

Highlight Review**Nanostructure-controlled Materials for Electrochemical Charging–Discharging****Isamu Moriguchi**Division of Chemistry and Materials Science, Graduate School of Engineering,
Nagasaki University, 1-14 Bunkyo-machi, Nagasaki 852-8521

(E-mail: mrgch@nagasaki-u.ac.jp)



Professor Isamu Moriguchi was born in Nagasaki, Japan in 1963. He received his Bachelor and Master degrees of Engineering in Kyushu University and Dr. of Engineering from Nagasaki University in 1996. After graduating the master course, he was appointed as Assistant Professor, Associate Professor, and Full Professor in Faculty of Engineering in Nagasaki University. The affiliation was changed to the present in 2012. He was a visiting scholar of Clarkson University (Supervisor: Prof. J. H. Fendler) in USA in 1997 and Researcher for Program of Precursory Research of Embryonic Science and Technology, Japan Science and Technology Agency (JST) from 2001 to 2005. His research interests are in the field of electrochemistry related to energy devices and colloid and interface chemistry.

Abstract

Down-sizing of Li-host materials is one of the recent research trends to develop high-performance electrode materials. Nano-sized materials are expected to show high rate capability and/or high capacities. Nanoporous materials are also candidates for high-performance electrode materials. This review introduces recent studies on nanosized and nanoporous electrode materials toward developing high-performance energy-storage devices.

Introduction

Recently there has been intensive interest in the development of electrode materials for energy-storage devices with both high energy and high power densities due to expected demand for power-grid applications as well as power sources for electric and/or hybrid electric vehicles.^{1,2} Lithium-ion secondary batteries (LIBs) are attractive power-storage devices, but the energy density is still not enough for power use, and the power density is generally low due to a large polarization at high charge-discharge rates.

Electrochemical reactions with charging-discharging of LIBs are composed of various processes; for example, Li-insertion reactions are accompanied with (1) transfer of solvated Li ions from the bulk electrolyte to the electrode surface, (2) charge-transfer reactions with desolvation of Li ions at the electrode interface, (3) Li diffusion in active material solids, and (4) electron transfer from the conductive substrate, as illustrated in Figure 1. The polarization due to these reactions should be suppressed to yield high-performance LIB. The process of (3) is generally thought to be a rate-determining step because of very low chemical diffusion coefficient (D) of Li ion in the solid phase (ca. 10^{-12} cm² s⁻¹). The diffusion length (L) of Li ion in solid phase, which can be expressed by $L \approx (Dt)^{1/2}$, where t is the diffusion time, should be shortened to overcome kinetic problems and to achieve high rate charging-discharging.³ Therefore, down-sizing of Li-host materials is a recent research trend to develop high-performance LIB electrode materials. In addition, it is worth noting that nanosized Li-host materials showed unique charge-discharge properties different from those of the bulk phases except for the mentioned above. This Highlight Review focuses on recent nanostructure-controlled materials from the aspects of enhanced electrochemical charge-discharge properties by nanosize effect, fabrication of nano-

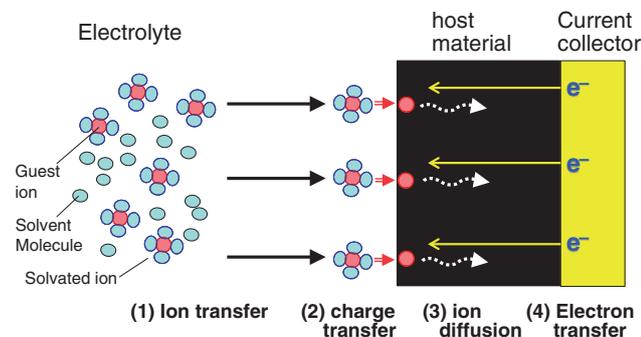


Figure 1. Schematics of electrode reaction processes during the insertion of guest ions into a host material.

porous secondary structures, and control of electrolyte ion transport.

Charge-Discharge Properties of Nano-sized Materials

Recent studies have demonstrated high rate charge-discharge properties of Li-host nanocrystallites. As for LiCoO₂, which is a representative Li-intercalation cathode material, the nanocrystallites were reported to show higher capacities at high discharge rates than the bulk crystal; discharge capacities at 100C (1C means the current density for de-intercalation in 1 h) were ca. 75 mA h g⁻¹ for nanocrystallites with an average thickness of 17 nm and ca. 36 mA h g⁻¹ for the bulk crystal.⁴ However, the down-sizing caused the decrease in capacities at low rates, lowering average discharge voltage, and lowering cyclability in comparison with those of bulk crystal, indicating negative effects on energy density and stability. The nanosize effect is thought to be due to broadening of Li-intercalation site energy in nanolayers at the material surface caused by lattice expansion. The effect of surface nanolayers on charge-discharge properties appears dominantly with decreasing the material size although such effect is negligibly small for bulk materials. Down-sizing was also effective to enhance charge-discharge properties of olivine materials such as LiFePO₄ when the electron conduction of electrodes is enough for the redox reactions by a sufficient addition of conductive additives such as carbon black.⁵⁻¹⁰ Bulk LiFePO₄ materials showed small capacities and low rate capability due to a kinetic barrier of phase transition between LiFePO₄ and FePO₄ phases. The enhancement of rate capability with the down-sizing was reported to be ascribable to the formation and extension of solid solution of Li_xFePO₄.¹¹ On the other hand, LiMnPO₄ needs greater size control at nanometer level to enhance charge-discharge properties because of larger kinetic barrier at the mismatched interface of MnPO₄-LiMnPO₄ than that of LiFePO₄.¹² LiMnPO₄ nanocrystallites with the crystalline size of 10–20 nm were reported to show high rate capability due to a formation of solid solution and an increase in Li-diffusion coefficient in the nanophase.^{13,14} Enhanced charge-discharge properties were also reported on LiMn₂O₄, of which redox reactions are generally observed around 4 and 3 V vs. Li/Li⁺.¹⁵ The latter redox is accompanied with rearrangement of atoms and large lattice volume change by the phase transition between cubic and tetragonal crystal phases; thus its capacity is very small for bulk LiMn₂O₄. However, the formation of solid solution with down-sizing to nanolevel facilitated the Li insertion-extraction reactions around 3 V and resulted in the increase in total capacity in the range of 4.3–2.5 V.¹⁵ Such findings are important for yielding not only high rate but also high capacity.

As for the development of high capacity materials, recent studies have focused on Li-host materials with more than one Li in the formula unit such as Li₂MSiO₄ (M = Fe and Mn). However, low capacities corresponding to the extraction-insertion of less than 1 Li ion per formula unit (i.e., <160 mA h g⁻¹) were realized in practice for most of the reports on orthosilicate cathodes.¹⁶⁻²⁸ The major drawback of orthosilicates is their very low intrinsic conductivities; for example, the conductivity of Li₂MnSiO₄ is below 10⁻¹⁶ S cm⁻¹ at room temperature.²⁹ Some recent reports have achieved high initial

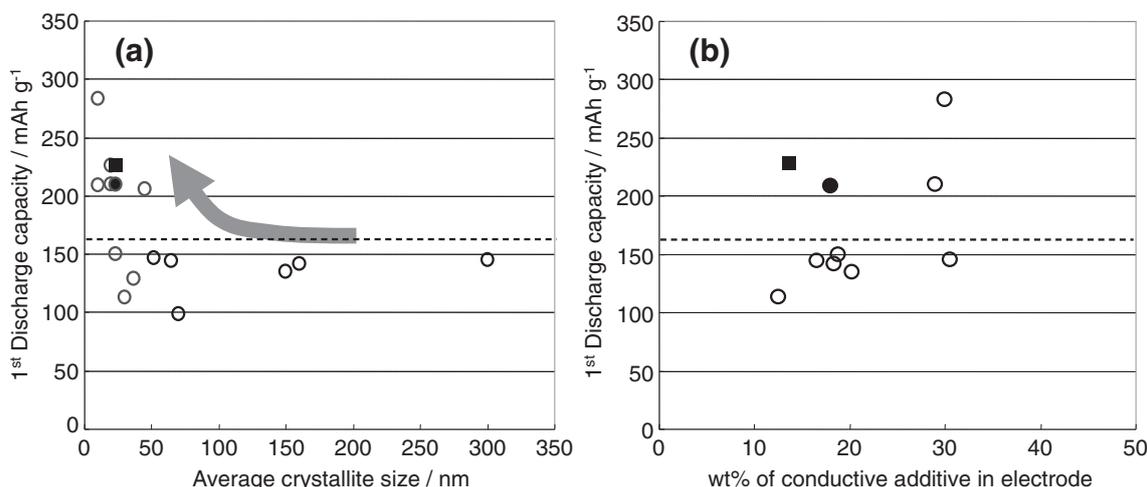


Figure 2. 1st discharge capacities at room temperature of LiMnSiO_4 samples dependent on (a) average crystallite size of LiMnSiO_4 and (b) wt % of conductive additives in electrodes. The data were collected from references of 16–34. The filled circle and square indicate the performance of a LiMnSiO_4 –carbon nanocomposite and a SWNTs-incorporated composite reported in ref 34, respectively.

capacities over 200 mA h g^{-1} for $\text{Li}_2\text{MnSiO}_4$ nanocrystallites post-coated with conductive materials.^{30–33} The reported charge–discharge properties on $\text{Li}_2\text{MnSiO}_4$ materials evaluated at room temperature are summarized in Figure 2. Initial discharge capacity tends to increase with decreasing the crystallite size, indicating the possibility of insertion–extraction of more than one Li ion from $\text{Li}_2\text{MnSiO}_4$ by the down-sizing. However, it is worth noting that high capacities of nanosized crystallites were obtained in the presence of much amount of conductive materials in the electrode, which means lowering the energy densities of electrode and cell. In addition, some were also accompanied with lowering the average discharge potential.^{31–33} To enhance the electrode performance, the composite structure of $\text{Li}_2\text{MnSiO}_4$ nanocrystallites and a conductive material should be precisely controlled at nanoscale for effective Li ion and electron transport with a minimized amount of conductive materials. Homogeneous nanocomposites of $\text{Li}_2\text{MnSiO}_4$ nanocrystallites and carbon (Figure 3), which were synthesized directly by using an organic–inorganic hybrid polymer, showed high capacities at room temperature (see the closed symbol in Figure 2).³⁴ Especially the composite incorporated additionally single-walled carbon nanotubes (SWNTs) showed excellent charge–discharge properties with reasonable discharge potential around 3 V vs. Li/Li^+ at low carbon content.

Nanoporous Materials as a Potential LIB Electrode Material

Since most Li-host materials have high electronic resistivity, electron-conductive paths are required in or near them for decreasing the polarization during charging–discharging. In general, conductive additives such as carbon black are mixed mechanically with Li-host material particles for conventional Li-battery electrodes. On this point, nanosized Li-host materials are not always suitable to practical electrodes due to the strong agglomeration which prevents homogeneous mixing with conductive and adhesive additives. Fabrication of secondary structures composed of Li-host nanocrystallites and carbon

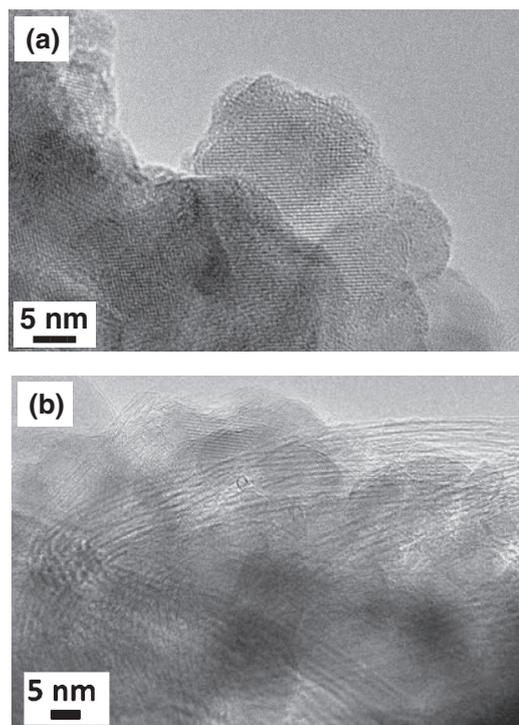


Figure 3. TEM images of (a) LiMnSiO_4 –carbon nanocomposite and (b) the SWNTs-incorporated composite reported in ref 34.

nanophase should be required to make the best use of nanosize effect to the development of high-performance electrodes.

Nanoporous materials are candidates for high-performance electrode materials because the large surface area decreases current density per unit surface area, the thin wall reduces Li-diffusion length in host solid phase, and nanopores enables electrolyte ions to transport smoothly. It has been reported that fabrication and control of nanoporous structure of Li-host materials such as TiO_2 and V_2O_5 were effective in improving

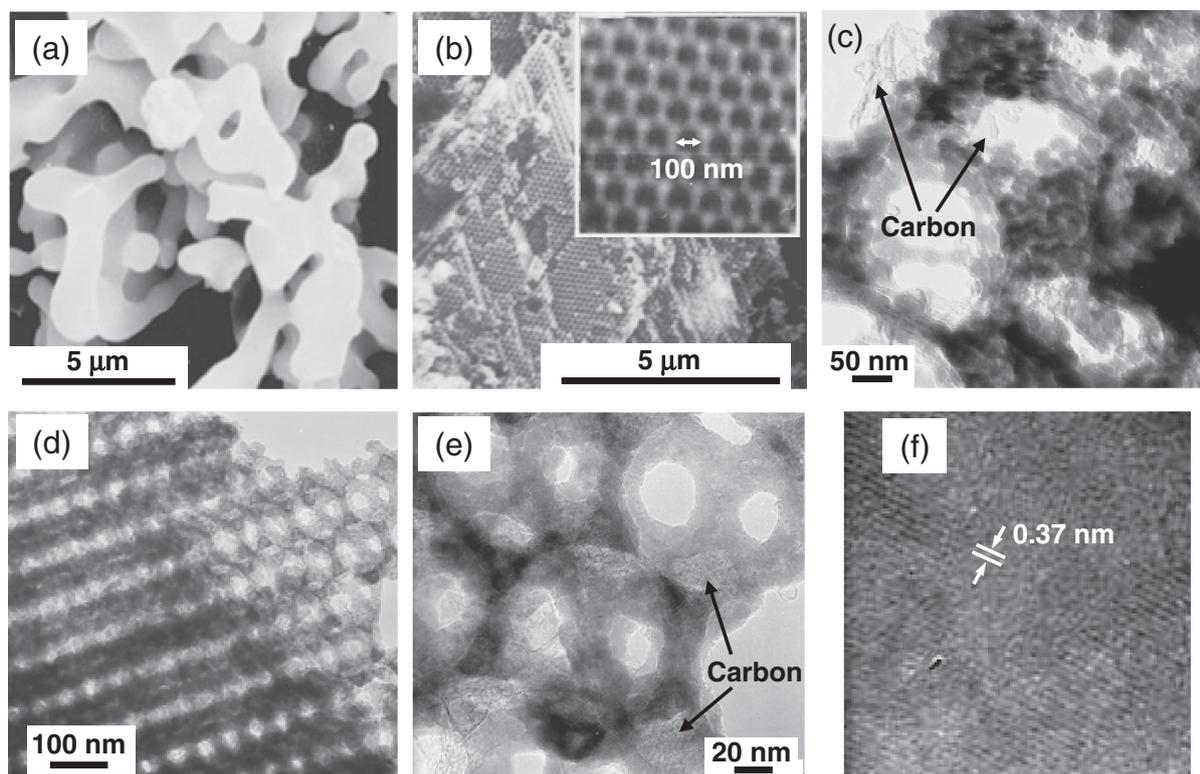


Figure 4. (a) SEM image of bulk LiFePO_4 (LFP), (b) SEM image of the CCT-derived LFP, (c) TEM image of the CCT-derived LFP, (d–f) TEM image of the LFP–carbon nanocomposite synthesized by the sucrose-added CCT process.⁴⁷

the rate capability of charging–discharging, but the capacity still decreased steeply at high rates.^{35–44} Most of the reported electrodes of nanoporous materials, which were made as a mechanical mixture of nanoporous materials and conductive additives or were made directly as a porous film on electronic conductive substrate, did not have sufficient electronic conductivity for high-rate Li insertion–extraction in the entire host material. The pore size of nanoporous materials is too small to incorporate the conventional conductive additives, and nanoporous materials usually have micrometer size bodies; thus the electron-supply for high-rate reaction is not enough at some parts in the materials far from the interface contacting with conductive additives and the current collector.

Nanoporous materials composed of Li host and carbon nanophases have been developed recently as an approach to overcome the problem mentioned above. Mesoporous and macroporous composites of TiO_2 and cut-SWNTs, which were synthesized by a bicontinuous microemulsion-aided process and a colloidal crystal-template (CCT) process, demonstrated excellent rate capability of Li insertion–extraction irrespective of a small amount incorporation of cut-SWNTs.^{45,46} Nanoporous composites of LiMPO_4 ($M = \text{Fe}$ and Mn) and carbon were obtained by a CCT process adding sucrose as a carbon source in the starting mineral solution.⁴⁷ Ordered nanoporous structures with a three-dimensionally continuous nanothick wall were successfully fabricated as shown in Figure 4, where the incorporation of amorphous carbon nanophases in the pore wall caused high ordering of the nanoporous composite structure. As shown in Figure 5, the capacity and rate capability of LiMPO_4

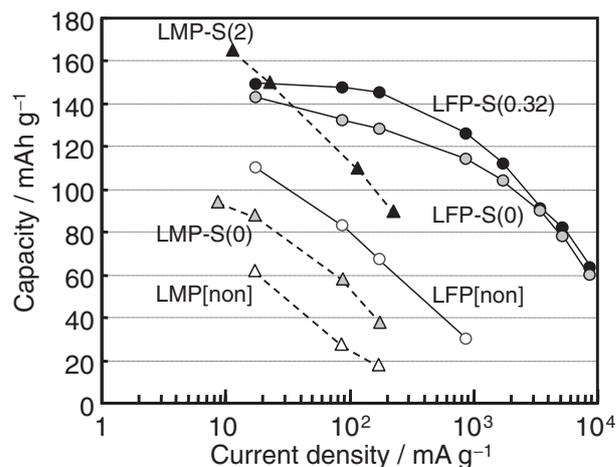


Figure 5. Rate capability of bulk LiFePO_4 and LiMnPO_4 samples (LFP[non] and LMP[non]), CCT-derived samples (LFP-S(0) and LMP-S(0)), and sucrose-added CCT-derived samples (LFP-S(0.32) and LMP-S(2)).⁴⁷

($M = \text{Fe}$ and Mn) were improved by the introduction of nanoporous structures (LFP-S(0) and LMP-S(0) in Figure 5), and were enhanced more by fabricating the nanoporous structures with the nanothick wall of LiMPO_4 –carbon composites (LFP-S(0.32) and LFP-S(2) in Figure 5).

Postmodification of porous carbons with Li-host nanomaterials is also attractive as another approach for a fabrication

of Li-host-carbon nanoporous electrode materials. MnO_2 nanoparticles incorporated inside the pore channels of CMK-3 mesoporous carbon showed higher discharge performance than a MnO_2 -coated acetylene black composite.⁴⁸ However, the capacity decreased with increasing MnO_2 -loading amount probably due to the decrease in mesoporous space with the incorporation of the particles. Similar behavior was also observed on LiMnPO_4 -embedded nanoporous carbons.¹³ A more suitable post modification should be coating with host nanolayer on the inner surface of porous carbons with appropriate pore size so as to provide nanopore channels for electrolyte transport. The possibility was demonstrated by a simulation, and actually prepared V_2O_5 nanolayer-coating of CCT-derived porous carbons maintained a high charge-discharge capacity up to extremely high current densities due to the rapid Li intercalation into whole V_2O_5 nanophasess.⁴⁹

Such porous materials may have a disadvantage of low volumetric capacity from the viewpoint of practical application to compact devices using a liquid electrolyte. The volumetric capacity can be increased theoretically by a modification of carbon nanopore surface with Li-host nanolayer with an appropriate thickness, where the pore size of nanoporous carbon should be minimized. The nanoporous composites are also useful for all-solid-state devices because large interface area of solid electrolyte-host material can be provided by filling a solid electrolyte in the pores to accelerate the solid-solid interface reactions.

Nanoporous Structure for Electrolyte Ion Transport

Although the fabrication of nanoporous electrode materials is one approach for developing high-performance energy-storage devices as mentioned above, the porous structure should be optimized to make the pore surface of materials accessible to electrolyte ions smoothly. Porous carbons are generally used as electrode materials for electric double-layer capacitors, thus the ion accessibility of nanoporous structure can be evaluated from the electric double-layer capacitance (EDLC) properties. The electric double-layer capacitance (C) is basically expressed by the equation $C = \varepsilon_0 \varepsilon_r S/d$, where ε_0 , ε_r , S , and d are the permittivity of vacuum, relative permittivity of dielectric material (electrolyte), surface area of electrode, and the thickness of electric double-layer at the electrode-electrolyte interface, respectively. The higher the electrode surface area and the concentration of electrolyte, the higher value of EDLC is expected theoretically. However, the proportionality between the EDLC and specific surface area of activated carbons are not always observed as shown in Figure 6. Micropores developed in the high-surface-area carbons such as activated carbons are generally considered not to be accessible to electrolyte and thus will not contribute to the total EDLC of the materials.^{50,59,60} On the other hand, mesoporous carbons, which were synthesized by the template process using mesoporous silica (MCM48)^{53,54,61} and aerogels,^{51,52} showed relatively high EDLC properties. 3D-ordered mesoporous and macroporous carbons, obtained by a CCT process, showed highly efficient EDLC properties; the specific capacitance based on weight increased linearly with increasing the specific surface area of samples.⁵⁵⁻⁵⁸ The nanoporous carbons derived by the CCT process were also superior

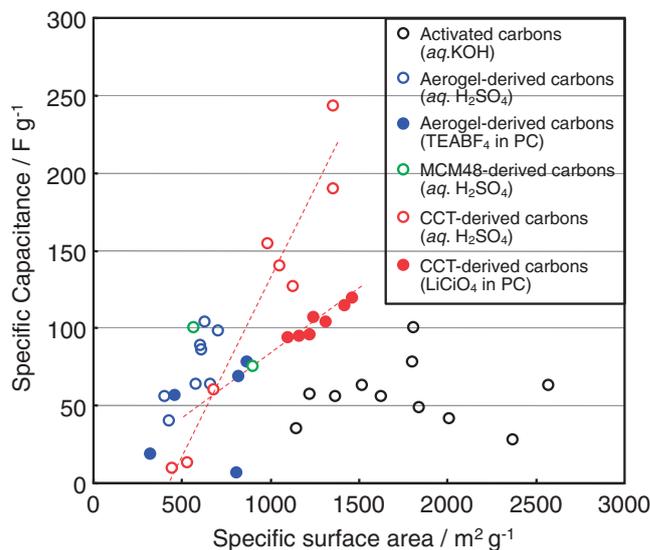


Figure 6. Specific EDLC based on weight vs. specific surface area plots of the reported activated carbons,⁵⁰ aerogel-derived carbons in an aqueous H_2SO_4 and in a PC solution of TEABF_4 ,^{51,52} MCM48-derived mesoporous carbons,^{53,54} CCT-derived meso- and macroporous carbons in an aqueous H_2SO_4 and in a PC solution of LiClO_4 .⁵⁵⁻⁵⁸

in rate capability to activated carbons and MCM48-derived mesoporous carbons. These results indicate that the nanoporous structure with pore size range of mesopore to macropore should be suitable for the effective access of electrolyte ions.

The EDLC was also affected by the kind of electrolyte solution. EDLCs in organic electrolytes were lower than those in aqueous solutions probably due to the low dielectric constant (ε_r) of organic electrolytes.⁵⁸ Specific capacitances per surface area, estimated from the slope of dotted lines in Figure 6, are ca. $22 \mu\text{F cm}^{-2}$ for the CCT-derived carbons in an aqueous H_2SO_4 and ca. $8.3 \mu\text{F cm}^{-2}$ in a propylene carbonate (PC) solution of LiClO_4 . The dependence of pore size on EDLCs was also different between aqueous and organic electrolytes. The contribution of micropore surface to EDLCs was generally thought to be very small in aqueous electrolytes, but it was recently reported that it is not always the case of organic electrolytes. The surface area-based specific capacitance of micropores with the pore size around solvated ion size was comparable to that of meso- and macropores for CCT-derived nanoporous carbons in the PC solution of LiClO_4 .⁵⁸ The remarkable increase in surface area-based specific capacitance was reported on carbide-derived microporous carbons in an acetonitrile solution of $\text{N}(\text{C}_2\text{H}_5)_4\text{BF}_4$ and an ionic liquid.⁶²⁻⁶⁵ The enhancement in EDLCs was ascribed to desolvated electrolyte ions derived from spatial restriction by the micropores. The desolvated electrolyte ions can approach the electrode surface more closely to decrease the thickness of electric double-layer (d). Consequently the EDLC is increased according to the mentioned equation of $C = \varepsilon_0 \varepsilon_r S/d$. These findings should contribute significantly toward developing not only electric double-layer capacitors but also LIBs because desolvation of Li ions at the electrode interface is one of the key reactions of LIB electrodes and because decreasing its activation energy will enhance LIB performance.

Conclusion

The development of high-performance energy-storage devices is required recently, but there are limitations of cost and amount of resources in order to apply the electrode materials to practical devices. Therefore, it is very important to enhance the material functions by a structural control rather than the development of new materials with varying elements. This Highlight Review has introduced recent research on nanosized materials and nanoporous materials. Such nanostructure-controlled materials have a high potential as electrode materials for energy-storage devices. However, we should pay attention to some expected disadvantages of nanosized materials such as low volumetric capacities and low stability as well as high reactivity of the surface which might induce side reactions. Further studies on nanostructure-controlled materials are in progress so as to fulfill the requirements for high-performance electrodes.

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