This article can be cited before page numbers have been issued, to do this please use: Y. Lan, M. Zhang, A. Zhang, X. Wang, Q. Huang, X. Zhu, X. Wang, L. Dong and S. Li, J. Mater. Chem. A, 2018, DOI: 10.1039/C8TA01062E.

This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the author guidelines.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the ethical guidelines, outlined in our author and reviewer resource centre, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
Encapsulating the ionic liquids into POM-based MOFs to improve their conductivity for superior lithium storage

Mi Zhang, A-Man Zhang, Xiaoxiao Wang, Qing Huang, Xiaoshu Zhu, Xiao-Li Wang, Long-Zhang Dong, Shun-Li Li* and Ya-Qian Lan*‡

Developing advanced anode materials with multi-electron reaction, adequate charge transport, and suppressed volume changes is highly desirable in lithium storage. Polyoxometalates (POMs) have the strong multi-electron redox properties and metal-organic frameworks (MOFs) possess high surface areas and controllable porosities, both of which are attractive candidates for the anode materials. However, the easy dissolution of POMs in the electrolyte and the intrinsically poor conductivity of MOFs result in the inferior rate performance and cycling capacity. In this paper, we skillfully encapsulate ionic liquids (ILs) into polyoxometalate-based metal-organic frameworks (POMOFs) to fabricate a series of ILs-functionalized POMOFs crystals (denoted as POMs-ILs@MOFs), which immobilize POMs in the cage of MOFs avoiding the leaching of POMs and obtain an enhanced conductivity by the modification of the ILs. One of POMs-ILs@MOFs (PMo12V2-Ils@MIL-100) crystals show superior cycling stability and high rate capability when they are used as anode materials, which are the best amongst all the reported MOFs, POMs and POMOFs crystals materials. The outstanding performances are attributed to the hybrid behavior of a battery-supercapacitor, which is a synergistic effect among ILs, POMs, and MOFs. And most importantly, we not only discover a series of new anode materials but also propose a new strategy to improve the conductivity of MOFs and POMOFs, which would guide the development of other electrode materials based on MOFs and POMOFs for Lithium storage.

1 Introduction

2 Environmental problem and energy shortage are two serious issues related to the life of human beings. Currently, looking for the new energy to replace the traditional fossil energy has aroused a lot of attentions. Lithium-ion batteries (LIBs) have been vastly applied in consumer electronics and are regarded as one of the best candidates for next generation power sources. Graphite is used as a commercial anode material for LIBs at present; however, it has a low theoretical capacity about 372 mAh g⁻¹ because of its tight stacked layered structure. In consequence, great efforts have been made to develop other proper anode materials. Among these potential anode materials, lots of work has been dedicated to transition metal oxides, silicon, and amorphous phosphorus. Nevertheless, these lithium storage anode materials still remain great challenge resulting from the slow processes of Lithium-ion diffusion. In comparison, supercapacitors, which work by the redox reactions of the pseudocapacitive active materials or the formation of electrical double-layer (EDL) capacitors, are hampered in application of electrochemical devices for their low-energy density. Several kinds of alternatives have been reported, however, continuous interest to fabricate new anode materials that combine the advantages of battery and supercapacitor for LIBs is still aroused. Polyoxometalates (POMs) as early transition metal anionic clusters have numerous applications in catalysis, magnetism, electronics, and energy conversion. Particularly, the high capability to accept a large number of electrons and the reversible multi-electron redox properties make POMs show potential for anode-active materials. However, when pristine POMs are used as anode materials, their anion is prone to dissolve in the electrolyte, which leads to an evident capacity degradation. To overcome this obstacle, POMs are usually linked to some proper substrates, such as metal-organic frameworks (MOFs), which possess high surface areas, controllable porosities and controllable flexibility, have aroused enormous research attention, and have been applied in gas storage, separation, sensor, drug delivery and energy storage. POMs can be encapsulated into MOFs to fabricate POMOFs materials, which possess both the advantage of POMs and MOFs and are attractive candidates for the anode materials in Lithium storage. However, the POMOFs have low cycling capacity and inferior rate performance for its poor conductivity. Recently, Much effort has been devoted to design...
some conductive MOFs, which were used as the active electrode materials for EDL supercapacitors with outstanding electrochemical performances. Nevertheless, these conductive MOFs are all two-dimension materials, which are not suitable for LIBs. Immobilization of POMs to circumvent these difficulties, it is necessary to adopt other synthesis strategies to improve electrode conductivity of POMOFs as the anode electrode material for LIBs. For example, our group has reported a novel nanocomposite based on the POMOFs/RGO for LIBs, which have enhanced battery performances. However, the synthesis of GO (Graphene Oxide) is a complex process, the homogeneity of this nanocomposite is crucial, which can directly determine the electrochemical properties of the anode materials. Because of high thermal and chemical stability, high ionic conductivity and wide redox stability of ILs, they have great potential as guest materials, which could tune or enhance the conductivity of POMOFs. Thus, the anode materials with high capacity, good cycling stability and rate behavior will be obtained when we encapsulate the ILs and POMs into the cage of MOFs simultaneously.

Herein, we synthesized PMo10V2-ILs@MIL-100 crystals based on ferric chloride (Fe3+), benzene-1,3,5-tricarboxylic acid (BTC), 1-ethyl-3-methylimidazolium bromide (ILs), and H2PMo10O40 (PMo10O40) for the following reasons: (1) We synthesized MIL-100 using the precursors of Fe3+ and BTC, which have high thermal, chemical stability, high surface area, mesoporous cage structure (≈25 and 8 Å) and the proper pentagonal and hexagonal windows (≈5.5 and 7.3 Å) (Fig. S1a). MIL-100 can encapsulate many of guest POMs due to the suitable size of these cavities and the mesoporous cage structure. (2) Keggin-type POMs such as PMo10O40 are widely used as anode materials owing to the proper size, high stability, good solubility and reversible redox property which is stronger than that of PMo12 for the V (V) atoms in the cluster can increase the redox potential of the first electron transfer reaction. PMo10V2 can be confined into the mesoporous cage of MIL-100 owing to the size of PMo10V2 (≈10.47 Å) (Fig. S1b) is bigger than the window size of the cage. PMo10V2 is inserted into the cages of MIL-100 to play the role of the bridge; thus, the ILs are prone to disperse into the mesoporous cages of MIL-100 and react with PMo10V2 to form PMo10V2-ILs by the ion exchange procedure. (3) ILs, especially imidazolium ILs, possess high ionic conductivity and wide redox stability, which makes them attractive to improve the conductivity of POMOFs. The ILs in the POMOFs not only can enhance the contact between electrolyte and electrode but also improve the ionic and electronic conductivity of POMOFs to avoid the solid-electrolyte interphase (SEI) film formation. Thus, as an anode material for LIBs, the PMo10V2-ILs@MIL-100 crystals achieved a high, reversible capacity of 1248 mAh g\(^{-1}\) after 100 cycles at 0.2 A g\(^{-1}\), an excellent rate capability of 480 mA h g\(^{-1}\) at 2.0 A g\(^{-1}\), and very long lifetime of 400 cycles with about 600 mA h g\(^{-1}\) retained after 100 cycles at 1.0 A g\(^{-1}\). More importantly, the performances of PMo10V2-ILs@MIL-100 are the same as those of the well-known MOFs, POMs, POMOFs-based crystal materials and are comparable to the most excellent anode electrodes. Besides, the lithium storage behavior of PMo10V2-ILs@MIL-100 and PMo10V2-ILs@HKUST-1 crystals investigated by cyclic voltammogram (CV) measurement. It is observed that both the samples show the hybrid behavior of battery and supercapacitor, and the larger mesoporous cages and the larger surface area of MIL-100 are beneficial to improve the contribution of the capacitance. Although the synthesis of PMo10V2-ILs@MIL-100 crystals are complex and the ionic liquids are not cheap, the most important purpose of this work is to provide a new strategy to improve the conductivity of MOFs and POMOFs and enhance their hybrid behavior of battery and supercapacitor performances, which would help the development of other electrode materials based on MOFs and POMOFs for Lithium storage.

Experimental

Materials and Synthetic procedures

Materials. All the raw chemicals were obtained commercially and used without additional purification. The PMo10V2 precursor was synthesized according to a procedure described in the literature.

Synthesis of MIL-100(Fe) crystals. FeCl3·6H2O (1.62 g) and BTC (0.834 g) were dissolved in 30 mL of H2O. The mixture was then transferred to Teflon-lined autoclave and heated at 130 °C for 72 h. The product was filtered, washed with acetone.

Synthesis of PMo10V2@MIL-100 crystals. FeCl3·6H2O (0.945 g), BTC (0.68 g), PMo10V2 (2.036 g) were dissolved in 25 mL of H2O. The mixture was then heated at 130 °C for 72 h in a Teflon-lined autoclave. The product was filtered, washed with ethanol and ether.

Synthesis of PMo10V2@HKUST-1 crystals. Cu(OAc)2·H2O (0.2 g) and PMo10V2 (0.22 g) were dissolved in 10 mL of H2O. BTC (0.14 g) was dissolved in 10 mL of alcohol, and this solution was added dropwise to above mixture with continuous stirring. The precipitate was collected by centrifugation and washed with alcohol and deionized water.

Synthesis of PMo10V2-ILs@MIL-100 crystals and other control samples. An excess of the ILs was dissolved in 25 mL of H2O and then PMo10V2@MIL-100 (2.0 g) was dispersed into the mixture. After that, the mixture was stirred at room temperature for 24 h. Finally, the product was collected by centrifugation, washed with diethyl ether. For comparison, PMo10V2-ILs@MIL-100, PMo10V2-ILs@HKUST-1 and MIL-100 was synthesized through the same method except that PMo10V2@MIL-100, PMo10V2@HKUST-1 or MIL-100 was used to replace PMo10V2@MIL-100.

Material characterization

The PXRD patterns were collected on a D/max 2500 VL/PC diffractometer (Japan) equipped with graphite monochromatized Cu Kα radiation (λ=1.54060 Å). The FTIR was collected on a Nexus 670 spectrometer. The TGA was carried out by using a DSC 800 from PerkinElmer under N2 flowing with a heating rate of 10 °C min\(^{-1}\) from room temperature to 700 °C. Nitrogen adsorption-desorption isotherms were evaluated at 77K on a Micromeritics ASAP 2050 system, while the pore size distributions were calculated according to the Barrett-Joyner-Halenda (BJH) method. 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-dispersive X-ray spectroscopy.
spectrum. XPS measurements was collected on scanning X-ray photoelectron spectrometer. XPS measurements was collected on scanning X-ray photoelectron spectrometer. XPS measurements was collected on scanning X-ray photoelectron spectrometer. XPS measurements was collected on scanning X-ray photoelectron spectrometer.

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 LiPF₆ in ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 in Volume) as the electrolyte and 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 to a pressure of ≈1 GPa.

Results and discussion

The preparation process of PMo₁₀V₂-ILs@MIL-100 crystals is illustrated in Scheme 1. We firstly synthesized PMo₁₀V₂@MIL-100 using a facile hydrothermal method of 130 °C for 72 h by the simple mixture of Fe³⁺, BTC and PMo₁₀V₂. And then, ILs dispersed into the mesoporous cages of MIL-100 and reacted with PMo₁₀V₂ to form PMo₁₀V₂-ILs by the ion exchange procedure. The crystal structure of PMo₁₀V₂-ILs@MIL-100 reveals that every trinuclear iron cluster is bridged six BTC ligands to generate a 3D network (MIL-100) and PMO₁₀V₂@MIL-100 crystals are displayed in Fig. S4. 

Powder X-ray diffraction (PXRD) was used to analyse the crystalline structure of the MIL-100, PMo₁₀V₂@MIL-100 and PMo₁₀V₂-ILs@MIL-100 crystals. The crystalline structure of MIL-100 and PMo₁₀V₂@MIL-100 is in agreement with the corresponding simulated patterns as observed from PXRD studies, demonstrating that they have been synthesized successfully (Fig. 1a). The XRD patterns of PMo₁₀V₂-ILs@MIL-100 and PMo₁₀V₂@MIL-100 crystals are analogous, which indicates that the diffusion of the ILs into MIL-100 doesn’t break the POMOFs’ structure. The Fourier-transform infrared (FTIR) spectra of PMo₁₀V₂-ILs@MIL-100 crystals as well as the other samples are shown in Fig. 1b. The bands at 1708 and 1366 cm⁻¹ in MIL-100, PMo₁₀V₂@MIL-100 and PMo₁₀V₂-ILs@MIL-100 crystals are attributed to the stretching vibrations of n(C=O) and n(C-O) originated from aromatic groups. In terms of the PMo₁₀V₂, PMo₁₀V₂@MIL-100 and PMo₁₀V₂-ILs@MIL-100 samples, the four observed characteristic bands centered at 1057, 961, 865 and 776 cm⁻¹ are ascribed to P-O₃, Mo=O₃, Mo-O₃-Mo and Mo=O-Mo stretching vibrations. Particularly, the bands at 3144 and 1582 cm⁻¹ in PMo₁₀V₂-ILs@MIL-100 are attributed to n(C-H) and n(C=N) stretching vibrations in the ILs, indicating that the ILs has been successfully implanted into PMo₁₀V₂@MIL-100. The N₂ adsorption-desorption isotherms and pore size distributions of MIL-100, PMo₁₀V₂@MIL-100 and PMo₁₀V₂-ILs@MIL-100 crystals are shown in Fig. S3. The surface area and the BJH pore size distribution also reflect the surface area and volume changes during the encapsulation process. The thermogravimetric analysis (TGA) analyses of MIL-100, PMo₁₀V₂@MIL-100 and PMo₁₀V₂-ILs@MIL-100 crystals are displayed in Fig. S4.
The electrochemical properties of PMo$_{10}$V$_2$-ILs encapsulate the PMo$_{10}$V$_2$-ILs@MIL-100 crystals and the corresponding mapping image of PMo$_{10}$V$_2$-ILs@MIL-100, as shown in Fig. S7 and Fig. S8. The cycle performances of PMo$_{10}$V$_2$-ILs@MIL-100 crystals maintain its capacity advantage over the control samples and a reversible capacity of 1258.5 mAh g$^{-1}$ achieved after 100 cycles (Fig. 2c), which is more than twice as large as that of MIL-100 (581.4 mAh g$^{-1}$), three times larger than that of PMo$_{10}$V$_2$-ILs@MIL-100 (310.5 mAh g$^{-1}$) and significantly exceeds that of MIL-100 (75.7 mAh g$^{-1}$) and PMo$_{10}$V$_2$ (242.3 mAh g$^{-1}$).

Fig. 2 (a) CV profiles of PMo$_{10}$V$_2$-ILs@MIL-100 crystals at a scan rate of 0.1 mV s$^{-1}$. (b) Galvanotactic charge-discharge curves of PMo$_{10}$V$_2$-ILs@MIL-100 crystals as LIBs anodes for different cycles at 100 mA g$^{-1}$. (c) Charge/discharge capacity and coulombic efficiency of PMo$_{10}$V$_2$-ILs@MIL-100, ILs@MIL-100 and PMo$_{10}$V$_2$-ILs@MIL-100 crystals at 0.1 A g$^{-1}$. (d) Rate performance of PMo$_{10}$V$_2$-ILs@MIL-100 crystals from 0.1 A g$^{-1}$ to 3 A g$^{-1}$. (e) Cycling performance of PMo$_{10}$V$_2$-ILs@MIL-100 crystals at 1.0 A g$^{-1}$ after a few cycles at 0.1 A g$^{-1}$. The cycle performances of PMo$_{10}$V$_2$-ILs@MIL-100 crystals and other samples between 0.01 and 3 V at 0.1 A g$^{-1}$ are displayed in Fig. 2c. PMo$_{10}$V$_2$-ILs@MIL-100 crystals display an initial discharge capacity of 1665.5 mAh g$^{-1}$ and a high reversible capacity of 1114.9 mAh g$^{-1}$ (Fig. 2b and c). In contrast, the control samples merely deliver initial discharge capacities of 1070.2 mAh g$^{-1}$ (PMo$_{10}$V$_2$-ILs@MIL-100), 1376.5 mAh g$^{-1}$ (ILs@MIL-100), 1031.4 mAh g$^{-1}$ (PMo$_{10}$V$_2$) and 1259 mAh g$^{-1}$ (MIL-100) (Fig. 510). The initial coulombic efficiency of PMo$_{10}$V$_2$-ILs@MIL-100 crystals is 66.94%, much higher than that of PMo$_{10}$V$_2$-ILs@MIL-100 (49.2%), ILs@MIL-100 (44.5%), PMo$_{10}$V$_2$ (12.56%) and MIL-100 (12.91%). In the subsequent cycles, PMo$_{10}$V$_2$-ILs@MIL-100 crystals maintain its capacity advantage over the control samples and a reversible capacity of 1258.5 mAh g$^{-1}$ achieved after 100 cycles (Fig. 2c), which is more than twice as large as that of MIL-100 (581.4 mAh g$^{-1}$), three times larger than that of PMo$_{10}$V$_2$-ILs@MIL-100 (310.5 mAh g$^{-1}$) and significantly exceeds that of MIL-100 (75.7 mAh g$^{-1}$) and PMo$_{10}$V$_2$ (242.3 mAh g$^{-1}$).
More importantly, the PMo$_{10}$V$_2$-ILs@MIL-100 crystals also display superior rate performance (Fig. 2d). As the current density increased from 0.1 to 0.2, 0.5, 1, 2, and 3 A g$^{-1}$, the charge capacity of PMo$_{10}$V$_2$-ILs@MIL-100 crystals decrease slightly from 1032.8 mAh g$^{-1}$ to 929.2, 774.7, 633.6, 5 and 347.5 mAh g$^{-1}$, respectively. The capacitive effect of the battery system was studied according to the CV curves of the PMo$_{10}$V$_2$-ILs@MIL-100 crystals (Fig. 3a) and PMo$_{10}$V$_2$-ILs@HKUST-1 (Fig. 3sa) at different sweep rates from 0.1 to 10 mV s$^{-1}$. These results can be used to calculate the capacitance contribution in the electrochemical process on account of power law $i = a \cdot \nu^{b}$, where $i$ represents the current, $\nu$ stands for the sweeping rate, and $a$ and $b$ are adjustable values. In general, a b-value of 0.5 indicates that the electrochemical reaction is mainly controlled by capacitance. A b-value of 1 means that it is regarded as a behavior which is controlled by the diffusion of Li$^+$. When b-values are located between 0.5 and 1, both them contribute to the electrochemical process. As shown in Fig. 3b, the b is 0.811 for the cathodic peaks and the b is 0.721 for the anodic one, which demonstrate a hybrid of capacitance and Li$^+$ insertion/extraction. Furthermore, the PMo$_{10}$V$_2$-ILs@MIL-100 exhibits larger b-values in both cathodic and anodic scans in contrast to that of PMo$_{10}$V$_2$-ILs@HKUST-1 crystals (Fig. 3sb), improving the corrected rate performance and cycling capacity. The contributions of the capacitance and intercalation capacity can be further quantitatively calculated by the below equations

$$i(v) = k_1 \cdot i(v)^{0.5} + k_2 \cdot i(v)^{-0.5}$$

By determining both $k_1$ and $k_2$ constants, we can analyze the fraction of the current originated from surface capacitance and Li$^+$ diffusion at a given potentials. As in Fig. 3c, the capacitive-controlled capacity contributed about 66.03 % of the total Li$^+$ storage for PMo$_{10}$V$_2$-ILs@MIL-100 crystals at 1 mV s$^{-1}$ (the blue shaded area of the Fig. 3c). As the scan rate rises from 0.1 to 2 mV s$^{-1}$, the effect of capacitive contribution gradually increases (Fig. 3d) and obtains a maximum value of 78.55 % at 2 mV s$^{-1}$. However, as seen from Fig. S15c and d, PMo$_{10}$V$_2$-ILs@HKUST-1 crystals show a lower capacitive contribution with a value of 51.05 % at 1 mV s$^{-1}$ and 65.75 % at 2 mV s$^{-1}$, which confirm the larger mesoporous cages of MIL-100 can be beneficial to improve the contribution of the capacitance compared with HKUST-1.

This journal is © The Royal Society of Chemistry 20xx
contributions separated with cyclic voltammogram at 1 mV s\(^{-1}\) scan rate and limited (red) capacities at various scan rates.

As illustrated in Scheme S2, the improved performances might be attributed to the synergistic effect among ILs, POMs and MOFs. Firstly, the porous characteristics of MIL-100 can accommodate the volume expansion induced by intercalation/deintercalation of Li\(^{+}\) and alleviate the stress.

Secondly, the PMo\(_{3}V_{2}\)@MIL-100 crystals show a hybrid behavior of battery and supercapacitor. The battery behaviors of PMo\(_{3}V_{2}\) are achieved by the redox of Mo\(^{5+}\), V\(^{4+}\) and Fe\(^{3+}\). At the same time, capacitive behavior also promotes the performance which is ascribed by the mesoporous cages and the large surface area of MIL-100. Thirdly, ILs in the MOFs not only can enhance contact between electrolyte and electrode but also improve ion and electronic conductivity due to fast charge and Li\(^{+}\) transport. Accordingly, PMo\(_{3}V_{2}\)-ILs@MIL-100 crystals anode materials show excellent rate capability, remarkable cycling stability and long cycle life.

## Conclusions

In summary, we have successfully fabricated a series of POMs-ILs@MOFs crystals through encapsulating ILs within POMs. Owing to the strong redox properties of POMs and the high porosity of MOFs, the obtained crystals show the hybrid behavior of battery and supercapacitor. In addition, ILs in the MOFs not only can provide a rapid path for Li\(^{+}\) transfer but also improve electronic conductivity. Thus, PMo\(_{3}V_{2}\)-ILs@MIL-100 crystals used as anode materials for LIBs delivers a high capacity of 1248 mAh g\(^{-1}\) at 0.1 A g\(^{-1}\) after 100 cycles. The battery performances of PMo\(_{3}V_{2}\)-ILs@MIL-100 crystals include capacity, cycling stability and rate behavior, and significantly improved compared with the MIL-100, PMo\(_{3}V_{2}\), PMo\(_{3}V_{2}\)-ILs@MIL-100 crystals, and are the best amongst all the reported MOFs, POMs and POMOFs-based materials. The new strategy introduced herein to improve conductivity of MOFs and POMOFs offers new prospects for the design of the next generation of high-performance and sustainable energy-storage devices based on different MOFs and POMOFs.

## Conflicts of interest

There are no conflicts to declare.

## Acknowledgements

This work was financially supported by NSFC (No. 21622201), 21471080 and 2170010097), the NSF of Jiangsu Province of China (No. BK2017040708), the Natural Science Research of Jiangsu Higher Education Institutions and the Foundation of Jiangsu Collaborative Innovation Center of Biomedical Functional Materials.
32 D. Sheberla, J. C. Bachman, J. S. Elias, C.-J. Sun, Y. Shao-Horn
33 T. Wei, M. Zhang, P. Wu, Y.-J. Tang, S.-L. Li, F.-C. Shen, X.-L.
Wang, X.-P. Zhou and W.-Q. Lan, Nano Energy, 2017, 34, 205-
214.
34 S. S. Moganty, N. Jayaparakash, J. L. Nugent, J. Shen and L. A.
36 H. Wan, C. Chen, Z. Wu, Y. Que, Y. Feng, W. Wang, L. Wang, G.
Guan and X. Liu, ChemCatChem, 2015, 7, 441-449.
37 X. Qi, K.-Y. Pu, H. Li, X. Zhou, S. Wu, Q.-L. Fan, B. Liu, F. Boey,
W. Huang and H. Zhang, Angew. Chem. Int. Ed., 2010, 49,
9426-9429.
38 G. A. Tsigdinos and C. J. Hallada, Inorg. Chem., 1968, 7, 437-
441.
39 R. Canioni, C. Roch-Marchal, F. Sécheresse, P. Horcajada, C.
Serre, M. Hardi-Dan, G. Férey, J.-M. Grenèche, F. Lefebvre, J.-
S. Chang, Y.-K. Hwang, O. Lebedev, S. Turner and G. Van
40 D. Zhou and B.-H. Han, Adv. Funct. Mater., 2010, 20, 2717-
2722.
41 C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck and R.
43 C. Zhang, W. Hu, H. Jiang, J.-K. Chang, M. Zheng, Q.-H. Wu and
44 M. C. Biesinger, B. P. Payne, A. P. Grosvenor, L. W. M. Lau, A.
2717-2730.
46 J. Wang, H. Tang, L. Zhang, H. Ren, R. Yu, Q. Jin, J. Qi, D. Mao,
M. Yang, Y. Wang, P. Liu, Y. Zhang, Y. Wen, L. Gu, G. Ma, Z. Su,
47 T. Yuan, Y. Jiang, W. Sun, B. Xiang, Y. Li, M. Yan, B. Xu and S.
48 P. Simon, Y. Gogotsi and B. Dunn, Science, 2014, 343, 1210-
1211.
7, 1597-1614.
50 M. Zhang, T. Wei, A. M. Zhang, S.-L. Li, F.-C. Shen, L.-Z. Dong,

This journal is © The Royal Society of Chemistry 20xx
J. Name., 2013, 00, 1-3 | 7

Published on 11 April 2018. Downloaded by Nanjing Normal University on 17/04/2018 12:59:33.
Encapsulating the ionic liquids into POM-based MOFs to improve their conductivity for superior lithium storage

Mi Zhang, A-Man Zhang, Xiao-Xiao Wang, Qing Huang, Xiaoshu Zhu, Xiao-Li Wang, Long-Zhang Dong, Shun-Li Li* and Ya-Qian Lan*

Developing advanced anode materials with multi-electron reaction, adequate charge transport, and suppressed volume changes is highly desirable in Lithium storage. In this paper, we skillfully encapsulate ionic liquids (ILs) into polyoxometalate-based metal-organic frameworks (POMOFs) to fabricate a series of ILs-functionalized POMOFs crystals (denoted as POMs-ILs@MOFs), which immobilize POMs in the cage of MOFs avoiding the leaching of POMs and obtain an enhanced conductivity by the modification of the ILs. More importantly, it is observed that POMs-ILs@MOFs show the hybrid behavior of battery and supercapacitor because of the large mesoporous cages and the large surface area of MOFs. Thus, one of POMs-ILs@MOFs (PMo$_{10}$V$_2$-ILs@MIL-100) crystals shows high reversible capacity and superior cycling stability and rate capability when they are used as anode materials, which are the best amongst all the reported MOFs and POMs crystals materials.