Development of High-efficiency 3D Nanoporous Electrode Materials Based on Carbon-metal Composites

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論文内容要約

※題名については，「要約」として下さい。

Achieving a secure, sustainable, and inexpensive energy future is one greatest scientific and societal challenges of our time. Electrical energy storage (EES) will be more important in the future than at any time in the past. Among various EES technologies, lithium-ion batteries (LIBs), dominating the current market for electronic devices, have exerted a profound impact on our daily life, varied by portable electronics, electric vehicles, to grid-scale applications. However, inherent limitations make it difficult for Li-ion chemistries to meet the growing demands for energy density and in particular power density to deliver energy rapidly and efficiently. Supercapacitors (SCs), also known as electrochemical capacitors (ECs), is another EES device that can be charged in minutes if not seconds, ensuring fast energy collection, but they usually store only less than 10% of the energy stored in LIBs. Even so, the similar cell configurations of LIBs and SCs and their shared electrode materials make it possible to create their hybrids as the next generation devices for future EES, well beyond what is anticipated from improvements in traditional LIBs or carbon-based electrical double-layer capacitors (EDLC). Despite tremendous exciting prospects presented by several very recent review articles, up to date, little specific research results have been reported to realize "*this new generation that has an enormous impact on our future*" at a practical level, as stressed in *Nature Communications 7 (2016) 12647*.

To achieve this goal, it not only needs to attain profound understandings of the chemistry taking place in these devices, including interfacial chemistries, Li deposition behaviour, and the correlations among them, but also needs to design and prepare novel materials and system architectures, which can combine the best features of electrode materials for both LIBs and SCs. Hence, on the basis of the promising transition metal oxides (MO_x) and graphene-based electrode materials for LIBs and the most favored hierarchical 3D nanoporous architectures in achieving future hybrid EES in a cost-effective manner, the research contents in this thesis are organized in the following order: (i) metallic material with hybrid nanoporous configuration for electrode structure design, (ii) bilayer-graphene foam for fundamental Li-storage mechanism in graphene/graphite, (iii) 3D ordered macroporous (3DOM) nanocrystalline carbon-Ni hybrid monoliths toward practical EES applications, and (iv) the universal preparation mechanism for extensive 3DOM nanocrystalline

carbon-based functional materials.

Accordingly, all the contents of this thesis are arranged as follows:

In **Chapter 1**, current energy storage systems such as LIBs and SCs, various types of electrode materials, fundamentally electrochemical mechanisms, and the advanced electrode structure/design proposed in the literature, were briefly introduced, followed by the objective and outline of this thesis.

In **Chapter 2**, the preparation methods of the as-developed novel electrode materials, such as one 3D nanoporous Cu-Mn-hybrid material in **Chapter 3**, one bilayer-graphene foam in **Chapter 4**, one nanocrystalline C-Ni hybrid monolith (denoted as NiG) featuring 3DOM structure in **Chapter 5**, and extensive 3DOM graphene-matel-based materials in **Chapter 6**, the characterization methods, and the performance evaluation methods were presented, respectively.

In **Chapter 3**, around the specific nanoarchitecture of the 3D nanoporous Cu-Mn hybrid material, one easy and universal electrochemical dealloying preparation mechanism was firstly proposed. The synergetic Li-storage mechanism of this hybrid system was then discussed mainly from the kinetics and resistance angles, followed by the final evaluation of its Li-storage performances (capacitance and capacity) to highlight the unique electrode configuration design.

In **Chapter 4**, the bilayer-graphene foam with little defect was developed by one high-temperature-switched CVD process to make clear the Li-storage mechanism into graphene as well as commercial graphite anode in LIBs. The specific capacity, process, kinetics, and resistances of Li storage in this material was firstly determined, and then corroborated by theoretical calculations, various physiochemical characterizations were performed on the typically staged Li-bilayer graphene products.

In **Chapter 5**, inspired by the superior electrode structure proposed in **Chapter 3** and the fundamental Li-storage mechanism in graphene/graphite revealed in **Chapter 4**, the 3DOM nanocrystalline C-Ni hybrid material was prepared by developing a simple nickel nitrate-based hard-template preparation. Its Li-storage kinetics mechanism was firstly studied and then the monolithic performance was determined. To further prove its potential in practical application, commercial-level measurements were carried out, too.

In **Chapter 6**, the formation mechanism of this 3DOM graphene carbon-based material by this co-sacrificial-template preparation was studied systematically to expand potential graphene materials for extensive applications beyond energy storage.

In **Chapter 7**, the general conclusion of the key findings and the innovations of this thesis were summarized.

Consequently, the main results, together with the corresponding innovations for each research discussed in **Chapter 3** to **Chapter 6**, are as follows:

(1) **Chapter 3**: A self-assembled nanoporous hybrid architecture, constructed by the internal 3D mesoporous thick foam of "yolk–shell" MO_x(shell)@M(core) and the surface macroporous thin film of MO_x nanoarrays, has been

prepared by developing one simple electrochemical dealloying route using common transitional metal alloys (e.g., Cu-Mn and Ni-Mn foils) as precursor and neutral salt solution (e.g., NaCl) as electrolyte. The results show that, this unique composite configuration with both high ionic and electronic conductivities has achieved a much larger loading active mass (~9 mg cm^{-2}) than the present research level (most < 3 mg cm^{-2} even for a 10-time thicker electrode). Meanwhile, in addition to the inhibition on hazardous Li dendrite, it is found that the surface macroporous film can facilitate the well formation of the inevitable solid electrolyte interphase (SEI) film at the electrode-electrolyte interface to efficiently enhance the Li-ion diffusion into the internal MO_x even with intrinsically slow Li-storage kinetics. Benefited by the above, this freestanding electrode material with multiple favorable electrode structure is able to realize high-rate and large-capacity EES with enhanced cycling stability, which can greatly satisfy the present commercial requirements in either the areal specific capacity of 3 mAh cm^{-2} or the affordable current density of 4 mA cm^{-2}.

As a result, the innovation points of this chapter include: (i) developing an in-situ electrochemically integrated preparation for M-MO_x electrodes; (ii) creating a novel electrode configuration loading large active mass (~9 mg cm^{-2}); and (iii) revealing enhanced Li-diffusion mechanism by surface macroporous film.

(2) **Chapter 4**: A high-quality 3D bilayer-graphene foam has been successfully prepared by developing one high-temperature-switched chemical vapor deposited (CVD) process. Using it as the self-supporting electrode in Li-ion half battery, the Li-storage capacity, process, kinetics, resistances, and the related Li-intercalation phenomena, as well as the composition and structure of each staged product of Li-intercalated bilayer graphene, were systematically investigated. Corroborated by theoretical calculations, the multiply regular experimental results reveal that, the accommodation of Li atoms only takes place at the graphene interlayer, it needs four-time fractal-way Li intercalations to achieve the whole Li-storage process, and there is no essential difference between graphenes and commercial graphite in serving as anodes of LIBs. Besides, reasonable interpretation can be given to several unsolved phenomena about Li-storage in graphite in the literature. As a result, the clarifications of the two perplexing problems for LIBs, namely the real capacity of pure graphene and Li-storage process in graphite, can help establish the first 2D Li-storage model for graphene-based carbon materials, which not only updates the controversial Rüdorff or Daumas–Hérold models proposed for graphite nearly 50 years ago, but also makes this commercial electrode the first material with rather clear Li-intercalation process. Consequently, this work has both practical and theoretical significances to identify the development direction of graphene materials in LIBs or even the whole EES field.

As a result, the innovation points of this chapter include: (i) high-temperature-switched CVD preparation for graphene foam; (ii) the 1st bilayer-graphene foam; (iii) the 1st experimental verification of pure graphene's Li-storage-capacity; and (iv) the 1st 2D model for Li-storage mechanism in graphite.

(3) **Chapter 5**: Inspired by the above macroporous surface-enhanced Li-diffusion mechanism and the explored

Li-storage mechanism in defect-free graphene/graphite anode, a 3DOM monolithic material composed of uniform Ni and carbon nanocrystals (or called graphene quantum dots (GQDs)) has been prepared by developing a simple nickel nitrate-based polymethyl methacrylate (P-MMA)-template preparation. The abundant Li-storage sites and high electron and ion conductivities grant this freestanding C-Ni composite (> 400 μm thick and > 10 mg cm^{-2}) dominative capacitive Li-storage kinetics, high-rate capability, and large reversible capacity. The comprehensively excellent Li-storage performance can fully verify its great potential to replace the commercial graphite anode in present LIBs with limited performance. Consequently, in addition to addressing the great challenge of cost-effective, controlled, and massive production of graphene material, this 3DOM nanocrystalline carbon-metal strategy can greatly facilitate the real applications of graphene materials in EES of high efficiency.

(4) **Chapter 6**: Using common metal nitrates $M(NO_3)_x$ (e.g., M = Zn, Ni, Al, Mn, Fe, Cu, La, Na) as precursor salts, citric acid as chelating agent, and well-assembled P-MMA microspheres as colloidal crystal templates, the universality of the aforementioned co-sacrificial-template preparation strategy has been demonstrated and extensive N-doped GQDs-based materials with well-defined 3DOM morphology have been developed. The results show that the phase composition and graphene quality of the product are greatly dependent on the crystal facet parameter of the as-applied $M(NO_3)_x$ and the calcination temperature associated with its thermal decomposition behavior. Meanwhile, a potential atomic nanocasting mechanism using crystal face of some metal salts as substrate to fabricate graphene carbon at low temperature (250–300 °C in the P-MMA case) has been proved. It is the synergistic effect of this novel mechanism and the hard templating chemistry to account for low-temperature formation of such unique 3DOM GQDs-based materials. These discoveries would help enable graphene-carbon products to be economically and massively available for broad energy-related applications and beyond.

As a result, the innovation points of **Chapters 5** and **6** include: (i) one co-sacrificial-template preparation for 3DOM nanocrystalline carbon-matel materials; (ii) nanocasting mechanism of atomic dimension for low-temperature graphene-carbon synthesis; and (iii) the 1st pure graphene-based electrode for practical application in Li battery.

All in all, to achieve the real performance integration of LIBs and SCs and thus the high-efficiency hybrid EES in a cost-effective way, this thesis has set up a whole set of creating freestanding electrode materials in terms of structure design and fundamental Li-storage mechanism, such as (i) proposing several simple but universal material preparation methods, (ii) developing several unique electrode structures as well as electrode materials of high performance, and (iii) revealing several originally fundamental Li-storage mechanisms. All of these are believed to pave a way for the early accomplishment of this profound goal in commerce and industry.

Keywords: Energy storage; Lithium-ion battery; Supercapacitor; Transition metal oxide; Bilayer graphene; Nanocrystals/quantum dots; 3D nanoporous electrode