

Letter to the Editors

On the need for a rational nomenclature for the nickel hydroxide electrode

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Nickel hydroxide, $\text{Ni}(\text{OH})_2$, is a very useful material on account of its extensive application in alkaline batteries [1] and electrochromic devices [2]. In the electrochemical literature, the nickel hydroxide electrode is frequently referred to as the 'nickel oxide' electrode [2–6] or even as the 'nickel' electrode [7–9]. This practice is chemically erroneous and often misleading.

In the Ni–O system, the only well-characterized oxide of Ni is the monoxide of Ni(II), NiO. The latter has a rock-salt structure. Unlike the hydroxides of Fe(III) and Cr(III), $\text{Ni}(\text{OH})_2$ is a well-defined compound by itself; it has the hexagonal brucite structure. Nickel hydroxide can by no means be treated as a hydrated form of NiO, such as $\text{NiO} \cdot \text{H}_2\text{O}$. Further, $\text{Ni}(\text{OH})_2$ has a sharp nonhydrogen-bonded OH stretching frequency in its infrared spectrum. This would not be expected of a hydrated nickel oxide such as $\text{NiO} \cdot \text{H}_2\text{O}$. Therefore, it is chemically incorrect to refer to the nickel hydroxide electrode as the 'nickel oxide' electrode.

The electrochemical and electrochromic properties of $\text{Ni}(\text{OH})_2$ arise because of the material's ability to reversibly undergo redox reactions. NiO is not involved in any of these redox reactions. The redox reactions of $\text{Ni}(\text{OH})_2$ take place by a facile intercalation/deintercalation mechanism in which protons and alkali metal ions play a crucial role [10]. Such a mechanism can only be valid in a layered material such as $\text{Ni}(\text{OH})_2$, and would be quite impossible in a compact three-dimensional material such as NiO.

There is now increasing evidence that the charged form of the nickel hydroxide electrode, traditionally characterized as $\text{NiO}(\text{OH})$, is actually a nearly quadrivalent phase $\text{H}_{0.3}\text{NiO}_2$ [11, 12]. Such a material must be referred to as 'nickel dioxide' e.g., by analogy with MnO_2 , manganese dioxide. Earlier literature refers to this black ' $\text{NiO}_2 \cdot \text{aq}$ ' phase as 'nickel peroxide' [13]. This is also incorrect as the use of the term 'peroxide' implies the presence of Ni(II). Compounds of Ni(II) should be green in colour and be electrically insulating while, in fact, the charged form of $\text{Ni}(\text{OH})_2$ is black and has substantial conductivity.

The only difficulty that arises in the comparison of ' NiO_2 ' with MnO_2 lies with the crystal structures. While NiO_2 is layered, many known forms of MnO_2 have the rutile structure. But here again, recent evidence has shown that the rich polymorphism

exhibited by MnO_2 contains many layered phases, such as 'birnessite' [14]. Indeed, it is these layered forms that show electrochemical properties and not the compact rutile counterparts [15].

We have proposed [16] a common reaction scheme for all oxide electrodes in alkaline media to spell out this analogy. We suggest that the charged form of the nickel hydroxide electrode should be referred to as 'nickel dioxide', and the reference to any of these phases as 'nickel oxide' should be discontinued.

The ambiguous nomenclature presently prevalent has created significant confusion. Belanger and Laperriere [17] have studied the interaction between $\text{Ni}(\text{OH})_2$ and an anodic deposit from $\text{Mn}(\text{CH}_3\text{COO})_2$ which they refer to as $\text{Mn}(\text{OH})_2$. The cathodic and anodic reactions of nitrates and acetates have been discussed by Switzer [18]. Cathodic reduction of the anion yields the corresponding metal hydroxide, while the anodic oxidation of $\text{Mn}(\text{II})$ yields MnO_2 . To refer to this as $\text{Mn}(\text{OH})_2$ is incorrect and this confusion, we believe, arises partly from the absence of a rational and commonly-accepted nomenclature for these phases in the electrochemical literature.

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