Nanomaterials

DOI: 10.1002/anie.201209849

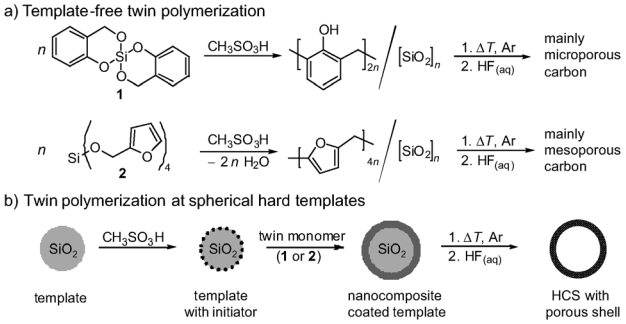
Twin Polymerization at Spherical Hard Templates: An Approach to Size-Adjustable Carbon Hollow Spheres with Micro- or Mesoporous Shells**

*Falko Böttger-Hiller, Patrick Kempe, Gerhard Cox, Alexander Panchenko, Nicole Janssen, Albrecht Petzold, Thomas Thurn-Albrecht, Lars Borchardt, Marcus Rose, Stefan Kaskel, Colin Georgi, Heinrich Lang, and Stefan Spange**

Hollow carbon spheres (HCSs) are widely used in gas-storage,[1] catalyst support,[2] and filters,[3] as a template for other hollow spheres,[4] as electrode materials for lithium ion batteries[5] and for water purification.[6] In recent years a number of methods for the production of HCSs have been described,[7] which are divided into hard-template syntheses[8] and solvothermal syntheses.[9]

Previous publications describe independent syntheses in which HCSs sometimes arise randomly, and analyze their properties.[8f,g,10] Few publications show how the inner diameter, the shell thickness of HCSs, or its morphology can be varied.[7d,8a,b,9f,11] An overview of the synthesis capabilities of HCSs with different features has to date only been given in review articles, which summarize the individual phenomena of independent HCS syntheses.[12]

With the twin polymerization at hard templates, we present an universal synthesis approach that allows the design of HCSs according to application-relevant properties. Template-free synthesis leads to a SiO_2/polymer nanocomposite. After carbonization and subsequent treatment with hydrofluoric acid, porous carbon is obtained. The pore texture of the carbon material depends on the used twin monomer. 2,2′-Spirobi[4*H*-1,3,2-benzodioxasiline][13] (**1**) leads to microporous ($d < 2$ nm, 72 vol%) and tetrafurfuryloxysilane[14] (**2**) to mainly mesoporous ($2\text{ nm} \le d < 50$ nm, 41 vol%) carbon with high specific surface areas, about 1400 or 1300 $m^2 g^{-1}$ (Scheme 1 a).[13,14]



Scheme 1. Synthesis of porous carbon by a) template-free twin polymerization and b) twin polymerization at SiO_2 particles.

For the template-assisted procedure, spherical SiO_2 particles with diameters of 7 nm (Aerosil 300), 40 nm (Aerosil OX 50), and 5–10 μm (LiChrospher 100) were used. In the first step, methanesulfonic acid, which acts as surface catalyst, was adsorbed at the particles[15] (further experimental details are given in the Supporting Information). After addition of **1** or **2**, the twin polymerization is initiated at the surface of the particles, which are inevitably included in the SiO_2/polymer nanocomposite (Scheme 1 b). The resulting hybrid materials were characterized by $^{13}C\{^1H\}$CP-MAS solid-state NMR spectroscopy, transmission electron microscopy (TEM), elemental analysis, and thermogravimetry (see the Supporting Information).

The polymer component of the hybrid material is converted into carbon by carbonizing. The SiO_2 phase obtained from twin polymerization as well as the SiO_2 template are controlled removed by treatment with aqueous hydrofluoric acid. Analogous to the template-free synthesis (Scheme 1 a), HCSs with a mainly microporous shell result when using twin monomer **1** and HCSs with a mainly mesoporous shell when using **2** (Scheme 1 b)

The size of produced HCSs is determined by the template particles. Thereby, the morphology of the HCSs is not influenced by the used twin monomer (see the Supporting Information). In Figure 1 a,b, Aerosil 300 was used as a template and HCSs with an inner diameter of about 7 nm were obtained. Synthesis with Aerosil OX 50 and LiChrosper 100 leads to HCSs with inner diameters of about 40 nm or 5–10 μm (Figure 1 c–f). In case of the micrometer-sized particles,

[*] F. Böttger-Hiller, P. Kempe, Prof. Dr. S. Spange
Professur für Polymerchemie, Technische Universität Chemnitz
09107 Chemnitz (Germany)
E-mail: stefan.spange@chemie.tu-chemnitz.de
C. Georgi, Prof. Dr. H. Lang
Professur für Anorganische Chemie
Technische Universität Chemnitz (Germany)
L. Borchardt, Dr. M. Rose, Prof. Dr. S. Kaskel
Professur für Anorganische Chemie
Technische Universität Dresden (Germany)
Dr. A. Petzold, Prof. Dr. T. Thurn-Albrecht
Professur für Experimentelle Polymerphysik
Martin-Luther-Universität Halle-Wittenberg (Germany)
Dr. G. Cox, Dr. A. Panchenko, Dr. N. Janssen
BASF SE Ludwigshafen (Germany)

[**] We thank the DFG (Project: Sp392/31-1) and BASF SE for the financial support, and Merck and Evonik for providing the template particles.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201209849.

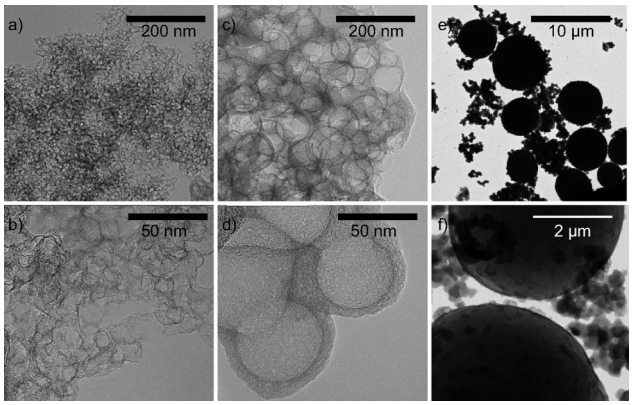


Figure 1. TEM images of HCSs obtained from a,b) Aerosil 300, c,d) Aerosil OX 50, and e,f) LiChrospher 100.

a byproduct from twin polymerization in solution occurs, which is favored by the worse adsorption of methanesulfonic acid at LiChrospher particles (Figure 1 e,f).

Further to the variation of the template, the morphology of the HCSs can be influenced by the monomer/substrate ratio. Here, the carbon content of the coated template correlates linearly with the amount of monomer (see the Supporting Information) and the shell thickness of the resulting HCSs can be adjusted by the amount of monomer (Figure 2).

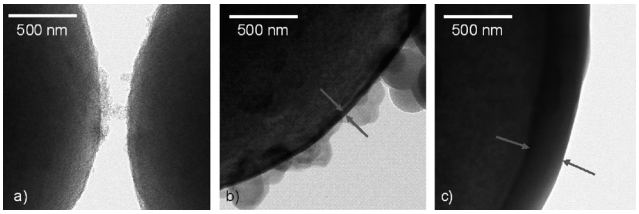


Figure 2. TEM images of HCSs obtained from LiChrospher 100 and a) 33 wt%, b) 67 wt%, and c) 89 wt% monomer **1**.

A monomer content of 33 wt% leads to HCSs with a shell thickness that is not measurable. In contrast, monomer contents of 67 wt% or 89 wt% lead to shell thicknesses of 40–50 nm or 250–350 nm.

The values of the inner diameters of the HCSs determined by TEM are confirmed by the results of X-ray small-angle scattering (SAXS) (see the Supporting Information). The SAXS can also be used to determine the pore structure of the HCSs. Thus, the SAXS patterns show a porous structure (high q values), which is assigned to the shell porosity.

The pore analysis by nitrogen-sorption experiments also shows a bimodal pore distribution. Thereby, small pores can be assigned to the spherical shell and large pores to the HCS interior. In this case, the inner diameters amount 20–100 nm (see the Supporting Information) and suggest that the obtained values by gas sorption are less accurate then the data from TEM and SAXS. The results for the pore diameter in the HCS shell obtained by the different methods vary, but in any case there is a dependence of the shell pores and the used twin monomer (see the Supporting Information). According to nitrogen sorption, the use of monomer **2** leads to pores twice larger as pores of carbon produced from **1**. The evaluation of the pore-size distribution according to DIN 66135 assigns mainly micropores to the shells of HCSs made from **1** and mainly mesopores to HCSs made from **2**.

Moreover, the used monomer/template ratio shows a significant influence on the pore texture. At nearly constant micropore volume, the number of mesopores increases with an increasing amount of the template (Figure 3).

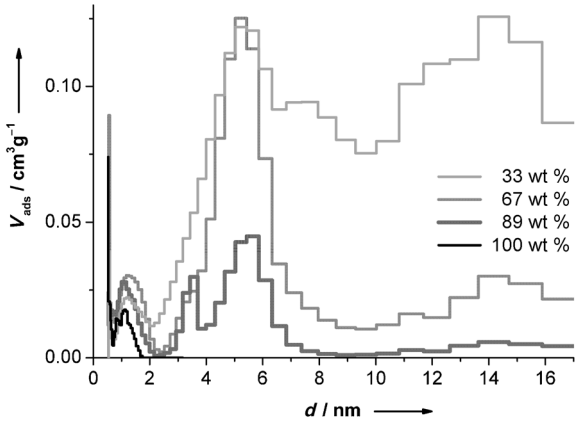


Figure 3. Pore-size distribution (histogram from DFT analysis) of porous carbon from template-free polymerization of **1** (100 wt%) and of HCSs resulting from twin polymerization of monomer **1** at Aerosil 300 particles (monomer content: 33 wt%, 67 wt%, or 89 wt%).

The carbon of the reference material from template-free synthesis (100 wt%) shows exclusively micropores. The absolute volume of micropores is almost identical in all samples, while the volume of the pores created from the template increases with increasing template ratio. The HCSs prepared using monomer **2** show a similar dependence (see the Supporting Information).

The synthesized HCSs have a high specific surface area (690–1370 m^2g^{-1}) and large total pore volume (0.49–2.33 cm^3g^{-1}; see the Supporting Information). Comparable HCSs[11d] ($d = 20$–60 nm) show a comparatively small specific surface area ($S_g = 670\ m^2g^{-1}$). Thereby, the pore volume amounts to $0.93\ cm^3g^{-1}$ and neither the inner diameter of the HCSs nor the pore-size distribution can be adjusted.

The morphology and porosity of the produced HCSs is determined substantially during polymerization and cannot be influenced after the formation of twin polymer at the template surfaces. However, shell properties, such as electrical conductivity and graphite content, can be changed by post treatment of the HCSs. The conductivity of HCSs can be affected in general during the carbonization. The higher the temperature, the higher the conductivity of the HCSs. According to SAXS and Raman spectra, the shell of the HCSs consists of amorphous carbon in every case (see the Supporting Information).

Furthermore, it is possible to graphitize the HCSs by a second carbonization step under addition of $FeCl_3$. The original spherical morphology is destroyed by the graphitiza-

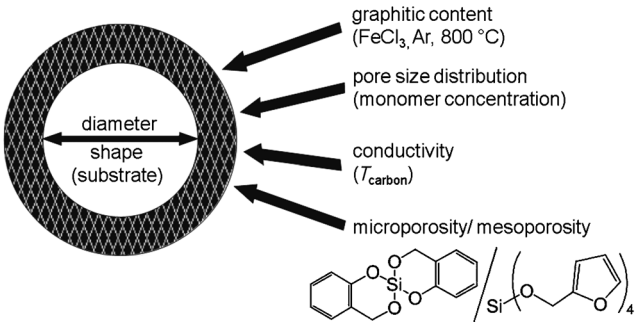


Figure 4. Modular concept of twin polymerization at hard templates for the individual synthesis of HCSs.

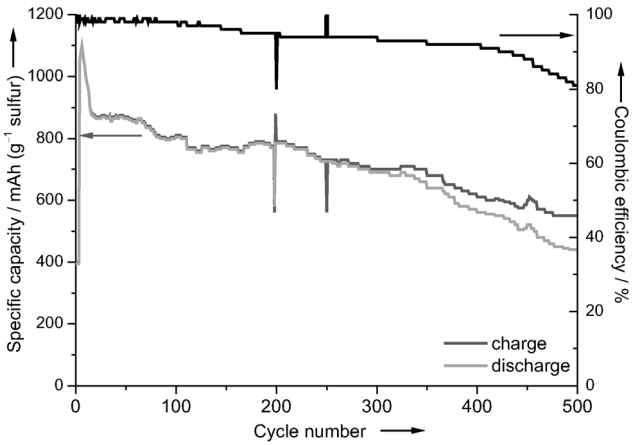


Figure 5. Cycling performance of a lithium–sulfur battery. The cathode material consists of a HCS/S_8 hybrid, which was made from a reaction of twin monomer **1** (67 wt%) and Aerosil 300.

tion and compact, graphitic spheres with a diameter of 0.4–1.0 μm occur (see the Supporting Information). Overall, the twin polymerization at spherical hard-templates offers the possibility to produce HCSs individually, according to a modular concept (Figure 4).

Selected HCSs were tested for hydrogen storage for use in fuel cells and as a new electrode material for lithium–sulfur batteries. Along with the method of storing hydrogen compressed in its liquid form, it can be stored by low-temperature adsorption in materials with large surface areas, such as the produced HCSs.[16] Hydrogen-sorption isotherms (see the Supporting Information) show that the hydrogen can be reversibly stored in the produced HCSs. The hydrogen uptake of the studied HCSs (values between 1.1 and 1.5 wt%) lies in a moderate range and is comparable to porous polymers (1.9 wt%).[17] The maximum values of microporous carbons (5.1 wt%)[18] or metal–organic frameworks (for example MOF-210: 8.6 wt%),[19] as a leading material, could not be reached.

As a more promising application, HCSs melted with sulfur at 140 °C were tested as C/S_8 hybrid materials in lithium–sulfur batteries. The prepared electrode materials have similar properties, as systems described by Gao et al.[20] or by Archer et al.,[21] based on microporous and mesoporous carbon spheres. The sulfur is located both in the pores and on the surface of the HCSs (see the Supporting Information). HCSs produced with Aerosil 300 give impressive results in lithium–sulfur batteries with a high cycling stability (Figure 5). A capacity of 850 mA h (g^{-1} sulfur) is achieved, which amounts 580 mA h (g^{-1} sulfur) after 500 cycles. The volume expansion and compression during charging and discharging as well as a weakening of the adsorption between sulfur and carbon may be the reasons for the decrease in the specific capacity. It should be noted that the anode has been changed owing to faster wear (dendrite formation) after 200 cycles, and the amplitudes in Figure 5 are to be regarded as a preparation artifacts. This situation can also lead to a more rapid reduction of the capacity in the following cycles.

Batteries of microporous carbon, prepared by template-free synthesis of **1**, show a capacity of 650 mA h (g^{-1} sulfur), and after 250 cycles still have a value of 390 mA h (g^{-1} sulfur). The results of the first battery tests using carbon from twin polymerization are comparable to recently published results, in which capacities of 600–1000 mA h (g^{-1} sulfur) were described and the measurements were stopped after 50 to 100 cycles.[22]

Battery tests of the materials presented substantiate the great potential of twin polymerization at hard templates. It is a suitable method to produce carbon materials, depending on the application requirements. In contrast to other work in the field of lithium–sulfur batteries, it is possible to vary the properties of HCSs, whereby the most suitable HCSs for a powerful lithium–sulfur battery can be evaluated.

The outer shape and the inner diameter of the HCSs are adjustable through the use of various templates. The monomer determines the layer thickness of the spherical shell, and thus the pore–size distribution of the overall material, wherein the type of the monomer influences the pore texture of the HCS shell. Tetrafurfuryloxysilane leads to HCSs with a mainly mesoporous structure and spirobi[4*H*-1,3,2-benzodioxasiline] with a mainly microporous shell. Thus the twin polymerization at hard templates offers a modular approach to produce a variety of HCSs.

In future work we will investigate possibilities of producing unimodal pore-size distributions by using multiple templates or twin monomers. Furthermore, it is planned to improve the production of electrodes and examine structure–property relationships between HCSs and derived lithium–sulfur batteries.

Received: December 10, 2012
Revised: February 13, 2013
Published online: April 25, 2013

Keywords: hollow carbon spheres · lithium–sulfur battery · porous carbon · twin polymerization

[1] a) H. Tamai, T. Sumi, H. Yasuda, *J. Colloid Interface Sci.* **1996**, *177*, 325–328; b) A. C. Dillon, M. J. Heben, *Appl. Phys. A* **2001**, *72*, 133–142.

[2] a) S. H. Joo, S. J. Choi, I. Oh, J. Kwak, Z. Liu, O. Terasaki, R. Ryoo, *Nature* **2001**, *412*, 169–172; b) G. S. Chai, S. B. Yoon, J. H. Kim, J.-S. Yu, *Chem. Commun.* **2004**, 2766–2767; c) S. Ikeda, S.

Ishino, T. Harada, N. Okamoto, T. Sakata, H. Mori, S. Kuwabata, T. Torimoto, M. Matsumura, *Angew. Chem.* **2006**, *118*, 7221 – 7224; *Angew. Chem. Int. Ed.* **2006**, *45*, 7063 – 7066.

[3] A. Vinu, M. Miyahara, T. Mori, K. Ariga, *J. Porous Mater.* **2006**, *13*, 379 – 383.

[4] G. M. Yang, H. W. Tian, X. Wang, W. T. Zheng, *J. Phys. D* **2008**, *41*, 195504 – 195509.

[5] K. T. Lee, Y. S. Jung, S. M. Oh, *J. Am. Chem. Soc.* **2003**, *125*, 5652 – 5653.

[6] S. Han, S. Kim, H. Lim, W. Choi, H. Park, J. Yoon, T. Hyeon, *Microporous Mesoporous Mater.* **2003**, *58*, 131 – 135.

[7] a) T. Zheng, J. Zhan, J. Pang, G. Tan, J. He, G. McPherson, Y. Lu, V. John, *Adv. Mater.* **2006**, *18*, 2735 – 2738; b) N. A. Katcho, E. Urones-Garrote, D. Ávila-Brande, A. Gómez-Herrero, S. Urbonaite, S. Csillag, E. Lomba, F. Agulló-Rueda, A. R. Landa-Cánovas, L. C. Otero-Díaz, *Chem. Mater.* **2007**, *19*, 2304 – 2309; c) S. Ding, C. Zhang, X. Qu, J. Liu, Y. Lu, Z. Yang, *Colloid Polym. Sci.* **2008**, *286*, 1093 – 1096; d) K. Niwase, T. Homae, K. G. Nakamura, K. Kondo, *Chem. Phys. Lett.* **2002**, *362*, 47 – 50.

[8] a) F. Su, X. S. Zhao, Y. Wang, L. Wang, J. Y. Lee, *J. Mater. Chem.* **2006**, *16*, 4413 – 4419; b) M. Kim, S. B. Yoon, K. Sohn, J. Y. Kim, C.-H. Shin, T. Hyeon, J.-S. Yu, *Microporous Mesoporous Mater.* **2003**, *63*, 1 – 9; c) Y. Ni, M. Shao, Y. Tong, G. Qian, X. Wei, *J. Solid State Chem.* **2005**, *178*, 908 – 911; d) M. Yang, J. Ma, S. Ding, Z. Meng, J. Liu, T. Zhao, L. Mao, Y. Shi, X. Jin, Y. Lu, Z. Yang, *Macromol. Chem. Phys.* **2006**, *207*, 1633 – 1639; e) V. V. Kovalevski, A. N. Safronov, *Carbon* **1998**, *36*, 963 – 968; f) S. B. Yoon, K. Sohn, J. Y. Kim, C.-H. Shin, J.-S. Yu, T. Hyeon, *Adv. Mater.* **2002**, *14*, 19 – 21; g) Y. D. Xia, R. Mokaya, *Adv. Mater.* **2004**, *16*, 886 – 891; h) R. J. White, K. Tauer, M. Antonietti, M.-M. Titirici, *J. Am. Chem. Soc.* **2010**, *132*, 17360 – 17363.

[9] a) B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti, M. M. Titirici, *Adv. Mater.* **2010**, *22*, 813 – 828; b) G. Hu, D. Ma, M. Cheng, L. Liu, X. Bao, *Chem. Commun.* **2002**, 1948 – 1949; c) J. Liu, M. Shao, Q. Tang, X. Chen, Z. Liu, Y. Qian, *Carbon* **2003**, *41*, 1682 – 1685; d) M. M. Titirici, A. Thomas, M. Antonietti, *Adv. Funct. Mater.* **2007**, *17*, 1010 – 1018; e) Z. L. Wang, J. S. Yin, *Chem. Phys. Lett.* **1998**, *289*, 189 – 192; f) D. Ni, L. Wang, Y. Sun, Z. Guan, S. Yang, K. Zhou, *Angew. Chem.* **2010**, *122*, 4319 – 4323; *Angew. Chem. Int. Ed.* **2010**, *49*, 4223 – 4227.

[10] a) Z. Zhi, J. Wang, G. Cui, M. Kastler, B. Schmaltz, U. Kolb, U. Jonas, K. Müllen, *Adv. Mater.* **2007**, *19*, 1849 – 1853; b) S. D. X. Yu, Z. Meng, J. Liu, X. Qu, Y. Lu, Z. Yang, *Colloid Polym. Sci.* **2008**, *286*, 1435 – 1536; c) N. Liu, W. Xinlu, Y. Wu, L. Wang, *Mater. Sci. Eng. B* **2009**, *158*, 79 – 81; d) L. Chen, R. K. Singh, P. Webley, *Microporous Mesoporous Mater.* **2007**, *102*, 159 – 170; e) A.-H. Lu, W.-C. Li, G.-P. Hao, B. Spliethoff, H.-J. Bongard, B. B. Schaack, F. Schüth, *Angew. Chem.* **2010**, *122*, 1659 – 1662; *Angew. Chem. Int. Ed.* **2010**, *49*, 1615 – 1618.

[11] a) Q. Wang, H. Li, L. Chen, X. Huang, *Carbon* **2001**, *39*, 2211 – 2214; b) Q. Wang, H. Li, L. Chen, X. Huang, *Solid State Ionics* **2002**, *43*, 152 – 153; c) C. Song, J. Du, J. Zhao, S. Feng, G. Du, Z. Zhu, *Chem. Mater.* **2009**, *21*, 1524 – 1530; d) Y. Fang, D. Gu, Y. Zou, Z. Wu, F. Li, R. Che, Y. Deng, B. Tu, D. Zhao, *Angew. Chem.* **2010**, *122*, 8159 – 8163; *Angew. Chem. Int. Ed.* **2010**, *49*, 7987 – 7991.

[12] a) A. Stein, Z. Wang, M. A. Fierke, *Adv. Mater.* **2009**, *21*, 265 – 293; b) T. N. Hoheisel, S. Schrettl, R. Szilluweit, H. Frauenrath, *Angew. Chem.* **2010**, *122*, 6644 – 6664; *Angew. Chem. Int. Ed.* **2010**, *49*, 6496 – 6515.

[13] S. Spange, P. Kempe, A. Seifert, A. Auer, P. Ecorchard, H. Lang, M. Falke, M. Hietschold, A. Pohlers, W. Hoyer, G. Cox, E. Kockrick, S. Kaskel, *Angew. Chem.* **2009**, *121*, 8403 – 8408; *Angew. Chem. Int. Ed.* **2009**, *48*, 8254 – 8258.

[14] S. Grund, P. Kempe, G. Baumann, A. Seifert, S. Spange, *Angew. Chem.* **2007**, *119*, 636 – 640; *Angew. Chem. Int. Ed.* **2007**, *46*, 628 – 632.

[15] S. Spange, *Prog. Polym. Sci.* **2000**, *25*, 781 – 849.

[16] U. Eberle, M. Felderhoff, F. Schüth, *Angew. Chem.* **2009**, *121*, 6732 – 6757; *Angew. Chem. Int. Ed.* **2009**, *48*, 6608 – 6630.

[17] M. G. Rabbani, H. M. El-Kaderi, *Chem. Mater.* **2011**, *23*, 1650 – 1653.

[18] F. Cheng, J. Liang, J. Zhao, Z. Tao, J. Chen, *Chem. Mater.* **2008**, *20*, 1889 – 1895.

[19] H. Furukawa, N. Ko, Y. Go, N. Aratani, S. B. Choi, E. Choi, A. Ö. Yazaydin, R. Q. Snurr, M. O. Keeffe, J. Kim, O. M. Yaghi, *Science* **2010**, *329*, 424 – 428.

[20] B. Zhang, X. Qin, G. R. Li, X. P. Gao, *Energy Environ. Sci.* **2010**, *3*, 1531 – 1537.

[21] N. Jayaprakash, J. Shen, S. S. Moganty, A. Corona, L. A. Archer, *Angew. Chem.* **2011**, *123*, 6026 – 6030; *Angew. Chem. Int. Ed.* **2011**, *50*, 5904 – 5908.

[22] a) G. Zheng, Y. Yang, J. J. Cha, S. S. Hong, Y. Cui, *Nano Lett.* **2011**, *11*, 4462 – 4467; b) N.-S. Choi, Z. Chen, S. A. Freunberger, X. Ji, Y.-K. Sun, K. Amine, G. Yushin, L. F. Nazar, J. Cho, P. G. Bruce, *Angew. Chem.* **2012**, *124*, 10134 – 10166; *Angew. Chem. Int. Ed.* **2012**, *51*, 9994 – 10024; c) S. Evers, L. F. Nazar, *Acc. Chem. Res.* **2012**, accepted; d) G. He, X. Ji, L. Nazar, *Energy Environ. Sci.* **2011**, *4*, 2878 – 2883; e) X. Ji, S. Evers, R. Black, L. F. Nazar, *Nat. Commun.* **2011**, *2*, 325 – 332; f) K. T. Lee, R. Black, T. Yim, X. Ji, L. F. Nazar, *Adv. Energy Mater.* **2012**, *2*, 1490 – 1496; g) J. Schuster, G. He, B. Mandlmeier, T. Yim, K. T. Lee, T. Bein, L. F. Nazar, *Angew. Chem.* **2012**, *124*, 3651 – 3655; *Angew. Chem. Int. Ed.* **2012**, *51*, 3591 – 3595; h) Y. Yang, G. Yu, J. J. Cha, H. Wu, M. Vosgueritchian, Y. Yao, Z. Bao, Y. Cui, *ACS Nano* **2011**, *5*, 9187 – 9193; i) Y. Yang, G. Zheng, S. Misra, J. Nelson, M. F. Toney, Y. Cui, *J. Am. Chem. Soc.* **2012**, *134*, 15387 – 15394.

