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Development of novel and ultrahigh-performance asymmetric supercapacitor based on redox electrode-electrolyte system

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ABSTRACT

The conventional enhancement in capacitive performance that only relies on electrode materials is limited. Here, based on the system-level design principle, we explore the possibility of enhancing capacitance through both electrode and electrolyte. A novel and ultrahigh-performance asymmetric supercapacitor has been fabricated using two redox electrode systems. The positive electrode system consists of graphene supported $Co(OH)_2$ nanosheet ($Co(OH)_2$/GNS) electrode and mixed KOH and $K_3Fe(CN)_6$ aqueous electrolyte. And the negative electrode system comprises carbon fiber paper supported activated carbon (AC/CFP) electrode in mixed KOH and p-phenylenediamine (PPD) aqueous electrolyte. The novel asymmetric supercapacitor exhibits a significantly improved capacitive performance (specific capacitance of 204.5 Fg^{-1}, operational voltage of 2.0 V) in comparison with that of the conventional asymmetric supercapacitor (66.8 Fg^{-1}, 1.5 V) fabricated without redox electrolyte. The improvement is attributed high reversibility and conductivity of electrode materials and redox electrolyte, as well as the synergistic effect between the two electrode systems, resulting in a ultrahigh energy density (114.5 $Whkg^{-1}$ at a power density of 1000 Wkg^{-1}), excellent power density (4000 Wkg^{-1} at an energy density of 31.6 $Whkg^{-1}$) and long-term cycling stability (after 20000 cycles, initial capacitance remains well). These encouraging results afford a facile and efficient way to fabricate ultrahigh-performance supercapacitors for the increasing demands on the energy storage devices.

1. Introduction

With the increasing power, energy and stability demands in next-generation energy devices, research efforts have mostly focused on developing compatible energy storage devices [1–3]. Supercapacitors (SCs), also known as electrochemical capacitors (ECs), have recently become promising candidates in the energy storage areas, owing to their higher power densities, longer cycle life and safer operation performance than batteries [4–7]. However, the disadvantages of limited energy density (usually less than 10 $Whkg^{-1}$ for commercial ECs) and high fabrication cost (expensive to obtain high-performance electrode materials, such as RuO_2) have been identified as the major challenge for the capacitive storage science. The energy density (E) is usually limited to the specific capacitance (C) and operating voltage (V) according to the equation $E = 1/2CV^2$. Therefore, developing ECs with high specific capacitance and wide operating voltage are two strategies to improve the energy density. However, two problems exist, firstly, although using organic electrolytes or ionic liquids can extend the operating voltage of ECs, the nonaqueous electrolytes suffer from low conductivity, high cost, flammability and environmental problems [8,9]; secondly, the researches for improving the capacitive performance of ECs mainly focus on the electrode materials recently, although developing nanostructured electrode materials can enhance specific capacitance, the enhancing is limited.

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An effective approach to increase energy density is to design aqueous asymmetric supercapacitors (ASCs) combining a battery-like faradic electrode as energy source and a capacitive electrode as power source [9–11]. The current aqueous symmetric supercapacitors are mainly electric double layer capacitors (EDLCs), based on high surface area carbon materials in the two electrodes, showing a relatively low energy density (less than 10 $Whkg^{-1}$) [6]. The restriction for symmetric supercapacitors is a limited operating voltage of about 1.23 V at which water decomposes [12]. To obtain high energy density, various types of aqueous ASCs, such as Li(Na, K)Mn_2O_4//activated carbon (AC) [13–15], M_xO_y//AC (M = Co, Ni, Mn, Mo, V, etc.) [8,16–18], $M_x(OH)_y$//AC (M = Co, Ni, Al etc.) [9,19,20], have been developed to achieve a high cell voltage of 1.4–2.0 V by taking advantage of different potential windows of the two electrodes to widen the device operating voltage. As shown in Table 1, advanced ASCs with pseudocapacitive materials as positive electrodes and carbon materials as negative electrode have been developed, providing a pronounced improvement in energy density (~50 $Whkg^{-1}$) by giving a specific capacitance about 2 ~ 10 times as large as that of carbon materials as well as an operating voltage higher than ~1 V of EDLCs for symmetric supercapacitors with aqueous electrolytes [21–35].

Although the construction of ASCs is an effective approach to extend the operating voltage window of aqueous electrolytes by electrode materials working in well-separated potential windows and thus improve the energy density, a problem exists that the specific capacitance for ASCs is not high enough to improve the energy density effectively compared with batteries. Since the ASCs research mainly focuses on the discovery of new electrode materials and new synthesis methodology, the specific capacitance cannot be improved significantly via only relying on the active electrode materials.

Recently, there have been a few reports that redox additives are introduced into the conventional electrolyte for symmetric carbon EDLCs to substantially enhance the capacitance via redox reactions of the additives between the electrode and electrolyte. For example, Chen et al. [36] have introduced $K_3Fe(CN)_6$ as a redox additives into conventional Na_2SO_4 electrolyte for the graphene-paper electrode, and a much higher areal specific capacitance (475 $mFcm^{-2}$) than that (93 $mFcm^{-2}$) with Na_2SO_4 electrolyte has been achieved. Similarly, Senthilkumar et al. [37] have reported that with KI introduced to conventional H_2SO_4 electrolyte, the AC|H_2SO_4-KI|AC supercapacitor system delivered a high specific capacitance and energy density of 912 Fg^{-1} at 2 $mAcm^{-2}$ and 19.04 $Whkg^{-1}$ at 224.43 Wkg^{-1}, which is nearly twice the specific capacitance and energy density of AC|H_2SO_4|AC (472 Fg^{-1}, 9.5 $Whkg^{-1}$). Based on these reports, it can be concluded that the redox additives can increase the original capacitance of the supercapacitor by contributing additional pseudocapacitance.

As mentioned above, although more attention has been paid to investigating either electrode or electrolyte for enhancing the capacitance, no any efforts have been done to improve both solid electrode and liquid electrolyte simultaneously for ASCs. In previous work, we have studied the performance of graphene supported $Co(OH)_2$ ($Co(OH)_2$/GNS) electrode in mixed KOH and $K_3Fe(CN)_6$ aqueous solution [38]. In this work, we prepared Co $(OH)_2$/GNS-KOH/$K_3Fe(CN)_6$ positive electrode system and AC/carbon fiber paper-KOH/p-phenylenediamine (AC/CFP-KOH/PPD) negative electrode system and fabricated an ASC with the novel positive and negative electrode system. We aimed at developing a novel ASC device based on redox electrode-electrolyte system with ultrahigh electrochemical performance, realizing that solid electrode and liquid electrolyte provide capacitance simultaneously and stably.

2. Experimental

2.1. Preparation of $Co(OH)_2$/GNS-KOH/$K_3Fe(CN)_6$ electrode system

Our previous work has confirmed the possibility of enhancing pseudocapacitance through both $Co(OH)_2$/GNS electrode and KOH/$K_3Fe(CN)_6$ electrolyte [38]. For the electrode material, vertically oriented GNS were synthesized by plasma-enhanced chemical vapour deposition on Ni foam, and that was used as substrates for cathodic electrodeposition of $Co(OH)_2$ nanosheets in $Co(NO_3)_2$ aqueous solution, the detailed description about the preparation of the $Co(OH)_2$/GNS electrode can be found in ref. [39]. The electrolytes were 1 M KOH aqueous solution mixed with 0.04 M $K_3Fe(CN)_6$.

2.2. Preparation of AC/CFP-KOH/PPD electrode system

The influence of AC on the performance of capacitor is very important, therefore high-quality commercial AC (TF-02, Xinjiang Tianfu Electric Co. Ltd) with a surface area of 2000 m^2g^{-1} and average particle size of 8 μm was chosen. The AC electrode was prepared by a simple and low-cost spray method. With high speed stirring and ultrasonic processing, 85 wt% AC, 5 wt% Nafion, and 10 wt% conductive graphite were mixed in ethanol to form homogeneous slurry. Then the homogeneous slurry was sprayed

Table 1
Summary of research describing energy storage parameters of the conventional ASC devices reported in literature. NR means not reported.

SC configuration	Electrolyte	CS (Fg^{-1})	Max V (V)	ES($Whkg^{-1}$)@ PS($kWkg^{-1}$)	CS retention (%)/cycle number	Ref.
CoO@Polypyrrole//AC	3 M NaOH	NR	1.8	43.5@5.5	91.5/20000	[21]
MnO_2/carbon nanofiber//AC	0.5 M Na_2SO_4	56.8	2.0	30.6@20.8	94/5000	[22]
$Co(OH)_2$/Co_3O_4//AC	2 M KOH	~62	1.5	22.3@3	104/2000	[23]
Co/Al LDHs//rGO	6MKOH	97.5	1.6	34.7@5.6	93/2000	[24]
$CoMn_2O_4$/GNR//GNR	0.5 M Na_2SO_4	~100	1.9	84.69@22	96/1500	[25]
$NiCo_2O_4$@MnO_2//AC	1 M NaOH	112	1.5	35@3	71/5000	[26]
NiCo2O4 NSs@HMRAs//AC	1 M KOH	70.04	1.5	15.42@7.8	106/2500	[27]
Ni–Co oxide NWAs//AC	1 M KOH	NR	1.8	25@3.57	73.1/3000	[28]
$NiCo_2O_4$@$Co_{0.33}Ni_{0.67}(OH)_2$//CMK-3	1 M KOH	87.9	1.6	31.2@3.96	82/3000	[29]
NiO//rGO	1 M KOH	50	1.7	39.9@4	95/3000	[30]
$NiMoO_4.xH_2O$//AC	2 M KOH	96.7	1.6	34.4@1.65	80.6/1000	[31]
Co_3O_4/$Co_3(VO_4)_2$//AC	2 M KOH	105	1.6	38@1.65	94.7/5000	[32]
Co_3O_4@MnO_2//graphene	1 M LiOH	49.8	1.8	17.7@158	81.1/10000	[33]
MnO_2//CNT-CNF	0.5 M Na_2SO_4	93.99	2.0	52.22@1	92/2000	[34]
$Co(OH)_2$/NMEG//PPy/rG-O	1 M KOH	74	1.6	24.9@0.224	60/6000	[35]
$Co(OH)_2$/GNS//AC/CFP	KOH + $K_3Fe(CN)_6$//KOH + PPD	204.5	2.0	114.5@4	100/20000	present work