

## Electrocatalytic Conducting Polymers: Oxygen Reduction by a Polythiophene–Cobalt Salen Hybrid

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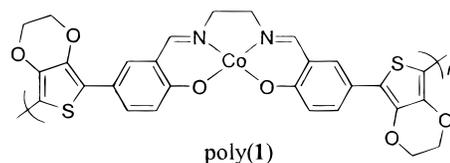
*Received November 8, 1999*

*Revised Manuscript Received January 3, 2000*

The electrocatalytic reduction of O<sub>2</sub> to H<sub>2</sub>O is critical to energy conversion (fuel cell) technologies. The fact that this process requires the near synchronous delivery of four electrons has resulted in many innovative catalyst designs, including catalysts containing redox reservoirs,<sup>1–10</sup> multinuclear complexes,<sup>1,11–19</sup> and the immobilization of catalysts on electrodes.<sup>1,11,12,14–19</sup> Ideal systems should exhibit durability, high current densities, selective reduction to H<sub>2</sub>O (i.e., no H<sub>2</sub>O<sub>2</sub> production), and function at the thermodynamic potential ( $E_{1/2} = +1.23$  V vs NHE). The stability of immobilized molecular catalysts is dependent on the rate of desorption from the electrode surface. One promising approach is the modification of electrode surfaces by the electrochemical polymerization of suitable catalyst monomers. Reduction of O<sub>2</sub> using polymers from the anodic polymerization of tetrakis(*o*-, *m*-, and *p*-aminophenyl)porphyrinatocobalt(II) complexes conformed to a nearly four-electron process in both acidic and basic media, as determined by the reduction current in the cyclic voltammogram.<sup>20</sup> A related *meso*-tetrakis[2,2]-*para*-cyclophanylporphyrinatocobalt(II)-based polymer showed similar four-electron reduction activity,<sup>21</sup> and anodically polymerized cobalt salen complexes perform this process

under neutral and basic conditions.<sup>22</sup> However, in the later case, substantial amounts of H<sub>2</sub>O<sub>2</sub> are produced. A critical requirement for efficient and selective catalysis in a polymerized film is the rapid delivery of four electrons to the catalytic site. Recognizing this feature, we have been interested in designing conductive polymeric systems wherein the well-defined catalyst is in essence amalgamated with a conductive support. By careful design, we report herein a system which retains the molecular identity of the transition metal catalyst and is intimately integrated in a highly conducting polymeric material.

We have recently reported the synthesis and electrochemistry of the cobalt salen-containing polymer, poly(**1**), which possesses 3,4-ethylenedioxythiophene (EDOT) moieties appended para to the phenolic oxygen.<sup>23</sup> This polymer is readily anodically deposited from its monomer on platinum or glassy carbon electrodes to give dark yellow films. The electron-rich nature of the organic backbone was chosen to affect a near perfect overlap of the polymer redox potential with that of the Co<sup>2+/3+</sup>



redox wave (−0.1 V vs Fc/Fc<sup>+</sup>). This redox matching produces high self-exchange/redox conductivity ( $\sigma = 42$  S/cm). We have further demonstrated that coordination of Lewis bases to the cobalt centers shifts the Co<sup>2+/3+</sup> redox wave to more negative potentials, as expected, with little loss of metal-centered electroactivity in the cyclic voltammogram.

Most previously investigated catalysts have been studied in acidic media to more closely simulate the conditions in fuel cells.<sup>1,11</sup> The cyclic voltammogram<sup>24</sup> of poly(**1**) in acidic media under an oxygen atmosphere displays a large reduction wave at +0.28 V in the initial sweep. Unfortunately, with continued cycling the peak potential shifted rapidly more negative, and the current density decreased with a concomitant loss of peak shape. This occurred in a variety of acidic media, including 0.05 M H<sub>2</sub>SO<sub>4</sub>, 0.5 M HClO<sub>4</sub>/0.5 M NH<sub>4</sub>PF<sub>6</sub>, and 1 M CF<sub>3</sub>-CO<sub>2</sub>H, and we believe that the most likely explanation is chemical degradation by the hydrolysis of the imine functionality in the salen core.

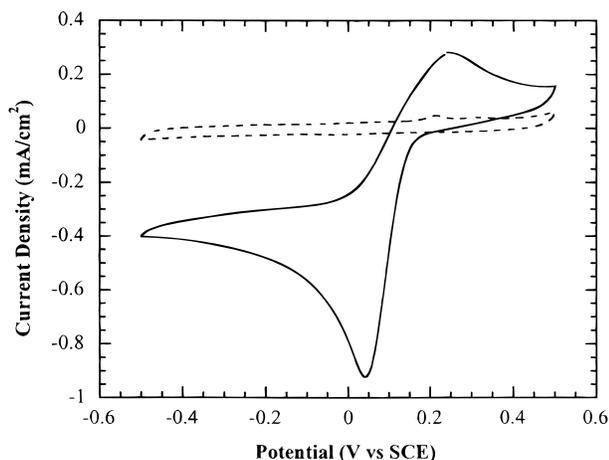
Films of poly(**1**) were subsequently examined in 0.1 M KH<sub>2</sub>PO<sub>4</sub>/K<sub>2</sub>HPO<sub>4</sub> buffer solutions (pH = 7) on a glassy carbon electrode under a nitrogen atmosphere (Figure 1). This neutral pH condition prevented chemical degradation of the polymer backbone due to acid attack. In the absence of O<sub>2</sub>, the polymer cyclic voltammogram is characterized by a nearly featureless trace with a

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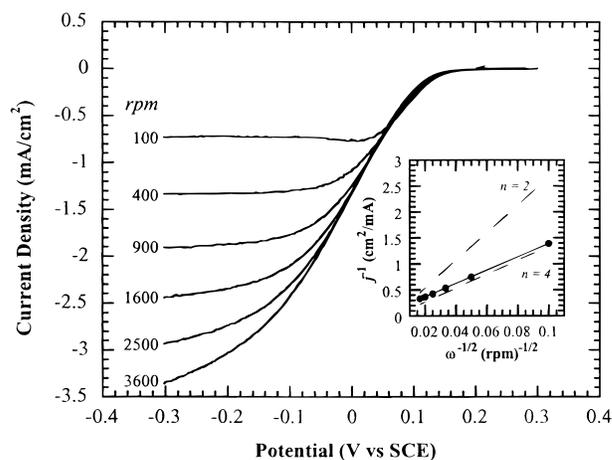
(24) Electrochemical measurements were made in a two-compartment cell with an isolated platinum wire counter electrode and a saturated calomel reference electrode against which all potentials are quoted for aqueous solutions.



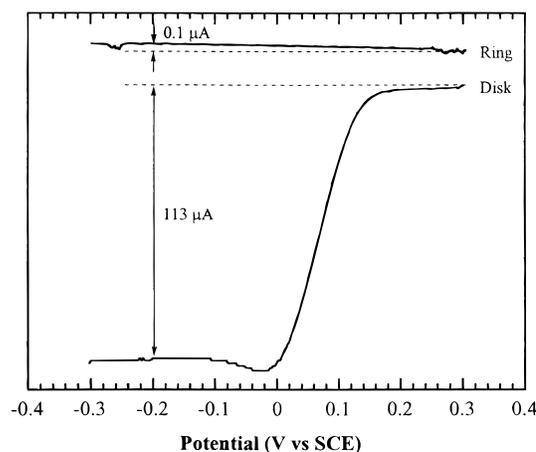
**Figure 1.** Cyclic voltammogram of poly(**1**) in 0.1 M  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  buffer solution on a  $0.07 \text{ cm}^2$  glassy carbon electrode at a sweep rate of  $100 \text{ mV/s}$  under oxygen (solid line) and nitrogen (dashed line) atmospheres.

small redox wave at  $0.1 \text{ V}$  vs SCE. Purging the solution with  $\text{O}_2$  and subsequently sweeping the same potentials resulted in the observation of a substantial enhancement of the reduction wave, corresponding to the electrocatalytic reduction of  $\text{O}_2$  by the polymer. At the start of the negative potential sweep from  $+0.5 \text{ V}$ , little current is observed until  $+0.15 \text{ V}$  when a reduction current increases dramatically until reaching a maximum at  $+0.05 \text{ V}$ . Oxygen reduction at a smooth Pt electrode under the same conditions reduced  $\text{O}_2$  at  $+0.48 \text{ V}$ .<sup>22</sup> At potentials lower than  $+0.05 \text{ V}$ , the reduction current from the polymer modified electrodes falls off as oxygen is consumed near the electrode surface. Oxygen reduction is accompanied by an oxidation wave at  $+0.25 \text{ V}$  on the return scan of varying current density depending upon the film. We attribute this process to polymer-bound oxygen species since ring–disk electrode experiments indicate the absence of significant quantities of free peroxide (vide infra). A sweep rate analysis of the  $\text{O}_2$  reduction afforded a slope of  $2.6 \text{ mA}/(\text{cm}^2 (\text{V/s})^{1/2})$  when plotting the current density,  $j$ , versus the square root of the sweep rate,  $v^{1/2}$ . The theoretical value for a four-electron process is  $3.2 \text{ mA}/(\text{cm}^2 (\text{V/s})^{1/2})$  assuming an  $\text{O}_2$  concentration of  $1.45 \times 10^{-3} \text{ M}$  (oxygen-saturated solutions<sup>25</sup>) and a diffusion coefficient,<sup>26</sup>  $D = 2.6 \times 10^{-5} \text{ cm}^2/\text{s}$ .

The electrochemistry of poly(**1**) immobilized on a glassy carbon rotating disk electrode is shown in Figure 2. As the electrode is rotated at a rate  $\omega$ , oxygenated electrolyte solution is swept toward the face of the electrode where it can interact with the polymer film. At low rotation speeds, the limiting current density,  $j$ , increases linearly with the square root of the rotation rate, indicative that the reduction current is dependent on the rate of oxygen arrival at the electrode surface.<sup>27</sup> The limiting current for this system was determined at  $-0.2 \text{ V}$ . Increasing the rotation rate induces a deviation from the Levich plot, which has been observed in other



**Figure 2.** Rotating disk voltammograms of poly(**1**) in 0.1 M  $\text{KH}_2\text{PO}_4/\text{K}_2\text{HPO}_4$  buffer solution on a  $0.1642 \text{ cm}^2$  glassy carbon disk electrode at a sweep rate of  $50 \text{ mV/s}$  under an oxygen atmosphere. Rotation rates are indicated. Inset: Koutecky–Levich plot showing the limiting current density,  $j$ , versus the square root of the rotation rate (kinematic viscosity  $0.01 \text{ cm}^2/\text{s}$ ).



**Figure 3.** Rotating ring–disk voltammograms of poly(**1**) with the platinum ring potential held at  $+0.86 \text{ V}$  using the same conditions as in Figure 2. The ring and disk current scales are different.

systems.<sup>4,5,10,14</sup> A Koutecky–Levich plot<sup>28</sup> of  $j^{-1}$  versus  $\omega^{-1/2}$  results in a linear relationship in the rotation rate range studied. Comparison of this slope to the theoretical slope for a two- and four-electron reduction of  $\text{O}_2$  shows that poly(**1**) affects a four-electron reduction of  $\text{O}_2$  to  $\text{H}_2\text{O}$ . The limiting currents observed for this catalyst are comparable to those observed by others.<sup>11,22</sup>

To ascertain the effectiveness of this catalyst for the four-electron reduction of  $\text{O}_2$ , ring–disk<sup>29</sup> measurements were performed.<sup>30</sup> The platinum ring was held at  $+0.86 \text{ V}$  to oxidize any  $\text{H}_2\text{O}_2$  byproducts that are swept by. Figure 3 shows a typical voltammogram at a rotation rate of  $100 \text{ rpm}$  and a sweep rate of  $50 \text{ mV/s}$ . Only a very small ring current is observed as the potential is swept through the electrocatalytic reduction potential, which indicates almost no  $\text{H}_2\text{O}_2$  production by the

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(30) The glassy carbon disk ( $0.1642 \text{ cm}^2$ )–platinum ring electrode (model AFMSRX, Pine Instrument Co.) had a  $0.018\text{-cm}$  gap between the disk and ring electrodes and a collection efficiency of  $0.22$ .

catalyst. The number of electrons involved in the reduction process may be estimated by comparison of the ring and disk currents, taking into account the possible H<sub>2</sub>O<sub>2</sub> diffusion difficulties with polymer modified electrodes,<sup>31</sup> by  $n = 4 - 2(i_r/i_d N_0)$ , where  $i_r$  and  $i_d$  are the ring and disk limiting currents and  $N_0$  is the collection efficiency. Calculation of this ratio shows that there is > 3.9 electron reduction of O<sub>2</sub> at the poly(**1**)-modified electrode. The nearly complete reduction of O<sub>2</sub> at the poly(**1**) surface is a substantial improvement over a previously reported related polymer, wherein poly[Co(salen)] displayed only a 39% conversion of O<sub>2</sub> to H<sub>2</sub>O.<sup>22</sup> The differences may be attributed to the highly conduc-

tive nature of poly(**1**), which can allow for rapid transfer of electrons from the electrode surface to the active metal centers.

In summary, we have demonstrated that a highly conducting transition metal–polythiophene hybrid material catalyzes the reduction of O<sub>2</sub>. Rotating ring–disk measurements suggest a selective four-electron reduction process takes place to produce H<sub>2</sub>O as the sole product. Currently, we are developing related hybrid materials designed to be more stable to acidic conditions as well as related sensory systems.

**Acknowledgment** is made to the Office of Naval Research for funding.

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