Journal of Electroanalytical Chemistry 632 (2009) 102–108

Contents lists available at ScienceDirect

Journal of Electroanalytical Chemistry

journal homepage: www.elsevier.com/locate/jelechem

Enhanced electrocatalytic reduction of oxygen with a molecule having multi-quinone moieties adsorbed in the nanofiber film

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A R T I C L E I N F O

Article history:
Received 17 December 2008
Received in revised form 28 March 2009
Accepted 1 April 2009
Available online 7 April 2009

Keywords:
Anthraquinone derivatives
Oxygen reduction
Electrocatalysis
Modified electrode

A B S T R A C T

The electrochemical reduction of oxygen has been studied on two novel anthraquinone derivatives, 1,5-bis(2-anthraquinonyloxy)-3-oxapentane (AQ1), and 1,11-bis(2-anthraquinonyloxy)-3,6,9-oxaundecane (AQ2) having two quinone moieties with cyclic voltammetry (CV) and hydrodynamic voltammetry (HV). Anthraquinone derivative modified electrodes exhibited a well defined redox couple in an aqueous solution which is corresponding to (AQ/AQH_2). The AQs adsorbed on the electrodes in the nanofiber network showed an electrocatalytic activity for the oxygen reduction with 620 mV positive potential shift and the current enhancement in a phosphate buffer solution (pH 7.0) as compared to a bare electrode. The compounds having two quinone moieties (AQ1, AQ2) showed the doubly increased catalytic current compared with that bearing a single quinine moiety (9,10-AQ). HVs with a rotating ring-disk electrode showed that the reduction of oxygen at the modified electrodes mostly occurs through the two-electron pathway to form H_2O_2 as a final product. The rate constant (k) for oxygen reduction with AQ1 and AQ2 modified electrodes was determined to be 2.4×10^5 and 2.7×10^5 M^{-1} s^{-1}, respectively.

1. Introduction

Oxygen reduction is one of the essential electrochemical reactions due to its importance in various applications, such as the electrochemical energy conversion systems and sensors [1–3]. The development of new catalysts to replace platinum for the catalytic reduction of oxygen is an important goal in environmental, medical, and industrial fields. To do this, chemical modification of electrodes are mostly used for examination of the catalyst performance at the first stage.

Chemical modification of electrode surfaces has attracted considerable interest over the past two decades as researchers attempt to exert more direct control over the nature of electrode surfaces [4]. Modified electrodes with diverse modifiers have been used for the electrocatalysis of oxygen reduction, such as porphyrin [5,6], and phenanthroline [7] complexes, bi-monolayer [8], wired enzymes [9–11], manganese oxide nanoparticles [12], dendrimer-encapsulated Pt nanoparticles [13], and multiwall carbon nanotube [14]. Previously, we have also studied diaminonaphthaline and glyoxal bis(2-hydroxyanil) metal complexes modified electrodes for the electrochemical reduction of oxygen [15–17]. The mechanism of oxygen reduction reaction at the modified electrode mainly depends on the kind of modifier and the pH of the medium.

Of the various species, quinone and its derivatives have received much attention as modifiers to electrocatalyze oxygen reduction, because these compounds play important roles in biocatalytics, analytical, and electroanalytical chemistry as excellent electron transfer mediators [18–20]. The modification of quinone compounds has been performed with different kinds of electrodes, such as glassy carbon, highly oriented pyrolytic graphite, boron-doped diamond [21–26]. The modification of quinones and anthraquinone podands on the electrode surfaces by adsorption also exhibited enhanced catalytic activity for the electrocatalytic reduction of dioxygen [27,28]. Although various anthraquinone derivatives-modified electrodes have been used to study the electrochemical reduction of oxygen, there is no report for studying the oxygen reduction reaction using anthraquinone derivative containing two AQ groups in a molecule until now. It is interesting to find out how the number of quinone moiety influence electrocatalytic reduction of oxygen. In the present study, we investigated the electrochemical reduction of oxygen using two novel anthraquinones derivatives, 1,5-bis(2-anthraquinonyloxy)-3-oxapentane (AQ1) and 1,11-bis(2-anthraquinonyloxy)-3,6,9-oxaundecane (AQ2) modified electrodes. The kinetics of the electrochemical reduction of oxygen on these modified electrodes was performed using cyclic voltammetry, and hydrodynamic technique with RDE and RRDE. As control experiments, we compared the electrocatalytic properties of molecules having two quinone moieties with that of a single quinone moiety. The parameters that could affect the electrocatalytic response of the modified electrodes for oxygen reduction

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doi:10.1016/j.jelechem.2009.04.003

were evaluated and discussed in terms of pHs of media, concentration of AQ, and temperature.

2. Experimental

2.1. Materials

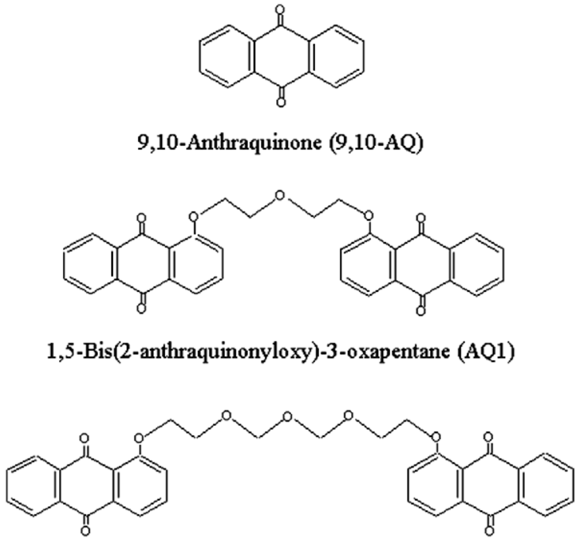
Two anthraquinone derivatives, 1,5-bis(2-anthraquinonyloxy)-3-oxapentane (AQ1) and 1,11-bis(2-anthraquinonyloxy)-3,6,9-oxaundecane (AQ2) (Scheme 1), were synthesized as follows:

2.1.1. Synthesis of 1,5-bis(1-anthraquinoyloxy)-3-oxapentane (AQ1)

A solution of the diethylene glycol (10 mmol) in dry THF (10 mL) was added slowly to a suspension of sodium hydride (1 g, 25 mmol; 60% oil dispersion was thoroughly washed with dry THF) in THF (100 mL) under an argon atmosphere, and the mixture was refluxed for 1 h. After the mixture was cooled to room temperature, a solution of 1-chloroanthraquinone (20 mmol) in THF (100 mL) was added, and the mixture was refluxed for 48 h under an argon atmosphere. The solvent was evaporated to from a solid residue. The residue was extracted with chloroform/water, and the remaining organic phase was successively washed with water (3 × 100 mL) thoroughly. The solid product was dried over anhydrous magnesium sulfate. The yellow solid was purified by column chromatography on silica using dichloromethane/methanol (30:1). Yield 65%, ^{1}H NMR ($CDCl_3$, $SiMe_4$, ppm): 8.18 (m, 4H, Ar), 7.94 (dd, 2H, Ar), 7.68 (m, 4H, Ar), 7.60 (*t*, 2H, Ar), 7.38 (dd, 2H, Ar), 4.38 (*t*, 4H, $-OCH_2-$), 4.21 (*t*, 4H, $-OCH_2-$). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.6, 182.3, 160.0, 135.9, 135.3, 135.1, 134.5, 133.5, 132.8, 127.4, 126.9, 122.2, 120.4, 120.1, 70.4, 70.1. IR (KBr, cm^{-1}): 2872 (m), 1680 (s), 1264 (m).

2.1.2. Synthesis of 1,11-bis(1-anthraquinoyloxy)-3,6,9-oxapentane (AQ2)

This compound was synthesized by the procedure using tetraethylene glycol instead of diethylene glycol. Yellow solid precipitated was obtained in 42% yield. ^{1}H NMR($CDCl_3$, $SiMe_4$, ppm): $\delta = 8.20$ (m, 4H, Ar), 7.93 (dd, 2H, Ar), 7.70 (m, 4H, Ar), 7.64 (*t*, 2H, Ar), 7.35 (dd, 2H, Ar), 4.31 (*t*, 4H, $-OCH_2-$), 4.02 (*t*, 4H, $-OCH_2-$), 3.86 (*t*, 4H, $-OCH_2-$), 3.73 (*t*, 4H, $-OCH_2-$). ^{13}C NMR ($CDCl_3$, $SiMe_4$, ppm): 183.6, 182.2, 159.9, 135.8, 135.2, 135.0, 134.4, 133.3, 132.7, 127.3, 126.8, 122.2, 120.4, 120.2, 71.4, 70.9, 70.5, 69.7. IR (KBr, cm^{-1}): 2889 (m), 1664 (s), 1260 (m).



Scheme 1. Chemical structure of anthraquinone derivatives used.

Tetrabutylammonium perchlorate (TBAP) purchased from Fluka (USA) was purified in ethyl alcohol and dried under vacuum at 10^{-5} Torr. Dichloromethane and acetonitrile (99.8%, anhydrous, sealed under nitrogen gas) were received from Aldrich (USA). 9,10-anthraquinone, citric acid, sodium dihydrogen phosphate, and disodium hydrogen phosphate were obtained from Sigma (USA). Nitrogen and oxygen gas (99.99%) were used for maintain deoxygenate and oxygen saturation in the measurement cell. All aqueous solutions were prepared in doubly distilled water, which were obtained from a Milli-Q water purifying system (18 M Ω cm).

2.2. Instruments

Cyclic voltammograms were recorded using Potentiostat/Galvanostat, Kosentech model PT-1 (S. Korea). RDE and RRDE voltammograms were recorded using a Kosentech bipotentiostat (Model Bipot-1) with the EG&G PAR model 636 rotating ring-disk electrode system. Three electrodes system consisting of a glassy carbon (area = 0.07 cm^2), an Ag/AgCl, and a platinum wire as working, reference, and counter electrodes were used. Scanning electron microscopy (SEM) images were obtained using a Cambridge Stereoscan 240 at the Korea Basic Science Institute (Busan). In hydrodynamic experiments, glassy carbon rotating disk and ring electrodes were used as the working electrode. Its disk and ring area were 0.24 and 0.18 cm^2, respectively. The collection efficiency was 0.127 as determined by the reduction of hexacyanoferrate.

2.3. Electrode modification

The glassy carbon electrode was polished with 0.5 μm alumina slurry on an emery paper to a mirror finish, and then rinsed with doubly distilled water. Electrochemical pretreatment of the electrode surface was performed by scanning the potential from −0.4 to 2 V in a 0.5 M sulfuric acid solution for 10 min. This process introduces active site on the GC surface, and may therefore act as templates for strong adsorption of the AQs from the solution. The modification of the electrode with AQ derivatives was performed by immersing the pretreated electrode in a 1.0 mM AQ derivatives containing acetonitrile solution for about 2 h. Then, the modified electrodes were washed with doubly distilled water to remove the excess AQs, and dried under nitrogen atmosphere. The modification of disk electrode of RRDE has also been performed in the same fashion. Where, the ring was not connected during the electrochemical treatment of RRDE. Thereafter, the ring surface was covered by electrically insulating tape to avoid any adsorption during RRDE modification with AQ.

3. Results and Discussion

3.1. Cyclic voltammetry of anthraquinone derivatives in a non-aqueous solution

Fig. 1 shows the CVs recorded for 1.0 mM anthraquinone derivatives of AQ1, AQ2, and 9,10-anthraquinone (9,10-AQ, that was used as a reference material for comparison of the redox properties) in a 0.1 M TBAP/CH_2Cl_2 solution. Two sets of redox peaks for AQ1 and AQ2 appeared in similar fashion of CV as previously reported in the literature for anthraquinones [29,30], which were related to the production of radicals [AQ^-] and dianions [AQ^{2-}], and the reaction followed the EE mechanism (electron transfer followed by electron transfer) [31]. It seemed that the first and second reduction peaks of AQs were expected to be two one-electron transfer processes since the AQ1 and AQ2 molecules contain two