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Electrocatalytic Reduction of Oxygen on PEDOT-Modified Glassy Carbon Electrode

Jinfu Ma[1*], *Xiaoe Wang*[2], *Xiangwei Jiao*[2]

[1]School of Materials Science and Engineering, Beifang University for Nationalities, Yinchuan 750021, PR China
[2]Office of Scientific Research，Beifang University for Nationalities, Yinchuan 750021, PR China

[*]E-mail: majf0870@163.com

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The poly(3,4-ethylenedioxythiophene)(PEDOT) was synthesized on glassy carbon electrode(GCE) by potentiostatic electropolymerisation, the linear sweep voltammogram (LSV) of EDOT aqueous solution containing Na_2SO_4 support electrolyte shows two oxidation peaks (+1.19V，+1.4V), which relate to the oxidation of monomer and the overoxidation of the PEDOT film. The cyclic voltammograms(CV) of PEDOT film modified GCE in 0.1M KOH alkaline solution with or without oxygen indicate that the PEDOT has good catalytic activity for oxygen reduction reaction(ORR). The Tafel plots show that ORR on PEDOT is a 2-electron transfer process with an intermediate product of HO_2^-.

Keywords: 3,4-ethylenedioxythiophene(PEDOT)；oxygen reduction reaction；Fuel cell

1. INTRODUCTION

Fuel cells are considered promising power sources because of their high-energy conversion efficiency, environmental compatibility, reliability, and quiet operation. The air electrode, which reduces oxygen, is a critical component in energy generation and storage applications such as fuel cells and metal/air batteries. The highest current densities are achieved with platinum(Pt), but in addition to its cost and scarcity, Pt particles in composite electrodes tend to be inactivated by contact with carbon monoxide (CO) or by agglomeration[1]. So, it is significant to research non-precious metal catalysts for fuel cells, especially high activity catalyst for cathodic reaction, in our previous works, the metals phthalocyanine (MPcs)[2-3] as cathode catalyst used in alkaline solution (direct borohydride fuel cells), and the MPcs has high activity for ORR and acceptable tolerance for anodic reaction.

As a type of conductive polymer, PEDOT was originally synthesized by the German Bayer company[4], the methods of PEDOT preparation[4-10], especially electropolymerise[7-10] were studied widely. The PEDOT was used mainly in electrochromic displays [11], as an antistatic coating on different materials [12], and also for use in slight-emitting diodes (OLEDs) [13]in solar[14] and fuel cells as anode catalyst support and improve the anodic catalyst[16-19], etc. In recent paper, A PEDOT/Goretex electrode[1] produced by vapor phase–polymerization method use the Iron(III) *para*-toluenesulfonate(Iron(III)PTS) as the oxidant, was used as electrochemical catalyst for ORR, and its catalytic activity and stability higher than the precious metals Pt, this findings not only expand the use of PEDOT, but also , it has great significant for the development of fuel cells.

In this article, PEDOT modified glassy carbon electrode(GCE) was prepared by electrochemical polymerization, and the electrochemical oxygen reduction reaction(ORR) catalyzed behavior was investigated.

2. EXPERIMENTAL

All chemicals were reagent grade, used without further purification. The monomer, EDOT, has been obtained from Aldrich.

The cyclic voltammograms (CV) and galvanostatic line sweep voltammograms (LSV) were carried out in a conventional three-electrode arrangement using a computer controlled CHI650C Electrochemistry Workstation (CH Instrument, Inc. USA). The GCE served as the working electrode, a Hg/HgO/6 M KOH electrode as a reference electrode, and a Pt wire as a counter electrode. The reference electrode was connected to the main body of the cell through a Luggin capillary, whose end was centered on the working electrode and positioned closed to the electrode surface. EIS measurements were acquired at the frequency range was 100 kHz to 1 Hz with an AC perturbation signal of 5 mV, and the results were simulated by ZSimpWin software.

3. RESULTS AND DISCUSSION

3.1 Electropolymerisation of EDOT

The value of the applied potential is one of the most significant parameters in an electropolymerisation process; therefore, experiments to establish the highest and lowest potential values at which it is possible to obtain polymer films with satisfactory value is conditioned by the fact that the polymer has not to be overoxidised.

3,4-Ethylenedioxythiophene is poorly soluble in aqueous solutions, so that low enough concentrations have been used in order to guarantee homogeneous media. The solution of 0.01 M EDOT+0.1 M Na_2SO_4 was standing for 24h, the color of the mixture solution changed to yellow which indicate that the oligomer was generated. Fig.1 shows the linear sweep voltammogram of 0.01M EDOT aqueous solution containing 0.1M Na_2SO_4 at sweep rate of 10 mVs^{-1}. Two oxidation peaks, P1 and P2, are apparent around +1.19 and 1.40V, respectively. The two peak potential values are in agreement with previously reported data. According to them the first peak (P1) has been related to the oxidation of monomer, adsorbed or not on the electrode surface. The second peak (P2) has been related either to the oxidation of EDOT species diffusing close to the electrode (and/or dimmer or oligomers formed during the first step), or to the overoxidation of the PEDOT film if an enough amount of polymer was deposited on the electrode. Therefore, from the results shown in Fig.1, potential of +1.19V was selected for electropolymerisation process.

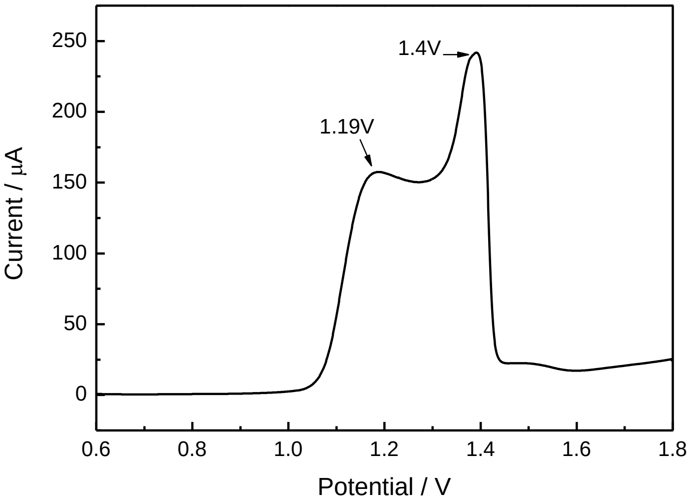

Figure 1. Linear voltammogram of 1×10^{-3}M EDOT in 0.1M Na_2SO_4 using a GCE (scan rate:10mv.s^{1})

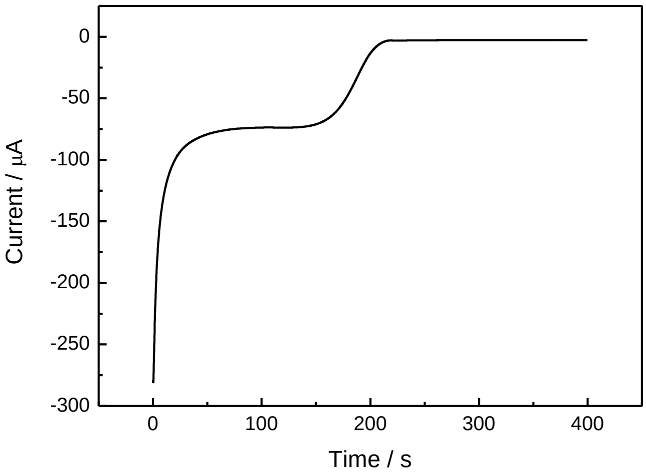

Figure 2. The current-time curve for electropolymerisation of EDOT at 1.19V on GCE.

Fig.2 shows current-time curve for polymerization of EDOT monomer under the conditions of 1.19V. It can be seen from Fig.2, the aggregate current is about 75μA when the reaction time of smaller than 180s, when electropolymerisation time is more than 180s, the aggregate current rapidly decreased to 0μA (210s), which showed that the amount of PEDOTGCE surface has reached saturation. It was determined that aggregate consumption is-1.602e-2C.

3.2 Electrocatalytic behavior of PEDOT for ORR

In order to investigate the electrochemical catalytic behavior of PEDOT for ORR, the electrochemical behavior of PEDOT-modified GCE was studied by cyclic voltammetry in 1M KOH solution. As shown in Fig.2, at scan potential window of 0.2 ~-0.8V and scan rate of 50mVs^{-1}, the green curve express the electrochemical behavior of bare GCE in argon saturated KOH solution, there is no obvious polarization current and redox peak. An irreversible reduction peak occurs in O_2 saturated KOH solution in the CV curve (black) at -0.30V, the results show that GCE has a certain catalytic activity for ORR. From the blue curve, it indicates that the character of CV curve PEDOT modified GCE in argon saturated solution is similar to bare GCE in argon saturated system, however, the difference of black curve compare to green curve is due to the double layer capacitance caused by PEDOT film.

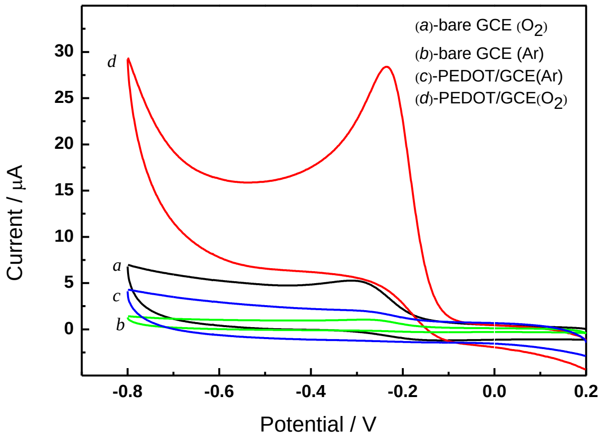

Figure 3. Cyclic voltammograms of :(a)bare GCE with O_2;(b)bare GCE with Ar; (c) PEDOT-modified GCE with Ar; (d)PEDOT-modified GCE with O_2. (Scan rate = 50 mV.s$^{-1)}$

The red curve indicate that there is an obvious irreversible reduction peak at -0.20V with PEDOT modified GCE in O_2 saturated KOH solution, compares to the unmodified GCE, the potential peak shifts positively 0.10V , the peak current increase of nearly 6 times, the results show that, PEDOT has a good electrochemical catalytic effect for ORR in the alkaline solution, this finding has great value for research on alternative precious metal cathodic catalyst on alkaline fuel cells or batteries such as direct borohydride fuel cells and Zn/air batteries.

3.3 The Kinetic Behavior of ORR Catalyzed by PEDOT

The electrochemical reduction reaction of oxygen at a PEDOT-modified GCE in 1M KOH solution is a irreversible process.

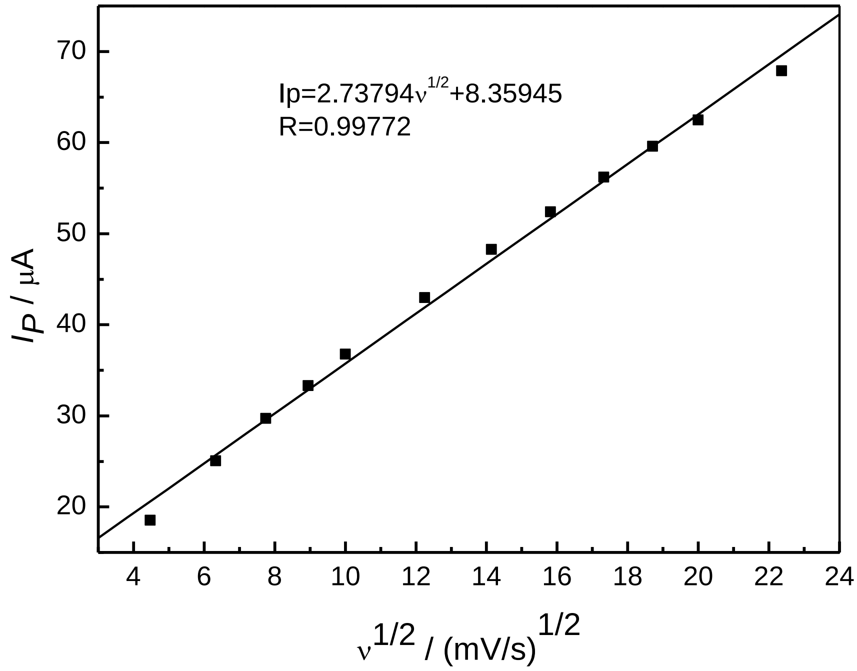

Figure 4. The relationship of I_p vs. $v^{1/2}$

As shown in Fig.4, at scan rate ranging 20~500 mV.s^{-1}, the plot of peak current versus the square root of the scan rate($v^{1/2}$) is a straight line, as expected for a diffusion-limited electrochemical process.

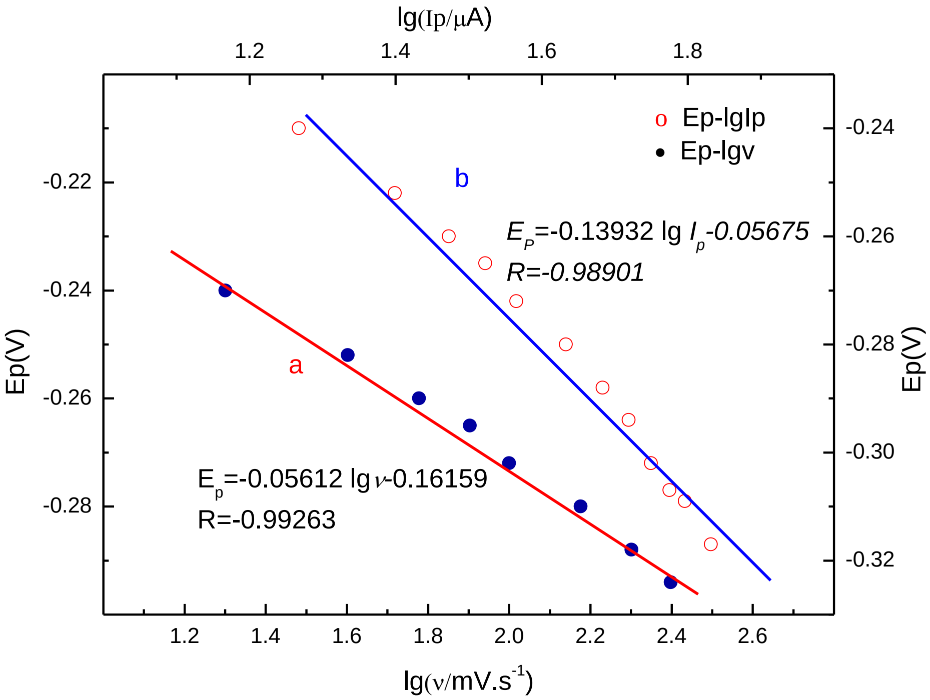

Figure 5. Tafel plot of AFc and sulfite: (a) E_P vs. Log v ; (b) E_P vs. log I_P.

In addition, with increasing scan rate, the catalytic reduction peak potential (Ep) shifts to more negative values and there is a linear correlation between the peak potential and the logarithm of scan rate, log (ν/mV.s^{-1}), as is illustrated in Fig.5a, the tafel slope b can be obtained from the linear relationship of Ep vs.log (ν/mVs^{-1}) by using the following equation[20]:

$$Ep = (b/2) \log (\nu/mV.s^{-1}) + constant \quad (1)$$

On the basis of Eq. (1), the slope of Ep vs. log (ν) plot is b/2, where b indicates the Tafel slope. The plot of Ep versus log (ν) indicates a linear variation for scan rates ranging 20–500 mV.s^{-1} . The slope is ∂Ep /∂log (ν), which was found to be 0.112 V in this work. So, b = 2 × 0.104 V = 0.224 V. Assuming the number of electrons transferred in the rate-limiting step, n is equal to 2, a transfer coefficient, α, was estimated as 0.26. If we assumed n = 1, α would then be equal to 0.52 which is not a common value, because for most electrode processes α equals to 0.2±0.02 due to the slow kinetics of ORR in alkaline solution[21].

The other Tafel slope (Fig. 5b) has been obtained by another method, A slope of 0.139V per decade is obtained, indicating a a transfer coefficient of α= 0.21 assuming two-electron transfer process.

The results show that ORR on PEDOT is an 2-electron transfer process with an intermediate product of HO_2^-.

3.4 EIS Spectra of ORR Catalysed by PEDOT-Modified GCE

EIS data were fitted with the circuit shown in Fig.6. The elements have the following meanings: R1 is the solution ohmic resistance; Rct is the charge transfer resistance; CPE is a constant phase element, used instead of a capacitance due to the inhomogeneous surface of the electrode.

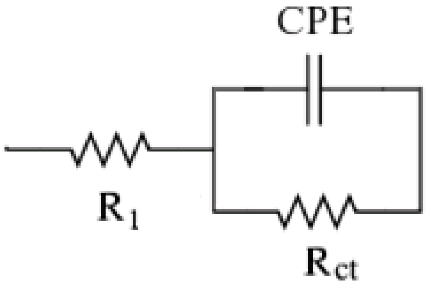

Figure 6. Equivalent circuit used to fit the experimental EIS data.

Fig.7 shows the complex plane plots of PEDOT-modified GCE in O2-saturated alkaline solution. The plots show single time-constant arcs, at positive polarization potential, the high charge transfer resistance (Rct) due to the ORR does not occur for 0.2 V~0, Decreasing the polarization from 0 to -0.2 V reduces the ORR charge transfer resistance (Rct) because of the enhanced electrochemical kinetics[22,23], but a further decrease to -0.6 V results in a larger resistance. The increase in Rct at such potential indicates a transition from an electrochemical kinetic dominated process to a mass transport dominated process with increasing polarization. At higher polarizations in Fig.7, the impedance spectra are dominated by the diffusion of species. Thus, the Rct values become progressively larger.

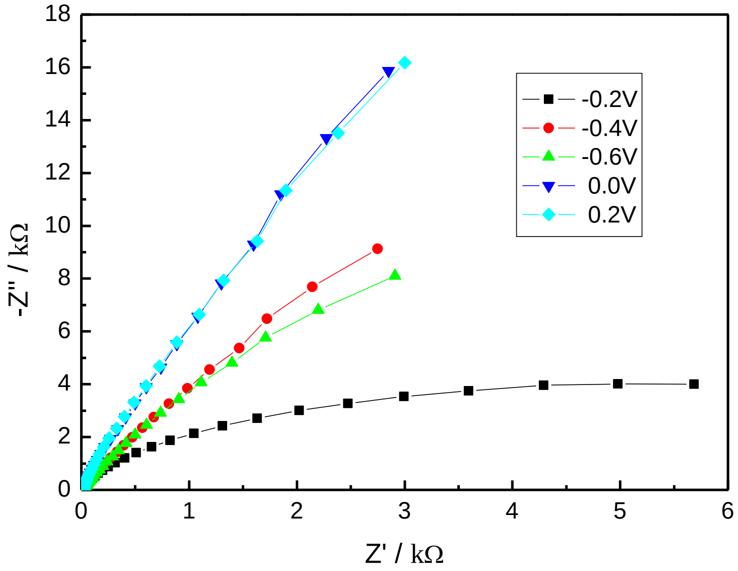

Figure 7. Simulated curves of EIS impedance at different potentials.

4. CONCLUSIONS

The poly(3,4-ethylenedioxythiophene)(PEDOT) was synthesized on glassy carbon electrode(GCE) by potentiostatic electropolymerisation. The electrochemical experiments show that, the ORR can be catalysed by PEDOT in alkaline solution, and the ORR on PEDOT is a 2-electron transfer process with an intermediate product of HO_2^-.

However, this article aims to examine the electrochemical PEDOT on the ORR catalytic behavior, other parameters such as the supporting electrolyte, catalyst for polymerization, and the mechanism of ORR catalysed by PEDOT should be conducted detailed investigating in further research.

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