Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2015

Supplementary info for:

MIL-101(Fe) as a Lithium-ion Battery Electrode Material: Relaxation and Intercalation Mechanism During Lithium Insertion

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1. Supplementary Discussion

MIL-101(Fe) was lithiated with roughly 0.6 Li/Fe when discharged down to 2.0 V. Compared to MIL-53(Fe), one of the previous MOFs which showed most promise in LIB, MIL-101(Fe) had a higher voltage cut-off by 0.5 V. Such advancement may be due to the fact that MIL-101(Fe) has larger pores than MIL-53(Fe). Li⁺ can be solvated by either two (174.5 Å³) or four (350 Å³) DMC molecules.¹ Only MIL-101(Fe) has large enough pores and pore windows to allow solvated Li⁺ to diffuse in and out of the material (figure 1b).

Five reduction peaks were observed in differential capacity (dQ/dV) plot (figure 2b). In MIL-53(Fe), lithium insertion process primarily involves two reactions. The first is a kinetically limited solid-solution reaction. The second is a two-phase reaction.¹ Like MIL-53(Fe), it is expected that the lithiation of MIL-101(Fe) also proceeds with a series of solid-solution reactions followed by a series of two phase reactions. Evidence of solid-solution and two phase reaction are provided by ex-situ EXAFS (figure S4). No clear change in Fe coordination during lithiation to 2.5 V suggests a solid solution reaction, while a change in Fe coordination during lithiation from 2.5 V to 2.0 V suggests a two phase reaction (figure 5 and figure S4).

In the PXRD results, some irreversible structural changes were observed to occur at lower d-spacing (figure S5). To further diagnose the diffraction patterns, the three synchrotron PXRD patterns were profile matched with Fd-3m cubic symmetry (figure S6, S7, and S8).² Overall, the peaks matched well with some exceptions in the lower d-spacing. Three peaks in which did not match well in the cubic symmetry were near 9.7, 9.6, and 9.1 Å. The impure peak observed near 9.7 Å started to disappear upon lithiation and completely disappeared upon de-lithiation. Comparing PXRD result of as-synthesized material and the pristine which had been ball milled with Super-P (SP) the conductive carbon additive, the peak near 9.7 Å, was a product of ball milling SP and the MOF together (figure S9). A new

peak near 9.6 and 9.1 Å appeared as 9.7 Å peak disappeared. Since the ball milled SP is known to have irreversible electrochemical reaction, these peak can be attributed to the decomposition of SP during electrochemical test.³ Regardless of the impurities, the irreversibilities were not related to the cubic MIL-101(Fe) framework.

In the higher d-spacing, there were increase in intensity for some peaks including the (022) peak. The increased peaks reversibly decreased in intensity after the de-lithiation. To comprehend this phenomenon, some diffraction patterns were simulated (figure S10). A MIL-101(Cr) was simulated from the reported crystal information file (CIF). The CIF contains oxygen atoms from solvent molecules. After deleting the oxygen atoms from solvent molecules, PXRD pattern was simulated again. Clearly, a decrease in intensity of (022) peak was observed for desolvated PXRD simulation. The same trend was observed when Cr was changed to Fe. Upon lithiation, electrolyte solvent molecules will be co-intercalating with Li⁺. We suspect that when the Li⁺ are intercalating inside the MOF, the solvent molecules will also intercalate. Therefore, the reversible peak intensity changes are likely due to electrolyte solvent molecules intercalating in the MOF.

2. Supplementary figures



Figure S1: Magnetic susceptibility plot of MIL-101(Fe) with H_2O vs. DMC. The MIL-101(Fe) H_2O sample is the MIL-101(Fe) electrode exposed in air. The MIL-101(Fe) DMC sample is the MIL-101(Fe) electrode soaked in DMC. The magnetic susceptibility is zero field cooled and temperature sweep was done in 2 K/min rate and in 5000 Oe. A shift in the magnetic susceptibility is observed and signifies the change in coordination environment of Fe from H_2O to DMC.



Figure S2: a) Trimer and b) TrimerDMC model used for the Gibbs free energy calculation. There are three Fe per model but there are only two different Fe environments as Fe2 and Fe3 are degenerate. Iron, oxygen, carbon, and hydrogen atoms are colored blue, red, grey, and white, respectively.



Figure S3: XANES region of the MIL-101(Fe)'s ex-situ XAS results at pristine state, lithiation to 2.5 V, lithiation to 2.0 V, and delithiation to 3.5 V.



Figure S4: Fourier transformed EXAFS region of the MIL-101(Fe)'s ex-situ XAS results at pristine state, lithiation to 2.5 V, lithiation to 2.0 V, and delithiation to 3.5 V.



Figure S5: dQ/dV plot of the 5th to 10th cycles at a C/40 rate. Both reductive peaks and oxidative peaks decrease continuously.



Figure S6: Lower d-spacing PXRD of MIL-101(Fe) at its pristine, lithiation and de-lithiated states. Irreversible peak disappearance and appearances are labeled with "*" sign.



Figure S7: a) PXRD comparison of MIL-101(Fe) at its as-synthesized state, electrode (pristine) state, and simulated state. b) Lower d-spacing PXRD of a). The as-synthesized PXRD pattern is collected using a Bruker D8 Advance diffractometer at 40 KV, 40 mA for Cu K α (λ =1.5418 Å), with scan speed of 0.1 sec/step, a step size of 0.02° in 2 θ and a 2 θ range

of 1.0 to 55°. The experimental backgrounds were corrected using Jade 5.0 software package.

The pristine PXRD pattern is collected from APS 1-BM using synchrotron source as

described in this paper. A secondary phase near 9.7 Å d-spacing is labeled with "*".



Figure S8: a) Profile matched MIL-101(Fe) pristine synchrotron PXRD pattern. b) Lower d-spacing PXRD of a). Regions associated with the secondary phase were excluded from the fit.



Figure S9: a) Profile matched MIL-101(Fe) lithiated synchrotron PXRD pattern. b) Lower d-spacing PXRD of a). Regions associated with the secondary phase were excluded from the fit.



Figure S10: a) Profile matched MIL-101(Fe) de-lithiated synchrotron PXRD pattern. b) Lower d-spacing PXRD of a). Regions associated with the secondary phase were excluded from the fit.

MIL-101(Fe)	a (Å)	X ²	Space	Lamda (Å)	Excluded regions
			Group		(Å)
Prsinte	89.781(3)	1.014	Fd-3m	0.6168	~9.5-9.7
Lithiated	89.687(3)	2.179	Fd-3m	0.6168	~8.8-8.9,~9.3-9.7,
					~9.9-10.0
De-lithiated	89.690(2)	0.3262	Fd-3m	0.6168	~8.8-8.9, ~9.3-9.7

Table S1: Profile matching parameters for MIL-101(Fe) synchrotron PXRD patterns.



Figure S11: a) Simulated PXRD patterns using solvated MIL-101(Cr), desolvated MIL-101(Cr), solvated MIL-101(Fr), and desolvated MIL-101(Fe). b) Higher d-spacing PXRD of a). One of the intensity changing peaks (022) is labeled with solid red line.



Figure S12: Voltage profile of MIL-101(Fe) cycled at a C/20 rate between a voltage range of 1.0 - 3.5 V. Li/Li⁺ was used as the counter electrode. A rapid decrease in capacity is associated with an irreversible conversion reaction.



Figure S13: Spin densities of the respective calculations. First row shows the results obtained from the Trimer model. Second row shows the results obtained from the TrimerDMC model. Spin density, oxygen, carbon, and hydrogen atoms are colored blue, red, grey, and white, respectively. Third row describes the electronic structure of the calculation. The three circles represent Fe nuclei. Blue means trivalent and olive means divalent.



Figure S14: a) Voltage profile and b) cycle capacity of an alternative voltage cut-off (2.5 - 4.0 V).

Table S2: List of computation conditions and their respective results. HS has all three Fespins up. BS1 has only Fe1 spin state down. BS2 has only Fe1 spin state down. BS3 has onlyFe1 spin state down.

Model	Reduction state	Spin State	Energy (keV	Total Spin (S²) 🔽	Decontaminated Energy (keV)
Trimer	Pristine	HS	-152.7917767	63.7724	N/A
		BS1	-152.7919557	13.6159	-152.7917838
		BS3	-152.7918162	13.7084	-152.7917854
	Reduce A	HS	-152.7949151	56.0435	N/A
		BS1	-152.7950053	15.9146	-152.7949196
		BS2	-152.7950653	10.8916	-152.7949218
		BS3	-152.7949871	10.9323	-152.7949183
	Reduce B	HS	-152.7949152	56.0435	N/A
		BS1	-152.7950593	10.8878	-152.7949216
		BS3	-152.7946393	15.9733	-152.7949014
	Reduce C	HS	-152.7951707	48.7842	N/A
		BS1	-152.7952647	12.6672	-152.7951759
		BS2	-152.7952107	8.6362	-152.7951727
		BS3	-152.7951166	48.7854	-152.7951166
	Reduce D	HS	-152.7951853	12.6638	N/A
		BS1	-152.7951113	8.6112	-152.7951163
		BS3	-152.7951878	12.7043	-152.7951205
TrimerDMC	Pristine	HS	-149.6101776	63.7702	N/A
		BS1	-149.6103224	13.6399	-149.6101834
		BS3	-149.6103053	13.6504	-149.6101827
	Reduce A	HS	-149.6166378	56.0555	N/A
		BS1	-149.6166383	15.918	-149.6166378
		BS2	-149.6167581	10.8877	-149.6166431
		BS3	-149.6167601	10.884	-149.6166432
	Reduce B	HS	-149.6166361	56.0554	N/A
		BS1	-149.6168128	10.8838	-149.616644
		BS3	-149.6166971	15.9284	-149.6166392
	Reduce C	HS	-149.6191745	48.7758	N/A
		BS1	-149.6192814	12.6601	-149.6191804
		BS2	-149.6193124	8.6136	-149.6191813
		BS3	-149.6192338	12.6815	-149.6191778
	Reduce D	HS	-149.6191745	48.7758	N/A
		BS1	-149.6192368	12.6614	-149.6191779
		BS3	-149.6193094	8.6088	-149.6191812

3. References

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