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Synergistic interaction between redox-active electrolytes and functionalized carbon in increasing the performance of electric double-layer capacitors

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ABSTRACT

The increasing demand of high-performance supercapacitors has aroused great interest in developing specific capacitance and energy density. Active carbon (AC) has attracted much attention as a promising electrode material for electric double-layer capacitors (EDLCs). Here, a facile strategy has been employed to fabricate high-performance EDLCs using the surface-oxygen functionalized active carbon (FAC) as an electrode and 2 M KOH with $K_3Fe(CN)_6$ as an electrolyte. In this system, $K_3Fe(CN)_6$ was used as a redox additive to enhance the performance of EDLCs. A 38.5% increase in specific capacitance (207.7 F g^{-1}) was achieved compared with the KOH electrolyte without adding $K_3Fe(CN)_6$ (152.9 F g^{-1}), due to the synergistic effects between oxygenic functional groups and redox electrolyte. These findings provide an alternative route to improve the performance of EDLCs, which are promising candidates for the broad applications of high-performance supercapacitors.

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1. Introduction

Electrochemical supercapacitors (ECs) have been considered as one of the most promising candidates for energy storage, main assistant power supply in portable electronics, hybrid electric vehicles, and unmanned aircrafts and have attracted great interest for a variety of applications due to their high power densities and long cycle life [1,2]. Carbon materials are most commonly used as the ideal electrode material for ECs because of its large surface area and high electrical conductivity [3–5]. Among various alternative carbon materials, the AC, with low cost and outstanding physico-chemical stability, has been explored as a promising candidate for electrode material [6,7]. Based on the charge storage mechanism, charge storage properties are typically attributed to the separation of charges and their accumulation on the electrode/electrolyte interface, forming what is called the electric double layer (EDL) [8–10], and in some cases the capacitance could be improved by the pseudocapacitance arising from quick faradaic reactions due to the surface functionalities (such as oxygen and nitrogen) [11,12]. Li et al. [13] prepared nitrogen-doped activated carbons with ex-

cellent specific capacitance ($\sim 185 \text{ F g}^{-1}$ at 0.4 A g^{-1}) and high energy densities (230 W h kg^{-1}). Tiruyea et al. [14] synthesized functional porous carbon nanospheres as the electrode, and the specific capacitance and energy density were as high as 110 F g^{-1} and 33 W h kg^{-1} PYR14FSI ionic liquid electrolytes. However, the above-mentioned strategies to introduce functional groups require expensive reagents and a complex process. In light of this, it is much more preferable to develop a simple and low-cost method to modify the carbon-based materials.

On the other hand, to improve the specific capacitance of the carbon electrode, multiple redox species can be directly added into the electrolyte to form the redox-active electrolytes, which involve aqueous electrolytes [15–17], organic solvents [18–20], and ionic liquids [21–23], such as KI in H_2SO_4 [15], $Na_2S_2O_8$ in KOH [16], $VOSO_4$ in acidic solutions [17], sulfonated polyaniline in H_2SO_4 electrolytes [18], *p*-phenylenediamine in KOH [19], and 1-ethyl-3-methylimidazolium tetrafluoroborate ionic liquid [21]. In addition, the aqueous electrolyte is safer, cleaner, and inexpensive and has attracted wide attention. Recently, Senthilkumar et al. [15] added KI into the H_2SO_4 electrolyte, which produced a nearly two fold increase in specific capacitance and energy density, 912 F g^{-1} and $19.04 \text{ W h kg}^{-1}$ respectively, than that of pure H_2SO_4 electrolytes. Rold et al. [22] added the hydroquinone to the KOH electrolyte, in which the capacitance values were observed to be at

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44 least two times higher after the addition of the redox compound.
45 The redox reaction of the electrolytes will lead to an increase in
46 its overall capacitance. Jänes et al. [23] studied the effect of 1,2-
47 dimethoxyethane (1,2-DME) addition (from 0 to 90 vol%) on the
48 electrochemical behaviour of 1-ethyl-3-methylimidazolium bis (tri-
49 fluoromethylsulphonyl) imide (EMImTFSI) as an electrolyte for su-
50 percapacitors. They demonstrated that the supercapacitors based
51 on the 40 vol% of 1,2-DME deliver higher power density at the
52 constant energy density, showing an excellent characteristics ap-
53 plicable in high rate supercapacitor devices at cell potentials up to
54 $E \leq 2.7$ V.

55 As mentioned above, the electrode materials and electrolyte
56 can both decide the capacitance performance of EDLCs. Inspired
57 by this, in the present work, we adopted a facile method to im-
58 prove supercapacitor performance of the carbon electrode through
59 a synergistic interaction between redox-active electrolytes and
60 surface functionalities, which is achieved by adding $K_3Fe(CN)_6$
61 into aqueous KOH as electrolyte and using functionalized carbon
62 as the electrode. Unlike conventional approaches, the functional
63 groups on the surface of ACs not only contribute to the pseu-
64 docapacitance but also improve the electrochemical activity of
65 $Fe(CN)_6^{3-}/Fe(CN)_6^{4-}$ redox pair, thus leading to high capacitance.

66 2. Experimental

67 2.1. Electrode and electrolytes

68 All the chemical reagents in this experiment were analytical
69 grade. The AC was purchased from Sunrise Power Co., Ltd. Briefly,
70 0.2 g AC was dispersed into 70 mL 30 wt% H_2O_2 solution and
71 stirred for 10 min. Then the mixed solution was transferred to a
72 100 mL Teflon-lined stainless steel autoclave and hydrothermally
73 treated at 120 °C for 1 h. After cooling to room temperature,
74 the obtained sample was washed several times with distilled wa-
75 ter and collected by centrifugation. Finally, it was dried at 60 °C
76 overnight. The sample was named functionalized active carbon
77 (FAC) after being dried at 60 °C overnight.

78 Two types of electrolytes were used in electrochemical mea-
79 surement: (1) 2 M KOH aqueous electrolyte and (2) a mixed
80 solution containing 2 M KOH aqueous electrolyte and 0.04 M
81 $K_3Fe(CN)_6$. In this work, the redox of $Fe(CN)_6^{3-}$ was added into the
82 conventional KOH electrolyte to enhance the overall capacitance of
83 carbon materials.

84 2.2. Physical and electrochemical measurement

85 Surface functional groups of the samples were verified by FTIR
86 spectroscopy (FTIR BRUKER TENSOR 27, Germany). The crystal
87 structure was characterized by X-ray diffraction (XRD, Panalytical,
88 Netherlands) with a Rigaku D/max UltimaIII using $Cu K\alpha$ radiation
89 ($\lambda = 0.150405$ nm) at a scanning rate of 10° to 80°. Specific surface
90 areas and pore size distribution (PSD) curve determined by nitro-
91 gen adsorption/desorption measurement at 77 K (ASAP 2020).

92 The electrode was prepared by pressing a mixture of active
93 materials (AC or FAC), acetylene black, and polytetrafluoroethylene
94 (60 wt% dispersion in water) with a weight ratio of 80:10:10 on
95 nickel foam (1 cm × 1 cm). A Pt plate and saturated calomel
96 electrode (SCE) were used as counter and reference electrodes,
97 respectively. The electrochemical measurements were carried out
98 by using a conventional three-electrode system with an aque-
99 ous solution (electrolyte: 2 M KOH or 2 M KOH- $K_3Fe(CN)_6$).
100 The cyclic voltammetry (CV) and electrochemical impedance spec-
101 troscopy (EIS) measurements were performed using an AUTOLAB
102 (ECO CHEMIE, PGSTAT 100). The galvanostatic charge-discharge
103 and cycling performance were tested using a CT2001A battery pro-
104 gram controlling test system (China-Land Com. Ltd).

3. Results and discussion

105 The chemical composition of the carbon materials was charac-
106 terized by FT-IR spectroscopy and is shown in Fig. 1(a). The AC and
107 FAC both exhibit a broad band around 3400 cm^{-1} corresponding
108 to the O-H stretching and deformation vibrations. After hydrother-
109 mal treatment, the functionalized AC obviously shows the signal of
110 adsorbed species: the peaks between 2980 and 2840 cm^{-1} are the
111 stretching vibration signal of the CH band from CH_2 or CH_3 groups,
112 the carbonyl (C=O) stretching band at 1729 cm^{-1} and conjugated
113 carbonyl (-CO-) band at 1662 cm^{-1} [24,25].

114 The spectral analysis results suggest that functional groups are
115 mostly presented on the surface of the active carbon after hy-
116 drothermal treatment, which will improve the capacitance perfor-
117 mance. Moreover, Fig. 1(b) shows the extended oxygen functional
118 groups on the surface of carbon materials. The surface functional
119 groups such as -OH, C-O, and C=C increased to 1.75 $mmol g^{-1}$
120 after H_2O_2 hydrothermal treatment, which not only improve the
121 surface wettability of the electrode materials but also provide the
122 pseudocapacitance to enhance the capacitance of the electrode
123 [26].

124 The capacitance performance of the EDLCs relates directly to
125 the specific surface area and the pore structure of the carbon ma-
126 terials, N_2 adsorption and desorption measurements are employed,
127 and the nitrogen adsorption-desorption isotherm and the pore size
128 distribution curves are described in Fig. 2(c) and (d). Both the
129 plots exhibit the patterns of type IV isotherms with a hysteresis
130 loop ($0.45 < p/p_0 < 0.97$), indicating the coexisting micro-meso-
131 macropores and large pore volume. The BET surface areas of the AC
132 and FAC were 1790 and 1671 $m^2 g^{-1}$, respectively. The pore size
133 distribution calculated from the Barrett-Joyner-Halenda method
134 was 3.27 and 3.30 nm, which is an ideal pore structure for ion dif-
135 fusion. No essential difference in textural structure was observed
136 for FAC, except a slight decrease in both specific surface area and
137 total pore volume (Table 1), which corresponds to the collapse of
138 the carbon skeleton after H_2O_2 treatment.

139 Furthermore, the unique electrochemical performance of the
140 FAC electrode was exposed. The CV curves of the AC and FAC in
141 KOH electrolyte and KOH- $K_3Fe(CN)_6$ at the scan rate of 10 $mV s^{-1}$
142 are shown in Fig. 2(a). The CV curves became much broader in
143 shape, but the rectangular shapes of the curves were unchanged in
144 KOH electrolyte, implying an ideal capacitive behavior, and the less
145 rectangular shape confirms a higher pseudocapacitance of the FAC
146 electrode. The oxygen functional groups can enhance the capaci-
147 tance performance of FAC by introducing abundant pseudocapaci-
148 tance active sites through reversible Faradic redox reactions [27].
149 Furthermore, carbon materials with functionalized surface were
150 found to have better surface wettability in aqueous electrolytes,
151 which is beneficial in the electron/ion diffusion between the elec-
152 trode and electrolyte [28,29]. Additionally, it can be seen that both
153 CV curves of AC and FAC in the KOH- $K_3Fe(CN)_6$ electrolyte show
154 the oxidation and reduction peaks are around 0.3 V, implying a
155 typical pseudocapacitive behavior, and the near symmetrical redox
156 peaks indicate good kinetic reversibility in the redox process. Par-
157 ticularly, the peaks' current values on the CV curves of the FAC
158 electrode are higher than that of the AC electrode due to the syn-
159 ergistic properties between the functional groups on the surface
160 and the redox pair in the electrolyte, that is, the surface functional
161

Table 1. Structure and parameters of the AC and FAC.

Sample	BET area ($m^2 g^{-1}$)	Total pore volume ($cm^3 g^{-1}$)/ $cm^3 g^{-1}$	Average pore size (nm)
AC	1790	3.36	3.27
FAC	1761	3.28	3.30

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