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Short review

The preparation and application of mesoporous materials for energy storage

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ABSTRACT

Designing new energy storage system is necessary for renewable energy development. With the large surface area and appropriate pore structure for good electrolyte wetting and rapid ionic motion, electric double layer capacitors (EDLC), as an ultracapacitor, have the potential to meet this challenge. As the constructing materials for EDLC, the prepration of ordered mesoporous materials, including silica-based mesoporous materials, carbon nitride, ordered mesoporous carbons as well as metal oxides, are summarized. Further researches on pore size control and morphology control of mesoporous materials have also been reviewed. These mesoporous materials, with high surface area, narrow distribution of pore size, good corrosion resistance, high stability, and tunable pore structure and easy surface modification, are widely used as electrocatalyst support and electrode in EDLC. The large surface area and small pore diameter can improve the specific capacitance. The tunable pore structure and surface functionalization are beneficial for capacitance improvement.

1. Introduction

The rapid development of renewable energy such as solar and wind raise the awareness of the need for electric storage system for continuous energy supply. And energy storage has become one of the great challenges in the twenty-first century. Therefore, it is essential to find a low-cost and environmentally-friendly energy conversion and storage system to address this problem [1]. The performance of the storage system strongly depends on the properties of the materials included in the system. Up to date, the most common electric energy storage systems are batteries and electrochemical capacitors.

Both batteries and electrochemical capacitors are widely used in portable(digital) electronic devices, supports for fuel cells, uninterruptible power supplies, memory protection of computer electronics and cellular devices [2,3]. Batteries with high energy density generally suffer from limited power density (charge/discharge rate). What is worse, continued high rate cycling deleteriously affects both battery performance and lifetime. To extend the lifetime, a lower rate is necessary, which requires battery-based energy storage system has to be oversized to accommodate peak. Additionally, low temperature environments will lead to the loss of energy storage capacity. Battery lifetime is limited to a few years at best and is further decreased with continuous cycling and harsh environmental conditions. So regular maintenance and replacement are required, especially in winter or under stormy weather conditions.

Different from a battery, ultracapacitors, also known as electrochemical capacitors, offer a promising alternative approach to meeting the increasing power demands of energy storage systems from portable (digital) equipment to electric vehicles. Ultracapacitors are similar to batteries in design and manufacture (two electrodes, separator and electrolyte), but the unique mechanism makes ultracapacitors available for the application requiring high power and long cycle life (>100 times of battery life) [4,5]. Another advantage of ultracapacitors is that they can store a higher amount of energy within a shorter time. Threfore, systems employing ultracapacitors are smaller and lighter and do not need to be oversized to accommodate high power cycling. Furthermore, the wide operating temperature range (−40 °C to +65 °C), long lifetime and outstanding cycling stability ensure a maintenance-free operation for the ultracapacitor-based system. Additionally, ultracapacitors are known to be a green technology due to their high efficiency and the materials used during manufacture. Fig. 1

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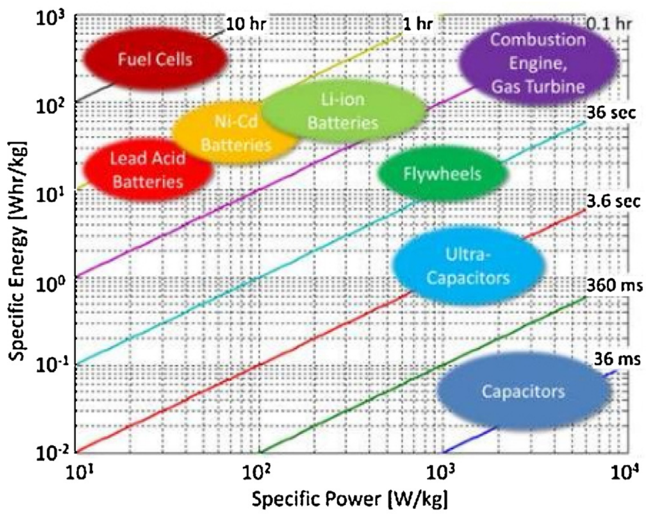

Fig. 1. Ragone plot of various energy storage technologies.

summarizes the different performance of current energy storage techniques [6].

In terms of their energy storage mechanism, the electrochemical ultracapacitors are summarized into two categories: electric double layer capacitors (EDLCs) and pseudocapacitors [1]. Their distinction is illustrated in Fig. 2. For EDLCs, a thin double-layer is placed at the interface between eltrolyte and the electrode, which is used to store charge. Their capacitance (C) is dependent upon the surface area of the electrode [7]:

$$C = \frac{\varepsilon S}{d}$$

where ε is the relative permittivity, S is the surface area, and d is the thickness of the double-layer. The value of d, dependent on electrolyte ion and solvent dimensions, is usually quite small. Thus the capacitance of EDLCs is much higher than those of traditional dielectric capacitors [8]. For the ideal capacitor, the rectangular ("mirror") cyclic voltammogram (CV) will be observed because of the independent relationship between current and. But the real situation is that the adsorption of ions on the surface shows mostly rectangular CVs in spite of some potential dependence can occur

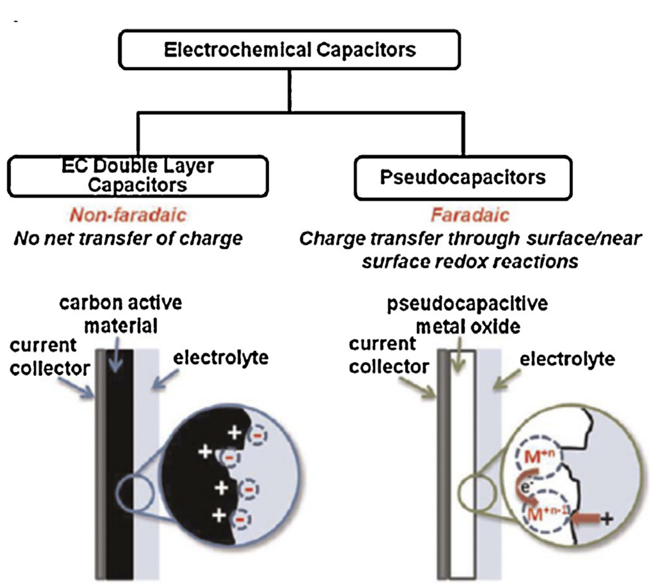

Fig. 2. Mechanisms for capacitive charge storage at an electrode surface.

through overscreening and crowding at the double-layer [9]. The pseudocapacitors (redox ultracapacitors) usually have surface or near-surface redox reactions in the faradaic. Pseudocapacitance often exhibits a dependence on potential because it involves redox reactions,

Compared with batteries, whose cycle life is limited because of the repeated contraction and expansion of the electrode in the cycling process, EDLC's lifetime is infinite in principle for they are based on electrostatic surface charge accumulation. The first patent describing a double-layer capacitor was published in 1957 [5]. EDLC utilize electric double layers formed at the interface of the electrode/electrolyte, where electric charges are accumulated on the electrode surface and ions of opposite charge are arranged on the electrolyte side of the interface [10]. EDLC electrode materials are expected to have a large surface area for effective charge accumulation and an appropriate pore structure for good electrolyte wetting and rapid ionic motion.

Porous carbon materials have received a great deal of attention and have wide applications [11–15]. They were used in areas such as gas separation, water purification, catalyst supports, and electrodes and fuel cells. According to the International Union of Pure and Applied Chemistry (IUPAC), porous carbon materials, based on their pore diameters, can be classified into three types: microporous materials with a dimension less than 2 nm, mesoporous materials with a dimension between 2 nm and 50 nm, and macroporous materials with a dimension larger than 50 nm. In recent years, many researchers have conducted studies by using mesoporous carbon as ultracapacitor electrode material. These capacitors are built to make use of the unique chemical and physical properties of mesoporous materials such high conductivity, large surface-area, excellent corrosion resistance, high temperature stability, controlled pore structure, processability and compatibility in composite materials and relatively low cost [16–20]. Generally, the first two of these properties are critical to the construction of ultracapacitors.

Mesoporous materials are of interest in electrochemistry for several reasons. First, their highly porous and regularly ordered 3D structure should ensure good accessibility and fast mass transport to the active centers. This might be useful to enhance the sensitivity in preconcentration electroanalysis (voltammetric detection subsequent to open-circuit accumulation). Moreover, the possibility of immobilizing a great variety of organo-functional groups opens the door to improvements in selectivity of the recognition event. Secondly, the materials bearing redox-active moieties can be promising to induce intra-silica electron transfer chains or to act as electron shuttles or mediators, with promising applications in electrocatalysis. Third, the possibility for nano-bioencapsulation (e.g., enzyme immobilization58–61) in such functionalized and mesostructured reactors could result in the development of integrated systems combining molecular recognition, catalysis and signal transduction, with applications in the field of electrochemical biosensors.

2. Mesoporous materials

In the early 1990s, Japanese scientists and Mobil researchers separately reported the synthesis of mesostructured silicates [21]. The formation of mesoporous silicate molecular sieves with crystal templates is undoubtedly one of the most exciting discoveries in the field of materials synthesis during the last few decades. The synthesis of these ordered mesoporous materials provides not only a new family of materials that possess large uniform pore sizes (10 nm), highly ordered nanochannels, large surface areas and attractive liquid-crystal structures but also an idea of designing periodic arrangements of inorganic–organic composite nano-arrays. Tremendous efforts were made in the area of the syntheses