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Short review

Colloidal supercapacitor electrode materials

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ABSTRACT

Key issues for supercapacitor electrode materials are their low energy density and slow ion/electron diffusion/transfer kinetics. The formations of nanostructured materials and composite materials with blending/coating conductive additives have been developed to solve above problems. For more efficiently using electroactive metal cations in pseudocapacitance electrode materials, one kind of colloidal supercapacitor electrode materials was introduced to get both high energy and power densities. Colloidal supercapacitor electrode materials have overwhelming advantages, i.e. quasi-ionic state cations, short ion diffusion length and high specific surface area, which is a tradeoff between confined active cations and facile cation diffusion. Multiple-electron transferred Faradaic reactions can occur within the whole colloid, leading to high specific capacitance. The development of colloidal supercapacitor electrode materials can promote the advance of supercapacitors and make their energy densities larger than 100 Wh/kg or more, resulting in replacing batteries.

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1. Introduction

Nowadays, supercapacitors can provide high power density (10 kW/kg), but they do not have sufficient high energy density to compete with batteries (150–200 Wh/kg) [1–3]. The energy density of the state-of-the-art lithium ion battery can reach 330 Wh/kg [4,5]. The energy density of supercapacitors can reach 10–20 Wh/kg for carbon-based symmetry devices [6,7]. The state-of-the-art carbon-based symmetric supercapacitors have the energy density of 63.0 Wh/kg with relative to the active materials mass (41.0 Wh/kg with relative to the total mass of devices) at the power density of 44 kW/kg [8]. Therefore, the key challenge for supercapacitors is still to increase their energy densities. The energy density (E) of supercapacitors can be described as:

$$E = V \int_{V1}^{V2} C dV \tag{1}$$

where C is specific capacitance (F/g), V is working potential (V). It should be noted that pseudocapacitance electrode materials have both classic charge storage (double layer capacitances) as well as electrochemical (or redox) charge storage, where C is dependent on V. Therefore, the energy density of supercapacitors is the function of specific capacitance and potential. The specific capacitance can be determined by positive and negative electrode materials. The specific capacitances of electrode materials can be adjusted by various materials design methods, i.e. size control, structure control, morphology control [9–11].

For electrode materials with charge storage mechanism of electrical double-layer capacitance (EDLC), their specific capacitances are mainly determined by their surface area. Although activated carbon materials have very large surface area of $\sim$2180–3100 m^2/g, their specific capacitances is still low, $\sim$250 F/g [12,13]. Graphene have a large theoretical capacitance of $\sim$550 F/g due to its large conductivity and high specific surface area of $\sim$2630 m^2/g [14,15]. Pseudocapacitive electrode materials have very large theoretical capacitance, i.e. 1380 F/g for MnO$_2$ (0.9 V) [16], 2584 F/g for NiO (0.5 V) [17], 3560 F/g for Co$_3$O$_4$ (0.45 V) [18]. Theoretical capacitance of pseudocapacitive materials can be written as:

$$C = \frac{nF}{3.6M} \tag{2}$$

where n is the number of the transferred electron, F is Faradaic constant, M is molar molecule weight. Therefore, electrode materials with the occurrence of multiple-electron transfer reaction can increase the specific capacitance [19]. Metal oxides often show low electronic conductivity and slow ion diffusion, leading to slow response to redox reactions. Ion diffusion time is the function of particle size (L) and diffusion coefficient (D^*).
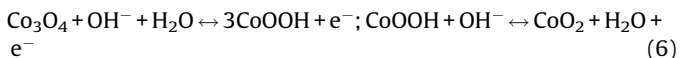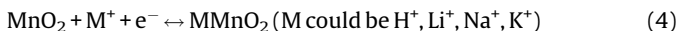
$$\tau = \frac{L^2}{4\pi D^*} \tag{3}$$

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Many researchers have synthesized nanostructured electrode materials and grew composite electrode materials with blending/coating conductive additives to shorten ion diffusion length and increase electronic conductivity [20,21]. Because the Faradaic reaction only occurs at or near the surface of materials, materials changed from micrometer scale to nanostructure indeed increase their specific capacitances (Fig. 1). It is reported that nanomaterials with the size less than 10 nm can enable pseudocapacitive materials to overcome diffusion limitations for surface Faradaic redox reactions [22,23]. However, these nanomaterials are difficult to synthesize and still have dead zone in the interior of materials. One kind of novel colloidal supercapacitor electrode materials can efficiently utilize electroactive metal cations and show high capacitance. In this review, we introduced the advantages and progress of colloidal supercapacitor electrode materials.

2. Advantages of colloidal supercapacitor electrode materials

The construction of nanostructured materials can indeed increase the electrochemical performance of the present electrode materials [23,24]. However, fully releasing the energy storage potential of pseudocapacitance electrode materials needs more novel ideas. Faradaic redox reactions of MnO_2, NiO, and Co_3O_4 electrode materials are shown as following:

$$MnO_2 + M^+ + e^- \leftrightarrow MMnO_2 \, (M \, could \, be \, H^+, Li^+, Na^+, K^+) \quad (4)$$

$$NiO + OH^- \leftrightarrow NiOOH + e^- \quad (5)$$

$$Co_3O_4 + OH^- + H_2O \leftrightarrow 3CoOOH + e^-; CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (6)$$

They mainly include redox reactions between metal cations with different oxidation states, i.e. $Mn^{4+} \leftrightarrow Mn^{3+}$, $Ni^{3+} \leftrightarrow Ni^{2+}$, $Co^{4+} \leftrightarrow Co^{3+}$, $Co^{3+} \leftrightarrow Co^{2+}$ [25–28]. According to Eq. (2), specific capacitance is dependent on the electron transfer number of metal cations. Because pseudocapacitance reaction occurs at or near the surface of electrode materials, charge storage capacitances of traditional materials are difficult to approach their theoretical capacitance values. Only when the size of electrode materials can reduce to ion size scale, the kinetic processes of redox reactions, ion diffusions and electron transfer are more facile compared with nanosized solid materials with long-range ordered crystallized structures [29,30]. Novel electrode materials with high specific capacitance need to satisfy following requirements: short ion diffusion length, free metal cations within confined space, inhibiting the dissolution of free cations into electrolyte. Fortunately, colloidal system can fulfill above requirements, which possess the characteristics of quasi-ionic state, short ion diffusion length and high specific surface area (Fig. 2) [31,32]. The principle of colloidal ionic supercapacitor systems has been proven in multiple-valence metal cations of Cu^{2+} [33], Fe^{3+} [34,35], Co^{2+} [28], Ni^{2+} [36], Sn^{4+} [37], Yb^{3+} [38] and Er^{3+} [39] ionic systems. In addition, binary A_xB_{1-x} ionic pseudocapacitor systems involving Mn, Fe, Co, and Ni have also been developed [40]. All of these colloidal ionic electrode materials can show high specific capacitances approaching their theoretical values.

3. Examples of colloidal supercapacitor electrode materials

In this section, two examples of Mn- and Ce-based colloidal ionic electrode materials were provided to prove the overwhelming superiority (high electroactivity) of colloidal ionc electrode materials compared with the traditional electrode materials of MnO_2 and CeO_2.
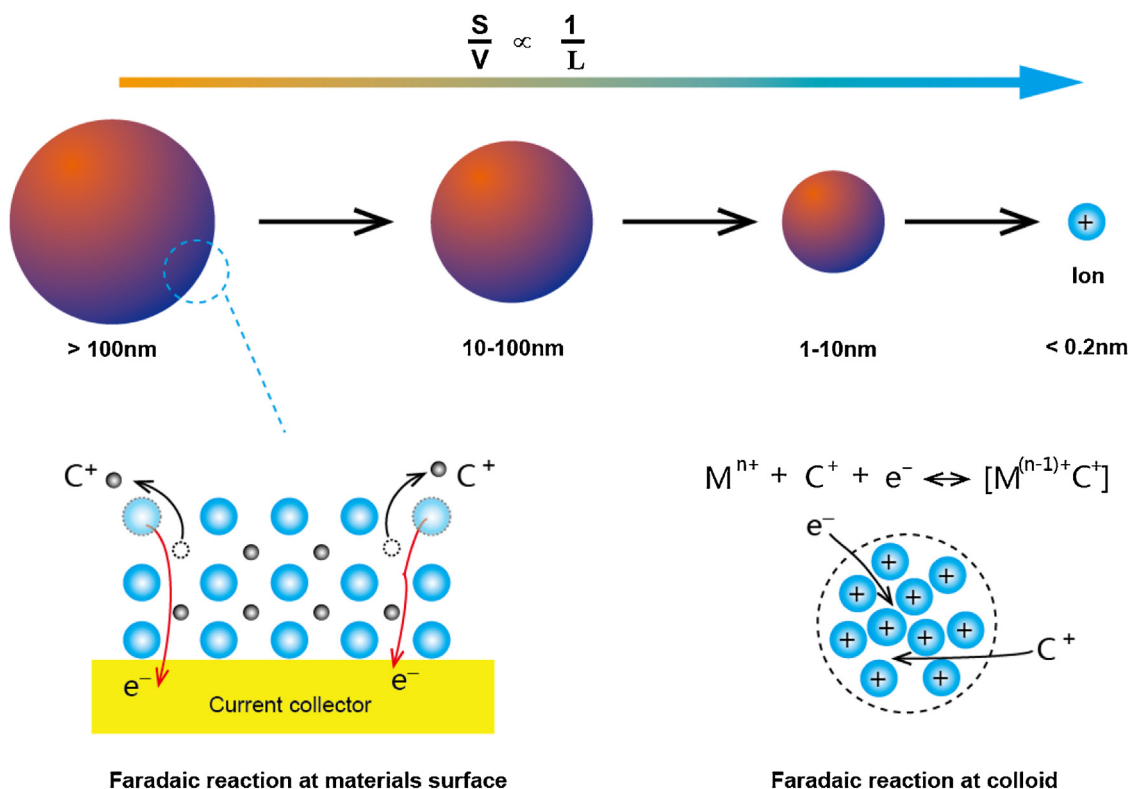

Fig. 1. Change of specific surface area with the reduction of particles size, Faradaic redox reactions at or near the surface of nanostructured materials and within whole colloidal ion particles used in supercapacitors. C represents alkaline metal cations (Li$^+$, Na$^+$, K$^+$). S is surface area of particle, V is volume of particle, L is the particle size (or diffusion length).