Analysis of local structure of Ru$_{1-x}$Ni$_x$O$_2$ electrocatalytic materials

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Abstract. Nanocrystalline Ru$_{1-x}$Ni$_x$O$_2$ materials were synthesized by a solution method. Local structure around doped Ni atoms was characterized by extended X-ray absorption fine structure (EXAFS) functions obtained from X-ray absorption spectra acquired at Ni-K edge (8333eV). It was found that Ni ions are confined to the Ru site in the RuO$_2$ rutile-type crystal structure, and Ni atoms tend to group by entering neighbouring sites along the body diagonal of rutile lattice. Such a neighbourhood of two Ni atoms may act as an active site for oxygen evolution by promoting simultaneous two electron transfer from the absorbed molecule of water. The refined Ni-O bond distances suggest that oxidation state of Ni ions is between +2 and +3.

1. Introduction

The electrochemistry of oxygen attracts a lot of attention due to its relevance for the efficient energy utilization and energy conversion in the context of polymer electrolyte fuel cells (oxygen reduction) and electrochemical splitting of water (oxygen evolution). Oxygen evolution itself may be regarded as either a desired but kinetically limiting step in the electrolysis of water or as a parasitic process in the chloro-alkali industry during chlorine production. Understanding and thus controlling the electrochemical oxygen evolution is one of the major challenges of current research in electrocatalysis.

The noble metals oxides with rutile crystal structure such as RuO$_2$ or IrO$_2$ exhibit catalytic properties in the electrochemical oxidation of water and can be considered as benchmark electrocatalytic materials for oxygen evolution. [1] In particular, ruthenium oxide has very favorable thermodynamics with respect to electrolytic oxygen generation [2] and further improvement of its catalytic activity may be achieved by changing the strength of metal-oxygen bonds in the vicinity of the surface-electrolyte interface. Therefore, from the viewpoint of a materials chemist, doping by a transition metal would be one of the possible options to improve the material performance. It was reported that heterovalent substitution of Ru in RuO$_2$ structure with Fe [3], Co [4] and Ni [5] improved the electrocatalytic properties of the materials, and Ni substitution yields the most active catalyst in that series. To rationalize the observed effects of transitions elements in the RuO$_2$ host on the enhancement of the electrocatalytic activity and to identify the nature of “active sites” for oxygen generation, adequate information about the local structure of such materials is required.
In this work we examined the local structure in the vicinity of doped Ni cations in the nanocrystalline Ru$_{1-x}$Ni$_x$O$_2$ electrocatalytic materials using X-ray absorption spectroscopy (XAS) data collected at Ni-K edge.

2. Experimental
Ru$_{1-x}$Ni$_x$O$_2$ (x=0.10, 0.30) materials were prepared by a coprecipitation method combined with solvothermal ageing described in ref. [5] followed by the annealing of the obtained amorphous powders at 400°C for 2h in air. In the typical synthesis the solutions containing Ru(NO)(NO$_3$)$_3$(OH)$_2$ (31.4 wt% Ru, Alpha Aesar) and Ni(NO$_3$)$_2$·6H$_2$O in the ethanol - propane-2-ol (1:1) (Aldrich, ACS grade) solvent were introduced dropwise into the aqueous solution of tetramethylammonium hydroxide (25% Alpha Aesar) under constant stirring. The precipitates were subjected to aging in a PTFE lined autoclave at 100°C for 40 h. The powders were separated on the centrifuge, washed several times and treated with H$_2$O$_2$ solution (1%) followed by drying in oven and annealing at 400 °C to obtain nanocrystalline powders. To simulate the conditions in the electrochemical cell, the powder was washed with 0.1M aqueous solution of HClO$_4$ for 12h under constant stirring, rinsed with water and dried. NiTa$_2$O$_6$ reference compound was synthesized by solid state reaction between Ni(NO$_3$)$_2$·6H$_2$O and Ta$_2$O$_5$ heat treated at 1000°C for 24h with one intermediate grinding.

The prepared materials were characterized by powder X-ray diffraction (Bruker D8 Advance diffractometer with Vantec-1 detector and CuKa radiation) and SEM-EDX using Hitachi S4800 scanning electron microscope (SEM) equipped with a Nanotrace EDX detector (Thermo Electron). The X-ray absorption spectra (XAS) were collected in transmission mode using pellets of Ru$_{1-x}$Ni$_x$O$_2$ samples diluted with boron nitride. The dilution factors for each sample were calculated to maximize the edge step, while maintaining at least 10% transmission at both Ru-K edge (22118eV) and Ni-K edge (8333eV) energies. The XAS spectra at Ni-K edge were measured at BL-12C beam line of 2.5GeV ring of Photon Factory (KEK, Japan). The data for etched Ru$_{1-x}$Ni$_x$O$_2$ x=0.3 sample and NiTa$_2$O$_6$ were collected at the X18B beam line of NSLS at Brookhaven National Laboratory (USA).

Data handling and analysis of local structure by full-profile EXAFS function refinement was carried out using IFEFFIT software package with FEFF6.2 library [6]. The model for refinement was generated using structural parameters of an ideal Ru$_2$O$_7$ rutile crystal; the initial structure was allowed to expand isotropically and the values of amplitude, phase shift $\Delta E_0$, and Debye-Waller factors for cations and anions were refined using least squares minimization with $k$-weighting factor equals to 1 and 2. Then the isotropic expansion/contraction was kept only for the first metal-oxygen coordination shell and for the other core metal-oxygen distances, while the distances from the core cation to other cations were allowed to change independently. Evaluation of metal site occupancies in the two nearest coordination shells was done by refinement of an additional parameter linking the amplitude and the degeneracy of the corresponding paths. The data in the range of $k=3$-14Å$^{-1}$ for Ni-EXAFS were used. In the R-space (real space) the ranges of $R=1$-4Å were applied.

3. Results and Discussions
All samples after annealing at 400°C were single phase according to the XRD phase analysis. The unit cell volume decreased with increase of Ni content suggesting formation of Ru$_{1-x}$Ni$_x$O$_2$ solid solutions till x=0.3. The powders with higher concentration of Ni contained NiO as an impurity phase and were not used for further studies. According to EDX analysis, bulk Ni concentration increased consistently with increase of Ni concentration as set by the stoichiometry. However analysis of anodes after electrochemical characterizations revealed selective Ni etching from the materials, and it seemed that stable composition of solid solutions corresponded approximately to x=0.1-0.15.

Figure 1a presents $k^2$-normalized Ni-EXAFS function of NiTa$_2$O$_6$. This compound conforms to the tri-rutile crystal structure, which possesses the same symmetry as rutile (P 4$_2$/mmm), but due to the ordering of Ni and Ta in metal sites the dimension of the unit cell along c-axis becomes tripled. The local environment of cations resembles that of rutile rather closely up to ~6Å, which makes NiTa$_2$O$_6$ compound a convenient reference for analysis of local structure around Ni in RuO$_2$ doped materials.
Figure 1. Fourier transformed Ni-EXAFS functions of (a) NiTa_2O_6; Ru_{1-x}Ni_xO_2 (b) x=0.1; (c) x=0.3 as synthesized and (d) x=0.3 after etching in HClO_4. k-weighting factor equals to 2.

Moreover, the concentration of Ni in the NiTa_2O_6 compound with respect to all metal sites is 33.3%, which is very close to the Ru_{1-x}Ni_xO_2 (x=0.3) oxides with the highest possible concentration of Ni. As one may notice, the k^2-normalized Ni-EXAFS function of Ru_{1-x}Ni_xO_2 (x=0.1) oxide in Fig. 1b resembles the Ni-EXAFS function of NiTa_2O_6 rather closely, which indicates that Ni ions substitute Ru ions in the rutile lattice of RuO_2. However, this situation changes for the oxides with high concentration of Ni. The k^2-normalized Ni-EXAFS function of as-synthesized Ru_{1-x}Ni_xO_2 (x=0.3) material is presented in Fig. 1c. One may see that in addition to the characteristic features of the EXAFS function of rutile crystal, a new feature at 2.8 Å has developed. Although one may anticipate shortening of Ni-Ni distance from 3.09Å typical for metal-metal distances in RuO_2 along c-axis it is still impossible to reproduce the magnitude of the peak based on the rutile structural model. This fact suggests that at high doping level Ni tends to form Ni-rich defects, however at this stage we do not have a solid structural model explaining this new peak in EXAFS function. On the other hand, presence of this structural feature in the Ni-rich compositions seems to be irrelevant for electrochemical performance of the materials. The EXAFS function of the same sample after etching in HClO_4 presented in Fig. 1d clearly shows, that such Ni-rich defects are unstable under the conditions of electrochemical experiment; they dissolve in the acidic solution and only Ni ions incorporated into the rutile lattice remain within the Ru_{1-x}Ni_xO_2 crystallites. Of course, one can not completely rule out that dissolved Ni-rich defects may enhance electrocatalitic activities of the Ru_{1-x}Ni_xO_2 materials by restructuring the surface of the catalyst in the particular favorable way that becomes exposed to the solution after dissolution of the defects. However, dramatic improvement in oxygen evolution achieved by 5-10 at% doping with Ni [5] suggests that it is Ni ions in the rutile host lattice that play the essential role in the electrochemical properties of Ru_{1-x}Ni_xO_2 solid solutions.

To understand the details of the Ni local environment we carried our full profile refinement using Ni-EXAFS function of Ru_{1-x}Ni_xO_2 (x=0.3) material after etching in the acid. The experimental and theoretical EXAFS functions based on the refined model are presented in Fig. 2. The elucidated local structure exhibits two important features: i) the refined value of Ni-O bond distances is 1.98Å, which is considerably shorter than Ni-O distances in NiO (2.09Å) or in NiTa_2O_6 (2.05Å and 2.08Å) suggesting higher average oxidation state of Ni than +2. On the other hand, Ni ions are located in the center of undistorted NiO_6 octahedra even though the Ru environment in the host structure allows to distinguish clearly the difference between apical and equatorial Ru-O bonds (1.94Å and 2.01Å). Such incongruence of Ni and Ru environment in the same lattice may speak against the localized charge on Ni ions since one would expect a Jahn-Teller distortion for the d^9 electronic configuration of Ni^{3+}; ii) the refined occupancies of Ru/Ni sites in the nearest and next nearest metal-metal coordination environments revealed 0.007(100) occupancy by Ni of the neighboring metal site along c-axis characterized by CN=2 and 3.08Å metal-metal distance, while the fraction of Ni in the metal site along the body diagonal of rutile lattice with CN=8 and 3.53Å was found to be 0.25(10). These values deviate significantly from 0.12 value of site occupancy, which should be expected based on the results.
Figure 2. $k^2$-normalized Fourier transformed Ni-EXAFS function of Ru$_{1-x}$Ni$_x$O$_2$ $x=0.3$ material after etching in HClO$_4$ (squares) and theoretical function for the refined structural model (solid line). Inset shows corresponding experimental and calculated spectra in $k$-space. Goodness of the fit $R=0.018$, $k$ range 3.0 – 14 Å$^{-1}$, $R$ range 1-4 Å, amplitude = 0.738, $E_0$=-2.43eV.

Figure 3. Possible arrangements of Ni ions in Ru$_{1-x}$Ni$_x$O$_2$ as suggested by the refined local structures based of the Ni-EXAFS functions.

of chemical analysis of this sample by EDX and indicate that on average each Ni atom is coordinated by two Ru atoms along c-axis of the rutile unit cell and should have two Ni neighbors along body diagonal forming a Ni-rich cluster. Such restrictions allow to propose three types of the most likely arrangements of Ni atoms in these areas. The possible local architecture around Ni ions is presented in Fig. 3. In principle all three types of clusters may be accountable for the catalytic activity of oxygen evolution depending on the particular crystal facet exposed to the solution. One may assume that the catalytic effect of such an arrangement is achieved due to simultaneous transfer of two electrons from one oxygen atom of the absorbed water molecule to two neighboring Ni ions, which would alter the mechanism of the elementary reaction step. However, this idea can not be tested based on the static EXAFS data alone and in situ XANES data for the polarized electrocatalyst – electrolyte interface is further required to validate the hypothesis about the mechanism of electron transfer.

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