**Supporting information**

## Materials:

All reagents were purchased and used without further purifications. MIL-101(Fe) were synthesized according to the literature method[32] with a slight modification.

$FeCl_3 \cdot 6H_2O$ (541 mg, 2 mmol), $H_2bdc$ (166 mg, 1 mmol) were dissolved into 10 mL of dehydrated DMF and stand at 120 °C for 20 hours. The resultant powder was washed with DMF and methanol and dried. Elemental analysis calcd (found) % for $Fe_3(O)Cl(C_8H_4O_4)_3(C_3H_7NO)$: C 41.34 (41.25), H 2.44 (2.36), N 1.79 (1.50).

## Methods:

The obtained sample was characterized with XRPD (Bruker D2 Phaser), ATR-FTIR (Shimadzu IRTracer-100 equipped with DuraSamplIR II, Smiths Detection) and SEM (Hitachi SU-9000) measurements as shown in Fig. S1 S2 and S3, respectively.

For battery test, same amount of Ketjen black (Lion Co. Ltd.), PTFE (60wt% dispersion in $H_2O$, Adlrich) and MIL-101(Fe) were mixed in agate mortar with an addition of several drops of ethanol, and coin-shaped pellet was formed before drying at 80 °C for three hours. SEM image of the mixture was shown in Fig. S4. The obtained pellet was used as cathode.

The sample pellet was placed into a caukless cell (Miclab co. ltd.) with glass filter and lithium metal, and were added with electrolyte (1 M $LiPF_6$ in EC : DEC = 1 : 2). Charge and discharge tests and cyclic voltammetry were executed with Solartron 1470E.

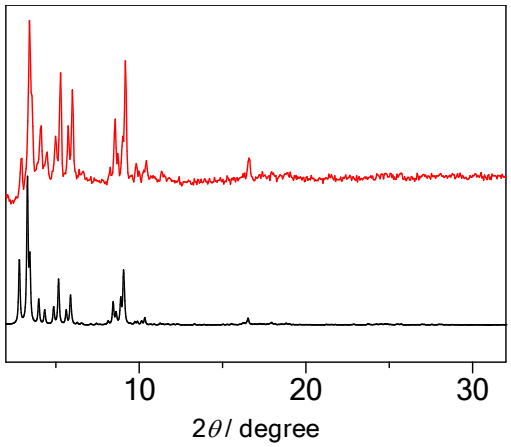


Fig. S1, X-ray powder diffraction of MIL-101(Fe) (red). Simulated pattern from MIL-101(Cr) was shown as black line.

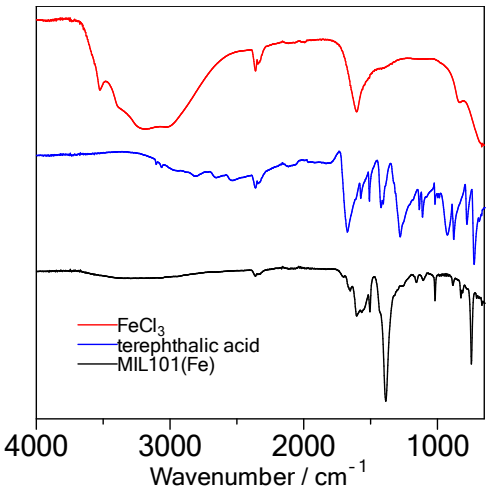


Fig. S2 FT-IR spectrum of MIL-101(Fe) (Black line). IR Spectra of $FeCl_3$ (Red) and terephthalic acid (Blue) were overwritten for comparison.

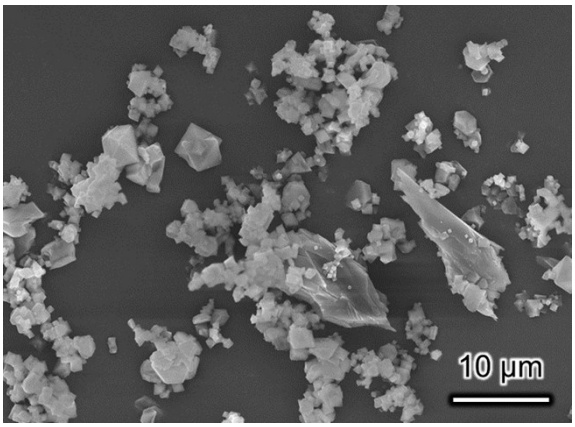


Fig. S3 SEM image of MIL-101.

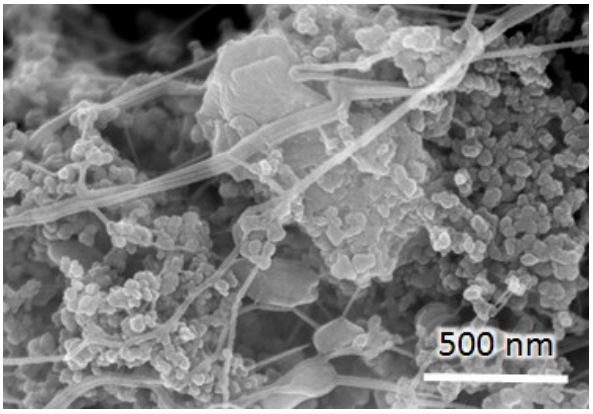


Fig. S4 SEM image of cathode mixture. Small spherical powders (ca. 50 nm), fibers and large angulated powders (ca. 100 to 1,000 nm) were Ketjen black, PTFE and MIL-101, respectively.

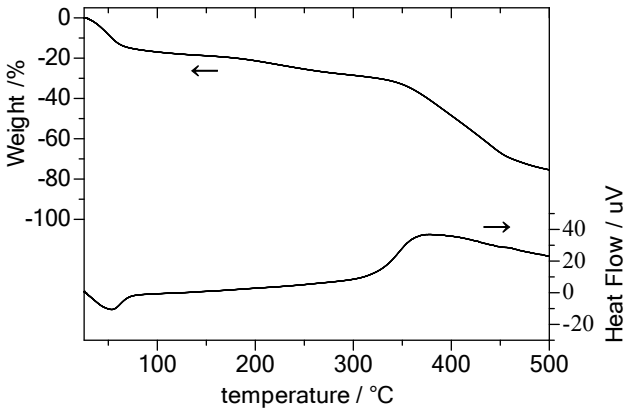


Fig. S5 Results of thermogravimetry (TG) and differential thermal analysis (DTA) of MIL-101(Fe).

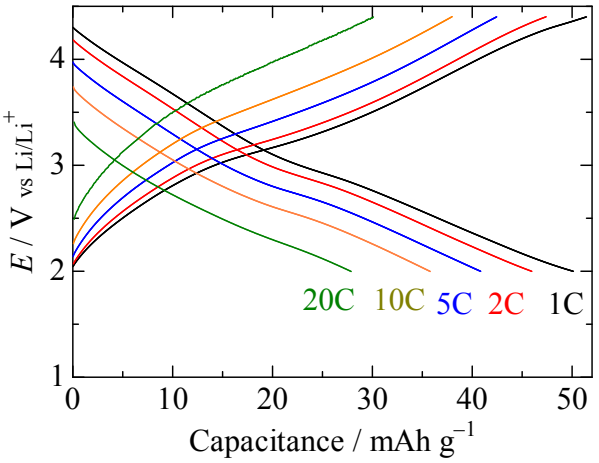


Fig. S6 High rate test of MIL-101(Fe) cathode from 1 to 20 C rate.

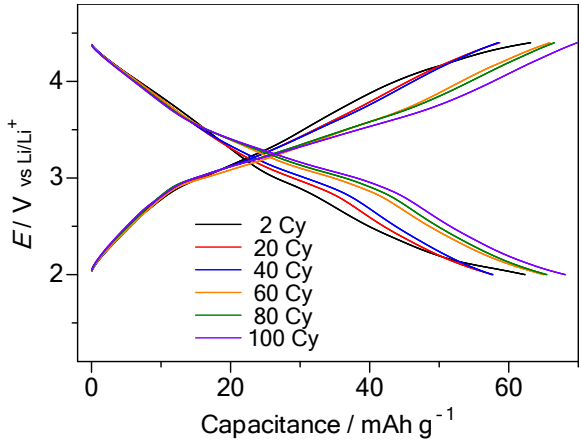


Fig. S7 Capacitance of MIL-101(Fe) cathode during charge and discharge cycles at C/5 rate.

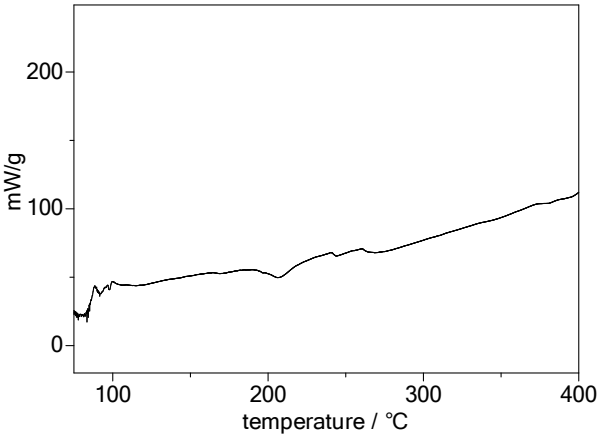


Fig. S8 Heat flow curves of mixture of 25 mg of electrolyte (1 M $LiPF_6$ / EC + DMC (1 : 2)) and 10 mg of cathode material at a heating ratio of 0.2 K / min.