



Suppression of the $\alpha \rightarrow \beta$ -nickel hydroxide transformation in concentrated alkali: Role of dissolved cations

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Abstract

The presence of dissolved cations such as Al and Zn in alkaline electrolyte (6 M KOH) suppresses the $\alpha \rightarrow \beta$ -nickel hydroxide transformation. The uptake of Al (10 mol%) and Zn (30 mol%) exhibited by the active material likely stabilizes the α -phase. Dissolved Al is deleterious to the performance of the nickel hydroxide electrode, whereas, dissolved Zn enhances the specific discharge capacity of nickel hydroxide by approximately 25% showing that the mode of metal uptake is different in the two cases.

1. Introduction

Nickel hydroxide, the positive electrode material of all nickel-based alkaline secondary cells, crystallizes in two polymorphic modifications known as α and β [1]. Consequently, the reversible reactions of nickel hydroxide, involve two redox couples, namely, the α/γ and the β/β [2]. Of these, the former reversibly exchanges 1.7 e per Ni atom (390 mAh g⁻¹) compared to the theoretical capacity of the latter derived from a 1 e exchange (290 mAh g⁻¹) [3]. However, the α/γ couple is not stable in the alkaline electrolyte (6 M KOH) and rapidly ages to the β/β couple, on account of which, the superior properties of the α/γ couple have not been exploited in working batteries. There is therefore considerable interest in stabilizing the α/γ couple in the operational conditions of Ni-based alkaline batteries. There are two approaches.

- (1) Impart thermodynamic stability to the α/γ couple by *modifying* the structure and composition of α -nickel hydroxide.
- (2) Suppress the $\alpha \rightarrow \beta$ transformation of nickel hydroxide.

By adopting the first strategy, we succeeded in designing Al [4, 5] and Zn [6] substituted, alkali-stable, high performance α -nickel hydroxides. Subsequently, other groups [7–10] worked on these systems.

In this paper, we report for the first time, results of our exploration of the second strategy. The $\alpha \rightarrow \beta$ transformation of nickel hydroxide occurs via a dissolution–reprecipitation mechanism [11]. It is therefore, logical to assume, species predissolved in the alkaline electrolyte, interfere with this transformation by affecting the solubility of α -nickel hydroxide. Dissolved

anions such as sulfate, oxalate, tartarate, thiosulfate and chromate aggressively catalyze the oxygen evolution reaction, a feature deleterious to battery performance and were discarded [12]. It was then decided to examine the effect of dissolved cations such as Al and Zn; these are often found as a result of anode dissolution in the alkaline electrolyte during battery operation conditions [13, 14]. We report here the suppression of the $\alpha \rightarrow \beta$ transformation in the presence of dissolved Al and Zn.

2. Experimental details

α -Nickel hydroxide was synthesized by galvanostatic (current density, 1.3 mA cm⁻²) cathodic reduction of an aqueous nickel nitrate solution (concentration, 1 M) using a nickel plate cathode (surface area, 38.5 cm²) in a divided cell (time, 22 h) [15]. The deposit in the cathode chamber was recovered by filtration and copiously washed with distilled water and dried to constant weight at 65 °C.

Thin films of nickel hydroxide were also electro-deposited (1 mA cm⁻², 40 s) on a Pt flange electrode (surface area, 3.75 cm²) from aqueous nickel nitrate (concentration, 0.1 M) solutions for cyclic voltammetry studies (counter electrode, Pt mesh of geometric area 27 cm²). Prior to electrodeposition, the platinum flag electrode was cleaned electrochemically as described elsewhere [16].

The electrolyte (E) used for control cells was 6 M KOH. Aluminum saturated electrolyte (Al-E) was prepared by suspending 0.5 g of aluminum powder in 100 ml of 6 M KOH for 1 h and then filtering it. Zinc saturated electrolyte (Zn-E) was similarly prepared by suspending 7 g of ZnO in 100 ml of 6 M KOH.

To study the effect of aging, 0.2 g batches of α -nickel hydroxide were suspended in 25 ml of E, Al-E and Zn-E, respectively for a 15-day period. In separate experiments 0.2 g batches of α -nickel hydroxide were suspended in 115 ml of each of the three electrolytes and hydrothermally treated (140 °C, 18 h) in 150 ml autoclaves (autogenous pressure, 75% filling). All samples were then recovered by filtration, washed free of alkali and dried to constant weight at 65 °C.

2.1. Physical characterization

All samples were characterized by powder X-ray diffractometry (Jeol JDX8P powder X-ray diffractometer, $\text{CuK}\alpha$, $\lambda=1.54$ Å or $\text{CoK}\alpha$, $\lambda=1.79$ Å radiation, 600 W), infrared spectroscopy (Nicolet Model Impact 400D FTIR spectrometer, KBr pellets, resolution, 4 cm^{-1}), scanning electron microscopy (SEM) (Jeol JSM 840A scanning microscope fitted with a Link ISIS, OXFORD Model EDX analyzer) and thermogravimetric analysis (lab. built system, heating rate, 5 °C min^{-1}).

2.2. Wet chemical analysis

The nickel content of the hydroxide was determined by gravimetry. The hydroxyl content was determined by dissolving an accurately weighed amount of hydroxide in excess acid and back titrating the excess against a standard base using a pH meter. The hydroxyl content was found to be substoichiometric in α -nickel hydroxide. The hydroxyl deficiency was compensated by the inclusion of nitrate ions for charge neutrality. The unaccounted weight was attributed to water in order to obtain an approximate formula, which was found to match with the TG results within acceptable limits of accuracy.

2.3. Electrochemical studies

2.3.1. Cyclic voltammetry

All cyclic voltammograms were recorded using a Versastat Model II A (EG&G PARC) scanning potentiostat driven by Model M270 electrochemistry software. The nickel hydroxide films were scanned ($v=10$ mV s^{-1}) from 0 to 700 mV with respect to a $\text{Hg}/\text{HgO}/\text{OH}^-$ reference. Forty cycles were studied in E, Al-E and Zn-E respectively to understand the effect of dissolved species on the cycling behavior of nickel hydroxide films. The experiments were done in triplicate to check for reproducibility.

2.3.2. Charge–discharge studies

Electrodes for galvanostatic charge–discharge studies were prepared by mixing the active material (α -nickel hydroxide, 0.3 g) with graphite powder and an aqueous suspension of PTFE in the ratio of 6:3:1. The mixtures were thoroughly ground to obtain a paste like consistency. This paste was pressed at 120 kg cm^{-2} on either sides of the nickel foam (2.9×2.3 cm^2) at the ambient temperature. The electrodes were dried at 65 °C and

soaked in the appropriate electrolyte for 24 h before being galvanostatically (current, 2.7 mA cm^{-2}) charged to 200% of the theoretical capacity computed for a 1.7 e exchange [3]. Nickel plates were used as counters and all potentials were measured using a $\text{Hg}/\text{HgO}/\text{OH}^-$ reference. These electrodes were then discharged at C rate to a cutoff voltage of 0 V at the ambient temperature (28–30 °C).

In all, six electrodes were prepared and divided into three sets of two each. One set was used as control and cycled in electrolyte E 20 times. In test experiments, the other two sets of electrodes were cycled 10 times in Al-E and Zn-E respectively, after which they were washed free of alkali and transferred into E and cycled a further 10 times.

3. Results and discussion

Figure 1 shows the powder X-ray diffraction pattern of electrosynthesized nickel hydroxide. It has the following characteristics. (a) A low angle peak at 7.6 Å followed by another at half this value, which can be assigned to the (0 0 1) and (0 0 2) reflections respectively. (b) Two saw tooth shaped reflections at 2.65 and 1.54 Å, which can be assigned to the two-dimensional (10) and (11) reflections of a turbostratically disordered layered phase [1]. These are unmistakable characteristics of α -nickel hydroxide. α -Nickel hydroxide is a hydroxyl deficient phase, which incorporates anions to restore charge neutrality [17]. As the samples in the present study have been obtained from a nitrate bath, the incorporated anions are nitrates. The intercalated nitrates have been characterized by IR spectroscopy and the details are published elsewhere [18, 19]. The water content and the anion incorporation can differ from batch to batch. The approximate formula of the α -nickel hydroxide used in the present study is $\text{Ni}(\text{OH})_{1.77}(\text{NO}_3)_{0.23} \cdot 0.73\text{H}_2\text{O}$.

On aging in the electrolyte E, α -nickel hydroxide transforms to the badly crystalline β - $\text{Ni}(\text{OH})_2$ phase, designated as β_{bc} (badly crystalline) (see Figure 2A) under ambient conditions and to crystalline β - $\text{Ni}(\text{OH})_2$ under hydrothermal conditions (see Figure 3A). The β - $\text{Ni}(\text{OH})_2$ is a stoichiometric phase comprised of a hexagonal close packing of hydroxyl ions with nickel(II) ions occupying alternate layers of octahedral sites. The layers are charge neutral and the β -phase is characterized by reflections at 4.6, 2.7, 1.75, 1.56 and 1.48 Å respectively (PDF 14-117). The β_{bc} exhibits a similar

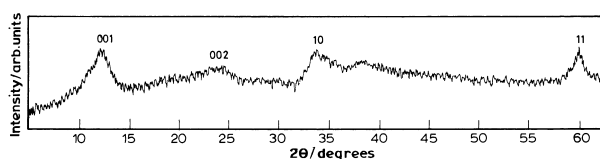


Fig. 1. Powder XRD pattern (source, $\text{CuK}\alpha$) of electrosynthesized α -nickel hydroxide.

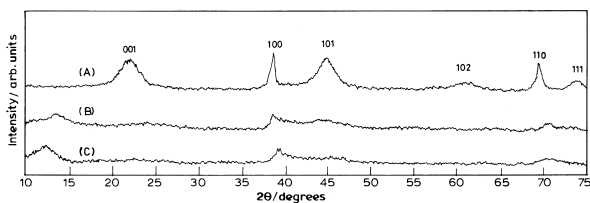


Fig. 2. Powder XRD patterns (source, $\text{CoK}\alpha$) of α -nickel hydroxide aged in electrolytes (A) E, (B) Al-E and (C) Zn-E for 15 days.

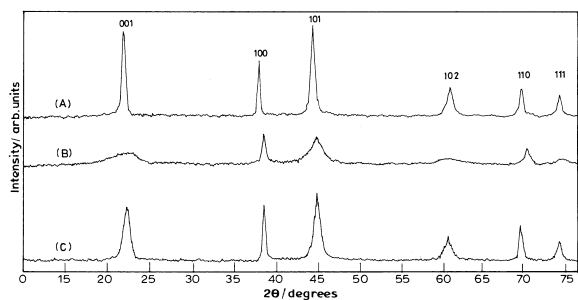


Fig. 3. Powder XRD patterns (source, $\text{CoK}\alpha$) of α -nickel hydroxide hydrothermally treated in electrolytes (A) E, (B) Al-E and (C) Zn-E for 18 h at 140 °C.

pattern, but with characteristic broadening of the non ($h k 0$) reflections [20]. This sequence of transformations $\alpha \rightarrow \beta_{bc} \rightarrow \beta$ has been reported by other authors as well [11].

In complete contrast with these observations, α -nickel hydroxide is observed to retain all its structural features on aging in electrolytes Al-E and Zn-E (see Figure 2B and C respectively) under ambient conditions. Under hydrothermal conditions, the emergence of the β_{bc} phase can be observed (see Figure 3B and C respectively). Under conditions investigated in the current study, the crystalline β is not observed in these modified electrolytes. Clearly the transformations of the α phase are retarded in the modified electrolytes.

The retention of the α -phase on aging in the ambient can occur by two mechanisms.

(a) Formation of double hydroxide phases isostructural with α -nickel hydroxide by the incorporation of Al [4] or Zn [6] in the $\text{Ni}(\text{OH})_2$ slabs. The double hydroxides of Ni with Al are layered phases comprising positively charged layers of the composition $[\text{Ni}_{1-x}\text{Al}_x(\text{OH})_2]^{x+}$ obtained by the partial isomorphous substitution of nickel(II) with aluminum(III) [4]. These layers incorporate anions (usually carbonates) in the interlayer region in exactly the same fashion as α -nickel hydroxide. The double hydroxide of Ni with Zn adopts a slightly different structure with a layer composition $[\text{Ni}_{1-x}\text{Zn}_x(\text{OH})_2]^{2x+}$ [6, 10]. These phases are alkali-stable by virtue of the higher coulombic attraction between the positively charged layers and the anions pillared in the interlayer region. These compounds are well known as layered double hydroxides (LDHs) [21].

Table 1. EDXA of α -nickel hydroxide samples aged and hydrothermally treated in electrolyte E, Al-E and Zn-E

Electrolyte composition	E %Ni	Al-E		Zn-E	
		%Ni	%Al	%Ni	%Zn
Aged	100	90	10	70	30
Hydrothermal	–	97	3 ^a	88	12

All compositions expressed in atomic percentages.

^a Within instrumental error range.

(b) Intercalation of AlO_2^- and ZnO_2^{2-} species from the modified electrolytes into the interlamellar regions of α -nickel hydroxide. Intercalation of oxoanions especially those of higher charge in the interlayer region can also bestow stability on layered phases. This mechanism leads to the formation of anion-exchanged α -nickel hydroxide [22].

The Al and Zn uptake was measured by SEM/EDXA and the results are given in Table 1. The scanning electron micrographs of all samples, as-prepared and aged, are similar. The samples consist predominantly of irregularly shaped chunky particles (A in Figure 4). Included between these and sometimes sticking to their faces are smaller granular particles (B in Figure 4). On aging in Al-E and Zn-E, the chunks show an uptake of 10% Al and 30% Zn respectively. The metal uptake by the smaller particles is even less (7% Al, 26% Zn). The uptake of Al is far below the extent (20 mol%) [4] required to stabilize the LDH in the alkaline solution, eliminating the role of mechanism (a) above. Therefore, α -phase retention in this case likely takes place by the incorporation of the metal oxoanion, AlO_2^- in the interlamellar region of α -nickel hydroxide [mechanism (b)]. On the other hand, Zn uptake is sufficient to yield the double hydroxide with a composition corresponding to $x=0.17$, according to mechanism (a) above. It therefore appears that different mechanisms are involved in α phase retention in the two cases. However in either case, metal uptake does not lead to ideal

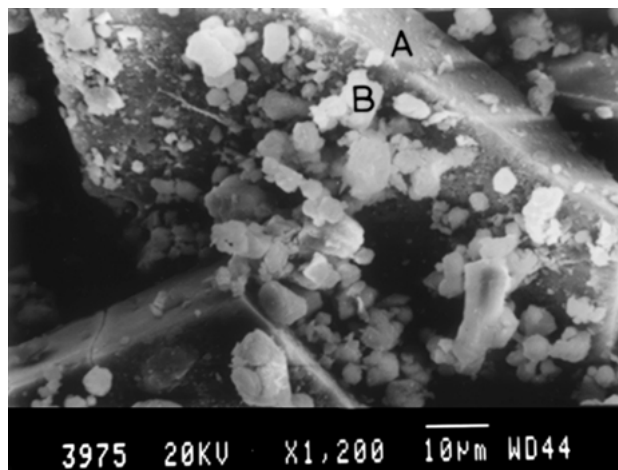


Fig. 4. Scanning electron micrograph of α -nickel hydroxide aged in Al-E indicating chunky (A) and small particles (B).

compositions whereby the α -phase acquires only moderate stability. Therefore hydrothermal treatment results in the birth of the β_{bc} .

This conjecture is also supported by the IR spectra. As prepared α -nickel hydroxide exhibits vibrations due to the intercalated nitrate ion, which appear in the 1500–900 cm^{-1} range, as described elsewhere [18, 19]. On aging in the ambient, in electrolyte E, $\alpha \rightarrow \beta$ transformation takes place and the aged sample does not exhibit any anion-related vibrations (Figure 5A). On aging in electrolytes Al-E and Zn-E, carbonate intercalation from the alkaline electrolyte is expected, in the event of LDH formation. No carbonate vibrations are seen in the spectra of α -nickel hydroxides aged in Al-E (Figure 5B) while the sample aged in Zn-E in the ambient exhibits two absorptions in the 1600–1400 cm^{-1} range corresponding to the symmetric and asymmetric stretching vibrations of the intercalated carbonate ions (Figure 5C). These observations also suggest that different mechanisms are involved in the two cases.

To examine the effect of these dissolved species on the redox reactions of α -nickel hydroxide, electrodeposited thin films were studied in E, Al-E and Zn-E by cyclic voltammetry. Forty cycles were monitored (see Figure 6). The effect of dissolved cations began to manifest in later cycles and the anodic peaks were found to shift to more positive potentials in Al-E and Zn-E compared to the control, E. The peak potentials are given in Table 2. In E and Al-E, the integrated charge computed from the

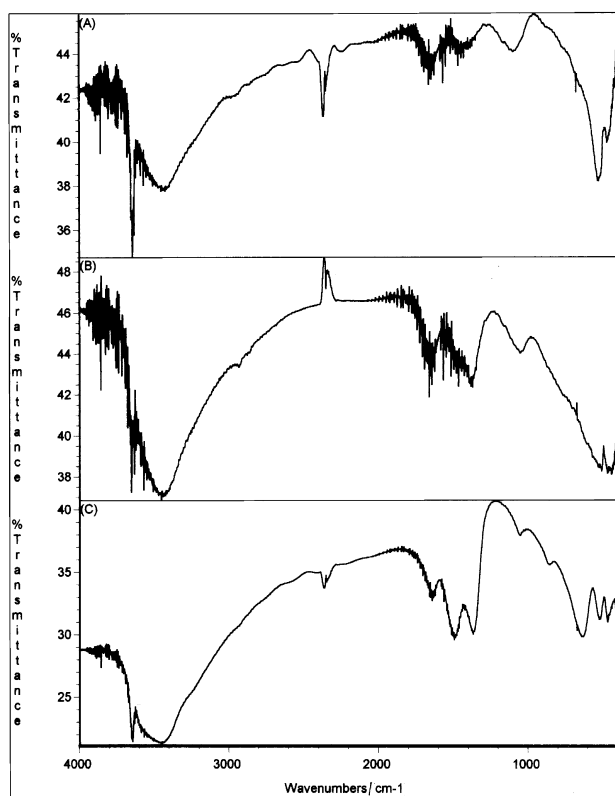


Fig. 5. IR spectra of α -nickel hydroxide aged in electrolytes (A) E, (B) Al-E and (C) Zn-E for 15 days.

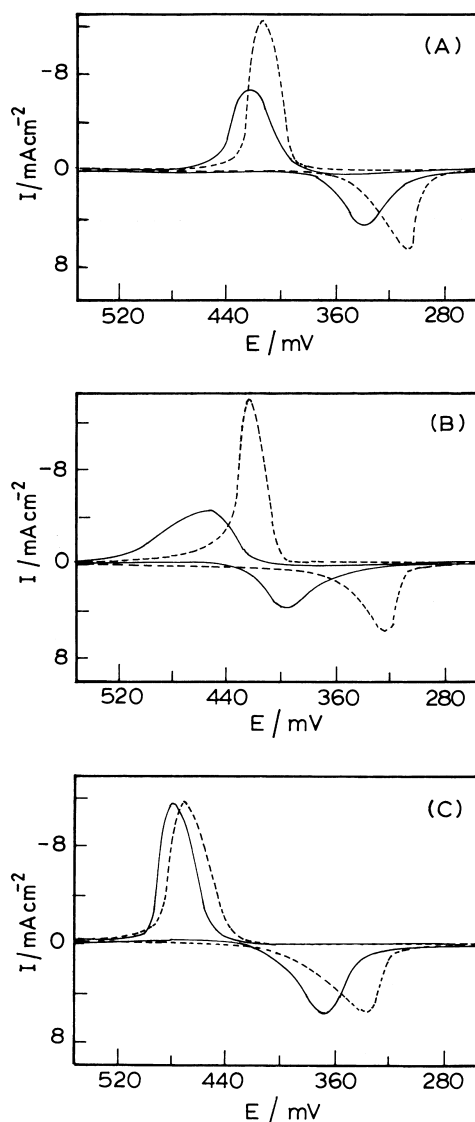


Fig. 6. Cyclic voltammograms of electrodeposited nickel hydroxide films in electrolyte (A) E, (B) Al-E and (C) Zn-E. Dotted and full lines indicate the 1st and 40th cycles respectively.

Table 2. Cyclic voltammetry data of electrodeposited nickel hydroxide in electrolytes E, Al-E and Zn-E

Electrolyte	Anodic peak/mV		Cathodic peak/mV	
	1st cycle	40th cycle	1st cycle	40th cycle
E	416	426	308	340
Al-E	424	456	320	395
Zn-E	470	480	336	365

area under the anodic peak is found to steadily decrease by 22 and 31% respectively on cycling indicating a progressively lowered material utilization. This effect is absent in Zn-E as the double hydroxide phases exhibit superior electrochemical properties. These observations clearly indicate that the cations dissolved in the alkaline electrolyte significantly affect the redox reactions of nickel hydroxide electrodes.

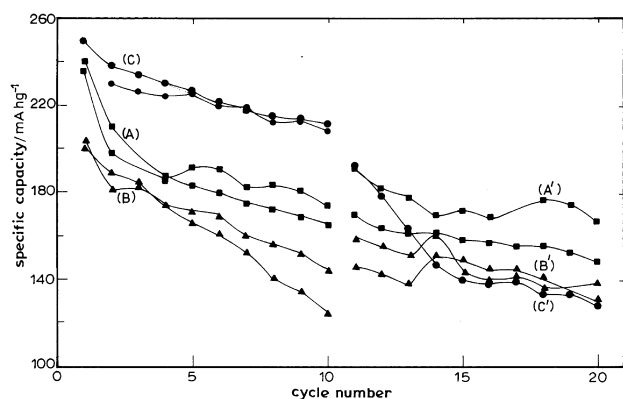
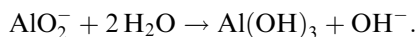


Fig. 7. Cycle life data of α -nickel hydroxide cycled 10 times in (A) E, (B) Al-E and (C) Zn-E. A', B' and C' indicate the cycle life data of A, B and C electrodes respectively cycled further 10 times in electrolyte E.

Figure 7 shows the variation in the specific discharge capacity of α -nickel hydroxide in E, Al-E and Zn-E. The discharge capacity in the early cycles in the control electrolyte E, is 240 mAh g^{-1} (corresponding to a 1.04 e exchange per Ni atom; estimated as per the experimentally determined approximate formula). This value is similar to the capacity of the β_{bc} nickel hydroxide (0.9 e per Ni) [23]. However on cycling, the capacity steadily fades, reaching a stabilized value of 170 mAh g^{-1} (0.72 e exchange) in the 10th cycle. A high initial capacity followed by capacity fading on cycling is typical of the $\alpha \rightarrow \beta$ transformation. In Al-E, the discharge capacity is found to steadily fall from 200 mAh g^{-1} (0.88 e exchange; 1st cycle) to 145 mAh g^{-1} (0.62 e exchange; 10th cycle). In contrast, the discharge capacity of α -nickel hydroxide in Zn-E varies around 249 mAh g^{-1} and stabilizes at 210 mAh g^{-1} (0.9 e exchange; 10th cycle), a value higher by 25% than what is observed in the control electrolyte, E.

The interlamellar region of α -nickel hydroxide contains 0.6 to 1.0 molecule of water per formula unit of nickel hydroxide [24–26]. The oxoanion of Al is known to undergo hydrolysis on prolonged standing in alkali. We speculate that a similar hydrolysis reaction in the interlayer region can occur as



Bernard [13] has recently shown that formation of $\text{Al}(\text{OH})_3$ is deleterious to the storage capacity of nickel hydroxide. Our results agree with these observations. In the case of Zn, in situ LDH formation by Zn incorporation during the battery operational conditions, results in a higher stabilized discharge capacity.

In further experiments, we continued cycling (cycles 11–20) these electrodes in the control electrolyte E, to confirm the effect of dissolved species on the performance of α -nickel hydroxide electrodes. It was noted that all the electrodes rendered capacities tending to similar values in the E medium (see Figure 7A', B' and C'). The discharge capacity of electrodes cycled in Al-E,

improved from 145 to 160 mAh g^{-1} on soaking in electrolyte E. On the other hand, the electrodes cycled in Zn-E, exhibited a fall in capacity from 210 to 190 mAh g^{-1} in the electrolyte E. We attribute this behavior to the leaching out of the intercalated AlO_2^- and the aging of the Ni–Zn LDH in the control electrolyte. These experiments show that the variation in performance in cycles 1–10 were due to the effect of dissolved cations.

In conclusion, we report for the first time the suppression of the α - to β -nickel hydroxide transformation by the modification of the alkaline electrolyte. The presence of dissolved Al is deleterious to the performance of α -nickel hydroxide while the presence of dissolved Zn improves electrode performance. The oxoanions of Al and Zn play a key role in the retention of the α -phase in concentrated alkali.

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