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## Technical Note

# Revised EMF-pH Diagram for Nickel\*

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Thermodynamic EMF-pH diagrams currently used for the nickel-water system contain most of the same nickel compounds that are in Pourbaix's atlas.<sup>1</sup> Thermodynamic, spectro-

scopic, and electrochemical characterization studies<sup>2-10</sup> conducted since the original compilation have suggested that some of the compounds, especially those containing nickel with valence greater than two, either do not exist or exist in a different form. The purpose of this note is to present an EMF-pH diagram which contains those nickel compounds which are consistent with the results of the characterization studies.

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**TABLE 1 — Species Considered for Original EMF-pH Diagram<sup>1</sup>**

Component	Free Energy of Formation at 298K (joule/mole)
Ni	0
NiO, Hydrated	-215700
Ni <sub>3</sub> O <sub>4</sub> , Hydrated	-711200
Ni <sub>2</sub> O <sub>3</sub> , Hydrated	-469300
NiO <sub>2</sub> , Hydrated	-214900
Ni <sup>+2</sup>	-48200
HNiO <sub>2</sub> <sup>-</sup>	-348900

Table 1 shows the nickel compounds used in the original diagrams.<sup>1</sup> Hydrated NiO, Ni<sub>3</sub>O<sub>4</sub>, Ni<sub>2</sub>O<sub>3</sub>, and NiO<sub>2</sub> were noted to correspond to Ni(OH)<sub>2</sub>, Ni<sub>3</sub>O<sub>4</sub>·2H<sub>2</sub>O, Ni<sub>2</sub>O<sub>3</sub>·H<sub>2</sub>O, and NiO<sub>2</sub>·2H<sub>2</sub>O.<sup>1</sup> Only two ionic species, Ni<sup>+2</sup> and HNiO<sub>2</sub><sup>-</sup>, were included. Though NiO<sub>4</sub><sup>-2</sup> was not considered, it was placed on the original diagram by Pourbaix.<sup>1</sup> Results from work on the nickel electrode in alkaline solutions has suggested a need to reexamine some of these compounds.

Two forms of Ni(OH)<sub>2</sub>, α and β, have been proposed.<sup>2</sup> On standing in alkaline solutions, the α form may revert to the β form. This latter form is consistent with the hydrated NiO shown in Table 1 and used in the original diagram.

Ni<sub>3</sub>O<sub>4</sub> or Ni<sub>3</sub>O<sub>4</sub>·2H<sub>2</sub>O does not seem to exist as a compound. Novakovskii and Uflyand<sup>3</sup> have compared measured and theoretical equilibrium potentials versus the oxygen to nickel ratio in a nickel electrode. No change in equilibrium potential was found when the ratio was changed from about 1.1 to about 1.45. Significant change in equilibrium potential was found for lower and higher ratios. This finding suggests that a compound with an oxygen to nickel ratio lying between 1.1 and 1.45 does not exist. Since Ni<sub>3</sub>O<sub>4</sub> has a ratio of 1.33, this result suggests that Ni<sub>3</sub>O<sub>4</sub> should not be considered as a unique compound. XRD results have also failed to indicate a structure corresponding to Ni<sub>3</sub>O<sub>4</sub> or Ni<sub>3</sub>O<sub>4</sub>·2H<sub>2</sub>O.<sup>4</sup>

Further work using X-ray diffraction and electron microscopy on the nickel electrode has indicated that in alkaline solutions nickel compounds containing Ni<sup>+3</sup> are βNiO(OH) and γNiO(OH), not Ni<sub>2</sub>O<sub>3</sub>.<sup>4</sup> Most likely βNiO(OH) contains nickel in the +3 state only. γNiO(OH) has been suggested to contain some nickel in a +4 state.<sup>5</sup> The γ form may revert to the β form upon aging.<sup>2</sup>

Nickel oxidation to higher than a +3 state may be possible.<sup>2,5,6</sup> However, X-ray diffraction results have not revealed the structure of the corresponding compounds.<sup>7</sup> They may be related to the NiO<sub>2</sub>·2H<sub>2</sub>O structure proposed by Pourbaix.<sup>1</sup> They are unstable compounds.<sup>7</sup>

The ionic species shown in Table 1 seem to be incomplete. Nickel ion in the +2 state seems to be capable of being hydrolyzed to NiOH<sup>+</sup>, dissolved Ni(OH)<sub>2</sub>, and Ni(OH)<sub>3</sub><sup>-</sup>.<sup>8,9</sup> More complex hydrolyses seem to be possible at high nickel concentrations. This data suggests that HNiO<sub>2</sub><sup>-</sup> should be written as Ni(OH)<sub>3</sub><sup>-</sup>. In addition, the existence of NiO<sub>4</sub><sup>-2</sup> has been questioned.<sup>10</sup> Further work is needed to verify if this ion can, indeed, be formed.

Table 2 shows the compounds that have been considered in the revised diagram. The compounds NiO<sub>2</sub>·2H<sub>2</sub>O and NiO<sub>4</sub><sup>-2</sup> have not been included because of the questions about their existence; however, they may exist. The free energy of formation of NiO(OH) is the average of predictions of Dibrov and Grigor'eva, -334820 joule/mole<sup>11</sup> and Novakovskii and Uflyand, -323950 joule/mole.<sup>3</sup> βNiO(OH) and γNiO(OH) seem to have similar free energies of formation.<sup>11</sup> Thus, NiO(OH) in Table 2 stands for either βNiO(OH) or γNiO(OH).

**TABLE 2 — Species Considered for Revised EMF-pH Diagram**

Component	Free Energy of Formation at 298K (joule/mole)	Reference
Ni	0	—
Ni(OH) <sub>2</sub> SOL (Solid)	-458600	13
Ni(OH) <sub>2</sub> DIS (Dissolved)	-410100	9
NiO(OH)	-329400	See Text
Ni <sup>+2</sup>	-43900	9
NiOH <sup>+</sup>	-224900	9
Ni(OH) <sub>3</sub> <sup>-</sup>	-590200	9

The diagrams calculated from the data in Tables 1 and 2 are shown in Figures 1 and 2 for 10<sup>-6</sup> activity for all ions. The program that generated these diagrams uses the algorithm written by Fronig, *et al*,<sup>12</sup> modified to include subroutines for plotting and for calculations at elevated temperature. Only 25 C was used to construct Figures 1 and 2 since measured heat capacity data is missing for some compounds.

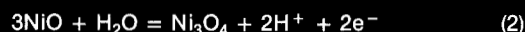
The revised diagram has some new characteristics. Since Ni<sub>3</sub>O<sub>4</sub> is absent, the equilibrium between Ni<sup>+2</sup> and solid Ni(OH)<sub>2</sub> at 25 C extends over the entire region of stability of water. Only one solid compound with Ni(III) is indicated. However, NiO(OH) exists in two forms with similar free energies of formation. This similarity suggests that both compounds may form under nonequilibrium conditions. If so, separated areas of γ NiO(OH) (with possibly some Ni<sup>+4</sup>) and of βNiO(OH) (no Ni<sup>+4</sup>) may arise.

The data shown by Verink<sup>14</sup> suggests that between pH values of 8 and 11, pitting seems to occur at somewhat lower potentials, relative to other values of pH. Though experimental and theoretical EMF-pH diagrams cannot be compared directly, the additional dissolution pathway to dissolved Ni(OH)<sub>2</sub> suggested in the revised diagram may help to explain the above observation. In this pH range, solid Ni(OH)<sub>2</sub> and dissolved Ni(OH)<sub>2</sub> can be in equilibrium. If this pathway results in a lower activation energy relative to formation of other hydrolyzed species, metal loss might be possible at lower potentials.

Sato and Okamoto<sup>15</sup> compared the measured pH dependence of the second arrest potential in 1N H<sub>2</sub>SO<sub>4</sub>,

$$E = 0.48 - 0.060 \text{ pH} \quad (1)$$

where E = potential (volts), to that calculated for the reaction

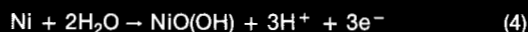


where

$$E = E^\circ - 0.059 \text{ pH} \quad (3)$$

The agreement led them to conclude that Ni<sub>3</sub>O<sub>4</sub> is the passive oxide formed at the second arrest potential even at a pH of about 1. This same conclusion was reached by Latansion and Staehle.<sup>16</sup>

The revised diagram suggests an alternate possibility. One reaction that may be possible under the nonequilibrium conditions of a polarization scan or a potential relaxation is:



This reaction has a potential-pH relationship of

$$E = 0.50 - 0.059 \text{ pH} \quad (5)$$

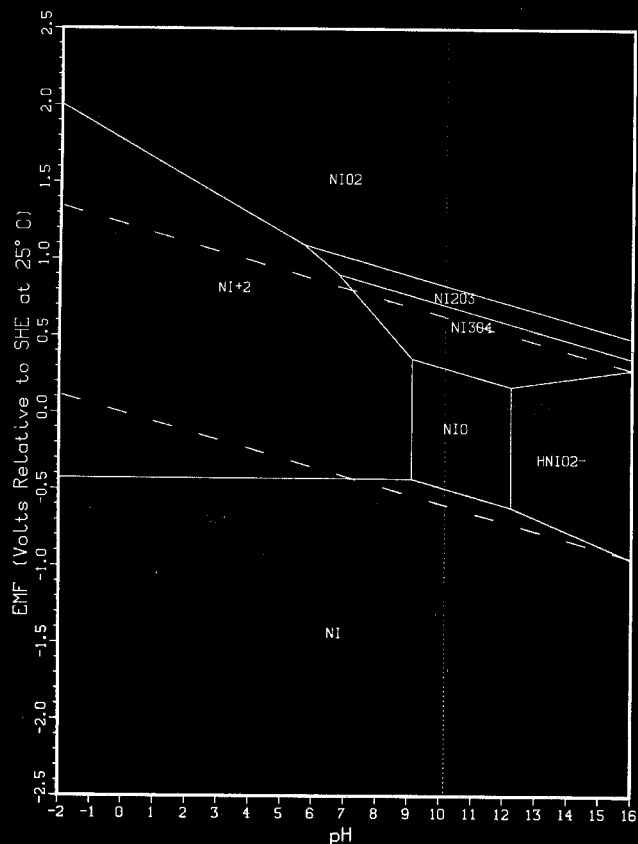


FIGURE 1 — Nickel-water EMF-pH diagram at 25 C using compounds originally considered by Pourbaix (Table 1). All metal containing ionic species are at  $10^{-6}$  activity.

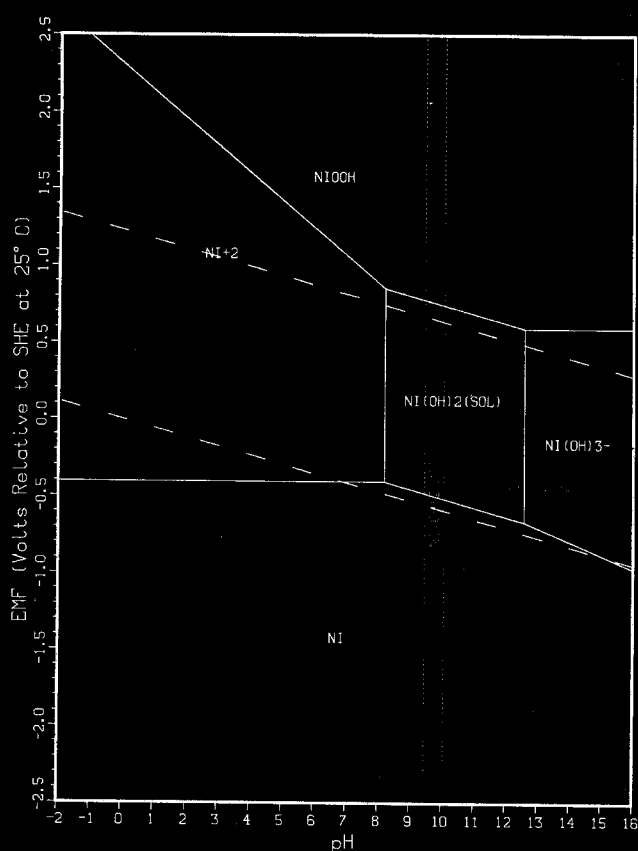
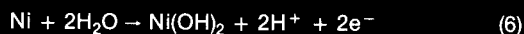


FIGURE 2 — Revised nickel-water EMF-pH diagram at 25 C. All metal containing ionic species are at  $10^{-6}$  activity.

in good arrangement with Equation (1). The revised diagram would suggest that NiO(OH) was the passive oxide that was observed.<sup>15,16</sup> The revised diagram does agree with the first arrest potential corresponding to the reaction:



In addition, note that the revised diagram predicts dissolved nickel to have a valence of +2 to rather high potentials. This prediction agrees with Okamoto, *et al.*<sup>17</sup> At some point, a dissolved Ni(III) ionic species may be formed, but no characterization data is yet available.

The revised diagram is consistent with current results of nickel spectroscopic and electrochemical characterization studies. However, further solid and solution characterization studies are needed especially at higher potentials and lower pH to more completely define the EMF-pH diagram of nickel. Of particular interest are the questions about the existence and properties of higher valent nickel species such as  $\text{NiO}_4^{-2}$  and  $\text{NiO}_2 \cdot 2\text{H}_2\text{O}$  and the role that  $\beta$ - and  $\gamma$ -NiO(OH) might play in nickel passivation.

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