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Review

Aligned carbon nanostructures based 3D electrodes for energy storage

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ABSTRACT

Electrochemical energy storage systems with high specific energy and power as well as long cyclic stability attract increasing attention in new energy technologies. The principles for rational design of electrodes are discussed to reduce the activation, concentration, and resistance overpotentials and improve the active material efficiency in order to simultaneously achieve high specific energy and power. Three dimensional (3D) nanocomposites are currently considered as promising electrode materials due to their large surface area, reduced electronic and ionic diffusion distances, and synergistic effects. This paper reviews the most recent progress on the synthesis and application of 3D thin film nanoelectrode arrays based on aligned carbon nanotubes (ACNTs) directly grown on metal foils for energy storages and special attentions are paid on our own representative works. These novel 3D nanoelectrode arrays on metal foil exhibit improved electrochemical performances in terms of specific energy, specific power and cyclic stability due to their unique structures. In this active materials coated ACNTs over conductive substrate structures, each component is tailored to address a different demand. The electrochemical active material is used to store energy, while the ACNTs are employed to provide a large surface area to support the active material and nanocable arrays to facilitate the electron transport. The thin film of active materials can not only reduce ion transport resistance by shortening the diffusion length but also make the film elastic enough to tolerate significant volume changes during charge and discharge cycles. The conductive substrate is used as the current collector and the direct contact of the ACNT arrays with the substrate reduces significantly the contact resistance. The principles obtained from ACNT based electrodes are extended to aligned graphene based electrodes. Similar improvements have been achieved which confirms the reliability of the principles obtained. In addition, we also discuss and view the ongoing trends in development of aligned carbon nanostructures based electrodes for energy storage.

1. Introduction

The development of highly efficient, low cost, and environmentally benign electrochemical energy storage systems (ESS) is critical for addressing the urgent energy and environmental issues, and also plays a key role for the efficient utilization of renewable energy [1–7]. Supercapacitors (SCs) [8–11] and lithium ion batteries (LIBs) [12–17] have attracted considerable interest as ESS for applications in portable electronic devices and are being considered for electric vehicles and smart grid application. However, in order to meet the requirements of future applications, the next generations ESS are expected with higher specific energy and power, better cyclic stability, more safety, and lower cost [18]. Compared with LIBs, SCs can deliver a higher specific power, and offer a much better cyclic stability. However, LIBs exhibit much higher specific energy relative to SCs. Therefore, a major scientific challenge is to either significantly increase the specific energy of SCs or dramatically improve the specific power and cyclic stability of LIBs [19–21].

SCs are characterized by their specific power and cyclic stability resulted from the energy storage mechanism [19]. They can be categorized as electric double-layer capacitors and redox pseudocapacitors according to the energy storage mechanism [8]. The former as shown in Fig. 1 is based on physical charge separation at the electrode/electrolyte interface, while the latter utilizes fast and reversible redox reactions occurring at the electrode surface or subsurface. SCs show a higher specific power and better cyclic stability owing to the fast and reversible charge separation and surface redox reaction. However, they exhibit relatively lower specific energy compared with LIBs due to the surface energy storage mechanism. Previous attempts to increase the specific energy of SCs include the utilization of electrode materials with enhanced specific capacitances [23,24] and electrolyte with wider operation voltage window [25–27]. Therefore, carbon nanomaterials with large specific surface area [23], nanostructured transition metal oxides [28–31] and conducting polymers [32,33] with enhanced pseudocapacitance have attracted widespread interest for high specific energy SCs. The utilization of electrolyte with wide operation voltage window, such as

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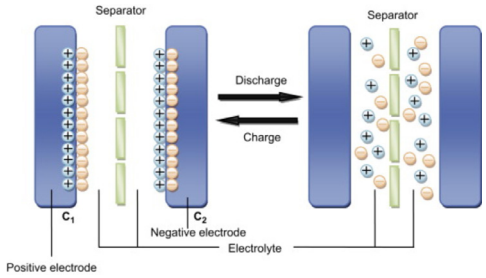

Fig. 1. Charged and discharged states of an electric double-layer capacitor [22].

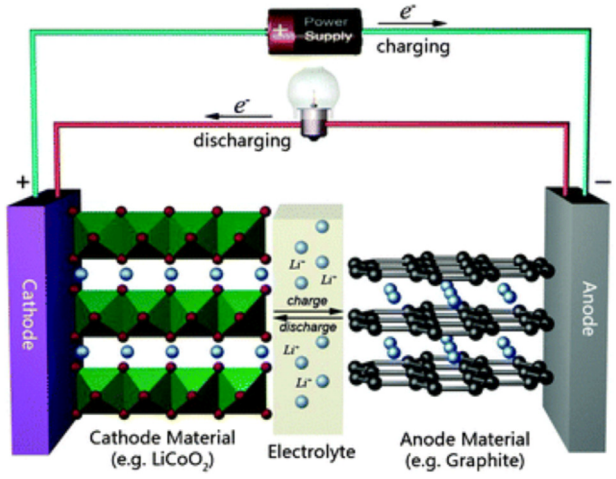

Fig. 2. Typical commercial LIBs showing the charge/discharge intercalation mechanism [6].

organic electrolyte and ionic liquid, is another route to increase the specific energy of SCs [25,26,34].

Typical LIBs comprise a negative electrode, a polymer separator permeated with non-aqueous liquid electrolyte, and a positive electrode (Fig. 2). Lithium ions are extracted from anode, transferred across the non-aqueous lithium ion containing organic electrolyte and intercalated into the cathode which is accompanying by the electrons transport from anode to cathode through the external circuit during discharge, and vice versa during charge. LIBs store electrochemical energy through Faradaic reactions in the bulk of the active material. This bulk energy storage mechanism provides a much higher specific energy as compared with SCs. However, storing lithium ions in the bulk of a material implies that lithium ions must transfer in the bulk electrode materials during charge and discharge. Because of the low solid state diffusion rates, this process is generally a rate limited step. As a result, LIBs deliver a very low specific power, requiring typically hours for charge and discharge. Additionally, due to a vast amount of side reactions occurring during overcharge or overdischarge which cause electrolyte decomposition, passive film formation, active material dissolution, and also other phenomena, LIBs suffer from capacity fading with cycling which results in poor cyclic stability [35].

The demand of safe ESS with large specific energy and high specific power is continuously increasing. Exploring full potential of present materials and searching for new electrode materials and electrolytes have been carried out around the world to improve the performance of present ESS [15]. One strategy to explore the full potential of present electrode materials is the fabrication of active materials into 3D nanostructures. This route can enlarge the specific energy of SCs by increasing specific surface area and improve the specific power of LIBs by reducing the lithium ion and electron diffusion distances. This review focuses on the applications of aligned carbon nanotubes (ACNTs) and aligned graphene based 3D electrodes for SCs and LIBs. We start with a discussion of the rational design of ESS, in terms of higher specific energy and specific power, and better cyclic stability, based on thermodynamic and kinetic analysis of elementary steps involved in the energy storage process (Section 2). The synthesis methods of ACNTs on metal foils and coating of thin layer of active materials such as conducting polymers and metal oxides, and their applications in energy storage are reviewed in Sections 3 and 4, respectively. Additionally, the latest progresses on aligned graphene for ESS have been summarized in Section 5. Finally, the ongoing trends of aligned carbon nanostructures based 3D electrodes for energy storages are discussed (Section 6).

2. Rational design

ESS involves a series of complex physical and chemical processes such as mass, ionic and electron transport, heat transfer as well as reactions in a multiphase system. Existing electrodes needs to be significantly improved in terms of such processes in order to meet future requirement. In this section, we will provide fundamental principles to achieve high specific energy and power from a chemical reaction engineering point view, by means of thermodynamic and kinetic analyses of the physical and chemical processes involved. We start to summarize fundaments of electrochemical processes in energy storage, although they can be found in many textbooks, to provide fundamental principles of rational design of electrodes.

2.1. Specific energy

2.1.1. Theoretical specific energy

The theoretical specific energy (E_{tse}) of SCs can be calculated according to the following equation:

$$E_{tse} = \frac{1}{2} C \Delta U^2 \quad (1)$$

where, C and ΔU are specific capacitance and maximum cell voltage, respectively [52]. Accordingly, the specific energy of SCs depends on the specific capacitance and the maximum operation voltage. The maximum operation voltage is limited by the stability of the electrolyte, which is beneath 1.23 V for aqueous electrolyte due to the hydrogen or oxygen evolution. The operation voltage window can be widened by employing organic electrolyte and ionic liquid up to around 3 and 4 V, respectively [26,34].

For SCs storing energy based on charge separation, the specific capacitance is measured as [43,53]

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} \quad (2)$$

where, ε_r, ε_0, A, and d are electrolyte dielectric constant, vacuum dielectric constant, specific surface area of the electrode materials, and the effective thickness of the electric double-layer, respectively. Therefore, a general strategy to increase the specific capacitance of an electrode material is to increase its effective specific surface area. Hence, many researches have been focused on the investigation of different high surface area carbon based materials for SCs, such as carbon nanotubes, graphene, active carbon and their composites [26,34,54].

Electric double-layer capacitance is present in any electrochemical cell. In the case of an electrode material also exhibiting a pseudocapacitance, the pseudocapacitance is coupled in a parallel way with electric double-layer capacitance [8]. Therefore, the theoretical specific capacitance of electrode material participating redox reaction can be estimated by the contributions from both the electric double-layer and the faradic redox reaction according to Equation (3) [33],

$$C = \frac{\varepsilon_r \varepsilon_0 A}{d} + \frac{nF}{M \Delta U} \quad (3)$$