

A DISCUSSION OF THE CAUSES OF BLISTERING OF SINTERED NICKEL HYDROXIDE ELECTRODES

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Summary

The blistering of sintered nickel hydroxide electrodes has been of continuing concern to users of long life batteries containing these electrodes. In this study it has been determined that blistering can be affected by many parameters that are sensitive to both the manufacturing processes and to the electrodes' operating conditions. Some of these parameters are the active material loading level and the ability of the electrode to vent gases due to overcharge. Also, the active material impregnation process can enhance blister formation.

A mechanism for blister formation is proposed that primarily relies on the existence of mechanical shear stresses within the electrode. Microscopic studies of several blistered electrodes provide the basis of evidence supporting the proposed model.

Introduction

The blistering of sintered nickel hydroxide electrodes has been a commonly observed "failure mechanism" in virtually all cells using nickel electrodes. The use of the term failure mechanism with respect to blistering is probably not strictly correct, as this author knows of no cell whose failure could be directly attributed to electrode blistering. Rather, blistering is probably indicative of an inferior product or of a malfunctioning cell. Thus, blistering is more appropriately viewed as a symptom of a more fundamental problem.

In this paper it is shown that blistering is influenced by several variables including the presence of macropores, loading level, gas venting capability, degree of overcharge, and the impregnation process used. In addition, it may also be influenced by the rate of local recombination occurring in a cell. Other parameters expected to influence blistering, but which are not discussed here, are sinter mechanical properties, types of additives used in the electrode, and additive levels.

Experimental

The emphasis of the experimental effort was to fabricate electrodes, in a controlled manner, that would be expected to blister. Two approaches were used: (1) fabricating electrodes with macropores in them; (2) using an impregnation process, on standard plaque, that is known to cause severe cyclic strain.

Three electrodes were constructed with controlled macropores. The electrodes were 1.27 cm wide by 7.62 cm long by 1.09 mm thick, having two macropores across their width whose dimensions were 12 μm by 1 mm. A polyvinyl film was used as the pore former. The pores were nominally 0.475 mm below the surface of the electrode. The electrodes had a wire screen current collector and a porosity of 78%.

The electrodes were electrochemically impregnated by the Pickett process [1] using a 50% ethanol solution with 9% $\text{Co}(\text{NO}_3)_2$ at a pH of 3.5 and a temperature of 80 °C. The active material loadings were determined by weight gain measurements after three formation cycles.

Two of the electrodes were loaded to 0.96 g/cm^3 void and one to 1.92 g/cm^3 void. The edges of one of the lightly loaded electrodes were sealed with Plexiglass to prevent gas from escaping through the ends of the macropore.

During tests of the electrodes, the percent. of overcharge for each electrode was such that the amount of gas generated for each electrode would be approximately equal. To detect blistering, the surfaces of the electrodes were observed through a binocular microscope (6X - 30X). They were charged and discharged at the 1.6 C rate.

The second set of test electrodes was fabricated from commercially manufactured plaque having a wire grid current collector, a 78% porosity, and a thickness of 0.75 mm. The impregnation process used for the electrodes was the same as before, except that the ethanol and $\text{Co}(\text{NO}_3)_2$ were eliminated from the impregnation bath. It has been shown previously that these impregnation conditions result in severe electrode growth [2]. It should be noted, for future reference, that the $\text{Ni}(\text{OH})_2$ active material from this impregnation process is strongly hydrated. This was determined by both its green color and its characteristic density of 2.85 g/cm^3 . The three test electrodes used had loadings of 1.68 g/cm^3 void, 1.89 g/cm^3 void, and 2.05 g/cm^3 void.

The testing of the electrodes was carried out at the 1.25 C rate and the degree of overcharge was 25%.

Results

The test sequence and the results for the macropore electrodes are shown in Table 1.

The cycling regimes, 20 - 100% depth of discharge, and 12% and 25% overcharge to 80% depth of discharge, were chosen to provide a qualitative

TABLE 1
Summary of the macropore blister test

Electrode	Cycle regime	Cycles	Result
0.96 g/cm ³ void unsealed	20 - 100% depth of discharge	0 - 483	No change
	25% overcharge to 80% depth of discharge	484 - 847	No change
0.96 g/cm ³ void sealed	20 - 100% depth of discharge	0 - 96	No change
	25% overcharge to 80% depth of discharge	97 - 425	Blister at one end of pore, rest of pore indented.
1.92 g/cm ³ void unsealed	20 - 100% depth of discharge	0 - 96	Blister in middle of pore, rest of pore indented.
	12% overcharge to 80% depth of discharge	97 - 165	Blister rises and falls with each cycle finally fractures to vent gas

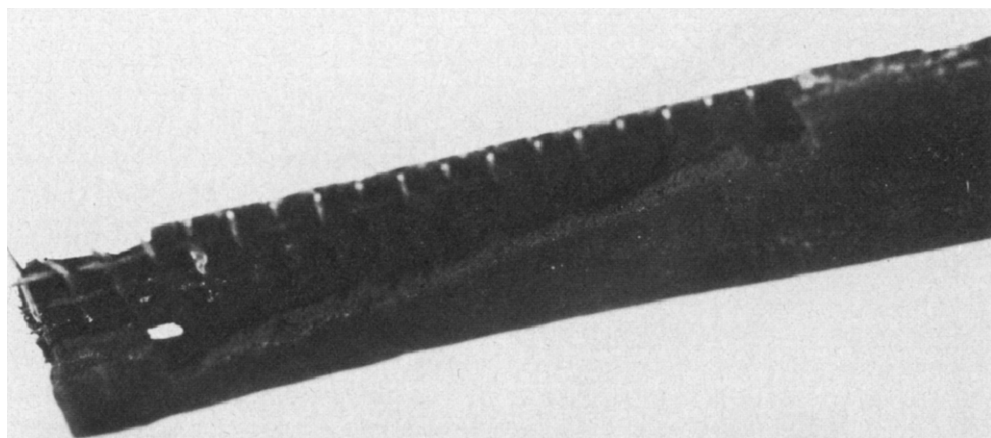


Fig. 1. Blister damage done to electrode loaded at 1.68 g/cm³ void.

description of the effects of oxygen evolution due to overcharge on blister formation. That is, it is assumed that no significant gassing occurs during the 20 - 100% cycling, thus, blister formation during this phase would be attributed to causes other than gas pressure. The number of cycles chosen for each electrode was based primarily on the stability of the experimental results. If the electrode appeared stable over a significant number of cycles, the data obtained were considered to be typical of the particular conditions of that test.

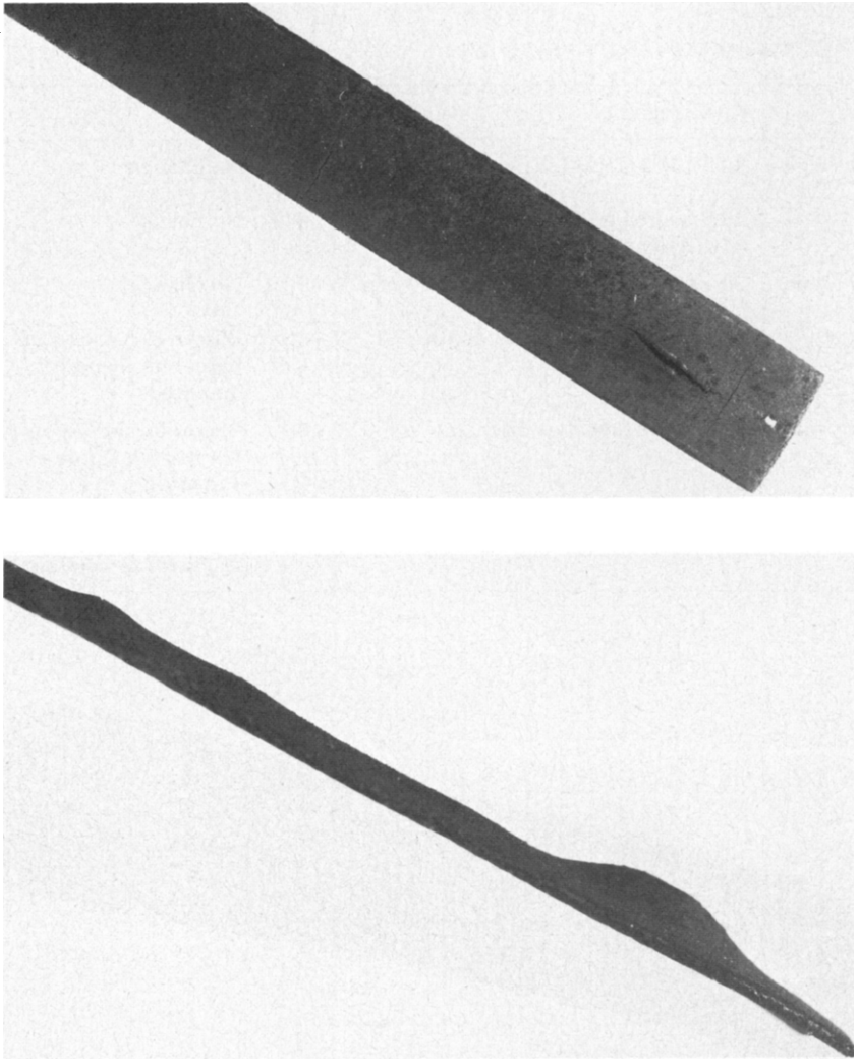


Fig. 2. Blister damage done to electrode loaded at 1.89 g/cm^3 void.

The first electrode of Table 1, lightly loaded and not sealed, did not show any tendency to blister. During the overcharge portion of the cycles, gas could be observed exiting the electrode at the unsealed ends of the macropores rather than through the sinter over the pore.

The other two electrodes of Table 1 appeared to gas in a normal manner, *i.e.*, a uniform distribution of surface bubbles. This continued until the blister on the third electrode in Table 1 fractured, whereupon the gas formed in the pore vented through the fracture.

The results for the three conventional electrodes with the modified impregnation process are shown in Figs. 1, 2 and 3. These electrodes were each

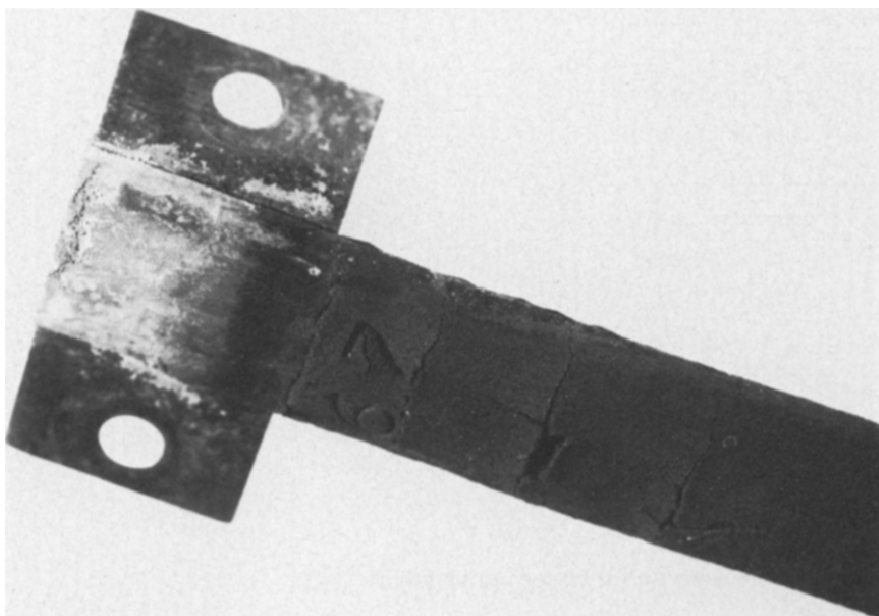


Fig. 3. Blister damage done to electrode loaded at 2.05 g/cm^3 void.

cycled for less than 30 cycles, and were accompanied by comparatively dramatic damage, as is evident from the Figures.

Discussion

The discussion portion of this paper is divided into two sections; the first discusses the specially prepared electrodes previously described, and the second section discusses the blistering of the electrodes in a nickel-hydrogen cell assembled in this laboratory [3].

From Table 1, it is seen that a macropore can serve as a blister site. Additionally, from the results of the first and second electrodes listed, electrode gassing due to overcharge enhances blistering unless there is an available path for the gas to escape. A comparison of the second and third electrode results suggests that blistering is also loading sensitive. This part of the effort was not carried out in sufficient depth to allow quantitative separation of the individual effects of these parameters, but it appears safe to assume that macropores in the sinter are not desirable from a blister point of view.

The damage done to the three conventional electrodes, Figs. 1, 2, and 3, is important, because a mechanism for a blister in formation is suggested. This proposed mechanism is shown in Fig. 4(a) and (d). In Fig. 4(a), it is supposed that a zone of severe shear stress exists next to the current collector. This is due to the large difference in rigidity between the current collector region and the unsupported sinter [4]. Thus, as the electrode is charged

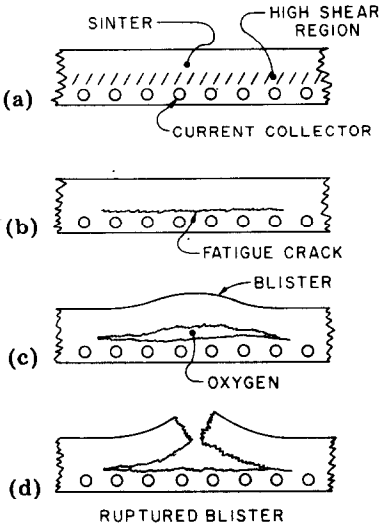


Fig. 4. Schematic of mechanism for blister formation.



Fig. 5. Fully developed blister from Fig. 3, X6.



Fig. 6. Sectioned view of blister from Fig. 5, X15.

and discharged, the sinter undergoes larger cyclic strains [5] (due to active material molar volume changes) than the current collector region. The resulting difference in strains results in a fatigue failure by shear, Fig. 4(b), of the sinter in the shear zone, thus forming a macropore. Conceptually, the

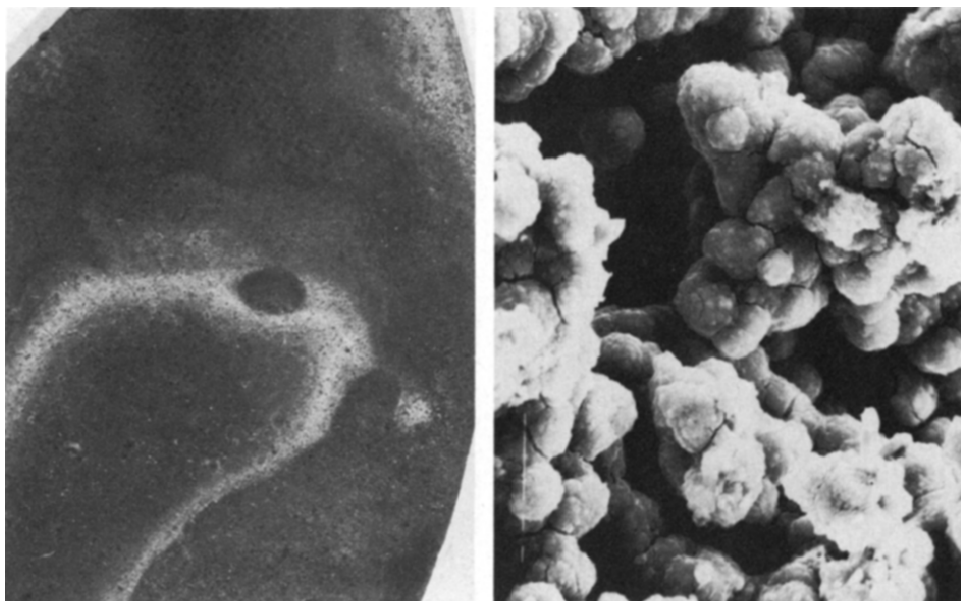


Fig. 7. Blister formed in nickel-hydrogen cell.

Fig. 8. Crystalline morphology of $\text{Ni}(\text{OH})_2$ in nickel-hydrogen cell before cycling.

next step in the process is shown in Fig. 4(c), where the oxygen pressure from overcharge causes the fatigue crack to open, thus lifting the surface into a blister. The final step, Fig. 4(d), is the rupture of the blister such that no further damage by oxygen pressure can take place. The breakup of nickel sinter due to internal gas pressure has previously been considered by Gross [6], but his proposed mechanism is on a sinter particle scale and substantially different from that proposed here.

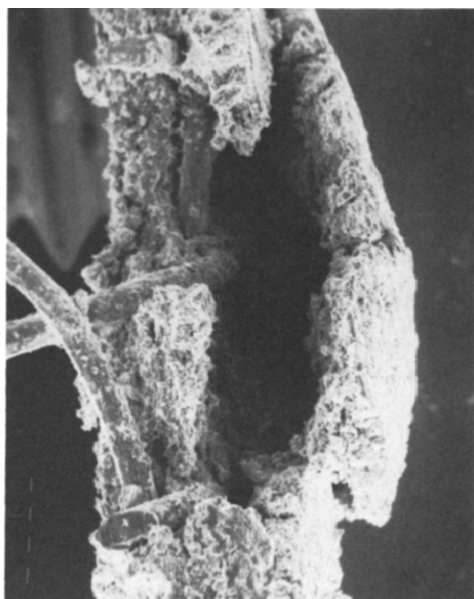
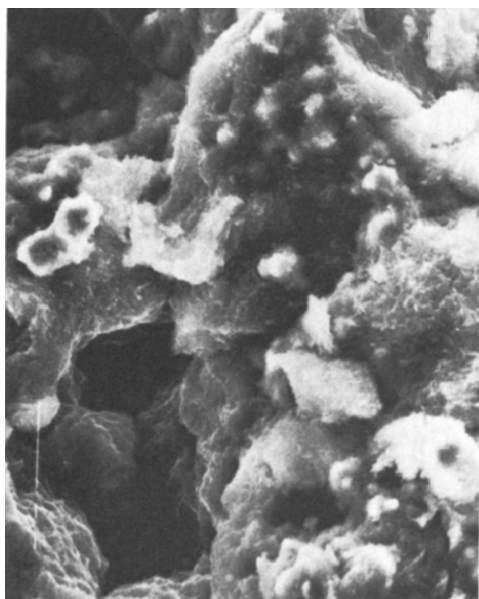
In Figs. 5 and 6, one of the blisters of Fig. 3 is examined in more detail. The full blister is shown in Fig. 5. In Fig. 6, one of the blister sections has been removed to demonstrate the uniformity of the blister thickness. The "fracture zone" for this blister was about 0.3 mm beneath the electrode surface over the entire region affected. This is taken as additional evidence that the blister process is the result of the existence of a shear zone that is due to nonuniform properties in the thickness direction, that is, the uniform blister depth would not be expected unless a depth dependent stress mechanism existed. All the blisters shown in Figs. 1 - 3 had the same uniform depth property.

The proposed shear model of blister formation appears to be valid in the actual cells, as evidenced by the results of this laboratory's investigation of nickel-hydrogen cells [3]. In the test cell reported on, blisters were formed on the nickel electrodes as shown in Fig. 7. The electrodes used in this cell were impregnated by the Pickett Process [1], and the particular

TABLE 2

Nickel hydroxide water coordination

Cycles	Location	Water coordination
Uncycled electrode	Random	$\text{Ni}(\text{OH})_2 \cdot (0.9)\text{H}_2\text{O}$
1200	2 cm from blister	$\text{Ni}(\text{OH})_2 \cdot (1.22)\text{H}_2\text{O}$
1200	at blister	$\text{Ni}(\text{OH})_2 \cdot (1.72)\text{H}_2\text{O}$

Fig. 9. Crystalline morphology of $\text{Ni}(\text{OH})_2$ in nickel-hydrogen cell after 1200 cycles.Fig. 10. Sectioned view of blister from Fig. 7, $\times 25$.

electrode shown had a loading of 1.09 g/cm^3 void. The mechanism of Fig. 4 seems consistent with the blisters formed provided certain assumptions about precursor steps are true. These assumptions are: (1) hydrogen-oxygen recombination occurs locally diluting the electrolyte; (2) over long term cycling, the nickel hydroxide is locally hydrated by the recombination process. Assumption number one is supported by the observation that the separator material had a burn spot at the blister location. This indicates that hydrogen-oxygen recombination was occurring here. The second assumption was established as being correct by determining the amount of coordinated water in the electrode shown. This was done by heating portions of the electrode in a differential thermal analyzer until after the dehydration peak, and recording the weight loss due to the dehydration. From the weight loss and loading, the number of water molecules coordinated with each nickel

hydroxide molecule was calculated. The results are shown in Table 2. It is apparent from Table 2 that the blistered electrode was being hydrated during cycling. Before and after micrographs of this electrode, Figs. 8 and 9, show a marked morphological change of the active material, further supporting the validity of the second assumption.

The blister of Fig. 7 was broken away at one end, and a cross-sectional view taken. The result is shown in Fig. 10. Note that the fracture occurred at the current collector, which is where shear forces are expected to be maximum for a uniformly loaded electrode. Thus, the complete blister model for the nickel-hydrogen electrode is

- (1) the electrode is locally hydrated, partially aided by hydrogen-oxygen recombination,
 - (2) the hydrated region has unfavorable growth characteristics,
 - (3) the sinter is broken in shear at the sinter/current collector interface,
- and
- (4) the gas pressure lifts a blister in the fractured region.

It should be emphasized that the above description implies that excess localized recombination occurred and does not imply that an inferior nickel electrode was used.

The mechanism proposed here depends primarily on the nonuniform structural properties inherent in conventional sintered electrodes. It is quite possible that the same shear zone condition could result from non-uniform impregnation of the active materials or possibly from certain cycling conditions.

Conclusions

The major conclusion of this effort is that macropores in sintered nickel hydroxide electrodes are a source of blisters. The macropores can be the result of a defect in the sinter, or they can develop during normal cycling by localized fatigue failure of the sinter.

The parameters shown to influence the formation of blisters are loading level, gas venting path within the sinter, degree of overcharge, and the impregnation process. Also, it is implicit in the proposed shear model of blister formation that blistering is dependent on the number of cycles. In addition, other cell components may indirectly influence the blister process by causing local recombination, thus altering the structure of the active materials.

Acknowledgements

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