



## Biomimetic Copper Complex Containing Polymer Modified Electrode for Electrocatalytic Reduction of Oxygen

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### ABSTRACT

The development of non-precious metal based electrocatalysts is highly desired for the oxygen reduction reaction (ORR) as alternatives to noble metal based ORR electrocatalysts. Herein, we report mononuclear copper(II) complex [CuLbpy]ClO<sub>4</sub> (L=4-[(2-hydroxyphenylimino)methyl]benzoic acid) containing poly(allylamine.HCl) polymer (PAIACuLbpy) as an electrocatalyst for oxygen reduction reaction (ORR). PAIACuLbpy was mixed with poly(acrylic acid) and tetraethylorthosilicate to prepare a composite and then deposited on the screen printed electrode surface. The modified electrode (PAIACuLbpy/PCE) is highly stable and showed a quasi-reversible redox behavior with  $E_{1/2} = -0.2$  V vs. Ag/AgCl(3 M KCl) in 0.1 M phosphate buffer at pH 7 under argon atmosphere. PAIACuLbpy/PCE exhibited a remarkable ORR activity with an onset potential of -0.1 V vs Ag/AgCl in 0.1 M PB (pH 7) in the presence of oxygen. The kinetics for ORR was studied by rotating disk voltammetry in neutral aqueous medium and the results indicated that the number of electrons involving in the ORR is four and the conversion products are water and hydrogen peroxide.

**Keywords :** Bio-mimicking, Hydrophilic polymer, Copper complex, Modified electrode, Oxygen reduction reaction

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### 1. Introduction

Copper oxidase enzymes such as laccase, ceruloplasmin and ascorbate oxidase catalyze the four-electron reduction of dioxygen to water coupled with substrate oxidation [1-2]. These multicopper oxidases contain three types of copper showing distinctly different EPR spectral features (types 1-3) with type 3 being a coupled binuclear copper. The type 2 and type 3 centers form a trinuclear copper cluster, which is the active site for both binding and multi-electron reduction of dioxygen to water [4-7]. The electrochemical oxygen reduction reaction is fundamentally important in the development of electrochemical devices such as fuel cell and zinc-air batteries and as electrochemical oxygen sensors [8-9].

The copper containing enzyme laccase [10] and bilirubin oxidase [11] modified electrodes reduce oxygen directly to water at higher positive potentials. Heller *et al.*, reported a fuel cell cathode based on laccase for the reduction of oxygen that operates with only 70 mV of over potential [12]. Another class of efficient and the most promising electrocatalysts for oxygen reduction are the noble metal, platinum, platinum nano-particles and its alloys with other metals. The formation of -OH species which will hinder the ORR, the cost and relatively low abundance of Pt in nature are the drawbacks of the Pt based electrocatalysts [13-14].

The advancement of biomimetic chemistry attracts the researchers to utilize it for several applications like catalysts in organic transformations, electrocatalysts, etc., [15-19]. In this context, electrocatalytic reduction of oxygen is achieved by using metalloporphyrins, metallophthalocyanines and metal oxides and

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other non-precious metal electrocatalysts [20-21]. Recently, various efforts have been devoted to study the electrocatalytic activities of copper complexes [22] and copper complex derived electrode surfaces [23-25]. Several research groups have investigated the electrocatalytic performance of copper complexes with different ligands; (a) Cu(II) complex of 4,7-diphenyl-1,10-phenanthroline disulfonate adsorbed on graphite electrodes [26-27] (b) Cu(II) hexaazamacrocyclic complex on glassy carbon electrode [28] (c) copper(II)-2,4,6-tris(2-pyridyl)-1,3,5-triazine complex adsorbed on a graphite electrode [29] (d) copper(II)-tris(3-aminopropyl)amine and imidazole complex on pyrolytic graphite electrode [30], (e) substituted-1,10-phenanthroline-copper complexes on graphite [31] and edge-plane graphite electrodes [32]. The copper complex, 1,5-diaminonaphthalene copper was attached to the conducting polymer poly-terthiophene carboxylic acid, which further deposited on GCE and studied ORR [33]. Gewirth et al reported a very high ORR activity for a synthetic copper based electrocatalyst, copper complex of 3,5-diamino-1,2,4-triazole supported on carbon black [34].

In the present study, we intend to prepare a copper complex, which mimics the type 3 copper center by taking into account of biomimetic chemistry for oxygen reduction reaction. In the present study, we incorporated the redox-active mononuclear copper complex [CuLbpy]ClO<sub>4</sub> (L = 4-[2-hydroxyphenylimino) methyl] benzoic acid) into hydrophilic poly(allylamine.HCl) polymer backbone through amide linkage. The redox polymers derived from hydrophilic polymer have special characteristics such as when they are cross linked on the electrode, they become insoluble, but swell in water to form hydrogel. The increased segmental mobility and swelling upon hydration increase the frequency of electron-transferring collision between the redox centers and thus increase the electronic conductivity [35,36]. The precursors and polymer were characterized by FTIR and elemental analysis and cyclic voltammetric techniques. The electrochemical and electrocatalytic behavior towards ORR of the modified electrode were studied. The electrocatalytic kinetics of ORR was determined by rotating disc voltammetry.

## 2. Experimental Section

4-Formylbenzoic acid, 2-aminophenol, copper(II)

perchlorate hexahydrate, poly(allylamine hydrochloride) (PAIA, Mw : 35,000), poly(acrylic acid) (PAA, Mw : 90,000), tetraethyl orthosilicate (TEOS), dimethylacetamide (DMAC) were purchased from Sigma-Aldrich and used without any further purification. (Caution: perchlorate salts are explosive; hence care should be taken while handling the compounds). Water purified from Milipore system was used in all experiments.

The synthetic procedures of the ligand and its mononuclear copper(II) complex, and their characterization are given in supplementary information.

### 2.1 Synthesis of [CuLbpy]ClO<sub>4</sub> Incorporated PAIA Polymer (PAIACuLbpy)

Poly(allylamine.HCl) (0.1 g) was dissolved in 10 mL deionized water and [CuLbpy]ClO<sub>4</sub> (0.5 mole equivalent to PAA.HCl monomer unit) in 10 mL methanol was added in the presence of EDC (0.4 g; 0.5 mole equivalent). The resulting solution was stirred for 12 h and then, the resulting precipitate was filtered off and the solvent was removed under reduced pressure to get the product. The resulting copper incorporated polymer was washed several times with methanol to remove the un-reacted complex. The copper complex incorporated polymer PAIACuLbpy is soluble in hot water or dimethylacetamide.

### 2.2 Synthesis of PAIACuLbpy-Poly(acrylic acid)-TEOS Composite

The composite of PAIACuLbpy with polyacrylic acid and TEOS was prepared as follows. Solutions of PAIACuLbpy (10 mg/mL) and polyacrylic acid (10 mg/mL) were prepared by dissolving in DMAC and in water respectively. Then equal volume (100 mL) of the two solutions were mixed along with 40 mL of TEOS and stirred overnight to form the composite.

### 2.3 Immobilization on PCE

The immobilization of composite on plasma treated printed carbon electrode (PCE; SE100, Zensor R&D, Taiwan, id = 5 mm, i.e., area = 0.196 cm<sup>2</sup>) was carried out by drop coating of 2  $\mu$ L of the polymer-composite. The electrode named as PAIACuLbpy/PCE was dried at room temp and used for the further experiments.

### 2.4 Spectroscopic Characterizations

FT-IR spectra were recorded with Nicolet Avatar

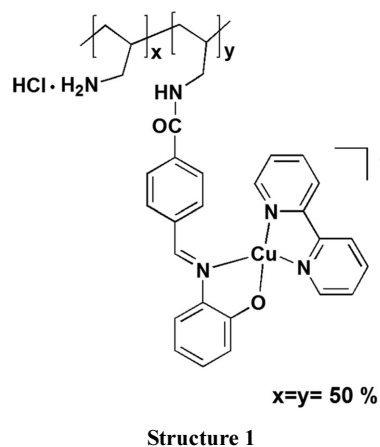
330FTIR (Thermo Electron Corporation) in dry KBr. Electronic spectrum of 1% PAIACuLbpy in DMAC: water mixture(1:1) was recorded on a Agilent 8453 single beam spectrophotometer in the range 250 - 800 nm. The Scanning Electron Microscopy (SEM) images were recorded with Hitachi S-4300 at 15 KV.

## 2.5 Electrochemical Measurements

Cyclic voltammetry (CV) experiments were performed with an electrochemical analyzer (CHI 900, CH Instrument Inc.) with three-electrode system comprising a glassy carbon (3 mm, Bioanalytical Systems) or PAIACuLbpy/PCE electrode (5 mm) as working electrode, Ag/AgCl (3M KCl) as reference electrode and a platinum wire as counter electrode. Phosphate buffer (0.1M, pH 7) was used as an electrolyte solution. All measurements were done under argon, air and oxygen atmosphere at room temperature. In the case of the RDE and RRDE experiments, a glassy carbon rotating disk electrode was used as the working electrode and the disk area is 0.196 cm<sup>2</sup>. GC electrode was polished with 0.3 μm alumina powder and cleaned by sonication in 50% ethanol solution before use.

## 3. Results and Discussion

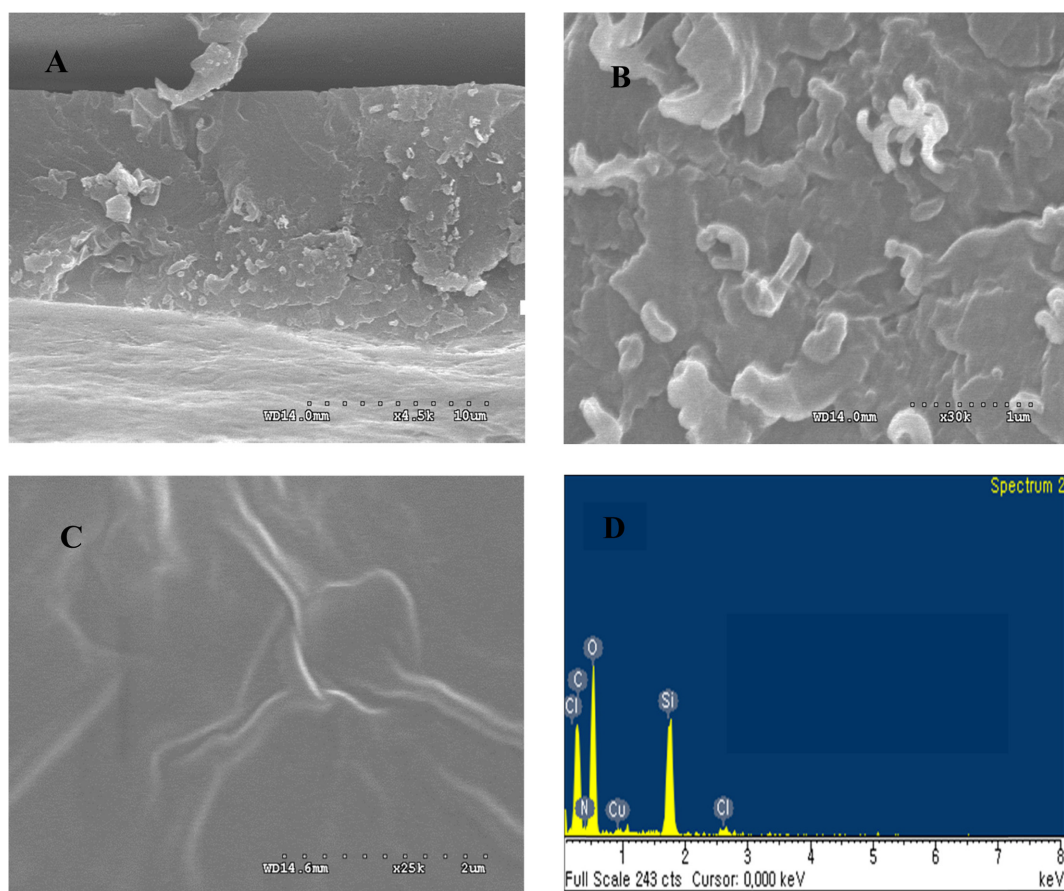
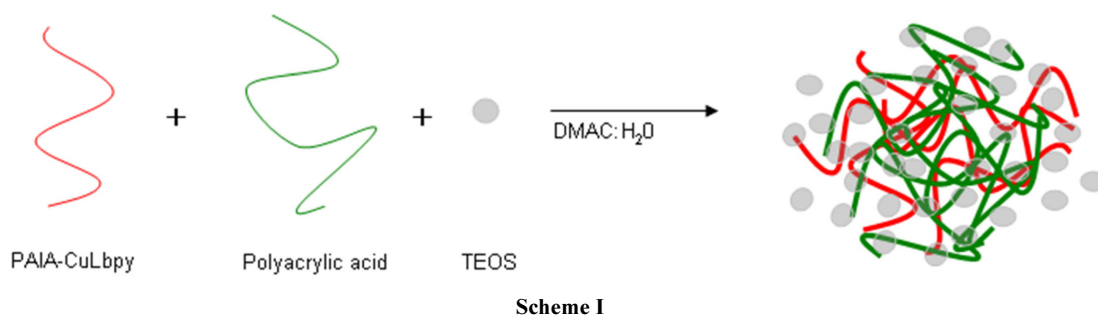
The mononuclear copper(II) complex [CuLbpy]ClO<sub>4</sub> is designed to mimic the activity of type 3 copper center to achieve the ORR. The synthesized copper complex was incorporated into polyallylamine polymer (**structure 1**) to immobilize on the electrode. In the first step, ligand and its mononuclear copper(II) complex containing free COOH group were synthesized (Supplementary data; scheme S1). In the next step, the mononuclear copper complex was condensed into polyallylamine through amide linkage and the polymer is having about 50% of complex modification. The polymer is well soluble in DMAC and hot water. The modification of poly(allylamine) by copper complex is confirmed by CHN analysis and FT-IR and UV-visible spectroscopy. From the elemental analysis, the percentage of C, H, and N was found to be 52.17, 3.65 and 9.7 respectively for PAIACuLbpy and these values are close to the extent of substitution of 50%. The FT-IR spectrum of the polymer is shown in supplementary Fig. S2. The polymer showed the oximidato C=O stretching



vibration at 1602 cm<sup>-1</sup> along with C=N stretching vibration 1686 cm<sup>-1</sup>, which prove the incorporation of copper complex. The polymer showed a single broad band at 1089 cm<sup>-1</sup> (ν<sub>3</sub> antisymmetric stretching), which does not show any split, and a medium band at 650 cm<sup>-1</sup> (ν<sub>4</sub> antisymmetric bending) due to uncoordinated perchlorate ion [37]. The UV-vis spectrum (Fig. S3 in supplementary) of polymer exhibited a d-d transition around 620 nm which is consistent with a tetra-coordinate Cu atom in a nearly square-pyramidal geometry with weak coordination of water.

Polyelectrolyte composite of PAIACuLbpy was prepared with poly(acrylic acid) or poly(phosphonic acid) or poly(vinyl alcohol) in the ratio of 1:1 by mechanical mixing to fabricate the electrode. From these blending mixtures, a stable modification on PCE was not achieved as it is leaching out on continuous potential scan in phosphate buffer. A stable film on the electrode was obtained when PAIACuLbpy was mixed with poly(acrylic acid) and TEOS. TEOS forms a silica network on acid hydrolysis, consequently it entangles the PAIACuLbpy and poly(acrylic acid) tightly, lead to sol-gel as shown in scheme 1. Apart from silica network, the electrostatic interactions between the polymers PAIACuLbpy and poly(acrylic acid) viz NH<sub>2</sub> & COOH groups further influences the stability of the electrode.

The physical appearance and surface characteristics of the sol-gel composite material were studied. Fig. 1 shows the SEM images of the composite material. As mentioned above, the composite with silica was prepared by the sol-gel method under acid catalysis. From the SEM images, it is clearly observed



**Fig. 1.** SEM images of the PAIACuLbpy/PCE, cross-section (A&B) and surface (C) EDAX (D) and Scale bars A: 20, B: 2, and C: 2  $\mu\text{m}$ .

that the composite is crack free and homogeneous in nature. From the cross-section images, molecular level and even distribution of silica was noticed throughout the nanocomposite polymeric film. The sol-gel composite is free from any precipitation and any phase separation during its preparation.

The cyclic voltammograms of PAIACuLbpy-composite coated on printed carbon electrode, PAIACuLbpy/PCE was recorded in 0.1 M phosphate buffer at pH 7 under argon atmosphere. The stability of the modified electrode was checked by carrying out the continuous cycling of

voltammograms. A quasi-reversible redox couple with  $E_{1/2} = -0.2$  V vs Ag/AgCl (3M KCl) was observed which can be attributed to the redox couple of Cu(II)/Cu(I). The peak current of copper (II) reduction peak is not changed appreciably, which indicates that the modification of electrode is stable and not detachable from the electrode surface (supporting information S5). Fig. 2 shows the cyclic voltammograms of the modified electrode at different scan rates and presented in Fig. 3. The peak potential changed gradually when the scan rate is varied from 100 mV/s to 5 mV/s. The cathodic peak was shifted to negative direction and anodic peak was shifted to more positive with increasing the scan rate. The plot of peak current versus scan rates is shown in the inset of Fig. 2 and the cathodic currents are proportional to the scan rate. This trend suggests that the electroactive copper complex is adsorbed on the electrode surface. The concentration of copper(II) species on the electrode film was calculated as follows; the charge consumed to reduce the film was estimated by integrating the anodic wave of CV at 2 mV/s and the amount of copper(II) species was calculated by Faraday's law assuming that the number of electron involved in the reduction process is 1. The volume of the film was assumed to be 2  $\mu$ L which is the volume of the solution used to preparing the electrode by drop-coating. The concentration of the copper(II) species is found to be  $7.8 \times 10^{-10}$  moles/cm<sup>2</sup>.

### 3.1 Electrocatalytic Oxygen Reduction Reaction

It is obvious that copper containing enzymes and copper ion modified electrodes are showing electrocatalytic activity towards many biological processes [10-12] along with number of other biological species. Particularly, Cu-containing fungal laccase enzymes reduce O<sub>2</sub> directly to water at remarkable positive potentials. Herewith, the functional activity of Cu-enzymes is mimicked by using the PAIACuLbpy/PCE in neutral aqueous medium. The modified electrode exhibited an excellent electrocatalytic activity towards oxygen reduction reaction (ORR) in phosphate buffer (pH 7) and observed a current corresponding to an electrocatalytic oxygen reduction under air and oxygen as shown in Fig. 3. It is known that the catalytic oxygen reduction peak appears along with copper(II) reduction peak with enhanced peak current as shown in Fig. 3 in the presence of air

and oxygen. In the presence of oxygen, the catalytic current commenced at about -0.1 V, which is 0.3 V more positive than that of the bare PCE electrode (Fig. 3). When comparing the electrocatalytic currents under air with oxygen atmosphere,  $i_{O_2}/i_{air}$  is nearly 7, showing a good accessibility of oxygen. Moreover, while removing the oxygen atmosphere by purging argon, the current of copper(II) peak of the modified electrode is returned back to its original position and this result indicates that the oxygen binds with the copper ion reversibly. The ORR takes place in the same region of similar reported copper complex-polymer modified electrodes, -0.05 to -0.2 V [33].

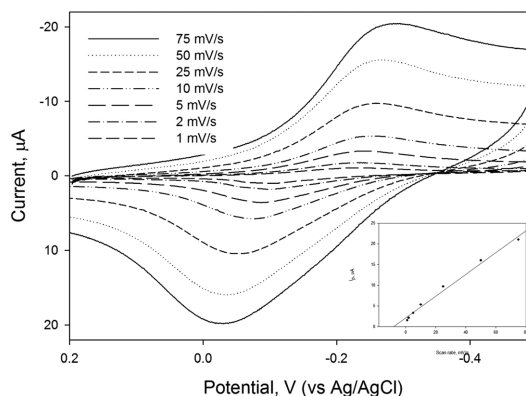


Fig. 2. Cyclic voltammograms of PAIACuLbpy/PCE at scan rates in 0.1 M phosphate buffer, pH 7 vs Ag/AgCl(3M KCl) under argon atmosphere; inset: peak current vs scan rates.

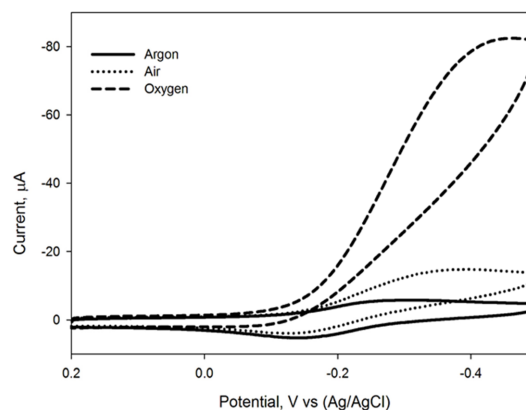


Fig. 3. Cyclic voltammograms of oxygen reduction on PAIACuLbpy/PCE in 0.1 M phosphate buffer, pH 7 at 5 mV/s vs Ag/AgCl(3M KCl) under oxygen and air.

### 3.2. Hydrodynamic studies

A kinetic study of the electrocatalytic oxygen reduction was performed with rotating disc (RDE) electrode modified with PAIACuLbpy-composite. Fig. 4 shows RDE voltammograms of PAIACuLbpy/PCE in 0.1M phosphate buffer (pH7) saturated with oxygen at various rotating rates from 0 to 1500 rpm with an increment of 300 rpm. The catalytic currents responsible for oxygen reduction start to flow around -0.1 V. A single stage of limiting current is observed when the potential is scanned from 0 to -0.6 V, indicating the electrocatalytic reduction of oxygen on PAIACuLbpy/PCE is controlled by the diffusion process. The Koutecky-Levich plots obtained from the RDE voltammograms are shown in Fig. 5, which are calculated at -0.5 V.

The diffusion limited currents for O<sub>2</sub> reduction at the rotating disk electrode were calculated by the Levich equation employing the following parameters: diffusion coefficient of O<sub>2</sub>,  $D_{O_2} = 2.5 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ , kinematic viscosity of aqueous solution,  $\nu = 0.01 \text{ cm}^2 \text{ s}^{-1}$ , concentration of oxygen in oxygen-saturated solution,  $C_{O_2} = 2.9 \times 10^{-4} \text{ mol cm}^{-3}$ , the Faraday constant,  $F = 96,485 \text{ C/mol}$ , and area of the disk electrode,  $A = 0.186 \text{ cm}^2$

$$i_{\text{lim}} = 0.620nFAD^{2/3}\omega^{1/2}\nu^{-1/6}C_{O_2} \quad (1)$$

From the slope of the Koutecky-Levich plot (-0.5 V), the number of electrons involved in the catalytic reduction of O<sub>2</sub> is calculated to be 3.8, which indicates that the catalytic reduction of oxygen on PAIACuLbpy/PCE is four electron process. The electroreduction of oxygen on a bare GCE is known to be around 2 electron process [37]. The extrapolated Koutecky-Levich plot is not passing through zero, which is probably due to the equilibrium between O<sub>2</sub> and H<sub>2</sub>O<sub>2</sub>. Both two and four electron reduction of oxygen is previously reported for Cu(II)-complex adsorbed EPG surfaces [26,38]. From the kinetic studies, it is observed that the electroreduction of O<sub>2</sub> was catalyzed by surface adsorbed Cu complex, through an unstable dioxygen adduct as an intermediate, proceeded by an inner sphere mechanism. Based on the above results, the following inner-sphere mechanism is proposed for the electrocatalytic reduction of O<sub>2</sub>.

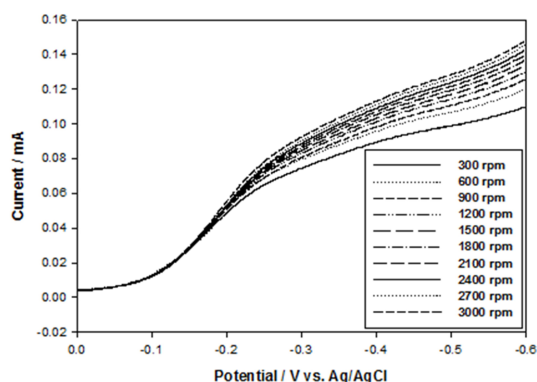
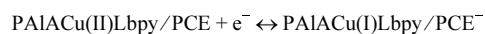


Fig. 4. Current-potential curves for the oxygen reduction on a PAIACuLbpy/RDE in 0.1M phosphate buffer, pH 7 at 5 mV/s under oxygen.

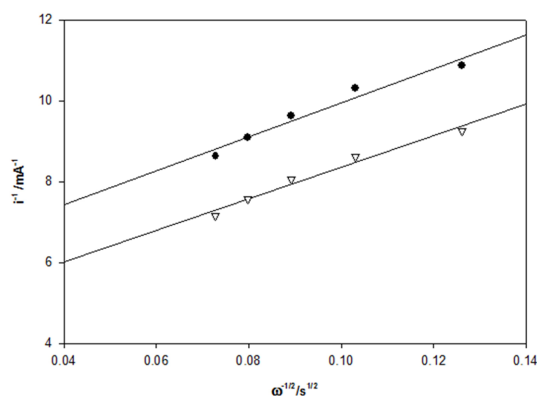
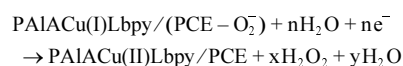
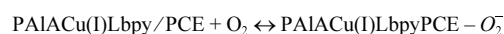


Fig. 5. Koutecky-Levich plot for the oxygen reduction with a PAIACuLbpy/RDE (at -0.5 V) in 0.1M phosphate buffer, pH 7 at 5 mV/s. (●) Two electron and (▽) four electron process.



A sensitive assessment was carried out to obtain the reaction stoichiometry by a rotating ring disc electrode RRDE. The potential of the ring was kept constant at 1.0 V to detect the generation of H<sub>2</sub>O<sub>2</sub>. The upper part of Fig. 6 shows the current-potential curve for the reduction of O<sub>2</sub> at PAIACuLbpy modified disk electrode. In the lower part of 6, the corresponding anodic current at the Pt ring electrode indicates that the reduction of O<sub>2</sub> at the disk produces



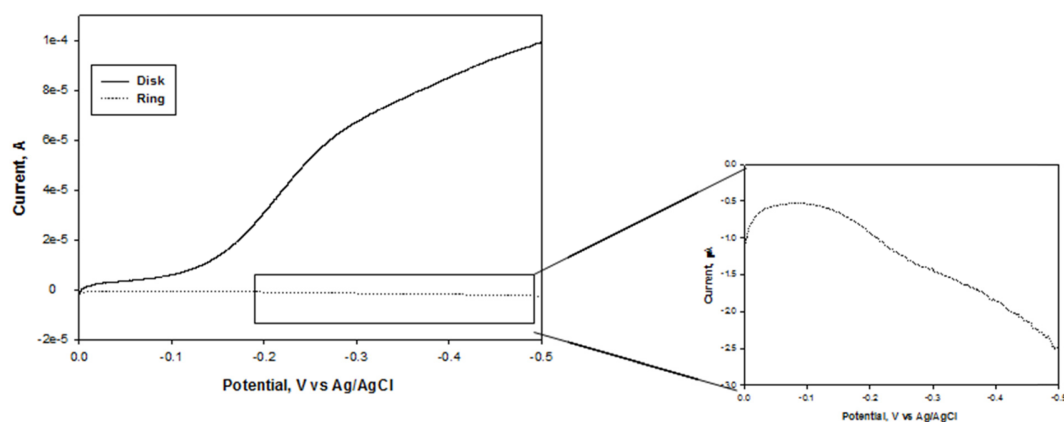


Fig. 6. Current-potential curves for the oxygen reduction on a RDE (0.1M phosphate buffer, pH 7, 50 mV/s).

both  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ . This observation suggests the possibility of a parallel catalytic pathway where oxygen is reduced to  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}_2$ .

#### 4. Conclusion

A hydrophilic mononuclear copper(II) complex containing poly(allylamine.HCl) polymer was synthesized. Composite of polymer with poly(acrylic acid) and TEOS was prepared to modify the electrode surface. A stable modification on PCE was obtained by drop coating the composite. The modified electrode PAIACuLbpy/PCE exhibited a quasi-reversible redox couple with  $E_{1/2} = -0.2$  V vs. Ag/AgCl (3M KCl) in 0.1M phosphate buffer (pH 7). The modified electrode PAIACuLbpy/PCE is utilized for ORR and it showed an excellent electrocatalytic response for the reduction of oxygen in phosphate buffer (pH 7) under oxygen at onset of -0.1 V, which is 0.3 V more positive than bare electrode. The kinetics involved in the catalytic reduction of oxygen was studied by rotating disk voltammetric technique. The results indicated that the number of electrons involved in the ORR are four with conversion of water and  $\text{H}_2\text{O}_2$ .

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