Materials Science

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Analysis of local structure in nano-crystalline electrocatalytic materials $Ru_{1-x}Ni_xO_{2-y}$ with different selectivity towards oxygen/chlorine production.

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Introduction

Nanocrystalline RuO_2 based materials doped with 3d metals demonstrate selectivity towards chlorine evolution in the electrolytic chlorine, chlorate and oxygen production [1]. Electrolytic chlorine and chlorate production is the most convenient technology for the generation of these industrially important chemicals, while oxygen forms as an undesired by-product of water electrolysis, resulting in the loss of large fraction of energy. Therefore, control of electrocatalytic properties of the anode materials and their selectivity is of practical importance. However, detailed understanding of nature of "active sites" for both oxygen and chlorine evolution processes is poorly understood due to the lack of structural information for these RuO_2 based materials.

Experimental

$Ru_{1-x}Ni_xO_{2-y}$ (x=0.0-0.3) materials were prepared by a "wet" chemistry method described in ref. [2]. The powders were characterized by XRD and their chemical composition was confirmed by SEM/EDX. The X-ray absorption spectra (XAFS) were collected in the transmission mode using samples diluted with BN and pressed into the pellets of 13mm diameter. The dilution factors were calculated to maximize the edge step, while maintaining at least 10% transmission. The spectrum of x=0.05 material at Ni-K edge was acquired in the fluorescence mode using Lytle detector. The XAFS spectra at Ru-K edge (22118eV) were collected at AR-NW10A beam-line (6.5GeV ring, average current - 530mA, Si(311) monochromator), and Ni-K edge (8333eV) spectra were acquired at BL-12C station (2.5GeV, average current - 380mA and Si(111) monochromator). Ru-K scans extended to $20Å^{-1}$ and Ni-K data extended $15Å^{-1}$. Extraction of EXAFS functions and refinement of local structure was performed by the IFEFFIT package [3]. The k vector for the Fourier transform of spectra was kept in the range of k=3-$18Å^{-1}$ for Ru-EXAFS and k=3-$14Å^{-1}$ for Ni-EXAFS.

Results and discussion

XRD analysis shows that prepared $Ru_{1-x}Ni_xO_{2-y}$ oxides were single phase and lattice parameters were changing linearly with x in the range of $0.0<x\leq0.3$. Comparison of the Ru- and Ni-EXAFS functions (Fig.1a,b) revealed that

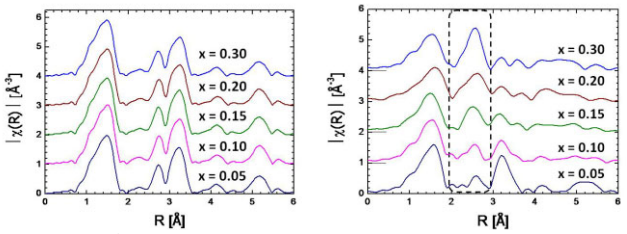

Fig. 1 k^2 normalized EXAFS functions of $Ru_{1-x}Ni_xO_{2-y}$ oxides at (a) Ru-K and (b) Ni-K edges.

the local structure around Ru atoms undergoes little change with increase of Ni content, while rather dramatic evolution of local structure takes place around Ni and new features appear in Ni-EXAFS functions (Fig. 1b).

Full-profile refinement of EXAFS spectra revealed that for $x\leq0.1$ the materials can be described in terms of Ni substitution into Ru site of RuO_2. The deviation of Ni_{Ru} site occupancies from the statistically expected values indicates tendency of Ni towards clustering. For $Ru_{1-x}Ni_xO_2$ materials with x>0.1, one should assume formation of defects with rock salt motif (Fig. 2) to interpret local structure around Ni. Such Ni-rich defects with the architecture similar to shear planes in rutile-based structures and their protrusion on the surface may be possible sites of the electrocatalytic activity in oxygen or chlorine evolution reaction.

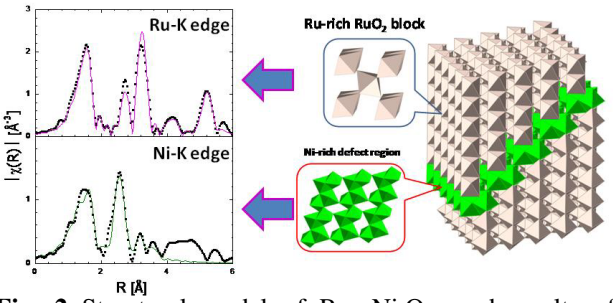

Fig. 2 Structural model of $Ru_{1-x}Ni_xO_{2-y}$ and results of refinement using Ni-EXAFS and Ru- EXAFS for x=0.30.

References

[1] K.Macounova et al., J.Electrochem.Soc. 154, A1077 (2007)
[2] S. Music, et al., Mater.Lett. 58, 1431 (2004).
[3] M. Neville, J.Synchrotron.Rad., 8, 322 (2001).

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