

Anthraquinone-2-Carboxylic-Allyl Ester as a New Electrocatalyst for Dioxygen Reduction to Produce H₂O₂

Trevor Wilson¹, Jiujun Zhang^{2,*}, Colin C. Oloman¹ and Danial D. M. Wayner³

¹Department of Chemical Engineering, The University of British Columbia, Vancouver, British Columbia, Canada V6T 1Z4

²Institute for Fuel Cell Innovation, National Research Council Canada, Vancouver, British Columbia, Canada V6T 1W5

³Steele Institute for Molecular Sciences, National Research Council Canada, Ottawa, Ontario, Canada, K1A 0R6

*E-mail: jiujun.zhang@nrc.gc.ca

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The irreversibly adsorbed anthraquinone-2-carboxylic-allyl ester (abbreviated as ACAE) on a graphite electrode displays strong electrocatalytical activity for the two-electron reduction of oxygen to form hydrogen peroxide. The surface electrochemistry of ACAE was examined by cyclic voltammetry. A two-electron, two-proton electrochemical redox process of the quinone group in the ACAE molecule was identified. A rotating disk electrode method was used to obtain the kinetic parameters of the electrocatalyzed reduction of oxygen. The high selectivity of ACAE for the two-electron reduction of oxygen in pH<7 aqueous solution was demonstrated. The possible application of ACAE in H₂O₂ production is also explored in this paper.

Keywords: Oxygen reduction, Electro-catalysis, Anthraquinone-2-carboxylic-allyl ester, Graphite electrode, Hydrogen peroxide production

1. INTRODUCTION

Electrochemical production of hydrogen peroxide by the reduction of oxygen on carbon electrodes has been studied for many years [1-8]. In recent years, attention has been given to the electrocatalytical aspect of this process [8-11].

Various metal-complexes have been found to be effective electro-catalysts for dioxygen four-electron reduction to H₂O, a reaction which can be potentially used in fuel cells [12-17]. However, our interest here is in the two-electron reduction from O₂ to H₂O₂ for the purpose of H₂O₂ production. Our experiments with several metal-phthalocyanide complex coated graphite electrodes in O₂ saturated

aqueous solution have shown poor efficiency for H_2O_2 production, that is believed to be caused by the decomposition of the product H_2O_2 to H_2O on the catalyst metal centers [8]. In recent years, the search has been shifted from metal-complex catalysts to anthraquinone-like organic compound [18-22]. In this paper, we are reporting a newly synthesized electrocatalyst in our laboratory, anthraquinone-2-carboxylic-allyl ester (abbreviated as ACAE), which can strongly adsorb on the graphite electrode, and catalyze the two-electron reduction of oxygen to produce H_2O_2 with high current efficiency.

The electrocatalytic activity of quinone-like compounds toward the oxygen reduction has been studied widely [8-11] and the 9,10-anthraquinone derivatives have been reported to be effective catalysts for the electrochemical reduction of O_2 to H_2O_2 on an illuminated semiconductive electrode [11], and the modified glass carbon electrodes [23, 24]. As reported here, the surface electrochemistry of ACAE on a graphite electrode was investigated and a two-electron, two-proton surface process was identified. A rotating disk electrode coated with ACAE was then used to examine the kinetics of the electrocatalytic reduction of oxygen to hydrogen peroxide.

2. EXPERIMENTAL PART

2.1. Reagents and solutions

The anthraquinone-2-carboxylic-allyl ester (Figure 1) was synthesized and purified according to the following procedure: Anthraquinone-2-carboxylic acid (Aldrich, 4g, 16 mmol) was dissolved in 50 ml of thionyl chloride and refluxed in an oil bath for three hours. Excess thionyl chloride was removed by distillation and the yellow-green solid was dried under vacuum at room temperature for 30 minutes. The acid chloride was dissolved in 50 ml of pyridine and cooled to 0°C . Allyl alcohol (1.2 equivalents) was added dropwise and the solution was stirred at 0°C for 90 minutes. Once the reaction subsided, excess pyridine was distilled off and the light yellow product obtained was dried under vacuum then recrystallized from petroleum ether. The product was characterized by FTIR and confirmed that its chemical structure is as shown in Figure 1. Other reagent-grade chemicals were used without further purification. Water was purified by double distillation with KMnO_4 .

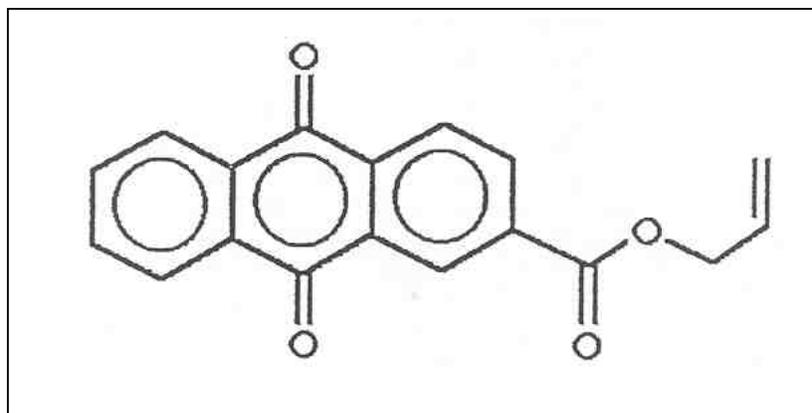


Figure 1. Structure of anthraquinone-2- carboxylic-allyl ester (abbreviated as ACAE).

The solution pH was adjusted with 0.1 M solution of CH₃COOH/CH₃COONa/NaOH, and 0.1M Na₂SO₄ was used as supporting electrolyte. Pure nitrogen gas (99.9%) was used to remove dissolved oxygen in the cyclic voltammetric experiments. In O₂ reduction experiments, pure O₂ (99.9%) gas was bubbled through the testing solution for 30 minutes before recording data.

2.2. Electrode preparation

The pyrolytic graphite (BPG, Union Carbide) disk electrode was sealed to a stainless steel shaft with polyolefin heat-shrinkable tubing. The electrode was mounted with the basal plane of the graphite exposed, and polished with 0.3 μm alumina powder, sonicated in water for 5 minutes, then rinsed with acetone and water before each experiment. The area of the electrode, 0.14 cm², was calibrated using a solution of 1x10⁻³ M K₃[Fe(CN)₆]. In the long-term H₂O₂ production experiments, an electrode of area of 0.79 cm² was used. The electrodes were modified by soaking a freshly polished electrode in a DMF solution saturated with ACAE for 3-30s, then washed with water and transferred into the testing solution to record electrodynamic data.

A platinum plate was used as a counter electrode, and a saturated calomel electrode was employed as the reference electrode.

2.3. Apparatus

Electrochemical measurements were performed with a conventional three-compartment cell and carried out with an RDE3 potentiostat, an electrode rotator (Pine Instruments) and an x-y recorder.

2.4. Procedures

For calculation of the diffusion-convection-limited current at rotating disk electrodes, the following parameters were employed [16, 17]: D_{O₂} (the diffusion coefficient of O₂) = 1.7x10⁻⁵ cm² s⁻¹; kinematic viscosity of aqueous solutions = 0.01 cm² s⁻¹; concentration of O₂ in its saturated aqueous solution = 1.3x10⁻³ M.

For the measurements of the current efficiency of O₂ reduction to H₂O₂, the standard iodometric Na₂S₂O₃ titration was used to analyze the concentration of H₂O₂ produced during the long-term run.

All experiments were carried out at ambient laboratory temperature and pressure (i.e. 22°C, 101 kPa(abs)).

3. RESULTS AND DISCUSSION

3.1. Surface electrochemistry of anthraquinone-2-carboxylic-allyl ester on a graphite electrode

Figure 2 shows the surface cyclic voltammograms of a graphite electrode coated with 5.1x10⁻¹⁰ mol.cm⁻² of ACAE, recorded in a pure supporting electrolyte solution (pH=5.8, under N₂, and without

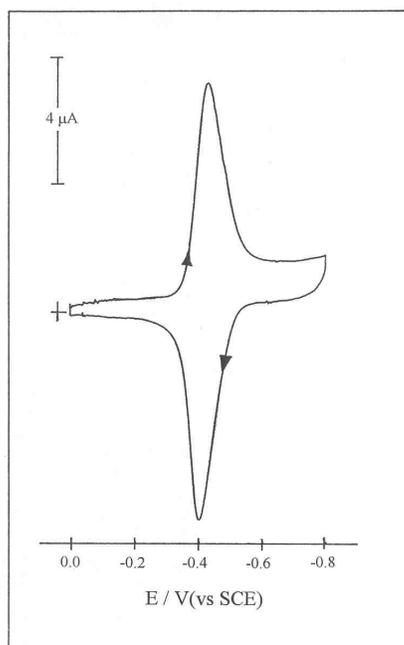


Figure 2. Cyclic voltammograms of a BPG surface adsorbed by $8.9 \times 10^{-10} \text{ mol.cm}^{-2}$ of ACAE in electrolyte: 0.1 M Na_2SO_4 + 0.1 M $\text{CH}_3\text{COOH}/\text{CH}_3\text{COONa}$ (pH 5.8). Potential scan rate: 100 mV.s^{-1}

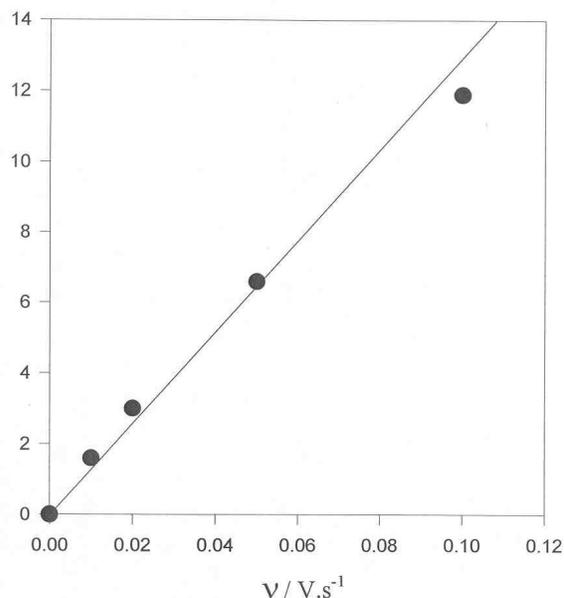


Figure 3. The scan rate dependence of the average of the anodic and cathodic peak currents on cyclic voltammograms as in Figure 2.

dissolved ACAE). A wave near -0.4 V (vs. SCE, all potentials in this paper are relative to the potential of a saturated calomel electrode) can be observed. The measurement was carried out in a pure supporting electrolyte, therefore the current response of the wave near -0.4 V only contains the contribution of adsorbed ACAE molecules. The average peak current, plotted as a function of potential scan rate, is shown in Figure 3. The linear relationship is typical of a surface confined electroactive reactant [25, 26].

Assuming that the wave near -0.4 V is a reversible electrochemical process, equation (1) can be employed to estimate the electron number involved in the current response [25, 26]:

$$i_p = (n^2 F^2 v A \Gamma^0) / (4RT) \quad (1)$$

where i_p (Amp) is the peak current, n the electron number involved in the response, F the Faraday's constant (96487 C.mol^{-1}), v the potential scan rate (V.s^{-1}), A the area of the electrode (cm^2), Γ^0 the surface concentration of the adsorbed reactant (mol.cm^{-2}), R and T the common meanings. The electron number, n can be obtained if i_p , F , v , A , Γ^0 , R and T are known. Γ^0 was obtained by measuring the area under the current response wave near -0.4 V in Figure 2, that is $5.1 \times 10^{-10} \text{ mol.cm}^{-2}$. The slope of the linear relationship between i_p and potential scan rate in Figure 3 gives a value of 2.1 for the

electron number (n), indicating a two-electron surface electrochemical process of ACAE on the graphite electrode.

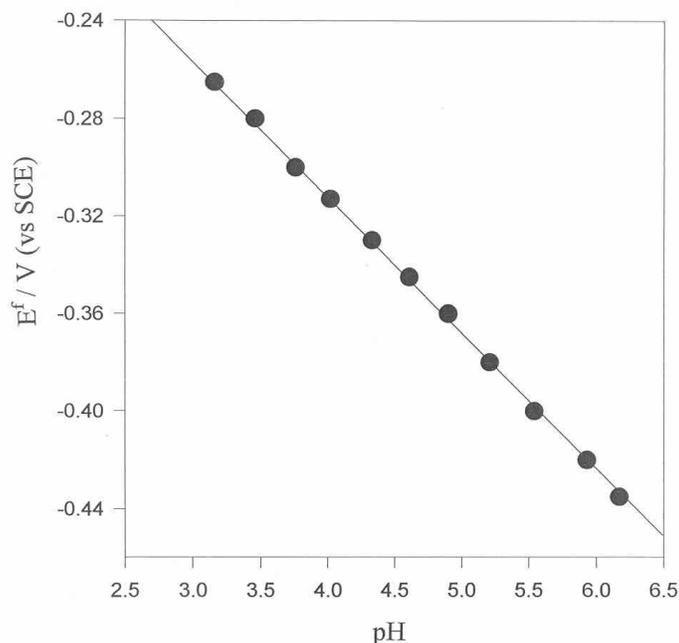
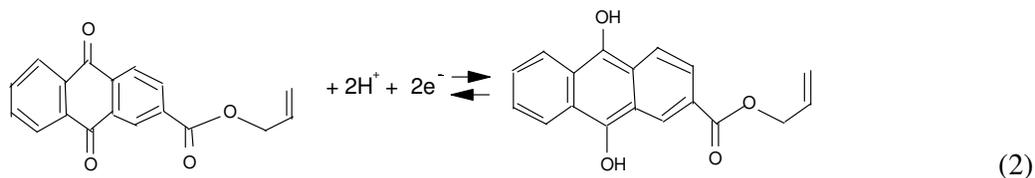


Figure 4. The pH dependence of the formal potential of the wave in Figure 2 estimated by averaging the anodic and cathodic peak potentials. Electrolytes as in Figure 2. Potential scan rate: $20 \text{ mV}\cdot\text{s}^{-1}$.

The formal potential of the electrochemical couple (wave near -0.4V in Figure 2) was estimated by averaging the anodic and cathodic peak potentials of the wave, and plotted as a function of solution pH, as shown in Figure 4. A linear relationship with a slope of $57 \text{ mV}\cdot\text{pH}^{-1}$ can be observed, indicating that the one proton per electron process is involved. For a two-electron process of the wave near -0.4V (Figure 2), indicated by Figure 3, two protons are involved. Therefore the response indicated by wave near -0.4 V (Figure 2) is a two-electron, two proton electrochemical process. This response can be assigned to a well-known redox process of the anthraquinone group [17, 27-30] in the ACAE molecule:



The attachment of adsorbed ACAE coating on the graphite electrode is stable. The coated electrode can be scanned between 0 and -0.8 V in a pH 5.6 solution for 4 hours without apparent decrease in the magnitude of the peak current of the wave near -0.4V .

3.2. Electrocatalytic activity of adsorbed ACAE toward the reduction of O_2 to H_2O_2

The ACAE coated graphite electrode was examined in an oxygen saturated solution (under oxygen at 101 kPa(abs)) by cyclic voltammetry, with typical results as shown in Figure 5B.

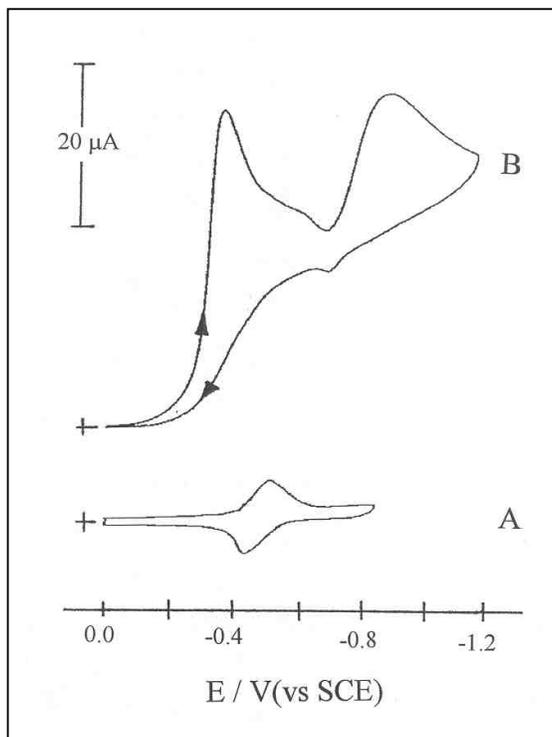


Figure 5. Cyclic voltammograms of a BPG electrode coated with 9.0×10^{-10} mol.cm⁻² of ACAE in pure supporting electrolyte (a), and 1.3×10^{-3} M of O_2 (b). Supporting electrolyte as in Figure 2 (pH 5.6). Potential scan rate: $10 \text{ mV} \cdot \text{s}^{-1}$.

The peak near -0.45 V is believed to be a two-electron process of O_2 reduction to H_2O_2 . The second peak near -0.87 V is a two-electron process of reduction of H_2O_2 , produced during the wave at -0.45 V , to H_2O . This second reduction was confirmed by the following experiment. In the same conditions as those in Figure 5B, H_2O_2 was added into the solution, then the cyclic voltammograms were recorded. The proportional increase with added H_2O_2 in the magnitude of the peak current near -0.87 V could be observed, while the first peak current near -0.45 V remained unchanged. The second process from H_2O_2 to H_2O is not our special interest, so no further investigation was pursued here. A bare graphite electrode was also tested in the same solution as that of Figure 5B (the CV is not shown here). Two waves which are similar to Figure 5B but with poor peak separation can also be observed. However, the recorded currents for both waves are approximately half of those recorded in the presence of adsorbed ACAE, and this demonstrates the catalytic activity of ACAE. The potential position of two-electron reduction from O_2 to H_2O_2 (first wave in Figure 5B) commences near the potential where the

reduction of ACAE occurs (Figure 5A), indicating that the electrocatalytic O₂ reduction process does involve the ACAE red/ox couple.

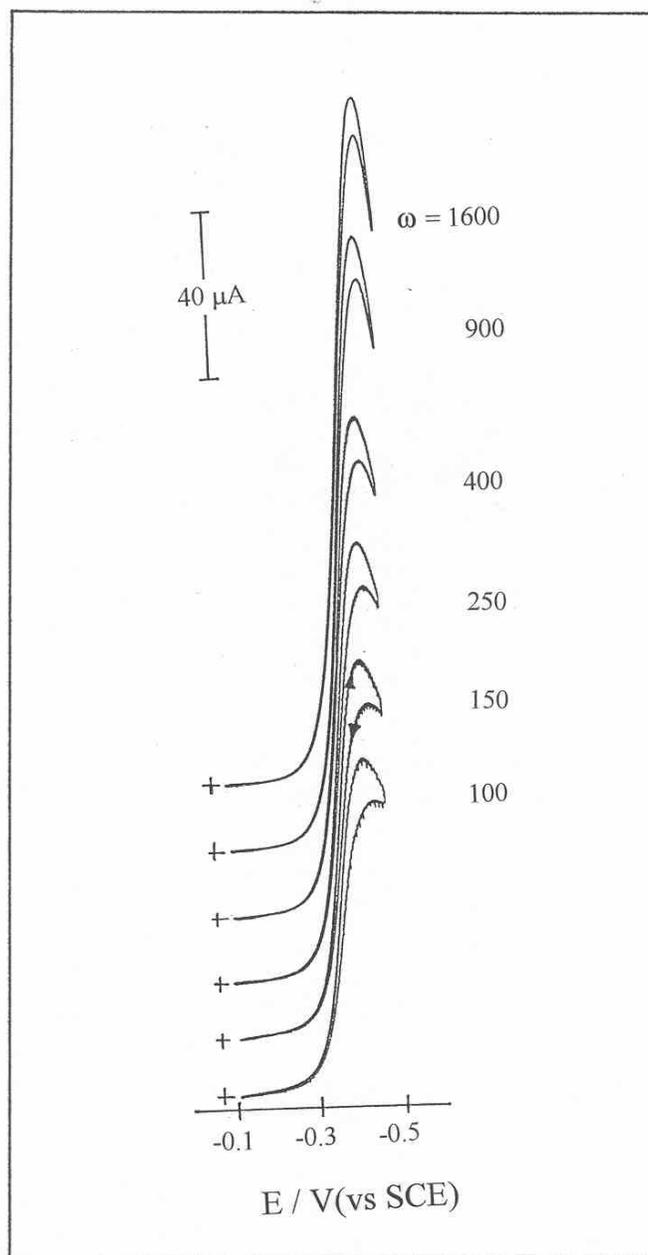


Figure 6. Electroreduction of 1.3×10^{-3} M O₂ on a rotating BPG electrode coated with 1.0×10^{-9} mol.cm⁻² of ACAE. The electrode rotating rates: (a) 100 rpm; (b) 150 rpm); (c) 250 rpm; (d) 400 rpm; (e) 900 rpm; and (f) 1600 rpm. Supporting electrolyte as in Figure 1 (pH5.6). Potential scan rate: 10 mV.s⁻¹.

For the quantitative assesment of the catalytic activity, the O₂ reduction was measured at a rotating disk electrode on which the ACAE had been irreversibly adsorbed. A set of typical current-

potential curves for the reduction of O_2 is shown in Figure 6. The current-potential curves exhibit maxima rather than true plateau currents. The decrease in the magnitude of the catalytic current after the maximum diffusion current may reflect the change in chemical nature or structure of the catalyst during the reduction of the substrate [31, 32]. The process is reversible since similar behaviour can be observed if the potential scan is reversed. The Levich and Koutecky-Levich theories [33, 34] were employed approximately here to describe quantitatively the electrocatalytic O_2 reduction. The representative Koutecky-Levich plots are shown in Figure 7.

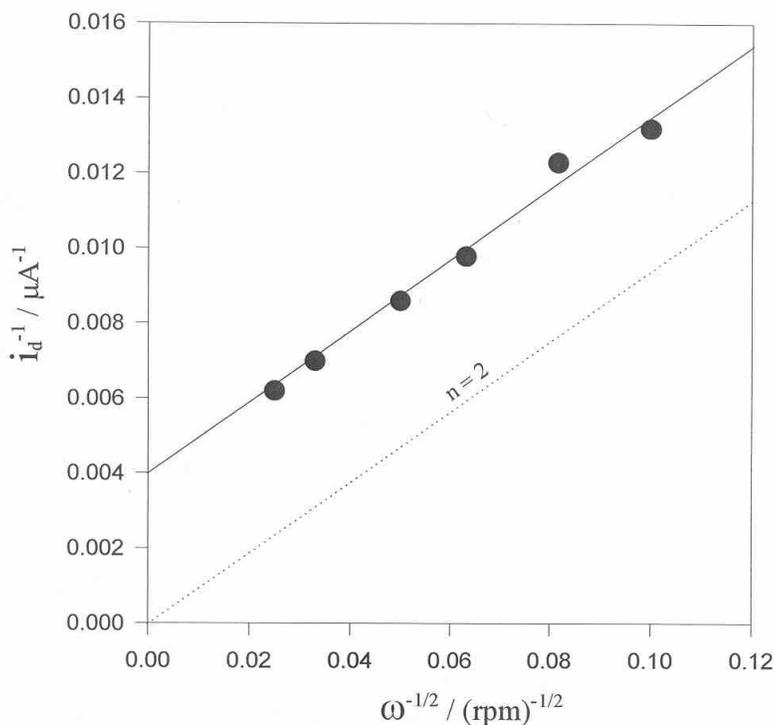


Figure 7. Koutecky-Levich plot for data in Figure 6. The dashed line corresponds to the calculated response for the diffusion-convection-controlled curve for two-electron reduction of O_2 .

The slope of the measured plot (Figure 7, solid line) is nearly parallel to that calculated (Figure 7, dashed line) for the two-electron reduction of O_2 , confirming the result of the two-electron transfer process discussed for Figure 5. The reciprocal intercept of the Koutecky-Levich plot can give a kinetic current $(i_k)_{O_2}$, which may be defined in equation (3) [25]:

$$(i_k)_{O_2} = nFAk_{O_2}\Gamma_{ACAE}C_{O_2} \quad (3)$$

where n , F , and A are the same meanings as in equation (1), k_{O_2} is the rate constant of the current-limiting reaction ($M^{-1}.s^{-1}$), Γ_{ACAE} is the surface concentration of catalyst (mol.cm^{-2}), and C_{O_2} is the bulk concentration of O_2 (mol.cm^{-3}). For example, in an O_2 saturated solution ($C_{O_2} = 1.3 \times 10^{-6} \text{ mol.cm}^{-3}$), the obtained rate constant is $8.4 \times 10^3 \text{ M}^{-1}.s^{-1}$ on an ACAE coated graphite electrode ($\Gamma_{ACAE} = 8.9 \times 10^{-10} \text{ mol.cm}^{-2}$).

Experiments with different quantities of ACAE adsorbed on the electrode showed the approximately linear dependence of $(i_k)_{O_2}$ on Γ_{ACAE} when Γ_{ACAE} is less than $1.0 \times 10^{-9} \text{ mol.cm}^{-2}$, While if the quantity of catalyst is in excess of $1.1 \times 10^{-9} \text{ mol.cm}^{-2}$, the $(i_k)_{O_2}$ becomes almost independent of Γ_{ACAE} , indicating that only those catalyst molecules in direct contact with or near the electrode surface participate in the catalytic cycle. Another factor is that at higher coverage, O_2 permeation through the adsorption layer and/or electron propagation within the layer may become a rate limiting step [35], that can also cause the $(i_k)_{O_2}$ independent behaviour.

Values of $(i_k)_{O_2}$ were obtained with various concentrations of O_2 , and a linear relationship between $(i_k)_{O_2}$ and C_{O_2} was observed in the O_2 concentration range of 1×10^{-4} - $1.3 \times 10^{-3} \text{ M}$, which confirms that equation (3) is probably a suitable model for describing the kinetic behaviour of the electrocatalytic reduction of O_2 .

3.3. A mechanistic comment

As indicated in Figure 5, the reduction of O_2 to form H_2O_2 occurs at approximately the same potential as that of the ACAE couple, providing reasonable evidence that the reduced ACAE (two-electron and two-proton process) is the actual reductant, which is confined to the electrode surface and promotes the catalytic process for O_2 reduction. The catalytic reduction of O_2 here is believed to be through an outer-sphere mechanism because it is unlikely for a non metal-complex catalyst (such as ACAE) to perform via an inner-sphere mechanism [36, 37].

For the reduction of O_2 catalyzed by surface ACAE, the first step should be the surface reduction of ACAE, as described by Equation (2), to form surface species of H_2ACAE . The followed electron transfer from H_2ACAE to O_2 can be described by Equation (4):



Since one of the products is the regenerated ACAE, the process is electrocatalytic. Actually, the mechanism may not be as simple as described by reactions (2) and (4). More detailed assessment of the mechanism would be the further work.

3.4. Long-term H_2O_2 production

A rotating graphite disk electrode (0.79 cm^2 , rotated at 400 rpm) coated with $1.1 \times 10^{-9} \text{ mol.cm}^{-2}$ of ACAE was employed in an O_2 saturated solution (under 101 kPa(abs) oxygen pressure, pH=5.6, 200 ml) to examine the long-term production of H_2O_2 . The result of a three-day run is shown in Figure 8. The current efficiency for H_2O_2 drops gradually with time from 97% to 74% as the H_2O_2 concentration increases from 0 to 3.8 mM. The same electrode but without ACAE coating was also tested in the same conditions, a low current efficiency for H_2O_2 (the concentration of H_2O_2 was from 0 to 0.4 mM) was observed, which suggests the utility of a catalyst such as ACAE for the electro-synthesis of peroxide especially in weak acidic solution.

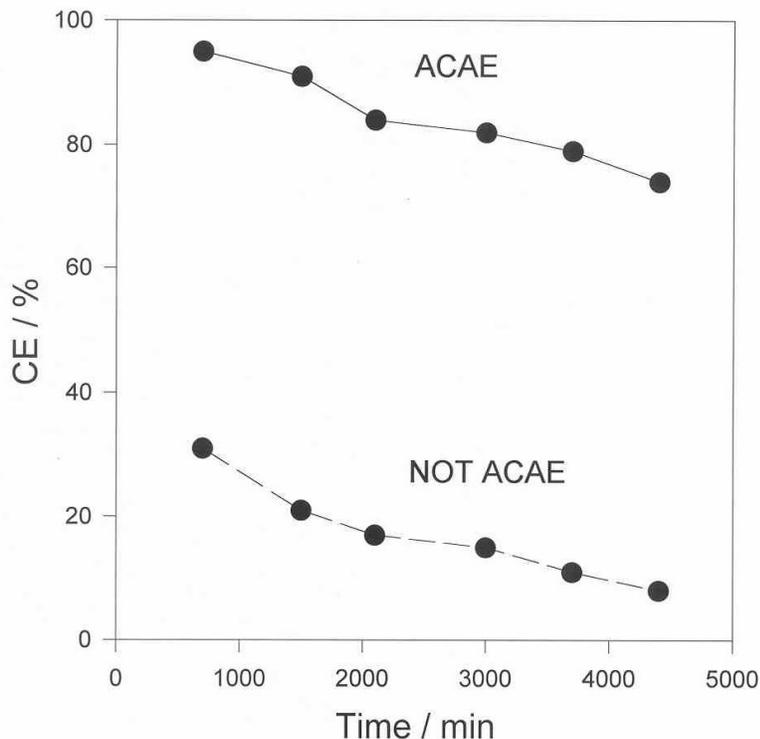


Figure 8. The current efficiencies of a three-day run. The data were obtained with a BPG electrode (0.79 cm^2) coated with $1.1 \times 10^{-9} \text{ mol.cm}^{-2}$ of ACAЕ (upper curve), and the same electrode but without catalyst (bottom curve), rotated at 400 rpm, in $1.3 \times 10^{-3} \text{ M O}_2$ solution (pH5.6). Supporting electrolyte as in Figure 2. Current density of electrolysis: $160 \mu\text{A.cm}^{-2}$.

4. CONCLUSIONS

Anthraquinone-2-Carboxylic-Allyl Ester (ACAЕ) is found to be electrocatalytically active toward the two-electron reduction of O_2 to produce H_2O_2 . The surface cyclic voltammetry reveals the two-electron, two-proton process of this catalyst, which probably involves an outer-sphere mechanism to catalyze O_2 reduction. The kinetics of this electrocatalytic reduction of O_2 are examined on an ACAЕ coated rotating graphite electrode, to show a rate constant of $8.4 \times 10^3 \text{ M}^{-1} \cdot \text{s}^{-1}$ at 22°C .

The stability of ACAЕ together with its high selectivity for catalytic reduction from O_2 to H_2O_2 may make it feasible to employ this modified electrode for H_2O_2 production in weak acidic solutions.

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