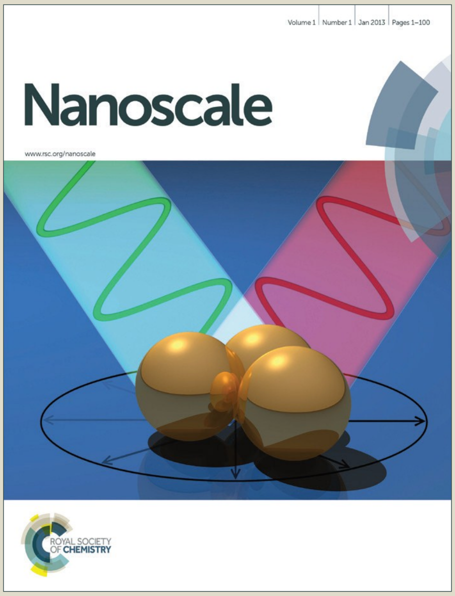
Nanoscale

Accepted Manuscript



ROYAL SOCIETY OF CHEMISTRY

www.rsc.org/nanoscale

Journal Name

ARTICLE

Received 00th January 20xx,

Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Mini review of designed mesoporous materials for energy-storage applications: from electric double-layer capacitors to hybrid supercapacitors

Eunho Lim,‡[a] Changshin Jo,‡[b] and Jinwoo Lee*[ab]

In recent years, porous materials have attracted significant attentions in various research fields because of their structural merits. In particular, well-designed mesoporous structures with two- or three-dimensionally interconnected pores have been recognized as electrode materials of particular promise for achieving high-performance electrochemical capacitors (ECs). In this mini review, recent progress in the design of mesoporous electrode materials for ECs, from electric double-layer capacitors (EDLCs) and pseudocapacitors (PCs) to hybrid supercapacitors (HSCs), and research challenges for the development of new mesoporous electrode materials will be discussed.

1. Introduction

Due to the fast charge-discharge performance and stable cycle life of electrochemical capacitors (ECs or supercapacitors),[1] there is increasing interest in their use in applications ranging from portable devices to large-scale technologies, and they have been the focus of a considerable research effort. Based on their energy-storage mechanisms (*e.g.,* non-Faradaic or Faradaic reactions) and cell configurations (*e.g.,* symmetric or asymmetric systems), ECs can be categorized as follows: (i) electric double-layer capacitors (EDLCs),[2, 3] (ii) pseudocapacitors (PCs),[4, 5] and (iii) hybrid energy-storage systems (*e.g.,* hybrid supercapacitors (HSCs)).[6, 7] EDLCs (Figure 1a) utilize the high surface area of carbonaceous materials for constructing an electric double-layer at the interface between the electrode and electrolyte, while PCs (Figure 1b) store charge by a redox reaction at the surface or near-surface of electrodes.[8] These traditional EC systems exhibit a high power density (> 10 kW kg^{-1}) and an excellent cycle life (>10,000 cycles in EDLCs). However, they have a lower energy density (< 30 W h kg^{-1}) than Li-ion batteries (LIBs, ~150 W h kg^{-1}) because of the low areal capacitance of electrode materials and narrow operating potentials. To improve the energy density, therefore, recent EC research has moved to merge the electrodes of ECs with high capacitance electrodes such as intercalation materials of LIBs under organic electrolyte systems containing Li-salts.[9] For example, HSCs, defined in this review as hybrid energy-storage systems using capacitor electrodes with battery-type electrodes, simultaneously exhibited high energy density (> 50 W h kg^{-1}) and power density (> 10 kW kg^{-1}) with stable cycle life.[10] In this regard, they are considered one of the most promising ECs.

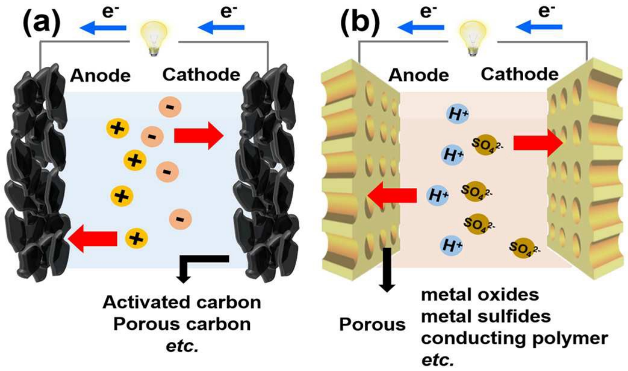


Figure 1. Schematic diagram of (a) an electrical double-layer capacitor (EDLC) and (b) a pseudocapacitor (PC).

To achieve high-performance in ECs, active materials designed with controlled nanoscale morphologies have been regarded as one of the most highly effective strategies, because the electrochemical reactions mainly occur at the electrode and electrolyte interfaces. Nanostructured electrode materials improve the capacitance and rate performance of active materials by increasing the number of reaction sites and shortening the diffusion lengths of ions and/or electrons.[11]

In particular, well-designed mesoporous materials, which possess two- or three-dimensionally interconnected pores with a diameter of 2-50 nm, have been recognized as being among the most appealing electrode materials. Compared with same materials in the bulk form, the active ordered mesoporous materials have various merits for EC applications:

---

[a] School of Environmental Science and Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-gu, Pohang, Gyeongbuk 37673, Republic of Korea. E-mail: jinwoo03@postech.ac.kr
[b] Department of Chemical Engineering, Pohang University of Science and Technology (POSTECH), 77 Cheongam-Ro, Nam-Gu, Pohang, Gyeongbuk 37673, Republic of Korea.

‡ E. Lim and C. Jo equally contributed to this work.

(i) a high surface area provides numerous charge storage sites, (ii) interconnected mesopores facilitate electrolyte transportation, (iii) nanometer-sized walls develop small crystallites and grain boundaries, resulting in enhancement of the areal capacitance of active materials, and (iv) porous structures can act as a host material for impregnating high capacitance guest materials inside the pores.[12, 13]

In this mini review, we summarize recent trends in the study of mesoporous materials for EC applications. First, we describe the synthetic approaches for well-designed mesoporous materials. Next, we discuss recent progress in their applications in EDLCs, PCs, and HSCs. Finally, we suggest current challenges and future prospects for mesoporous electrode materials in EC applications.

2. Synthesis of designed mesoporous materials

Since the first report of mesoporous silica materials in the 1990s,[14, 15] various synthetic approaches have been applied to develop mesoporous metal oxides,[16] non-oxides,[17] carbons,[18] and polymers.[19] Preparation methods generally fall into two categories: soft-template and hard-template strategies. The former method creates an ordered mesoporous structure *via* self-assembly and/or aggregation between organic surfactants and precursors (Figures 2a and 2c).[20, 21] The latter uses pre-formed nano-templates, such as mesoporous silica, carbon, and aggregates of nanoparticles, for nanocasting precursors into the inner pores of templates (Figures 2b and 2d).[22, 23]

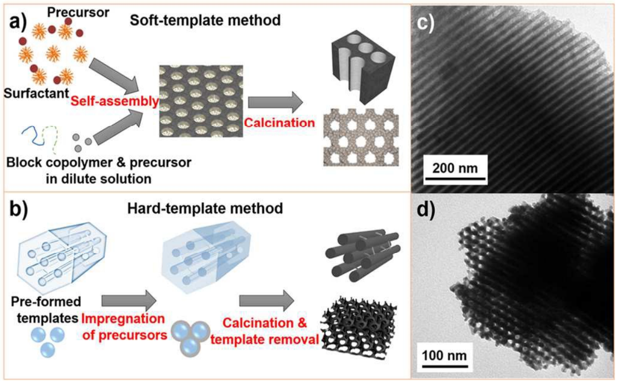


Figure 2. Schematic representations of (a) soft- and (b) hard-template methods. Transmission electron microscope (TEM) images of (c) soft-templated mesoporous carbon and (d) hard-templated mesoporous reduced tungsten oxide.

In the soft-template method, the cooperative interaction between building blocks (*e.g.,* inorganic sols, polymers, and nanoparticles) and surfactants is the most important factor for the construction of ordered mesoporous structures. During soft-template syntheses based on the surfactants and precursors, the materials are prepared in various ways including direct precipitations,[14] liquid crystals[24] in aqueous solution and evaporation-induced self-assembly (EISA).[25] The EISA method, which develops the ordered mesostructure during the evaporation of an organic solvent, is especially powerful and versatile because it offers a wide choice of surfactants and precursors.[26, 27] On the other hand, hard-template methods are advantageous for treating the materials at high temperature; commercial surfactants for the soft-template method are thermally unstable (usually functional at < 500 ^{o}C). Moreover, relatively inexpensive metal salts such as nitrates and chlorides can be used in hard-template methods. However, multiple and tedious steps including the preparation of template, nano-casting, calcination, and removal of the template are drawbacks of the hard-template method.

Recently, a new synthetic approach that combines the merits of soft- and hard-template methods has been reported.[28] Designed mesoporous materials with various pore sizes and structures, and aligned components have been actively investigated by varying the surfactant/precursor pairs and adjusting their compositions.[29, 30]

These designed mesoporous materials with finely controlled structures have been applied to various EC applications, which will be discussed in the next chapters.

3. Electric double-layer capacitors

As active materials in EDLC systems, ordered mesoporous carbons (OMCs) with accelerated ionic motion inside particles, have shown high capacitance and excellent rate capability.[31-33] Furthermore, OMC electrodes have provided a platform for basic and systematic studies of electrochemistry, including electrode morphology effects related to the ionic and electronic transports.[34-36] In this section, we summarize the recent studies on ELDCs using OMC electrodes for improved high areal capacitance and electrical conductivity.

The doping of OMCs with heteroatoms can modify the surface of the carbons, resulting in enlarged areal capacitance and improved rate capability.[37] In this respect, doping strategies with electron-donating or -withdrawing heteroatoms such as B,[38] N,[39] O,[40] P,[41] and S[42] have been reported for EDLCs. For example, Zhao *et al.* synthesized N-doped OMCs with controllable nitrogen contents (up to 15 wt%), the electrochemical analyses of which are shown in Figure 3a.[43] In 6 M KOH solution, the N-doped OMC electrode exhibited a higher capacitance (~230 F g^{-1}) than the un-doped OMC (~143 F g^{-1}). The improved capacitance is attributed to the modified electronic properties, surface chemistry, or contribution of the pseudocapacitive reaction on the doped surface.[44-46]

The graphitization of OMCs (Figure 3b) is another effective approach to improve their areal capacitance and electron conductivity with a small internal resistance.[47, 48] Graphitized OMCs with different morphologies have synthesized by a heat-treatment with metal salts (Fe, Co, and *etc.*).[49] The areal capacitance of a graphitized CMK-3 electrode in an organic electrolyte system was 6.8 μF cm^{-2}, whereas a capacitance of only 4.1 μF cm^{-2} was achieved for a pure CMK-3 electrode.[50] In addition, graphite functionalized mesocellular carbon foams (MSU-F-C-G) electrode delivered an areal capacitance of 23.5 μF cm^{-2} in 2 M H$_2$SO$_4$ electrolyte, a value much higher than that of pure MSU-F-C electrodes (11.7 μF cm^{-2}).[51] It should also be noted that the graphitization process can improve the volumetric capacitance of the electrodes and the rate capability by enhancement of the electronic conductivity.

However, the capacitance, stored within the EDL, is theoretically limited to exceed the present level; the areal capacitance on the carbon surface is lower than 30 μF cm^{-2}. In this respect, the studies of EDLCs have stagnated.

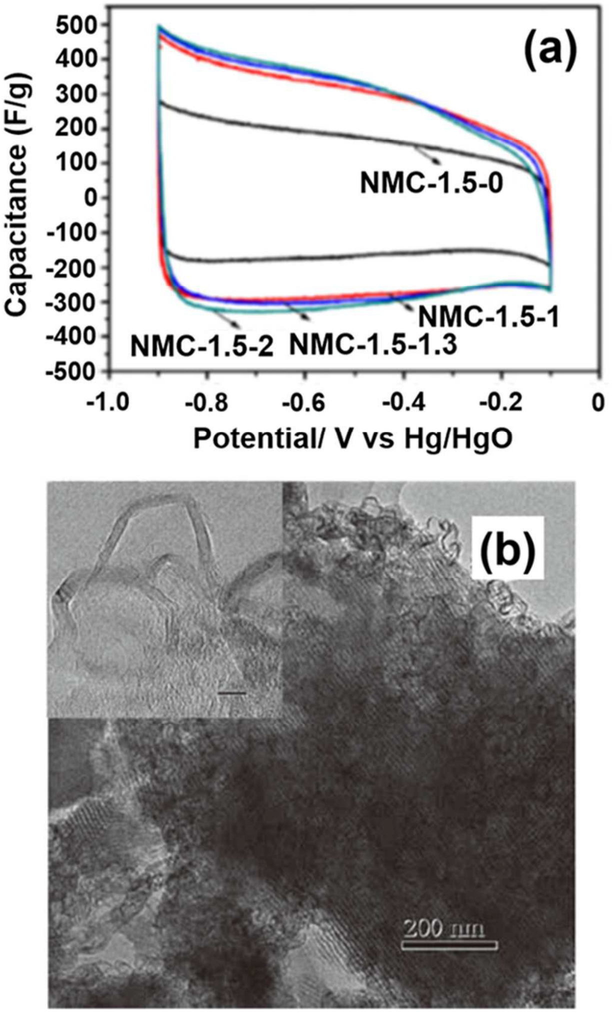


Figure 3. (a) Cyclic voltammetry (CV) data of OMCs with controlled nitrogen contents at a scan rate of 2 mV s^{-1} (Reproduced from Ref. [43] with permission from the Elsevier). (b) TEM image of graphitic OMC (Reproduced from Ref. [49] with permission from the WILEY-VCH).

4. Pseudocapacitors

In contrast to the charge storage mechanism of EDLCs, PCs use a faradaic reaction for charge storage. Numerous redox materials including metal oxides,[52] sulfides,[53] and conducting polymers[54] have been applied in PC systems and they have exhibited a lager capacitance than the electrodes of EDLCs. However, the PC electrodes usually suffer from a poor cycle performance during the repetitive redox reactions, and a large internal resistance caused by poor electrical conductivity. These result in a voltage loss (IR drop), with a reduction of both energy and power densities.

PC electrodes with mesoporous morphologies exhibit increased reversible capacitances and excellent rate capabilities, owing to the enlarged surface area and interconnected porous structures, respectively.[55, 56] To solve the conductivity problems, further processes such as thermal reduction and addition of carbon sources have been applied in PC electrodes. For example, the reduced form of mesoporous tungsten oxide (m-WO_{3-x}, Figure 4a) exhibited highly improved capacitance and rate performance, compared with mesoporous and bulk tungsten oxides (m-WO_3 and b-WO_{3-x}) as can be seen Figure 4b.[57-59]

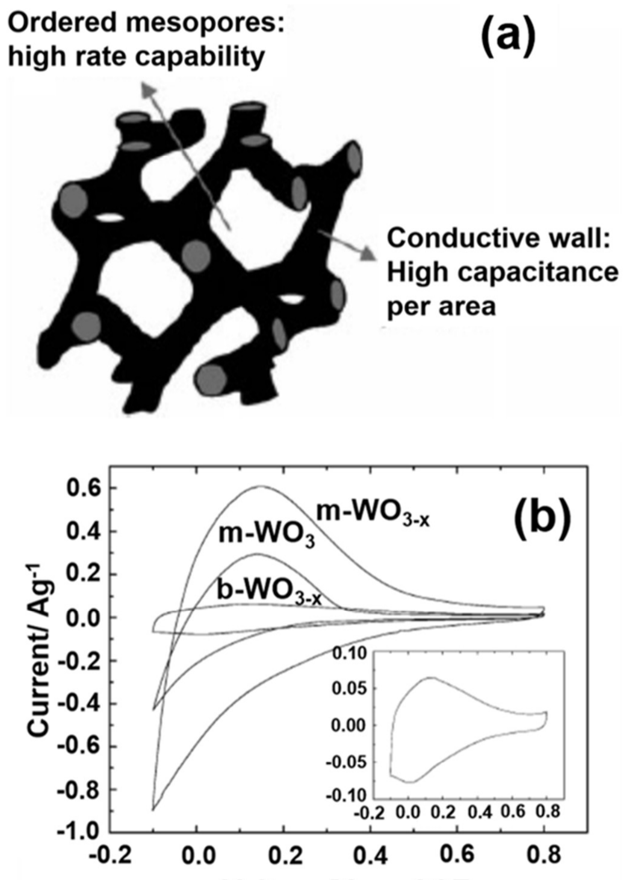


Figure 4. (a) Schematic explanation of the improved capacitance and, high conductivity of the m-WO_{3-x} electrode, and (b) CV curves of m-WO_{3-x}, m-WO_3, and b-WO_{3-x} at a scan rate of 5 mV s^{-1} (inset: enlarged CV curve of b-WO_{3-x}) (Reproduced from Ref. [57] with permission from the Royal Society of Chemistry).

As another example of designed mesoporous PC electrodes, high capacitance electrode materials such as hydrous RuO_2, MnO_2, polypyrrole, and polyaniline have been incorporated into ordered mesoporous supports to obtain the well-dispersed active materials or high conductivity composite materials.[60-63] As a result, the mesoporous composite materials show high reversible capacitance, highly stable cycle life, and excellent rate performance. Xia *et al.* reported that the capacitance of whisker-like polyaniline grown on OMC surface was as high as 1,221 F g^{-1}, the highest value measured in studies of polyaniline.[62] However, most of the PC electrodes store charges under aqueous electrolyte solutions, resulting in limited operating potentials.

Recently, Dunn and co-workers presented a non-aqueous PC system based on ordered mesoporous metal oxide films synthesized by using block copolymer coassembly.[64, 65] With structural advantages including large reaction sites, good electrolyte accessibility, and a short diffusion path from the nanometer-thick walls, the thin film electrode exhibited fast charge storage properties using an intercalation pseudocapacitive reaction under an organic electrolyte containing Li-salts. These studies imply that nano-engineering could change the charge storage mechanisms from intercalation (battery-type) to pseudocapacitance by maximizing the reaction contribution occurring at the surface or near-surface region.[66]

5. Hybrid supercapacitors as promising devices and outlook for new porous electrodes

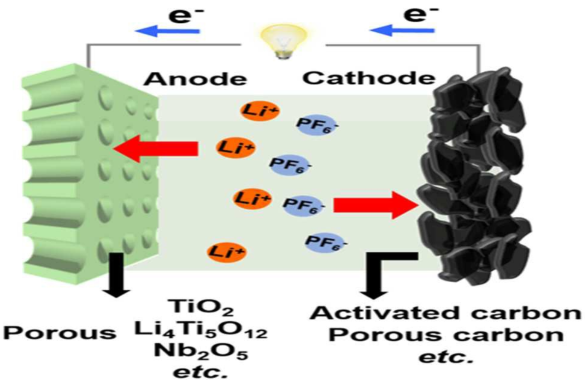


Figure 3. Schematic diagram of a hybrid supercapacitor (HSC).

Despite the various research directions, the energy density of traditional ECs remains unsatisfactory, because of restricted capacitance and narrow operating potentials. Such limitations have motivated many researchers to develop a new type of capacitor.

HSCs can deliver higher energy densities compared with traditional ECs, by utilizing the different energy-storage mechanisms at the anode and cathode. Since the first paper on the HSC was published in 2001, non-aqueous HSCs using battery-type electrolytes (*e.g.,* Li-salt/carbonate solvents) have been intensively studied, primarily because they have a wider working voltage range than aqueous ECs.[67] In the charge process of non-aqueous HSCs (Figure 5), Li-ions from the electrolyte are intercalated to battery-type anodes, resulting in higher capacitance (high energy density). Conversely, anions such as PF_6^- and BF_4^- are physically adsorbed on the surface of carbon-based cathodes, leading to high power capability. Therefore, the main issue in HSC research is to develop faster the cation-intercalation kinetics to balance the rate performances at each electrodes.

In this regard, intrinsically high-rate battery anodes such as TiO_2, $Li_4Ti_5O_{12}$, and Nb_2O_5 have been actively applied as anodes in HSCs. By developing nano-composites with carbonaceous materials (*e.g.,* graphene,[68] amorphous carbon,[69] and carbon nanotube[70]), researchers have developed HSCs with a high energy density (30–40 W h kg^{-1}) compared to those of traditional ECs. Recently, an HSC using an ordered mesoporous Nb_2O_5/carbon composite (m-Nb_2O_5-C) anode and an activated carbon cathode exhibited noticeable energy and power densities (~74 W h kg^{-1} and ~19 kW kg^{-1}, respectively) with stable cycle performance (capacity retention: ~90% at 1 A g^{-1} during 1000 cycles).[71] In addition, HSCs comprising mesoporous carbon cathodes (*e.g.,* CMK-3[72] and CMK-5[73]) and pseudocapacitive anode materials in the form of nanowires have achieved high energy and power density values (40–90 W h kg^{-1} and 11–40 kW kg^{-1}). Such results are comparable to both the high power/stable cycle life of EDLCs and the high energy density of LIBs, bridging the performance gap between traditional ECs and LIBs.

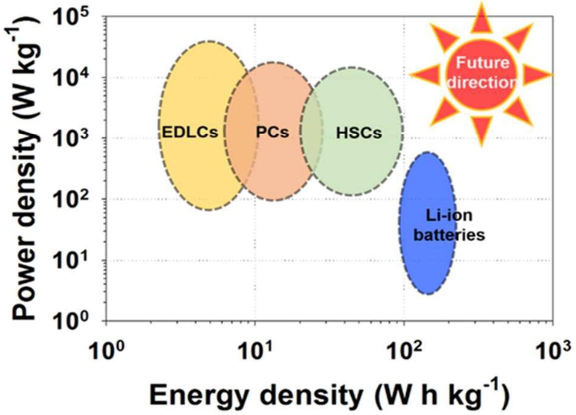


Figure 6. Ragone plot for various energy-storage applications.

As shown in Figure 6, HSCs are gradually being acknowledged as next-generation energy-storage devices. Their potential will be realized if the kinetics gap between anodes and cathodes of HSCs can be further narrowed, and the capacitance of carbonaceous cathodes increases *via* the development of suitable electrode materials.

Based on mini review, we can predict the future directions in the field of mesoporous research, since there remain challenges for the design of advanced mesoporous electrodes for application to HSCs. The current limitations of mesoporous materials are their monotonous pore sizes and irregular particle shapes or sizes. Monotonous pore structures are not able to induce sufficient electrolyte transport, and result in limited rate-capability. Moreover, particle shapes and sizes that deviate from uniform standard patterns can cause a low electrode density. Therefore, the important challenges in the field of designed mesoporous materials in the near future will be to create precisely controlled mesoporous materials, with uniform nano- or micrometer-sized spherical particles that exhibit hierarchically porous structures, which simultaneously possess macro/meso/microscale pores, as depicted in Figure 7. This strategy will enable the development of materials that allow easy wettability and mass transport of electrolytes with high capacitance and fabrication of high density electrodes.

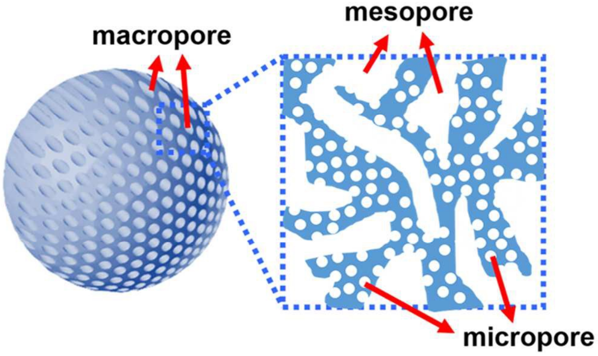


Figure 7. Schematic diagram of a nano- or micrometer-sized sphere with a hierarchically porous structure.

6. Summary

To date, there is a tremendous research effort on ECs using designed mesoporous materials. From previous studies, it has been clearly confirmed that the well-designed mesoporous materials are suitable as electrodes in the ECs, mainly due to their various advantages, such as large surface areas, well-interconnected mesopores, and frameworks composed of nano-sized crystals. These advantages have resulted in improved capacitance, fast charge-discharge rate, and stable cyclability. We eagerly anticipate the development, in the immediate future, of versatile synthesis methods for advanced porous materials.

Acknowledgements

This research was supported by the Center for C1 Gas Refinery grant funded by the Korea government (Ministry of Science, ICT & Future Planning). This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (NRF-2013R1A1A2074550). This work was supported by the Industrial Strategic Technology Development Program (10053302, Development of mesoporous magnetic ceramic material for diagnostics of pathogenic virus and bacteria) funded by the Ministry of Trade, industry & Energy (MI, Korea).

References

1 P. Simon and Y. Gogotsi, *Nat. Mater.*, 2008, **7**, 845-854.
2 K. Jost, G. Dion and Y. Gogotsi, *J. Mater. Chem. A*, 2014, **2**, 10776-10787.
3 A. Pandolfo and A. Hollenkamp, *J. Power Sources*, 2006, **157**, 11-27.
4 P. Simon, Y. Gogotsi and B. Dunn, *Science*, 2014, **343**, pp. 1210-1211.
5 M. Zhi, C. Xiang, J. Li, M. Li and N. Wu, *Nanoscale*, 2013, **5**, 72-88.
6 K. Naoi, S. Ishimoto, J.-i. Miyamoto and W. Naoi, *Energy Environ. Sci.*, 2012, **5**, 9363-9373.
7 V. Aravindan, J. Gnanaraj, Y.-S. Lee and S. Madhavi, *Chem. Rev.*, 2014, **114**, 11619-11635.
8 W. Gu and G. Yushin, *WIREs Energy Environ.*, 2014, **3**, 424-473.
9 K. Naoi, W. Naoi, S. Aoyagi, J.-i. Miyamoto and T. Kamino, *Acc. Chem. Res.*, 2012, **46**, 1075-1083.
10 D. Dubal, O. Ayyad, V. Ruiz and P. Gómez-Romero, *Chem. Soc. Rev.*, 2015, **44**, 1777-1790.
11 G. Wang, L. Zhang and J. Zhang, *Chem. Soc. Rev.*, 2012, **41**, 797-828.
12 I. E. Rauda, V. Augustyn, B. Dunn and S. H. Tolbert, *Acc. Chem. Res.*, 2013, **46**, 1113-1124.
13 Y. Ye, C. Jo, I. Jeong and J. Lee, *Nanoscale*, 2013, **5**, 4584-4605.
14 C. Kresge, M. Leonowicz, W. Roth, J. Vartuli and J. Beck, *Nature*, 1992, **359**, 710-712.
15 T. Yanagisawa, T. Shimizu, K. Kuroda and C. Kato, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 988-992.
16 D. Gu and F. Schüth, *Chem. Soc. Rev.*, 2014, **43**, 313-344.
17 Y. Shi, Y. Wan and D. Zhao, *Chem. Soc. Rev.*, 2011, **40**, 3854-3878.
18 C. Liang, Z. Li and S. Dai, *Angew. Chem. Int. Ed.*, 2008, **47**, 3696-3717.
19 D. Wu, F. Xu, B. Sun, R. Fu, H. He and K. Matyjaszewski, *Chem. Rev.*, 2012, **112**, 3959-4015.
20 A. E. Palmqvist, *Curr. Opin. Coll. Interface Sci.*, 2003, **8**, 145-155.
21 Y. Wan and D. Zhao, *Chem. Rev.*, 2007, **107**, 2821-2860.
22 J. Lee, J. Kim and T. Hyeon, *Adv. Mater.*, 2006, **18**, 2073-2094.
23 F. Schüth, *Angew. Chem. Int. Ed.*, 2003, **42**, 3604-3622.
24 G. S. Attard, J. C. Glyde and C. G. Göltner, *Nature*, 1995, **378**, 366-368.
25 P. Yang, D. Zhao, D. I. Margolese, B. F. Chmelka and G. D. Stucky, *Nature*, 1998, **396**, 152-155.
26 D. Grosso, F. Cagnol, G. d. A. Soler-Illia, E. L. Crepaldi, H. Amenitsch, A. Brunet-Bruneau, A. Bourgeois and C. Sanchez, *Adv. Funct. Mater.*, 2004, **14**, 309-322.
27 M. C. Orilall and U. Wiesner, *Chem. Soc. Rev.*, 2011, **40**, 520-535.
28 J. Lee, M. C. Orilall, S. C. Warren, M. Kamperman, F. J. DiSalvo and U. Wiesner, *Nat. Mater.*, 2008, **7**, 222-228.
29 C. Jo, Y. Kim, J. Hwang, J. Shim, J. Chun and J. Lee, *Chem. Mater.*, 2014, **26**, 3508-3514.
30 J. Hwang, S. H. Woo, J. Shim, C. Jo, K. T. Lee and J. Lee, *ACS Nano*, 2013, **7**, 1036-1044.
31 H. Zhou, S. Zhu, M. Hibino and I. Honma, *J. Power Sources*, 2003, **122**, 219-223.
32 S. Oh and K. Kim, *Chem. Commun.*, 1999, 2177-2178.
33 Y. Korenblit, M. Rose, E. Kockrick, L. Borchardt, A. Kvit, S. Kaskel and G. Yushin, *ACS Nano*, 2010, **4**, 1337-1344.
34 S. Yoon, S. M. Oh, C. W. Lee and J.-W. Lee, *J. Electrochem. Soc.*, 2010, **157**, A1229-A1235.
35 W. Xing, S. Qiao, R. Ding, F. Li, G. Lu, Z. Yan and H. Cheng, *Carbon*, 2006, **44**, 216-224.
36 D. Lozano-Castello, D. Cazorla-Amorós, A. Linares-Solano, S. Shiraishi, H. Kurihara and A. Oya, *Carbon*, 2003, **41**, 1765-1775.
37 D.-W. Wang, F. Li, Z.-G. Chen, G. Q. Lu and H.-M. Cheng, *Chem. Mater.*, 2008, **20**, 7195-7200.
38 T. Durkić, A. Perić, M. Laušević, A. Dekanski, O. Nešković, M. Veljković and Z. Laušević, *Carbon*, 1997, **35**, 1567-1572.
39 C. O. Ania, V. Khomenko, E. Raymundo-Piñero, J. B. Parra and F. Beguin, *Adv. Funct. Mater.*, 2007, **17**.

40 H. Oda, A. Yamashita, S. Minoura, M. Okamoto and T. Morimoto, *J. Power Sources*, 2006, **158**, 1510-1516.
41 X. Zhao, Q. Zhang, B. Zhang, C.-M. Chen, A. Wang, T. Zhang and D. S. Su, *J. Mater. Chem.*, 2012, **22**, 4963-4969.
42 H.-K. Jeong, M. Jin, E. J. Ra, K. Y. Sheem, G. H. Han, S. Arepalli and Y. H. Lee, *ACS Nano*, 2010, **4**, 1162-1166.
43 Q. Shi, R. Zhang, Y. Lv, Y. Deng, A. A. Elzatahrya and D. Zhao, *Carbon*, 2015, **84**, 335-346.
44 D. Zhang, Y. Hao, L. Zheng, Y. Ma, H. Feng and H. Luo, *J. Mater. Chem. A*, 2013, **1**, 7584-7591.
45 M. Seredych and T. J. Bandosz, *J. Mater. Chem. A*, 2013, **1**, 11717-11727.
46 L. Zhao, L. Z. Fan, M. Q. Zhou, H. Guan, S. Qiao, M. Antonietti and M. M. Titirici, *Adv. Mater.*, 2010, **22**, 5202-5206.
47 D. W. Wang, F. Li, M. Liu, G. Q. Lu and H. M. Cheng, *Angew. Chem. Int. Ed.*, 2008, **120**, 379-382.
48 Y. Mun, C. Jo, T. Hyeon, J. Lee, K.-S. Ha, K.-W. Jun, S.-H. Lee, S.-W. Hong, H. I. Lee and S. Yoon, *Carbon*, 2013, **64**, 391-402.
49 W. Gao, Y. Wan, Y. Dou and D. Zhao, *Adv. Energy Mater.*, 2011, **1**, 115-123.
50 S. Inagaki, Y. Yokoo, T. Miki and Y. Kubota, *Micropor. Mesopor. Mater.*, 2013, **179**, 136-143.
51 C. Jo, S. An, Y. Kim, J. Shim, S. Yoon and J. Lee, *Phys. Chem. Chem. Phys.*, 2012, **14**, 5695-5704.
52 X.-H. Xia, J.-P. Tu, X.-L. Wang, C.-D. Gu and X.-B. Zhao, *Chem. Commun.*, 2011, **47**, 5786-5788.
53 L. Shen, L. Yu, H. B. Wu, X.-Y. Yu, X. Zhang and X. W. D. Lou, *Nat. Commun.*, 2015, **6**.
54 T. Liu, L. Finn, M. Yu, H. Wang, T. Zhai, X. Lu, Y. Tong and Y. Li, *Nano Lett.*, 2014, **14**, 2522-2527.
55 W. Sugimoto, S. Makino, R. Mukai, Y. Tatsumi, K. Fukuda, Y. Takasu and Y. Yamauchi, *J. Power Sources*, 2012, **204**, 244-248.
56 L. An, Q. Ren, W. Li, K. Xu, Y. Cao, T. Ji, R. Zou, Z. Chen and J. Hu, *J. Mater. Chem. A*, 2015, **3**, 11503-11510.
57 S. Yoon, E. Kang, J. K. Kim, C. W. Lee and J. Lee, *Chem. Commun.*, 2011, **47**, 1021-1023.
58 C. Jo, I. Hwang, J. Lee, C. W. Lee and S. Yoon, *J. Phys. Chem. C*, 2011, **115**, 11880-11886.
59 C. Jo, J. Hwang, H. Song, A. H. Dao, Y. T. Kim, S. H. Lee, S. W. Hong, S. Yoon and J. Lee, *Adv. Funct. Mater.*, 2013, **23**, 3747-3754.
60 H. S. Huang, K. H. Chang, N. Suzuki, Y. Yamauchi, C. C. Hu and K. C. W. Wu, *Small*, 2013, **9**, 2520-2526.
61 J. H. Jang, S. Han, T. Hyeon and S. M. Oh, *J. Power Sources*, 2003, **123**, 79-85.
62 Y. G. Wang, H. Q. Li and Y. Y. Xia, *Adv. Mater.*, 2006, **18**, 2619-2623.
63 Z. Lei, X. Sun, H. Wang, Z. Liu and X. Zhao, *ACS Appl. Mater. Interfaces*, 2013, **5**, 7501-7508.
64 K. Brezesinski, J. Wang, J. Haetge, C. Reitz, S. O. Steinmueller, S. H. Tolbert, B. M. Smarsly, B. Dunn and T. Brezesinski, *J. Am. Chem. Soc.*, 2010, **132**, 6982-6990.
65 T. Brezesinski, J. Wang, S. H. Tolbert and B. Dunn, *Nat. Mater.*, 2010, **9**, 146-151.
66 J. Wang, J. Polleux, J. Lim and B. Dunn, *J. Phys. Chem. C*, 2007, **111**, 14925-14931.
67 R. Yi, S. Chen, J. Song, M. L. Gordin, A. Manivannan and D. Wang, *Adv. Funct. Mater.*, 2014, **24**, 7433-7439.
68 H. Kim, M. Y. Cho, M. H. Kim, K. Y. Park, H. Gwon, Y. Lee, K. C. Roh and K. Kang, *Adv. Energy Mater.*, 2013, **3**, 1500-1506.
69 H.-G. Jung, N. Venugopal, B. Scrosati and Y.-K. Sun, *J. Power Sources*, 2013, **221**, 266-271.
70 X. Wang, G. Li, Z. Chen, V. Augustyn, X. Ma, G. Wang, B. Dunn and Y. Lu, *Adv. Energy Mater.*, 2011, **1**, 1089-1093.
71 E. Lim, H. Kim, C. Jo, J. Chun, K. Ku, S. Kim, H. I. Lee, I.-S. Nam, S. Yoon and K. Kang, *ACS Nano*, 2014, **8**, 8968-8978.
72 Y. Wang, Z. Hong, M. Wei and Y. Xia, *Adv. Funct. Mater.*, 2012, **22**, 5185-5193.
73 Y. Wang, D. Zhou, D. Zhao, M. Hou, C. Wang and Y. Xia, *J. Electrochem. Soc.*, 2013, **160**, A98-A104.