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Large performance improvement of carbon-based supercapacitors using dual-redox additives phosphotungstic acid and potassium ferricyanide

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ABSTRACT

In this work, highly porous and hierarchical carbon materials with a BET surface area of 2085 $m^2 g^{-1}$ and pore volume of 2.80 $cm^3 g^{-1}$ were produced by a simple but effective template carbonization approach using ZnO as the hard template. Furthermore, to significantly improve the energy density of the supercapacitors, dual-redox additives of phosphotungstic acid (PTA) and potassium ferricyanide (KFC) have been developed based on their integrative effect. The sample prepared by mixing PTA and KFC at equal concentrations of 15 mmol L^{-1} in 1 mol L^{-1} H_2SO_4 delivers a large capacitance of 77 F g^{-1}, as well as an optimum energy density of 21.1 W h kg^{-1}, which are much larger than those obtained with PTA or KFC alone. In addition, introducing PTA, KFC or their mixture can result in diffusion-controlled redox processes. Moreover, the redox reaction of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ occurs on the positive electrode, and opposite PTA species with various chemical valences are on the negative electrode. The dual-redox additives of PTA and KFC are effective, integrative and easy to operate at ambient conditions, and thus, they are anticipated to exert a crucial role in remarkably elevating the energy density of supercapacitors.

1. Introduction

Supercapacitors can provide high specific power (10 kW kg^{-1}), long cycle life (>10^5), and fast charge/discharge propagation (within seconds), and therefore, they offer a promising approach to meet the increasing power demands of energy storage systems [1]. In addition, in the past decades, nanoporous carbon materials have been shown to be capable candidates as electrode materials for supercapacitors, mainly due to their large surface areas, high pore volumes, good chemical inertness and low cost, etc. [2]. Notwithstanding, the energy density of supercapacitors (approximately 5 W h kg^{-1}) is much lower than that of batteries, greatly limiting the optimal discharge time to less than a minute. However, many applications clearly need more time [3]. Hence, to efficaciously elevate the energy density of supercapacitors remains an interesting challenge for practical applications.

Currently, from a practical point of view, the most important challenge for supercapacitors is to increase the energy density above 10 W h kg^{-1} while maintaining a low fabrication cost and using environmentally benign materials [4]. Generally, increasing the energy density of supercapacitors can be realized by improving the capacitance and/or operating cell voltage (based on the well-known equation for energy density: $E = 0.5CV^2$). To increase the capacitance, many crucial factors, including surface area, pore volume, electrical conductivity, and additional redox capacitance, are commonly involved [5]. So far, most efforts have been devoted to increasing the surface area and pore volume of carbon materials while retaining the conductivity as much as possible [6]. To achieve this goal, the template carbonization method that ordinarily adopts a hard/soft template to form pores without the additional use of any activation reagent is a powerful tool for producing carbon materials with precisely controlled structures at the nanometer level [7], and many research studies have been completed,

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especially concerning the choice/combination of various kinds of templates [8,9].

Moreover, the enhancement of supercapacitor capacitance has also been actualized by introducing redox additives into aqueous electrolytes (commonly H_2SO_4, KOH, or Na_2SO_4), which can offer additional faradic pseudocapacitance to the overall capacitance with redox reactions at the interface of the electrode materials and electrolyte (although some confusion still exists about the correlative concept, storage mechanism, etc.) [10]. Basically, redox additives have been categorized into inorganic and organic species [11]. Inorganic additives usually exhibit diverse chemical valences and provide electron/proton transfer during the charging/discharging process, such as $Fe(CN)_6^{-3}$ with the redox pair of $Fe(CN)_6^{-3}/Fe(CN)_6^{-4}$; I^- with the redox reaction between $3I^-/I_3^-$, $2I^-/I_2$, $2I_3^-/I_2$, and I_2/IO_3^- [12–14]; and Br^- with the pair of $3Br^-/Br_3^-$ [15,16]. Additionally, organic compounds, especially those with the functional groups of hydroquinone, quinone, and amine, have been used as redox additives, such as benzoquinone-hydroquinone [17], hydroquinone sulfonate [18], and 9,10-anthraquinone-2,7-disulfonic acid [19]. It should also be noted that most of the redox additives for enhancing capacitance have been, to date, implemented individually.

To synchronously elevate the capacitance at the positive and negative electrodes, dual redox additives such as $KI/VOSO_4$ [20,21] and anthraquinone-2,7-disulfonate/$K_4Fe(CN)_6$ [22] have been utilized and ensuring that each of them participates in a faradaic reaction at one electrode is proving to be interesting and highly effective. Some redox additives are composed of two different functional constituents, while others exhibiting single unit structures in composition have also been reported. For instance, viologen (1,1′-diethyl-4,4′-bipyridinium bromide) can serve as an individual species for improving performance, and the redox reactions of bromide and 1,1′-diethyl-4,4′-bipyridinium ions occur at both positive and negative electrodes simultaneously, resulting in a maximum specific energy density of 23.0 W h kg^{-1} at 0.25 A g^{-1} [23]. Viologen dibromide incorporates pentyl viologen as the anolyte and bromide as the catholyte and can result in a high energy density of 48.5 W h kg^{-1} at 0.5 A g^{-1} [24]. As a consequence, choosing two different redox additives (or a single one with two different functional constituents) that cause redox reactions to simultaneously happen at positive and negative electrodes and unite different voltage windows into a complete one within available voltage scopes provides us a facile but efficient protocol for further elevating the energy density of supercapacitors.

Herein, we first prepared nanoporous carbon materials by the template carbonization method using potassium citrate monohydrate as the carbon source and ZnO as the hard template. Next, phosphotungstic acid and potassium ferricyanide were adopted as dual-redox additives to elevate the capacitance as well as the energy density of supercapacitors by an integrative effect. The redox reaction mechanism involved was thoroughly investigated by means of electrochemical techniques.

2. Experimental section

All the analytical-grade chemicals were purchased from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

For convenience, the pristine carbon without any added PTA or KFC is termed the ***Carbon-blank*** sample; the samples prepared by adding 10, 15 and 20 mmol L^{-1} PTA in 1 mol L^{-1} H_2SO_4 are named the ***PTA-10***, ***PTA-15***, ***PTA-20*** samples, respectively; the sample prepared by adding 15 mmol L^{-1} KFC in 1 mol $L^{-1}$$H_2SO_4$ is named the ***KFC-15*** sample; and the one created by mixing PTA and KFC with equal concentrations of 15 mmol L^{-1} in 1 mol L^{-1} H_2SO_4 is called the ***PTA-KFC-1:1*** sample. The overall samples are summarized in Table 1.

Polyoxometalates (POMs) are nanometric oxide clusters that consist of three or more transition metal oxyanions linked together by shared oxygen atoms to form closed 3-dimensional frameworks, which show reversible redox activities; they can be used as building blocks for a variety of materials and applications [25]. These molecular clusters are very stable and present strong interactions with various electrode materials. However, only a few recent examples are found concerning the applications of polyoxometalate-based materials in supercapacitors, particularly using POMs as redox additives in aqueous electrolytes.

As is well known, phosphotungstic acid (PTA) is a polyoxometalate species in which tungsten has diverse chemical valences, predominantly including +4, +5 and + 6. It is expected to deliver pseudocapacitive behavior during the charging-discharging process when used as a redox additive for supercapacitor applications, primarily due to the redox reactions between tungsten species with different valences. Therefore, we first tested the CV profile at 20 mV s^{-1} of the ***PTA-15*** sample, and the resultant CV, shown in Fig. 1a, indicates a pair of redox peaks around −0.2–0.2 V. Notwithstanding, another long period of 0.2–0.8 V in Fig. 1a remains flat (without the occurrence of redox peaks), and therefore, how to take full advantage of this CV profile is intriguing.

From another point of view, potassium ferricyanide (KFC) contains iron species with different chemical valences of +2 and + 3, which can give us a CV profile possessing redox peaks at 0.4–0.8 V, as depicted in Fig. 1b. Consequently, synchronously utilizing PTA and KFC as dual-redox additives seems to be perfect and might accomplish a CV profile with the entire scan rate profile from −0.2–0.8 V. In the present work, when testing the ***PTA-KFC-1:1*** sample by mixing PTA and KFC in an H_2SO_4 solution, one convincing CV profile showing the integrative effect appears, as given in Fig. 1c. To be brief, in the scan scope of −0.2–0.8 V, PTA and KFC can serve as efficient dual-redox additives in an H_2SO_4 solution, which is anticipated to notably improve the capacitance as well as the resultant energy density of supercapacitors. Additionally, the unit structures of $H_3PW_{12}O_{40}$ and $K_3Fe(CN)_6$ are simply depicted in Fig. 1d.

2.1. *Typical synthesis procedure for nanoporous carbon materials*

Potassium citrate monohydrate ($K_3C_6H_5O_7 \cdot H_2O$) and zinc oxide (ZnO), at a mass ratio of 3:1, were carbonized in a tube furnace up to the desired temperature of 800 °C at a rate of 4 °C min^{-1} under an Ar atmosphere and held at this temperature for 2 h. The obtained black products were then immersed in a 1 mol L^{-1} HCl solution, washed with sufficient deionized water, distilled and dried at 120 °C for 12 h under vacuum to finally obtain the ***Carbon-blank*** sample.

2.2. *Typical preparation procedure for the redox additive electrolyte*

Phosphotungstic acid hydrate, $H_3PW_{12}O_{40}$, was added into 100 mL of 1 mol L^{-1} H_2SO_4 solution under magnetic stirring at

Table 1
Summary of samples with different incorporations of PTA and KFC.

Samples	PTA (mmol L^{-1})	KFC (mmol L^{-1})
Carbon-blank	/	/
PTA-10	10	/
PTA-15	15	/
PTA-15	20	/
KFC-15	/	15
PTA-KFC-1:1	15	15