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Review paper

Recent development in spinel cobaltites for supercapacitor application

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Abstract

Precious metal oxides exhibit impressive characteristics that caught worldwide attention due to their promising capacitive performance, excellent electrochemical stability and low resistance, and these metal oxides have been extensively employed in supercapacitor application. This type of supercapacitors is known as redox supercapacitors or pseudocapacitors which applied faradaic process in storing energy in their systems. Thus, new materials with impressive electrochemical performance are highly demanded. In this aspect, cobaltite system with spinel structure has been the subject of intense research due to its established applications in electrochemistry. Besides, carbonaceous materials like activated carbons, carbon nanotubes, graphites, graphenes and fullerenes utilize electric double-layer capacitance whereby energy is stored by charge separation at an electrode/electrolyte interface. With greater development conducted on metal oxides and carbonaceous materials for supercapacitor application, introduction of hybrid and composite electrodes comprise of these two types of materials have been well received.

Keywords: B. Composites; D. Transition metal oxides; E. Electrodes; Supercapacitors

Contents

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1. Introduction

Depletion of fossil fuels has prompted the alarming situation in search for alternative energy storage and conversion systems. Moreover, the escalating power demand in worldwide nowadays, has ensured a lot of emphasis been placed on the development of devices with high power, high energy as well as robust in withstanding hundreds of thousands of charge/discharge cycles without degrading. Therefore, supercapacitor which is also referred to as 'electrochemical capacitor (EC)', 'double-layer capacitor' or 'ultracapacitor' is considered as an innovative technology due to its uniqueness that fills the gap between batteries and capacitors. This device possesses remarkable characteristics and is efficient and capable to combine the energy properties of batteries and the power discharge characteristics of capacitors.

Electrochemical capacitors can be categorized into two groups namely double-layer capacitors and pseudocapacitors. Electrical energy storage in the former occurs at the phase boundary between an electrode (electronic conductor) and the electrolyte solution (liquid ionic conductor) [1] with no involvement of charge transfer. Moreover, the current generated in this type of capacitor is merely a displacement current due to charge rearrangement or better known as ideally polarized electrode [2]. Fast faradaic redox reactions caused by redox-active species involving metal oxides and conducting polymers are responsible in the potential determining charge transfer reaction that induces the charge storage mechanism of pseudocapacitors [3].

At the present time, worldwide research and development focuses on enhancing the performance and ensuring the cost reduction of electrochemical capacitors. However, the crucial importance is to maintain the power capability, fulfilling the cycle life requirements as well as to increase the capacitance and energy density performance. Various ways have been developed to achieve these criteria such as mixing the metal oxides to become binary or ternary oxides, compositing the metal oxides with carbonaceous materials like activated carbons, fibers, aerogels, xerogels, fullerenes, graphite, carbon nanotubes or graphene, as well as incorporation of the metal oxides with conducting polymers. Composite electrodes involve the combination of two types of materials within the same electrode whereas hybrid electrodes comprise of two different electrodes with different materials such as metal oxides with carbonaceous materials [4]. Adopting nanotechnology in optimizing the microstructure of the electroactive materials in the electrodes has become a notable issue as the charge storage system in pseudocapacitors involve the first few nanometers from the surface [5,6]. Moreover, active material with smaller particle size may contribute to higher capacitive performance due to the larger contact area between the electrode/electrolyte in nanostructured oxides. Greater power delivery and better cycling stability can be achieved as well [7]. Undoubtedly, nanodimensional materials possess high electrical conductivity that makes them as promising energy storage systems in the current situation whereby energy demand is expanding [8]. Therefore, much research effort has been poured in to develop effective methods in the preparation of nanostructured metal oxides and hydroxides in various forms like nanoparticles, nanofibres, nanorods, nanowires, nanotubes, nanosheets and so on. In this context, cobaltite system with spinel structure has gained recognition from worldwide researchers due to its strong establishment in the field of electrochemistry. For example, nickel cobaltite, $NiCo_2O_4$ is one of the promising metal oxides in the family of cobaltite materials which has a spinel structure AB_2O_4, with the nickel ions reside at A-sites and cobalt ions at B-sites. The spinel structure has received much attention by numerous researchers as more than 30 ions with radii ranging from 0.5 to 1.0 Å can be incorporated in the spinel-like phases [9]. The A and B ions occupy one-eighth of the tetrahedral interstices and half of the octahedral interstices in this cubic structure ($a \approx 8$ Å).

It is known that the fundamental and physicochemical properties of cobaltite systems are dependent on the methods of preparation, composition of oxides and temperatures of thermal decomposition. When the size of cobaltite nanoparticles is reduced to the nanometer range, some of their properties can be different compared to samples in micron range. It is believed that by mixing two or more individual oxides together will lead to synergistic effects that may help in the enhancement of the performance of the synthesized materials. This helps to densify the prepared oxides with lower sintering temperature as well as to enhance the grain growth [10]. Researchers have given a considerable attention in synthesizing cobaltite system by exploring the precursors used, preparation methods, processing control and firing temperatures [11–15]. They have developed different preparative methods in synthesizing cobaltite systems not only in nanosized but in micron sized particles as well to be utilized in fuel cells [16,17], electrooxidation of phenol [18], electrocatalysis of oxygen evolution reaction [19–28], thermal decomposition of ammonium perchlorate [29], removal of toluene [30], CO oxidation [31–33], decomposition of nitrous oxide [34], conversion of *p*-nitrophenol to *p*-aminophenol [35], gas sensors [36], batteries [37,38], electrochemical capacitors [39–51] and others. Cobaltites can be synthesized via co-precipitation [52–54], thermal decomposition [54,55–58], sol–gel [55,57,59–62], hydrothermal [63], microwave hydrothermal [64], spin coating [65], chemical bath deposition [45,66], electrochemical deposition [67–72], electrophoretic deposition [73], plasma deposition [74], sputtering [75–77], electrospinning [78,79], spray pyrolysis [54,80], combustion [81], cryochemical [54] and so on.

This paper provides an overview of the background of supercapacitor, present commercial pursuit, current research attempts,