ELECTROCATALYTIC REDUCTION OF OXYGEN AT VAPOR PHASE POLYMERIZED POLY(3,4-ETHYLENEDIOXIDETHIOPHENE) MODIFIED GLASSY CARBON ELECTRODE

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ABSTRACT. We successfully polymerized poly(3,4-ethylenedioxidethiophene) by vapor phase polymerization technique on rotating glassy carbon disk electrode. The catalytic activity of this electrode towards oxygen reduction reaction was investigated and showed remarkable activity. Rotating disk voltammetry was used to study the kinetics of oxygen reduction reaction by plotting Levich, Koutecky Levich and Tafel plots. It was found that the reduction was mixed diffusion and kinetic controlled. The O_2 reduction underwent through four electron transfer reaction. The Tafel slope was obtained as 55 mV/dec. The limiting current density was higher by a factor of more than 10^3 times the exchange current density.

KEYWORDS: Poly(3,4-ethylenedioxidethiophene), Vapor phase polymerization, Oxygen reduction, Glassy carbon electrode

INTRODUCTION

One of the difficult situations in the widespread use of alternative renewable energy sources like solar and hydroelectric energy sources for sustainable power generation is the growing energy demand that does not correlate with the actual available energy from these sources. This calls for an efficient means of storing excess energy when the sun is shining or when the weather is good enough to supply the water needed for hydroelectric power plants. Electrochemical energy conversion like fuel cells are most attractive technologies for efficiently storing the excess electrical energy in to chemical fuels and later use it for different applications ranging from powering small portable devices to generating several megawatts of electrical energy for stationary power generation and for transportation purposes [1-4]. Several different types of fuel cells such as polymer electrolyte membrane [5], alkaline [6], phosphoric acid [7], molten carbonate [8], solid oxide [9] and biofuel cells [10] are under development [11].

In all fuel cell devices, the reduction of O_2 to H_2O plays a critical role. The sluggish nature of the oxygen reduction reaction requires an expensive electrocatalyst like platinum. The high cost of platinum is the main reason for keeping consumers from reaping the benefits of the clean energy afforded by fuel cell technology for transportation and stationary power generation applications. Because of this, a vast worldwide research effort is underway to identify and synthesize cheaper electrocatalysts to reduce the amount of platinum loading or completely replace it with non-platinum based catalysts. Materials like clays, zeolites, quinones, anthraquinone and their derivatives, nanotubes and metal nanoparticles alone and in combination with conducting polymers are also under intensive investigations for their catalytic behavior towards oxygen reduction [12-20].

Conducting polymers synthesized electrochemically, chemically as well using vapor phase polymerization techniques found interesting electrocatalytic activity towards oxygen reduction for reducing the amount of platinum loading or completely replace it with cheap and efficient non-platinum based electrocatalysts [21-24]. Particularly, poly(3,4-ethylenedioxythiophene), which is commonly used in organic electronic devices show quite remarkable behavior when synthesized through vapor phase method which results from its high conductivity and we

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characterized and investigated its potential applications in organic electronics [25-28]. In this study, we report to our knowledge for the first time the electrocatalytic behavior of this material for oxygen reduction at rotating glassy carbon disk electrode.

EXPERIMENTAL

The glassy carbon rotating disk electrode of 0.0707 cm^2 area was first polished to a mirror finish using 0.05 mm alumina prior to each experiment. The VPP PEDOT was prepared on the polished glassy carbon electrode following similar procedures reported earlier [25-28]. Briefly, 0.585 mL of pyridine was added to 20 mL of Baytron C 40% iron(III) tosylate in butanol (H. C. Starck Newton, MA) and the mixture was then spin coated on a polished glassy carbon electrode for 1 min at 2500 rpm. The sample was then inverted and transferred to a reaction chamber where 3,4-ethylenedioxythiophene was allowed to evaporate at 65 °C for 30 min, allowing the polymerization reaction to occur directly on the electrode surface. Finally, the sample was left at room temperature for 30 min before rinsing the unreacted oxidant with ethanol. The average film thickness we obtained when vapour phase synthesis was made on different substrates under these conditions was about 120 nm [26].

For the electrosynthesis of PEDOT, a 0.01 M EDOT monomer was dissolved in a 0.1 M tetrabutylammonium tetrafluoroborate (Bu_4NBF_4) in acetonitrile as the solvent. The EDOT was then electropolymerized on the dried GC by running cyclic voltammetry from 0.0 to 1.3 V (*versus* Ag/AgCl) for ten cycles. After electropolymerization, the PEDOT modified GC electrode was carefully washed with acetonitrile. Then the modified electrode was cycled between -0.8 to 0.8 V in monomer free 0.1 M Bu_4NBF_4/acetonitrile solution until stable film is obtained.

Cyclic voltammetric investigations and rotating disk experiments were carried out using Epsilon electrochemical workstation. A three-electrode system consisting of VPP PEDOT/GCE or ECP PEDOT/GC as a working electrode, a Ag/AgCl reference electrode and a platinum wire counter electrode were used for the electrochemical measurements.

RESULTS AND DISCUSSION

Figure 1 shows the cyclic voltammograms of the vapor phase polymerized (VPP) PEDOT modified glassy carbon electrode (GCE), and electrochemically polymerized (ECP) PEDOT modified GCE and bare GCE in oxygen and argon saturated 0.5 M H_2SO_4 solution, respectively. The comparison of the electrocatalytic activity of the different electrodes toward oxygen reduction revealed that the oxygen reduction potential is shifted to more positive value and the peak current is highest in the VPP PEDOT in oxygen saturated 0.5 M H_2SO_4 solution (Figure 1). No significant electrocatalytic activity is observed for the ECP PEDOT modified GCE in oxygen saturated 0.5 M H_2SO_4 solution as reported earlier by other groups [29].

Rotating disk voltammograms for VPP PEDOT modified GCE in oxygen saturated 0.5 M H_2SO_4 at different rotation speeds (100-3200 rpm) are shown in Figure 2. The currents associated with O_2 reduction begins to flow around -0.1 V (Ag/AgCl) and exhibit plateaus at around -0.63 V (Ag/AgCl). The diffusion limiting current was observed and increased with increasing rotation speed. The current density under pure argon atmosphere is also shown and is independent of the rotation speed.
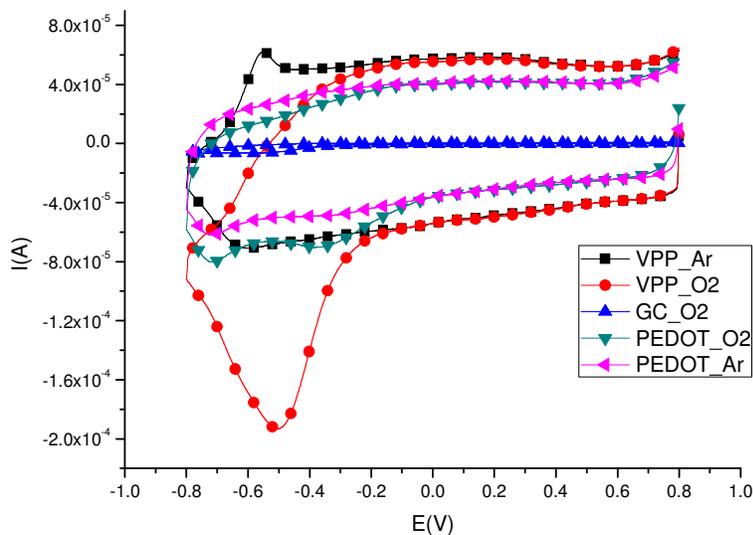
Figure 1. Comparative cyclic voltammograms of the modified and bare electrodes in oxygen saturated 0.5 M H$_2$SO$_4$. Scan rate 100 mV/s.
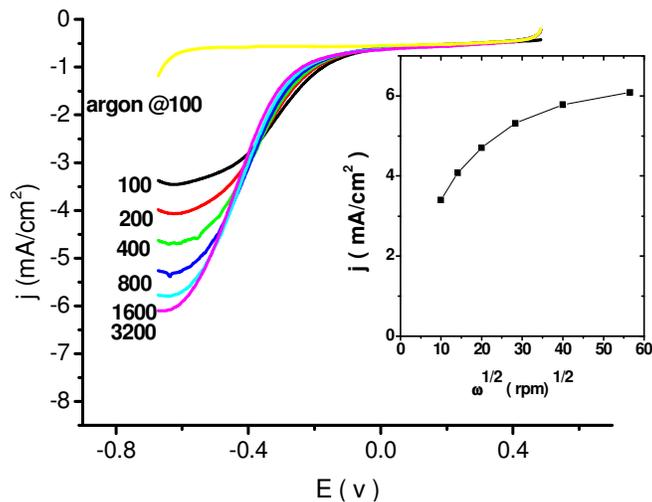

Figure 2. Rotating disk voltamograms at different rotation speeds for O$_2$ reduction on a VPP PEDOT modified GCE in oxygen and Argon saturated 0.5 M H$_2$SO$_4$; respectively, at scan rate of 10 mV/s between potential of 0.4 V to -0.672 V (*versus* Ag/AgCl). The inset shows Levich plot of limiting current at potential of -0.63 V (*versus* Ag/AgCl) for O$_2$ saturated 0.5 M H$_2$SO$_4$ at VPP PEDOT modified GCE.

The rotating disk electrode (RDE) data were analyzed using the Levich and the Koutecky-Levich equations. The Levich equation is expressed as equation 1:

$$I_l = 0.62\, nFAC_oD^{\frac{2}{3}}v^{-\frac{1}{6}}\omega^{\frac{1}{2}} \tag{1}$$

where n is the number of electrons, F is the Faraday constant (96485Cmol^{-1}), A is the electrode area (0.0707 cm^2), C_o is concentration of O_2 (1.1 x 10^{-6} mol/cm^3), D is the diffusion coefficient (1.4 x 10^{-5}cm^2/s) of oxygen, ν is kinematic viscosity of O_2 (1.1 x 10^{-2} cm^2/s) taken from the literature value and ω angular velocity (in rpm) [30]. The nonlinear Levich plot and the highest value of the current plateau reached for oxygen reduction at VPP PEDOT modified GCE in an O_2 saturated 0.5 M H_2SO_4 solution (Figure 2 insert), suggests that the oxygen reduction is mixed diffusion and kinetic controlled reaction [31].

The kinetic contribution to the current is given by equation 2:

$$I_k = nFAC_ok_o\exp\left(\frac{-\alpha nF(E-E_o)}{RT}\right) = nFAk_fC_o\Gamma \tag{2}$$

where k_o is the standard heterogeneous rate constant, k_f is the heterogeneous rate constant, Γ is the surface coverage by active species, E_o is the formal potential, E is electrode potential, T is temperature and R is gas constant. The electrode current for case in mixed transport–kinetic control is described by the above equation. The combination of these equations produces the so called Kouteky-Levich equation 3:

$$\frac{1}{i} = \frac{1}{i_k} + \frac{1}{i_l} = \frac{1}{nFAk_fC\Gamma} + \frac{1}{0.62nFAC_oD^{\frac{2}{3}}v^{-\frac{1}{6}}\omega^{\frac{1}{2}}} \tag{3}$$

The plot of $\dfrac{1}{i_l}$ vs $\dfrac{1}{\omega^{\frac{1}{2}}}$ for constant value of k_f i.e. fixed η are predicted to generate straight line

having slope proportional to 1/n and intercept proportional to $\dfrac{1}{k_f}$ [31].

The Kouteky–Levich plot (current density corrected from the background yielded straight lines with the intercept corresponding to the inverse of the kinetic current.

The data from the slope of Koutectky-Levich plot at -0.63 V was also used to calculate the number of electrons and found to be n = 3.12. The slope of the Koutectky-Levich plot is close to the theoretical value of the four electron reduction O_2 directly to H_2O. This confirms that the oxygen reduction reaction at the VPP PEDOT modified GCE in oxygen saturated 0.5 M H_2SO_4 solution is not a two electron reaction via the formation of H_2O_2. Similar results are obtained for carbonized polyaniline nanostructures and micro/mesoporous conducting nitrogen-containing carbon nanorods/nanotubes with high surface area, and excellent electrocatalytic activity for the oxygen reduction reaction, which also belong to the classes of non-precious catalysts as VPP PEDOT [32, 33].

The intercept at the origin of the Koutecky-Levich plot gives the inverse of the kinetic current I_k as a function of potential. The Tafel slope (b = 55 mV/dec) and the exchange current (I_o = 1.48 x 10^{-7} A) were determined by plotting (Figure 3) the potential E *versus* $\ln\left|\dfrac{I_l*I_k}{I_l-I_k}\right|$

using the equation 4 [34]:

$$E = E_{eq} - b\left[\ln\left(\frac{j_l}{j_o}\right) + \ln\left|\frac{j_k}{j_l-j_k}\right|\right] \tag{4}$$

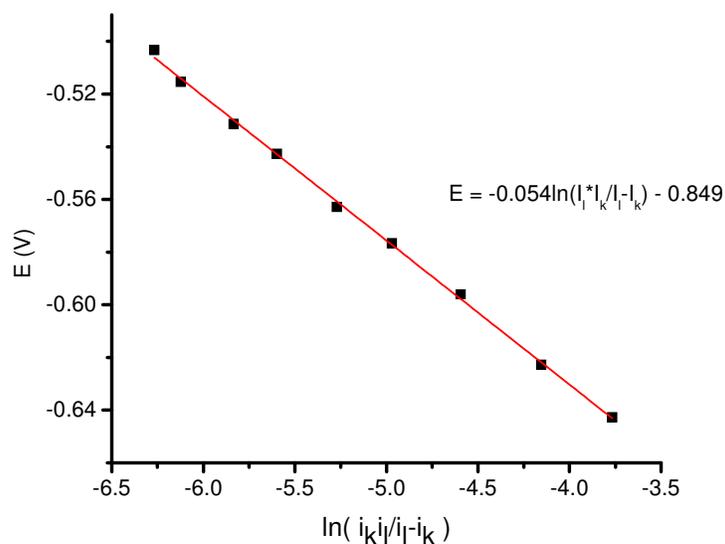where I_l is the limiting current (5.035x10^{-4} A).

Figure 3. Plot of E *versus* $\ln\left|\dfrac{I_l * I_k}{I_l - I_k}\right|$ for oxygen reduction at VPP-PEDOT modified GCE in oxygen saturated 0.5 M H_2SO_4.

The value of the Tafel slope obtained (b = 55 mv dec^{-1}) indicates Temkin adsorption isotherm [35-37]. The limiting current, I_l is much higher (by a factor of more than 10^3 times) than that of the exchange current, I_o [34, 31].

CONCLUSIONS

The electrocatalytic reduction of oxygen was studied on the VPP-PEDOT modified GCE using cyclic voltammetry and rotation disk voltammetry. The VPP-PEDOT modified GCE was found to have significant effect on the catalytic activity. The kinetic parameters like I_o, I_l and Tafel slope were evaluated. The results showed that VPP-PEDOT was a promising catalyst and can also serve as a catalyst support of platinum or non-platinum based metals for oxygen reduction reaction.

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