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Searching for electrode materials with high electrochemical reactivity

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Abstract

The most key materials in electrochemical energy storage devices are electrode materials mainly including inorganic cathode and anode materials. However, inorganic electroactive materials often suffer from low conductivity, low capacity, low cycling life. In order to solve these problems, much research work focused on the design of electrode materials and the construction of novel electrode structures in the field of electrochemical energy storage. In this review, we reported the latest development of the design principles of the high-performance electrodes for lithium ion batteries and supercapacitors. We mainly discussed three kinds of examples, blended electrode, integrated electrode and in-situ formed electrode, to display the principles of electrode materials design and electrode construction. The new-developed integrated electrode and in-situ formed electrode maybe the promising candidates for next-generation high-performance energy storage devices. In addition, we conclude this review with personal perspectives on the directions toward which future research in this field might take.

Keywords: Materials design; Electrode construction; Lithium ion battery; Supercapacitor; Integrated electrode

1. Introduction

Electrical energy storage is one of key routes to solve energy challenges that our society is facing, which can be used in transportation and consumer electronics [1,2]. The rechargeable electrochemical energy storage devices mainly include lithium-ion batteries, supercapacitors, sodium-ion batteries, metal-air batteries used in mobile phone, laptop, electric vehicles, etc.[3–5] In battery systems, the charge storage mechanisms include the insertion of secondary species into solid electrodes, alloying and conversion reaction with secondary species (H^+, Li^+, Na^+, K^+) [6]. Electrode materials with alloying and conversion mechanism often exhibit a much higher specific capacity than that of the intercalation electrode materials. Supercapacitors can provide larger power density and longer cycling ability than rechargeable batteries. The charge storage mechanisms of supercapacitors mainly originate from electrical double-layered capacitance (EDLC) at the electrode/electrolyte interface and surface Faradaic redox reactions at the surface of electrode materials (named pseudocapacitance) [7]. To increase the energy density and charge–discharge rate of these devices, the electrode materials should have high electrochemical activity, and can deliver more charge with fast electron and ion transfer/diffusion rate [8]. In order to achieve these goals, the design of active electrode materials with high surface area, short diffusion length, more active sites and high conductivity is more needed. For example, hollow, 1D, 2D, porous, nanosize structural materials have been designed to satisfy above demands [9–11]. However, the pure inorganic electrode materials often suffer from poor cyclability and low capacity, which is mainly caused by their low conductivity and by the large volume change during the charge–discharge cycles [12,13]. In an attempt to solve this problem, powdered electrode materials are often blended with conductive carbon and polymer binders to coat on the metal current collector, which are the standard industrial electrode preparation methods [13,14]. However, the

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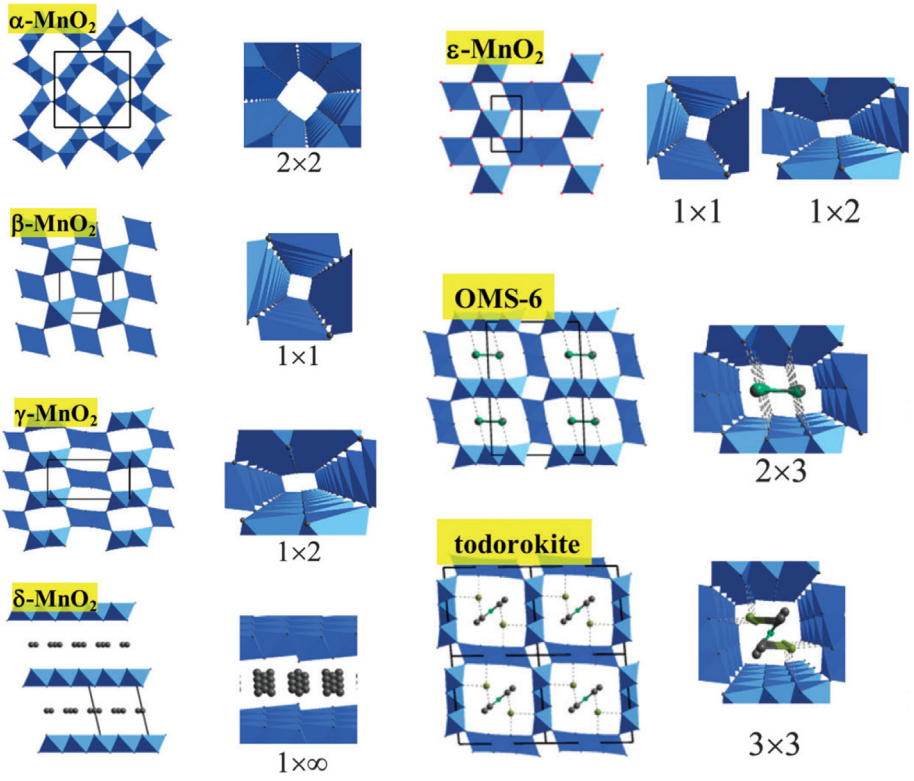

Fig. 1. Crystallographic structures of α-, β-, γ-, δ-, ε-, OMS-6, and todorokite-MnO_2. Reprinted with permission from Ref. [17]. Copyright 2015 Royal Society of Chemistry.

blended electrodes often suffer from phase-separation and the use of many non-active materials.

The design of electrode construction forms is another method to improve the electrochemical performance of these electrochemical energy storage devices. For example, the integrated active materials/current-collector electrode can show two main advantages: (1) the absence of both binder and carbon black is favorable for the direct study of their morphology and phase evolution upon electrochemical cycling (2) the integrated active materials on current collector can effectively enhance the electronic conductivity, and shorten electron transfer length [15,16]. The in-situ formed electrode in practical application environment can display high electrochemical activity because it can form active structured electrode materials compared with materials synthesis in the separate environment.

Although the scalable fabrication and the cost of electrode materials are also the key issues for the scale practical application of energy storage devices, in this review, we mainly focus on the study of the design principle of electrode material and electrode structure in electrochemical energy storage devices. Blended electrode, integrated electrode and in-situ formed electrode are used as three examples to review the recent progress about electrode material design and electrode construction for high-performance electrochemical energy storage devices, mainly including lithium ion batteries and supercapacitors.

2. Blended electrode

The blended electrodes, which are often used in commercial electrochemical energy storage devices, are prepared by blending electroactive materials (i.e., MnO_2, CuO, Fe_2O_3, $LiMn_2O_4$, $LiFeO_2$) with conductive carbon and polymer binders and coating on the current collector [17–20]. The electrochemical performance of the blended electrode is

Table 1
Discharge capacities of MnO_2 samples obtained by hydrothermal only, microwave only and coupled microwave-hydrothermal method in the designed $MnCl_2$–$KMnO_4$ aqueous system as lithium-ion batteries. Reprinted with permission from Ref. [27]. Copyright 2013 American Chemical Society.

Reaction conditions	Composition	Anode discharge capacity/ mAh g^{-1}			Cathode discharge capacity/ mAh g^{-1}		
		1st	2nd	15th	1st	2nd	15th
Hydrothermal only at 160 °C for 1 h	γ	1259.4	354.4	84.5	168.3	137.9	88.7
Microwave only for 10 min	γ	1244.2	256.4	26.9	181.9	175.1	129.2
Microwave-hydrothermal at 160 °C for 10 min	γ(dominant)	1379.7	636.3	286.7	151.1	111.9	77.6
Microwave-hydrothermal at 160 °C for 1 h	β(dominant)	1505.4	446.9	196.0	57.9	39.5	28.3