

## XANES Studies on Fe-N-C/Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene as Electrocatalyst for Oxygen Reduction Reaction for Proton Exchange Membrane Fuel Cell

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### Abstract

We found that Fe-N-C catalyst supported on two-dimensional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (MXene, T = -O, -OH, or -F) showed a high activity towards the oxygen reduction reaction. This catalyst contains no precious metals such as Pt and is expected as a next-generation catalyst for fuel cells. By fitting the XANES spectra using those of Fe and Fe oxides, the oxidation states of Fe in Fe-N-C/MXene prepared under different conditions were estimated.

**Keywords:** Fe-N-C/MXene, Fuel Cell Catalyst, Oxidation States, XANES

### Research Background

The wide commercialization of proton exchange membrane fuel cell (PEMFC) as clean energy generation technology has been hindered by the high components cost due to the use of noble Pt catalyst. Recent studies have shown that the abundantly available and low-cost noble-free catalyst of Fe-N-C possess promising oxygen reduction activity, hence has emerged as the potential candidate as alternative catalyst [1]. Yet, its performance in actual PEMFC operation has not achieved the desired target to-date.

The two main challenges in this type of catalysts are the lower intrinsic oxygen reduction activity and the blockage of water on the active sites of the hydrophilic Fe-N-C catalyst that results in rapid performance deterioration. This project is aimed to introduce a novel two-dimensional Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> (MXene, T = -O, -OH, or -F) materials as the support for Fe-N-C, replacing the convention carbon-based support such as graphene.

Despite that XPS can reveal the chemical bonding states, such as Fe-N, Fe<sup>2+</sup> and Fe<sup>3+</sup>, the low attenuation length and large cross-section of Fe 2*p* electron with low Fe composition could lead to lower accuracy on the measurement. In addition, XPS is unable to inform of the local atomic coordination structures of the catalysts which can be in different coordination numbers, such as Fe-N<sub>2</sub> and Fe-N<sub>4</sub> moieties, or other possible metal-metal coordination could reveal more information on the active sites of the catalyst. Hence, employing X-ray absorption near edge structure XANES is a favorable method that can reveal the abovementioned information to provide more insight on the identification of the active sites, thus enable us to further tailor the molecular structure for higher reactivity.

This work is expected to unleash the potential of the novel Fe-N-C/porous MXene as the promising and stable noble-free catalyst for PEMFC. This finding would benefit the fuel cell community in the search for more active and stable Pt-free catalysts to be used in proton exchange membrane fuel cells for clean energy generation using hydrogen fuel, as one promising method in realizing carbon neutral community and more sustainable living.

### Experimental

Samples used are as follows:

1. Fe-N-C (FeNC\_No1)
2. MXene (reference sample, not used for XANES)
3. Fe-N-C/MXene (4:1)  
3 samples with different synthesis conditions, namely FeNC\_No2, FeNC\_No3, and FeNC\_No4.
4. Fe-N-C/MXene (1:1) (FeNC\_No5)

All samples are in powder form. The elemental compositions of the samples were determined via Energy Dispersive X-ray (EDX) analysis and X-ray Photoelectron Spectroscopy (XPS) and their estimated mass compositions are tabulated in Table 1.

**Table 1. Estimated mass compositions on different samples**

Element	Fe-N-C (ZIF) <sup>a</sup>	MXene <sup>a</sup> (reference)	Fe-N-C/Mxene-1 (4:1) <sup>a</sup>	Fe-N-C/Mxene-1 (4:1) <sup>b</sup>	Fe-N-C/Mxene-2 (4:1) <sup>c</sup>	Fe-N-C/Mxene (1:1) <sup>c</sup>
C	70.6	7.6	73.6	70.88	70.88	56.75
Ti	-	40	13.9	7.07	7.07	17.08
O	-	26.3	8.1	14.86	14.86	18.84
Fe	24	-	3.2	1.17	1.17	0.90
F	-	26.1	1.2	1.07	1.07	2.58
N	5.4	-	0.0	4.95	4.95	3.83

### XANES Measurements

To identify the coordination states of Fe in each sample, fluorescence XAFS spectra of Fe K-edge were obtained at the beamline BL14B2 of SPring-8 at room temperature in air on all samples contained in plastic bags.

### Results

Fig. 1 shows the XANES spectra of Fe foil, FeO, Fe<sub>2</sub>O<sub>3</sub> ( $\gamma$ ), and Fe-N-C/MXene (FeNC\_No4). Comparing also the data of the four samples, it was confirmed that the oxidation states of Fe in all Fe-N-C/MXene samples were between 2 and 3.

The XANES data of Fe-N-C/MXene samples were fit with the linear combination of those of Fe metal (Fe foil) and Fe<sub>2</sub>O<sub>3</sub> ( $\gamma$ ) with small R-factors between 0.002 and 0.005 [2,3]. As an example, Fig. 2 shows the fitting result of the spectrum of FeNC\_No1.

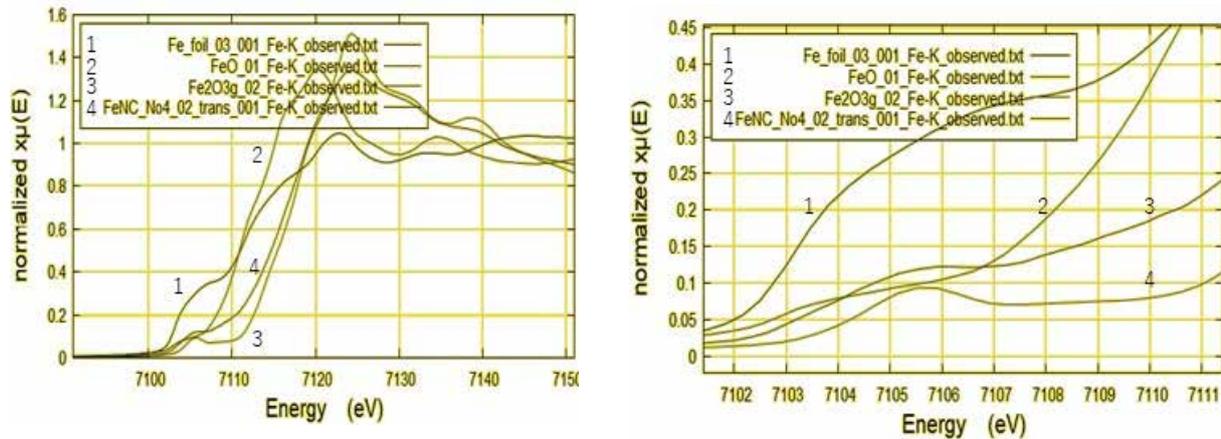


Fig. 1 XANES spectra of Fe (1), FeO (2), Fe<sub>2</sub>O<sub>3</sub> (3), and Fe-N-C/MXene (FeNC\_No4) (4). The onsets were enlarged and shown on the right.

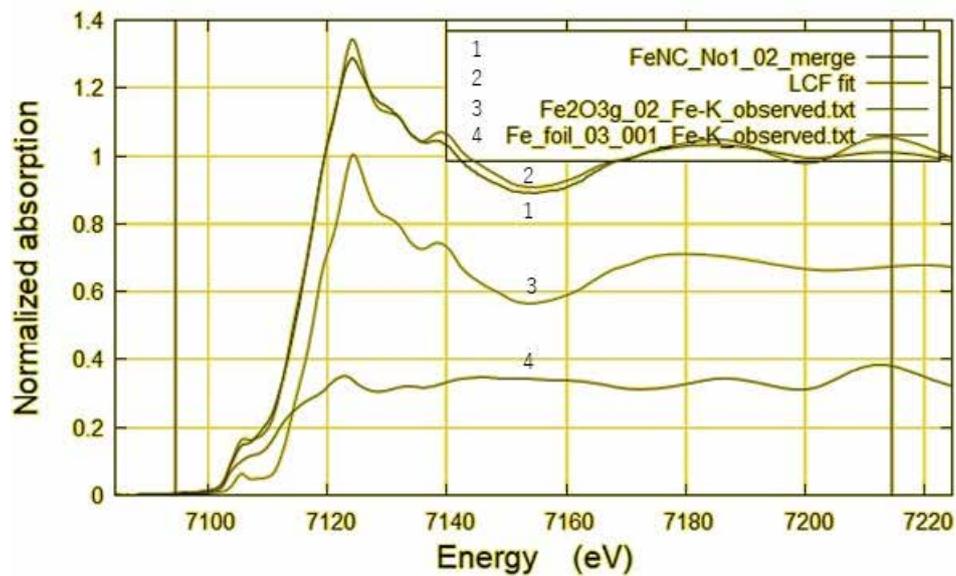


Fig. 2 XANES data of Fe-N-C/MXene (FeNC\_No4) (1), Fe (2), and Fe<sub>2</sub>O<sub>3</sub> (3). The linear combination of the curves of Fe (2) and Fe<sub>2</sub>O<sub>3</sub> (3) is shown as (4), where the averaged oxidation number was 2.32.

From the linear combination of the curves of Fe and Fe<sub>2</sub>O<sub>4</sub>, the averaged oxidation numbers were obtained for the five samples.

- No.1: 1.99
- No.2: 2.18
- No.3: 2.05
- No.4: 2.32
- No.5: 2.34

### Summary and Future Perspective

The XANES data of Fe-N-C/MXene samples were successfully obtained under the ambient conditions. The averaged oxidation numbers were estimated. The in-situ measurements are planned in the future.

### References

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