Supercapacitors

Conductive Metal–Organic Framework Nanowire Array Electrodes for High-Performance Solid-State Supercapacitors

Wen-Hua Li, Kui Ding, Han-Rui Tian, Ming-Shui Yao, Bhaskar Nath, Wei-Hua Deng, Yaobing Wang,* and Gang Xu*

The application of conventional metal-organic frameworks (MOFs) as electrode materials in supercapacitors is largely hindered by their conventionally poor electrical conductivity. This study reports the fabrication of conductive MOF nanowire arrays (NWAs) and the application of them as the sole electrode material for solid-state supercapacitors. By taking advantage of the nanostructure and making full use of the high porosity and excellent conductivity, the MOF NWAs in solid-state supercapacitor show the highest areal capacitance and best rate performance of all reported MOF materials for supercapacitors, which is even comparable to most carbon materials.

1. Introduction

Supercapacitors are among the most promising types of devices for next-generation energy storage owing to their high power density, fast charge/discharge process, and excellent cyclability.^[1] Compared to liquid electrolyte supercapacitors, solidstate ones are smaller, more lightweight, and easier to handle. Solid-state supercapacitors also have higher level of reliability and safety, and a wider range of operating temperatures. These features make them suitable for wearable and miniaturized electronics.^[2] Various capacitive materials, such as transition metal oxides, carbon allotropes, and conductive polymers, have been extensively studied.^[3] Compared with conventional electrode materials, metal-organic frameworks (MOFs) are a newly emerging type of electrode materials that have attracted increasing attention owing to their fascinating structural features.^[4] MOFs are crystalline sponge-like materials that are constructed by connecting metal sites with organic linkers.

W.-H. Li, K. Ding, H.-R. Tian, Dr. M.-S. Yao, Dr. B. Nath, W.-H. Deng, Prof. Y. Wang, Prof. G. Xu
State Key Laboratory of Structural Chemistry
Key Laboratory of Design and Assembly of Functional Nanostructures
Fujian Provincial Key Laboratory of Nanomaterials
Fujian Institute of Research on the Structure of Matter
Chinese Academy of Sciences (CAS)
155 Yangqiao Road West, Fuzhou, Fujian 350002, P. R. China
E-mail: wangyb@fjirsm.ac.cn; gxu@fjirsm.ac.cn
W.-H. Li, K. Ding
University of Chinese Academy of Sciences

Beijing 100049, China

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/adfm.201702067.

DOI: 10.1002/adfm.201702067

Their large specific surface area (over 7000 m² g⁻¹) enables MOFs to substantially adsorb ions from the electrolyte, which is beneficial to generate large electrical double-layer (EDL) capacitance.^[5] In addition, the well-established structural tunability of MOFs enables the rational design of their pores into a highly ordered arrangement and strictly limited into fewnanometer size. This condition facilitates desolvation of ions, thereby enhancing the capacitance.^[6,7]

However, the application of conventional MOFs as electrode materials on

supercapacitors is largely hindered by their conventionally poor electrical conductivity. To improve their conductivity, MOFs are either pyrolyzed into carbons (not MOF anymore) or mixed with conductive materials, such as carbon black, graphene, and polyaniline, and then glued to the current collector by polymeric binders.^[8-11] However, the use of conductive additives and polymer binders would decrease the effective surface area of MOFs.^[12] Recently, Dincă and co-workers reported the first successful example of using the pressed powder pellet of a conductive MOF, Ni₃(HITP)₂, (HITP = 2, 3, 6, 7, 10, 11-hexaiminotriphenylene), as the active electrode material for EDL supercapacitors without conductive additives or other binders.^[13] This conductive MOF-based supercapacitor shows very exciting specific surface area normalized capacitance (denoted as "areal capacitance" thereafter) that is even higher than those of most carbon material-based supercapacitors. Nevertheless, further studies are extremely desired to obtain better rate capacity by engineering MOFs at nanoscale, to realize better mechanical properties by contacting MOF material to current collector through chemical bonding and to achieve higher capacitance by incorporating pseudocapacitive components. However, the preparation of MOF materials into nanowires on current collector remains a challenge, and conductive MOF nanowires have not been reported.

We report, for the first time, the fabrication of conductive MOF nanowire arrays (NWAs) and the application as the sole electrode for solid-state supercapacitors. The conductive MOF, namely, Cu–CAT, was grown onto carbon fiber paper to form crystalline NWAs in a controlled manner, thereby enabling this material to be directly used as integrated electrodes for supercapacitors without conductive additives and binders. By taking advantage of the nanostructure and making full use of the high porosity and excellent conductivity, Cu–CAT NWAs in



FUNCTIONAL MATERIALS



Figure 1. a) Crystal structure of Cu–CAT viewed along the *c*-axis. b) SEM and photographic image (inset) of the carbon fiber paper. c,d) SEM and photographic image (inset in c) of the Cu–CAT NWAs growing on carbon fiber paper.

solid-state supercapacitor showed the highest areal capacitance and the best rate performance in all MOF materials reported for supercapacitors, which is even comparable to most carbon materials (based on the mass of active material).

2. Results and Discussion

2.1. Morphology and Structural Analysis

Cu–CAT was first synthesized by Yaghi and co-workers and exhibits conductivity as high as 20 S m⁻¹, which is one of the highest values in reported MOF materials.^[14,15] The crystal structure of Cu–CAT is shown in **Figure 1**a. Cu ions coordinate to 2, 3, 6, 7, 10, 11-hexahydroxytriphenylene (HHTP) ligands in *ab* plane to construct a 2D hexagonal lattice which further packs along the *c*-axis with a slipped-parallel AB stacking model to form a honeycomb-like porous structure. Cu–CAT has 1D channels along the *c*-axis with open-window size of ≈1.8 nm. Effective orbital overlaps between Cu ions and organic ligands endow Cu–CAT with good property of charge transport.^[16]

Cu–CAT crystallite powder with irregular morphology (Figure S1, Supporting Information) was synthesized by the reaction between copper acetate and HHTP in water/N,N-dimethylformamide (DMF) (v/v = 4:1) at 85 °C (for details, see the Experimental Section). Cu–CAT NWAs was directly grown on carbon paper by immersing carbon paper into reaction solution (see the Experimental section for details). Controlling the oriented growth of the nanostructured MOFs remains a big challenge. However, when fixing other experimental conditions, the diameter of Cu–CAT nanowires was controlled in 200–250 nm, and its length was modulated from 3 to 15 μ m

by elongating the reaction time from 1 to 24 h (Figure S2, Supporting Information).

As shown in the digital photographs (insets of Figure 1b,c), the blank carbon fiber paper $(1.5 \times 1.5 \text{ cm}^2)$ is gray and uniformly turns to dark blue after being covered by Cu-CAT NWAs. The scanning electron microscopy (SEM) image in Figure 1b shows that the blank carbon fibers have very smooth surface and diameters of $\approx 2 \,\mu m$. After synthesis, numerous oriented nanowires with high density homogeneously covered the whole fibers (Figure 1c). The high-magnification SEM image in Figure 1d shows that the nanowires have uniform hexagonalprism shape and hexagonal top facet. The transmission electron microscopy (TEM) images are shown in Figure 2a,b. The distance of 1.83 nm between lattice fringes coincides with the lattice spacing in hexagonal crystal system and can be assigned to the (100) face. The bright and independent diffraction points in the selected area electron diffraction (SAED) (the inset of Figure 2b) further reveal the single crystal feature of the nanowire. The well-defined diffraction dots in SAED pattern correspond to the {001} and {100} facets. This information, together with the [100] lattice fringes in Figure 2b, demonstrates that the growth direction of the nanowire is along [001]. Therefore, the 1D channels in the crystal structure of Cu-CAT are extended along the growth direction of the nanowires and should be perpendicular to the hexagonal top facets of the nanowires (Figure S3, Supporting Information), which may facilitate the transport of electrolyte ions to achieve rapid charge/discharge transfer reaction and result to high rate performance.^[17]

Powder X-ray diffraction (PXRD) data, as shown in Figure 2c, verifies that the nanowires are the crystal of Cu–CAT. N_2 and water vapor sorption results reveal that Cu–CAT possesses microporous structure with a Brunauer–Emmett–Teller (BET)

FUNCTIONAL MATERIALS www.afm-iournal.de



Figure 2. a,b) TEM images of Cu-CAT nanowire (insets: SAED pattern). c) PXRD patterns for Cu-CAT. d) N2 sorption isotherms of Cu-CAT at 77 K.

surface area of 540 m² g⁻¹, and can be wetted and accessed by aqueous electrolytes easily (Figure 2d; and Figures S4 and S5, Supporting Information). These results suggest that the Cu–CAT NWAs is a promising electrode for supercapacitors owing to its high effective porosity and wettability.

2.2. Supercapacitors Performance

Figure 3a shows the typical CV curves of Cu-CAT NWAs electrode in a three-electrode cell using 3 м KCl as aqueous electrolyte. The working potential window was explored by cycling cathodically between the open circuit potential of 0 and -0.4 V and anodically between 0 and 0.5 V (vs Ag/AgCl) (Figure S6a, Supporting Information). CV of blank carbon paper electrode at least from -0.4 to +0.4 V (vs Ag/AgCl) was shown in Figure S6b (Supporting Information). The carbon paper did not show any redox activity and has almost no contribution to the capacitance. The galvanostatic charge and discharge curves of Cu-CAT NWAs electrode (Figure 3b) exhibit that its specific capacitances remains as high as 66% (202-134 F g⁻¹) when current densities increase 20 times (0.5-10 A g⁻¹). As shown in Figure 3c, it retains 80% of its initial capacitance after 5000 cycles at 800 mV $\ensuremath{\mathrm{s}}^{-1}\xspace$, which is comparable to other MOF-based supercapacitors.^[18] Moreover, there is no change of the PXRD pattern of Cu-CAT NWAs after 5000 cycling, suggesting the excellent electrochemical stability of Cu-CAT NWAs (Figure S7, Supporting Information).

For comparison, Cu-CAT powder electrode was made by mixing Cu-CAT crystallite powder with polymer binder and then coated onto carbon paper with the traditional slurrycoating method without conductive additives. It is observed that the Cu-CAT NWAs electrode shows much better performance than its powder electrode (Figure 3d). The NWAs electrode has two times higher capacitance than the powder electrode. Meanwhile, the NWAs electrode has ≈66% retention when increasing current density from 0.5 to 10 A g⁻¹, which is significantly higher than the \approx 33% retention of the powder electrode. As shown in Figure 3e, electrochemical impedance spectra were conducted to reveal the reasons for above observations.^[19] The ohmic resistance and the charge transfer resistance at the electrode/electrolyte interface of NWAs electrode (1.2 and 0.5Ω , respectively) are both significantly lower than those of the powder electrode (3.6 and 7.4 Ω , respectively) (Figure 3e; and Figure S8, Supporting Information). For the powder electrode, the MOF particles attach to current collector with the help of polymer binder, which possesses large inter-particle resistance and contact resistance between MOF nanoparticles and current collector. Differently, the NWAs electrode exhibits single crystal nanowires directly grown on the carbon fibers with firmly adhesion. This kind of nanostructured electrode can significantly reduce its intrinsic resistance and charge transfer resistance at the electrode/electrolyte interface, enabling effective charge/ electron transport on the interface of nanowires array and electrolyte.^[3,13,20] Further, the straight tail of the NWAs electrode at low frequency is more parallel to the imaginary axis than that of the powder electrode, which confirms that electrolyte has faster







Figure 3. Electrochemical performances of Cu–CAT NWAs electrode in a three-electrode cell. a) CVs at different scan rates. b) Galvanostatic charge and discharge curves at different current densities. c) Cycling performance. d) Rate-dependent specific capacitance. e) Nyquist electrochemical impedance spectra. f) Comparison of the specific capacitances of the electrodes of different MOF materials.

diffusion speed in NWAs electrode than in powder electrode. These results explain why NWAs electrode has much higher rate performance than that of the powder electrode.^[21]

The electrochemical performance of the conductive Cu–CAT was also compared with other well-known low conductive MOF materials (UiO-66, ZIF-8, ZIF-67, MIL-100, and MIL-101) (see the Experimental Section, Figure 3f; and Figure S9 and Table S1, Supporting Information for details).^[22] Without conductive agent, ZIF-67 shows the highest capacitance of 0.133 F g⁻¹ among these MOFs, which is 260 times lower than that of Cu–CAT powder. These results indicate that the low conductivity of these MOFs severely inhibits the electron transport on the framework and the ion diffusion inside the pores, which induces their low capacitances.

The excellent electrochemical performance of Cu–CAT NWAs electrode inspires us to explore the possibility to apply it on the solid-state supercapacitor. A symmetric solid-state

supercapacitor was fabricated by pressing two identical pieces of Cu–CAT NWAs electrodes $(1.5 \times 1.5 \text{ cm}^2)$ together in parallel with PVA/KCl (PVA = polyvinyl alcohol) gel as solid electrolyte (Figure S10, Supporting Information). The CV and galvanostatic charge and discharge of a symmetrical cell were shown in Figure 4a,b, respectively. The Cu-CAT NWAs-based solid-state supercapacitor has good cycling stability, which retains more than 85% of its initial capacitance after 5000 cycles at 50 mV s⁻¹ (Figure 4c). The Nyquist plot is almost unchanged after cycling (Figure S11, Supporting Information), which further demonstrates the high stability of Cu-CAT NWAs electrode. Meanwhile, solid-state electrolyte supercapacitor normally has lower capacitance than liquid electrolyte supercapacitor with the same electrode material.^[23] However, the carbon paper supported Cu-CAT NWAs electrode can exhibits EDL capacitance of 120 F g^{-1} at current densities of 0.5 A g^{-1} (based on the mass of total active materials). This result reveals the device has specific





www.afm-journal.de



Figure 4. Device performances of Cu–CAT NWA-based supercapacitor: a) CVs at different scan rates. b) Galvanostatic charge and discharge curves at different current densities. c) Cycling performance. d) Performance comparison of Cu–CAT NWAs and carbon materials based symmetric solid-state supercapacitors. e) Comparison of rate performance of Cu–CAT NWAs and Cu–CAT powder. f) Structure of the solid-state supercapacitor (left) and photograph of a red light-emitting-diode powered by the three supercapacitors connected in series (right).

surface area normalized capacitance of ~22 $\mu F~cm^{-2}$. This value also surpasses the reported values of the activated carbon and single walled carbon nanotube (SWCNT)-based symmetric solid-state supercapacitors (<10 $\mu F~cm^{-2}$) and is comparable to those of graphene-based symmetric solid-state supercapacitors (18.9–25 $\mu F~cm^{-2}$) with exception of 3D graphene hydrogel-based one (45 $\mu F~cm^{-2}$) (Figure 4d; and Table S2, Supporting Information).^[24]

Cu–CAT powder-based capacitor can only retain 23% of the initial capacitance, when increasing the current density from 0.25 to 5 A g^{-1} (Figure 4e). Comparatively, Cu–CAT NWAs supercapacitor with electrode mass loading of 0.50 mg cm⁻² has capacitance retention as high as 55% when the current density changed in the same range. The electrode with 4 times higher mass loading (2.01 mg cm⁻²) can still remain the retention of 45% (Figure S12, Supporting Information). These results demonstrate the nanowire array structured electrode can keep good

retention in higher mass loading. This significantly improved rate ability attributes to the unique nanowire-arrays-structured electrode as discussed above.

The gravimetric energy density of the Cu–CAT NWAs supercapacitor ≈ 2.6 W h kg⁻¹ as the gravimetric power density is ≈ 0.2 kW kg⁻¹ (Figure S13, Supporting Information). A red light-emitting diode (1.5 V) was successfully lighted for more than 60 s by three series-connected devices (Figure 4f), demonstrating the potential of the Cu–CAT NWAs supercapacitor.

3. Conclusion

In summary, conductive MOFs are a new class of promising microporous electrode materials for supercapacitors. Our work demonstrated the possibility to apply one of them (i.e., Cu– CAT) in a high-performance solid-state supercapacitor. Highly





oriented NWAs of conductive MOF material was successfully prepared for the first time as conductive additives and binders free electrode. Based on this, a solid-state supercapacitor was constructed and achieved a very high surface area-normalized capacitance of $\approx 22 \ \mu F \ cm^{-2}$, which is beyond the previously reported values for other MOF-based supercapacitors and most porous carbon- (such as activated carbon, carbon nanotube) based symmetric solid-state supercapacitors. Most importantly, our work reveals that the electrochemical performances of MOF materials, such as rate performance and capacitance, can be significantly improved by engineering its morphology from irregularly shaped crystallite to highly oriented nanowire arrays and making full use of the high porosity and excellent conductivity. At present, conductive MOFs seems to be just beginning of the field of conductive MOF for energy storage applications. In future, much work should focus on overcoming the challenges like, higher energy density, longer cycling performance, and higher mass loading of the active materials. However, given that MOFs possess well-established structure and property tunability, the results of this work provide a great prospect for developing MOFs as an ideal class of electrode materials for supercapacitors.

4. Experimental Section

Synthesis of Cu-CAT Powder and Cu-CAT NWAs on Carbon Fibre Papers: Copper acetate monohydrate (8 mg, 0.04 mmol) and HHTP (6.5 mg, 0.02 mmol), were dispersed in 1 mL solvent mixture of water/ DMF (v: v = 1:1) under sonication for 10 min in a 20 mL glass vial. The clean carbon fiber paper was immersed into the reaction solution and heated in an oven at 85 °C and then cooled to room temperature within 30 min. The length of the Cu-CAT nanowires was controlled by the reaction time. After that, the gray carbon paper was uniformly coated with a layer of dark blue Cu-CAT NWAs. The Cu-CAT NWAs coated carbon paper was collected and washed thoroughly with deionized water for 5 times and then treated by freeze-drying technique. The activation process and weighting of the electrode: Carbon fiber paper was first cleaned by ultrasonically in deionized (DI) water/acetone/isopropanol (v/v/v = 1:1:1) for 30 min, and then washed in ethanol for 3 times, and dried in an oven for 12 h at 100 °C. The mass of the blank electrodes were carefully weighted using a SHIMADZU AUW 120D balance (d =0.01 mg) with a platform vibration isolator. After growth, the Cu-CAT NWAs coated carbon papers were collected and washed carefully with deionized water for 5 times. Then the Cu-CAT NWAs coated carbon papers were immersed to DI water in a capped vial at 85 °C for 4 h. The same procedure was repeated again with the final immersion step for 15 h. Then, the Cu-CAT NWAs coated carbon papers were immersed to CH₃OH in the capped vial at 65 °C for 5 h. This procedure was also repeated again. Then the Cu-CAT NWAs coated carbon papers were dried under vacuum at 85 $^\circ C$ for 15 h. The mass of the Cu–CAT NWAs coated carbon papers were carefully weighted. The weight difference before and after mass loading is the weight of Cu-CAT NWAs. By control the synthesis process, the mass of Cu-CAT NWAs grown on carbon papers is from ${\approx}0.90$ to ${\approx}4.53$ mg, and the mass loading is increased from 0.40 to 2.01 mg cm⁻². Cu-CAT crystallite powder with irregular morphology can be collected at the bottom of the glass vial.

Synthesis of Typical Low Conductive MOF Materials: UiO-66, ZIF-8, ZIF-67, MIL-100, and MIL-101 were synthesized under solvothermal conditions as previously reported, respectively.^[25]

Preparation of the Electrodes for Electrochemical Measurements in a Three-Electrode Cell: The electrochemical performances of Cu–CAT NWAs were performed by directly using Cu–CAT NWAs on carbon paper (mass loading 0.60 mg cm⁻²) as the working electrode. The electrodes of

Cu–CAT crystallite or other low conductive MOF powders were prepared by the traditional slurry coating method but without conductive carbon additives (mass loading 0.40 mg cm⁻²). The active materials were mixed with polyvinylidene fluoride (80:20, w/w) in N-methyl-2-pyrrolidene solution by stirring \approx 12 h to form a sticky slurry, then the slurry was coated on carbon fiber paper and then dried at 80 °C overnight under vacuum. The electrochemical performances of these materials were studied in a three-electrode cell in 3 $\,$ KCl aqueous electrolytes, with Ag/AgCl and Pt plate as the reference electrode and counter electrode, respectively.

Fabrication of the Solid-State Supercapacitor. The gel electrolyte for supercapacitor was prepared as follows: 6 g PVA powder was dissolved in 60 mL 3 M KCl aqueous solution slowly under vigorous stirring at 85 °C until the mixture became a clear and transparent solution. The process of fabricating the all-solid-state supercapacitor was as follows: a piece of separator membrane (NKK TF40) was sandwiched in between two identical pieces of Cu–CAT NWAs electrodes ($1.5 \times 1.5 \text{ cm}^2$; mass loading 0.5-2.0 mg cm⁻²) with PVA/KCl gel as solid-state electrolyte. In general, the electrodes with mass loading of $\approx 2.0 \text{ mg cm}^{-2}$ were used for performances measurements. Before assembling, Cu-CAT NWAs electrodes were immersed into the PVA/KCl solution for 5 min to allow the electrolyte to contact with the microporous structure of the activated sample. After that, they were allowed to dry under ambient conditions for 15 min. This gel coating process was repeated two times. Then a symmetrical solid-state supercapacitor device was assembled. The device assembly process was optimized by controlling suitable pressure among separator and two electrodes as well as elongating standing time (for 10 h) of the assembly device to allow better penetration of electrolyte into electrodes. The process of fabricating the all-solid-state supercapacitor with Cu-CAT powder electrode is the same as Cu-CAT NWAs.

Characterization: All reagents were purchased commercially and used without further purification. PXRD patterns were recorded on a Rigaku MiniFlex II diffractometer using Cu K_{α} radiation. The morphology and microstructure of the fabricated materials are characterized by a field emission scanning electron microscopy, JEOL model JSM-6700 FE-SEM, operating at an accelerating voltage of 1.5 or 5.0 kV. TEM images were obtained on a IEOL- 2010 transmission electron microscope at an acceleration voltage of 200 kV. Nitrogen sorption isotherms were measured at 77 K on Micromeritics ASAP 2020 analyze after refluxed the samples in methanol over night for three times and then pretreated under vacuum at 100 °C for 10 h. The specific surface area was calculated from the N₂ adsorption isotherm using the BET equation. The pore size distribution was determined by NLDFT modeling. The conductivity of MOF powder pellets was measured with a two-probe method using Keithley 4200 (Table S1, Supporting Information). The pellets of MOFs were pressed at a pressure of ≈ 1 GPa. Electrical measurements were performed in air at a constant temperature of 297 K and in the absence of light. The electrochemical characteristics in a three-electrode cell with liquid electrolyte or in a two-electrode system with solid-state electrolyte were performed with CHI660e electrochemical working station (CH Instrument Inc.). The Nyquist plots of the samples were studied by CompactStat-Plus2 (Ivium) in a frequency range of 0.01 to 1 000 000 Hz.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

W.-H.L. and K.D. contributed equally to this work. This work was supported by the NSF of China (Nos. 51402293, 21501173, and 21550110194), the Strategic Priority Research Program, CAS (No. XDB20000000), Key Research Program of Frontier Science, CAS (No.

SCIENCE NEWS _____ www.advancedsciencenews.com

QYZDB-SSW-SLH023), and NSF of Fujian Province (Nos. 2016J06006, 2015J01230, and 2014J05027). The authors thank Prof. L. M. Zheng and Dr. S. S. Bao (Nanjing University, China) for their help with gas sorption measurements.

Conflict of Interest

The authors declare no conflict of interest.

Keywords

conductivity, metal-organic frameworks, nanowire arrays, porous structures, supercapacitors

Received: April 19, 2017 Published online: May 26, 2017

- a) M. Salanne, B. Rotenberg, K. Naoi, K. Kaneko, P. L. Taberna, C. P. Grey, B. Dunn, P. Simon, *Nat. Energy* **2016**, *1*, 16070;
 b) Z. Yu, L. Tetard, L. Zhai, J. Thomas, *Energy Environ. Sci.* **2015**, *8*, 702.
- [2] X. Lu, M. Yu, G. Wang, Y. Tong, Y. Li, Energy Environ. Sci. 2014, 7, 2160.
- [3] a) P. Simon, Y. Gogotsi, Nat. Mater. 2008, 7, 845; b) G. Wang,
 L. Zhang, J. Zhang, Chem. Soc. Rev. 2012, 41, 797; c) Z. Wu, L. Li,
 J. Yan, X. Zhang, Adv. Sci. 2016, DOI: 10.1002/advs.201600382.
- [4] L. Wang, Y. Han, X. Feng, J. Zhou, P. Qi, B. Wang, Coord. Chem. Rev. 2016, 307, 361.
- [5] O. K. Farha, I. Eryazici, N. C. Jeong, B. G. Hauser, C. E. Wilmer, A. A. Sarjeant, R. Q. Snurr, S. T. Nguyen, A. O. Yazaydin, J. T. Hupp, J. Am. Chem. Soc. 2012, 134, 15016.
- [6] H. Furukawa, K. E. Cordova, M. O'Keeffe, O. M. Yaghi, Science 2013, 341, 1230444.
- [7] J. Chmiola, G. Yushin, Y. Gogotsi, C. Portet, P. Simon, P. L. Taberna, *Science* 2006, 313, 1760.
- [8] a) B. Liu, H. Shioyama, H. Jiang, X. Zhang, Q. Xu, Carbon 2010, 48, 456; b) H. L. Jiang, B. Liu, Y. Q. Lan, K. Kuratani, T. Akita, H. Shioyama, F. Zong, Q. Xu, J. Am. Chem. Soc. 2011, 133, 11854; c) R. R. Salunkhe, J. Tang, Y. Kamachi, T. Nakato, J. H. Kim, Y. Yamauchi, ACS Nano 2015, 9, 6288; d) J. Tang, R. R. Salunkhe, J. Liu, N. L. Torad, M. Imura, S. Furukawa, Y. Yamauchi, J. Am. Chem. Soc. 2015, 137, 1572; e) P. Pachfule, D. Shinde, M. Majumder, Q. Xu, Nat. Chem. 2016, 8, 718; f) F. Cao, M. Zhao, Y. Yu, B. Chen, Y. Huang, J. Yang, X. Cao, Q. Lu, X. Zhang, Z. Zhang, C. Tan, H. Zhang, J. Am. Chem. Soc. 2016, 138, 6924; g) J. Tang, Y. Yamauchi, Nat. Chem. 2016, 8, 638; h) R. R. Salunkhe, Y. V. Kaneti, J. Kim, J. H. Kim, Y. Yamauchi, Acc. Chem. Res. 2016, 49, 2796; i) R. R. Salunkhe, C. Young, J. Tang, T. Takei, Y. Ide, N. Kobayashi, Y. Yamauchi, Chem. Commun. 2016, 52, 4764; j) R. R. Salunkhe, Y. Kamachi, N. L. Torad, S. M. Hwang, Z. Sun, S. X. Dou, Y. Yamauchi, J. Mater. Chem. A 2014, 2, 19848.



www.afm-journal.de

- [9] a) X. Liu, C. Shi, C. Zhai, M. Cheng, Q. Liu, G. Wang, ACS Appl. Mater. Interfaces 2016, 8, 4585; b) J. Yang, P. Xiong, C. Zheng, H. Qiu, M. Wei, J. Mater. Chem. A 2014, 2, 16640; c) D. O. Miles, D. Jiang, A. D. Burrows, J. E. Halls, F. Marken, Electrochem. Commun. 2013, 27, 9.
- [10] K. M. Choi, H. M. Jeong, J. H. Park, Y. B. Zhang, J. K. Kang, O. M. Yaghi, ACS Nano 2014, 8, 7451.
- [11] L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, J. Am. Chem. Soc. 2015, 137, 4920.
- [12] L. Shen, B. Ding, P. Nie, G. Cao, X. Zhang, Adv. Energy Mater. 2013, 3, 1484.
- [13] D. Sheberla, J. C. Bachman, J. S. Elias, C. J. Sun, Y. Shao-Horn, M. Dincă, Nat. Mater. 2017, 16, 220.
- [14] M. Hmadeh, Z. Lu, Z. Liu, F. Gándara, H. Furukawa, S. Wan, V. Augustyn, R. Chang, L. Liao, F. Zhou, E. Perre, V. Ozolins, K. Suenaga, X. Duan, B. Dunn, Y. Yamamto, O. Terasaki, O. M. Yaghi, *Chem. Mater.* **2012**, *24*, 3511.
- [15] L. Sun, M. G. Campbell, M. Dincă, Angew. Chem. Int. Ed. 2016, 55, 2.
- [16] S. S. Park, E. R. Hontz, L. Sun, C. H. Hendon, A. Walsh, T. Van Voorhis, M. Dincă, J. Am. Chem. Soc. 2015, 137, 1774.
- [17] a) L. Dai, D. W. Chang, J. B. Baek, W. Lu, Small 2012, 8, 1130;
 b) X. Yang, C. Cheng, Y. Wang, L. Qiu, D. Li, Science 2013, 341, 534.
- [18] a) X. Liu, C. Shi, C. Zhai, M. Cheng, Q. Liu, G. Wang, ACS Appl. Mater. Interfaces 2016, 8, 4585; b) J. Yang, P. Xiong, C. Zheng, H. Qiu, M. Wei, J. Mater. Chem. A 2014, 2, 16640; c) D. O. Miles, D. Jiang, A. D. Burrows, J. E. Halls, F. Marken, Electrochem. Commun. 2013, 27, 9.
- [19] D. A. Harrington, B. E. Conway, Electrochim. Acta 1987, 32, 1703.
- [20] L. Shen, Q. Che, H. Li, X. Zhang, Adv. Funct. Mater. 2014, 24, 2630.
- [21] L. Wang, X. Feng, L. Ren, Q. Piao, J. Zhong, Y. Wang, H. Li, Y. Chen, B. Wang, J. Am. Chem. Soc. 2015, 137, 4920.
- [22] a) M. Miyamoto, S. Kohmura, H. Iwatsuka, Y. Oumi, S. Uemiya, CrystEngComm. 2015, 17, 3422; b) Z. Jiang, Z. Li, Z. Qin, H. Sun, X. Jiao, D. Chen, Nanoscale 2013, 5, 11770; c) Y. Pan, Y. Liu, G. Zeng, L. Zhao, Z. Lai, Chem. Commun. 2011, 47, 2071; d) P. L. Llewellyn, S. Bourrelly, C. Serre, A. Vimont, M. Daturi, L. Hamon, G. De Weireld, J. S. Chang, D. Y. Hong, Y. K. Hwang, S. H. Jhung, G. Férey, Langmuir 2008, 24, 7245; e) M. Latroche, S. Surble, C. Serre, C. Mellot-Draznieks, P. L. Llewellyn, J. H. Lee, J. S. Chang, S. H. Jhung, G. Férey, Angew. Chem. Int. Ed. 2006, 45, 8227.
- [23] a) C. Meng, C. Liu, L. Chen, C. Hu, S. Fan, *Nano Lett.* 2010, *10*, 4025; b) Y. J. Kang, S. J. Chun, S. S. Lee, B. Y. Kim, J. H. Kim, H. Chung, S. Y. Lee, W. Kim, *ACS Nano* 2012, *6*, 6400.
- [24] W. Gu, G. Yushin, Wiley Interdiscip. Rev.: Energy Environ. 2014, 3, 424.
- [25] a) C. H. Lau, R. Babarao, M. R. Hill, *Chem. Commun.* 2013, 49, 3634; b) S. A. Moggach, T. D. Bennett, A. K. Cheetham, *Angew. Chem. Int. Ed.* 2009, 121, 7221; c) Z. Jiang, Z. Li, Z. Qin, H. Sun, X. Jiao, D. Chen, *Nanoscale* 2013, 5, 11770; d) G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour, I. Margiolaki, *Angew. Chem. Int. Ed.* 2004, 116, 6456; e) G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé, I. Margiolaki, *Science* 2005, 309, 2040.