

Polyoxometalate based metallogels as anode materials for lithium ion batteries

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Material characterization

The PXRD patterns were collected on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu K_{α} radiation ($\lambda = 1.54060 \text{ \AA}$). The FTIR was collected on a Nexus 670 spectrometer. The TGA was carried out by using a DSC 800 from PerkinElmer under N_2 flowing with a heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ from room temperature to $700 \text{ }^{\circ}\text{C}$. The TEM and HRTEM images were performed on JEOL-2100F apparatus and JEOL JSM-6700 M scanning electron microscope, respectively. The EDS were performed on JSM-5160LV-Vantage typed energy spectrometer. XPS measurements was collected on scanning X-ray microprobe (PHI 5000 Versa, ULAC-PHI, Inc.) using excitation energy of 1486.6 eV (Al K_{α}) and the C1s line at 284.8 eV as energy referencing.

Electrochemical characterization

To prepare working electrode, active materials, carbon black and poly (vinylidene fluoride) (PVDF) with a weight ratio of 7:2:1 were pasted on a piece of Cu foil. The active materials loading for the electrode was around 1 mg . The half-coin cells were assembled in an argon filled glove box utilizing a Li metal as the negative electrode, a solution of 1 M LiPF_6 in ethylene carbonate (EC), dimethyl carbonate (DMC) (1:1 in Volume) as the electrolyte and a Celgard 2400 membrane as separator. The galvanostatic charge/discharge measurement was conducted by a LAND CT2001A multichannel battery between 0.01 and 3.0 V . Electrochemical impedance spectra (EIS) measurements and CV were conducted on CHI 660D (Shanghai, China) electrochemical workstation. The conductivity of samples pellets was measured with a two-probe method using Keithley 4200. The pellets of samples were pressed at a pressure of $\approx 1 \text{ GPa}$.

Synthesis of MOGs

$\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (540 mg , 2 mmol), were dissolved in ethonal (2 mL), forming homogenous solution (solution A). Then H_3BTC (84 mg , 0.4 mmol) and a certain quality of PMo_{12} (0.05 mmol , 0.1 mmol , or 0.3 mmol) were dissolved in ethonal (2 mL) (solution B). Solution B was added dropwisely into solution A, and place it alone.

Brown MOGs were obtained, and filtered out, then washed with distilled water and ethanol for 6 times to remove the remaining reactants. The remaining precipitate was obtained after drying at 60 °C for 24 h.

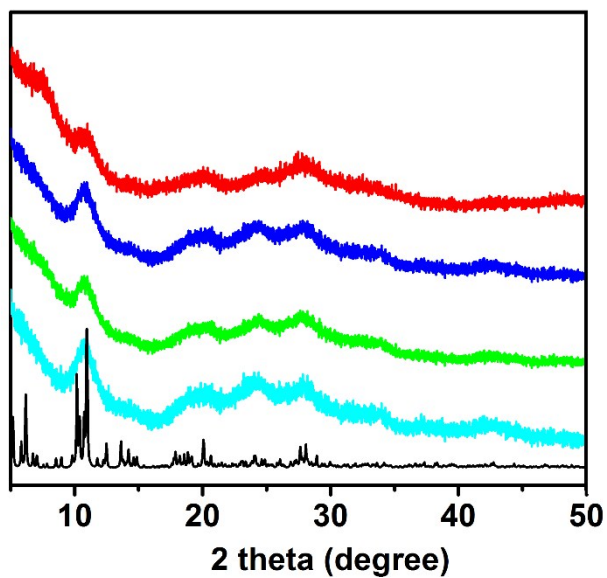


Fig. S1 PXRD patterns of simulated MIL-100 (black), FeBTC (light blue), PMo₁₂@FeBTC-1 (green), PMo₁₂@FeBTC-2 (blue), and PMo₁₂@FeBTC-3 (red).

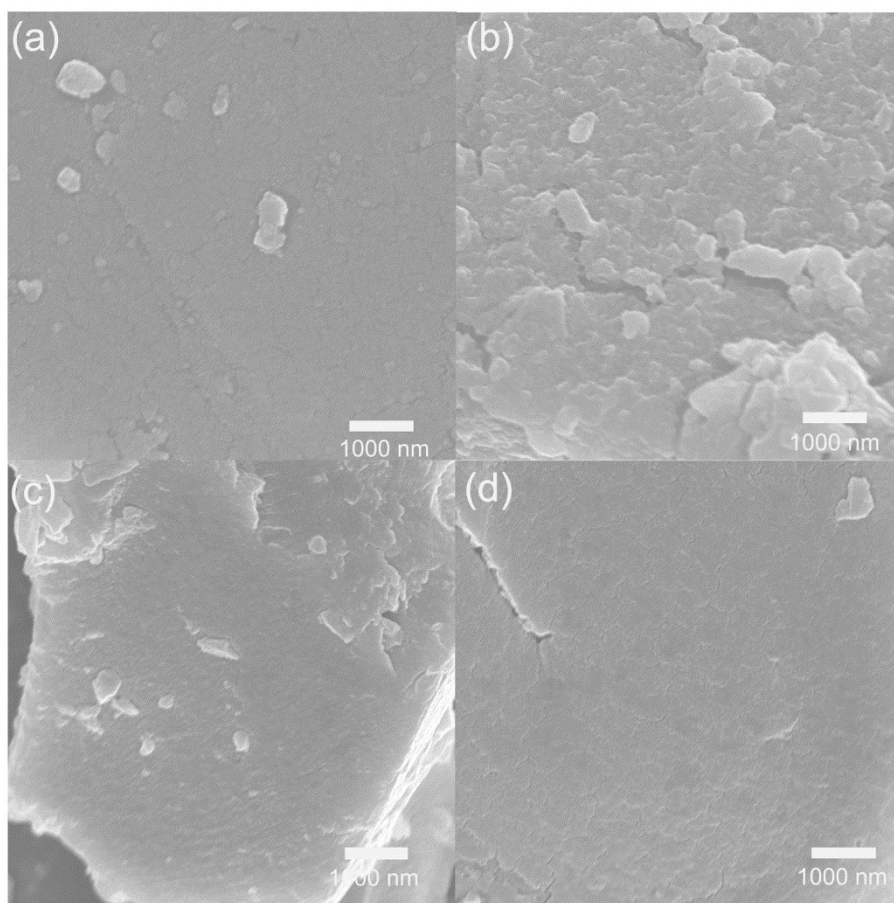


Fig. S2 The SEM images of $\text{PMo}_{12}@FeBTC-1$ (a), $\text{PMo}_{12}@FeBTC-2$ (b), $\text{PMo}_{12}@FeBTC-3$ (c), and FeBTC (d).

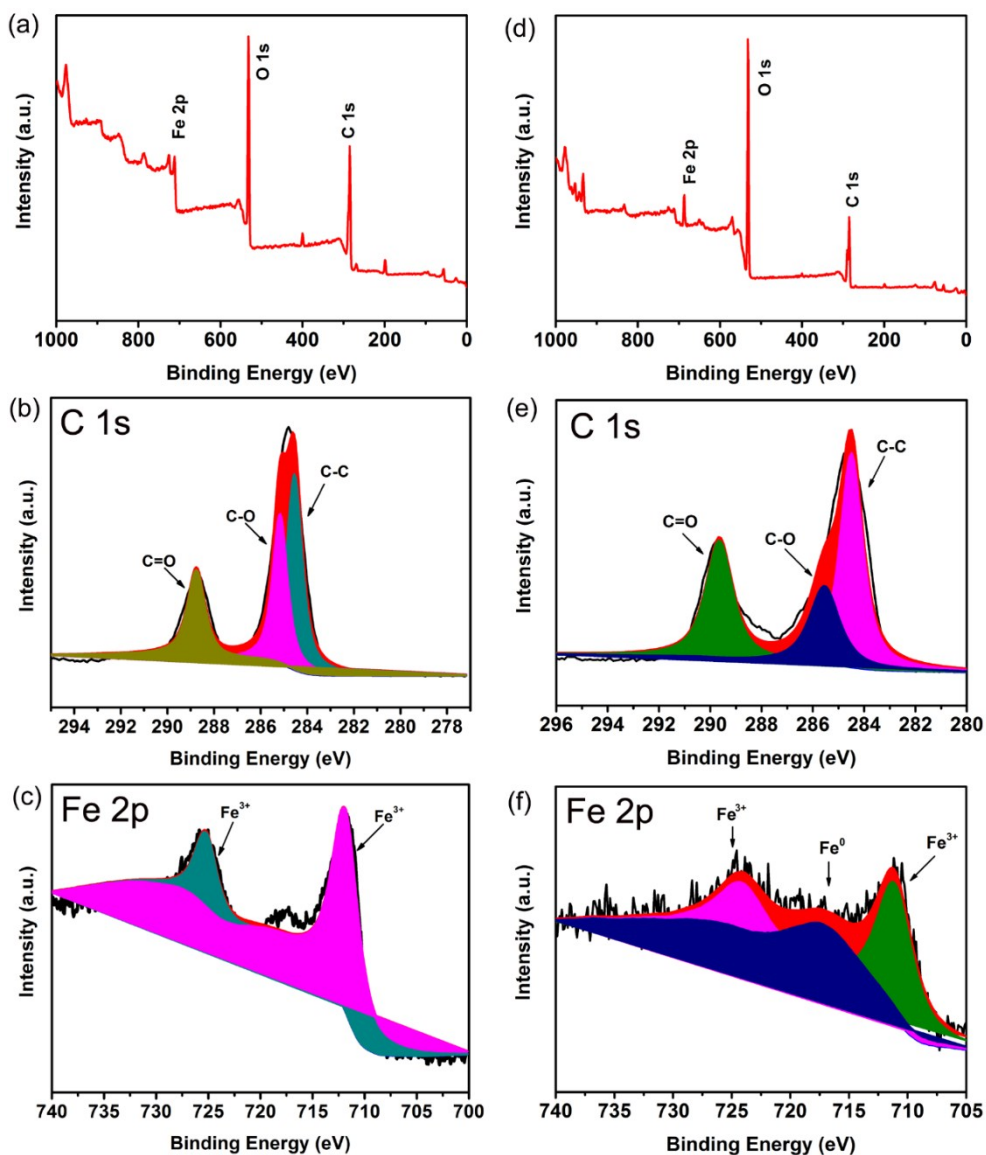


Fig. S3 XPS spectra of FeBTC before and after discharged to 0.01 V, (a-c): survey scan of as-synthesized FeBTC (a), C 1s (b), and Fe 2p (c), respectively, (d-f): Discharged at 0.01 V, survey scan (d), C 1s (e), and Fe 2p (f), respectively.

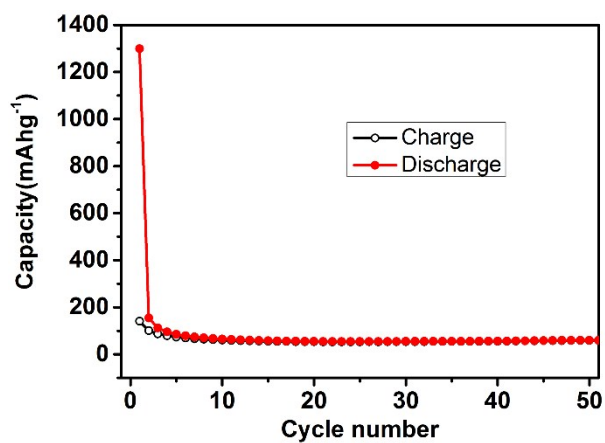


Fig. S4 Cycling stability of FeBTC at a current density of 100 mA g⁻¹.

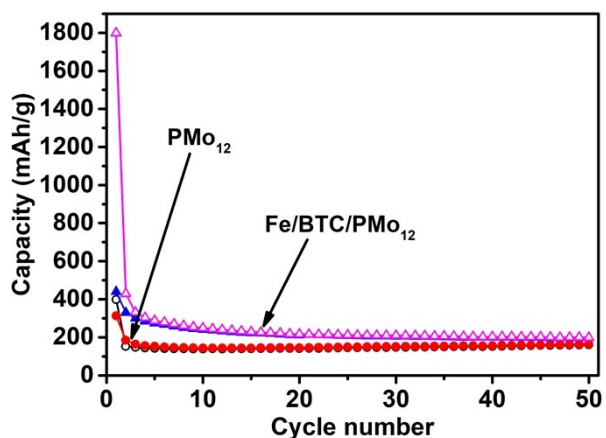


Fig. S5 Cycling stability of pure PMo₁₂ as well as the mixture (Fe/BTC/PMo₁₂) based on PMo₁₂, FeCl₃·6H₂O and BTC at a current density of 100 mA g⁻¹.

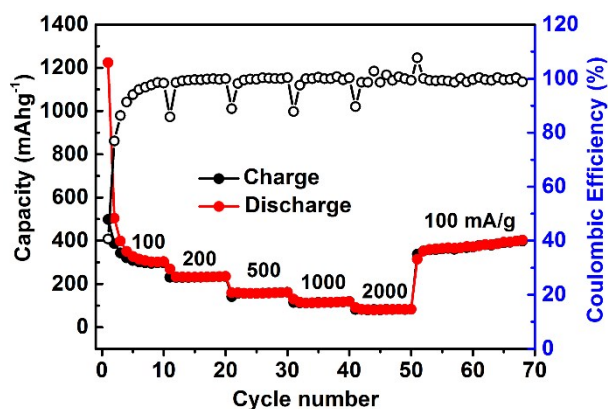


Fig. S6 Cycle capability test for the PMo₁₂@FeBTC-1 at various current densities (0.1-2 A g⁻¹).

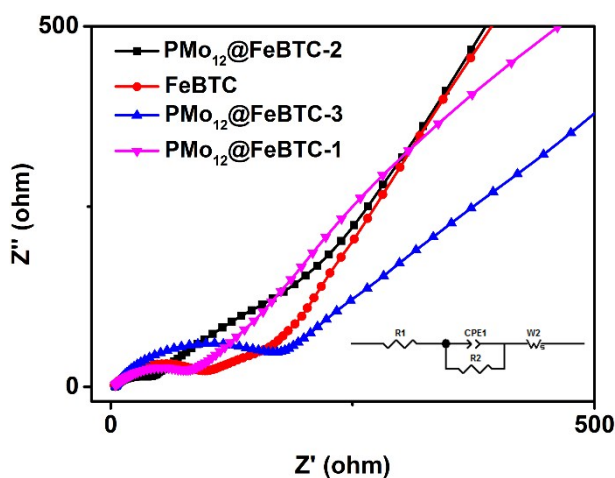


Fig. S7 Nyquist plots of the PMo₁₂@FeBTC-1, PMo₁₂@FeBTC-2, PMo₁₂@FeBTC-3,

and FeBTC after third cycles.

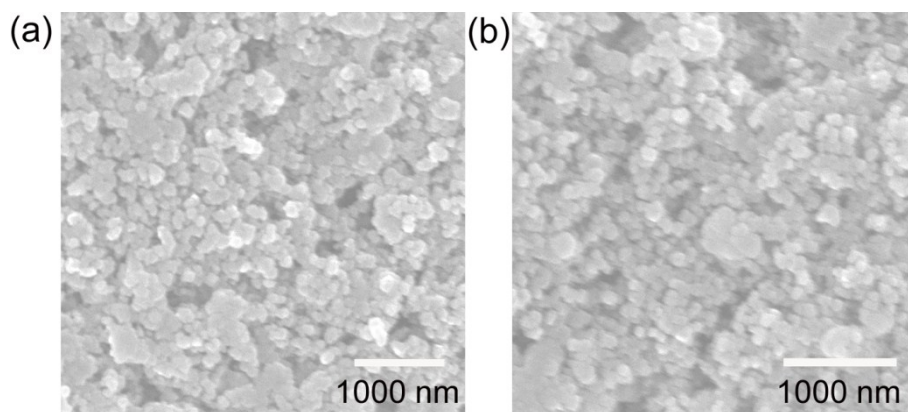


Fig. S8 SEM images of PMo₁₂@FeBTC-2 electrode before (a) and after 100 cycles (b) performed with a current density of 0.5 A g⁻¹.

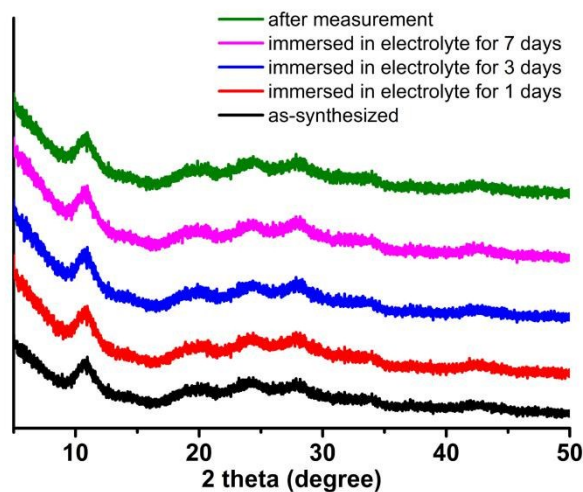


Fig. S9 PXRD patterns of as-synthesized PMo₁₂@FeBTC-2, immersed in electrolyte for 1 day, 3 days, 7 days and after electrochemical measurement.

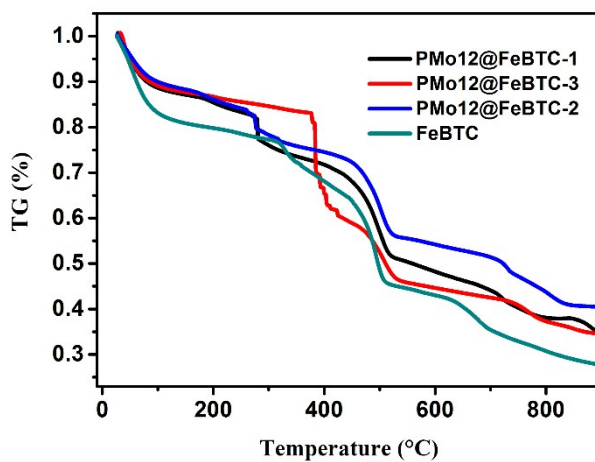


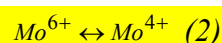
Fig. S10 TGA results of PMo₁₂@FeBTC-1, PMo₁₂@FeBTC-2, PMo₁₂@FeBTC-3, and FeBTC.

The theoretical capacity has been calculated according to equation 1:

$$Q = \frac{nF}{3.6M} = \frac{96500n}{3.6M} \quad (1)$$

Where Q is the reversible charging–discharging capacity, n is the number of electrons passed during the redox reaction, and M is the molecular weight.

Owing to the intercalation mechanism for Li storage (equation 2), we consider the redox reactions of metal ions Mo, which is also confirmed by the XPS results.



The molecular formula of PMO₁₂ is H₃PMo₁₂O₄₀. If 12 Mo⁶⁺ ions are reduced to Mo⁴⁺, maximum of $n = 24$, $Q = 352 \text{ mAh g}^{-1}$

Therefore, the theoretical energy capacity of PMO₁₂ is 352 mAh g⁻¹.

Table S1 Gelation tests at RT and various Fe:PMo₁₂ ratios

Fe ³⁺ /mmol	H ₃ BTC/mmol	PMo ₁₂ /mmol	Fe:BTC:PMo ₁₂	Result	Name
2	0.4	0.05	40:8:1	gel	PMo ₁₂ @FeBTC-1
2	0.4	0.1	20:4:1	gel	PMo ₁₂ @FeBTC-2
2	0.4	0.3	20:4:3	gel	PMo ₁₂ @FeBTC-3
2	0.4	0.5	20:4:5	gel	Not defined
2	0.4	0.6	20:4:6	gel	Not defined
2	0.4	0.7	20:4:7	solution	Not defined
2	0.4	0.8	20:4:8	solution	Not defined
2	0.4	0.9	20:4:9	solution	Not defined

Table S2 Comparison of PMo₁₂@FeBTC-2 with other pristine MOFs and POMs based anodes materials

Materials	CD/mA/g	Cycle/RC (mAh/g)	Ref.
Mn–LCP	50	50/390	Inorg. Chem. 2013, 52, 2817

Mn-BTC	103	100/694	ACS Appl. Mater. Interfaces 2015, 7, 16357
Zn(IM) _{1.5} (abIM) _{0.5}	100	200/190	Chem. Commun. 2015, 51, 697
Asp-Cu	50	200/233	RSC Adv. 2015, 5, 20386
POMOF-1	1.25 C	500/350	J. Mater. Chem. A 2015, 3, 22989
Fe/Co-BTC	200	70/639	Small 2016, 12, 2982
NENU-507	100	100/640	Chem. Commun. 2017, 53, 5204

RC: Reversible capacity. CD: Current density.