



Diphenylcarbazide-based carbon materials: Novel redox additives for simply and largely improving the electrochemical performance



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ARTICLE INFO

Article history:

Received 16 July 2015

Received in revised form 25 August 2015

Accepted 5 September 2015

Available online 10 September 2015

Keywords:

Redox

Additive

Carbon materials

Supercapacitor

ABSTRACT

In this work, we demonstrate two kinds of novel redox additives, diphenylcarbazide (abbr. **DC**) and phenylazoformic acid 2-phenylhydrazide (abbr. **PP**), with quick and reversible redox reaction incorporated into carbon-based supercapacitors. It is revealed that the 4-electron and 4-proton transfer occurring in the redox additive–carbon material system within the electrode can result in additional capacitance. When introducing 24 mg **DC** or **PP** substance into 24 mg carbon system, largely improved specific capacitances of 544.3 or 427.6 F g⁻¹ are achieved, which are almost 4.31 and 3.39 times, respectively, than that of the pristine carbon (126.1 F g⁻¹) at the current density of 2 A g⁻¹. Besides, their corresponding capacitance retentions can reach up to 78.9% and 75.6%, respectively, after 5000 charge–discharge cycles, and both of them are somewhat smaller than that of the pristine carbon (96.8%) due to the incremental electronic resistances. The present commercially available, low-cost and highly effective redox additives of **DC** and **PP** are quite promising and expected to be implemented for high performance supercapacitors.

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1. Introduction

Carbon-based materials have been widely used in supercapacitors due to their controlled pore structures, relatively narrow pore size distributions and chemical stabilities [1–3]. However, their practical applications are restricted by relatively low capacitances as well as energy densities [4]. As far as we know, this obstacle can be overcome via the following three strategies: (i) incorporating heteroatoms into carbon matrix, such as sulfur [5], nitrogen [6], phosphorus [7], oxygen [8] and boron [9]. As a result, these functional groups delivered enriched capacitances, but the equivalent series resistance (ESR) and durability are inferior in comparison to ideal supercapacitors [10]. (ii) Preparing composites with pseudocapacitive metal oxides/hydroxides, such as Fe₂O₃ [11], MnO₂ [12], Ni(OH)₂ [13] and Co(OH)₂ [14]. However, in most cases, those metal oxides/hydroxides have their own drawbacks of low rate capability and poor cyclability because of their poor electrical conductivity [15], and (iii) introducing a small amount of organic/inorganic redox additives in the aqueous electrolyte.

Alternatively, introducing redox additives into the electrolyte is an efficient and simple way to improve the specific capacitance, which can store extra energy by the self-discharge reaction of redox additives [16]. For example, Su et al. [17] added K₃Fe(CN)₆/K₄Fe(CN)₆ into the KOH aqueous electrolyte with Co–Al layered double hydroxide

electrode. The capacitance was increased from 226 F g⁻¹ to 712 F g⁻¹/317 F g⁻¹ by introduction of 0.1 M K₃Fe(CN)₆/K₄Fe(CN)₆ into 1 M KOH aqueous electrolyte. Senthilkumar et al. [18] have reported the improvement of specific capacitance via addition of 0.08 M KI to 1 M H₂SO₄ aqueous solution as mixed electrolyte. The specific capacitance of the mixed electrolyte was increased from 472 F g⁻¹ to 912 F g⁻¹. Wu et al. [19] has increased specific capacitance by using *p*-phenyl-enediamine (PPD) as redox additive. The mixed electrolyte of 2 M KOH + 0.050 g PPD exhibited high capacitance value of 605.225 F g⁻¹ which is nearly four-fold in comparison with the 2 M KOH electrolyte (144.037 F g⁻¹). Similarly, indigo carmine [20], *m*-phenylenediamine [21], methylene blue [22] and Na₂S/S powder [23] were also researched as redox additive, prominently increasing the performance of the electrodes. Although the above-mentioned redox additives have improved the capacitive performance of electrodes, exploring new redox additives with high capacitances is still interesting and challenging.

In the present work, we employed **DC** and **PP** as redox additives into carbon-based supercapacitors. Interestingly, both of them have the aniline groups on the benzene rings, which are also anticipated to generate the redox reactions at the interface between the surface of electrode and electrolyte. More importantly, the reaction at the electrode–electrolyte interface can store extra energy, and it is expected that the electrochemical properties of the electrodes can be significantly improved. In addition, introducing **DC** or **PP** substance into the carbon system can overcome the drawback of their being slightly soluble or insoluble in

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Table 1
The materials and their components for preparing the mixture electrodes.

Sample no.	DC content (mg)	PP content (mg)	Carbon (mg)	Acetylene black (mg)	PTFE (mg)
Carbon-blank	/	/	48	9	3
DC-1	16	/	32	9	3
DC-2	24	/	24	9	3
PP-1	/	16	32	9	3
PP-2	/	24	24	9	3

water (DC is slightly soluble and PP insoluble in water). On the other hand, the redox additive–carbon material system can overcome phase separation and association of free ions that derive from excessive concentration of electrolytic salts in comparison with the traditional method for introducing redox additives into electrolyte [21].

2. Experimental

All the chemicals were purchased from Sinopharm Chemical Reagent (Shanghai) Co. Ltd with analytical grade, and used as received without further treatment.

2.1. Preparation procedure of carbon material

In the work, the carbon material was prepared by carbonization method, in which DC was used as carbon source and ZnCl_2 used as activation agent, respectively. The mass ratio of DC to ZnCl_2 was 1:3. Then the mixture was heated to 700 °C at a rate of 5 °C min^{-1} and kept for 2 h under N_2 atmosphere. Finally, the combustion product was treated with dilute HCl solution and adequate deionized water to remove impurities and then dried at 110 °C, resulting in the formation of the **carbon-blank** sample.

2.2. Preparation procedure of mixture electrodes

Mixtures of polytetrafluoroethylene (PTFE 3 mg), acetylene black (9 mg), certain amount of prepared carbon and DC/PP were fabricated using ethanol as a solvent. The materials together with their components investigated in our work are listed in Table 1. Then a slurry of the above mixtures was subsequently pressed onto nickel foam under a pressure of 20 MPa, serving as the current collector. Finally, the prepared supercapacitors were dried at 60 °C in an oven for 24 h to achieve the **carbon** and **DC-1**, **DC-2**, **PP-1**, **PP-2** samples. The mass of carbon materials on each supercapacitor was measured to be ~1.0–1.3 mg.

2.3. Measurements conducted in a three-electrode system using 2 M KOH as electrolyte

A three-electrode experimental setup taking a 2 M KOH aqueous solution as electrolyte was used in cyclic voltammetry (CV) and galvanostatic charge–discharge (GCD) measurements on an electrochemical working station (CHI660D, ChenHua Instruments Co. Ltd., Shanghai). Here, the prepared electrode, platinum foil (6 cm^2) and saturated calomel electrode (SCE) were used as the working, counter and reference electrodes, respectively.

Specific capacitances derived from galvanostatic tests can be calculated from the equation:

$$C = \frac{I\Delta t}{m\Delta V}$$

where C (F g^{-1}) is the specific capacitance; I (A) is the discharge current; Δt (s) is the discharge time; ΔV (V) is the voltage window; and m (mg) is the mass of active materials loaded in the working electrode.

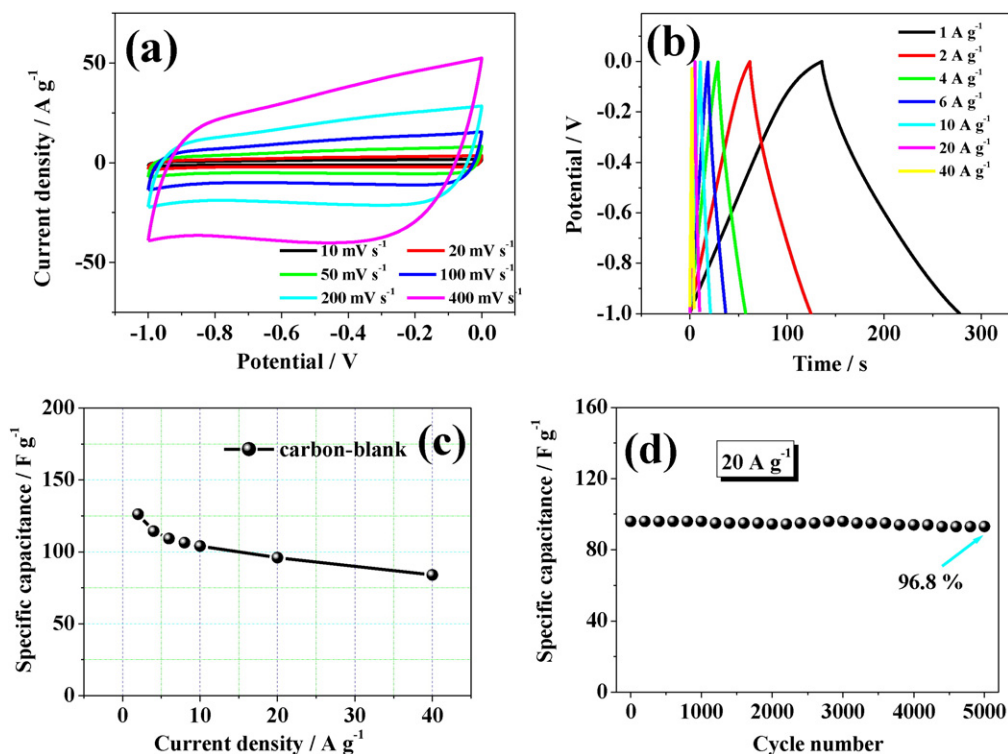


Fig. 1. The **carbon-blank** sample: (a) CV curves; (b) GCD curves; (c) specific capacitances as a function of current density; (d) cycling performance for 5000 cycles at 20 A g^{-1} .

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