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Novel organic redox catalyst for the electroreduction of oxygen to hydrogen peroxide

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ABSTRACT

The organic redox catalysis of O₂ electroreduction to H₂O₂ in acidic media has been investigated using several quinone and riboflavin catalysts supported on Vulcan XC72 carbon. The synthesis of a novel riboflavinyl–anthraquinone 2-carboxylate ester (RF–AQ) is reported. The activity and selectivity of organic redox catalysts (riboflavin, anthraquinone derivatives and riboflavinyl–anthraquinone 2-carboxylate ester) for the electrosynthesis of H₂O₂ were investigated by the rotating ring–disk electrode (RRDE) method and potentiostatic electrolysis. Electrodes with 10 wt% RF–AQ loading on Vulcan XC-72 showed excellent electrocatalytic activity toward the two-electron oxygen reduction coupled with very good catalyst layer stability. The reaction mechanism for the organic redox catalysis by RF–AQ is discussed. Electroreduction of O₂ dissolved in 0.5 M H₂SO₄ under potentiostatic conditions (0.1 V vs. RHE) at 21 °C using the composite RF–AQ/Vulcan XC72 catalyst (total loading 2.5 mg cm⁻²) deposited on unteflonated Toray[®] carbon paper, generated H₂O₂ with an initial rate of 21 μ mol h⁻¹ cm_{geo}⁻² and a stable current efficiency of 70%.

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1. Introduction

Hydrogen peroxide has an expanding market with a wide range of applications in industries including pulp and paper (50%), propylene oxide production (40%), textile, food and environmental sectors (10%) [1]. The global demand for H_2O_2 is over two million ton per annum. The major commercial production method is the Riedl–Pfleiderer process, which accounts for over 90% of the global H_2O_2 production. This process involves an alkyl anthraquinone, dissolved in a mixture of polar and nonpolar solvents (such as polyalkylated benzenes and alkyl phosphates), cycled between hydrogenation, catalyzed by suspended Raney Ni or Pd, and autooxidation in air to generate H_2O_2 . Further purification by extraction and distillation produces H_2O_2 up to 70 wt% with over 95% yield [1]. The capital and energy intensive Riedl–Pfleiderer process is advantageous only with the economy of scale, and is not applicable to smaller scale synthesis of H_2O_2 .

Alternative methods of H_2O_2 synthesis include reduction of O_2 to H_2O_2 via electrochemical routes, such as trickle-bed reactors using alkaline electrolyte and high-surface graphite cathodes [2,3], and in H_2-O_2 fuel cells operated in either alkaline or acidic media [4–6]. Under acidic or neutral conditions, to overcome the electrode kinetic limitation of the two-electron O_2 reduction, the electrocatalysis of this reaction has been extensively studied. Recently,

Bonakdarpour et al. reported that Co–C based electrocatalysts can be effective in acidic media [7]. The electrocatalysis of O_2 electroreduction to H_2O_2 has been intensely investigated by research groups under the CLETEPEG Project and the European Union Framework Program [8–14].

The Riedl–Pfleiderer process, where an anthraquinone compound is shuttled between reduction and oxidation (i.e. redox catalysis), served as an inspiration for electrocatalysis as well. Since it is well established that hydrogenated 9,10-anthraquinone derivatives spontaneously react with molecular oxygen to form hydrogen peroxide [15], Gyenge and Oloman used an emulsion of 2-ethylanthraquinone with a cationic surfactant, and reticulated vitreous carbon or graphite felt as the cathode to produce up to 0.6 M of H₂O₂ in 2 M Na₂SO₄ electrolyte at 800 A m⁻² at about 50% current efficiency [16,17].

Much effort has been made to carry out O_2 electroreduction to H_2O_2 mediated by surface immobilized quinones. Tammeveski et al. investigated the quinone mediated two-electron O_2 electroreduction in alkaline solutions [9,12–14]. However, the quinone reduction potential shifts towards more negative values with increasing pH [8], leading to high cathodic overpotentials.

Methods of surface immobilization included: irreversible adsorption [18–20], covalent attachment of diazonium salts of quinones [8–14], and anodic polymerization of aminoanthraquinone over the electrode surface [21–23]. Berchmans and Vijayavalli attached riboflavin to glassy carbon electrodes through covalent linkage of the amine or alcohol groups to the surface carboxylic groups of the carbon substrate [24]. Manisankar et al.

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modified the electrode described by Berchmans and Vijavavalli with several 9,10-anthraquinones and reported that riboflavin was beneficial to the quinone reduction and thus, the subsequent rate of O₂ reduction in buffered pH neutral electrolytes increased as well [25,26]. The majority of these investigations involved modification of glassy carbon electrodes, where the presence of quinones or riboflavin (on the order of 10^{-9} mol cm⁻²) shifts the potential of

Riboflavinyl–anthroquinone-2-carboxylate ester (RF–AQ) was synthesized as shown in Eq. (1), by first chlorinating CAQ with thionyl chloride (Fluka) refluxed at 80 °C for three hours. After distilling off the excess thionyl chloride, the acyl chloride was dissolved in pyridine (Fisher Scientific) and allowed to react with riboflavin. The excess pyridine was distilled off, and the final product was purified by recrystallization in hexanes (Fisher Scientific), followed by vacuum drying.



 O_2 reduction to more positive values. Lobyntseva et al. prepared a membrane-electrode assembly with Vulcan XC72 grafted with diazonium-anthraquinone as the cathode, but the H_2O_2 current efficiencies were less than 1% [10].

This paper presents results using organic redox catalysts supported on Vulcan XC72 for the electrosynthesis of H₂O₂ in acidic media. A carboxylate ester of anthraquinone and riboflavin was synthesized and deposited on the Vulcan XC72 support, and investigated for the first time for electrocatalytic activity by the rotating ring-disk electrode (RRDE) method. Potentiostatic batch electrolysis experiments were performed using gas diffusion cathode coated with the novel organic redox catalyst to demonstrate the long term H₂O₂ production rate and the electrode durability. The effort of this paper aims to contribute to the development of an onsite H₂O₂ electrosynthesis unit for drinking water treatment that could eliminate the cost and risks involved in transporting, storing and handling concentrated H₂O₂. This work is part of the Res'eau WaterNET, a nationally funded research network in Canada, which is dedicated to solving challenges faced by remote communities with respect to drinking water supply. The Res'eau WaterNET identified the UV/H₂O₂ disinfection processes as very promising for drinking water treatment.

2. Experimental methods

2.1. Chemicals

The quinone compound and riboflavin were purchased from Sigma–Aldrich at the highest purity available and used directly without further purification: anthraquinone-2-carboxylic acid (CAQ) 98%, and riboflavin (RF) 98%. Vulcan XC72 carbon powder was purchased from Cabot Inc. All solutions were prepared with deionized water of $18.2 \text{ M}\Omega \text{ cm}^{-1}$ resistivity at $21 \,^{\circ}\text{C}$ (Siemens Purelab). Cyclic voltammetric measurements were performed in 0.1 M H₂SO₄ (GFS Chemicals). Oxygen (Praxair, 99.998%) was purged in the electrolyte through a 5 μ m porous dispersion tube (Ace Glass) during the measurements.

The structures of CAQ, RF and the product RF–AQ were analyzed by Fourier transform infrared (FTIR) spectroscopy. These measurements were performed by a Bruker IFS 55 system using the KBr pellet technique. IR spectra were collected in the mid IR range $(4000-400 \text{ cm}^{-1})$ with a resolution of 0.5 cm⁻¹.

2.2. Catalyst ink and electrode preparation

The catalyst in this paper refers to the composite of the organic redox catalyst and Vulcan XC72 carbon powder. The appropriate amount of quinone or riboflavin redox catalyst and Vulcan XC72 powder was sonicated in 280 μ L of DI water and 70 μ L of ethanol for 15 min, followed by the addition of 100 μ L of 5 wt% Nafion solution (Alfa Aesar) and sonication for 30 min to make a well-mixed suspension.

For cyclic voltammetry (CV), 7 μ L of the ink was placed on the glassy carbon (GC) disk electrode and air dried at 21 °C to achieve a catalyst loading of 0.66 mg cm⁻²_{geo.} The typical dry weight ratio of the catalyst layer components is 1:9:4.4 in the order of redox catalyst:Vulcan XC72:Nafion.

For electrolysis measurements, Toray[®] paper with no Teflon[®] treatment (TGP-H-060 Fuel Cell Earth) was cut into $2 \text{ cm} \times 2 \text{ cm}$ squares with a 0.5 cm stem for electrical connection. The catalyst ink was deposited on the 4 cm^2 electrode in aliquots of $25 \,\mu$ L, followed by air drying at $21 \,^{\circ}$ C. After the entire area of the electrode was covered with the desired amount of the catalyst, it was dried in an oven at $80 \,^{\circ}$ C for 12 h. Total composite catalyst (the organic redox catalyst, Vulcan XC72 and Nafion) loadings of 1.7 to $3.5 \,\text{mg cm}^{-2}_{geo}$ were determined by weighing the electrode before and after the deposition.

2.3. Electrochemical measurements

Cyclic voltammetry (CV) measurements were performed using the CBP Bipotentiostat system (Pine Instruments) in a single compartment electrochemical cell. The working electrode consisted of a Pine (AFE6R2GCPT) rotating-ring disk electrode (RRDE) with a glassy carbon disk (0.2376 cm²) and a platinum ring electrode



Fig. 1. Mid-Infrared spectra of (a) CAQ, (b) RF and (c) RF-AQ.

 (0.2356 cm^2) with a collection efficiency of about 38%. A platinum wire counter electrode and a mercury/mercurous sulfate reference electrode (Radiometer Analytical) were used for all measurements, all immersed in about 100 mL of 0.1 M H₂SO₄.

All measurements were performed at 21 ± 0.5 °C and 1 bar. The Pt ring electrode was cleaned by cycling between 0 and 1.2 V vs. RHE until steady state CVs were obtained. During the measurements, the ring electrode was held constant at 1.2 V vs. RHE to record the H₂O₂ oxidation current.

First, a CV in the N₂-purged electrolyte was recorded to characterize the redox behavior of the quinone based catalysts. Next, O₂ was purged for 30 min in the electrolyte, and its saturation in the electrolyte was maintained by allowing an O₂ blanket above the solution for the short-term duration of the oxygen reduction reaction (ORR). After the ORR, a second CV measurement in the N₂purged electrolyte was again performed to determine the adhesion of the quinone-based catalysts on the carbon support. ORR was performed with the RRDE assembly rotating at fixed rotation speeds of 100, 400 and 900 rpm.

Bulk electrolysis experiments were performed using an Hcell connected to the same CBP Bipotentiostat system. The anode and cathode were housed in chambers separated by Nafion[®] 112 (Dupont) membrane, which was pretreated by a three step boiling treatment in 3 wt% H₂O₂, DI water, and 0.5 M H₂SO₄. The cathodic potential was fixed at 0.1 V vs. RHE throughout the 24 h duration of the electrosynthesis. O_2 was purged for 30 min before the experiments and continued during the experiments to maintain O₂ saturation in the electrolyte. The cathodic chamber contained 136 mL of the electrolyte $(0.5 \text{ M H}_2 \text{SO}_4)$ with constant stirring. 0.5 M H₂SO₄ was used to provide sufficient ionic conductivity and protons for the reaction. Moreover, the flooded batch electrolysis cell setup will provide a qualitative indication of the catalyst's performance in solid polymer fuel cells employing a Nafion[®] membrane. Samples of 3.5 mL were periodically taken from the cathode chamber and replaced with fresh electrolyte. A Hg/Hg₂SO₄ reference electrode was used and located in the reference electrode chamber connected to the cathode chamber by a porous ceramic frit.

All the potential measurements reported are referenced to the reversible hydrogen electrode (RHE). The RHE scale for the Hg/Hg₂SO₄ reference electrode was established by purging H₂ in the electrolyte and recording the open circuit potential difference between the reference electrode and a Pt wire electrode in the same chamber.

2.4. H_2O_2 analysis by UV-vis spectrophotometry

The concentration of H_2O_2 was determined by the UV spectrophotometric method described by Klassen et al. [27]. The UV absorption measurements were performed with a Varian Cary 100 UV–vis spectrophotometer. The sample pH had a significant impact on the absorption [28], and therefore, the reference measurements were conducted using the fresh electrolyte (0.5 M H₂SO₄) with the corresponding pH. This method is sensitive in the μ M range.

3. Results and discussion

3.1. Structural characterization of

riboflavinyl-anthroquinone-2-carboxylate ester

The structures of anthraquinone-2-carboxylic acid (CAQ), riboflavin (RF) and riboflavinyl-anthraquinone-2-carboxylate ester (RF-AQ) are shown in Eq. (1). The mid IR spectra of CAQ, RF and RF-AQ are presented in Fig. 1. The broad peak at about 3330 cm⁻¹ (Fig. 1b and c) is due to the O—H stretch of H-bonded alcohol groups observed in both RF and RF-AQ. Peaks at 1730, 1240 and 1080 cm⁻¹ (Fig. 1c) are generated by one C=O stretch and two C–O stretch modes of an unsaturated ester, which in this case is a characteristic feature of RF-AQ. The peak at about 1720 cm⁻¹ observed in Fig. 1b is due to the C=O stretch of the ketone groups in RF. This peak in Fig. 1c is likely merged with the more prominent C=O stretch of the ester at 1730 cm⁻¹ in the RF-AQ spectrum. Another C=O stretch



Fig. 2. Organic redox catalyst screening by cyclic voltammetry in N₂ and O₂ purged electrolytes: (a) Vulcan XC-72 (support baseline), (b) 10 wt% RF-AQ, (c) 10 wt% CAQ, and (d) 10 wt% RF. The experiments were performed using a total composite catalyst (organic redox catalyst and Vulcan XC-72) loading of 0.66 mg cm⁻² on the RRDE tip, 0.1 M H₂SO₄ electrolyte, at 21 °C and 1 bar pressure.

mode is observed at 1680 cm^{-1} for both RF–AQ (Fig. 1c) and CAQ (Fig. 1a), due to the ketone groups of anthraquinone. C–N stretch modes of aromatic amines are observed for both RF–AQ (Fig. 1c) and RF (Fig. 1b) at about 1270 and 1340 cm⁻¹.

The spectral features of CAQ that are unique to the carboxylic acid group (Fig. 1a) are not observed in RF–AQ (Fig. 1c), validating therefore that the esterification reaction (1) with RF has occured and the RF–AQ product was well purified. Thus, the very broad band between 3400 and 2400 cm⁻¹ due to the O–H stretch of carboxylic acid is only observed for CAQ (Fig. 1c). Moreover, the peaks at 1700, 1280 and 930 cm⁻¹ representing the stretch modes of C=O, C–O and O–H respectively of the carboxylic acid group, are observed only in the CAQ spectrum (Fig. 1c). Thus, the IR analysis supports the structure of RF–AQ shown in Eq. (1).

3.2. Electroanalytical and electrolysis measurements

3.2.1. Screening of organic redox catalysts

Organic redox catalysts supported on Vulcan XC72 with a loading of 10 wt% redox catalyst were examined by cyclic voltammetry in 0.1 M H₂SO₄, including riboflavinyl–anthroquinone-2-carboxylate ester (RF–AQ), anthraquinone-2-carboxylic acid (CAQ), and riboflavin (RF). Fig. 2 shows the cyclic voltammograms for the investigated catalysts on the RRDE electrode, in N₂-purged and O₂-purged 0.1 M H₂SO₄, respectively. The oxygen reduction onset potential defined at -0.1 mA cm⁻² is about 0.2 V vs. RHE on the bare Vulcan XC72 (Fig. 2a). In de-aerated 0.1 M H₂SO₄, the formal redox potential for both RF–AQ (Fig. 2b) and RF (Fig. 2d) is about 0.2 V whereas for CAQ, it is about 0.15 V (Fig. 2c). All the organic redox catalysts are electrochemically active.

It was observed that RF (molecular weight 376 g mol^{-1}) showed a lower reduction peak current density than CAQ (MW 252 g mol^{-1}) in the de-aerated electrolyte, for the same redox catalyst loadings on a weight basis. It was also observed that RF–AQ (MW 610g mol⁻¹) with a much lower molar loading showed almost as large a reduction peak current density as CAQ; however, its reduction peak potential was the same as that of RF. This could be attributed to the reduction of the RF constituent in RF–AQ, and subsequently mediating the reduction of the AQ constituent.

In the O₂-saturated electrolyte all three catalysts generated reduction peaks at potentials virtually equal to the characteristic catalyst reduction peak potential in the absence of O₂. The corresponding reduction peak current densities are composed of two electrode reactions: net O₂ electroreduction and redox catalyst electroreduction, respectively (Fig. 2b–d). RF–AQ generated the highest reduction peak current density, -1.6 mA cm^{-2} followed by RF with -1 mA cm^{-2} and lastly CAQ with -0.75 mA cm^{-2} .

Fig. 3a shows the net faradaic current due to O_2 electroreduction, after correction for the charging and discharging of the double layer capacitance and the intrinsic catalyst reduction in the absence of O_2 (measurements in N₂-purged electrolyte). Fig. 3b presents the oxidation current of H₂O₂ collected at the ring electrode (collection efficiency equal to 38%). The selectivity of the catalysts towards H₂O₂ formation, shown in Fig. 3c was calculated from the disk and ring currents as follows:

Selectivity =
$$\frac{200 \times I_{\text{ring}}}{N \times |I_{\text{disk}}| + I_{\text{ring}}}$$
 (2)

where *N*, I_{ring} and I_{disk} refer to the collection efficiency of the ring, ring current, and disk current respectively [29].

The standard potential of oxygen reduction to H_2O_2 is 0.70 V vs. SHE [30]. Modifications of the Vulcan XC72 by RF–AQ(10 wt%) or RF (10 wt%) increased the onset potential of the O_2 reduction to H_2O_2 by up to 50 mV compared to Vulcan XC72 and CAQ(Fig. 3a). Furthermore, for disk electrode potentials between 0.25 V and -0.1 V the



Fig. 3. Oxygen electroreduction study on rotating ring-disk electrode (RRDE) using 10 wt% organic redox catalyst loading on Vulcan XC-72. (a) O₂ reduction measurements obtained from the rotating disk electrode, (b) ring current densities, and (c) Selectivity of the catalysts for reduction of O₂ to H₂O₂. The experiments were performed using a total composite catalyst loading of 0.66 mg cm⁻² on the RRDE tip, 0.1 M H₂SO₄ electrolyte, at 21 °C and 1 bar pressure.

 H_2O_2 generation rate was the fastest in case of the RF–AQ catalyst as shown by the higher H_2O_2 oxidation ring current densities (up to 0.5 mA cm⁻², Fig. 3b) compared to the other catalysts. For disk electrode potentials below 0.1 V, a selectivity for H_2O_2 of $85 \pm 5\%$ is observed for the RF–AQ catalyst, which is 20% higher than for the baseline Vulcan XC72 (Fig. 3c). The selectivity is influenced by the competing secondary reaction, which is the reduction of H_2O_2 to H_2O :

$$H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O, \quad E_0 = 0.53 \frac{V}{V \text{ vs. SHE}}$$
 (3)

Riboflavin (RF) itself shows pronounced activity towards O_2 reduction to H_2O_2 , as well as assistance to the quinone reduction (Fig. 3a–c). The constitutional groups of the redox catalyst have profound impact on the catalyst's activity towards O_2 electroreduction. Among the investigated organic redox catalysts, RF–AQ has been found to be the most active and selective for O_2 reduction to H_2O_2 . Therefore it was down selected for further studies.



Fig. 4. RF–AQ redox waves with 10 wt% RF–AQ loading. (a) Redox waves of the RF–AQ couple, and (b) averaged peak current density as a function of potential sweep rate. The experiments were performed using a total composite catalyst loading of 0.66 mg cm⁻² on the RRDE tip, 0.1 M H₂SO₄ electrolyte, at 295 K and 1 bar pressure.

3.2.2. Reaction mechanism of O_2 reduction to H_2O_2 catalyzed by RF-AQ

Fig. 4a shows cyclic voltammograms as a function of sweep rate, recorded in N₂-saturated 0.1 M H₂SO₄ electrolyte using the 10 wt% RF–AQ catalyst deposited onto the RRDE GC tip with an effective RF–AQ coverage of 1.07×10^{-7} mol cm⁻²_{geo} (calculated from the composite catalyst composition). A reversible wave is observed with a formal redox potential at 0.2 V vs. RHE. The reduction peak current density was a linear function of the potential sweep rate (Fig. 4b). Thus, assuming Nernstian behavior of the surface modified electrode, the number of electrons can be estimated from the peak current densities [31]:

$$j_{\rm p} = \frac{n^2 F^2 v A \ \Gamma_{\rm RF-AQ}^*}{4RT} \tag{4}$$

where n, v, A and $\Gamma^*_{\text{RF-AQ}}$ represent the number of electrons transferred, potential sweep rate, geometric area of the electrode, and the coverage of RF–AQ, respectively.

The one electron reduction of RF–AQ in the N₂-purged electrolyte raises the question whether the anthraquinone structural unit or the riboflavin constituent participate in the electroreduction and mediation of the O₂ reduction. It is evident that RF has a pronounced effect in the mediated O₂ reduction reaction. The mechanism by which the anthraquinone constituent improved the H₂O₂ yield and selectivity (Fig. 3b and c) is unknown and deserves further investigation.

A reaction scheme for the mediated O_2 reduction is proposed in Fig. 5, where the radicals (b or c) formed by the one-electron reduction of RF (a) is responsible for the electrocatalytic activity for O_2 reduction, as supported by reports of mediated O_2 reduction by many quinoid compounds [19]. The radicals (b or c), stabilized by a number of resonant structures, reacts thermochemically with O_2 to form peroxyl radical adducts (d or e). The formation of the adducts has been proposed as the rate determining step [34,35]. H_2O_2 is thereafter formed via the subsequent electro-reduction of adduct (d or e) to adduct (f or g) followed by its molecular rearrangement with simultaneous regeneration of the riboflavin structural unit (referred to also as redox mediation).

Riboflavin has been reported to assist the reduction of quinones [25,26]. In the present study, it is evident that the RF structural unit is active for the $2e^- O_2$ reduction in the RF–AQ catalyst. The



Fig. 5. Proposed reaction mechanism scheme of RF-AQ mediated O₂ electroreduction to H₂O₂.

molecular and electronic interaction of the RF and AQ is unknown at present but it could involve activation of the thermochemical reaction between the semiquinol radical and O₂ and/or stabilization of the adduct (d or e).

From the RRDE experiments of the RF–AQ modified Vulcan XC72 carbon with 5 and 10 wt% RF–AQ contents, and the unmodified Vulcan XC72 catalysts at rotation speeds of 100, 400, 900 and 1200 rpm, the Koutecky–Levich relationship at 0.1 V vs. RHE was generated and it is shown in Fig. 6:

$$\frac{1}{j_{\rm F}} = \frac{1}{j_{\rm k}} + \frac{1}{j_{\rm dl}} = -\frac{1}{nFkC_{\rm O_2,b}} - \frac{1}{0.62nFD_{\rm O_2}^{2/3}\nu^{-1/6}C_{\rm O_2,b}\omega^{1/2}}$$
(5)

where j_F , j_k , j_{dl} , k, C_b , F, D, n, ν and ω represent the total faradaic current density, kinetic current density, diffusion limited current density, electrochemical rate constant for O₂ reduction, bulk concentration of the analyte (dissolved oxygen), Faraday's constant, diffusivity of the analyte, number of electrons transferred, viscosity of the electrolyte, and angular velocity of the rotating electrode, respectively.

Using the literature reported values of $C_{0_2,b} = 1.26 \times 10^{-6}$ mol cm⁻³, $D_{0_2} = 1.93 \times 10^{-5}$ cm² s⁻¹, and $\nu = 1.009 \times 10^{-2}$ cm² s⁻¹ [32], and the reciprocal of the slopes in Fig. 6, *n* is estimated to be about 2, confirming the two electron reduction of O₂ mediated by the catalysts. From the reciprocal intercept of the Koutecky–Levich plots, the electrochemical rate constants (at 0.1 V vs. RHE) are estimated to be 1.51 × 10⁻⁶, 4.53 × 10⁻⁶, and 6.91 × 10⁻⁶ cm s⁻¹ for the Vulcan XC72 carbon baseline, 5 wt% RF–AQ modified Vulcan XC72, and 10 wt% RF–AQ modified Vulcan XC72 catalysts, respectively. Thus, the RF–AQ modification significantly improved the kinetics of O₂ reduction.

3.2.3. Adhesion and monolayer coverage of RF–AQ on Vulcan XC-72

The adhesion of RF–AQ to Vulcan XC72 and the RF–AQ/Vulcan XC72 catalyst to the GC disk were examined by comparing the cyclic voltammograms recorded in the N₂ purged electrolyte before

and after performing the oxygen reduction experiments. The redox waves of the immobilized RF–AQ showed no decrease in peaks, suggesting good adhesion to the GC tip of the RRDE during the entire time of measurements. Furthermore, the ORR voltammograms were also stable for several cycles. The immobilization is attributed to the π – π interaction between the polycyclic aromatics and the carbon support [33].



Fig. 6. Koutecky–Levich plot for O_2 reduction on the unmodified Vulcan XC72, 5 wt% and 10 wt% RF–AQ on Vulcan XC72 catalysts. The experiments were performed using a total composite catalyst loading of 0.66 mg cm⁻², 0.1 M H₂SO₄ electrolyte, at 21 °C and 1 bar pressure. Oxygen saturated electrolyte.



Fig. 7. The effect of the RF–AQ redox catalyst on H_2O_2 generation in a batch electrolysis cell. (a) current efficiency of H_2O_2 generation. (b) Cathodic current density, and (c) H_2O_2 accumulative production normalized by the cathode geometric area and H_2O_2 concentration as a function of time. The experiments were performed using RF–AQ 10 wt% on Vulcan XC72 carbon, 0.5 M H_2SO_4 electrolyte, at 0.1 V vs. RHE, 1 bar pressure and 21 °C or 50 °C as specified. The total composite catalyst loading (10 wt% RF–AQ and Vulcan XC72) on the unteflonated Toray carbon paper is given in the legend.

To approximate the maximum RF-AQ loading on the carbon support for complete monolayer coverage, the molecular volume of RF-AQ was estimated by total energy minimization in vacuum to be 685 Å³. A trial version of CambridgeSoft ChemBio 3D software was used to perform the computation using the Hartree-Fock method with the Gaussian algorithm and 6-31G basis set [34,35]. For comparison, a van der Waals volume of 504Å³ was calculated from the correlation developed by Zhao et al. [36], which is about 25% less than that predicted by the computational chemistry method, since the correlation only considers the atoms and number of bonds present in the molecule. Assuming the active surface area of the Vulcan XC72 powder substrate is $200 \text{ m}^2 \text{ g}^{-1}$ from N₂ adsorption isotherms [37], and that the RF-AQ molecules are rigid spheres with a volume estimated by the computational chemistry method, the complete RF-AQ monolayer coverage of Vulcan XC72 is estimated to occur at an RF-AQ loading of 17.7 wt%. This assumption however does not consider the molecular shape and orientation of RF-AQ over the carbon substrate. During CV experiments in the de-aerated electrolyte, decrease in redox waves of the second scan cycle from the first was observed for RF-AQ loadings over 15 wt%, indicating desorption of the RF-AQ from the carbon support at high loadings.

3.2.4. Chronoamperometric batch H₂O₂ electrosynthesis

Fig. 7 shows the H₂O₂ yield and current efficiency of the Vulcan XC72 carbon baseline and a number of RF–AQ modified Vulcan XC72 catalyst in the electrolysis cell described in Section 2.3 using O₂ purged 0.5 M H₂SO₄. The H₂O₂ generation is expressed both as accumulative concentration in parts per million (ppm) and in molar quantities normalized by the electrode's geometric surface area (μ mol cm⁻²_{geo}). The catholyte volume was kept constant (136 mL) throughout the electrolysis experiments, such that the two *y*-axes correspond in value.

The RF–AQ modification improved both the H₂O₂ yield and the current efficiency. With a total composite catalyst loading of $2.50 \pm 0.05 \text{ mg cm}_{geo}^{-2}$ (10 wt% RF–AQ, Vulcan XC-72 and Nafion) on the Toray[®] carbon paper, 432 ppm H₂O₂ was produced at 21 °C with 70 ± 5% current efficiency after 24 h. The initial H₂O₂ production rate was 21 µmol h⁻¹ cm_{geo}⁻² during the first two hours. For the unmodified Vulcan XC72 only about 170 ppm H₂O₂ was produced at 21 °C with 55 ± 5% current efficiency after 24 h (Fig. 7a and c). A higher total composite catalyst loading of 3.40 mg cm_{geo}⁻² produced about 500 ppm of H₂O₂ after 24 h, but with about 10% lower efficiency. This lower efficiency was likely due to the thicker porous catalyst layer retaining the generated H₂O₂, which subsequently underwent further reduction to H₂O.

The elevated temperature of 50 °C considerably improved the H_2O_2 production rate of the RF–AQ redox catalyst, by increasing the rate of the limiting thermochemical reaction of the HRF–OO* adduct formation (Fig. 5d or e). Much higher H_2O_2 concentration, 628 ppm after 24 h, was achieved but at this temperature H_2O_2 decomposition was also significant as shown by the drop of the apparent current efficiency from $80 \pm 5\%$ initially to about $60 \pm 5\%$ after 24 h at 50 °C (Fig. 7a and c). The effect of temperature on the Vulcan XC72 catalyst was much less pronounced, and the H_2O_2 concentration was below 200 ppm after 24 h. The current densities for all electrolysis experiments were stable at both 21 and 50 °C, and no noticeable desorption of the immobilized RF–AQ was observed during the 24 h experiments.

4. Conclusions

Riboflavinyl–anthraquinone-2-carboxylate ester (RF–AQ) is electrochemically active toward the two-electron reduction of O_2 to H_2O_2 in acidic media based on a redox catalysis mechanism. Among the various derivatives of AQ and RF compounds studied, the synthesized RF–AQ compound supported on Vulcan XC72 carbon showed the highest electrocatalytic activity followed by RF and CAQ, RF–AQ at 10 wt% content showed irreversible adsorption over the Vulcan XC72 carbon support, which was estimated to be equivalent to a surface coverage of 0.56. Full monolayer of RF–AQ coverage is estimated at 17.7 wt% loading on Vulcan XC72.

The RF–AQ modified electrode had a $2e^- O_2$ electroreduction rate constant of $6.9 \times 10^{-6} \text{ cm s}^{-1}$ (0.1 V vs. RHE, at $21 \,^{\circ}\text{C}$). Batch electrolysis using a composite catalyst loading of 2.5 mg cm⁻², with dissolved O_2 in 0.5 M H₂SO₄ at 21 $^{\circ}\text{C}$, produced H₂O₂ at an initial rate of about 21 µmol cm⁻²_{geo} h⁻¹ with current efficiencies up to 70% at a constant cathode potential of 0.1 V vs. RHE. Electrolysis using the same composite catalyst loading, at 50 $^{\circ}\text{C}$ promoted the thermochemical step of the mediated O₂ reduction reaction and produced H₂O₂ at an initial rate of 46 µmol cm⁻²_{geo} h⁻¹ with about 75% current efficiency under the same potentiostatic conditions. However, at 50 $^{\circ}\text{C}$ the apparent current efficiency dropped below 70% when the H₂O₂ concentration exceeded 200 ppm. This loss in apparent current efficiency, observed at 50 $^{\circ}\text{C}$ but not at 21 $^{\circ}\text{C}$, may be primarily due to H_2O_2 disproportionation more pronounced at higher temperatures.

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