



Simpler and greener grafting method for improving the stability of anthraquinone-modified carbon electrode in alkaline media



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ABSTRACT

Black Pearls, a high surface carbon black, was modified by surface grafting of anthraquinone molecules. Firstly, the modification involved the adsorption of 2-aminoanthraquinone on the porous carbon powder. Secondly, the resulting powder was used to form a composite film electrode by mixing with a carbon additive and a binder. Thirdly, grafting of anthraquinone molecules was either electrochemically induced or left to occur spontaneously in aqueous acidic media. Overall, this procedure requires a much smaller volume of solvents and is simpler than the traditional method, which involves numerous washing steps with several organic solvents to remove unreacted species. The resulting anthraquinone modified electrodes, when tested in aqueous 1 M KOH, delivered a comparable specific capacitance and found to be more stable upon charge/discharge cycling than electrodes prepared by the traditional method. Our new electrochemical method allowed to improve the grafting efficiency and to decrease the amount of non-covalently adsorbed anthraquinone molecules, which are desorbed upon cycling.

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1. Introduction

Quinones are molecules that play an important role in biological systems, in chemical synthesis, as drugs and in electrochemical systems [1–4]. Applications in the latter systems obviously stem from their rich redox chemistry, which has been studied in great details as a function of pH [2,3,5]. These studies are extremely relevant for electrochemical applications that require working in the whole range of pH including very acidic and alkaline electrolytes [5]. Accordingly, quinones have been used for the development of sensors [6,7], oxygen reduction catalyst [8], electrochemical production of H₂O₂ [9–15], polymer-air battery [16] and electrochemical capacitors [17–24]. For these electrochemical systems, several methods have been investigated for the modification of surfaces with quinones. These methods include impregnation in a porous material [18], grafting to polymer backbone [16], electrodeposition [25] and spontaneous modification [22] by reduction of diazonium ions. Furthermore, various supports such as glassy carbon electrode [26], carbon fabrics [19,27,28], highly oriented

pyrolytic graphite [13,29] and porous carbons [20,22–24] were used for the immobilization of quinone molecules.

In electrochemical capacitors, quinone-modified carbons have demonstrated promising electrochemical properties for use as active electrode material [17,19–24,27,28]. Modification of the carbon materials with quinone have led to a significant increase of the specific capacitance of the carbon due to the contribution of the redox reaction of the immobilized quinone molecules which involves typically one electron per carbonyl unit as illustrated in Scheme 1 for anthraquinone (AQ) in acidic electrolyte.

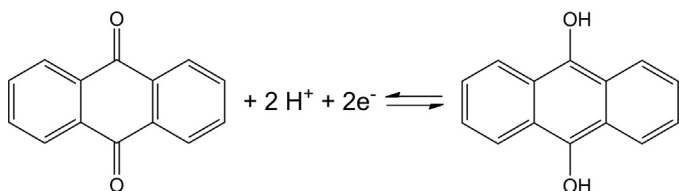
So far the electrolyte of choice for electrochemical capacitor applications of quinone-modified carbon electrodes has been an aqueous H₂SO₄ solution [17,19,20,22–24]. For example, anthraquinone-modified carbon electrodes display a relatively good stability in acidic media [22,23]. On the other hand, the number of studies describing the use of alkaline electrolyte in energy conversion systems is more limited [5,16]. The redox reaction of AQ in alkaline electrolyte is illustrated in Scheme 2 and involves the transfer of two electrons and the charge compensation being done by water molecules or cationic species (M⁺)[3] (Scheme 2).

Here, we report a new procedure for the chemical grafting of anthraquinone molecules at the surface of Black Pearls (BP) powder and the electrochemical behavior of anthraquinone-modified Black Pearls carbon electrode in alkaline electrolyte with an emphasis on its stability upon cycling. The motivation of this work stems from

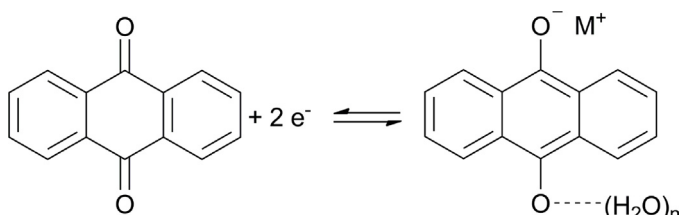
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Scheme 1. Redox reaction of anthraquinone in acidic media.



Scheme 2. Redox reaction of anthraquinone in alkaline media where the charges of the dianionic reduced form is compensated by hydrogen bonds and/or alkaline cations (eg. K^+ or Na^+).

the possible use of a quinone-modified carbon electrode as negative electrode in hybrid electrochemical capacitor based on alkaline electrolyte with nickel oxide positive electrode [30,31]. Our initial results in this work indicated a continuous decrease of the intensity of the redox waves associated to the anthraquinone molecules upon potential cycling. Thereafter, UV-visible spectroscopy was used to investigate the degradation mechanism. Subsequently, approaches to develop more stable electrodes were investigated. More importantly, a simpler and “greener” synthesis method for modification of carbon is proposed in this work. Indeed, the modification of activated carbon powder by reduction of in-situ generated diazonium ions requires several filtration steps using significant volume of organic solvents in order to remove unreacted molecules and loosely adsorbed species. This novel modification method requires much smaller volumes of solvents compared to the commonly used method in our laboratory [22]. It involves the formation of a carbon composite electrode, which has been previously loaded with the anthraquinone precursor, prior to the spontaneous or electrochemical functionalization step.

2. Experimental

2.1. Reagents

Black Pearls 2000 was obtained from the Cabot Corporation, 2-aminoanthraquinone (2-aminoAQ) (97%) and tert-butyl nitrite (90% solution in acetonitrile) were purchased from Aldrich. Unless otherwise stated, all reagents were obtained from Aldrich and were used without further purification.

2.2. Carbon modification

2.2.1. Classical procedure [32,33]

A mass of 2-aminoAQ (186 mg, 0.1 equivalent compared to carbon) was added to 150 mL of acetonitrile. The solution was kept under stirring until complete dissolution of the quinone derivative. Then, one equivalent (with respect to the quinone) of tert-butyl nitrite was added. The mixture was stirred for 30 min and 100 mg of activated carbon was added. Thereafter, every 30 min, another 1 equivalent of tert-butyl nitrite was added directly to the organic suspension, which was kept at ambient temperature for 4 h. The reaction mixture was finally vacuum filtered on a Nylon filtration membrane having a pore size diameter of 0.47 μm (Pall) and the carbon powder washed by successive aliquots of acetonitrile, DMF,

acetone and methanol (about 300 ml for each solvent) and dried under vacuum overnight at 70 °C. The resulting modified BP powder was heat treated in air at 225 °C during 1 h to remove solvents trapped in the pores of the materials.

The working electrode consists of a composite electrode prepared by mixing, in a small volume of ethanol, the modified activated carbon (40 mg), acetylene black carbon (3.75 mg), graphite (3.75 mg) and polytetrafluoroethylene (PTFE) (2.5 mg) as binder in a 80:7.5:7.5:5 wt.% ratio until a homogenized paste-like consistency was obtained. The paste was cold rolled and a small square of approximately 0.25 cm^2 in size and 1.5 mg in weight was placed in a stainless steel grid (80 mesh, 0.127 mm, Alfa Aesar) used as current collector and was pressed at 0.9 MPa. Thus, the electrode loading was 6 mg cm^{-2} and therefore technologically relevant for electrochemical capacitor devices.

2.2.2. New chemical grafting method

A mass of 2-aminoAQ (215 mg or 21.5 mg, 0.1 and 0.01 equivalent compared to carbon) was dissolved in to 150 mL of acetonitrile. After complete dissolution 100 mg of carbon BP was added and the mixture kept under stirring overnight. The solution was vacuum filtered on a Nylon filtration membrane having a pore size of 47 μm (Pall). The resulting powder was dried without washing under vacuum at 60 °C for 1 or 24 h. Then, a composite paste was prepared by mixing, in a small volume of ethanol, the 2-aminoAQ adsorbed activated carbons (40 mg), acetylene black carbon (3.75 mg), graphite (3.75 mg) and PTFE (2.5 mg) as binder in a 80:7.5:7.5:5 wt.% ratio until a homogenized paste-like consistency was obtained. The paste was cold rolled and a small square of approximately 0.25 cm^2 in size and 1.5 mg in weight was soaked in a 0.1 M H_2SO_4 solution containing 2 mM or 20 mM of NaNO_2 . After 15 min of reaction, the paste was rinsed with deionized water and dried under vacuum at 60 °C overnight. The effect of the quantity of amine (0.1 and 0.01 equivalent) and NaNO_2 (2 or 20 mM) as well as the duration of adsorption (1 or 24 hours) was evaluated.

2.2.3. New electrochemical grafting method

The composite paste containing 2-aminoAQ adsorbed BP was prepared as detailed above and an electrode was fabricated by pressing the paste on a stainless steel mesh. Prior to any experiments, the electrode is immersed in 20 mL of degassed 0.1 M H_2SO_4 electrolyte for 15 minutes and 20 mg of NaNO_2 was directly added to the solution. The grafting procedure consists in applying successively the open circuit potential ($E_{\text{OCV}} \sim 0.7 \text{ V vs. Ag/AgCl}$) and a potential E_1 more negative than the reduction potential of the anthraquinone diazonium ions ($E_{\text{reduction}} \sim \text{about } 0.3 \text{ V vs. Ag/AgCl}$). The influence of E_1 , the duration of the pulse (t_{pulse}) and the duration of the relaxation at the OCV (t_{OCV}) was studied.

2.3. Electrochemical characterization

A three-electrode configuration was used in a one-compartment cell for the electrochemical characterization of the single activated carbon electrode. The counter electrode consists of a 20 mm \times 60 mm piece of carbon paper (Spectracarb 2050A-6060) placed at 20 mm of the working electrode. To evaluate the electrode stability, all potentials are referred to Hg/HgO (in 1 M KOH) reference electrode placed at 5 mm of the working electrode. Degassed aqueous 1 M KOH was used as electrolyte. Prior to any measurement, the working electrode was dipped in the electrolyte for 15 min in order to allow the electrolyte to impregnate the electrode porosity. Cyclic voltammetry was carried out using a VMP3 multipotentiostat (BioLogic) and the electrochemical setups were controlled with EC-Lab software.

For pristine carbon electrodes the capacitance is expressed in F g^{-1} by integrating the voltammetric charge (C g^{-1}) in the cyclic

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