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Review

Core-shell materials for advanced batteries

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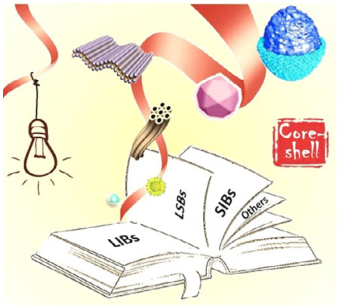
HIGHLIGHTS

- Core-shell structures show a great potential in advanced batteries.
- Core-shell structures with different morphologies have been summarized in detail.
- Core-shell structures with various materials compositions have been discussed.
- The connection between electrodes and electrochemical performances is given.

GRAPHICAL ABSTRACT

Design of core-shell materials for advanced batteries is given in this review.



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ABSTRACT

Nowadays, materials with a core-shell structure have been widely explored for applications in advanced batteries owing to their superb properties. Core-shell structures based on the electrode type, including anodes and cathodes, and the material compositions of the cores and shells have been summarized. In this review, we focus on core-shell materials for applications in advanced batteries such as LIBs, LSBs and SIBs. Firstly, a novel concept of aggregates of spherical core-shell architectures and their aggregates, linear core-shell architectures and their aggregates, sheet-like core-shell architectures and their aggregates and special core-shell architectures and their aggregates are involved. Secondly, the main material compositions of carbon/Si-based, carbon/metal-based, metal-based materials and organic-based composites are introduced along with the synthesis and electrochemical performances of core-shell nanostructured materials. Finally, the emerging challenges and prospects of core-shell materials are briefly discussed.

1. Introduction

Dramatic climate change and the limited availability of fossil fuels have spurred international interest in developing renewable energy technologies [1]. Efficient and environmental-friendly rechargeable batteries such as lithium-ion batteries (LIBs), lithium-sulfur batteries (LSBs) and sodium-ion batteries (SIBs) have been widely explored, which can be ascribed to their operational safety, high capacity and good cycle stability.

Core-shell nanostructures often possess superb chemical and physical properties compared to their single-component counterparts. Hence, they are widely employed in optics, biomedicine, energy conversion, storage, etc [2]. Core-shell structures can be broadly defined as a combination of a core (inner material) and a shell (outer layer material). In general, many considerable efforts on core-shell materials have been reported, such as nanoparticles (NPs) [3–5], spheres [6,7], nanowires [8–14], nanorods [15–18], nanotubes [19], nanobelts [20], nanofibers [21], nanoplates [22], nanosheets [23,24], cubes [25],

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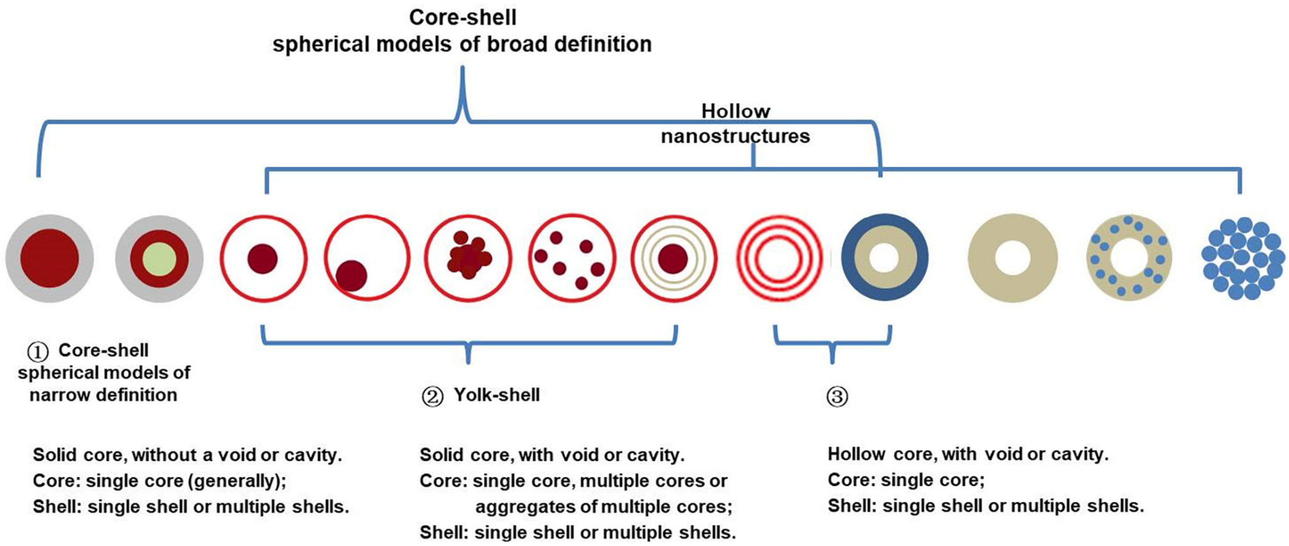

Fig. 1. Schematic illustration of core-shell structures, yolk-shell and hollow structures.

flowers [26], etc. Based on above-mentioned research, the main advantages of core-shell structures are as follows. The core-shell structures can 1) protect the core from the effect of environmental changes outside; 2) intensify or bring new chemical or physical capabilities; 3) limit volume expansion and maintain structural integrity; 4) protect the core from aggregating into large particles; and 5) percolate ions or molecules onto the core selectively [2].

In a broad sense, core-shell structures are defined as a sum of core-shell structures of narrow definition, yolk-shell structures and part of hollow structures (Fig. 1). In a narrow sense, the core-shell structures are composed of a solid inner core coated with one or more layers (shells) of different materials. Yolk-shell structures as a special class of core-shell structures have a distinctive core@void@shell configuration, which are composed of a core within a hollow cavity surrounded by a porous outer shell. Hollow structures are composed of functional shells and inner voids, including yolk-shell structures, structures with hollow core and one or more layers (shells), etc.

Due to a large number of publications on core-shell structures (Fig. 2a), a few reviews focusing on the morphologies of core-shell structures are reported. Tan et al. summarized the development, synthesis methods, characterization techniques, advantages as well as relationship between morphologies and compositions of core-shell structures in the field of epitaxial growth of hybrid nanostructures [27]. Su et al. reviewed the development of core-shell materials for LIBs, and the preparation, electrochemical performances and structural stability of core-shell nanostructured materials for LIBs were expounded by the classification of cathode materials and anode materials [2]. Hou et al. illustrated the design principles along with formation mechanism of core-shell and concentration-gradient cathode materials, then discussed the core-shell materials applied to LIBs according to different electrode shapes [28]. In addition, Yu et al. focused on the current development of hollow structures formed by self-templated methods and their applications in electrochemical energy-related technologies [29]. Feng et al. discussed carbon-based core-shell structures with different composites and provided a perspective for the development of these materials [30]. We conclude two approaches can be employed to improve the electrochemical performances of advanced batteries as presented in Fig. 2b: 1) introduction of conductive materials for improving the conductivity; 2) fabrication of core-shell structures for weakening the mechanical strain of volume change and the barrier for Li^+ transport. The publications of core-shell materials for advanced batteries increased obviously in recent years in order to meet the huge demands of high performance batteries. Thus, it is necessary to summarize the development in this field systematically and promote further investigation.

In this review, we focus on the core-shell structures employed in advanced batteries including LIBs, LSBs, SIBs, etc. Core-shell structures are innovatively classified into four categories and discussed systematically based on spherical core-shell architectures and their aggregates (NPs, spheres, NPs encapsuled in hollow spheres, etc.), linear core-shell architectures and their aggregates (nanowires, nanorods, nanotubes, nanobelts and nanofibers, etc.), sheet-like core-shell architectures and their aggregates (nanoplates, nanosheets, nanowalls, etc.) and special core-shell architectures (nanorings, cubes, etc.) (Fig. 3). Core-shell composites are mainly composed of carbon/Si-based materials, carbon/metal-based materials, metal-based materials and organic-based composites. The relationships between material compositions, structures and electrochemical performances are also presented in detail. Furthermore, the challenges and future perspectives of core-shell materials are concisely given.

2. Core-shell materials for lithium-ion batteries

In traditional LIBs, graphite with a relatively modest theoretical capacity of 372 mA h g^{-1} has often been chosen as the anode [31,32]. Recently, novel core-shell structures for LIB applications have also been widely exploited due to the modest volume expansion and good cyclability, while common nanomaterials show disadvantages of low density, inferior electronic conductivity and the high tendency for side reactions [2,33–35].

2.1. Spherical core-shell architectures and their aggregates as anodes

2.1.1. Nanoparticle

NPs with sizes of less than 100 nm in the x, y and z directions such as carbon/Si-based [33,36–38], carbon/metal-based (carbon@metal [39–41], carbon@metal oxide [42–44]) and metal-based materials [4,45–47] have been developed for LIB applications. In this section, carbon materials refer to amorphous carbon, which is obtained *via* heat treatment. Comparisons of the synthesis methods and electrochemical performance of the spherical core-shell materials for LIBs are shown in Table 1.

2.1.1.1. Carbon/Si-based composites with nanoparticle morphology. Si is one of the most widely employed materials in LIBs as it is inexpensive, easy to obtain and has a high theoretical capacity (4200 mA h g^{-1})