



# Lawrence Berkeley Laboratory

UNIVERSITY OF CALIFORNIA

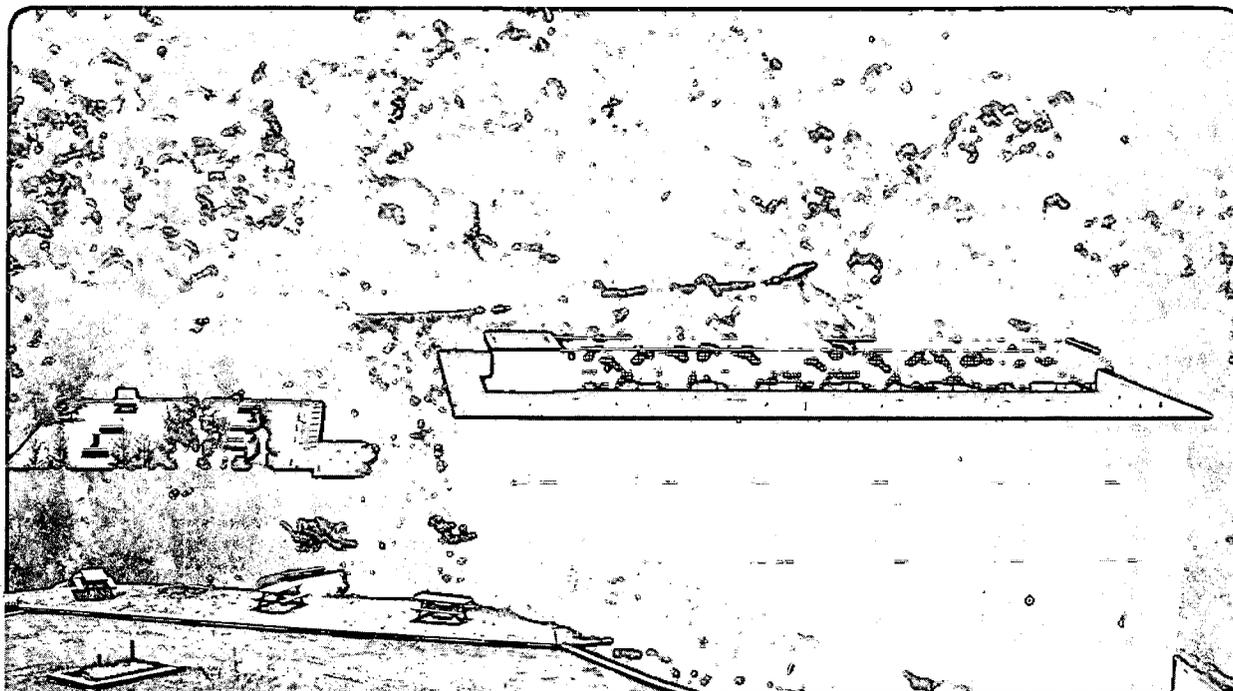
## Materials Sciences Division

Presented at the Electrochemical Society Meeting,  
Toronto, CANADA, October 11-16, 1992,  
and to be published in the Proceedings

### Structural Transformation of Nickel Hydroxide Films during Anodic Oxidation

R.W. Crocker and R.H. Muller

May 1992



REFERENCE COPY |  
Does Not |  
Circulate |  
Bldg. 50 Library.

LBL-32417

#### DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. Neither the United States Government nor any agency thereof, nor The Regents of the University of California, 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 its 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, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or The Regents of the University of California and shall not be used for advertising or product endorsement purposes.

Lawrence Berkeley Laboratory is an equal opportunity employer.

## **DISCLAIMER**

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor the Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or the Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof or the Regents of the University of California.

## **Structural Transformation of Nickel Hydroxide Films during Anodic Oxidation**

Robert W. Crocker  
Rolf H. Muller  
Materials Sciences Division  
Lawrence Berkeley Laboratory  
and Department of Chemical Engineering  
University of California  
Berkeley, CA 94720

### **75 Word Abstract**

Investigation of anodically formed nickel hydroxide/oxy-hydroxide electrodes has determined that the phase boundary between the materials evolves via a nodular structure within the electrode film during the anodic oxidation reaction. This nodular growth mechanism is caused by the disparity in conductivity between the phases. Unconverted material is trapped within the film by an overlayer which forms across the film/electrolyte interface. Scanning tunneling microscopy and spectroscopic ellipsometry experiments support this structure model.

The transformation of anodically formed nickel hydroxide/oxy-hydroxide electrodes has been investigated. The search for the structure evolution of the phase boundary between nickel hydroxide and nickel oxy-hydroxide during the anodic solid-solid oxidation reaction has led to a nodular structure within the electrode film.

In our proposed structural mechanism of the anodic oxidation reaction, illustrated schematically in figure 1, the initial condition for the system is a planar nickel hydroxide film on a nickel metal substrate, immersed in concentrated alkaline electrolyte. (figure 1a) As the film is oxidized, small nodules of nickel oxy-hydroxide form at the metal/film interface. (figure 1b) Experiments by Kuchinskii and Erschler<sup>1</sup> on single grains of nickel hydroxide supported on a platinum pin confirm that the oxidation occurs near the metal current collector.

Since the electronic conductivity of nickel oxy-hydroxide is nearly one hundred times greater than the ionic conductivity of nickel hydroxide, the current density to the tips of the nodules is much greater than to the base. Calculations using typical values of the physical properties indicate that the current density to the peak of a small perturbation is at least twice as great as that to the valley. Under these conditions, the nodules grow rapidly to the film/electrolyte interface. (figure 1c)

The presence of the electronically conducting nickel oxy-hydroxide at the film/electrolyte interface facilitates a competing Faradaic reaction, oxygen evolution. Thermodynamically, oxygen evolution should occur at a lower potential than the nickel oxy-hydroxide formation, at 308 versus 424 millivolts (mercury/mercuric oxide reference). Dyer<sup>2</sup> and others have shown that the nickel hydroxide electrode catalyzes the oxygen evolution reaction. Unfortunately, oxygen evolution is a parasitic reaction to the storage

electrode charging process.

As further oxidation occurs, an overlayer of nickel oxy-hydroxide is created as the reaction boundary between the nickel hydroxide and oxy-hydroxide phases spreads laterally across the film/electrolyte interface. (figure 1c) Optical modeling of spectroscopic ellipsometer measurements provides evidence of the nickel oxy-hydroxide overlayer. The presence of the overlayer inhibits further conversion of nickel hydroxide, leaving pockets of unconverted nickel hydroxide within the film.

Scanning tunneling microscopy of the electrode in its charged state reveals direct evidence of nickel oxy-hydroxide nuclei within the nickel hydroxide film. (figure 2) Experiments show that these nodules disappear upon removal of the film from the nickel metal substrate, and hence, are not merely roughening of the substrate.

The topography of the oxidized films is substantially different from that of the substrates: The surface appears to be strewn with round nodules 30 to 50 Angstroms in diameter with an average separation of 50 to 80 Angstroms. The number density of the nodules is of the order of  $10^{12}$  per square centimeter.

Spectroscopic ellipsometry was employed to take advantage of the significant differences in the optical constant spectra of the nickel hydroxide and nickel oxy-hydroxide materials. Optical models of the film structures were fitted to the measured ellipsometer spectra to interpret the observed changes in the optical measurements. Optical constant spectra of the pure film materials and nickel substrate were determined separately to limit the fitting process to structural parameters only.

Optical models of the film transformation process were developed consisting of four film structure prototypes corresponding to the stages of the

transformation: a pure nickel hydroxide film, pure nickel hydroxide over an effective medium representation of nickel oxy-hydroxide nodules in nickel hydroxide, pure nickel oxy-hydroxide over an effective medium of nickel oxy-hydroxide nodules in nickel hydroxide, and a pure nickel oxy-hydroxide film. These models are illustrated schematically in figure 1.

The films were modeled using Fresnel reflectivities and Drude thin film interference equations. The self-consistent, Bruggemann effective medium approximation is an appropriate representation of the nodule layer since the theory was developed for small ellipsoidal inclusions in a continuous phase. The structural parameters in each model to be fitted were the thicknesses for each pure layer, and volume fraction and thickness for the nodule layer.

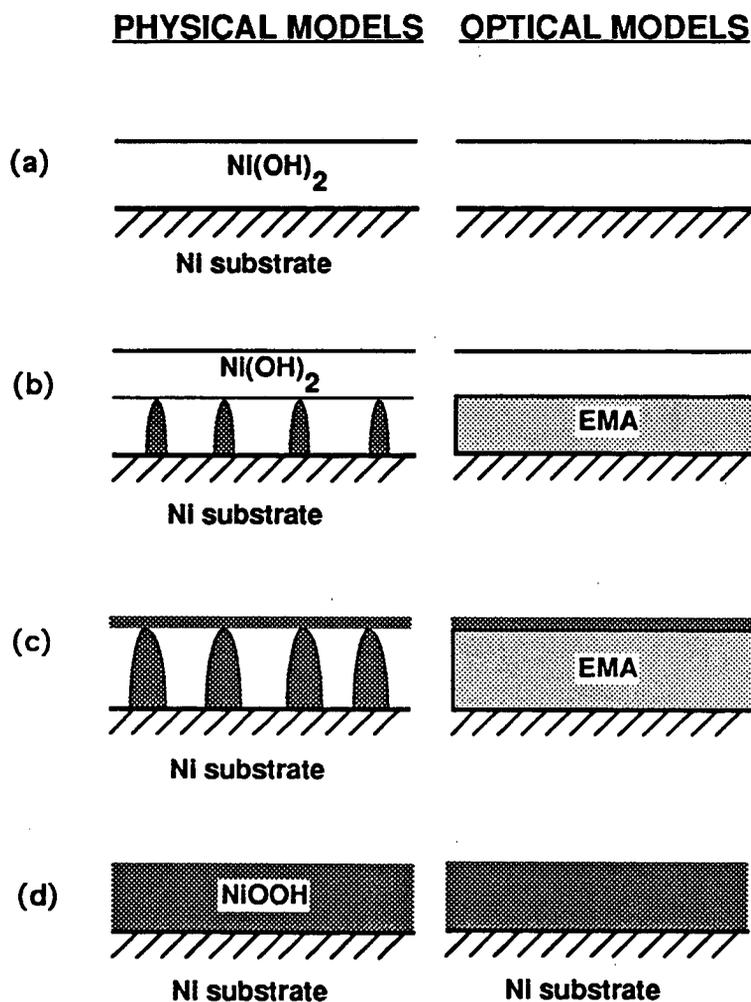
*In-situ* spectroscopic ellipsometer measurements of films held at various constant potentials agree quantitatively with predictions based on optical models of the nodular growth and subsequent overgrowth of the nickel oxy-hydroxide phase. The 16% volumetric contraction of the films during oxidation is consistent with the unit cell measurements of the beta nickel hydroxide and beta nickel oxy-hydroxide phases determined from X-ray<sup>3</sup> measurements in the literature.

In our optical measurements, the nickel oxy-hydroxide overlayer is found only while the potential is held above 500 millivolts versus the mercury/mercuric oxide reference electrode. The overlayer disappears when the oxidized film is allowed to stand at open circuit because of the spontaneous oxidation of hydroxide ions to form oxygen as the uppermost surface of the film is reduced to nickel hydroxide. This reaction is thermodynamically spontaneous by approximately 80 millivolts. The conversion of the uppermost surface to nickel hydroxide hinders transport and restricts the self-discharge reaction. These results are summarized in

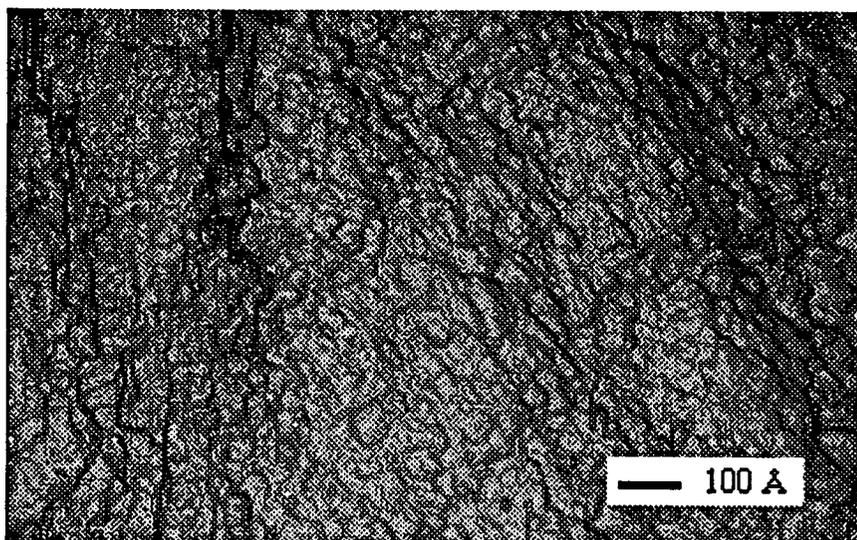
table 1. A comparison between the modeled and measured ellipsometer spectra for the overlayer structure is shown in figure 3.

This work was supported by the Assistant Secretary for Conservation and Renewable Energy, Office of Transportation Technologies, Electric and Hybrid Propulsion Division of the U.S. Department of Energy under Contract No. DE-AC03-76S00098

- 
- <sup>1</sup> E.M. Kuchinskii, B.V. Erschler, J. Phys Chem (USSR) **14**, 985 (1940)
  - <sup>2</sup> C.K. Dyer, J. Electrochem. Soc. **132**, 64 (1985)
  - <sup>3</sup> R.S. McEwen, J. Phys. Chem. **75**, <12>, 1784 (1971)



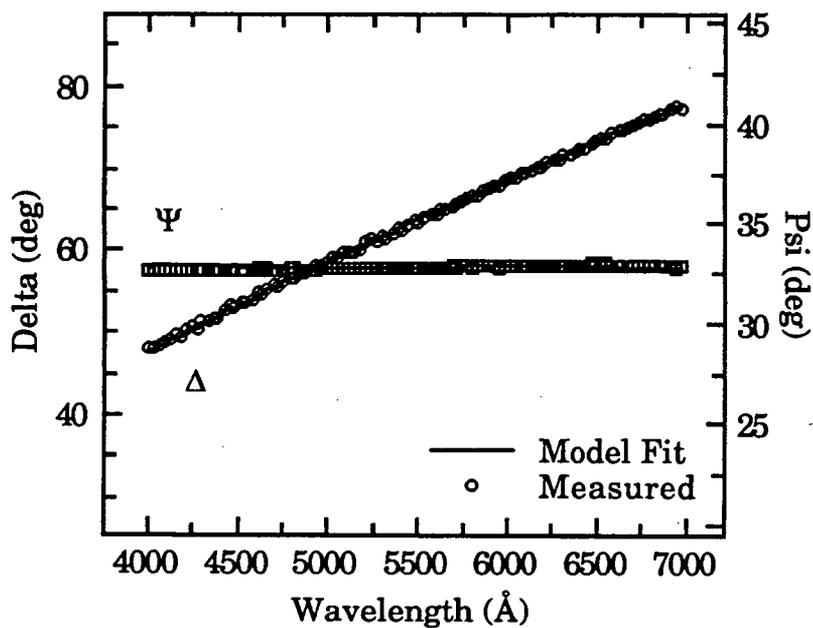
**Figure 1:** Physical and optical models for the anodic oxidation of nickel hydroxide film electrode. (a) Unconverted nickel hydroxide film. (b) Partially oxidized film with nickel oxy-hydroxide nodules below a layer of unconverted material. An effective medium approximation (EMA) was used for the optical properties of the nodule layer. (c) Partially converted film with nickel oxy-hydroxide overlayer shielding the nodule layer from further conversion. (d) Film completely converted by extended potentiostatic oxidation.



**Figure 2:** STM image of nickel oxy-hydroxide nodules within an oxidized nickel hydroxide film electrode on a nickel metal substrate. The nodules are 30–50 Å in diameter. The number density is approximately  $10^{12}$  nodules/cm<sup>2</sup>.

Measurement	1	2	3	4	5	6
Potential [mV]	-250	250	480*	-250	500	-250
Structure Figure	1a	1b	1b	1a.	1c	1a
<b>Nodule Layer</b>						
Thickness		25 Å	72.		98.	
Fraction NiOOH		51%	97%		88%	
<b>Overlayer</b>						
Ni(OH) <sub>2</sub> Thickness	97 Å	65.	8.	122.		123.
NiOOH Thickness					4.4	

**Table 1:** Structures determined by optical model fits to ellipsometer spectra of potentiostatic electrode films. Structures correspond to schematics in figure 1. \*Measurement 3 was made at open circuit after oxidation. Potentials are measured versus the mercury/mercuric oxide reference electrode. Measurements 2 is partially reduced after oxidation.,



**Figure 3:** Comparison of best optical model fit to experimental ellipsometer spectra of electrode film charged at 500 mV vs. HgO. The model corresponds to column 5 in table 1. The film consists of a 98 Å layer having 88%vol NiOOH with an overlayer of 4 Å of NiOOH.

LAWRENCE BERKELEY LABORATORY  
UNIVERSITY OF CALIFORNIA  
TECHNICAL INFORMATION DEPARTMENT  
BERKELEY, CALIFORNIA 94720