50$, $x = 0.025$, $y = 0.005$. 50°C .

played by metal-phthalocyanine modified electrodes in several electrocatalytic reactions.²⁹

The presence of Li^+ ion in the solution increases the efficiency and hinders the decay of the active material, particularly for $\text{Ni}(\text{OH})_2 + \text{Zn}(\text{OH})_2$ composed electrodes, it favors the Ni(II)/Ni(III) electrochemical cycling process as the polarization of the OER is increased, and it increases the contribution of the Ni(II)/Ni(III) redox couple at more positive potentials. This suggests that Li^+ ions are quite probably incorporated in the $\text{Ni}(\text{OH})_2$ lattice. It is possible that the intercalation of Li^+ ions into the metal hydroxide layer operates in a way similar to the proton transfer into the homogeneous phase, as it has been postulated by Kozawa for the case of alkaline MnO_2 cell.³⁰ Accordingly, the electroreduction reaction implies the formation of a Li^+ ion containing intercalation product such as $[\text{Ni}(\text{III}) \cdot \text{O}^{2-} \cdot \text{Li}^+(\text{OH})]$, making the reaction faster than in the absence of Li^+ ions in the oxide layer.

The presence of some foreign ions can also modify the kinetics of the OER, particularly when there is no possibility of the foreign cations producing intermediate oxidation levels at potentials lower than the equilibrium potential of the Ni(II)/Ni(III) redox couple. In this case, one should expect that for a certain concentration level of foreign cations an optimal electronic interaction can be reached, so that the energy distribution at reacting sites becomes, then, adequate for hindering the OER. This is apparently the case for the addition of Cd^{2+} -ion and Zn^{2+} -ion to the $\text{Ni}(\text{OH})_2$ layer.

The influence of foreign cations in binary composed hydroxide nickel layers can be tentatively approached in terms of an order-disorder gel-like structure in which the foreign cations participate by modifying the Ni-O bond, the H-bonding and electronic Ni-foreign metal interactions. These effects become specific and would imply a certain optimal concentration level of the foreign cation. The latter can operate by influencing either the proper Ni(II)/Ni(III) electrochemical reactions or the OER, depending on the possibility of offering intermediate oxidation levels at potentials preceding the equilibria potential of the Ni(II)/Ni(III) redox couple. This tentative explanation of the foreign cation effect in the kinetics of the nickel hydroxide electrode reactions justifies further work for establishing parametric relationships for operational purposes.

Conclusions

The presence of hydrous cobalt hydroxide appears to hinder the aging of unstable nickel hydroxide species. This effect suggests that a relatively loose nickel hydroxide structure is promoted by the addition of cobalt hydroxide. This structure remains practically unaltered for prolonged ORC and appears to be able to incorporate different ions including OH^- ions. The latter favors the Co(III)/Co(II) redox reactions and contributes to the diminution of the threshold potential for the Ni(II) \rightarrow Ni(III) electro-oxidation reaction.

The addition of zinc hydroxide to the hydrous nickel hydroxide has no apparently beneficial effect for the long term stability and good utilization efficiency. The initial formation of nickel hydrous zincate probably determines the electrochemical characteristics during the first potential cycles as the main oxidation product appears to be γ -NiOOH whose electroreduction yields α -Ni(OH)₂.^{25,31} However, the stabilized electrochemical response after prolonged ORC is mainly associated with the β -Ni(OH)₂/ β -NiOOH redox reaction.^{25,31-34} The influence of zinc hydroxide concentration as a performance enhancing additive appears also in the ORC charge stabilization.^{17,34}

The simultaneous addition of cobalt hydroxide and zinc hydroxide improve both the reversibility of the Ni(II)/Ni(III) redox reaction and the active material efficiency, provided that the metal ion concentration ratios and the layered structure composition profile are properly set. Then, the complex voltammetric response of the Ni(II)/Ni(III) reaction can be explained through a square-type reaction model including cross electrochemical reactions (see for instance reaction scheme II in Ref. 25). Long term aging effects are observed through voltammetric and open-circuit data under a wide variety of experimental conditions.

The incorporation of cadmium hydroxide increases strongly the polarization of the ORC, but the charge capacity of the nickel hydroxide electrode decreases slightly.

The type of modifications in the electrochemical response of the composite metal hydroxide electrodes can be explained by the influence of the different cations on the structure of the Ni(OH)₂ layer. In this case, the oxidation level, the hydration state, the solvodynamic radius, and the complexing capability of foreign cations in the hydroxide structure should influence the rate of the electrochemical reactions at the nickel hydroxide electrode.

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