

Effect of KOH concentration and anions on the performance of an Ni–H₂ battery positive plate¹

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Abstract

The capacity and voltage behavior of electrochemically impregnated sintered nickel positive plates was examined by galvanostatic charging and discharging in a flooded electrolyte cell. Three different concentrations of potassium hydroxide (KOH) (40%, 31% and 26%) and 31% KOH containing dissolved nitrate, sulfate, or silicate were investigated. The end-of-charge voltage at *C*/10 charge and at 10 °C showed the following order: 40% KOH > 31% KOH alone, and in the presence of the anions > 26% KOH. The mid-discharge voltage at *C*/2 discharge was higher in 26% KOH, almost the same for 31% KOH with and without the added contaminants, and much lower for 40% KOH. The plate capacity was marginally affected by cycling in all cases except for 40% KOH, where the capacity declined after 1000 cycles at 80% depth-of-discharge (DOD). At the end of cycling all the plates tested experienced a weight loss, except in the case of 31% KOH, as a result of active material extrusion. Cyclic voltammetry of miniature electrodes in 31% KOH showed that the cathodic peak potentials are less polarized at –5 °C (compared to 25 °C) in the presence and absence of silicate. This indicates a slightly higher voltage during discharge in an Ni–H₂ battery. Furthermore, the features of the current–potential profile were practically unchanged in the presence of silicate.

Keywords: Potassium hydroxide; Positive plates; Electrodes; Nickel; Batteries; Anionic additives

1. Introduction

The Ni(OH)₂/NiOOH cathode has been used in aerospace batteries for the past three decades, and its manufacture and performance features have been extensively discussed by several authors [1–5]. This cathode is the capacity- and life-limiting component in Ni–H₂ cells, and its reaction, molecular composition, and structure are very complex. The active material in the cathode has a theoretical energy of 0.279 Ah/g, and the charge transfer reaction occurs between +2 and +3.6 valency states. This positive plate yields a practical energy of 0.12 Ah/g in Ni–H₂ cells, and it endures more continuous charge/discharge cycles than any other cathode used in batteries. Several methods can be employed to fabricate this cathode; the use of cationic additives such as Co²⁺, Cd²⁺, and Li⁺ is very common. The effects of additives and impurities have been examined by others, and generally the cationic types have been found to have beneficial effects [3,6,7]. Among the anions, carbonate is believed to increase

the ohmic resistance, sulfate is reported to increase the corrosion of the sintered matrix, and silicate and nitrate are reported to decrease the capacity [8]. The current study is directed at the effects of hydroxyl, sulfate, silicate, and nitrate on the performance of the Ni(OH)₂ cathode.

2. Experimental

The positive plates were of the sintered and electrochemical impregnated type with a 0.9 mm thickness and a 50 cm² area. Two types of plates, differing only in the nature of the sintered plaque, were used for the study. The chemical composition of the positive plate is given in Table 1; all of the

Table 1
Chemical composition of the positive plate

Item	Mass gram	Percent
Positive plate	14.29	100
Ni(OH) ₂	5.25	36.74
Co(OH) ₂	0.51	3.57
Nickel sintered plaque	8.45	59.13
Other (water)	0.08	0.56

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plates contained the cobalt hydroxide additive. The plates were tested individually by immersing them in a coolant-jacketed glass cell containing 800 ml of KOH. The counter electrode was a sheet of nickel, and the voltage was measured using a Hg/HgO reference electrode. First, the capacity of all 14 plates at 10°C was measured. Then, plates were repeat-

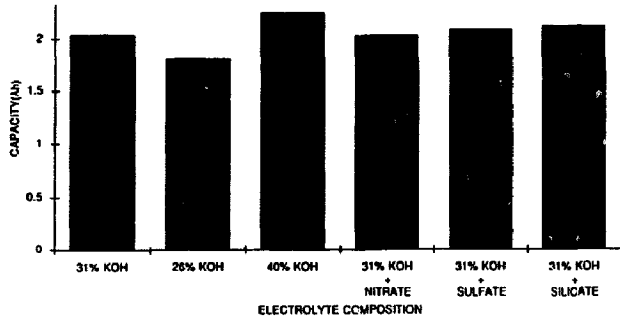


Fig. 1. Initial capacity of the plates.

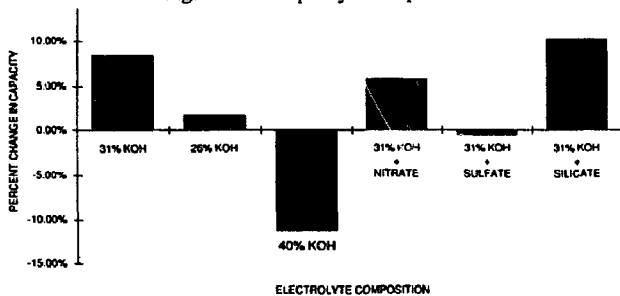


Fig. 2. Capacity vs. cycling.

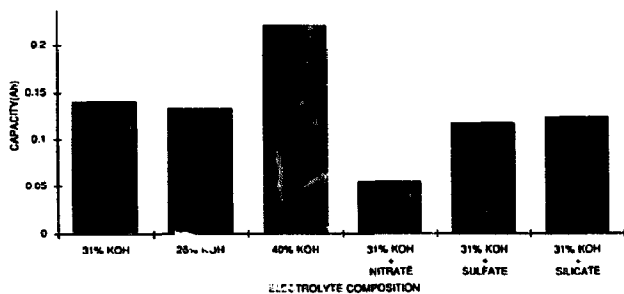


Fig. 3. Low voltage capacity in the plates.

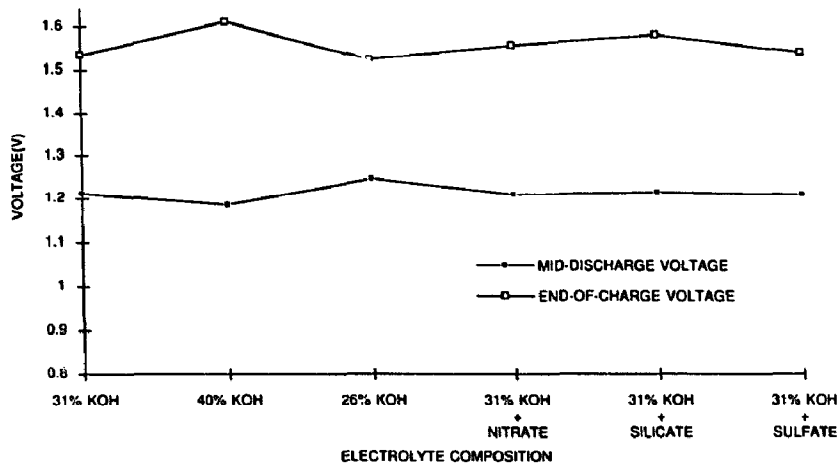


Fig. 4. End-of-charge and mid-discharge voltages.

edly charged and discharged in a cycling regime consisting of charge for 28 min and discharge for 17 min, with an overcharge of 5% and a depth-of-discharge of 80% at the rate of 32 cycles per day. The anionic additives were introduced immediately after the initial capacity determination. The sodium silicate level was 0.1% based on electrolyte weight, the potassium nitrate level was 0.5%, and the sodium sulfate level was 0.1%.

3. Capacity variation

Fig. 1 shows the capacities of the plates as a function of the electrolyte composition. The capacity was highest in 40% KOH and lowest in 26% KOH, the effect of nitrate, silicate, and sulfate being very minimum. The reason for the higher capacity in 40% KOH is the larger voltage window available for the plates during charge before predominant oxygen evolution sets in which increases the amount of oxidized species in the plates and/or higher proportions of Ni^{4+} in the charged state as a nickelate species. Fig. 2 depicts the variation of capacity with cycling (1000 cycles) for the plates. (For purposes of comparison, only plates using dry powder sintered plaque were included.) The capacity actually increased to varying degrees for all the plates except that in 40% KOH. The increase in capacity may be due to the active material formation effect. The smaller increase in capacity for 26% KOH was unexpected. Several reasons can account for the capacity loss for the plates in 40% KOH such as swelling of the plate, loss of active material due to extrusion, and increase in ohmic resistance between the sinter and the active material.

Fig. 3 shows the variation of capacity below 1 V (second plateau capacity) for the plates as a function of electrolyte composition. The plate tested in 40% KOH behaved differently than the rest, with significantly higher capacity at low voltage.

4. Voltage characteristics

The end-of-charge voltage after 16 h of charge at $C/10$ varied as a function of electrolyte composition, as shown in

Table 2
Physical changes due to cycling

Electrode number	Sinter type	Weight with TAB (g)	Electrolyte	Change in appearance after 1000 cycles
1A	Dry powder	17.68	31% KOH	Small blisters only on top of the plate
23A	Dry powder	18.13	31% KOH	Small blisters on top of the plate
3A	Slurry	16.26	31% KOH	Only two blisters
3A	Dry powder	17.71	26% KOH	Large blisters on top and bottom of the plate
21B	Dry powder	17.72	26% KOH	Many tiny blisters on top of the plate
7A	Dry powder	17.39	40% KOH	Warping
22A	Dry powder	17.72	40 KOH%	Warping and cracking
13A	Slurry	16.41	40 KOH%	Blisters on both sides of the plate
4A	Dry powder	17.73	31% KOH + KNO ₃	Many blisters on top and bottom of the plate
9A	Slurry	16.46	31% KOH + KNO ₃	Many blisters on bottom of the plate
15B	Dry powder	18.03	31% KOH + Na ₂ SO ₄	Slight warping, small blisters on bottom of the plate
6B	Slurry	15.84	31% KOH + Na ₂ SO ₄	Blisters on both sides of the plate
14B	Dry powder	18.08	31% KOH + Na ₂ SiO ₃	Slight warping
11B	Slurry	16.29	31% KOH + Na ₂ SiO ₃	Slight warping

Fig. 4. The end-of-charge voltage was insensitive to the presence of sulfate. Silicate ions increased the voltage by 48 mV, and nitrate by 23 mV, compared to that obtained in 31% KOH. The largest effect was in 40% KOH, where the end-of-charge voltage increased by 78 mV, compared to that obtained in 31% KOH. High voltage during charge is undesirable since it promotes anodic corrosion of the sintered nickel skeleton. Because high end-of-charge voltage increases the voltage requirements for the charging source, it is disadvantageous for aerospace Ni–H₂ batteries.

Fig. 4 plots the mid-discharge voltage obtained during discharge at $C/2$ as a function of the electrolyte composition. The presence of nitrate, silicate, and sulfate did not affect the voltage with respect to that obtained in 31% KOH. In the presence of 26% KOH, the voltage was 26 mV higher than that obtained in 31% KOH. In 40% KOH, the mid-discharge voltage was lower by 27 mV. This is a very interesting result. The reason for the higher voltage may be due to a slightly lower amount of K⁺ ions incorporated in the lattice of the charged active material (NiOOH) in 26% KOH and/or an increased amount of H₂O molecules.

5. Structural effects

In addition to being measured for weight and thickness, the plates were examined visually before and after cycling. The amount of extruded active material was determined by collecting and weighing the residue from the test cell. The microstructural features of the plates were determined by cross-sectioning, followed by back-scattered electron (BSE) image analysis using a procedure described in Ref. [9]. Visual examination of the plates at the end of cycling revealed several structural and mechanical imperfections such as blistering and warping. These are recorded in Table 2.

The increase in thickness of the plates as a result of cycling is recorded in Table 3. The expected increase in thickness at the end of 1000 cycles is about 1%, which was obtained for

Table 3
Swelling and extrusion of plate

Electrolyte	Swelling (%)	Weight loss (%)
31% KOH	1	0.18
26% KOH	4.90	0.85
40% KOH	12.36	6.31
31% KOH + nitrate	8.90	0.38
31% KOH + silicate	1.80	1.90
31% KOH + sulfate	2.40	0.75

the plates tested in 31% KOH with no additives. Except for 31% KOH, all other electrolyte compositions induced some noticeable imperfections irrespective of whether the plate was dry powder sinter or slurry sinter. The swelling was significantly higher in the presence of nitrate and in 40% KOH. Higher swelling in 26% KOH than in 31% KOH was observed in this test, and is in agreement with previous results for cycled positive plates in Ni–H₂ cells [10]. The reason for higher swelling in nitrate and 40% KOH is the higher corrosion of the sintered nickel in these electrolytes which weakens the sinter-to-sinter and sinter-to-substrate bonds.

Table 3 also records the active material weight loss in various electrolytes. The weight loss was significant in 40% KOH and in the electrolytes containing silicate. The reason for the higher weight loss in these electrolytes is the corrosion of the sintered nickel and the surface chemical effect which produces loosely held mossy structures.

Fig. 5 shows the microstructure of plates cycled in 26% KOH and 40% KOH. The micrographs, which were taken at a magnification of 60, indicate that, in the case of the plate cycled in 40% KOH, the microstructure has undergone considerable change in the distribution of the active material across the plate thickness. The surface of the plate is becoming depleted of active material, macrovoids have developed, and the plate thickness has increased compared to the one for 26% KOH. On the other hand, the plate cycled in 26% KOH

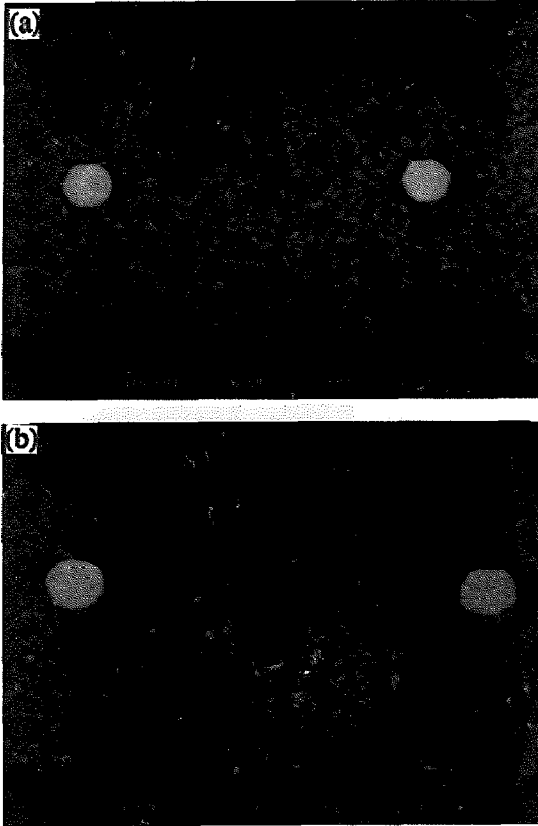


Fig. 5. (a) BSE image of a cross section of the positive plate cycled in 40% KOH, $\times 60$. (b) BSE image of a cross section of the positive plate cycled in 26% KOH, $\times 60$.

shows no evidence of any change in the microstructure. Figs. 6 and 7 show the distribution curves for the active material void and sinter fractions which were deduced from the

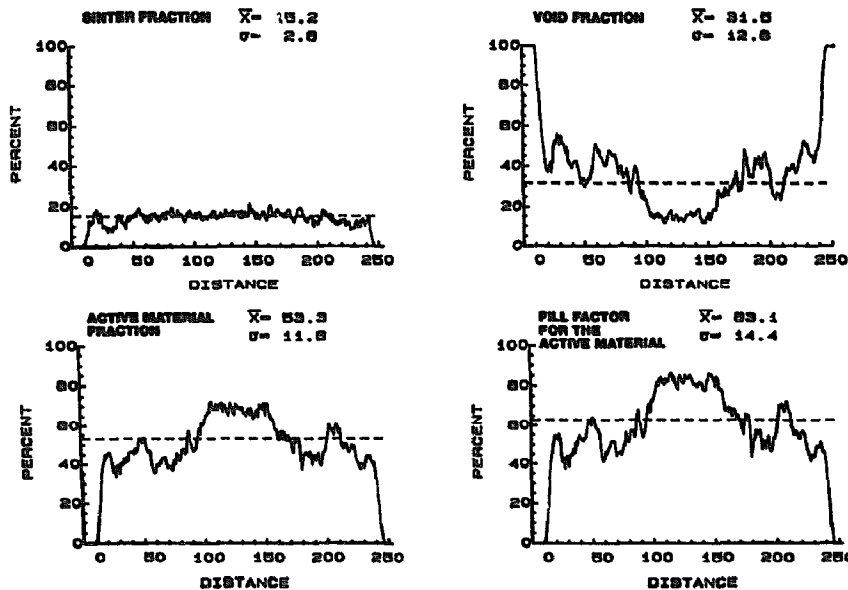


Fig. 6. Distribution profiles obtained by BSE image analysis for the plate after 1000 cycles in 40% KOH (\bar{x} = average, σ = standard deviation, distance = plate thickness in arbitrary units).

BSE images using the method described in Ref. [9] which consisted of grey level histogram plotting for the plate cycled in 26% and 40% KOH, respectively. The active material distribution is uniform across the thickness for the plate cycled in 26% KOH, and is very nonuniform for the plate cycled in 40% KOH. The calculated fill factor is only 63.1%, with a sigma of 14.4% for the active material in the 40% KOH plate. The results indicate considerable movement of active material in the plate structure if the plate is cycled in 40% KOH. Very stable conditions are indicated for the plate cycled in 26% KOH.

6. Cyclic voltammetry

The voltage profile of a miniature positive electrode (1 cm^2) was obtained by using cyclic voltammetry in 31% KOH. The potential of the positive plate was continuously changed using a triangle-wave generator and a potentiostat from -0.5 to 0.65 V (versus a Hg/HgO reference electrode) at a rate of 0.1 mV/s . Fig. 8 shows two voltage profiles: curve (A) corresponds to a plate in 31% KOH, and curve (B) to another plate in 31% KOH containing 0.1% sodium silicate. The plate exhibited two anodic peaks (peak I and peak II), an oxygen evolution maximum, and a cathodic peak (peak III). The two anodic peaks can be correlated with the oxidation of two different types of nickel species. Only one cathodic peak indicates reduction to a single nickel species. The peak potentials are listed in Table 4. The voltage profile of the positive plate in the presence and absence of 0.1% (by weight) sodium silicate at -5 and $25 \text{ }^\circ\text{C}$ was obtained, and the peak potentials obtained are included in Table 4. The data indicate the following:

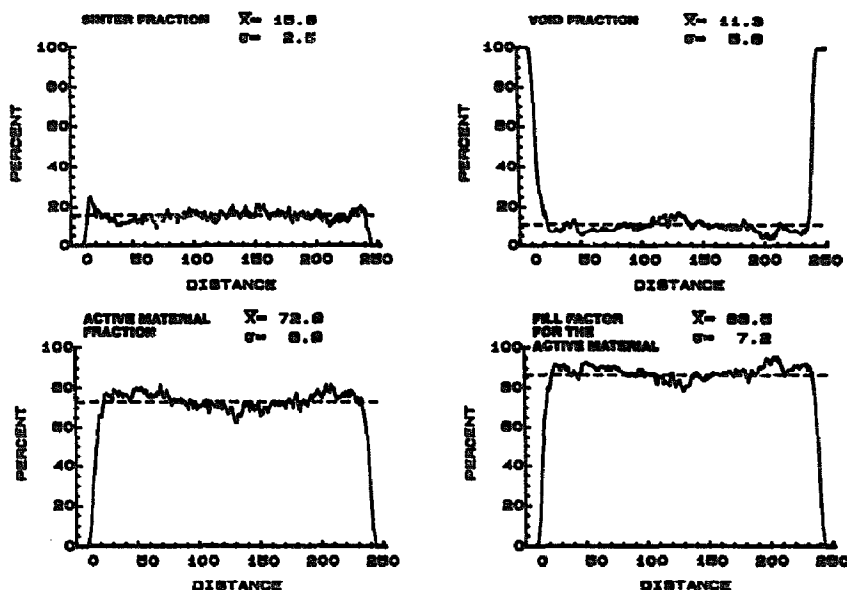


Fig. 7. Distribution profiles obtained by BSE image analysis for the plate after 1000 cycles in 26% KOH (\bar{x} = average, σ = standard deviation, distance = plate thickness in arbitrary units).

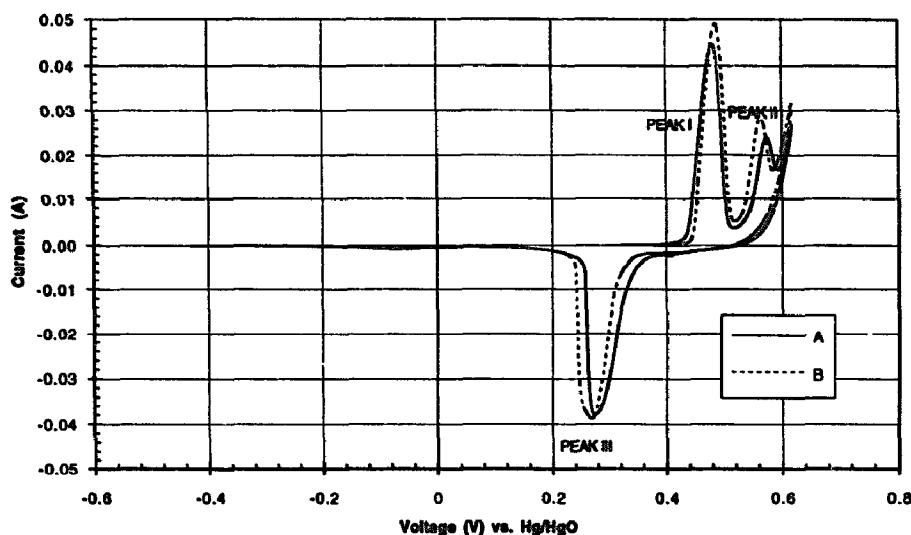


Fig. 8. Cyclic voltammograms obtained for the positive plates: curve (A) in 31% KOH, and curve (B) in 31% KOH + silicate.

(i) The cathodic peak potentials are less polarized at -5°C (compared to 25°C) in the presence and absence of silicate, indicating a slightly higher voltage during discharge in an Ni-H₂ battery.

(ii) The cathodic peak potentials are unaffected by the presence of silicate, indicating that the silicate does not influence the electrochemical reduction reaction.

(iii) The anodic peak I potential is unaffected by the presence of silicate and the peak II potential is marginally affected at -5°C . These data indicate that silicate does not influence the electrochemical reaction.

(iv) At 25°C , the anodic peak I and peak II potentials are lower in the presence of silicate. Absorption of silicate on the nickel hydroxide could explain the lowering of the peak potentials.

7. Mechanism of anions

A number of studies have shown that when inorganic salts are introduced during the processing of the electrode or in the cell electrolyte, cations such as Co^{2+} , Zn^{2+} , Cd^{2+} , K^{+} , and Li^{+} are incorporated in the crystal lattice of $\text{Ni}(\text{OH})_2$, which changes the lattice parameters [11]. The foreign cations are said to occupy the vacant sites to make up for the nickel deficit in the structure. On the other hand, anions are believed to be absorbed between layers of $\text{Ni}(\text{OH})_2$ [12]. Thus, the cationic additives alter the behavior of the nickel hydroxide by virtue of their ability to stabilize a higher valent nickel (Ni^{4+}), increase the ion transport by expanding the lattice, increase the degree of hydration by enlarging the interstitial spacing, and increase the conductivity by reducing the stoi-

Table 4
Peak potentials obtained by cyclic voltammetry

Temperature	Electrolyte	Anodic peak I potential (V)	Anodic peak II potential (V)	Sweep reversal O ₂ evolution potential (V)	Cathodic peak potential (V)
-5 °C	31% KOH	0.481	0.574	0.64	0.275
-5 °C	31% KOH + 0.1% Na ₂ SiO ₃	0.482	0.570	0.64	0.272
25 °C	31% KOH	0.495	0.544	0.64	0.262
25 °C	31% KOH + 0.1% Na ₂ SiO ₃	0.474	0.529	0.64	0.264

chiometry. Consequently, the presence of Co²⁺ increases the coefficient of utilization of the Ni(OH)₂ electrode, the presence of Cd²⁺ improves the charge efficiency at warmer temperatures [3], and the presence of Zn²⁺ improves the dimensional stability [6]. The effect of anions is limited to the alteration of surface texture. The reaction most affected by this is the electrocatalytic oxygen evolution on the charged active material NiOOH, since the oxygen evolution is very sensitive to surface conditions such as the structure of the double layer and adsorbed species. This is the reason for the increase in the end-of-charge voltage for the positive electrode in the presence of anions. The effect of anions on surface conditions is also reflected in the adhesion of the active material which in turn affects the extent of swelling and a resultant loss of active material. For aerospace application, the role of anionic impurities in the swelling of the electrode and spalling of the active material is of importance, since the processes are life-limiting. Therefore, minimizing anionic impurities is vital for long-life nickel electrodes.

8. Effect of KOH concentration

This study has highlighted differences in the behavior of the nickel electrode in 26% KOH — a new concentration for the electrolyte advocated by Lim and co-workers [10,13]. The results show that mid-discharge voltage is higher by 26 mV, uniform distribution of active material across the cross section is maintained with cycling, plate capacity is lower, and the initial increase in capacity due to plate formation is minimal. The observation of a slightly higher self-discharge rate, as reported by Stadnick and Rogers [14], and the formation of ice crystals during low-temperature operation, may be added to our results. It should be noted that, in the charged state, KOH is incorporated into the lattice structure of the nickel active material [2]. This results in a decrease in KOH concentration in the charged state of the Ni-H₂ cell, compared to the discharged state. One consequence of using 26% KOH in the cell is the development of too low a concentration of KOH in the charged state, which promotes water loss from the electrode stack in the Ni-H₂ cell by evaporation and condensation. Conditions such as high hydrogen pressure and a high vapor pressure of water favor evaporation and the condensation of water in colder parts of the cell, even when the temperature gradient is less than 8 °C. Thus, there are

both advantages and disadvantages of using 26% KOH as the electrolyte in Ni-H₂ cells.

9. Conclusions

The experimental results suggest the following conclusions:

1. An increase in KOH concentration (from 26 to 40%) significantly affects performance features such as capacity stability with cycling, end-of-charge voltage, and mid-discharge voltage more than trace amounts of nitrate, sulfate and silicate as impurities.
2. Trace amounts of nitrate increase plate swelling.
3. Trace amounts of silicate increase active material loss by extrusion.
4. The effect of anions like sulfate, silicate and nitrate are minor compared to that of cations like Co, Cd, and Zn. This is because cations are easily incorporated into the crystal lattice thus altering the lattice parameters. The anions influence the surface structure. This confirms the hypothesis of earlier work by other authors that in the charged state there is a predominance of nickelate species. The formation of nickelate can also account for the fractional valency of 3.6 for the charged species.
5. Although the positive plate electrochemistry appears to be tolerant to anionic impurities, such impurities are still undesirable from the standpoint of the mechanical strength and physical integrity which are required in batteries.
6. The effect of anions was the same whether the positive plate was based on slurry or dry powder sintered plaque.
7. BSE image analysis indicated that there is no movement of active material across the cross section of the plate in the case of 26% KOH.

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