Mechanism Study of Hydrazine Electrooxidation Reaction on Nickel Oxide Surface in Alkaline Electrolyte by In Situ XAFS

Tomokazu Sakamoto,a,∗ Hirofumi Kishi,a Susumu Yamaguchi,a Daiju Matsumura,b Kazuhisa Tamura,b,∗ Akihiro Horib,∗ Yousuke Horiuchi,c Alexey Serov,d Kateryna Artyshekova,c Plamen Atanassov,d,* and Hirohisa Tanaka*a,e

This study introduces a new insight on the mechanism of selective electrooxidation of hydrazine in alkaline media. The catalytic process takes place on nickel oxide surface of a Ni oxide nano-particle decorated carbon support (NiO/C). The catalyst was synthesized by wet impregnation and a liquid reduction procedure followed by thermal annealing. In-situ X-ray absorption fine structure (XAFS) spectroscopy was used to investigate the reaction mechanism for hydrazine electrooxidation on NiO surface. The spectra of X-ray absorption near-edge structure (XANES) of Ni K-edge indicated that adsorption of OH− on Ni site during the hydrazine electrooxidation reaction. Density functional theory (DFT) calculations were used to elucidate and suggest the mechanism of the electrooxidation and specifically propose the localization of electron density from OH− to 3d orbital of Ni in NiO. It is found that the accessibility of Ni atomic sites in NiO structure is critical for hydrazine electrooxidation. Based on this study, we propose a possible reaction mechanism for selective electrooxidation of hydrazine to water and nitrogen taking place on NiO surface as it is applicable to direct hydrazine alkaline membrane fuel cells.© The Author(s) 2016. Published by ECS. This is an open access article distributed under the terms of the Creative Commons Attribution 4.0 License (CC BY, http://creativecommons.org/licenses/by/4.0/), which permits unrestricted reuse of the work in any medium, provided the original work is properly cited. [DOI: 10.1149/2.0571610jes] All rights reserved.

Diversification of fuel is important to enhance the versatility of fuel cells as viable power devices for the next generation. Liquid fuel such as methanol, ethanol, borohydride, formic acid, 2-propanol, dimethyl ether and hydrazine are liquid chemical substances that include hydrogen and are considered an energy source in which hydrogen is an electron carrier. The advantages of liquid fuels include, but are not limited to high energy density and ease of handling at both the energy supply and demand sides. In the case of liquid fuel, simple/existing infrastructure, such as conventional petrol stations, is sufficient as for fuel supply, and while the geographic and temporal gap between energy supply and receipt are being filled this would allow to concentrate and leveraging off energy contribution to the expansion of and market penetration of fuel cell technology.

Direct hydrazine hydrate fuel cells (DHFCs) utilizing an anion exchange membrane have recently attracted attention as a clean power device. Hydrazine contains no carbon and excretes harmless nitrogen and water by theoretical electroreduction and non-platinum group metal (PGM) catalysts such as Fe, Co, and Ni. These catalysts have been demonstrated for both the anode and cathode electrodes as shown in Fig. 1a. The fuel cell vehicle equipped with no PGM as catalysts was demonstrated at SPRing-8 in 2013. We believe this demonstration of DHFCs as a power device contributes to the reduction of CO2 emissions and begins to address the fossil fuel resource problem. If zero CO2 emission fuel cell vehicles (FCVs), are to be deployed using carbon-free liquid fuel, the emissions of CO2 would be associated only with the liquid fuel manufacturing facility side and the measures of reduction of CO2 emission by the transportation sector are being supported by the deployment of Carbon Capture and Storage (CCS) technology in general.

Much effort has been devoted to the development of new Ni-based catalysts for hydrazine electrooxidation for DHFCs.1−4 We have researched Ni-Zn,5 Ni-Co,6,7 and Ni-La,8,9 and other Ni-based binary and ternary catalysts10 for hydrazine electrooxidation and confirmed that alloy effect and synergy effect contribute to increased catalytic activity. This is the case especially for Ni-Zn catalysts, which we have applied to the anode catalyst for anion exchange membrane fuel cell vehicles and accomplished successful test driving using non-platinum group metals for both electrodes.51 This demonstration leads to the need for a better understanding of the mechanism of the hydrazine electrooxidation reaction on a Ni surface. This is important for increased cell performance resulting in a reduction in size and weight of the fuel cell stack. Understanding the mechanism of hydrazine electrooxidation reaction on Ni oxide surface is critically important for the design and deployment of hydrazine hydrate-based fuel cell technology in realistic environment.

In this study, a carbon supported Ni oxide nano-particle catalyst was synthesized. The morphology and structure of the prepared catalyst were characterized by field emission scanning electron microscope (FE-SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), ex-situ X-ray absorption fine structure (XAFS), and X-ray photoelectron spectroscopy (XPS). Based on in-situ XAFS studies and density functional theory (DFT), we propose a possible reaction mechanism for catalyzed hydrazine electrooxidation.

Experimental

Catalyst synthesis.—A carbon supported Ni oxide catalyst was prepared using the impregnation liquid reduction procedure followed by thermal annealing. The catalyst contained 50 wt% total Ni metal on carbon support.12,13 First, 0.5 g of carbon black (Ketjenblack ECP600JD, Lion) was dispersed in deionized water of 0.4 l (>18.2 M cm, Millipore Direct Q 3 UV Water Purification System, Millipore). The aqueous metal nitrate solution made from precursor compounds of Ni(NO3)2·6H2O (98%, Kishida Chemical) and sodium borohydride (Hayashi Pure Chemical Ind., Co., Ltd.) of 6.4 g was injected to reduce the metal precursors. This final solution was rinsed with deionized water. The powder thus obtained was dried at 100°C in vacuum for 10 h. Then thermal annealing was performed at 400°C for 2 h in Ar.

Electrochemical measurements.—Electrochemical measurements were carried out with a conventional three-electrode electrochemical cell. A potentiostat (Als 660a, CH Instruments Inc.)
controlled by a computer and a rotating disk electrode system (Pine Instrument) was used for electrochemical measurements. A glassy carbon electrode (diameter: 5.0 mm) was used as the working electrode, and Hg/HgO (XR440, Radiometer) and platinum were used as the reference and counter electrodes, respectively. All measurements were carried out at 60°C.

The cell test of DHFC was performed under the following condition: the catalyst ink was directly sprayed onto an anionic electrolyte membrane (A201, Tokuyama Corp.) to form both the anode and cathode electrodes with catalyst loading of 2.6 mg cm⁻² and 1 mg cm⁻², respectively. Fe-AAPyr (AAPyr: aminoantipyrine, synthesized by Sacrificial Support Method, developed at University of New Mexico)¹⁴–¹⁹ was used as a cathode catalyst. The prepared MEAs were used as square shaped working electrodes with an area of 2 × 2 cm². The fuel was supplied to the anode at a flow rate of 2 ml min⁻¹. The air was supplied to the cathode at the flow rate of 500 ml min⁻¹. Cell temperature was controlled at 80°C.

**Material characterization.**—FE-SEM (SU8020, Hitachi High-Technologies Corporation) with the voltage acceleration of 3 kV and TEM (JEM-2100, Japan Electron Optics Laboratory Company Limited) with the voltage acceleration of 200 kV was performed to analyze catalyst morphology. The crystal structures of the prepared catalyst were examined using the 0–2θ XRD (RINT 2000, Rigaku) with the Cu Kα source operating at a potential of 40 kV and a current of 450 mA. 2θ diffraction angles ranged from 20° to 80° at 2° min⁻¹. Ex-situ XAFS measurements were carried out with transmission mode at room temperature with a mixture of boron nitride as a binder. XPS measurements were carried out using Ulvac Phi Inc., ESCA 5600 spectrometer with a focused monochromatized Al-Kα radiation (1486.6 eV). Pressure in the analysis chamber was controlled at 10⁻⁶ Pa range. The calibration of binding energy scale was performed with the C 1s line (284.6 eV) from the carbon support.

**XAFS measurement.**—All XAFS analyses were performed using the IFEFFIT suite version 1.2.11 (Copyright 2008, Mathew Newville, University of Chicago, http://cars9.uchicago.edu/ifeffit). All scans were carefully aligned and calibrated using the reference foil to account for any changes in beam energy throughout the course of the experiment. Background subtraction and normalization was performed using the AUTOBK algorithm in Athena (Bruce Ravel, Copyright 2006), a subroutine of IFEFFIT. For Δρ analysis of in-situ XAFS spectra, all XAFS spectra were carefully aligned and normalized over energy range from −30 to 100 eV. Difference spectra were calculated by subtracting the μ of a selected potential as reference. XANES spectrum of NiO/C drying sample has been chosen as reference spectrum.

The in-situ XAFS measurement system and a half-cell were explained in our previous study.²⁰ The working electrode was prepared by coating catalyst ink on carbon paper (CP, GDL 10AA, SGL Technologies GmbH). Hg/HgO (XR440, Radiometer) and Pt coils were used as reference and counter electrode, respectively. During experiments, the electrolyte was circulated by a circulation pump (PST-110, Iwaki). Electrode potential was controlled by a potentiostat (Als 660A, CH Instruments Inc.). In-situ XAFS measurements were carried out in transmission mode at room temperature. Experiments were performed at beamline BL14B1 at the Japan Atomic Energy Agency Facilities, SPring-8 with a Si(111) monochromatized beam in transmission mode.

**Calculation methods.**—Calculations were done with spin-polarized DFT under Kohn–Sham formalism, implemented in Quantum Espresso.²¹ Projector augmented wave (PAW) was used to represent core electrons.²² Exchange–correlation energy functional was expressed by using a generalized gradient approximation by Perdew–Burke–Ernzerhoff (GGA-PBE).²³ This is due to the fact that because of the strong electronic correlations between 3d electrons, a standard density functional theory (DFT) computation cannot give an accurate description of the electron structure of NiO. Electronic correlations were also included in a simple rotationally invariant DFT+U version.²⁴ Plane-wave basis sets were used with energy cutoff of 400 eV. The integration on Brillouin zone was done in 4 × 4 × 1 grid. Surfaces were modeled using four layer slabs for NiO(001). The adsorption structure of the OH molecule is relaxed and the bulk atomic arrangement of the NiO has been fixed to evaluate the most stable structure of the adsorbed molecules. For calculations of OH⁻ ion, total charge in unit cell is −1 (one additional electron).

**Results and Discussion**

**Catalytic activity of hydrazine electrooxidation.**—Fig. 2 shows cyclic voltammogram (CV) profiles for a glassy carbon electrode coated with the prepared catalyst, recorded in 1 M KOH + 0.1 M H₂O₂. For comparison, the same electrode was also used to evaluate a cyclic voltammogram under similar conditions without hydrazine in the alkaline electrolyte. It can be seen that in the presence of hydrazine, a large oxidation peak appeared at −0.95 V, indicating that the prepared catalyst had electrocatalytic activity toward hydrazine oxidation. Hydrogen oxidation anodic peak was not observed in the CV of 1 M KOH in this potential range as shown in Fig. 2b and an onset potential of hydrazine oxidation using the prepared catalyst was near 0 V vs. RHE (V vs. Hg/HgO = RHE + 0.94 V), these results indicate that the prepared catalyst directly oxidizes hydrazine in alkaline electrolyte.

Fig. 3 shows the cell performances of DHFCs using the prepared catalyst as an anode and Fe-AAPyr as cathode with differential concentration of hydrazine in fuel. The DHFCs showed high performance without any precious metals used as catalysts on either anode or cathode. The three I-V profiles have almost the same open circuit potential. The cell performance increases with increased hydrazine concentration in fuel due to improvement of material transportation of hydrazine in the anode catalyst layer.

![Figure 1](image_url)
Characterization.—Fig. 4 shows SEM and TEM micrographs of the prepared catalyst. The secondary electron images (SEI) show the catalyst morphology and backscattered electron images (BEI) in order to detect contrast between areas with different chemical compositions as shown in Figs. 4a and 4b, respectively. Agglomerated particles were not observed by SEM. The TEM image and the high-angle annular dark field scanning TEM (HAADF-STEM) image represent particle diameter on the carbon support in the range from 5 to 10 nm as shown in Figs. 4c and 4d. Both SEM and TEM analysis indicated NiO nano-particles are highly dispersed on the carbon support without agglomeration.

To obtain the crystal structure of the prepared catalyst, XRD analysis was performed. Fig. 5 shows XRD pattern of prepared catalyst. Diffraction peaks were observed at $2\theta = 25, 36, 43, 62, 74, 78^\circ$. The peak at $25^\circ$ is attributed to C(002) and peaks at 36, 43, 62, 74, and 78$^\circ$ are attributed to NiO(111), (200), (220), (311), and (222), respectively. All these peak positions of NiO can be indexed to the face-centered cubic (fcc) crystalline structure of NiO. It can be seen from Fig. 5 that the diffraction peaks are low and broad due to the nano size particles.

Fig. 6 shows X-ray absorption near-edge structure (XANES), extended X-ray absorption fine structure (EXAFS) spectra, and Fourier transforms of EXAFS spectra for Ni K-edge in NiO/C, together with Ni foil, NiO, Ni(OH)$_2$ as reference materials. The XANES and EXAFS data processing involves a normalization/background removal process using a background spline function ($-250$ eV $<$ pre-edge $<$ $-50$ eV, $150$ eV $<$ normalize $<$ $1000$ eV) in the Athena code. Fig. 6a shows absorption spectrum of Ni K-edge in NiO/C is almost consistent with the absorption spectrum of NiO reference. In generally, white line intensity depends on valence of materials. However, white line intensity makes a difference between NiO and Ni(OH)$_2$ of divalent as shown Fig. 6a. It is indicated that white line intensity depends on not only valence of materials but also ligand structure. In the Fourier transforms of EXAFS spectrum, the spectral structures for NiO/C and oxidized Ni (NiO and Ni(OH)$_2$) are similar as shown in Fig. 6c.

Fig. 7 shows XPS spectrum at Ni 2p region of prepared catalyst. The peaks at 850–870 eV and 870–890 eV with a main peak and a satellite peak are attributed to the Ni 2p$_3$/2 and Ni 2p$_1$/2 spin orbit levels of NiO. The main peak of Ni 2p$_3$/2 indicates surface structure is a higher oxidation state than that of NiO.$^{25}$ White line of XANES spectrum of NiO/C is slightly expanded compared with divalent reference materials such as NiO and Ni(OH)$_2$ in high energy region as shown in Fig. 6a. White line of NiO/C is indicated NiO/C partially includes...
higher ingredient than divalent. From these results of both XAFS and XPS measurement, the chemical composition of prepared nano-size NiO particles on carbon contains higher bivalent Ni in surface and NiO in bulk.

**In-situ XAFS study.**—In-situ XAFS study was focused on XANES region of the Ni K-edge to investigate the potential dependence of electronic structure of catalyst surface in dynamics of hydrazine electrooxidation in an alkaline electrolyte. Fig. 8 shows the linear sweep voltammogram (LSV) profiles of prepared catalyst coated on a carbon paper (CP) in 1 M KOH and 1 M KOH + 0.1 M hydrazine hydrate (HH). Absolut value of current by hydrazine oxidation is not agree with that of Fig. 2 which was evaluated by RDE because half-cell was used for in-situ XAFS. The anodic peak in the potential range over −1.0 V are ascribed to hydrazine electrooxidation as shown in Fig. 8. LSV in alkaline electrolyte was accurately analyzed using half-cell for in-situ XAFS. Arrows in the Fig. 8 indicate selected potential values for in-situ XAFS spectra collection.

Figs. 9a and 9b show the XANES spectra for Ni K-edge in the prepared catalyst coated on CP in 1 M KOH and 1 M KOH + 0.1 M HH, respectively. We focused on XANES region which is measured in a short time for in-situ XAFS measurement because generated and accumulated N2 gas on a catalyst layer affects the spectrum in EXAFS region. The XANES data processing involves a normalization/background removal process using a background spline function (−200 eV < pre-edge < −17 eV, 40 eV < normalize < 130 eV) in the Athena code. Figs. 9c and 9d show plot of Δμ at the indicated potentials using NiO/C as the clean reference in 1 M KOH, 1 M KOH + 0.1 M hydrazine hydrate, respectively. The peak intensity of Ni K absorption edge depended on the potential in alkaline electrolyte presence or absence HH as shown in Figs. 9a and 9b. Figs. 9c and 9d indicated difference in XANES spectra is observed at only white line region. The maximum peak intensity of Ni K-edge at each potential shown in Fig. 10 with peak intensity of drying NiO/C coated on CP as a reference to clearly explain the potential dependence.
Potential dependence of white line as shown Figs. 9 and 10 indicates possibility of a change in ligand structure caused by adsorption of OH\(^-\) onto the catalyst surface. The adsorption of OH\(^-\) is thought the oxidatively change. OH\(^-\) adsorbs onto catalyst surface at high potential region, OH\(^-\) desorbs from catalyst surface at low potential region in this experiment. The change in white line intensity was clearly observed from \(-1.2\) V to \(-1.0\) as shown in Figs. 9 and 10. The change in white line intensity is suggested that OH\(^-\) adsorbs onto catalyst surface at higher than \(-1.0\) V, OH\(^-\) desorbs from catalyst surface at \(-1.2\) V. In generally, white line intensity depends on valence value of materials. However, white line intensity makes a difference between materials. White line intensity of Ni(OH)\(_2\) is lower than that of NiO as shown Fig. 6a. This result of ex-situ XAFS well agree with in-situ XAFS which white line intensity was reduced at high potential region. Also, OH\(^-\) is believed to preferentially adsorb onto Ni surface in alkaline electrolyte presence hydrazine due to adsorption energy of OH\(^-\) onto the Ni surface is lower than that of hydrazine.\(^{26-28}\)

We tried specific calculation of adsorption structure using DFT first principle calculation to consider mentioned above hypothesis.

**DFT calculation.**—DFT calculation was used to examine the cause of catalytic activity of NiO for hydrazine oxidation. We compared the electronic state of 3d orbital of Ni in NiO between presence and absence OH\(^-\) onto the surface of NiO. Fig. 11 shows the local density of states (LDOS) of 3d orbital of Ni in NiO at the surface layer. Bandgap of Ni in clean NiO was estimated approximately 3 eV as shown in Fig. 11a. Electronic state of clean NiO was a confirmed insulator material. For confirmation, we calculated LDOS of NiO with desorbed OH\(^-\) in Fig. 11b adding extra electron charge in the unit cell to represent OH\(^-\) ion. Fig. 11b represent the same LDOS as Fig. 11a, so we confirmed that adding extra electron did not change electronic states of NiO and was charged desorbed OH\(^-\) correctly. Meanwhile electronic state in Fig. 11c indicating the conductivity was confirmed at Fermi energy of 3d orbital of Ni in adsorbed OH\(^-\) onto NiO. This result indicated that electronic state of NiO changes from an insulator to a conductive material due to OH\(^-\) adsorption onto the surface.

From these results, we propose a possible reaction mechanism for hydrazine electrooxidation on NiO surface in alkaline media as shown in Figure 12. In the first step, OH\(^-\) adsorbs onto the Ni in NiO surface; in the second step, electron of OH\(^-\) was localized to 3d orbital of Ni in NiO in; in the third step, hydrazine electrochemically reacts with adsorbed OH\(^-\) producing \(\text{N}_2\) and \(\text{H}_2\text{O}\). For confirmation of the proposed reaction mechanism, we evaluated total valance electron of Ni in NiO surface and OH\(^-\) with Bader charge analysis\(^{29}\) as shown in Table I. The results showed that valance electron of Ni and OH\(^-\) increased with OH\(^-\) adsorption. This means that the electron localized at Ni adsorbed OH\(^-\) is consistent with the second step in the reaction mechanism. Furthermore reaction
Figure 11. LDOS of 3d orbital of Ni in NiO. (a) without OH\(^-\), (b) with desorbed OH\(^-\), (c) with adsorbed OH\(^-\) onto the surface of NiO.

Figure 12. Schematic of reaction mechanism of hydrazine electrooxidation on Ni oxide surface.

Figure 13. Comparison of reaction energy of hydrazine oxidation with or without OH\(^-\).

Conclusions

Carbon supported highly dispersive NiO nanoparticle catalyst for hydrazine electrooxidation was synthesized by impregnation liquid reduction procedure followed by thermal annealing. Morphology of the prepared catalyst was observed by FE-SEM and TEM. The bulk and surface structure of the prepared catalyst indicated higher bivalent Ni in surface and NiO in bulk by XRD, XAFS, and XPS analysis. In-situ XAFS study indicated that OH\(^-\) adsorbs onto the catalyst surface at a hydrazine electrooxidation potential. DFT calculations were used to examine the cause of catalytic activity of NiO for hydrazine oxidation. DFT studies indicated that the electronic state of NiO changes from insulator to conductive due to OH\(^-\) adsorption onto the surface. Based on in-situ XAFS and DFT study, we propose a possible reaction mechanism for catalyzed hydrazine electrooxidation.

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