



# Determination of the “NiOOH” charge and discharge mechanisms at ideal activity



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## ABSTRACT

Optimization of electrodeposition conditions produced Ni(OH)<sub>2</sub> deposits chargeable up to  $1.84 \pm 0.02$  e<sup>-</sup> per Ni on and the resulting nickel oxide/hydroxide active material could subsequently deliver  $1.58 \pm 0.02$  e<sup>-</sup> per Ni ion (462 mA h/g) over a potential range <0.2 V. The ability of the “NiOOH” active material to deliver an approximately ideal charge and discharge facilitated a coulometric and thermodynamic analysis through which the charge/discharge mechanisms were determined from known enthalpies of formation. The (dis)charge states were confirmed with *in situ* Raman spectroscopy. The mechanisms were additionally evaluated with respect to pH and potential dependence, charge quantities, hysteresis, and fluoride ion partial inhibition of the charge mechanism. The results indicate that the “NiOOH” (dis)charges as a solid-state system with mechanisms consistent with known nickel and oxygen redox reactions. A defect chemistry mechanism known for the LiNiO<sub>2</sub> system also occurs for “NiOOH” to cause both high activity and hysteresis. Similar to other cation insertion nickel oxides, the activity of the “NiOOH” mechanism is predominantly due to oxygen redox activity and does not involve the Ni<sup>4+</sup> oxidation state. The “NiOOH” was produced from cathodic electrodeposition of Ni(OH)<sub>2</sub> from nickel nitrate solutions onto highly oriented pyrolytic graphite at ideal electrodeposition current efficiencies and the deposition mechanism was also characterized.

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## 1. Introduction

Nickel oxides have been the dominant cathode material for secondary batteries over many years and Li-ion batteries have only recently emerged as a superior alternative due to their higher energy densities. Still, batteries with nickel oxide cathodes have several features that are superior to Li-ion batteries with regards to higher power densities, non-flammable electrolytes, and less costs [1,2]. In practice, the nickel oxide material is the limiting electrode for energy density in the battery with an activity of 0.4 e<sup>-</sup> per Ni ion or 115 mA h/g Ni(OH)<sub>2</sub> [2,3]. Nickel oxide materials have been reported in the literature to reach high activities of up to 1.65 e<sup>-</sup> per Ni ion or 475 mA h/g Ni(OH)<sub>2</sub> yet this higher performance has never been realized in practical batteries [2–4]. An improvement in the energy density of nickel oxides by a factor of 3–4 could restore interest in this battery material. Both the highly active nickel oxide mechanisms and the mechanisms for producing the highly active nickel oxide materials are further investigated here in order to facilitate the practical implementation of more active nickel oxide materials.

Recent developments in spectroscopic analysis, theoretical modeling, and the analysis of nickel oxide materials in Li-ion batteries challenge the conventionally assumed nickel oxide mechanism in aqueous conditions and indicate that the mechanism needs revision. The conventionally assumed mechanism for the energy producing reaction in nickel oxide/hydroxide batteries is based upon the oxidation of nickel ions from Ni<sup>2+</sup> to Ni<sup>4+</sup> [3,5]. The only evidence specifically supporting the Ni<sup>4+</sup> state is the similarity in the first Ni–O bond length or Ni K-edge shift energy observed though X-ray absorption studies [6–10]. The actual Ni<sup>4+</sup> valence state has been conventionally thought to occur in the fully oxidized γ-NiOOH state because of the X-ray adsorption experiments in which BaNiO<sub>3</sub> or KNiO<sub>6</sub> reference materials were assumed to represent an actual Ni<sup>4+</sup> state. These materials were originally assumed to contain nickel in the Ni<sup>4+</sup> valence state because there was reasonable confusion between the formal and actual valence states at the time [11]. A formal oxidation state of Ni<sup>4+</sup> includes the possibility that the actual valence state is Ni<sup>3+</sup> because oxidation of oxide has occurred. It has now been well-established (even by some of the same authors, O’Grady and Mansour) from Mössbauer, magnetic susceptibility, and X-ray photoelectron spectroscopy (XPS) experiments that the BaNiO<sub>3</sub> or KNiO<sub>6</sub> reference materials (as well as Li<sub>(1-x)</sub>NiO<sub>2</sub> and γ-NiOOH) all have the same

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$D_{5d}$  space group symmetry involving a  $Ni^{3+}$  which has been somewhat distorted due to the oxidation of some  $O^{2-}$  [12–18]. XPS experiments specifically indicate that nickel is  $Ni^{3+}$  in  $\gamma$ -NiOOH and not  $Ni^{4+}$  [19–22]. The uncertainty involved with Jahn-Teller distortions causes the modeling of nickel oxide structures and bond lengths alone to be insufficient for determining nickel oxidation states despite the numerous attempts to do so [14,15,18].

Recent experiment and theoretical modeling of the  $Li_xNiO_2$  electrode in lithium batteries has also indicated that oxygen redox chemistry is primarily responsible for the charge storage instead of the oxidation of nickel ions to the 4+ state [16,18,23–26]. The oxygen redox chemistry occurs when electron vacancy forms on  $O^{2-}$  instead of on  $Ni^{3+}$  and so the nickel ions are not being oxidized to an actual  $Ni^{4+}$  valence state. Similarly, the electron vacancies in  $Li_xNi_{(1-x)}O$  also occur on oxygen species to form  $O^-$  plus  $Ni^{2+}$  when  $X < 0.4$  and the electron vacancy only shifts to nickel to form  $O^{2-}$  plus  $Ni^{3+}$  as  $X$  approaches the 0.5 of  $LiNiO_2$  [17,27–30]. It should therefore be expected that the aqueous “NiOOH” mechanism involves oxygen redox activity instead of the actual  $Ni^{4+}$  state. A more thorough and comprehensive review and analysis of the “NiOOH” mechanism is available online in the Supporting Information section. We develop a new mechanism for the charging mechanism of nickel oxide materials which is consistent with both our experimental results and the literature. This mechanism incorporates the oxygen redox activity caused by electron vacancies on oxide species. A better understanding of oxygen redox center formation and stabilization could lead to better battery active materials regardless of whether it is a  $H^+$ -insertion system of an aqueous battery or a  $Li^+$ -insertion systems of a  $Li^+$  ion battery.

“NiOOH” in its most active form is expected to constitute the optimal condition for mechanistic analysis. Minimizing the presence of side reactions will improve the resolution in the thermodynamic analysis and minimizing the presence of inactive states will improve the clarity of spectroscopic analysis. The oxidation of  $Ni(OH)_2$  produced from cathodic electrodeposition from nickel nitrate solutions has resulted in the highest “NiOOH” activity (1.65  $e^-$  per Ni ion) reported in the literature and will therefore be implemented here [4]. The cathodic electrodeposition of  $Ni(OH)_2$  from nickel nitrate and other nickel solutions is likely more complex than the conventional mechanism typically presupposed in the literature because of the multiplicity of possible reaction pathways. The five reactions of Table 1 collectively cause the four different mechanisms (i–iv) below through which  $Ni(OH)_2$  can be cathodically deposited.  $Ni(OH)_2$  electrodeposition mechanisms (i) and (ii) have been previously proposed in the literature. It is not likely that electrodeposition mechanisms (i) and (ii) can achieve ideal electrodeposition current efficiency because they depend upon the chemical precipitation of  $Ni(OH)_2$  from  $OH^-$  concentration gradients. The observation that the most highly active nickel oxide materials are produced under the condition of ideal electrodeposition current efficiency motivates the re-evaluation of the electrodeposition mechanism and the introduction of mechanisms

(iii) and (iv) [4]. The characterization of the cathodic electrodeposition mechanism is relevant for explaining why deposits of  $Ni(OH)_2$  with optimum activity as “NiOOH” can only be produced in a relatively narrow range of conditions as well as why the limited conditions may be challenging for practical implementation in batteries.

- i. The  $OH^-$  gradient generated by the electrochemical reduction of  $NO_3^-$  through (1) chemically precipitates  $Ni^{2+}$  as  $Ni(OH)_2$  according to (2) in an 1  $Ni(OH)_2$  per 2  $e^-$  ratio [4,31–33]. The further reduction of  $NO_3^-$  to either  $N_2$  or  $NH_4^+$  can also electrochemically generate a pH gradient, both with an additional 2  $Ni(OH)_2$  per 3  $e^-$  ratio [34].
- ii. The reduction of water to form molecular hydrogen,  $H_2$ , according to reaction (3) is another mechanism which can electrochemically an  $OH^-$  gradient for chemically precipitating  $Ni(OH)_2$  through reaction (2) in a 1  $Ni(OH)_2$  per 2  $e^-$  ratio [5]. This mechanism is a likely mechanism when  $NO_3^-$  is absent from the electrodeposition solution.
- iii. The reduction of  $Ni^{2+}$  to the metallic state  $Ni^0$  according to (4) occurs at relevantly cathodic potentials and leads to two more possible cathodic deposition mechanisms. Water is not electrochemically stable on Ni at moderate potentials and will oxidize  $Ni^0$  to  $Ni^{2+}$  through (4) or to  $Ni(OH)_2$  through (5), depending upon pH [34,35].
- iv. The nitrate ion is such a strong oxidizing agent that it can oxidize  $Ni^0$  even under a large, negative potential bias. The direct coupling of nitrate reduction (1) to  $Ni^0$  oxidation (4) is expected to cause the immediate precipitation of  $Ni(OH)_2$  before either the  $Ni^{2+}$  or  $OH^-$  products could diffuse back into the bulk electrolyte phase and should therefore be expected when ideal electrodeposition current efficiency is occurring.

## 2. Methods

General electrochemical experiments were performed in a Teflon electrochemical cell. A Teflon face plate and corrosion-resistant silicone gasket (McMaster-Carr) exposed a circular, 1 cm diameter (0.785  $cm^2$ ) working electrode surface of highly oriented pyrolytic graphite (HOPG, ZYH grade, Bruker AFM Probes) on the bottom of the chamber. A 2  $cm^2$  HOPG (ZYH grade, K-Tek Nanotechnology) was used in conjunction with a 1.75 cm diameter Teflon face plate for *in situ* Raman experiments. Used HOPG surfaces were removed with (Scotch) tape to expose a new, clean surface. A 30 ga platinum wire (Hauser & Miller) counter electrode was coiled around the tip of a double junction SCE reference electrode (Radiometer Analytical) to be jointly inserted into the cell chamber from the top. The general electrochemical experiments were performed with a Biologic VSP electrochemical workstation while the *in situ* Raman spectroscopy experiments were performed with a Biologic SP200. Raman spectra were collected with Nicolet Almega XR dispersive micro-Raman spectrometer, using 633 nm excitation length and a water immiscible Olympus LumPlanFl 60x objective for collecting the Raman scattered radiation. The *in situ* Raman samples were prepared by electrodeposition onto HOPG from 0.08 M  $Ni(NO_3)_2$  solutions at  $-1.0$  mA/ $cm^2$  for 10 min. The spectra were collected for the first discharge and the second charge in 3 M KOH. The “NiOOH” was initially charged at 20 C, the potential was held constant for approximately 15 min during spectra collection, and the potential was changed between spectra at 1 mV/s. Metallic nickel layers of about 20 nm in thickness were deposited onto HOPG substrates from Techni Nickel HT-2 solutions (Technic Inc.) at 10 mA/ $cm^2$  current density for 5 s.

Masses of the  $Ni(OH)_2$  active material were determined by dissolving samples in 2 ml of 10% weight/volume nitric acid under

**Table 1**  
Eqs. (1)–(5): the reactions of the  $Ni(OH)_2$  deposition mechanisms [32].

$NO_3^- + 2e^- + H_2O \leftrightarrow NO_2^- + 2OH^-$	(1)
$E_0(1) = 0.835 - 0.0592 \cdot pH + 0.0296 \cdot \log([NO_3^-]/[NO_2^-])$	
$Ni^{2+} + 2OH^- \leftrightarrow Ni(OH)_2$	(2)
$\log(Ni^{2+}) = 12.18 - 2 \cdot pH$	
$2H_2O + 2e^- \leftrightarrow H_2 + 2OH^-$	(3)
$E_0(3) = 0.000 - 0.0592 \cdot pH$	
$Ni^{2+} + 2e^- \leftrightarrow Ni$	(4)
$E_0(4) = -0.250 + 0.0296 \cdot \log([Ni^{2+}])$	
$Ni + 2H_2O \leftrightarrow Ni(OH)_2 + 2e^- + 2H^+$	(5)
$E_0(5) = 0.110 - 0.0592 \cdot pH$	

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