

Perspective

An Era of Powerful Supercapacitors: Materials Science and Engineering toward the System-Level Design of Ionic Supercapacitor Electrode and Electrolyte

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Electrochemical energy storage technologies are the most promising for solving the demand for energy and the concerns of environmental pollution, but to meet the needs of different applications in terms of energy, power, cycle life, safety, and cost, different systems, such as lithium ion batteries, redox flow batteries, and supercapacitors, need be considered [1]. Electrochemical capacitors, also called supercapacitors, are highly desirable energy storage devices because they can deliver high levels of electrical power and offer long operating lifetime, which have had an important role in complementing or replacing battery [2,3]. Supercapacitors have been developed for more than fifty years. First patent of supercapacitors date back to 1957 where a capacitor based on high surface area carbon was described by Becker [4]. Later in 1969 first attempts to market such devices were undertaken by SOHIO [5]. Only in the nineties electrochemical capacitors became famous in the context of hybrid electric vehicles [6]. Today many companies in electrochemical capacitors are developing [7]. However, the main bottleneck that hinders the practical application of supercapacitors is their low energy density. The charge is confined to the material surface, so the energy density of electrochemical double layer capacitors is less than batteries [8]. In the 1970s, Conway et al. recognized that reversible redox reaction can occur at or near the surface of an appropriate electrode material [3], which can result in much greater charge storage. Due to the progress of nanotechnology, nanostructured electrode materials have been developed to enhance the energy density of supercapacitors [9]. However, the application of nanostructured materials certainly does not automatically lead to the enhancement in energy density.

System-level planning of theoretical and experimental efforts is increasingly important for the development of modern materials science [10]. Nowhere has this become more obvious than in the area of energy storage and conversion, where it seems clear there is a trend towards an emerging new field of integrated systems materials engineering [10]. Based on the system- and ion-level design, for the first time, we reported the proof-of-principle of a new concept

of ionic supercapacitor systems [11,12]. These systems include the transition metal salt electrode and an alkaline electrolyte operating at room temperature, which can show ultrahigh specific capacitance and energy density [13-16]. For example, CuCl_2 electrodes deliver a very high specific pseudocapacitance ~ 5442 F/g, which exceeds the one-electron transfer theoretical capacitance of ~ 5061 F/g [12]. YbCl_3 pseudocapacitor can show the specific capacitance of 2210 F/g, which also exceeds one-electron redox theoretical capacitance of ~ 1358 F/g [15]. These new alkaline ionic supercapacitor systems are launching an era of powerful supercapacitors by the system-level design of ionic supercapacitor electrode and electrolyte.

The capacitive behavior of inorganic pseudocapacitor is associated primarily with the redox reactions of the cations or changes in oxidation states of the cations in electrode materials during operation [3]. In order to increase the energy density of pseudocapacitors, redox-active metal cations in these electrode materials must be fully utilized in Faradaic reaction. Figure 1 shows the charge storage mechanisms of new ionic pseudocapacitors systems and traditional pseudocapacitors. In ionic pseudocapacitor system, highly active ionic state colloids were designed as electrode material, which can facilitate cooperate with electrolyte. Thus, the Faradaic redox reaction of Cu^{2+} , Co^{2+} , Ce^{3+} , Yb^{3+} , Sn^{4+} cations can occur in the whole colloids; thus high cations utilization can lead to high energy density. In addition, this specific structure can shorten the transport paths for ions and electrons, which can maintain high power density. The efficient manipulation of active cations is a powerful way for developing high performance pseudocapacitors.

In our designed pseudocapacitor system, commercial metal salts were mixed with carbon black and poly(vinylidene fluoride) (PVDF) to form slurry, which were dispersed on a Ni foam current collector as working electrode (Figure 2a). When measured in 2 M KOH electrolyte, electroactive hydroxide colloids were formed by electric field assisted chemical coprecipitation (Figure 2b). At the same time, pseudocapacitive Faradaic reaction was occurred at the same electrode. After undergoing the in-situ crystallization process, subsequently integrated into practical electrode structures can simultaneously occur. The specific electrode configuration with the highly reactive colloids adsorbed at the surface of carbon spheres was formed via the chemical/electrochemical coprecipitation and Faradaic reactions. The specific configuration can shorten diffusion path of ion/electron and can enhance electrochemical utilization of active metal cations, thus high specific capacitance can be obtained. Other significant advantages of water-soluble salts pseudocapacitors systems are: 1) water-soluble inorganic salts are promising candidates to utilize active cations, 2) the use of commercial inorganic salt as pseudocapacitor does not need complex synthesis procedures.

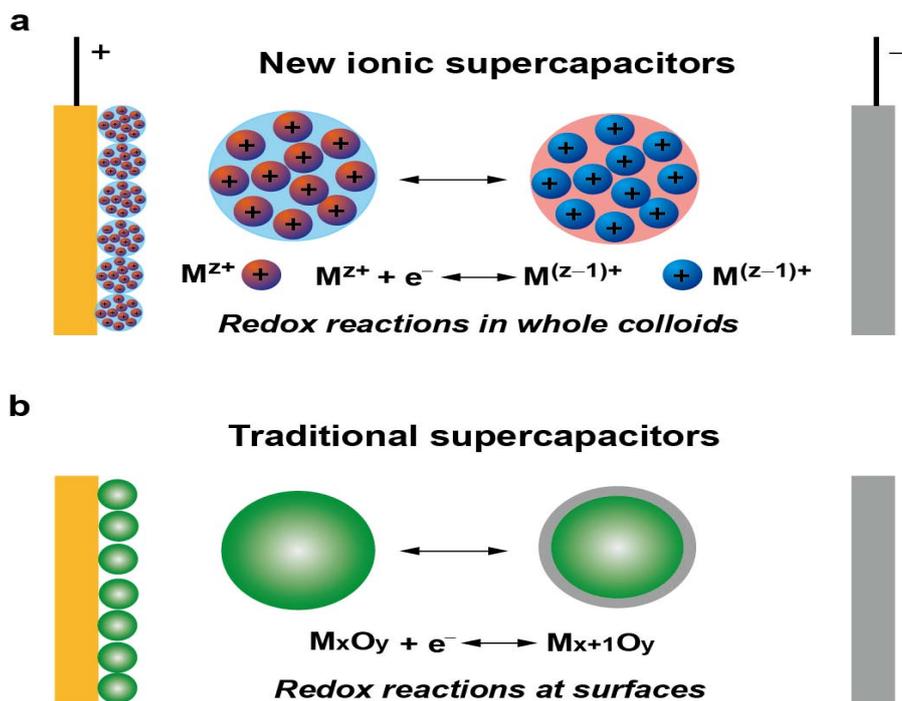


Figure 1: Comparison of new ionic and traditional pseudo capacitors. (a) New ionic pseudo capacitors. With highly active ionic state colloids as electrode material, Faradaic redox reaction can occur in whole colloids. The high cation utilization can deliver high energy density. (b) Traditional pseudo capacitor. Reversible redox reaction can occur only at or near the surface of an appropriate electrode material. The most part of material cannot be used toward to Faradaic redox reaction (called "dead zone"). The low cation utilization leads to low energy density.

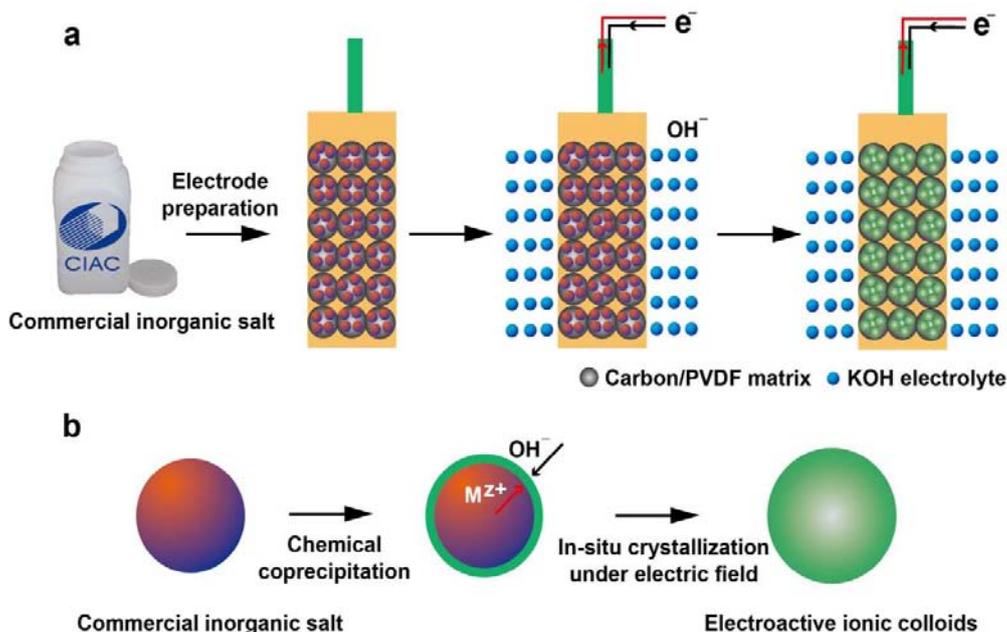


Figure 2: Schematic of system-level design of ionic supercapacitor electrode and electrolyte. (a) The preparation and reaction process of inorganic salts electrode in KOH electrolyte. (b) Highly electroactive colloids were formed by electric field assisted chemical coprecipitation. Faradaic reactions of electroactive colloids were occurred at the same time and the same electrode, with the corresponding Faradaic redox reactions of $M^{z+} \leftrightarrow M^{(z-1)+}$. The enhanced electrochemical performance mainly originates from the in-situ electric field assisted activation of colloids during the chemical coprecipitation.

Pseudocapacitors and batteries both rely on electrochemical redox reaction processes, where electric energy is stored as chemical energy by the valence change of active cations. Both theoretical capacities of pseudocapacitors and batteries are a function of the transferred electron number during redox reaction. In our designed alkaline ionic supercapacitor system, the ionic state colloids can deliver high energy density and power density, due to the high cations utilization and the short transport paths for ions and electrons. Therefore, both increasing the power density of batteries and enhancing the energy density of supercapacitors can be achieved by fully delivering the charge of cations at a fast rate, narrowing the gap between inorganic pseudocapacitors and batteries. The new ionic supercapacitor systems are not only launching an era of powerful supercapacitors, but also an era of powerful electrical energy storage systems.

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