

Changes in Crystal Structure and Battery Performance of MIL-101 (Fe) upon Introduction of Substituent NH₂

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MIL-101 (Fe) (MIL = Matériaux de l'Institut Lavoisier) was used to fabricate MIL-101 (Fe)-NH₂ by replacing the 1,4-benzenedicarboxylate (BDC) ligand with 2-aminoterephthalate (BDC-NH₂), wherein substituent NH₂ was introduced into the crystal structure. Powder X-ray diffraction and Fe K-edge X-ray absorption fine structure (XAFS) studies revealed that MIL-101 (Fe) had a crystal structure different from that of MIL-101 (Fe)-NH₂, and the local structure around the Fe ion in their bulk did not change. However, Fe L-edge XAFS studies revealed that the Fe ions on the surface of MIL-101 (Fe) were reduced, indicating that the change in electronic structures on the surface could affect the electrochemical properties of MIL-101 (Fe). Charge–discharge measurements of lithium-ion batteries, with either MIL-101 (Fe) or MIL-101 (Fe)-NH₂ as the positive electrode active material, showed that batteries with MIL-101 (Fe)-NH₂ electrodes had a higher capacity and initial potential than those with MIL-101 (Fe) electrodes. These results suggest that the chemical structure on the surface of MIL-101 (Fe) affected its capacity and initial potential.

1. Introduction

Metal–organic frameworks (MOFs) are porous hybrid materials constructed via coordination bonding between organic ligands and metal ions. Owing to the large voids and high redox activity of metal ions and ligands, their applications in various fields such as gas storage[1] and electrode active materials[2] have been studied. Among them, MIL-101 (Fe) (MIL = Matériaux de l'Institut Lavoisier) has been reported to function as a positive active material for realizing highly stable Li-ion batteries because of the reversible redox reaction of Fe³⁺ ions contained in the secondary building unit (SBU) [Fe₃(O)Cl(BDC)₆] (BDC = 1,4-benzenedicarboxylate) [3]. In recent years, the preparation of MIL-101 (Fe)-NH₂ production has been reported via replacement of the organic ligand BDC with 2-aminoterephthalate (BDC-NH₂) [4]. A polar organic compound is selectively adsorbed via hydrogen bonding by the change in the surface property of MIL-101 (Fe)-NH₂ [5], and the cyclic voltammetry of MIL-101 (Fe)-NH₂ on a grassy carbon electrode has demonstrated an increase in the current density due to redox reaction of Fe³⁺/Fe²⁺ up to three times that of MIL-101 (Fe) [6]. Thus, by substituent of NH₂, the surface physical properties of MIL-101 (Fe) have changed, and the electrochemical properties have enhanced. In this study, we investigated the factors contributing to the excellent electrochemical properties of MIL-101 (Fe)-NH₂ from the viewpoint of the crystal structures and electronic structures of MIL-101 (Fe) and MIL-101 (Fe)-NH₂, via powder X-ray diffraction (PXRD) and X-ray absorption fine structure (XAFS) measurements.

2. Experimental

Preparation of MIL-101 (Fe) and MIL-101 (Fe)-NH₂

To synthesize MIL-101 (Fe), we used FeCl₃·6H₂O (Tokyo Chemicals Co., Ltd.), 1,4-benzenedicarboxylic acid (H₂BDC, Tokyo Chemicals Co., Ltd.), and *N,N*-dimethylformamide (DMF, Fujifilm Wako Pure Product). First, FeCl₃·6H₂O (2.506 mmol) was dissolved in DMF (15 mL) and kept under air for 24 h. Thereafter, H₂BDC (1.227 mmol) was added to the solution, which was sonicated for 15 minutes and then heated at 110 °C for 24 h. The resulting powder were washed three times with 5 mL of DMF and 5 mL of ethanol and collected via natural filtration. MIL-101 (Fe)-NH₂ was synthesized using 2-aminoterephthalic acid (H₂BDC-NH₂, 1.242 mmol, Tokyo Chemicals), instead of H₂BDC, as per the same method described above.

Characterization

After the synthesis, PXRD was performed using a X-ray diffractometer (Ultima-IV, Rigaku) with a horizontal sample mount and a Cu-Kα X-ray source operated at a voltage of 40 kV and current of 40 mA. For infrared (IR) measurement, an FT/IR-680 Plus (JASCO) was used. IR light irradiated on powders of H₂BDC, MIL-101 (Fe), and MIL-101 (Fe)-NH₂ sandwiched between calcium fluoride windows (Applied Koken Kogyo Co., Ltd.) was measured in the wavenumber region of 1000–4000 cm⁻¹. To obtain spectra with a resolution of 2 cm⁻¹, 256 integrations were collected.

XAFS measurements

Fe K-edge XAFS measurements were performed

using the transmission mode of BL-4 at the SR center (Ritsumeikan University). For the analysis, pellets ($\phi 10$ mm) composed of a mixture of either 10.2 mg of MIL-101 (Fe) or 10.1 mg of MIL-101 (Fe)-NH₂ with 145.1 mg of boron nitride at 20 MPa were used. Incidentally, the required amounts of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ were calculated using SAMPLEM so that the absorption amount was $\Delta\mu t = 1$ for both pellet types. In addition, soft X-ray XAFS studies were performed at BL-11 in SR center (Ritsumeikan University). Fe L_{II, III}-edge XAFS measurements were performed using partial electron yield mode. O K-edge and C K-edge XAFS measurements were performed using the total electron yield mode. The MIL-101 (Fe) and MIL-101 (Fe)-NH₂ powders were pasted on carbon tape and measured under vacuum.

Charge-discharge measurements

To fabricate positive electrodes, active materials (MIL-101 (Fe), MIL-101 (Fe)-NH₂), acetylene black (AB), and polytetrafluoroethylene (PTFE) (weight ratio of 60 : 30 : 10) were used. Active materials and AB were mixed in a mortar for 10 min, following which PTFE was added and mixed until the mixture was rendered a paste. The paste was punched using a belt punch ($\phi 6$ mm) and sandwiched between two Ti mesh sheets ($\phi = 8$ mm, wire diameter = 0.10 mm, 100 mesh, Nilaco) via compression at 10 MPa. Two-electrode cells (Nippon Tomcell Co., Ltd.) were assembled using a MIL-101 (Fe) or MIL-101 (Fe)-NH₂ positive electrode, polypropylene separator, a lithium foil ($\phi 10$ mm, thickness: 0.2 mm, Honjo Metal), and 1 M LiPF₆ in EC/DMC (3:7 v/v, Kishida Chemicals) in an Ar-filled glove box. Charge and discharge measurements were performed at a rate of 0.2 C and a voltage of 2.0–4.2 V using a HJ1001SDE (Hokuto Denko) charge-discharge measurement system.

3. Results and Discussion

Fig. 1 shows the PXRD patterns of MIL-101 (Fe) and MIL-101 (Fe)-NH₂. The patterns with peaks at 8, 9° of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ were similar to the typical diffraction patterns of previously reported MIL-101 (Fe) and MIL-101 (Fe)-NH₂ [6], indicating that they both exhibited *Fd-3m* cubic symmetry [7]. However, the structure of MIL-101 (Fe)-NH₂ was different from that of MIL-101(Fe), indicating that new crystallographic phases were formed in MIL-101 (Fe)-NH₂ upon the introduction of the substituent NH₂ group into MIL-101 (Fe). This phenomenon has also been observed in the synthesis of MIL-101 (Cr) and MIL-101 (Cr)-NH₂, whose crystal structures were the same as MIL-101 (Fe) and MIL-101 (Fe)-NH₂ [8]. From this result, it was found that MIL-101 (Fe)-NH₂

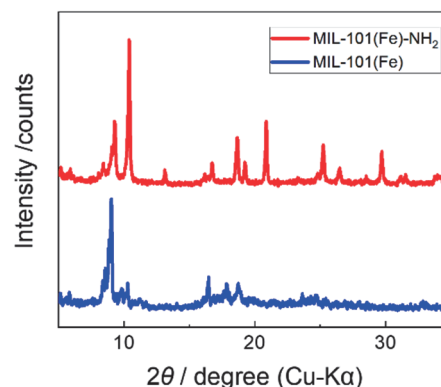


Fig. 1 PXRD patterns of MIL-101(Fe)-NH₂, (red) and MIL-101(Fe) (blue)

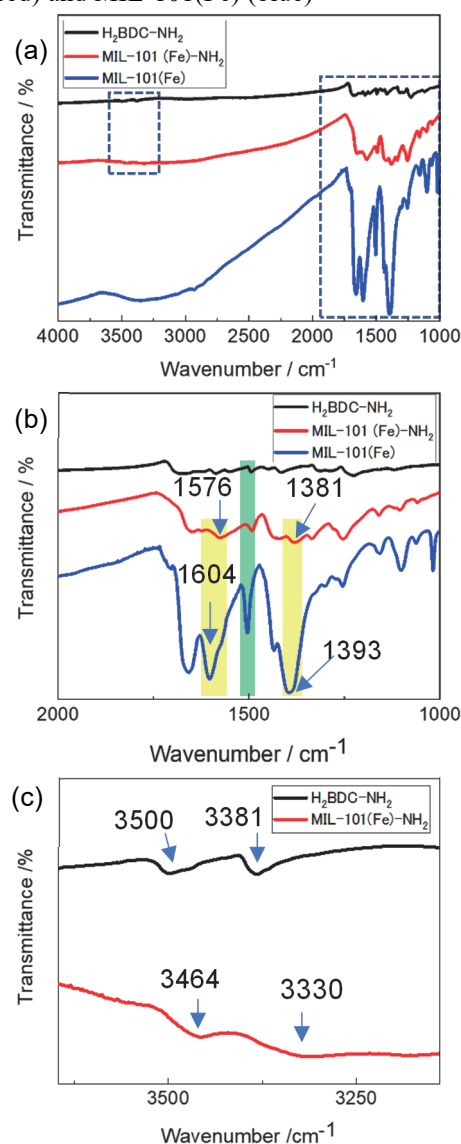


Fig. 2 (a) IR spectra of H₂BDC-NH₂ (black), MIL-101 (Fe)-NH₂ (red), and MIL-101 (Fe) (blue). Enlarged IR spectra for 1800–1000 cm⁻¹ (b) and 3200–3650 cm⁻¹ (c)

possesses a typical MIL-structure with a new crystallographic phase.

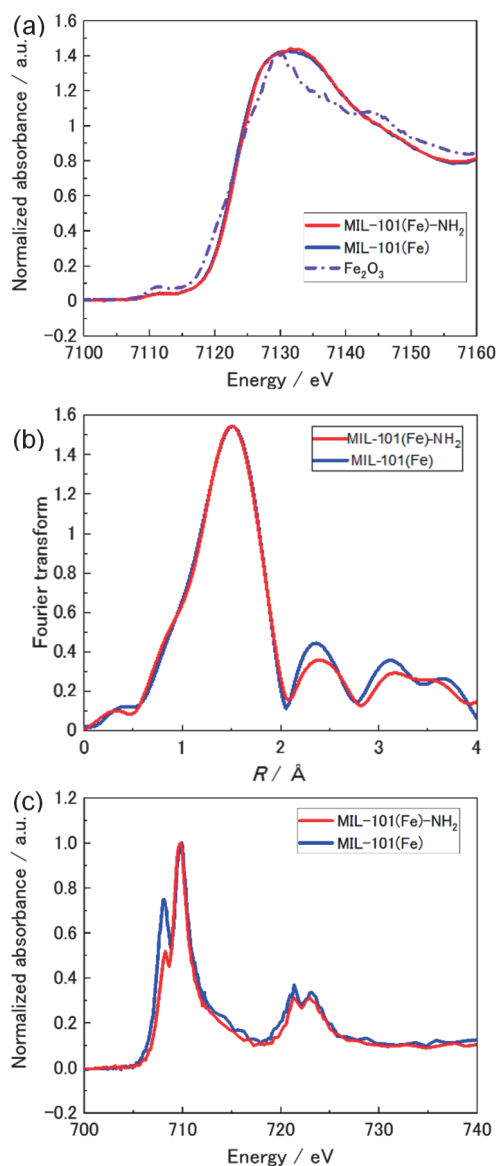


Fig. 3 Fe K-edge XANES spectra of MIL-101 (Fe)-NH₂ (red), MIL-101 (Fe) (blue) and Fe₂O₃ (black) (a), Fourier transform of EXAFS (b), and Fe L_{II,III}-edge XANES spectra MIL-101 (Fe)-NH₂ (red) and MIL-101 (Fe) (blue) (c)

The IR spectra of MIL-101 (Fe), MIL-101 (Fe)-NH₂, and H₂BDC-NH₂ are shown in Fig. 2(a). Fig. (b) and (c) are enlarged IR spectra for 1800–1000 cm⁻¹ and 3200–3650 cm⁻¹, which correspond to the typical regions of vibrations of carboxylates and N-H, respectively. As shown in Fig. 2 (b), peaks are observed at 1393 and 1604 cm⁻¹ in the spectrum of MIL-101 (Fe) and at 1381 and 1576 cm⁻¹ in the spectrum of MIL-101 (Fe)-NH₂. Weak-intensity peaks were observed in the spectra (Fig 2(c)) of MIL-101 (Fe)-NH₂ (3330 and 3464 cm⁻¹) and H₂BDC-NH₂ (3381 and 3500 cm⁻¹). These correspond to the stretching vibration of carboxylates [9] in the range of 1300–1700 cm⁻¹ and of N-H [9] in the range of

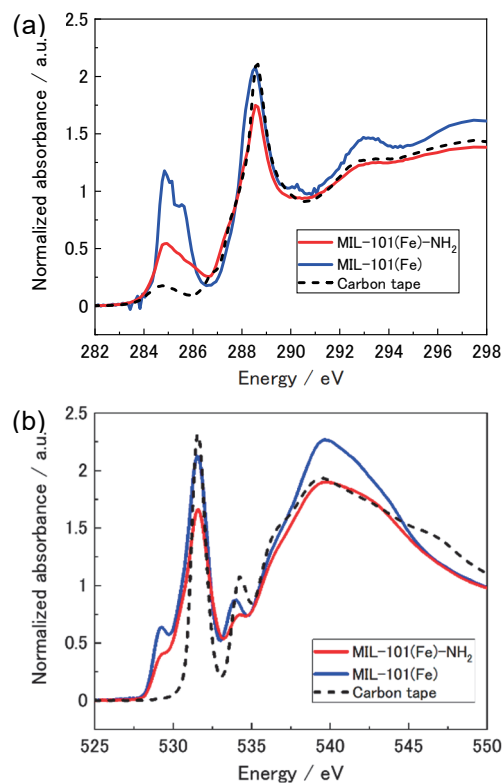


Fig. 4 C K-edge (a) and O K-edge (b) XANES spectra of MIL-101(Fe)-NH₂ (red), MIL-101(Fe) (blue), and carbon tape (black)

3330–3500 cm⁻¹. Furthermore, peaks were observed at 1492 and 1495, 1502 cm⁻¹ in the spectra of MIL-101 (Fe)-NH₂, H₂BDC-NH₂, and MIL-101 (Fe), indicating the C_{ring}-C_{ring} vibration of the BDC skeleton [10]. Therefore, it was found that MIL-101 (Fe) and MIL-101 (Fe)-NH₂ contain the ligands BDC and BDC-NH₂, respectively.

Fig. 3 (a) shows the Fe K-edge X-ray absorption near edge structure (XANES) spectra of MIL-101 (Fe) and MIL-101 (Fe)-NH₂. In the Fe K-edge XANES spectra, the spectra of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ were consistent. In addition, both MIL-101 (Fe) and MIL-101 (Fe)-NH₂ contained Fe³⁺ ions in their bulk because of the consistency with the absorbance at 7123 eV of Fe₂O₃. As shown in Fig. 3 (b), the peak at 1.5 Å was found in the Fourier transforms of the extended X-ray absorption fine structure (EXAFS) of MIL-101 (Fe) and MIL-101 (Fe)-NH₂. This peak was attributed to Fe-Cl and Fe-O bonds[11], although the peak position was not equal to bond the lengths due to no phase correction. Fig. 3 (c) shows the Fe L_{II,III}-edge XANES spectra of MIL-101 (Fe) and MIL-101 (Fe)-NH₂. MIL-101 (Fe)-NH₂ exhibited a peak at 709 eV with a higher intensity than that of the MIL-101 (Fe) peak, indicating that the Fe ions on the surface of only MIL-101 (Fe) were reduced, although Fe³⁺ ions were

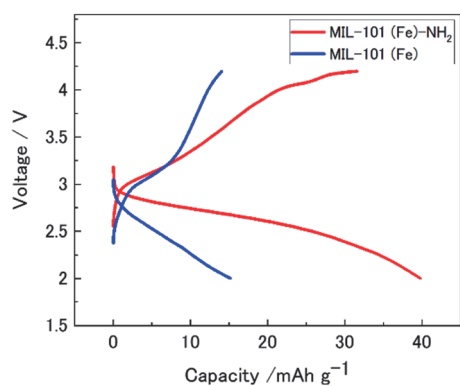


Fig. 5 Charge/discharge curves of MIL-101 (Fe)-NH₂ (red) and MIL-101 (Fe) (blue) at the rate of 0.2 C and voltages of 2.0–4.2 V

retained in the bulk of both MIL-101 (Fe) and MIL-101 (Fe)-NH₂ [12]. Thus, the change in electronic structures on the surface could change the electrochemical properties of MIL-101 (Fe).

The binding states of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ were identified from the C and O K-edge XANES spectra of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ shown in Figs 4 (a) and (b). The difference of peaks, at 285 eV in the C K-edge XANES spectrum of MIL-101 (Cr) can be attributed to π^* of benzene ring [13] in MIL-101 (Fe) and MIL-101 (Fe)-NH₂. In the O K-edge XANES spectra of MIL-101 (Fe) and MIL-101 (Fe)-NH₂, shoulder peaks were observed at 529 eV. This is probably owing to the hybridization of Fe 3d-O 2p [14,15], indicating secondary building units of MIL-101 (Fe) and MIL-101 (Fe)-NH₂ included Fe-O bonds.

Fig. 5 shows the charge–discharge curves of the secondary batteries for the two types of positive electrode active materials used. MIL-101 (Fe)-NH₂ showed an initial voltage of 3.19 V and a broad plateau region between 2.9 and 2.6 V. On the contrary, MIL-101 (Fe) showed an initial voltage of 3.05 V and a gradual voltage drop instead of a plateau region. Moreover, MIL-101 (Fe)-NH₂ exhibited a higher capacity of 39.8 mAh g⁻¹ than that of MIL-101 (Fe). This is probably because the surface of MIL-101 (Fe), whose Fe ions were reduced, was high resistant to lithium intercalation, which resulted in a voltage drop.

4. Conclusions

In this study, we investigated the chemical state of MIL-101 (Fe)-NH₂ from the viewpoint of the crystal structures and electronic structures of MIL-101 (Fe) and MIL-101 (Fe)-NH₂, via PXRD and XAFS measurements. Although the PXRD patterns indicated that MIL-101 (Fe)-NH₂ had a distinctly different structure from that of MIL-101 (Fe), Fe K-edge XAFS measurements indicated that the electronic structure and local structure in the bulk

of MIL-101 (Fe)-NH₂ were the same as those of MIL-101 (Fe). However, Fe L-edge XAFS revealed that the Fe ions on the surface of MIL-101 (Fe) were reduced, indicating that the surface of MIL-101 (Fe) had a different electronic structure from that of MIL-101 (Fe)-NH₂. The reduced Fe ions on the surface affected the voltage drop and resulted in a decrease in the capacity of MIL-101 (Fe). This is a significant result that proves that the chemical structure on the surface of active materials affects the capacity and initial voltage of batteries.

References

- [1] M. Kondo, T. Yoshitomi, H. Matsuzaka, S. Kitagawa, and K. Seki, *Angew. Chem., Int. Ed.*, **1997**, *36*, 1725.
- [2] G. Férey, F. Millange, M. Morcrette, C. Serre, M.-L. Doublet, J.-M. Grenèche, and J.-M. Tarascon, *Angew. Chem., Int. Ed.*, **2007**, *46*, 3259.
- [3] T. Yamada, K. Shiraishi, H. Kitagawa, and N. Kimizuka, *Chem. Commun.*, **2017**, *53*, 8215.
- [4] S. Bauer, C. Serre, T. Devic, P. Horcajada, J. Marrot, G. Férey, and N. Stock, *Inorg. Chem.*, **2008**, *47*, 7568.
- [5] M. Gao, W. Liu, X. Wang, Y. Li, P. Zhou, L. Shi, B. Ye, R. A. Dahlgren, and X. Wang, *Microchem. J.*, **2019**, *145*, 1151.
- [6] A. D.S. Barbosa, D. Julião, D. M. Fernandes, A. F. Peixoto, C. Freire, B. de Castro, C.M. Granadeiro, S.S. Balula, and L. C.-Silva, *Polyhedron*, **2017**, *127*, 464.
- [7] G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, and I. Margiolaki, *Science*, **2005**, *309*, 2040.
- [8] M. F. Dapaah, B. Liu, L. Cheng, *J. Environ. Chem. Eng.*, **2021**, *9*, 105275.
- [9] Z. Zhang, X. Li, B. Liu, Q. Zhao, and G. Chen, *RSC Adv.*, **2016**, *6*, 4289.
- [10] M. Karabacak, M. Cinar, Z. Unal, and M. Kurt, *J. Mol. Struct.*, **2010**, *982*, 22.
- [11] J. Shin, M. Kim, J. Cirera, S. Chen, G. J. Halder, T. A. Yersak, F. Paesani, S. M. Cohen, and Y.S. Meng, *J. Mater. Chem. A*, **2015**, *3*, 4738.
- [12] S. Yang, D. Wang, G. Liang, Y. M. Yiu, J. Wang, L. Liu, X. Sun, and T.-K. Sham, *Energy Environ. Sci.*, **2012**, *5*, 7007.
- [13] Y. Chen, H. Li, W. Zhao, W. Zhang, J. Li, W. Li, X. Zheng, W. Yan, W. Zhang, J. Zh, R. Si, and J. Zeng, *Nat. Commun.*, **2019**, *10*, 1885.
- [14] M. Pollak, M. Gautier, N. Thommat, S. Gota, W.C. Mackrodt, and V.R. Saunders, *Nucl. Instrum. Methods Phys. Res. Sect. B*, **1995**, *97*, 383.
- [15] F. M. F. de Groot, M. Grioni, J. C. Fuggle, J. Ghijsen, G. A. Sawatzky, and H. Petersen, *Phys. Rev. B*, **1989**, *40*, 5715.