EUROPEAN SYNCHROTRON RADIATION FACILITY

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ESRF

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal (“relevant report”)

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *“preliminary report”),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as “relevant report(s)” in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Operando VtC-XES and HERFD-XANES Studies on the Water Oxidation Mechanisms of Active Metal-Carbodiimides	**Experiment number**: CH-6675
Beamline: ID 26	**Date of experiment**: from: 2023.6.13 at 8 am to: 2023.6.19 at 8 am	**Date of report**: 2023.08.29 *Received at ESRF:*
Shifts: 18	**Local contact(s)**: Pieter Glatzel	

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Report:

Background

Rechargeable metal-air battery can be a promising energy storage device for renewable energy due to its safety, high theoretical energy density and low cost.[1] Electrochemical oxygen catalysis, including oxygen evolution reaction (OER) and oxygen reduction reaction (ORR), plays the critical role in the capacity of metal-air batteries. To develop state-of-the-art metal-air batteries, it is significant to have a deep understanding of catalytic mechanism for OER/ORR, such as the potential structural reconstruction and the real active sites on catalysts.

VtC-XES and HERFD-XANES tests

Our previous experiment results indicate that metal carbodiimides (*M*NCN) can be a promising catalyst for oxygen catalysis. In this experiment at ID 26, valence to core X-ray emission spectroscopy (VtC-XES) and high-energy-resolution fluorescence-detected X-ray absorption near-edge structure (HERFD-XANES) spectroscopy were employed to uncover the subtle change of local geometry and electronic property in cobalt carbodiimide-based catalysts during ORR and OER. Experiments first started from the beam damage test for sample pellets to determine the measurement method. Next, ex-situ VtC-XES and HERFD-XANES spectra of samples, including pellets and electrodes, were recorded. Because of the serious influence from the bubbles caused by beam irradiation and the intense beam absorption from KOH electrolyte, the electrochemical reaction was performed under several potential in a cell for 1 hour in advance, and then the electrodes were dried quickly and measured. VtC-XES and HERFD-XANES spectra of CoNCN loading on oxidized carbon nanotubes (CoNCN/O-CNTs) during ORR and highly/lowly crystalline- (HC/LC-) CoNCN during OER were collected.

Results

The CoNCN/O-CNTs electrode was first investigated under various potential for ORR by HERFD-XANES. As shown in Figure 1(a), with the applied potential decreasing from 1.0 V to 0.5 V, the position of absorption edge does not show obvious change, indicating that the valence state of cobalt center still remains the same. It is noticed that the white line peak has a slight blue shift after contacting the KOH electrolyte possibly due to the absorption of oxygen-contained species on cobalt surface. Two peaks can be observed in pre-edge region. After the subtraction of the background, peak fitting was done for the pre-edge peak (Figure 1(b)). In CoNCN, cobalt center has an octahedral coordination with high spin state ($t_{2g}^5e_g^2$).[2] Because of this centrosymmetric geometry, the direct $3d^7 \rightarrow 1s^1 3d^8$ quadrupole transition is allowed while the dipole transition is forbidden.[3] Moreover, 3d-4p mixing is not allowed in octahedral coordination. Since there are two excited state configurations ($t_{2g}^6e_g^2$ and $t_{2g}^5e_g^3$), the first peak at lower energy can be attributed to the $1s \rightarrow t_{2g}$ transition while the second peak at higher energy can be regarded as the $1s \rightarrow e_g$ transition. In Figure 1(b), after the application of potential, the pre-edge peak position has the negligible change, but the contribution of $1s \rightarrow e_g$ transition shows an upward trend. Considering that there should be only one pre-edge peak at the similar position of $1s \rightarrow e_g$ transition for Co^{2+} with the low spin state theoretically, the average spin state of Co^{2+} in CoNCN/O-CNTs during ORR may decrease. In Figure 1(c), the position of two peaks in $K\beta_{2,5}$ region is similar. Thus, we concluded there is no irreversible phase transition in CoNCN/O-CNTs during ORR.

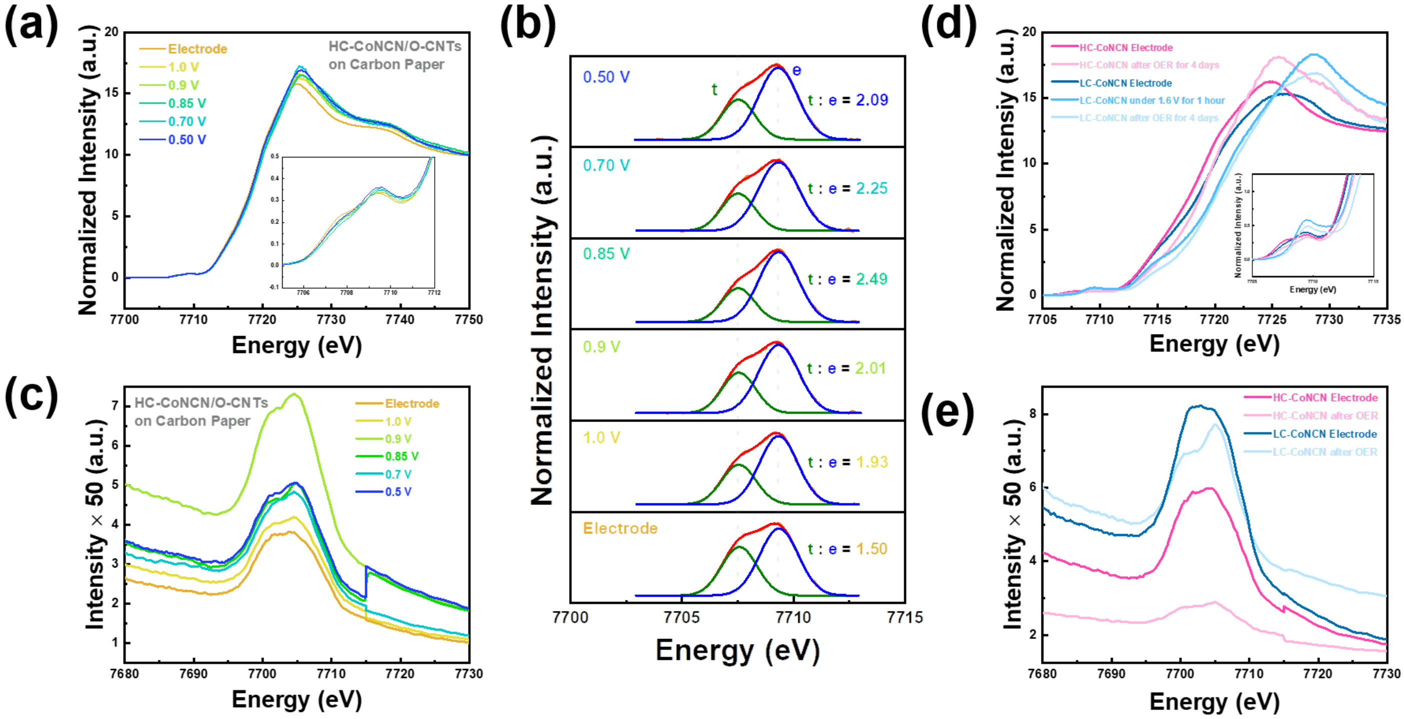

Figure 1. HERFD-XAENS spectroscopy (a), pre-edge peak fitting after background deduction (b), VtC-XES (c) of HC-CoNCN/O-CNTs electrode obtained after various ORR potential; HERFD-XAENS spectroscopy (d) and VtC-XES (e) of pre-/post-catalytic HC/LC-CoNCN electrode.

CoNCN with different crystallinity was also investigated before and after OER. Both of post-catalytic electrodes show a blue shift of absorption edge (Figure 1(d)), revealing an increase of the average valence state of Co. Interestingly, they display the different terminal state after OER according to the position of pre-edge and main absorption edge. While LC-CoNCN shows a remarkable phase transition, HC-CoNCN seems to partially keep the initial component. In VtC-XES region (Figure 1(e)), the shape change and peak shifting in $K\beta_{2,5}$ region demonstrate that both of two catalysts underwent structural reconstruction after OER. To have a clearer answer for some questions, like the exact coordination around cobalt after OER and the contribution of the transition in VtC region, we still need to combine theoretical calculation and other characterization technique.

References

[1] Wang, H.-F.; Tang, C.; Zhang, Q; *Adv. Funct. Mater.* **2018**, 28, 1803329.
[2] Neukirch, M.; Tragl, S.; Meyer, H.-J; *Inorg. Chem.* **2006**, 45, 8188–8193.
[3] Groot, F. de; Vankó, G.; Glatzel, P; *J. Phys.: Condens. Matter.* **2009**, 21, 104207.