Alternative method to obtain the Tafel plot for simple electrode reactions using batch injection analysis coupled with multiple-pulse amperometric detection

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ABSTRACT

The application of the batch injection analysis coupled with multiple-pulse amperometric (BIA-MPA) detection is proposed as an alternative method to obtain the kinetic parameters for simple redox reactions (e.g., $Fe(CN)_6^{3-/4-}$, $Ru(NH_3)_6^{3+/2+}$ and $Fe(H_2O)_6^{3+/2+}$) from analysis of the Tafel plot (TP). The kinetic studies were performed to permit the 'in situ' surface characterisation of thin, boron-doped diamond (BDD) films that exhibit a high conductivity. The evaluation of the apparent equilibrium electrode potential (E_{eq}) and the kinetic parameters comprising the exchange current (i_0), the anodic and cathodic charge-transfer coefficients (α_a and α_c), as well as the apparent heterogeneous rate constant (k^o), were evaluated through the analysis of the Tafel plots. According to the experimental values of k^o, the degree of reversibility strongly depends on the particular redox reaction occurring on the surface of BDD. The k^o values obtained for the different redox reactions from analysis of the Tafel plot were compared with those obtained using the electrochemical impedance spectroscopy (EIS) technique. A good agreement for the kinetic parameters determined for the different redox reactions using different experimental approaches (TP and EIS) was obtained through the statistical analysis based on the standard deviation obtained for the different k^o values, after five different measurements for each redox reaction. The use of the proposed alternative method for the study of simple electrode reactions can be very helpful because these reactions are often used as a 'probe' for the 'in situ' surface characterisation of new electrode materials developed for different purposes.

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1. Introduction

The batch injection analysis (BIA) system was originally proposed by Wang and Taha in 1991 [1] to obtain a simple and fast technique to be coupled with electrochemical detection methods. In this case, the solution containing the analyte can be injected directly onto the surface of the working electrode housed in a wall-jet electrochemical cell, whereby the solution can be stirred using an appropriate electrolyte volume. The theoretical aspects regarding the flow and current profiles for the BIA system during the amperometric and voltammetric detections were previously addressed by Brett and co-workers [2]. Despite the well-known advantages concerning the use of the BIA system, this technique has not been extensively explored in the last decades for the development of new electroanalytical methods [3].

Recently, the BIA system coupled to multiple-pulse amperometric (MPA) detection has been successfully used in several electroanalytical applications, such as the cases involving the simultaneous determination of two or more organic analytes [4–9] and the use of the internal standard to improve the accuracy of the injection step [10]. Using MPA detection, various pulse potentials can be applied at the working electrode in a short time interval,

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thus resulting in a fast acquisition of several amperograms. In addition to the electroanalytical applications, in principle, the BIA-MPA system can also be used for other purposes, such as in the study of simple (e.g., outer-sphere) redox reactions carried out to provide the 'in situ' surface characterisation of new electrode materials.

Electrodes composed of thin, polycrystalline, boron-doped diamond (BDD) films (e.g., 1–10 μm), heavily doped with boron (e.g., 1,000–10,000 ppm), exhibit metallic conductivities (e.g., $\rho \leq 0.01\ \Omega$ cm) and show a very low capacitive background current for a wide potential window of up to 3 V in aqueous media [11–15]. As a result, BDD electrodes are quite useful in electroanalytical applications, permitting the detection of small concentrations of several different analytes [4–6].

During the fabrication of BDDs using the chemical vapour deposition (CVD) method, the boron dopant is added to the source gas mixture (e.g., 0.3–1.0% CH_4 in H_2), often in the form of diborane (B_2H_6), at concentrations ranging from 1,000 to 10,000 ppm [11,15]. Therefore, depending on the specific experimental fabrication conditions, thin BDD films exhibiting different surface and electronic properties can be obtained [12,14,15].

The characterisation of BDD electrodes using different experimental techniques (e.g., cyclic voltammetric (CV), electrochemical impedance spectroscopy (EIS), conductive probe atomic force microscopy (CP-AFM), scanning electrochemical microscopy (SECM), etc.) has been reported in the literature [11–14]. However, there were no previous attempts that utilise the 'in situ' surface characterisation of thin, heavily doped BDD films using the BIA-MPA system.

It is well-known that the kinetic parameters (e.g., the standard heterogeneous rate constant (k^o) and charge-transfer coefficients (α_a and α_c)) for several types of electrode reactions can be evaluated from the experimental polarisation curves by means of analysis of the corresponding Tafel plots (E vs. $\log(i)$). Therefore, different experimental techniques have been employed to obtain the Tafel plot, as is the case of point-by-point potentiostatic polarisation (stationary method), linear sweep voltammetry at low scan rates (quasi-stationary method), voltammetry under hydrodynamic conditions using the rotating disc electrode, electrochemical impedance spectroscopy, etc. [16–18].

The kinetic parameters for simple electrode reactions can be evaluated from the Tafel plot according to the following equation [16–18]:

$$\log(i) = \log(i_0) + \frac{\alpha n F}{2.303 R T}\eta, \qquad (1)$$

where i (in A) is the faradaic current, i_0 (in A) is the exchange current, n is the number of electrons, α is the charge-transfer coefficient, and η (in V) is the overpotential ($\eta = E - E_{eq}$).

Taking into account the above considerations, the use of the BIA-MPA system as an alternative experimental approach to obtain the Tafel plot for simple electrode reactions using a polycrystalline, boron-doped diamond (BDD) electrode with a doping level of 8,000 ppm was proposed. When the MPA detection is associated with BIA, some advantages for obtaining the Tafel plot, such as the great reproducibility of the experimental findings, can be observed.

It is difficult to determine the heterogeneous rate constant (k^o) in the case of BDD electrodes because of their polycrystalline structure and local heterogeneous electric/electrochemical properties [11]. In fact, the electronic properties of the BDD electrode depend of several factors [11–15]: (i) dopant concentration and the resulting density of states (DOS); (ii) structural defects; (iii) non-diamond carbon impurities (e.g., sp^2 inclusions); (iv) crystallographic orientation; (v) surface termination (H, O), and (vi) fraction of grain boundaries.
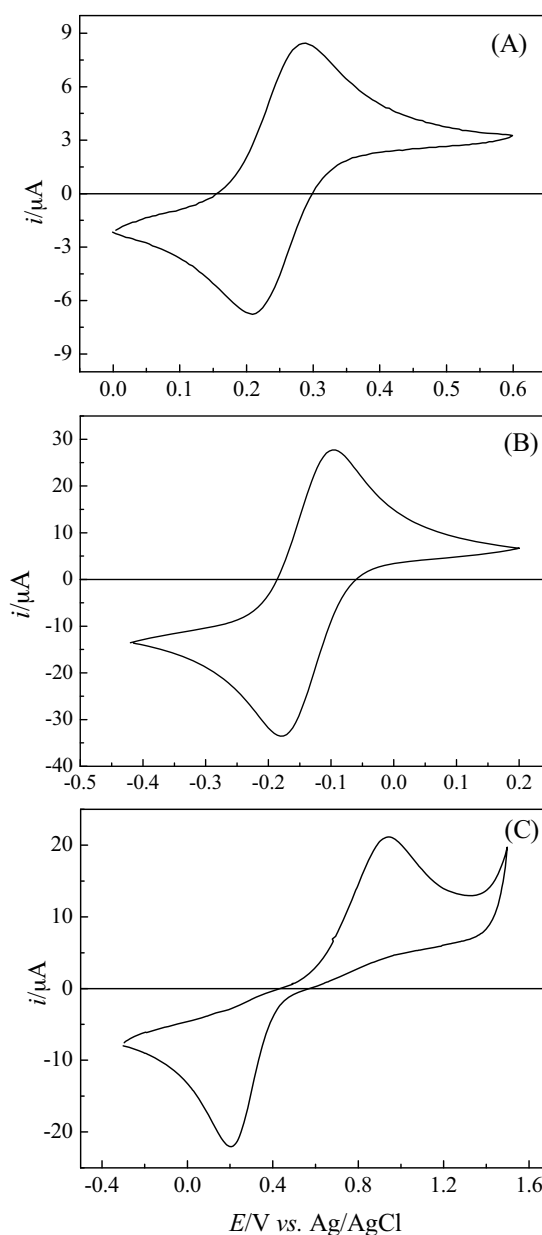

Fig. 1. Cyclic voltammograms obtained for the simple charge-transfer reactions occurring on the BBD electrode: (A) $Fe(CN)_6^{3-/4-}$, (B) $Ru(NH_3)^{3+/2+}$, and (C) $Fe(H_2O)_6^{3+/2+}$ Conditions: [redox couple] = 1.0 mmol L^{-1} in 0.1 mol L^{-1} KCl; v = 50 mV s^{-1} and T = 25 °C.

For instance, relatively slow kinetics have been reported for BDD electrodes even for outer-sphere redox couples, such as $Ru(NH_3)_6^{3+/2+}$ and $IrCl_6^{2-/3-}$, whose heterogeneous rate constants should be largely independent of the nature of the electrode surface [11]. In addition, Becker et al. [19] studied thin BDD films with doping levels between 200 and 6000 ppm using cyclic voltammetry and electrochemical impedance spectroscopy. They observed large deviations from reversible charge transfers for some well-known reactions (e.g., $Fe(CN)_6^{3-/4-}$ and $Ru(NH_3)^{3+/2+}$), commonly considered to be outer-sphere reactions, on electrodes like Pt. These experimental findings led to the suggestion of a geometric surface-blocking model, where only limited areas of the BDD film are believed to be electrically conducting; that is, the rate