



Synergistic capacitive behavior between polyaniline and carbon black



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ABSTRACT

Polyaniline (PANI) is an excellent electrode material with high pseudocapacitance for supercapacitors. Here the binder-free supercapacitor electrodes with high specific capacitance (458 F g^{-1} at 2 mV s^{-1}) and Coulombic efficiency (100%) are successfully synthesized via a one-step potentialdynamic co-deposition of PANI and carbon black (CB). Significant synergistic effect between PANI and CB is demonstrated. Particularly, CB as the secondary dopant of PANI has been found to play an important role in producing higher conductivity, extended conformation structure, improved porosity, higher oxidation state and depressed hydrolysis effect, leading to superior capacitive performance. This promotes better understanding about synergistic effect between active materials and carbon additives, and opens up new research direction for high performance electrode design.

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1. Introduction

Supercapacitors with high power density, long-term cycling stability and high reversibility have been rising as promising energy storage devices. There are three main types of electrode materials for supercapacitors, namely, carbon species, metal compounds and conducting polymers [1–4]. The combination of carbonaceous materials, metal compounds and conducting polymers in a composite system usually results in improved performance due to the synergistic effect of every component [5,6].

Polyaniline (PANI) has been extensively studied as electrode materials for supercapacitors for its excellent properties, including high pseudocapacitance, high conductivity, high flexibility and low cost [7–9]. The excellent capacitive properties and fast charge transfer usually result in high energy/power density and good rate capability for supercapacitors. Moreover, the flexibility makes PANI promising to fabricate flexible electrodes. However, the pseudocapacitance of PANI is not always high and its capacitive behaviors is significantly dependent on its structural and chemical properties [3,10]. PANI can exist in three different oxidation states: fully

reduced leucoemeraldine (LE), 50%-oxidized emeraldine base (EB) and fully oxidized pernigraniline (PE). EB is the most stable form of PANI, consisting of equal numbers of reduced amine ($-\text{NH}-$) and oxidized imine ($-\text{N}=\text{}$) units [11], as shown in Fig. 1a. Upon doping with acid, neutral EB, which is insulating with a wide band gap can be converted to protonated emeraldine salt (ES), which is electrically conducting. LE and PE are insulators, even when doped. PANI-ES with reduced amine and oxidized imine units possesses an asymmetric electronic structure in the energy band gap [12], where the protonation of imine ($-\text{N}=\text{}$) sites and the subsequent internal redox reaction induce two asymmetric polaron bands. The upper polaron band (p^*) is narrow and nearly degenerated in the conduction band while the lower band (p) is broad. Hence the protonation results in the shift of Fermi level from the middle of the band gap to the middle of the half-occupied lower polaron band (as schematically shown in Fig. 1b). The polaron bands facilitate the electron transition across the band gap, resulting in significantly enhanced conductivity of PANI-ES [13]. When PANI-EB is protonated, the polymer backbone is positively charged and the negative counterions like SO_4^{2-} could sit in the vicinity of polymer chains, resulting in the so-called PANI-ES. It will cause the change of the conformation, conjugation length of PANI, which are significantly related to the conductivity, as well as the electrochemical performance.

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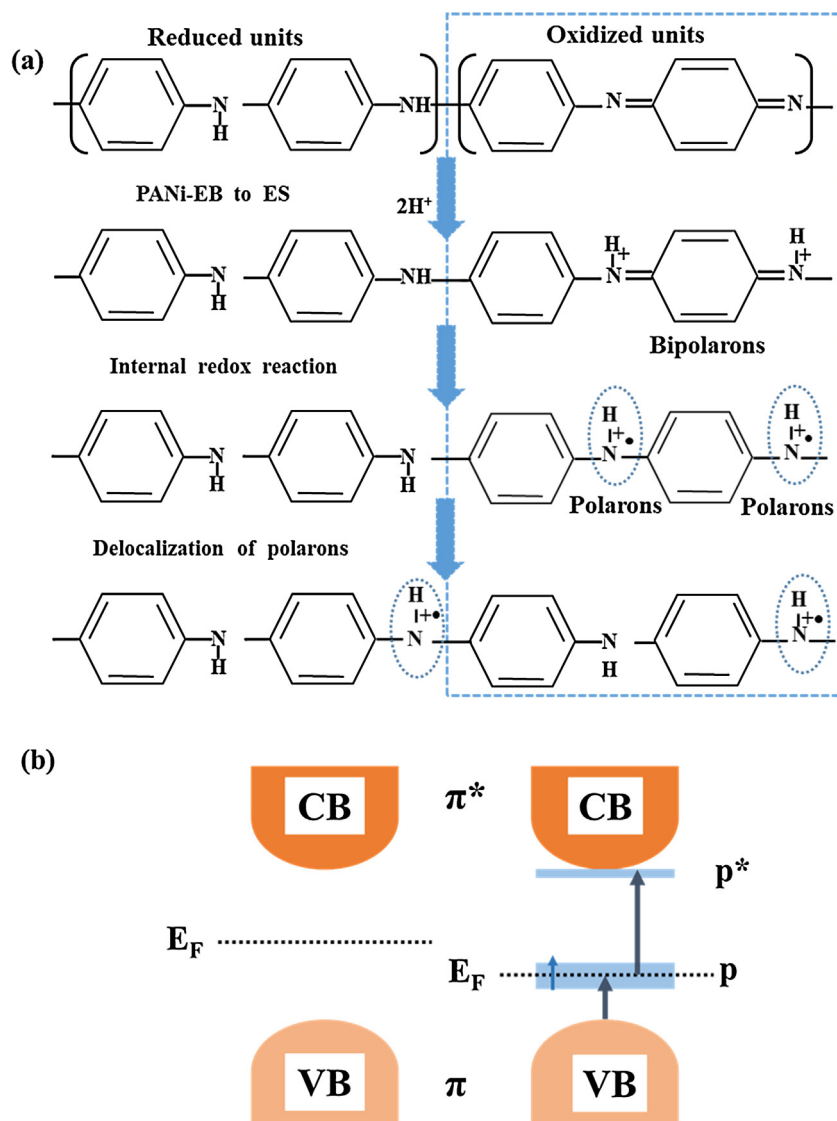


Fig. 1. (a) The polaron formation and conversion in PANi-ES. (b) the schematic energy band structure of PANi-ES with asymmetric upper (p^*) and lower polaron bands (p). CB (π^*) and VB (π) represent of conduction band and valence band, respectively.

Even the conductivity of PANi could be greatly increased by the doping of acid that increases the electrochemical performance, the inferior mechanical stability due to swelling, shrinkage or crack and the degradation due to side reactions during the polymerization and electrochemical test will restrict its application in supercapacitors. As mentioned above, PANi has three different forms based on the oxidation states. Besides, there are also unwanted side products like p-benzoquinone (BQ) and hydroquinone (HQ) due to the hydrolysis. The hydrolysis is unavoidable during the polymerization, which will affect the conductivity, reversibility and stability of PANi [14,15].

Carbon materials are common supercapacitor materials with high stability but low specific capacitance [16,17]. Recently, many PANi based composites containing nanostructured carbon materials such as carbon nanotubes (CNTs), graphene and various porous carbon materials have been reported with enhanced electrochemical performance for supercapacitors. The presence of nanostructured carbonaceous materials in hybrid PANi/C electrodes can significantly enhance the stability, conductivity and the dispersibility of PANi, resulting in enhanced electrochemical performance. Graphene and CNTs are popularly used in energy storage and show excellent intrinsic electronic, structural and mechanical properties

[18,19]. Many investigations have been conducted on PANi based composite electrodes involving graphene or CNTs, which show high specific capacitance over 500 F g^{-1} and good cycling stability of around 90% capacity retention after hundreds of electrochemical cycles [7–9,20–22]. However, the syntheses of graphene normally follow the Hummer's method with complicated chemical process [8]. The resulting graphene oxide (GO) suffers from low conductivity, which needs to be reduced to reduced graphene oxide (rGO). Several works focused on functional-rGO (frGO), such as nitrophenyl-rGO and aminophenyl-rGO, which were found to further enhance the performance of PANi/frGO [8]. Besides, CNTs are usually obtained through the chemical vapor deposition and surfactant of dopant is introduced to modify the surface properties of CNTs to facilitate the combination with PANi [20]. Most of these works were time consuming or cost ineffective due to complicated chemical process and prohibitive cost of graphene and CNTs, which could hamper the commercial application.

In this paper, we adopt a facile electrochemical co-deposition method to achieve freestanding PANi/CB electrode on porous graphite substrates, using low cost precursors. The potentialdynamic polymerization is employed because it can produce binder-free electrode with uniform porous-network in short reaction time with a

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