IS-T-1826

Synthesis and Characterization of Nickel Hydroxide Powders for
Battery Application

by

Widjaja, Agus

RECEIVED

MAY 20 1999

OSTI

MS Thesis submitted to Iowa State University

Ames Laboratory, U.S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: October 8, 1997

PREPARED FOR THE U.S. DEPARTMENT OF ENERGY

UNDER CONTRACT NO. W-7405-Eng-82.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED *ph*

MASTER

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

This report has been reproduced directly from the best available copy.

AVAILABILITY:

To DOE and DOE contractors: Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831

prices available from: (615) 576-8401
FTS: 626-8401

To the public: National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

This work was performed at Ames Laboratory under Contract No. W-7405-Eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1826 to this thesis.

TABLE OF CONTENTS

GENERAL INTRODUCTION	1
Thesis Organization	3
References	3

* SYNTHESIS OF NICKEL HYDROXIDE BY HOMOGENEOUS PRECIPITATION FROM UREA DECOMPOSITION * Preprint	5
ABSTRACT	5

INTRODUCTION	5
--------------	---

EXPERIMENTAL PROCEDURE	8
Materials	8
Precipitation	8
Characterization	9

RESULTS AND DISCUSSION	10
Yield	10
Morphology	13
Mechanism of Particle Growth	18
Effect of Dispersants	24
Thermal Analysis	29
Phase Analysis	32

SUMMARY	35
---------	----

REFERENCES	36
------------	----

* CYCLIC VOLTAMMETRIC STUDY OF NICKEL HYDROXIDE ELECTRODE PRODUCED BY HOMOGENEOUS PRECIPITATION * Preprint	38
ABSTRACT	38

INTRODUCTION	38
--------------	----

EXPERIMENTAL PROCEDURE	40
Materials	40
Aging in Aqueous KOH	40

* Removed for separate processing —

Preparation of Electrode	41
Cyclic Voltammetry	41
RESULTS AND DISCUSSION	42
Effect of Aging on Morphology	42
Phase Analysis	45
Electrochemical Behavior	52
SUMMARY	56
REFERENCES	57
GENERAL CONCLUSIONS	59
References	61

GENERAL INTRODUCTION

The interest in an electrical vehicle is mainly due to its emission-free nature which will reduce its impact on environmental pollution. This shift from conventional internal-combustion engine to electrically-powered vehicle is also of national interest since the change means less dependence on imported petroleum, thus reduction in the international trade deficit. However, the development of electrical vehicles that can compete in performance and cost with conventional vehicles has run into a technological barrier. The technology to date of battery¹ which is the key element of electrical vehicles, does not provide sufficient energy density, life cycle, charge capability, and other important performance criteria for a practical vehicle at an affordable cost.

Nickel-metal hydride (NiMH) battery has shown a promise for future use in electrical vehicles because of its high energy density and discharge rate capability, low environmental pollution, and it could replace environmentally hazardous Ni-Cd battery². A metal alloy which is utilized as the negative electrode, has the capability to store hydrogen as a solid hydride phase upon charging and release hydrogen upon discharging, while nickel hydroxide which is used as the positive electrode, is oxidized to nickel oxyhydroxide upon charging and reduced back to nickel hydroxide upon discharging. The charge and discharge reactions of the NiMH battery can be written as²:

charge

discharge

and overall

charge

discharge

During charging, water is split into hydrogen and hydroxyl ions where the hydrogen ion reacts with the metal to form metal hydride and the hydroxyl ion reacts with nickel hydroxide to form NiOOH. As a result, no net change in the electrolyte concentration is observed.

The primary purpose of this research is to investigate the synthesis and characterization of $Ni(OH)_2$ powders by homogeneous precipitation. An auxiliary objective of the investigation is to produce $Ni(OH)_2$ powders that have superior performance characteristics compared to the commercial powders currently available. The synthesis and characterization of nickel hydroxide have been studied extensively by many authors³⁻¹². Depending on the synthesis method, different phases of nickel hydroxide have been observed. Nickel hydroxide has a hexagonal structure and exhibits layered NiO_2 sheets between which protons are intercalated. The α -phase has a large interlayer distance ($c=8.0 \text{ \AA}$) because of its intercalated ligands and/or water. The layered structure is turbostratic and randomly oriented. This property of α - $Ni(OH)_2$ is desirable in that electrolyte and solvent have greater access to the reaction sites. The β - $Ni(OH)_2$ ($c=4.6 \text{ \AA}$) is more structured and does not have ligands and/or water intercalated. Although the α - $Ni(OH)_2$ is electrochemically more active than β - $Ni(OH)_2$, the β -phase is employed in battery applications because the α -phase is unstable in

aqueous KOH solution and transforms to β -phase in a relatively short period of time.

Previous researches have emphasized on the crystal structure of the particles produced, but the effect of particle morphology on the electrochemical activity was not evaluated. No attempts have been made to control the particle morphology. Hence, the purpose of this study was to synthesize nickel hydroxide powders by homogeneous precipitation from urea decomposition and to examine the electrochemical activity in relation to the crystal structure, morphology, size distribution, and surface area of the particles under various experimental conditions.

Thesis Organization

This thesis consists of two manuscripts prepared for publication. The first manuscript, "Synthesis of Nickel Hydroxide by Homogeneous Precipitation from Urea Decomposition" summarizes the composition, morphology, and yield of the powders produced and offers a plausible explanation of the particle growth mechanism. The second manuscript, "Cyclic Voltammetric Study of Nickel Hydroxide Electrode Produced by Homogeneous Precipitation" relates the surface area of the precipitate to its electrochemical activity, compares these results with those of previous research, and explains the aging mechanism of the electrode in concentrated KOH solution. A general conclusions chapter summarizes the relationship between particle morphology and the electrochemical behavior of the $\text{Ni}(\text{OH})_2$ electrodes produced in this study.

References

1. J. I. Kroschwitz, *Encyclopedia of Chemical Technology*, 4th ed., v. 3, John Wiley, New York, 1992, pp. 1028-1079.

2. S. R. Ovshinsky, M. A. Fetcenko, and J. Ross, "A Nickel Metal Hydride Battery for Electric Vehicles" *Science*, 1993, **260**, 176-181.
3. E. J. McHenry, "Electrochemical Precipitation of $\text{Ni}(\text{OH})_2$ into Porous Electrodes" *Electrochem. Tech.*, 1965, **5**, 275-279.
4. A. Delahaye-Vidal and M. Figlarz, "Textural and Structural Studies on Nickel Hydroxide Electrodes. II. Turbostratic Nickel (II) Hydroxide Submitted to Electrochemical Redox Cycling" *J. Applied Electrochem.*, 1987, **17**, 589-599.
5. B. Mani and J. P. de Neufville, "Dehydration of Chemically and Electrochemically Impregnated (CI and EI) Nickel Hydroxide Electrodes" *J. Electrochem. Soc.*, 1988, **135**(4), 800-803.
6. B. S. Maruthiprasad, M. N. Sastri, S. Rajagopal, K. Seshan, K. R. Krishnamurthy, and T. S. R. P. Rao, "A Novel Nickel Trihydroxy Isocyanate - Preparation and Characterization" *Proc. Ind. Acad. Sci.: Chemical Sciences*, 1988, **100**, 459-462.
7. K. Ohtsuka, J. Koga, M. Tsunoda, M. Suda, and M. Ono, "Epitaxial Growth of Nickel (II) Hydroxide on Layer Silicate and Derived Nickel-[Layer Silicate] Nanocomposite" *J. Am. Ceram. Soc.*, 1990, **73**(6), 1719-25.
8. F. Portemer, A. Delahaye-Vidal, and M. Figlarz, "Characterization of Active Material Deposited at the Nickel Hydroxide Electrode by Electrochemical Impregnation" *J. Electrochem. Soc.*, 1992, **139**(3), 671-678.
9. K. T. Ehlsissen, A. Delahaye-Vidal, P. Genin, M. Figlarz, and P. Willmann, "Preparation and Characterization of Turbostratic Ni/Al Layered Double Hydroxides for Nickel Hydroxide Electrode Applications" *J. Mater. Chem.*, 1993, **3**(8), 883-888.
10. P. V. Kamath, J. Ismail, M. F. Ahmed, G. N. Subbanna, and J. Gopalakrishnan, "Stabilization of α -Nickel Hydroxide in the Presence of Organic Additives: Chemical Route to Bulk Synthesis" *J. Mater. Chem.*, 1993, **3**(12), 1285-87.
11. M. J. Avena, M. V. Vazquez, R. E. Carbonio, C. P. de Pauli, and V. A. Macagno, "A Simple and Novel Method for Preparing $\text{Ni}(\text{OH})_2$. Part I: Structural Studies and Voltammetric Response" *J. Appl. Electrochem.*, 1994, **24**, 256-260.
12. M. Dixit, G. N. Subbanna, and P. V. Kamath, "Homogeneous Precipitation from Solution by Urea Hydrolysis: a Novel Chemical Route to the α -Hydroxides of Nickel and Cobalt" *J. Mater. Chem.*, 1996, **6**(8), 1429-1432.

GENERAL CONCLUSIONS

The primary objective of this research was to investigate the synthesis and characterization of $\text{Ni}(\text{OH})_2$ powders by homogeneous precipitation. Previous research¹⁻³ of the same method showed conflicting results and complete characterization of the particle morphology was not carried out. This study has produced precipitates having a composition of $2\text{Ni}(\text{OH})_2 \cdot \text{Ni}(\text{HCO}_3)_{1.85}(\text{NO}_3)_{0.15}$. The XRD patterns showed peaks commonly observed for $\alpha\text{-Ni}(\text{OH})_2$ ⁴⁻⁶.

The precipitates produced from low and high cation concentration solutions showed that the mean particle size and specific surface area increased with aging time. The increase in mean particle size was disrupted by a drop at around 120 minutes of aging time. A jump in the specific surface area was also observed at around the same time. The occurrence of both phenomenon coincided with the observation of the second nucleation event in the SEM micrographs and the pH vs. time plots. The second nucleation event occurred probably because the generation rate of carbonate and/or hydroxide ions in the solution was higher than its consumption rate in the growth process.

The high specific surface area measured suggested that the particle growth occurred through the aggregation of nanosized crystallites. The TEM micrographs confirmed that the particles were actually aggregates of thin films or sheets that were crumpled and intertwined together. From the XRD line broadening, the crystallite size was calculated to be approximately 9 nm in the (001) direction, corresponding to a specific surface area of 246 m^2/g . This surface area was significantly higher than the measured value of 167 m^2/g or less because the crystallite size measured from the (001) plane might have underestimated the

average crystallite size.

This work also investigated the effect of dispersant on the particle morphology. The addition of dispersants did not alter the density of the particles implying that the dispersants were not incorporated into the solid phase. A general decrease in mean particle size at each aging time was observed resulting in an increase in specific surface area. The use of dispersants provided steric hindrance for the particles in the solution to aggregate, thus smaller particles were observed.

Aging of the precipitates with and without dispersants were carried out in 6 M KOH solution in order to assess the stability of the α -Ni(OH)₂ produced. It was found that the use of dispersants did not affect the aging mechanism. The α -Ni(OH)₂ was completely transformed to β -phase after 2 days of aging. Upon 8 days of aging in KOH solution, the specific surface area values stabilized at around 160-170 m²/g, regardless of the use of dispersants. The increase in surface area was most probably due to the decrease in mean particle size upon aging. The specific surface area obtained for the aged-Ni(OH)₂ above was about 8 times as high as that of a β -Ni(OH)₂ commercially available.

Cyclic voltammetric tests were carried out to see if the high surface area Ni(OH)₂ produced in this work had superior performance characteristics compared to the commercial powders currently available. Indeed, the study showed that the homogeneously precipitated Ni(OH)₂ had higher coulombic efficiency and degree of reversibility than the commercial powders. The efficiency values of all the homogeneously precipitated powders were approximately 90%. The same efficiency values observed were probably due to the same specific surface areas of the powders after aging in KOH solution.

References

1. B. S. Maruthiprasad, M. N. Sastri, S. Rajagopal, K. Seshan, K. R. Krishnamurthy, and T. S. R. P. Rao, "A Novel Nickel Trihydroxy Isocyanate - Preparation and Characterization" *Proc. Ind. Acad. Sci.: Chemical Sciences*, 1988, **100**, 459-462.
2. M. J. Avena, M. V. Vazquez, R. E. Carbonio, C. P. de Pauli, and V. A. Macagno, "A Simple and Novel Method for Preparing Ni(OH)₂. Part I: Structural Studies and Voltammetric Response" *J. Appl. Electrochem.*, 1994, **24**, 256-260.
3. M. Dixit, G. N. Subbanna, and P. V. Kamath, "Homogeneous Precipitation from Solution by Urea Hydrolysis: a Novel Chemical Route to the α -Hydroxides of Nickel and Cobalt" *J. Mater. Chem.*, 1996, **6**(8), 1429-1432.
4. C. Faure, C. Delmas, and P. Willmann, "Preparation and Characterization of Cobalt-Substituted α -Nickel Hydroxide Stable in KOH Medium. Part II. α -Hydroxide with a Turbostratic Structure" *J. Power Sources*, 1991, **35**, 263-277.
5. K. T. Ehlssissen, A. Delahaye-Vidal, P. Genin, M. Figlarz, and P. Willmann, "Preparation and Characterization of Turbostratic Ni/Al Layered Double Hydroxides for Nickel Hydroxide Electrode Applications" *J. Mater. Chem.*, 1993, **3**(8), 883-888.
6. P. V. Kamath, J. Ismail, M. F. Ahmed, G. N. Subbanna, and J. Gopalakrishnan, "Stabilization of α -Nickel Hydroxide in the Presence of Organic Additives: Chemical Route to Bulk Synthesis" *J. Mater. Chem.*, 1993, **3**(12), 1285-87.