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PAN/PSF Composite Films as Supports of PtRu Particles for Methanol Electro-Oxidation

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The polyaniline/polysulfone (PAN/PSF) composite films are prepared by electropolymerization, and then PtRu particles are deposited into this composite film to obtain the PtRu-modified polyaniline/polysulfone (PtRu/PAN/PSF) electrodes. Their morphology and chemical component are characterized by scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDS), respectively. The cyclic votammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques are applied to investigate the electrocatalytic activity of the PtRu/PAN/PSF electrodes. The results show that the PtRu-modified composite film electrode significantly enhanced electrochemical activity towards methanol oxidation. Current–time measurements reveal that the PtRu-modified composite film electrode is relatively endurable for intermediate production. In addition, the effect of ratios of Pt to Ru for methanol oxidation is also investigated，which the ratio of Pt/Ru= 2:1 holds the best activity for methanol oxidation. Furthermore, the electrochemical behaviors of the PtRu/PAN/PSF electrode are also discussed.

Keywords: PtRu modified composite film electrode; Electrochemical preparation; Catalytic activity; Methanol oxidation

1. INTRODUCTION

In recent years, methanol oxidation has been attracting enormous research interest due to the possible application in direct methanol fuel cells (DMFC)， which show great promise as high-efficiency, low-emission future power sources[1-2]. However, there are several barriers to their application, including the poisoning of Pt electrocatalyst by adsorbed CO species, as well as substantial power losses due to the relatively low activity of the methanol oxidation catalysts [3]. Therefore, binary, multi-catalysts are considered as the best choice for anodic and cathodic fuel cell.

Nowadays, many different electrocatalysts have been investigated, such as PtPd， PtSn, PtMo[4-6] and ternary compounds such as PtRuNi, PdCoAu, and PtRuSn[7-9], while the PtRu catalyst is commonly accepted as the best electrocatalyst for methanol oxidation. The presence of Ru may increase the anode activity by reducing the effects of CO poisoning. In addition, the importance of the supporting material structure for the activity of the catalyst has been concerned [10,11]. Carbon and carbon nanotubes (CNTs), appeared to be promising supporting materials for platinum and platinum-based alloy catalysts. However, the pristine surface of these materials is relatively inert and difficult to support particles homogeneously [12-14], which often results in the agglomeration and drop of nanoparticles. To overcome these difficulties, conducting polymers such as polyaniline as a substrate offer great advantages easy to coat on various substrates. They own high accessible surface area, stability and low resistance [15].Consequently, dispersing metal particles into PAN films is an attractive method to prepare electrocatalysts [16,17]. Generally, these conductive polymers were directly deposited onto the surface of the conductive substrate as working electrode by electrochemical polymerization, but the brittleness, unsteady and desquamation of active deposited layer constitute major obstacles to its extensive application. Thus, preparing supporting materials with large porosity is necessary for PtRu namiparticls dispersion.

The porous bi-layer PAN/PSF composite film whose inner layer is conductive polyaniline and the outer layer is non-conductive polysolfone were prepared in our previous experiments [18-19]. In the composite film the conducting polyaniline layer furnishes the required conducting behavior and the non-conducting polysulfone matrix enhances the mechanical properties. Furthermore, the porous structure of the PAN/PSF composite films can accommodate a dispersed PtRu catalyst with a large surface area， preventing catalyst particles from agglomerating and consuming in working. So the composite film can be a promising supporting material for platinum and platinum-alloy-based catalysts.

In this report, the PAN/PSF composite films were prepared using the published method of our group with some modifications [19]. The platinum and ruthenium particles are deposited in PAN/PSF composite film by CV deposition. The cyclic votammetry (CV) and electrochemical impedance spectroscopy (EIS) techniques are applied to investigate the electrocatalytic activity of the PtRu/PAN/PSF electrodes and Pt/PAN/PSF electrodes. In addition, the effect of ratios of Pt to Ru for methanol oxidation is also investigated.

2. EXPERIMENTAL PART

2.1. Materials and electrochemistry

Aniline (CP, Shanghai) was distilled under decompression prior to use and stored in refrigerator. Polysulfone (Aldrich, Mn =26 kg mol^{-1}) was dried in vacuum at 60°C before use. All other chemicals used in this investigation were of analytical grade and used as received. All the solutions were prepared with twice distilled water.

All electrochemical experiments were carried out in a conventional three-electrode electrochemical cell by means of CHI660B electrochemical analyzer. The working electrode was a platinum disk encapsulated in epoxy resin (electrode geometric area: 0.0366 cm^2), a platinum wire and a saturated calomel (SCE) electrode were used as counter electrode and reference electrode, respectively.

The electrochemical properties of the PtRu/PAN/PSF composite film electrode were investigated in 1.0MCH_3OH+0.5MH_2SO_4 aqueous solutions. The impedance data were collected in ac frequency range from 0.01Hz to 100kHz with the same ac amplitude of 5 mV at the open circuit potential. All experiments were carried out at room temperature.

2.2. Preparation of PAN/PSF electrode

The composite films were prepared using the published method of our group with some modifications [19]. The amount of aniline monomer decrease to 1.8ml in 10ml polysulfone + N, N-dimethyl acetamide solution and a 1.5μL aliquot of the mixture solution was used to coat the Pt working electrode at each time. Then the electrodeposition was carried out between -0.1V and 0.9V for 15 circles at the scan rate of 50 mVs^{-1}.

2.3. Preparation of PtRu/PAN/PSF electrode

Onto thus obtained composite film electrodes, platinum and ruthenium particles were deposited in PAN/PSF composite film at the potential range from -0.25V to 0.65V at 50mVs^{-1} for 30 circles in a solution of 8mM H_2PtCl_6 + 4mM $RuCl_3{\cdot}xH_2O$+0.5MH_2SO_4. Prior to PtRu electrodeposition, the PAN/PSF composite film electrodes were kept in the 8mM H_2PtCl_6 +4mM $RuCl_3{\cdot}xH_2O$ +0.5M H_2SO_4 solutions for 15min. The resultant PtRu modified PAN/PSF composite film electrode can be directly used as working electrode for methanol oxidation.

2.4. Characterization of PtRu/PAN/PSF composite film

The FTIR measurements were performed in an ATR modelon Nicolet NEXUS 670 spectrometer to characterize the chemical component of the PAN/PSF composite films. The SEM images were obtained by a JSM-5600LV electron microscope. The EDS data was also collected to analysis the element component of the PtRu/PAN/PSF composite films.

3. RESULTS AND DISCUSSION

3.1. FTIR spectra

The FTIR spectra are almost the same as that of in our published paper [18]. This indicates that the PAN/PSF films are composed of two layers, in which the inner layer comprises polyaniline while the outer layer is composed of polysulfone.

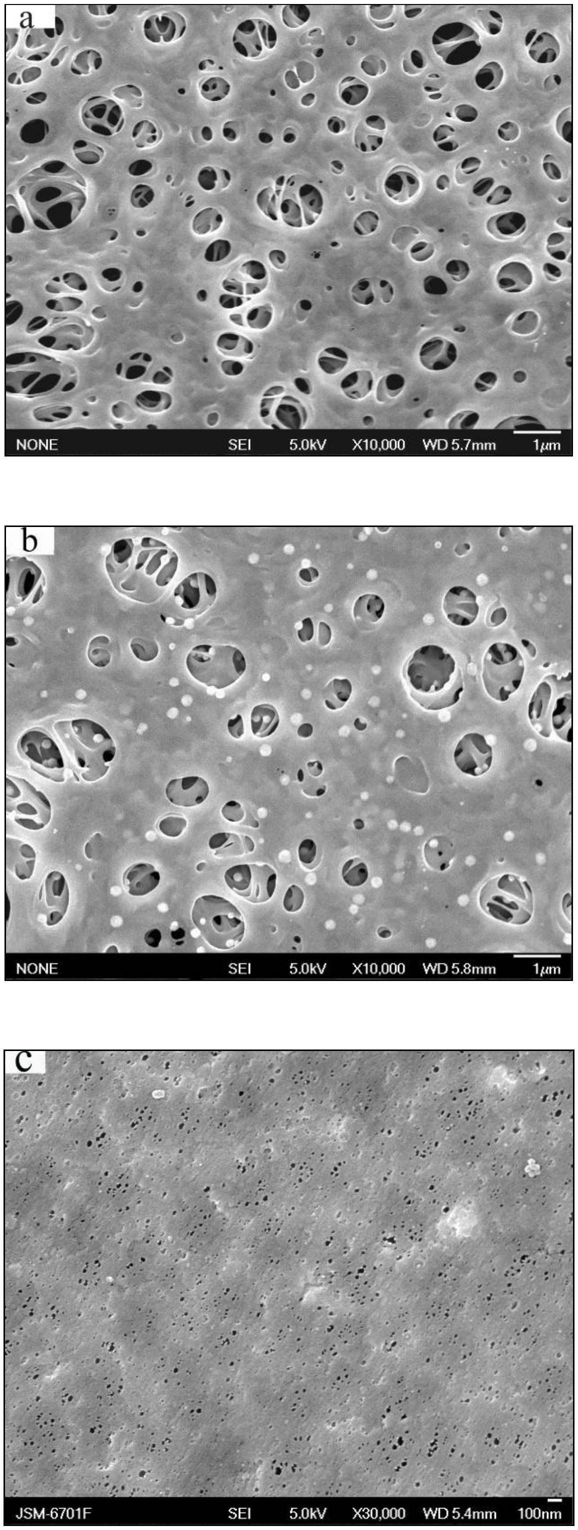

Figure 1. SEM micrographs of the polyaniline layer of the PAN/PSF film (a) and the inner layer (b) and outer layer (c) of PtRu modified PAN/PSF film.

3.2. SEM images and EDS analysis

The SEM images of the polyaniline layer of the PAN/PSF and the inner and outer layer of PtRu/PAN/PSF composite film are shown in Fig.1, respectively. As can be seen, the polyaniline layer of the PAN/PSF film has a porous structure with different pore diameters, while on the outer surface of the composite film there are a lot of small pores as Fig 1c is shown whose morphology is similar to that of our previous work [18]. From Fig.1b, we find that the PtRu particles disperse uniformly in the polyaniline layer. Some of the PtRu particles are dispersed on the framework of the porous structure, while the others are holden in the holes of the polyaniline layer. It is furthermore observed that the pores of the polyaniline layer exhibit the three-dimensional net structure, which offers many advantages as a supporting material for the electrocatalysts. Firstly, it provides a cross-link framework for depositing PtRu nanoparticles, facilitating to obtain loading without agglomeration as Fig 1b is shown. Secondly, its holes supply an unblocked path for transporting reaction components while its cross-link frameworks furnish the electrochemical reaction with large surface. So the composite film is an excellent substrate for depositing electrocatalysts.

The EDS data is shown in Fig.2. The obvious signal of platinum and ruthenium indicates that two kinds of particles have been deposited on the composite film. The peaks of C, N and S elements are due to polyaniline and polysulfone in the composite film.

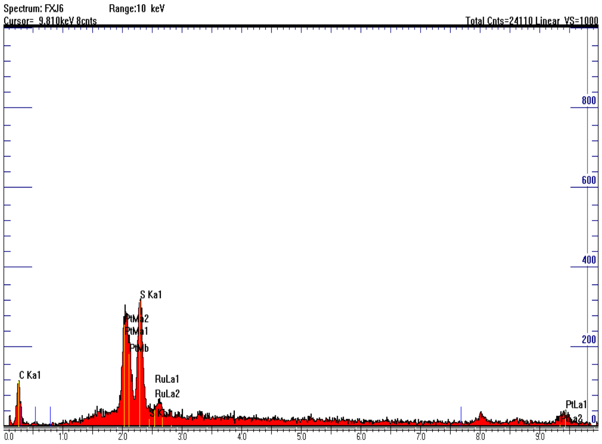

Figure 2. EDS patterns of the PtRu/PAN/PSF composite film electrode.

3.3. Electrochemical characterization of PtRu/PAN/PSF composite film electrode

To compare the electrochemical activity of the PtRu/PAN/PSF (a) and Pt/PAN/PSF (b) electrodes, the cyclic voltammetry of them were performed in 0.5M H_2SO_4 solution between -0.1 and 0.9 at a scan rate of 50mVs^{-1}. As shown in Fig. 3, the hydrogen adsorption/desorption peaks are clearly seen for two electrodes, but the current of the hydrogen region is higher for the PtRu/PAN/PSF. It infers that the PtRu modified electrode has the more active sites than Pt modified electrode. In addition, the large current in the double-layer region is observed on the PtRu/PAN/PSF electrode, which is ascribed to the adsorption of oxygen-containing species (probably OH) on Ru atoms. Another major difference is that the cathodic peak of oxygen-like species on PtRu sharpens and shifts towards more negative potentials. This implies that the oxygen-like species will form on the PtRu/PAN/PSF at lower potential, which helps to oxidize the adsorbed intermediates during methanol oxidation [20].

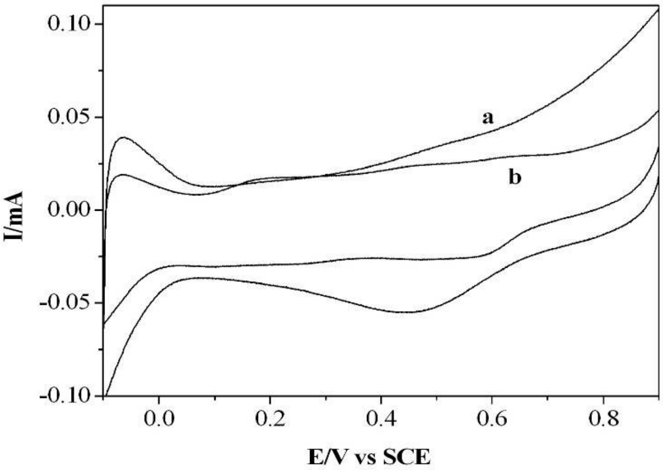

Figure 3. Cyclic voltammograms of PtRu/PAN/PSF (a) and Pt/PAN/PSF electrodes (b) in 0.5 M H_2SO_4 solution. Scan rate: 50 mVs^{-1}.

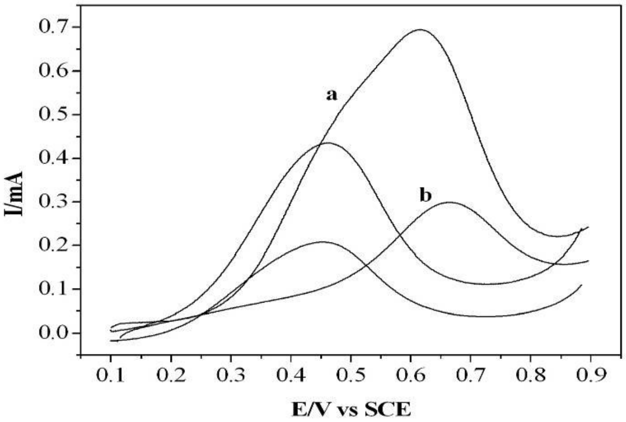

Figure 4. Cyclic voltammograms of PtRu/PAN/PSF (a) and Pt/PAN/PSF electrodes (b) in 1M CH_3OH+0.5 M H_2SO_4 solution. Scan rate: 50 mVs^{-1}.

3.4. Methanol electrooxidation

3.4.1. Cyclic voltammetry for methanol electrooxidation

The cyclic voltammetry curves of PtRu/PAN/PSF electrode (a) and Pt/PAN/PSF electrode (b) for methanol electrooxidation are shown in Fig.4, respectively. From the figure, we can see clearly that two electrodes have good electrocatalytic activity for methanol oxidation. The reason is that an ideal nano-construction of the catalyst in the electrodes enhances their electrocatalytic activity. In addition, the rich porosity structure of the composite film can offer more interfaces for electrochemical reactions. Moreover, a significant difference that the peak potential is negatively shifted and peak current is higher is observed in the case of PtRu modified PAN/PSF due to an important role of Ru in the electrocatalytic process. The presence of Ru transfers effectively oxygen and reduces the poisoning of anode catalysts, which may lead to the larger accessible electrochemical areas of the electrode. Thus, the prepared PtRu/PAN/PSF has a potential application in DMFCs as an anode electrocatalyst for methanol electrooxidation.

Further investigation was made into the transport characteristics of methanol in the modified composite film electrode. From Fig.5, it can be seen that the peak currents of methanol oxidation increase with the increase of scan rates and the peak potentials almost have no change. The anodic peak currents are linearly proportional to the square root of scan rates (shown in inset), which suggests that the electrocatalytic oxidation of methanol on PtRu/PAN/PSF electrode is a diffusion -controlled process.

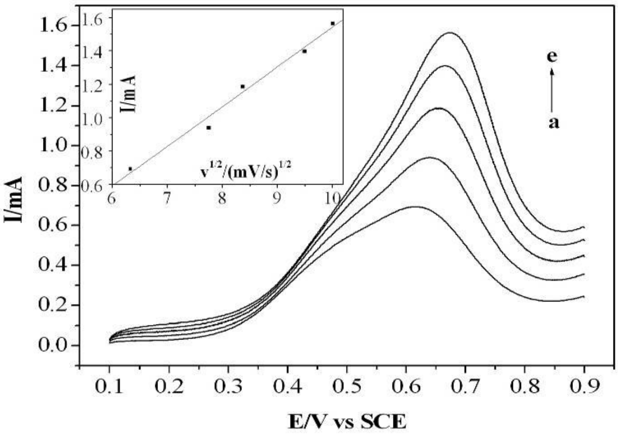

Figure 5. The anodic peak currents in 0.5M H_2SO_4 solutions at different scan rates. Scan rates from a to e are 40, 60, 70, 90 and $100mV^{-1}$, respectively. Inset shows dependence of the anodic peak currents on the square root of scan rates.

3.4.2. Current–time curves for methanol electrooxidation

To evaluate the endurance of the composite electrodes, the electrolysis was performed at constant potential of 0.65V in 1.0M CH_3OH with 0.5M H_2SO_4 solution for 1h. Fig.6. shows typical current–time responses on PtRu/PAN/PSF (a) and Pt/PAN/PSF (b) electrodes. As shown in the figure, both of them present a current decay in current–time measurements, which was also observed for traditional Pt [21] and PtRu catalysts [22] attributing to the formation of some Pt oxide or adsorbed intermediates such as CO in methanol electrooxidation reaction [23]. However, the most interesting feature deserving our attention is that the current decay on the PtRu/PAN/PSF electrode is less than on

Pt/PAN/PSF electrode. This is supposed that the PtRu-modified composite film electrode is relatively endurable for intermediate production.

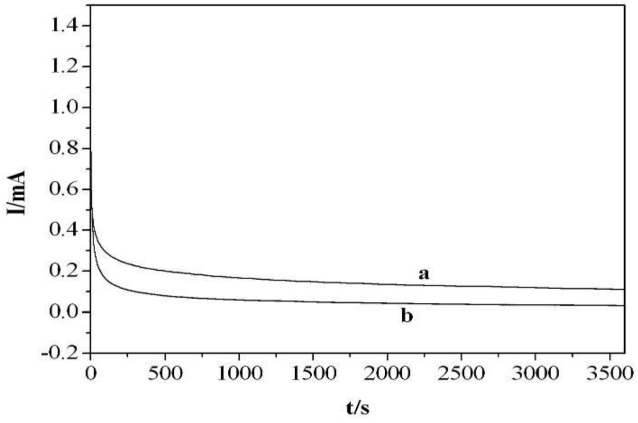

Figure 6. Current-time curves at 0.65V for 1h of PtRu/PAN/PSF (a) Pt/PAN/PSF electrodes (b) in 1 M CH_3OH +0.5 M H_2SO_4 solution.

3.4.3. Effect of Pt-Ru compositions for methanol oxidation

In order to investigate the effect of the ratio of Pt to Ru in PAN/PSF composite film electrodes towards methanol oxidation, the concentration of Pt is kept constant (8mMl^{-1}) and the content of Ru is changed from 4 to 16mMl^{-1} during the electrochemical synthesis of PtRu/PAN/PSF electrodes. The electrochemical oxidation of methanol on the PtRu/PAN/PSF electrodes with different $R_{Pt/Ru}$ has been investigated by cyclic voltammetry. The forward peak current and forward peak potential with $R_{Pt/Ru}$ are shown in Fig7. From Fig.7A, it can be seen that Ep shifts to the negative direction with the content of Ru increases. When electrocatalyst is changed from single Pt to PtRu ($R_{Pt/Ru}$ = 2/4), the shift of Ep is up to 70 mV. This implies that the electrooxidation of methanol is easier on the PtRu catalyst than that on the single Pt. As shown in figure 3, sufficient amounts of oxygen-like species such as OH_{ad} exist at lower potentials on Ru sites(above≈0. 44V) than on the single Pt sites(above≈0. 57V) because Ru has higher affinity towards oxygen-containing species. It is generally considered that the oxygen-like species facilitates removal of the adsorbed CO on Pt, which regenerates the active sites poisoned by intermediate product and CO, and promotes the activation of electrcatalysts.

Fig.7B shows the dependence of the peak currents on the content of Ru. The maximum of peak current is found at around $R_{Pt/Ru}$ = 2/1. Compared with single Pt catalyst, a certain amount of Ru can improve the catalytical activity of the catalyst. It is suggested that Ru provide for oxygenated species in the vicinity of Pt sites, creating additional active sites for CO_{ads} oxidation, which provides increasing activity of catalyst towards methanol oxidation [24]. On the other hand, the exceed amount of Ru content in PtRu nanoparticles modified electrode results in the decrease of the electrocatalytical activity of the catalyst as it is well known that Ru has no catalytic activity for the electrooxidation of methanol [25].This result infers that Pt is responsible for the true catalytic effect and Ru acts as a promoter for methanol electro-oxidation.

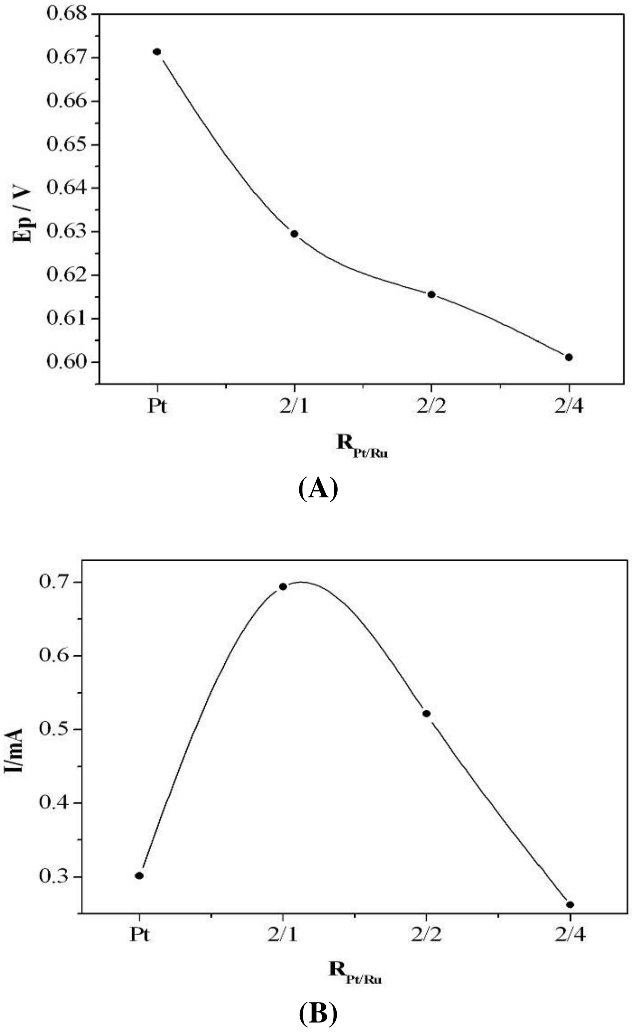

Figure 7. The different ratio of Pt to Ru in deposition solution on the peak potential (A) and peak current (B) for methanol oxidation at PtRu/PAN/PSF electrodes. Deposition solution, 8mM H_2PtCl_6 + 4mM $RuCl_3$ ($R_{Pt/Ru}$=2). Scan rate: 50 mVs^{-1}.

3.4.4. Electrochemical impedance spectroscopy for methanol electrooxidation

In order to further compare the activity of methanol electrooxidation of PtRu/PAN/PSF (a) and Pt/PAN/PSF (b) electrodes in 0.5M H_2SO_4 solution with 1.0M CH_3OH. The EIS of two electrodes were carried about at different potentials. Fig.8. shows the impedance plots of methanol oxidation at potentials of 0.30V, 0.55V and 0.65V. The EIS results indicate that the methanol electrooxidation on two electrodes at various potentials shows different impedance behaviors. At 0.30V, an arc is clearly evident in the complex-plane plots, which indicates the presence of a resistive component. The resistive component may be due to the reaction resistant of the methanol dehydrogenation reaction. At 0.55V, pseudo-inductive behavior is observed (positive Z'' values). This pseudo-inductive behavior

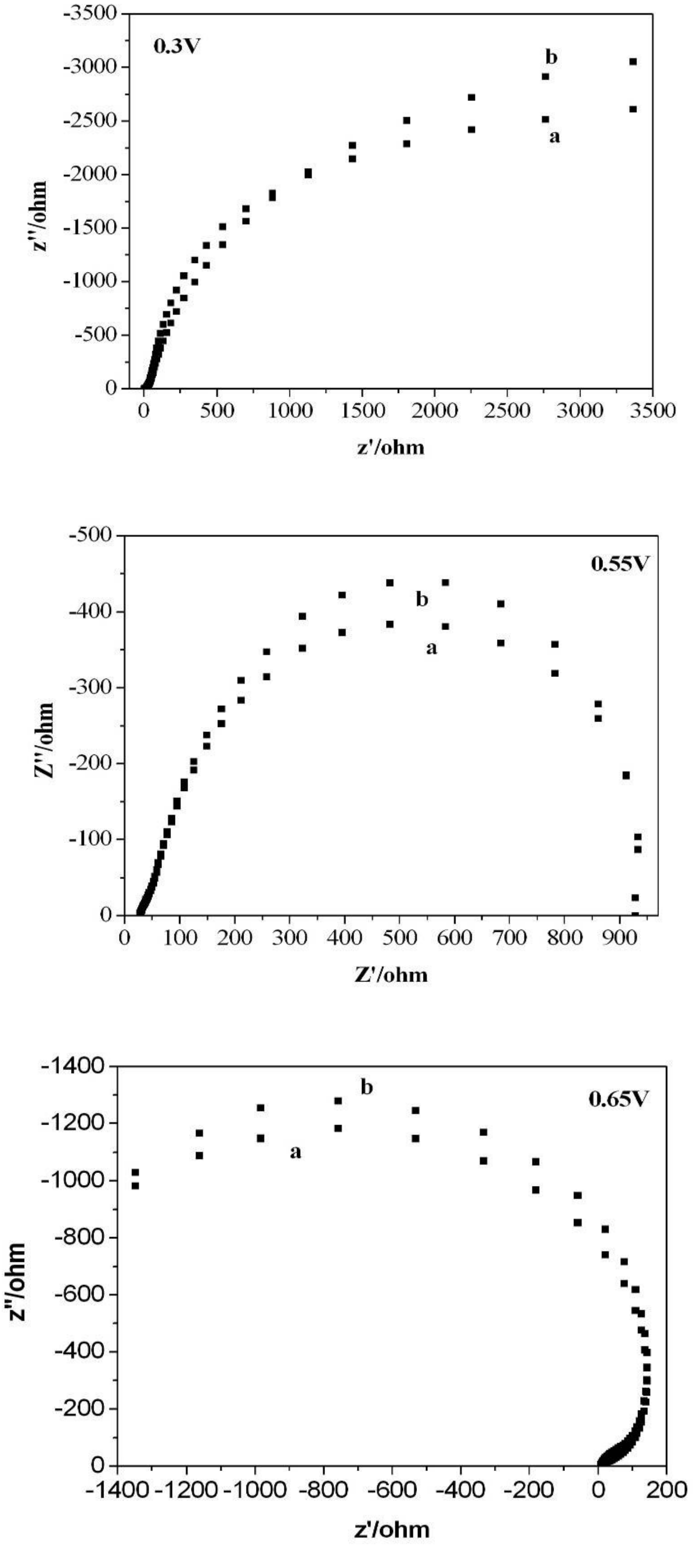

Figure 8. EIS of PtRu/PAN/PSF (a) and Pt/PAN/PSF electrodes (b) in 1 M CH_3OH +0.5 M H_2SO_4 solution at 0.30V, 0.55V and 0.65V potential, respectively.

has been attributed to CO_{ad} oxidation [26-27]. In addition, we can see that there exists a smaller diameter on the PtRu/PAN/PSF electrode than Pt/PAN/PSF electrode which shows the oxidation of CO_{ads} with the OH_{ads} on Ru sites is faster. When methanol oxidation is at high potential of 0.65V, the electrode may be produce surface passivation, which makes the real component of the impedance becoming negative. The passivation of the electrode during methanol electrooxidation is probably due to the reversible formation of oxide species. The oxidation of CO_{ads} is very slow, so the passivation at higher potentials can inhibit adsorption of methanol on Pt sites in the Pt/PAN/PSF and PtRu/PAN/PSF electrodes.

The methanol oxidation reaction should involve many parallel processes with reaction intermediates. The impedance data in this study proves two major reactions, namely the CH_3OH to CO_{ad} and CO_{ad} to CO_2 oxidation reactions. For methanol electrooxidation, methanol dehydrogenation is rate-determining step at low potential (0.3V). At intermediate potential (0.55V), the rate of CH_3OH to CO_{ad} reaction is increasing with an increase of potential, but is not enough to exceed the rate of reaction CO_{ad} to CO_2 obviously. So in this case the rate-determining step of methanol electrooxidation is in transition region. When methanol electrooxidation is at high potential (0.65V), reaction CO_{ad} to CO_2 can be assumed as rate-determining step. It is shown that CO only is intermediate not poisoning substrate at PtRu/PAN/PSF electrodes.

4. CONCLUSIONS

The PtRu/PAN/PSF composite film electrodes with bi-layer asymmetrical porous structure were successfully prepared by the electrochemical method. Its polyaniline layer exhibits the three-dimensional net porous structure and a cross-link framework, offering several advantages for the composite films as the supporting materials of electrocatalysts. Firstly, it facilitates to obtain loading without agglomeration. Secondly, its holes supply an unblocked path for transporting reaction components while its cross-link frameworks furnish the electrochemical reaction with large surface. Lastly, the polysulfone layer is located outer so that it is directly in contact with the solution phase, which its conductive layer and deposited PtRu particles will be kept from damaging in the reaction process. The analysis of cyclic voltammetry indicates that PtRu modified composite film electrodes have a more excellent activity for methanol oxidation in comparison with Pt modified composite film electrodes. The ratios of Pt to Ru are infective for electroactivities of the catalyst. The ratios of Pt/Ru= 2:1 hold the best activity for methanol oxidation. Furthermore, the PtRu modified electrodes exhibit better endurance than Pt modified electrode for the intermediates during methanol oxidation.

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