

## Identification of Fe<sup>3+</sup> single-atom sites for CO<sub>2</sub> conversion to CO using *operando* X-ray absorption spectroscopy

Efficiently converting carbon dioxide (CO<sub>2</sub>) to carbon-based chemicals and fuels presents a promising catalytic approach to reduce the anthropogenic CO<sub>2</sub> emission. To achieve high energy efficiency and scalability, the electroreduction of CO<sub>2</sub> must occur rapidly and selectively at low overpotentials. To date, precious gold (Au) and silver (Ag) have been to be demonstrated the most efficient at low overpotentials, exhibiting a high Faradaic efficiency of carbon monoxide (CO) above 90%. Unfortunately, catalysts composed solely of Earthabundant elements typically have low selectivity for CO production. Recently, many single-atom catalysts have been developed, in which numerous catalytic metal sites, especially iron (Fe), cobalt (Co) and nickel (Ni), were atomically dispersed and coordinated to the conductive carbon support. Although these nonprecious metal catalysts show comparable Faradaic efficiency for CO to those of Au and Ag catalysts, much larger overpotentials are required to obtain the same partial current density  $(j_{CO})$ . Here, we report a catalyst with atomically dispersed Fe<sup>3+</sup> sites with ultrahigh activity at low overpotentials for CO<sub>2</sub> electroreduction to CO.

The Fe catalyst (Fe<sup>3+</sup>-N-C) was prepared through the pyrolysis of Fe-doped zinc (Zn) 2-methylimidazolate framework (ZIF-8) under nitrogen atmosphere at 900°C. To investigate the atomic structures and oxidation states of the asprepared Fe<sup>3+</sup>-N-C catalyst, we have conducted X-ray absorption experiments using SPring-8 BL12B2 beamline [1]. The Fe K-edge X-ray absorption nearedge structure (XANES) spectrum of Fe<sup>3+</sup>-N-C showed the binding and edge energies close to those of Fe<sub>2</sub>O<sub>3</sub> and Fe<sup>3+</sup>TPPCI (tetraphenylphosphonium chloride), indicating that the Fe ions in the catalyst were in the +3 oxidation state (Fig. 1(a)). Moreover, the Fe K-edge extended X-ray absorption fine structure (EXAFS) spectrum supported the atomic dispersion of Fe sites and their planar  $Fe-X_4$  (X = N or C) structures in Fe<sup>3+</sup>-N-C (Fig. 1(b)). The catalytic activity toward CO<sub>2</sub> electroreduction was then evaluated using a gas diffusion electrode in a flow cell. At -0.45 V versus reversible hydrogen electrode (RHE), the Fe<sup>3+</sup>-N-C catalyst exhibited a high  $j_{CO}$  reaching 94 mA cm<sup>-2</sup> with a Faradaic efficiency of CO above 90%. The  $j_{CO}$  for Fe<sup>3+</sup>-N-C measured in an H-cell between -0.2 and -0.5 V versus RHE was also observed considerably high, which even overwhelmed that attained by other previously reported Fe single-atom catalysts. Notably,

the performance of  $Fe^{3+}$ -N-C could be stable between –0.2 and –0.5 V versus RHE, although at potentials more negative than –0.5 V versus RHE, the activity became unstable, indicating some changes in the  $Fe^{3+}$ -N-C around –0.5 V versus RHE.

We further conducted operando XAS experiments using SPring-8 BL12B2, which enabled the precise monitoring of changes in the catalysts under working conditions. Fe K-edge spectra were obtained on dry samples and on samples that were loaded on glassy carbon electrodes and immersed in the electrolyte at various potentials. For Fe<sup>3+</sup>-N-C catalyst (Fig. 2(a)), the Fe K-edge exhibited no obvious shift between the dry powder and the in situ sample at -0.4 V versus RHE, indicating that the Fe ions in Fe<sup>3+</sup>-N-C remained in the +3 oxidation state during CO<sub>2</sub> electroreduction. When the applied potential was shifted further negative, the Fe-edge shifted to lower energies, showing the reduction of Fe<sup>3+</sup> to Fe<sup>2+</sup>. Such reduction process occurred at the same potential as the abovementioned deactivation of Fe<sup>3+</sup>-N-C, implying that Fe<sup>3+</sup> sites were more active for generating CO. Moreover, the fitting of EXAFS spectra indicated that the reduction of Fe<sup>3+</sup> sites was accompanied by a change in local structure, where the first shell coordination



Fig. 1. (a) Fe *K*-edge XANES spectra of Fe<sup>3+</sup>-N-C and reference samples. (Inset) Enlargement of the main edges. (b) R-space Fe *K*-edge EXAFS spectra of Fe<sup>3+</sup>-N-C.

number of Fe was reduced from 4 to about 3. To investigate the origin of the improved activity of Fe<sup>3+</sup>-N-C, we also measured the *in situ* Fe *K*-edge XANES of previously reported single-atom Fe<sub>0.5</sub>d catalyst [2]. It was revealed a +2 rather than +3 oxidation state for the Fe sites under potentials between -0.2 and -0.5 V versus RHE, which might be due to different ligand environments with regard to the N atoms. For those previously reported Fe single-atom catalysts, Fe ions coordinated with four pyridinic N were proposed as the active sites [3]. By a sharp contrast, Fe<sup>3+</sup>-N-C was observed to be coordinated to pyrrolic N, as demonstrated by the N *K*-edge XANES spectrum.

Furthermore, we directly compared the Fe<sup>3+</sup>-N-C with an analogous Fe<sup>2+</sup>-N-C catalyst in which the Fe ions were coordinated by pyridinic N atoms. Fe *K*-edge XANES spectra showed a considerable number of Fe<sup>3+</sup> sites in the as-prepared sample of

Fe<sup>2+</sup>-N-C (Fig. 2(b)). Moreover, the *in situ* Fe K-edge exhibited that Fe<sup>3+</sup> sites in the Fe<sup>2+</sup>-N-C started to be reduced to Fe2+ at -0.1 to -0.2 V versus RHE, and at potentials more negative than -0.2 V versus RHE  $(CO_2 \text{ electroreduction})$ , the energy of the Fe K-edge was slightly lower than that of FeO, suggesting that Fe<sup>2+</sup>-N-C had an oxidation state of +2 or lower under reaction conditions. Correspondingly, the turnover frequency (TOF) of CO production of Fe<sup>2+</sup>-N-C is more than one order of magnitude lower than that of Fe<sup>3+</sup>-N-C under the same potential. The current density of Fe<sup>2+</sup>-N-C decreased markedly during 2 h chronoamperometry tests, indicating its lower stability as compared with the Fe<sup>3+</sup>-N-C catalyst. These data suggest that pyrrolic type ligands are significant to keep Fe sites in the +3 oxidation state during CO<sub>2</sub> electroreduction and consequently maintain the high activity and stability of Fe<sup>3+</sup> sites.



Fig. 2. *Operando* XAS characterization. (**a**, **b**) Fe *K*-edge XANES spectra (left) and the first derivative of the spectra (right) of (a)  $Fe^{3+}$ -N-C and (b)  $Fe^{2+}$ -N-C as dry powder and loaded on glassy carbon electrodes at various potentials.

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