

# XANES Study of Sol-Derived [Co-N-C]-based Catalysts for Proton Exchange Membrane Fuel Cells

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## Introduction

There is a major concern regarding how to reduce our environmental footprint. Fuel cells (FCs) are electrochemical devices that convert chemical energy to electrical energy in a clean and efficient manner. Proton Exchange Membrane FCs (PEM) are one of the most promising devices because of their low operating temperature and the potential to produce clean water as the only product, when H<sub>2</sub> is the fuel. Some of the major disadvantages of PEMFCs are their high cost and the slow activity of the Oxygen Reduction Reaction (ORR), which occurs at the cathode. Currently, platinum is used as the active metal in ORR catalysts. However,

it is costly and in limited supply, and thus our research group is developing a low cost sol-derived non-noble metal-based catalyst as a replacement for platinum. The structure of the active site within these catalysts is poorly understood. In order to systematically improve the catalyst activity, and ultimately, to be able to generate the power density levels required for most practical fuel cell applications, an unequivocal determination of the true active site structure is needed. For this purpose, XANES and XPS are the definitive methods of interest.

## Science

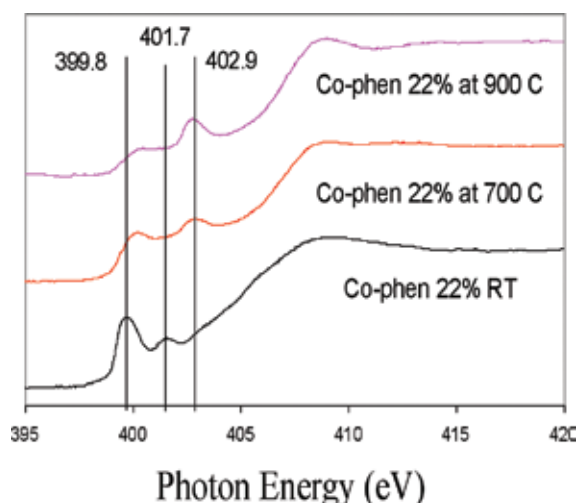
The catalysts were prepared using sol chemistry as follows: CoCl<sub>2</sub>·6H<sub>2</sub>O was dissolved in ethanol, refluxed for 6 hours and then stirred for 18 hours. Then, a 0.5 M phenylene diamine (phen) or a 10% (v/v) ethylenediamine (en) solution in ethanol/ethyl acetate solution was added to the refluxing Co sol mixture over a period of 2 days to give a 2:1 mole ratio of phen/en to Co. Concentrated catalyst samples were prepared by direct application of the solution to 0.25 g dry carbon powder, followed by air drying. The catalysts were then heat treated (HT) for 2 hours at 700 °C or 900 °C in N<sub>2</sub>.

X-ray absorption near edge structure (XANES) experiments of the N and C *K*-edges and Co *L*-edge were carried out using the Spherical Grating Monochromator (SGM) beamline 11ID-1. The spectra were recorded in total electron yield (TEY) using the specimen current.

## Results and Discussion

The absolute calibration of the photon energy was completed using the 1s → π\* transitions of pure gas-phase N<sub>2</sub> (400.8 eV) [1] and monitored over time using the same transition for Cu(NO<sub>3</sub>)<sub>2</sub>, which is located around 401.6 eV. In the case of the Co *L*-edge, the reference signals used along the experiments were the XANES corresponding to Co<sub>3</sub>O<sub>4</sub> and CoCO<sub>3</sub>.

Figure 1 shows the thermal evolution of the N *K*-edge of the Co-phen derived catalysts.



**Figure 1.** Temperature evolution of N *K*-edge of Co-phen derived oxygen reduction catalysts.

There are at least three N 1s → π\* transitions. The resonance at 399.8 eV was assigned to a pyridine-like chemical environment (=N-) [2]. At room temperature, no important changes were expected in the precursor compound, (i.e. Co-phen does not experience any conditions that should change its chemical nature). In principle, Co-phen does not have a pyridine-like N in its structure, but the presence of chelated Co may increase the electron density (or decrease the effective nuclear charge) around the absorbing N. As the temperature of thermal treatment is raised, the lower energy transition shifts to a higher energy around 400.3 eV. This change in energy suggests the formation of an oxidized form of pyridine during thermal treatment, even though this was done under an inert atmosphere. The oxygen source could be oxygen-containing functionalities on the original Vulcan carbon surface, or low levels of oxygen in the N<sub>2</sub> gas. Another explanation for this small shift in energy could be a change of the original interaction of N with Co and/or substrate C atoms.

The signal at 401.7 eV almost disappears with the thermal treatment, and another signal appears at 402.9 eV. This is a clear indication that the presence of the chelated Co in the Co-phen creates a pyridine-like environment around the absorbing N. Based on previous reports [3,4,5], the transition at 402.9 eV corresponds to a pyrrole N (=NH). This suggests the formation of five membered rings after thermal treatment. The absence of transitions between 404 and 405.5 eV is an indication that a quaternary N was not formed during thermal treatment at

high temperatures [5]. All of this information suggests that the N present in the Co-phen derived catalyst is surrounded by 5 and 6 membered rings, but that N is not incorporated into the graphene layer of the carbon support, as was reported by Sidik, et al. [6].

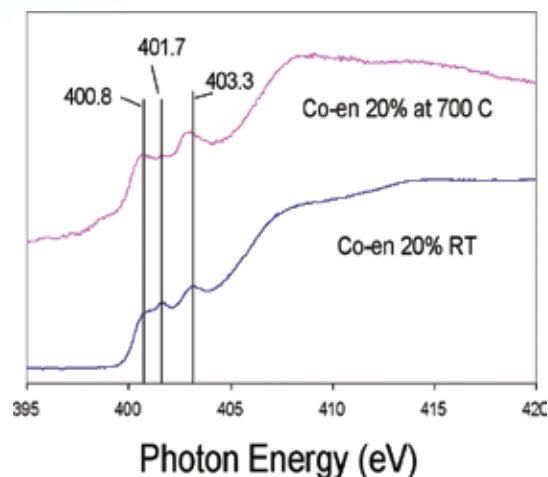


Figure 2. Temperature evolution of N K-edge of Co-en derived catalysts.

The nitrogen XANES of the Co-en derived catalysts (Figure 2) is not pyridinic in character, (i.e. no signal below 400 eV). The resonance at 400.8 eV has been attributed to the chelated Co in a tetraphenylporphine structure [5]. This peak becomes more defined as the catalyst undergoes thermal treatment. The resonance around 401.7 eV almost disappears after thermal treatment. This latter signal, as well as that at 403.3 eV, corresponds to a pyrrole environment. The appearance of both transitions is a clear indication of the pyrrolic nature of the absorbing N in Co-en derived catalysts, even after thermal treatment at 700°C.

Based on these XANES results, it is clear that N in a pyridine-like chemical environment seems to be the active species (or active site) in our sol-derived catalysts.

Figure 3 shows the Co L-edge for the catalysts studied in this work. It is clear that the Co signal for the Co-phen derived catalyst goes through important changes as temperature is increased. At RT, the Co L-edge resonance is similar, with minor differences in intensity and position, to the spectrum of CoO reported in [7]. In the case of the Co-en derived catalyst at RT, the Co L-edge transition has a complex structure but it is shifted as a whole towards higher energies. This suggests that the Co in this sample is in a higher oxidation state or that its electron density is smaller than in the Co present in the Co-phen derived catalysts.

As the temperature increases, the original Co L-edge signal becomes less well resolved, centred primarily around 773.7 eV. Something similar happens with the signal for the Co-en derived catalysts as the temperature is increased. The transition around 774 eV is still defined, even after heat treatment. This energy is similar to that of the intense peak found for Co<sub>3</sub>O<sub>4</sub> and reported previously [7]. Again, not every peak present in

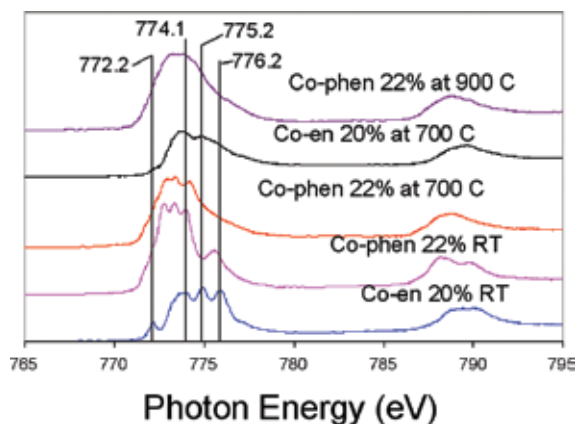


Figure 3: Co L-edge of Co-phen and Co-en derived catalysts.

our reference oxide is present in the Co L-edge transition of the Co-en derived catalysts. This could be an indication that Co in these catalysts may have a chemical environment similar to that in Co<sub>3</sub>O<sub>4</sub>, indicating a possible mixture of Co<sup>2+</sup> (T<sub>d</sub>) and Co<sup>3+</sup> (O<sub>h</sub>).

## Conclusions

These initial experiments have provided a better understanding of the nature of the sites that are active towards oxygen reduction, for application in PEM fuel cells. Moreover, these results will be used in order to select the optimum catalytic materials and conditions in order to carry out *in situ* XANES measurements in the near future.

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