

RECENT ADVANCES IN Ni-H₂ TECHNOLOGY AT NASA LEWIS RESEARCH CENTER

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ABSTRACT

NASA Lewis Research Center has concentrated its efforts on advancing the Ni-H₂ system technology for low earth orbit applications. Component technology as well as the design principles have been studied in an effort to understand the system behavior and failure mechanisms in order to increase performance and extend cycle life. The design principles have been previously addressed (Ref. 1, 2). This paper will discuss the component development, in particular the separator and nickel electrode and how these efforts will advance the Ni-H₂ system technology.

INTRODUCTION

The Ni-H₂ technology group at NASA Lewis Research Center has been developing Ni-H₂ cells primarily for LEO applications. The overall objective is to improve the components, design and operating characteristics of Ni-H₂ cells and batteries. An active program to address the anticipated decay modes and failure mechanisms is underway both on contract as well as in-house.

The types of shortcomings that are associated with Ni-H₂ devices which are related to electrolyte management, oxygen management, electrode growth management and performance degradation can all be traced to problems associated with the nickel electrode and/or separator. Therefore, they are considered the critical components. The nickel electrode is the life limiting component while the separator is the critical risk component due to unavailability of asbestos and the electrolyte and oxygen management problems associated with Zircar.

The LeRC has concentrated its efforts in separator development and the understanding of the nickel electrode behavior in order to improve cycle life. The closer we get to understanding the nickel electrode the more able we will be to deal with the problems associated with it either by correcting the cause or by reducing its impact on cycle life. An attempt to reduce the impact of current shortcomings by modifying the design of Ni-H₂ cells is currently underway, but an in-depth understanding of the causes and effects is sought. This will ultimately allow us to understand the effect of uncontrolled changes on the system and will provide us the necessary tools to take

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corrective measures so Ni-H₂ systems will be less affected by manufacturing and technology changes in the future.

The most recent advances in the nickel electrode and separator technology areas are expected to have a positive effect on life, weight, cost and performance. These include new separator materials, lightweight nickel electrodes and the understanding of the nickel electrode mechanism and structure.

SEPARATOR TECHNOLOGY

As part of the technology development at LeRC, a separator development program was designed to develop a separator that is resistant to penetration by oxygen and loose active material from the nickel electrode while retaining the required chemical and thermal stability, reservoir capability and high ionic conductivity. A close look at SOA separators, their properties and problem areas was undertaken to determine the necessary properties for a new improved separator. A set of standard properties were identified which would provide the necessary characteristics for short term performance while addressing the problems related to the long term performance of SOA separators.

Screening studies showed two laboratory separators which met the characteristic goals of electrolyte retention, bubble pressure, and conductivity, etc. These were 80% PKT-20% ZrO₂-10% EBL and PKT on ZrO₂ cloth where PKT is potassium titanate and EBL is emulsified butyl latex. These separators were incorporated into Ni-H₂ stacks and tested to examine their voltage characteristics and cell performance. The cells were submitted to the same characterization and testing as those with the baseline asbestos and Zircar separators. Cell characterization showed good cell voltage with mid-point and end of discharge voltages higher than either of the baseline separators (Ref. 3).

The results obtained from characterization and testing encouraged us to further pursue this effort. The process needed to be adapted and transferred from a laboratory operation to a manufacturing process since reproducibility and uniformity are important factors that will govern their future use and applications. The first step undertaken was to have the separators prepared by a commercial vendor (Quin-T) for further evaluation. The separators obtained lacked the necessary bubble pressure to prevent the oxygen produced at the nickel electrode from accessing the hydrogen electrode in a controlled fashion. This was due to small holes ~50 μm in diameter apparently caused by localized swirls during the filtering step.

In order to overcome the manufacturing problems we started an effort with Miami University. Miami University has a Paper Science and Engineering Department well experienced in the paper making process and is equipped with a small pilot paper making machine. They also have handsheet molds and testing capabilities that will allow timely testing and modification of the production techniques to easily adapt to the new materials. The objective is to demonstrate the feasibility of manufacturing the new separator materials using

standard paper making techniques. This effort is intended to bridge the gap between the handsheet operation and the commercial processes and establish the potential of these separators for use in a variety of different applications. The one-year effort will reproduce the original handsheet material and will gradually adapt the fabrication from the handsheet techniques to the production techniques. It will study the effect of these changes on the separator properties and manufacturability and modify them to achieve a high performance separator that will be easily reproduced.

The final result is to be a separator which will be reproducible using standard paper making technology that will ensure uniformity, availability and lower costs. The technology will lead to a higher performance and extended life of the Ni-H₂ systems.

NICKEL ELECTRODE TECHNOLOGY

LIGHTWEIGHT NICKEL ELECTRODE

The second part of the technology development program focuses on the nickel electrode which, in addition to being identified as the critical component, has also been identified as the heaviest component of the Ni-H₂ battery system. The NASA Lewis Research Center is developing nickel electrodes for Ni-H₂ batteries which will be lighter in weight and have higher energy densities when cycled under a low earth orbit (LEO) regime at deep depths of discharge.

The weight of components in a typical 125 AH Ni-H₂ bipolar battery is shown in figure 1. A major weight reduction of as much as 14% can be accomplished by the use of lightweight electrodes.

Several commercially available materials or plaques other than sintered plaque have potential as a support for the active material. These plaques are lightweight and some of them have pore sizes comparable to a typical commercial sintered nickel plaque. These lightweight plaques are less conductive, but in a bipolar design the current flow is perpendicular to the electrode surface; hence the need for high lateral conductivity is eliminated (Ref. 4).

Plaques other than sintered nickel plaques that may be used to support the active material are the nickel plated plastic plaque developed here at NASA Lewis Research Center (Ref. 5, 6), commercially available Feltmetal (TM) and a needle punched web (80% Ni, 20% Cr) from Brunswick Technetics, graphite fiber mat manufactured by American Cyanamid and Fibrex (TM), a fibrous mat manufactured by National Standard Company. The lightweight plaques except for the Feltmetal are about 50 to 90% lighter than the standard sintered nickel plaque. The Feltmetal is about 5% lighter than the sintered nickel plaque.

Figure 2 shows the pore size distribution of the lightweight plaques as compared with the standard sintered plaque. Most of these plaques have larger pore radii than the sintered plaque. The Nichrome needle punched web and the Fibrex materials have about the same broad distribution at about 20 to 40 μ m.

The nickel plated plastic, the nickel plated graphite and the Feltmetal show peaks in the pore size distribution at 10 to 18 μ m. The standard sintered plaque has the lowest pore size distribution peak at 7 μ m. Porosity and pore size distribution measurements were made by the mercury intrusion porosimeter method.

To evaluate the performance of the lightweight materials, the plaques were electrochemically impregnated in a saturated solution of nickel nitrate with cobalt nitrate using the Bell Telephone Laboratory method.¹ After washing the impregnated plaques, the electrodes were formed using the Eagle-Picher procedure which consists of eight cycles of 20 minutes charge and 20 minutes discharge at approximately the 3C rate. After formation, the electrodes were thoroughly rinsed in deionized water, dried and weighed. The theoretical C rate was determined from the weight of the active material in the electrode using the electrochemical equivalent of 0.289 AH/gram of nickel hydroxide. The electrochemical impregnation of these lightweight plaques using the aqueous bath yields loading levels comparable to commercial nickel electrodes.

The initial characterization screening testing of the electrodes is performed at five discharge levels, C/2, 1.0C, 1.37C, 2.0C and 2.74C rates. The voltage versus time and the capacities at each rate are recorded and compared with the sintered nickel electrode. After the initial characterization tests, the electrodes will be life cycle tested at a LEO regime to 80% depth of discharge. Capacities will be measured every 50 cycles during the duration of the test for the first 1000 cycles and every 500 cycles thereafter. The Feltmetal electrode has accumulated over 2000 cycles and is still being cycled.

A significant improvement in weight, thus an increase in energy density of the Ni-H₂ battery system can be achieved by the use of lightweight nickel electrodes using lightweight plaques. Life and performance are being investigated.

NICKEL ELECTRODE DEVELOPMENT - HUGHES CONTRACT

While the lightweight nickel electrode is under development, an effort is being made to improve the life of SOA nickel electrodes when cycled under a LEO regime at deep depths of discharge. For this reason a contract was awarded to Hughes Aircraft Company (Research Division) to develop a nickel electrode which will have a long cycle life when cycled to deep depths of discharge. The principal investigator for this contract is Dr. Hong Lim.

The approach taken was to investigate (1) the effect of electrode design parameters on cycle life of the nickel electrode, (2) the failure mechanism of the nickel electrode, (3) the effect of potassium hydroxide electrolyte concentration on performance and cycle life, and (4) the effect of electrolyte composition.

¹T. D. O'Sullivan, Bell Laboratories, Personal Communications

The results from studying the effect of the design parameters on the cycle life of the nickel electrode were the following: (1) the plaque mechanical strength had no significant effect on cycle life over the range of values tested, (2) the pore diameter had a significant effect with the largest pore plaque (16 μm) resulting in the shortest cycle lives, the optimum pore size was 13 μm ; (3) the active material loading level affected the cycle life the most with an optimum loading of 1.6 g/cc void volume. As a result of this effort a data base was established for optimum nickel electrode design parameters for maximum cycle life in Ni-H₂ cells.

A failure model of the nickel electrode based on the experimental data was advanced which suggests ways to further improve cycle life. Cell failure was due to loss of high rate capacity rather than an absolute loss in capacity. This could be explained by the active material expansion away from the current collecting nickel sinter due to cycling. This resulted in electrical isolation of active material and loss of high rate discharge capacity. Hence, control of active material expansion is the most important factor for increasing the cycle life.

It has been reported by others from work done in nickel cadmium cells that the nickel electrode growth was a function of the potassium hydroxide concentration. Another task was to investigate the effect of the KOH concentration (21, 26, 31, 36%) on the life of the nickel hydrogen cells. To date significant increases (greater than a factor of three) in cycle life of IPV Ni-H₂ cells have resulted from the reduction in KOH concentration from the traditional values of 31% to 26%. In this continuing test over 13,000 accelerated LEO cycles have been achieved thus far at 80% DOD. The significance of these results are the increased cycle life of Ni-H₂ cells; this will have a considerable effect on LEO applications in terms of life cost and enhanced performance.

The effect of alternate electrolyte compositions on the cycle life of the nickel electrode is scheduled to start in November 1985. It includes aqueous solutions of one or more of all alkali metal hydroxides and barium hydroxide with two level variation of the actual material loading of the nickel electrode. It is expected that with some electrolyte compositions, e.g. those containing LiOH, the active material expansion rate will be greatly reduced. The optimum loading level is expected to be higher than the 1.6 g/cc void found for the standard KOH electrolyte.

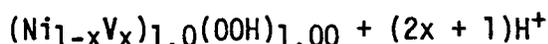
The overall results from this contract are an improved understanding of the various factors that effect cycle life of the nickel electrodes. The results provide an insight to the cycle life limitations and the failure mechanisms; they also indicate that control of the active material expansion is the most important factor for further improving cycle life in the Ni-H₂ systems.

NICKEL ELECTRODE STRUCTURE

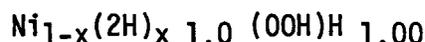
Research is also being carried out, both in-house and through grants and contracts, to learn more about the structures of the active materials and the mechanisms of the electrode reactions. Dr. Bahne Cornilsen at Michigan

Technological University has been studying Laser Raman spectroscopy of nickel oxides prepared by chemical and electrochemical means, both oxidized and reduced. Each preparation method gives somewhat different spectral features. Some of the results of this study are presented on Figure 3. The most significant finding is that both chemically and electrochemically oxidized materials, as well as reduced electrodes that have been cycled, do not exhibit any bands in the 3500-3700 cm^{-1} range that can be attributed to an OH stretch of free water. In addition, electrodes that have been cycled exhibit similar spectra in both the oxidized and reduced states. The spectra of all these materials are distinctly different from that of the well-crystallized beta $\text{Ni}(\text{OH})_2$.

The fact that no OH stretch is observed in most of these materials has led to a new interpretation of the structures of the various hydroxides in terms of a model which postulates a sizeable fraction of vacancies in the nickel lattice sites. These vacancies may be filled, either partially or completely, with hydrogen atoms or alkali metal ions. Additional hydrogen atoms can be accommodated in sites between the planes of oxygen atoms where they are hydrogen bonded between the layers. The symmetry of the crystal structure is such that the OH stretch modes are forbidden in the Raman spectra. General formulas for the oxidized and reduced forms are postulated.



and



where x represents the fraction of Ni lattice sites either vacant or occupied by H^+ or M^+ ions and can be up to about 0.27. V represents vacant Ni lattice sites. The protons can either occupy vacant lattice sites or bridge two adjacent oxygens. Alkali metal ions can also occupy lattice vacancies. Most of the postulated formulas in the literature fit into this scheme nicely. For example, Barnard's α - $\text{Ni}(\text{OH})_2$ with an empirical formula of $0.25\text{NiOOH} \cdot 0.75\text{Ni}(\text{OH})_2 \cdot 0.25\text{H}_2\text{O}$ with a Ni valence of 2.33 can be written as $\text{Ni}_{0.89}\text{V}_{0.11}(\text{OOH}_2)_{1.00}$. Barnard's β phases can be interpreted as having a vacancy ratio of about 0.11, while the γ phase, like the α phase, has about 0.25 Ni vacancies which in the case of γ are filled by alkali ions. Reinterpretation of the X-ray diffraction data is being carried out, and it appears that the data fit this scheme at least as well as the earlier structural formulations.

Other work in progress includes cyclic voltammetry studies, self-discharge measurements, and impedance studies of both planar and porous nickel electrodes. The data on the planar Ni electrodes is being interpreted as due to a variable resistance oxide film, with the resistance varying with both depth and potential, analogous to some studies of the passive film on Fe.

This research should lead to a better understanding of the nature of the active material which will assist in designing cells with improved life and performance.

CONCLUDING REMARKS

Improved performance and cycle life on the Ni-H₂ cells can be achieved by an understanding of the nickel electrode behavior and improved cell design and component technology development. Improving performance and cycle life as well as increasing the energy density of the system are the drivers of the technology development program at LeRC. Our means of achieving these goals are by developing lower cost, high performance separators and lightweight, longer life nickel electrodes. Our studies show that as much as a 14% system weight reduction and at least a three-fold increase in nickel electrode life can be achieved. These improvements have been possible through an improved understanding of the various factors affecting life and insights into cycle life limitations provided by the nickel electrode studies.

The most recent advances in the nickel electrode and the separator technology areas will have a positive effect in life, weight, cost and performance and will have a considerable effect on the use of Ni-H₂ systems for LEO applications.

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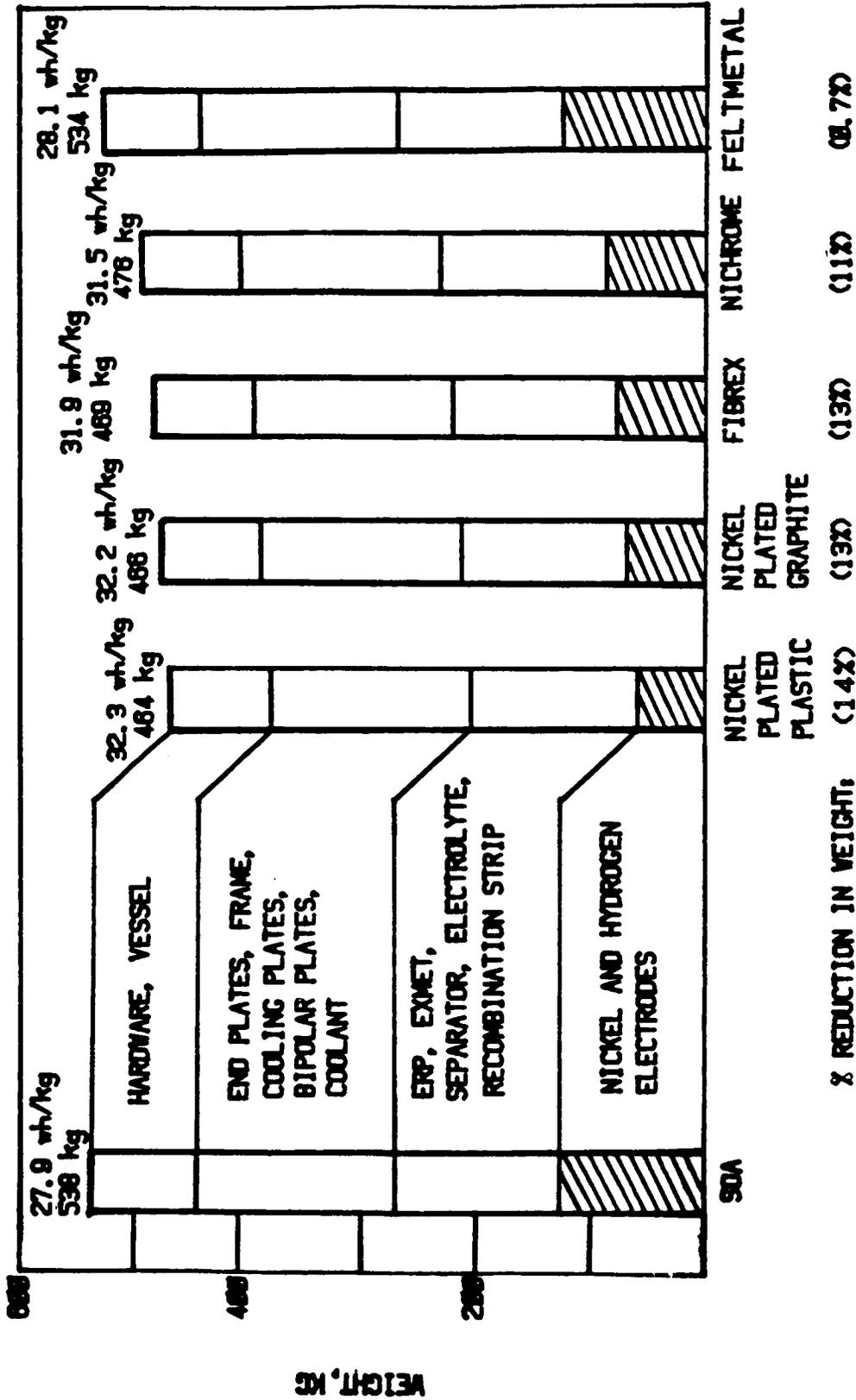


Figure 1. WEIGHT OF COMPONENTS IN A 125 Ah NiH₂ BIPOLAR BATTERY AND THE WEIGHT REDUCTION WITH LIGHTWEIGHT NICKEL ELECTRODES

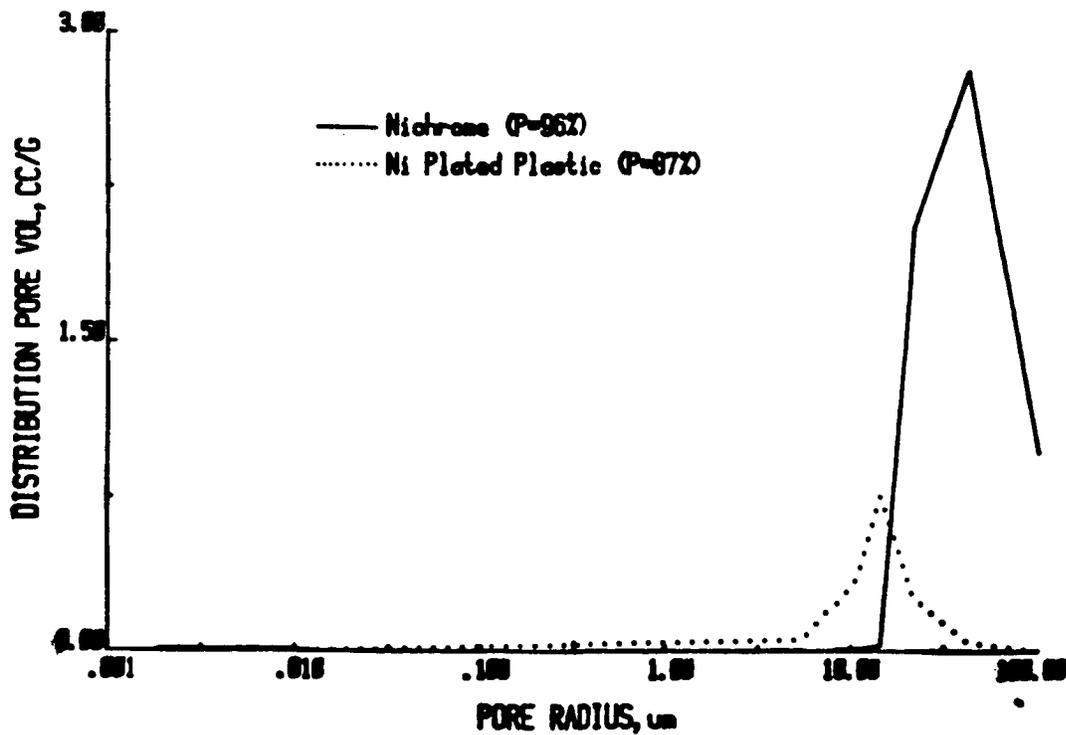
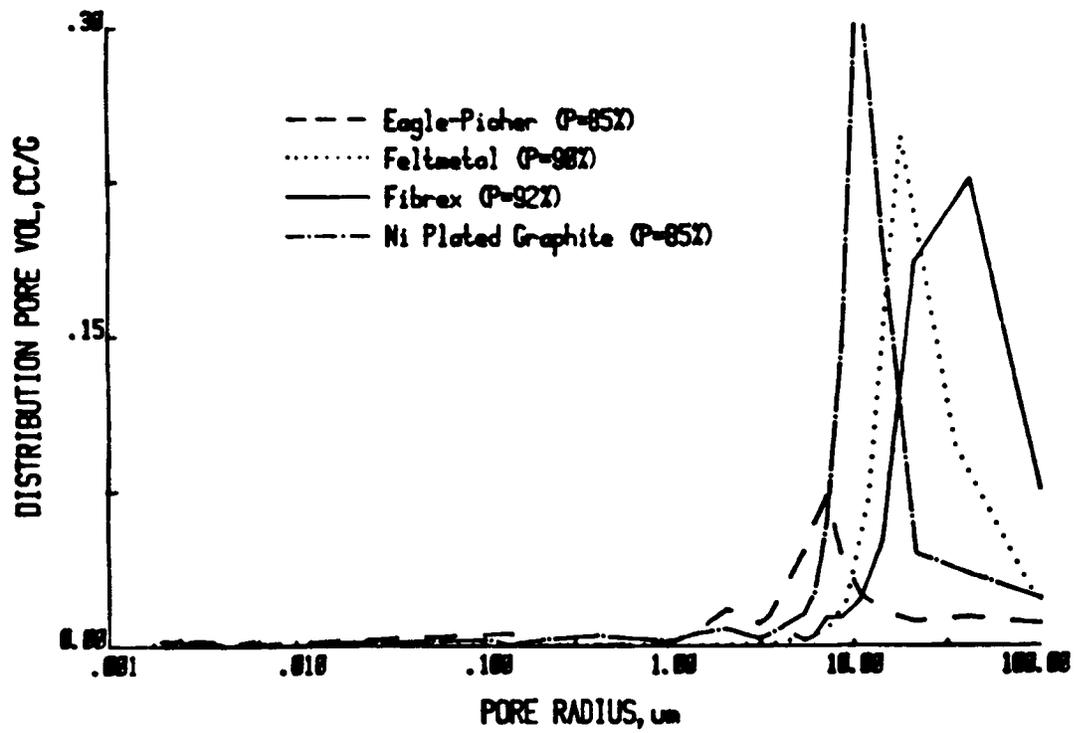
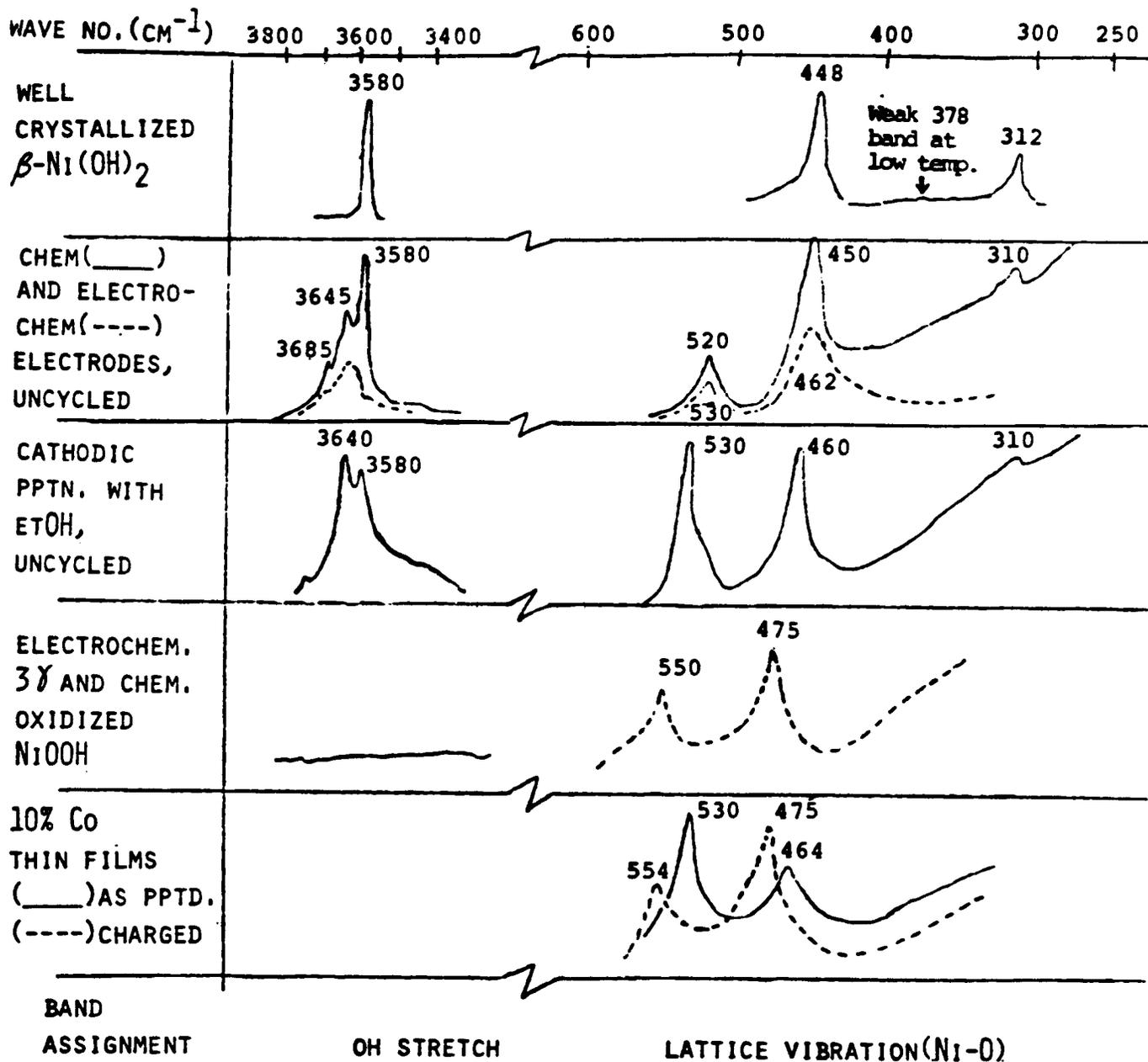


Figure 2. PORE SIZE DISTRIBUTION CURVES



OH STRETCH BANDS DISAPPEAR ON CYCLING.

BACKGROUND BELOW 450 CM⁻¹ RELATED TO PARTICLE SIZE EFFECTS, ALIGNMENT, AND SENSITIVITY.

DIFFERENT SPECTRA RUN WITH DIFFERENT SENSITIVITIES. RELATIVE INTENSITIES AND BACKGROUND MAY VARY SOMEWHAT.

WELL CYCLED ELECTRODES HAVE SPECTRA LIKE THE 10% Co THIN FILM-CHARGED.

Figure 3. RAMAN SPECTRA OF SELECTED NICKEL HYDROXIDES