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Review article

Review on α-Fe_2O_3 based negative electrode for high performance supercapacitors

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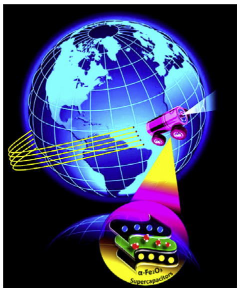
HIGHLIGHTS

- The recent progress of α-Fe_2O_3 as negative electrode in supercapacitor is reviewed.
- Discussed the possible ways to enhance the capacitive performance of α-Fe_2O_3.
- Provided future insight to develop high energy density supercapacitor using α-Fe_2O_3.

GRAPHICAL ABSTRACT



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ABSTRACT

Supercapacitor is an electrochemical energy storage device which has drawn attention of the researchers in recent years due to its high power density and long cycle life. Recently, an enormous effort has been imposed to improve the energy density of supercapacitor and might be attained through asymmetric cell configuration that offer wider potential window. Until now, a significant advancement has been achieved in the fabrication of positive electrodes for asymmetric cell. Nevertheless, the electrochemical performance of negative electrode materials is less explored, especially Hematite (α-Fe_2O_3). The α-Fe_2O_3 has been proved to be a promising negative electrode in supercapacitor application due to its wide operating potential, high redox activity, low cost, abundant availability and eco-friendliness. In this review, we have chosen α-Fe_2O_3 as the negative electrode and discussed its latest research progress with emphasis on various surface engineering synthesis strategies such as, carbon, polymer, metal-metal oxide, and ternary based α-Fe_2O_3 composites for supercapacitor. Besides, the importance of their synergistic effects over the supercapacitive performance in terms of specific capacitance, energy density, power density, cycling life and rate capability are highlighted. Also, an extensive analysis of the literature about its symmetric/asymmetric cell performance is explored.

1. Introduction

Energy crisis due to an increase in the global economy has forced researchers to develop new renewable energy technologies and the energy management strategies. However, these renewable energy systems are reliant on various environmental conditions,

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making them less controllable and predictable. Consequently, they trigger technologies associated with energy storage, which should be economically viable with minimal environmental impact. The miscellaneous energy storage systems include batteries, supercapacitors and fuel cells [1]. Among them, Supercapacitor establishes high power density (5–10 $kWkg^{-1}$), long cycle life (>5,00,000 cycles), long shelf life, high efficiency (95%), wide range of operating temperature (−40 to +70 °C), environmental friendly and safe [2]. It has attracted more attention among researchers and scientists following the patent work produced by General Electric in 1957 [3]. The main role of supercapacitor at that time was to provide necessary power for acceleration in hybrid electric vehicles in combination with batteries or fuel cells. As the supercapacitor technology develops, it plays a main role in complementing batteries or fuel cells and further it was considered as a future energy storage system by US Department of Energy. Nowadays they are widely used in consumer electronics, memory back-up, breaking systems, flash photography and hybrid electric vehicles.

Based on the charge storage mechanism, electrochemical capacitors are classified into two basic types such as an electric double layer capacitor (EDLC) and pseudocapacitor [4]. The energy storage in EDLC's arises due to the charge separation at the electrode-electrolyte interface [5]. Typically, EDLC utilizes materials with porosity, large surface area and high electronic conductivity. Carbon based materials such as activated carbon, carbon nanotubes, carbon aerogels and graphene are the main EDLC materials and the advantages of these materials are they possessed high specific surface area, better electronic conductivity, high chemical stability, abundant, low cost, easy processing and non-toxicity [6].

In Pseudocapacitors, the pseudocapacitance arises from the faradaic redox reactions between the electrolyte and electro-active surface of the electrode material. Metal oxides and conducting polymers are commonly utilized as pseudocapacitor electrodes [7]. Consecutively, the redox processes are highly dependent on the surface area of the electrode. Because of the number of ions involved in the redox reactions is high, the pseudocapacitors delivers a high specific capacitance when compared with EDLCs [8]. The performance of supercapacitor is mainly dependent on the specific capacitance, energy density, power density, cycling stability and rate capability. The energy density (E) and power density (P) of the supercapacitor are given by,

$$E = \frac{1}{2} C_{sp} V^2 \tag{1}$$

$$P = \frac{V^2}{4R_s} \tag{2}$$

where C_{sp} is the specific capacitance, V is the operating voltage window and R_s is the equivalent series resistance (ESR) [9]. The terms V, C and R_s are important factors determining the supercapacitor's performance. The power density could be enhanced by minimizing R_s. The ESR could be reduced by utilizing aqueous electrolytes and they are highly attractive due to its low ESR, cost-effective, secure and eco-friendliness. The electrolytes engaged in supercapacitor should mainly possess a wide potential range, high ionic conductivity, high stability, non-toxicity, low solvated ionic radius and low cost. Also, the aqueous electrolytes provide a higher ionic concentration and low resistance compared with organic electrolyte [10].

Subsequently, to increase the energy density (E), it is enviable to enhance the cell voltage (V) and the specific capacitance (C_{sp}) of the active material. The specific capacitance (C_{sp}) of the individual electrode is characterized using three electrode system consisting of working, reference and counter electrodes within the electrolyte. The electrochemical performance is analyzed using a cyclic voltammetry (CV), galvanostatic charge discharge (GCD) and the electrochemical impedance spectroscopic (EIS) analysis. In CV, the current is plotted against the potential of the working electrode. The area under the CV curve gives the specific capacitance (C_{sp}) of the material. The CV analysis is performed at various scan rates, where the C_{sp} is higher at lower scan rates while it decreases upon increasing scan rates. Aforementioned is a normal behavior observed in supercapacitor where the diffusion of ions is higher at lower scan rates and it declines at higher scan rates. The contribution of the inner and the outer electrode surface area to the charge storage mechanism of the material is found using the Trasatti plot. The total charge stored in the electrode material has its contribution from both inner and outer surfaces as given as $q^*_{(Total)} = q^*_{(Inner)} + q^*_{(Outer)}$ [11].

In GCD, the capacitance can be calculated from the slope of the GCD curve. While in EIS measurement, the impedance data is taken by applying small amplitude of alternative voltage over a wide range of frequencies. The Nyquist plot of EIS gives the charge transfer resistance which can be calculated from the diameter of the semicircle. In the impedance spectra; (i) high frequency ($>10^4$ Hz) region provides the information about the conductivity of both active materials and the electrolyte, (ii) high-to-medium frequency (*i.e.* 10^4 Hz–1 Hz) is due to the pseudo charge transfer resistance and (iii) low frequency ranges (<1 Hz) is the characteristic feature of pure capacitive behavior [7].

Nowadays, the commercial supercapacitors utilizes the carbon as electrode material (EDLC) because of its excellent cycling stability, economical, high cycle life time and corrosion resistance. However, the major drawback of carbon supercapacitor is the limited specific capacitance and a low energy density of 3–5 Wh Kg^{-1} which is much lower than commercial Li-ion batteries (10–250 Wh Kg^{-1}). This limits the usage of a supercapacitor in high density required applications such as electric vehicles, solar power plants, etc. Furthermore, to improve the energy density, transition metal oxides are considered as the best candidate because of their availability of the variable oxidation states for the charge storage mechanisms. The metal oxides engaged in the supercapacitor should meet following criteria such as high conductivity, possess two or more oxidation state, and their protons activity during the redox reactions without any phase changes [12].

Initially, hydrous ruthenium oxide ($RuO_2.xH_2O$) was studied as the pseudocapacitor electrode due to its high theoretical capacitance (2000 F g^{-1}), good chemical stability, high thermal stability, possess a wide potential window of 1.2 V and the high metallic electrical conductivity (10^5 S cm^{-1} at ambient temperature) [13]. In this regard, numerous works have been reported using RuO_2 as an electrode material in supercapacitor by various techniques such as, sol-gel [14], self assembly [15] and template synthesis [16]. Besides, it was prepared in various structures by controlling crystallinity and water content to attain maximum C_{sp}. Although it attains a maximum C_{sp} of 1300 F g^{-1} for nanotubular arrayed hydrous ruthenium oxides [17], the commercial applicability of RuO_2 was limited because of its high cost and toxicity to the environment. In general, the redox reaction of RuO_2 in acidic electrolyte involves the change of oxidation state of ruthenium from Ru (II) to Ru (IV) given by;

$$RuO_2 + xH^+ + xe^- \leftrightarrow RuO_{2-x}(OH)_x \tag{3}$$

Later, to replace the costlier RuO_2, a cost effective layered crystalline structured manganese oxide (MnO_2) with multiple oxidation states was explored as a supercapacitor electrode. MnO_2 is attractive due to its low cost, eco-friendliness, less toxicity and a high theoretical capacitance (1100–1300 F g^{-1}) [18]. The charge