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The Synergistic Influences of OH⁻ Concentration and Electrolyte Conductivity on the Redox Behavior of Ni(OH)₂/NiOOH

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The synergistic influences of the OH⁻ concentration and electrolyte conductivity on the redox behavior of NiOOH/Ni(OH)₂ for nickel oxide-coated graphite electrodes are clearly demonstrated by voltammetric and impedance analyses. The increase in the OH⁻ concentration and electrolyte conductivity effectively promote the utilization of active nickel species and the electrochemical reversibility of NiOOH/Ni(OH)₂, indicating the simultaneous involvement of OH⁻ and cations in the redox transition. The upper limit for utilizing Ni oxyhydroxides is mainly determined by the OH⁻ concentration, which is facilely reached by increasing the electrolyte conductivity (adding Na₂SO₄). The synergistic phenomena could be very important in the applications of Ni oxide-based batteries, supercapacitors, sensors, electrochromic devices, and organic synthesis. © 2008 The Electrochemical Society. [DOI: 10.1149/1.2945911] All rights reserved.

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Nickel-based oxyhydroxides in various structures show distinctive electrochemical properties, which are widely studied for several applications, e.g., nickel-based batteries,^{1,2} supercapacitors,³ electrocatalysis in organic synthesis,⁴ sensors,⁴⁻⁶ and electrochromic devices.⁷ To achieve a higher utilization of electroactive species, Ni-based oxyhydroxides were widely investigated in concentrated alkaline media (generally ≥ 1 M MOH, M: Li, Na, K).^{8,9} A model, the so-called Bode diagram,¹⁰ was proposed to clarify the redox transitions among α -Ni(OH)₂, β -Ni(OH)₂, β -NiOOH, and γ -NiOOH. The exact oxidation states of these well-defined oxyhydroxides are unclear, although their structures seem to be clarified. Actually, certain nonstoichiometric intermediates between these well-defined structures were proposed,^{4,11,12} indicating the complicated structures of various nickel oxyhydroxides.

It is well known that an increase in the OH⁻ concentration can effectively promote the utilization of electrochemically active nickel species (estimated from voltammetric charges) and electrochemical reversibility of NiOOH/Ni(OH)₂ (from the peak potential difference),^{8,9} suggesting that this complicated redox reaction involves the exchange of OH-. This action, however, results in an increase in the electrolyte conductivity, probably favoring the redox transition due to an increase in the cation concentration.^{13,14} Recently, the redox transitions among various oxyhydroxides on Ni(OH)₂ ultrathin films were systematically investigated by means of the electrochemical quartz microbalance (EQCM).¹³⁻¹⁸ These studies proposed several redox mechanisms involving the exchange of cations, differing in whether H⁺ or OH⁻ is transferred.¹⁸ However, contrary results were usually found when the mass of nickel oxyhydroxides was varied, ^{14,16,17} probably due to the influences of electronic conductivity of oxyhydroxides and/or the diffusion issues of ionic species involved in the redox transitions. Due to the much higher loading of Ni(OH)₂ for sensors, batteries, supercapacitors, and electrochromic devices than that studied in EQCM, the above issues have to be carefully considered in these applications.

Based on the above viewpoints, the influences of electrolyte conductivity and OH⁻ concentration on the redox behavior of NiOOH/Ni(OH)₂ with significant loading (ca. 0.20 mg cm⁻²) are worth investigating. In this work, the electrochemical reversibility and number of Ni oxyhydroxyl species active to the redox transitions have been demonstrated to strongly depend on the concentrations of OH⁻ and Na₂SO₄. Moreover, the pH window for the redox transition of NiOOH/Ni(OH)₂ has been effectively extended by adding Na₂SO₄ in the dilute NaOH electrolytes. Furthermore, this work demonstrates the enhancement in electrochemical kinetics of the NiOOH/Ni(OH)₂ couple by adding a neutral supporting electrolyte (i.e., Na₂SO₄) into a dilute NaOH media, although this redox transition is invisible in neutral solutions. The above synergistic influences of electrolyte conductivity and OH⁻ concentration on the redox behavior of NiOOH/Ni(OH)₂ could be very important in the wide applications of Ni oxyhydroxides.

Experimental

For NiO synthesis via the modified sol-gel method,19 NiCl₂·xH₂O precursors were dissolved and agitated in a solution with equal volumes of water and ethanol to form organometallic species at room temperature for 0.5 h. A 1 M NaOH solution was then added into the stirred solution until nickel oxide precipitates were clearly found (\approx pH 10). Nickel oxide precipitates could be easily obtained by means of a centrifuge, which was washed with pure water several times until the pH was close to 7. The precipitates were dried in a vacuum oven at room temperature for 8 h and then annealed in air at 400°C for 1 h. The annealed oxide powders were well dispersed in pure water in an ultrasonic bath for 20 min and dropped onto pretreated graphite substrates without any binder. These electrodes were dried in a vacuum oven at 85°C overnight. The loading of NiO, $0.20 \pm 0.03 \text{ mg cm}^{-2}$, is the weight difference before and after the oxide coating, which can be effectively controlled by the number of drops. The graphite substrates were first abraded with ultrafine SiC paper, degreased with acetone and water, then etched in a 0.1 M HCl solution at room temperature (ca. 26°C) for 10 min, and finally degreased with water in an ultrasonic bath. The exposed geometric area of these pretreated graphite supports was equal to 1 cm², while the other surface areas were insulated with polytetrafluorene ethylene coatings.

Electrochemical measurements were performed with an electrochemical analyzer system, CHI 633A (CH Instruments, Austin, TX) in a three-compartment cell. The impedance spectrum analyzer, IM6 (Zahner), with the Thales software was employed to measure and analyze the electrochemical impedance spectra (EIS) data. The potential amplitude of ac was equal to 10 mV; meanwhile, its frequency region was from 0.1 to 100 kHz. Before electrochemical tests, 150 cyclic voltammetry (CV) cycles were performed in 1 M NaOH between -0.15 and 0.7 V (vs Ag/AgCl) for every electrode to obtain the so-called Ni(OH)₂/G electrode (see Fig. 1A). A Ag/AgCl electrode (Argenthal, 3 M KCl, 0.207 V vs standard hydrogen electrode at 25°C) was used as the reference electrode. For convenient comparisons, however, data measured in the electrolytes with different pH values were referred to a reversible hydrogen electrode (RHE). A piece of platinum gauze with an exposed area of 4 cm²

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Figure 1. (A) Cyclic voltammograms of a NiO/G electrode measured at 25 mV s^{-1} in 1 M NaOH for 150 cycles. (B) XRD patterns of NiO powders (1) before and (2) after the CV activation employed in (A). (C),(D) FESEM photographs of a NiO/G electrode (C) before and (D) after the CV activation employed in (A).

was employed as the counter electrode. A Luggin capillary was used to minimize errors due to the potential drop of uncompensated resistance in the electrolytes.

X-ray diffraction (XRD) patterns were obtained from an X-ray diffractometer (Rigaku Miniflex system) using a Cu target (Cu K α = 1.5418 Å) at an angle speed of 4° (2 θ) min⁻¹. The morphologies of annealed NiO and the oxide with electrochemical activation for 150 CV cycles were observed using a field-emission scanning electron microscope (FESEM, Hitachi S4800 type I).

All solutions used in this work were prepared with 18 M Ω cm water produced by a reagent water system (Milli-Q SP, Japan), and all reagents not otherwise specified in this work were Merck, GR. The electrolytes for the electrochemical characterization of Ni(OH)_2/G electrodes were degassed with purified nitrogen gas before measurements and nitrogen was passed over the solution during the measurements. The solution temperature was maintained at 25°C by a water thermostat (Haake DC3 and K20).

Results and Discussion

The XRD pattern shown as curve 1 in Fig. 1B reveals the formation of crystalline NiO through the modified sol–gel synthesis process with annealing in air at 400°C for 1 h. The mean crystallite size of as-prepared NiO is ca. 15.4 nm estimated from the XRD peak (200). The size of the NiO nanoparticles with clear outlines (see Fig. 1C) is between 70 and 30 nm, suggesting a good quality of NiO nanocrystals. After 150 cycles of CV activation (see Fig. 1A), the morphology of the resultant Ni oxide is not significantly changed, suggesting that the 150-cycle CV activation occurs mainly in the solid state (see Fig. 1D).²⁰ A comparison of these scanning electron microscopy images also indicates no mechanical degradation during the 150-cycle CV activation. Moreover, Fig. 1A shows the gradual change in redox responses of a NiO-coated graphite electrode through a potentiodynamic activation process used in this work. The stabilized current density-potential (i-E) responses after the 150-cycle activation indicate the transformation of most NiO into nickel hydroxide [i.e., Ni(OH)2], because very weak diffraction peaks corresponding to NiO are still visible for the activated oxide (see curve 2 in Fig. 1B). The resultant electrode is therefore a socalled nickel hydroxide-coated graphite electrode [denoted as $Ni(OH)_2/G].$ Note that the effect of KOH concentration on the charge storage capability of NiO has been reported by Srinivasan and Weidner.⁸ However, the electrochemical characteristics of Ni(OH)₂/G prepared in this work are believed to be different from their case because their annealed nickel oxide was only stabilized by 25 cycles of CV in 3 wt % KOH (probably between -0.80 and 0.55 V vs saturated calomel electrode at 5 mV s^{-1}). Furthermore, the nickel oxide films used by these researchers were prepared by cathodic deposition with postdeposition annealing at temperatures \leq 450°C for 3 h, which is very different from the Ni(OH)₂/G electrode employed in this work. From a comparison of their CVs and those in Fig. 1A, their oxides were not effectively activated by CV (similar to curve 1 in Fig. 1A), which are not the typical nickel oxyhydroxides discussed in this work.

Figure 2 demonstrates the determinant influence of the NaOH concentration on the utilization and electrochemical reversibility of NiOOH/Ni(OH)₂ on Ni(OH)₂/G, although oxidation of Ni(OH)₂ commences at the same potential (in the RHE scale), suggesting neither super- nor sub-Nerstian responses. Note the decrease in the



Figure 2. Cyclic voltammograms of a Ni(OH)₂/G electrode measured at 25 mV s⁻¹ in (1) 1.0, (2) 0.1, (3) 0.025, and (4) 0.005 M NaOH.

peak potential difference of this redox couple from ca. 600-120 mV with increasing the NaOH concentration from 0.005 to 1.0 M. The voltammetric charge, attributed to the NiOOH/Ni(OH)₂ couple, also increases from 15.65 to 31.48 mC with increasing the NaOH concentration from 0.005 to 1.0 M. The above phenomena should be attributed to the limited OH⁻ availability in a dilute NaOH solution causing an increased concentration polarization. Due to the possible contribution of the oxygen evolution reaction (OER), the cathodic charge integrated on the negative sweeps is used to indicate the utilization of electroactive species. Because the *i-E* responses of curves 1 and 2 completely follow the same trace on the negative sweeps as the potential swept from 1.72 to 1.45 V, most active species should be oxidized into the higher oxidation state on the positive sweeps when the concentration of NaOH is ≥ 0.1 M. This statement is supported by the fact that the voltammetric charges on the negative sweeps of curves 1 and 2 are approximately the same.

utilization and electrochemical reversibility The of NiOOH/Ni(OH)₂ on Ni(OH)₂/G are definitely promoted by adding Na₂SO₄ to the dilute NaOH solutions, revealing the significant influences of electrolyte conductivity (i.e., cations and/or anions). On the positive sweep of curve 1 in Fig. 3A, the oxidation of $Ni(OH)_2$ commences at ca. 1.45 V and the anodic currents are gradually increased with the positive shift in potentials. Because anodic currents are visible on the negative sweep of this curve at potentials positive to 1.52 V, this redox transition is relatively irreversible. This statement is supported by the fact that the cathodic voltammetric charges on the negative sweeps are close to the sum of anodic charges on both positive and negative sweeps of curve 1. On the other hand, when Na₂SO₄ is added into this dilute NaOH solution, the electrochemical reversibility (from the peak potential difference) and utilization of electroactive species are improved simultaneously. Also, the voltammetric charges on the negative sweeps are slightly increased by increasing the Na₂SO₄ concentration in the electrolyte. These results suggest the involvement of cations in the redox transition, which has been found in the concentrated alkaline media through the EQCM analysis.¹

In Fig. 3B, an increase of the Na_2SO_4 concentration in the electrolyte significantly reduces the peak potential difference of NiOOH/Ni(OH)₂ and increases the voltammetric charge, very similar to the *i-E* responses found in Fig. 2. Based on the results and discussion of Fig. 2 and 3, the electrochemical reversibility of NiOOH/Ni(OH)₂ as well as the difference between the anodic peak potential of Ni(OH)₂ and the onset potential of OER depends not only upon the oxyhydroxide microstructures but also on the electrolyte composition. Moreover, a comparison of Fig. 3A and B reveals the synergistic effect by increasing the concentrations of NaOH and Na₂SO₄ on the utilization and reversibility of NiOOH/Ni(OH)₂ for



Figure 3. Cyclic voltammograms of a Ni(OH)₂/G electrode measured at 25 mV s⁻¹ in (A) 0.005 and (B) 0.1 M NaOH with the addition of (1) 0, (2) 0.1, (3) 0.3, and (4) 0.5 M Na₂SO₄.

 $Ni(OH)_2/G$. Note that the redox transition of $NiOOH/Ni(OH)_2$ is invisible in neutral solutions and the corresponding CV curves only represent the pure double-layer charge-discharge behavior. In dilute NaOH solutions, the electrochemical reversibility and number of oxyhydroxyl species active to the redox transitions are significantly enhanced by increasing the concentration of Na₂SO₄. Clearly, this indicates the synergy in utilizing the oxyhydroxyl species as well as in improving the electrochemical reversibility. This effect suggests an upper limit in utilizing active nickel species, which is mainly determined by the OH⁻ concentration. Because Ni(OH)₂ and OH⁻ are main reactants involving the redox process, it is reasonable to observe a critical concentration limit of OH- in utilizing active nickel species. Actually, an increase in the NaOH or KOH concentration also resulting in an increase in the electrolyte conductivity shows the same effect on the electrochemical reversibility and utilization of oxyhydroxyl species. This important finding is that, in dilute alkaline solutions, an increase in the concentration of a neutral species (i.e., Na₂SO₄) exhibits a similar effect of adding NaOH or KOH. This finding emphasizes the importance of electrolyte conductivity (including cations and anions) on the redox behavior of NiOOH/Ni(OH)₂. In addition, the pH window for the redox transition of NiOOH/Ni(OH)₂ has been effectively extended by adding Na₂SO₄ in the dilute NaOH electrolytes.

To clarify the above synergistic effect, the voltammetric responses of a Ni(OH)₂/G electrode measured in 0.449 M NaOH and 0.025 M NaOH with 0.9 M Na₂SO₄ ($\Lambda \sim 78$ mS cm⁻¹) are shown in Fig. 4 as curves 1 and 2, respectively. For a comparison purpose,



Figure 4. Cyclic voltammograms of a Ni(OH)₂/G electrode measured at 25 mV s⁻¹ in (1) 0.449 and (2) 0.025 M NaOH with 0.9 M Na₂SO₄, and (3) 0.1 M NaOH with 0.5 M Na₂SO₄.

the CV measured in 0.1 M NaOH with 0.5 M Na₂SO₄ (Λ ~ 67.2 mS cm⁻¹) is shown as curve 3. Curve 1 reveals the good electrochemical reversibility and high utilization of active species for this Ni(OH)2/G electrode in a relatively concentrated NaOH solution. The electrochemical reversibility and utilization of active species for this electrode become obviously poorer when it is measured in the solution containing 0.025 M NaOH and 0.9 M Na $_2$ SO₄, although the conductivity of both solutions is approximately the same. The voltammetric responses of curves 1 and 3 are almost overlapped in the whole potential region, although the electrolyte conductivity of the solution for curve 3 is lower than that for curve 1. The above results support the statement that the upper limit for utilizing NiOOH/Ni(OH)2 is mainly determined by the OH⁻ concentration. Based on all the above results and discussion, the utilization of active nickel oxyhydroxyl species on Ni(OH)2/G seems to approach a constant (i.e., the upper limit) when the NaOH concentration is ≥ 0.1 M, because the voltammetric charges from the CV curves measured in 1.0 M NaOH, 0.449 M NaOH, and 0.1 M NaOH + 0.5 M Na₂SO₄ are approximately the same. Clearly, an electrolyte of higher conductivity (e.g., 0.1 M NaOH + 0.5 M Na₂SO₄ in comparison with 0.1 M NaOH) significantly enhances the redox kinetics, favoring to reach this limit.

Figure 5A show the EIS measured in 0.025 M NaOH with various concentrations of Na₂SO₄ for a Ni(OH)₂/G electrode. The EIS spectra can be analyzed through a simple circuit model (see Fig. 5B) by assuming that the impedance behavior is dominated by three major processes occurring in the high-, medium-, and low-frequency regions, respectively. The high-frequency impedance arc is attributable to the processes occurring at the oxide–electrolyte interface. This process can be modeled as a double-layer capacitor (C_d) in parallel with an ionic charge–transfer resistor (R_{ict} ; see the mechanisms in Ref. 18) due to the discontinuity at the electrolyte/electrode interface (i.e., ionic conductive in the electrolyte phase and electronically conductive in the solid phase). Following this small impedance arc, there is a relatively large arc (see the inset in Fig. 5A), corresponding to the redox process involving the exchange of OH⁻ and cations, which are simply expressed as follows

$$NiOOH + H_2O + e = Ni(OH)_2 + OH^{-}$$

$$NiOOH + Na^{+} + e = Ni(OH)(ONa)$$
 [2]

The film impedance is attributable to the damping of electron hopping and OH⁻/cation diffusion due to the interparticle discontinuity of nickel oxide primary particulates, which can be modeled as a film capacitor (C_f) in parallel with an electron-transfer resistor (R_{ect}). The finite-length diffusion Warburg behavior (W) ascribes the im-



Figure 5. (A) EIS spectra of a $Ni(OH)_2/G$ electrode measured at 1.51 V in (1) 0.025 M NaOH with the addition of (2) 0.1, (3) 0.3, and (4) 0.5 M Na_2SO_4 ; and (B) the equivalent circuit.

pedance due to highly distributed anion and/or cation diffusion within the oxide.²¹ From a comparison of curves 2–4 in the inset of Fig. 5A, the diameter of both semicircles is significantly decreased with increasing the concentration of Na₂SO₄. Moreover, a similar phenomenon is also found with increasing the OH⁻ concentration, supporting the above viewpoint. In the low-frequency region, the slopes of all spectra are gradually increased up to ca. 80–85°, representing the capacitive-like responses. This pseudocapacitive behavior indicates that the redox reaction of NiOOH/Ni(OH)₂ is facile under such low frequencies. Thus, the electrochemical charge storage/delivery behavior in the low-frequency region can be modeled as a (pseudo)capacitor ($C_{\rm S}$), indicating the capacity of Ni oxy-hydroxides.

Through data fitting, both ionic and electronic charge-transfer resistances are reduced by increasing the conductivity of electrolytes and concentration of NaOH (see Table I). The geometric capacitance is promoted from ca. 6-22 mF cm⁻² by increasing the concentration of NaOH from 0.005 to 0.1 M. The capacitance is further enhanced by increasing the electrolyte conductivity (e.g., an increase from 10.84 to 22.36 mF cm⁻² in the solution containing 0.025 M NaOH and 0.5 M Na₂SO₄). These results indicate the fact that the increases in the conductivity of electrolytes and concentration of NaOH significantly enhance the redox kinetics by reducing both ionic and electronic charge-transfer resistances. Note that the influence of the finite-length diffusion Warburg element is slightly reduced by increasing the concentration of Na₂SO₄ when the NaOH concentration is relatively high (see the data measured from the 0.1 and 0.025 M NaOH solutions). This effect, however, becomes dominant in the very dilute NaOH solutions (0.005 M). Accordingly, the presence of an upper limit for utilizing nickel oxyhydroxyl species is presumably due to the OH⁻ exhaustion at the vicinity of the oxideelectrolyte interface²² as $Ni(OH)_2$ is oxidized into the higher oxidation state. The significant enhancements in the redox kinetics by reducing both ionic and electronic charge-transfer resistances through increasing the conductivity of electrolytes and concentration of NaOH favor reaching this limitation.

Table I. The electrolyte conductivity (A) and best-fitting values of the parameters in the equivalent circuit model shown in Fig. 5B for a Ni(OH)₂/G electrode measured at 1.51 V.

	0.1 M NaOH				0.025 M NaOH				0.005 M NaOH			
Na_2SO_4 Λ (mS/cm)	0 20.8	0.1 33.3	0.3 52.4	0.5 67.2	0 6.91	0.1 22.2	0.3 44.5	0.5 63.4	0 1.29	0.1 16.8	0.3 40.8	0.5 60.0
$R_{\rm S}/\Omega$	4.14	2.498	1.366	1.311	13.53	4.497	2.682	1.741	92.6	4.272	2.196	1.128
$\tilde{C_{\rm dl}}/\mu F$	167.5	294.9	389.5	407.5	120.8	206.7	241.7	347.4	107.6	176.5	230.1	335
α	0.663	0.680	0.666	0.603	0.690	0.689	0.646	0.645	0.766	0.624	0.618	0.592
$R_{\rm ict}/\Omega$	1.308	1.101	0.687	0.434	3.366	1.116	0.680	0.497	33.7	3.776	1.547	1.23
W/DW	8.294	7.253	6.995	6.085	8.527	7.592	7.027	6.668	52.7	42.08	33.38	31.59
$C_{\rm f}/{\rm mF}$	1.851	2.89	3.61	4.917	0.787	2.254	3.894	4.557	0.462	0.522	1.871	1.891
α	0.927	0.942	0.931	0.930	0.912	0.956	0.995	0.944	0.986	0.985	1	0.982
$R_{\rm ect}/\Omega$	5.181	3.463	2.359	1.532	15.49	5.027	2.133	1.793	30.76	25.08	4.671	4.529
$C_{\rm s}/\rm{mF}$	21.86	24.17	25.67	27.8	10.84	18.09	18.84	22.36	6.297	11.51	11.71	11.72
α	0.946	0.959	0.96	0.965	0.923	0.963	0.961	0.973	0.809	0.89	0.902	0.91

Conclusions

There is a synergistic influence of OH⁻ concentration and electrolyte conductivity on the electrochemical reversibility of NiOOH/Ni(OH)₂ and utilization of active nickel oxyhydroxyl species on $Ni(OH)_2/G$. The synergistic phenomenon is attributable to the exhaustion of OH⁻/cations when $Ni(OH)_2$ is oxidized into the higher oxidation states. The upper limit for utilizing Ni oxyhydroxyl species is mainly determined by the OH⁻ concentration. An increase in the electrolyte conductivity, significantly enhancing the redox kinetics by reducing both ionic and electronic charge-transfer resistances, favors reaching this limit.

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