

CAPACITIVE PROPERTIES OF QUINONE-GRAFTED CARBONS IN SALT AQUEOUS ELECTROLYTES

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Abstract

Various strategies based on pseudo-capacitive or faradaic contributions have been reported to enhance the capacitance of carbon/carbon capacitors in aqueous media. Such contributions were obtained by i) adding electrochemically active species such as quinones [1] and alkali metal iodides [2] in the electrolyte, ii) using carbon electrode materials undergoing redox reactions resulting from naturally occurring surface functionalities, hydrogen storage and chemically/electrochemically grafted active molecules such as quinone derivatives [3]. The later modification is generally realized by electrochemical or chemical [4] reduction of diazonium cations. The pH of the applied electrolyte has a significant influence on the possible redox mechanisms involving proton and electron transfer, and consequently on the capacitance properties of quinone-modified carbons. Surface functionalization enables an increase of the specific capacitance of the modified electrode even by a factor of two compared to the pristine carbon electrode in acid and basic aqueous electrolytes. However, the highly corrosive character of H_2SO_4 in presence of most metallic current collectors imposes using less corrosive media, such as neutral electrolytes.

In this work, the electrochemical response of carbon Black Pearl BP2000 grafted with phenanthrenequinone molecules (BP-PQ) is studied in 0.4 mol L^{-1} phosphate ($\text{pH}=7.2$) and 0.4 mol L^{-1} potassium hydrogen phthalate ($\text{pH}=4.0$) buffer solutions. As a result of grafting PQ molecules, the specific capacitance increases from 81 F g^{-1} for Black Pearls up to 225 F g^{-1} for Black Pearls-PQ and from 107 F g^{-1} for Black Pearls up to 164 F g^{-1} for Black Pearls-PQ in potassium hydrogen phthalate buffer and phosphate buffer, respectively. Reversible redox peaks are observed in the two buffer solutions, but the reversibility of the redox reaction is smaller in phosphate buffer as compared to potassium hydrogen phthalate. The peak-to-peak separation between anodic and cathodic peaks (ΔE_p) evaluated from CVs increases with the electrolyte pH, indicating that the overall process is kinetically much slower in the presence of phosphate buffer. At higher pH (phosphate buffer), the peaks current ratio (I_a/I_c) for peaks located at ca. 0.3 and 0 V was found to be greater than unity, which indicates possible kinetic disturbance in the electrode process, contrary to potassium hydrogen phthalate buffer.

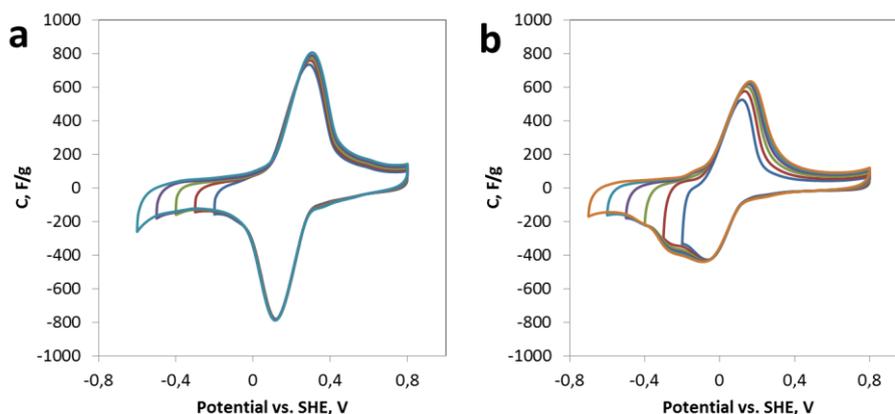


Figure 1. Cyclic voltammograms of BP-PQ in (a) 0.4 mol L^{-1} potassium hydrogen phthalate buffer ($\text{pH} = 4.0$), (b) 0.4 mol L^{-1} phosphate buffer ($\text{pH} = 7.2$).

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