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A comparative study on electrogeneration of hydrogen peroxide through oxygen reduction over various plasma-treated graphite electrodes

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ABSTRACT

The present study reports a simple modified method that enhanced the surface characteristics of graphite electrode towards greater hydrogen peroxide production. In this method, the plasmas of various gases vis. air, argon and nitrogen were used in alternating current glow discharge plasma (AC-GDP) technique to treat graphite surface. The morphology, microstructure, roughness, disorder degree, surface chemical composition and carbon state of the graphite samples were determined before and after plasma treatments. The formation of 3D nanostructures and enhancement in surface characteristics resulted in effective H_2O_2 generation over the plasma-treated electrodes. Particularly, air plasma-treated electrode showed higher efficiencies by producing 119 μmol/L H_2O_2, owing to etching effect of oxygen-content and improved wettability. Furthermore, the pH, applied current and electrolyte concentration had distinct effects on the H_2O_2 yield. The results indicated that AC-GDP using air plasma can be a promising technique for developing high efficient graphite electrodes for facile electro-generation of hydrogen peroxide.

1. Introduction

Hydrogen peroxide (H_2O_2) is a well-known oxidant for various chemical manufacturing. At industrial scale, H_2O_2 is produced by an indirect batch procedure which is known as anthraquinone process. This multistep process involves consecutive anthraquinone hydrogenation and oxidation and finally, the extraction of H_2O_2 which is not an energy-efficient method. Additionally, storing, handling and transporting bulk H_2O_2 is unsafe and difficult. In light of this, the in situ production and utilization of H_2O_2 is found to be more attractive for various applications. Cathodic reduction of dissolved oxygen is a promising ecofriendly method for continues in situ production of H_2O_2. Hence, cathode material has prominent effects on the H_2O_2 electrogeneration yield [1]. Carbonaceous materials are of the most utilized materials for fabrication of cathodes in electrochemical cells. From literature, graphite felt [2], graphene-carbon nanofiber [3], N-doped porous carbon [4], metal–carbon composite [5], and activated carbon/carbon nanotubes immobilized onto graphite surface [6] are number of the studied cases. Evidently, graphite is a subject of great interest in virtue of being highly conductive, stable, non-toxic and commercially available. Despite the large number of electrochemical investigations, attaining highly efficient graphitic electrodes, for two-electron-reduction of oxygen to H_2O_2, in terms of productivity, reaction kinetics and facial production method is still a focus of experimentation and controversy. Graphite, owing to its lateral grain size (L_a), occurs in a wide verity of products, each differing in properties from the rest. In addition, the structural defects, imperfections and surface impurities also have to be considered [7].

So far, many efforts have been made to enhance graphite physico-chemical properties by various approaches [8]. Surface modification though doping with other elements or compounds

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and inducing defects/functional groups on the graphite surface, in order to develop more active reaction sites and enhance the wettability are amongst the widely studied objectives. Recently, plasma-based techniques have been employed to modify the surface of various materials, leaving the bulk material unchanged [9]. The non-thermal plasmas are particularly of interest due to the low energy consumption and current condition (<1 A) and capability to empower reactions under relatively lower temperatures. Most recent research has concentrated on glow discharge plasma (GDP) methodology which is a practically simple and efficient tool for selective alteration on the target material via the application of a specific gas carrier. Herein, the energetic electrons and/or species are created via the activation of the applied gas which initiate the preferred chemical reactions under energy-saving condition. Hence, in the present study, air, nitrogen and argon plasmas were investigated in GPD to modify distinctive properties in graphite to develop higher electrochemical efficacies. With this intention, a number of nanostructured graphite electrodes were prepared using GDP method. To our best knowledge, there is no reported study on the application of alternating current (AC) GDP treatment of graphite electrodes. Being safe and energy-efficient, AC made the treatment procedure practical, feasible, and much easier. The changes on the surface of the treated samples were identified using various analysing methods and their efficiency were assessed and compared in terms of H_2O_2 generation. Furthermore, the effects of the main operating condition were assessed on the H_2O_2 electroproduction efficacy. The main objective of the current study was to introduce a facile method to improve graphite characteristics as cathodic material for enhanced two-electron-reduction of dissolved oxygen to H_2O_2.

2. Experimental

2.1. Materials

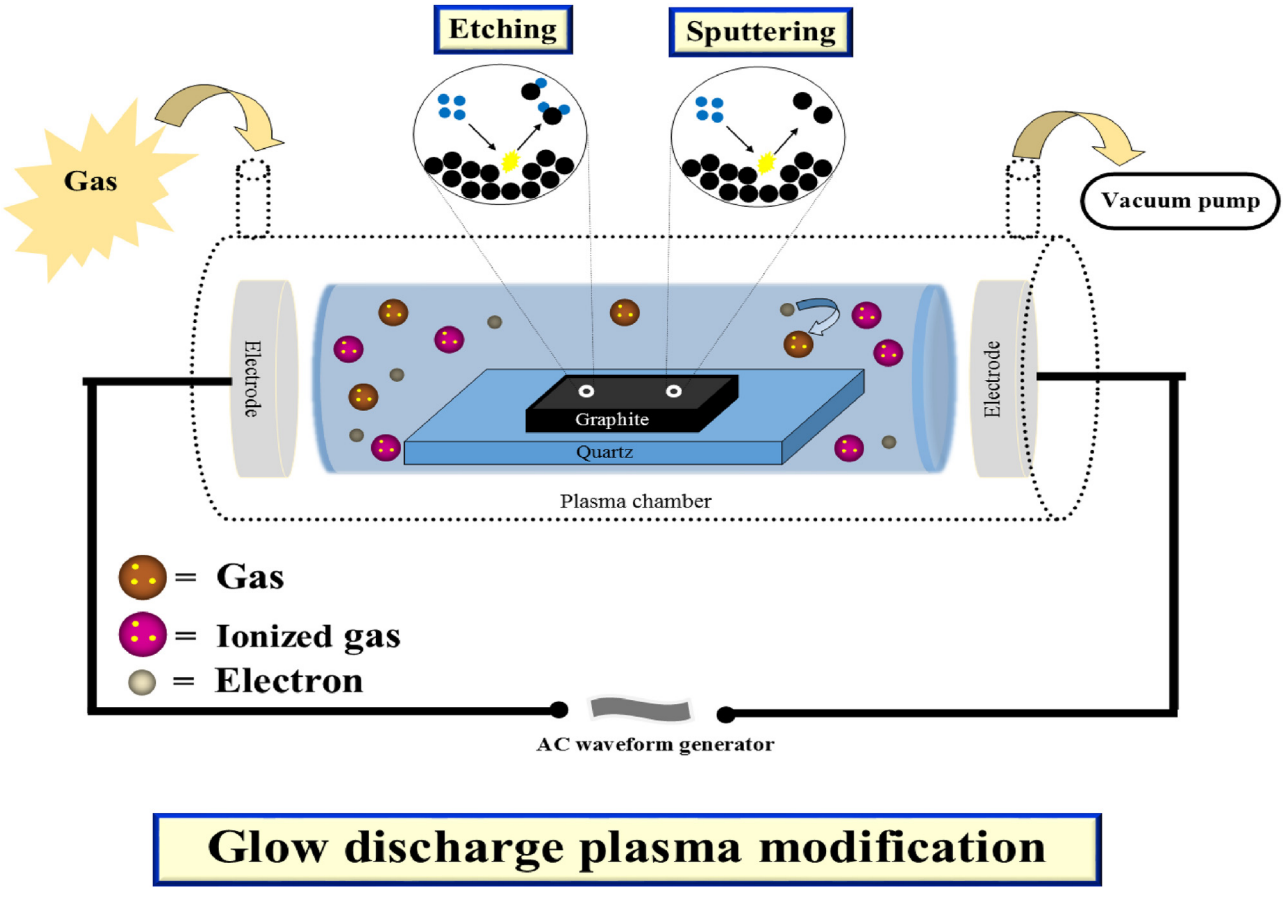
Analytical grade sulfuric acid, sodium hydroxide, sodium sulfate, acetone, potassium chloride, and potassium hexacyanoferrate were purchased from Merck (Germany). Industrial grade graphite sheet was purchased from Tabriz Zoghal Co. (Iran).

2.2. Plasma modification procedure

The following procedure was carried out to prepare the plasma treated graphite (PTG) samples: A graphite sheet of $1 \times 5\ cm^2$ was prepared, acetone-washed and dried at 100 °C for 24 h. Subsequently, the graphite sample was subjected to AC glow discharge plasma to generate nanostructured surface. For this purpose, the graphite sheet was sited on a quartz plate in a glow discharge plasma reactor which was consisted of a Pyrex tube sealed with two aluminum bonnets on both sides (D = 5 cm and L = 50 cm). A high voltage AC power supply directed by the aluminum bonnets provided an AC voltage of 12–18 kHz frequencies. Finally, the chamber was degassed to 10^{-2} torr and predesignated gas was led into the reactor to adjust the pressure to 0.2 torr. Each plasma modification procedure took 45 min. The schematic illustration of the AC-GDP treatment procedure is provided as Scheme 1.

2.3. Characterization of the PTG samples

Atomic force microscopy (AFM, with a scanning area of $8\ \mu m \times 8\ \mu m$, Nanosurf Mobile S, Nanosurf, Swiss), Raman



Scheme 1. Schematic illustration of the preparation of nanostructured graphite samples by treatment under air, N_2 and Ar plasmas.