

Influence of Surface Roughness of YSZ on Polarization of Pt Electrode Deposited on the Electrolyte

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Received: 19 April 2013 / Accepted: 2 June 2013 / Published: 1 July 2013

The influence of surface roughness of YSZ on polarization of Pt electrode deposited on the electrolyte was investigated in ambient air at 600°C, with emphasis put on the comparative analysis for the anodic and cathodic polarization of Pt electrode prepared by using different grade of diamond pastes. Generally, at the absolute over-potentials up to 0.3V, the limiting currents passing through the electrode during anodic polarization were lower than that under cathodic bias result from the depressed site-exchange reaction of oxygen and platinum atoms. However, while the electrode was polarized at the absolute over-potentials larger than 0.3V, the more pronounced electro-activity for oxidation was found ascribed to the promotion of site-exchange reaction. Although a relatively smaller quantity of oxygen anions oxidized at the limited interfaces of the electrode prepared by using 1000 grade diamond paste than that of the electrode prepared by using 400 grade paste, the site-exchange reaction might be actuated by the concentrated contact area in the former electrode, which made it exhibits the maximum electro-catalytic activity at the over-potentials lower than 0.4V. As the polarization signal increased, the second electrode won and held the best performance due to the saturation of site-exchange reaction. The further chronopotentiometric experiments demonstrated that the electrode was more active towards oxidation than towards reduction reactions under strong polarization. And the remarkable enhancement of electro-catalytic activity was not observed during both potentiostatic and amperostatic polarization experiments might be due to the short polarization time and relatively low temperature.

Keywords: surface roughness; Pt/YSZ electrode; polarization; chronoamperometry; chronopotentiometry

1. INTRODUCTION

Yttria stabilized zirconia (YSZ) has been still the most widely studied and employed oxygen conductor at temperatures above 300 °C due to its high ionic conductivity and stability for over 50 years, by application of different electrodes on YSZ substrates, the solid electrolyte cells for gas sensors [1-5], gas pumps [6-7], solid oxide fuel cells [8-12] and electrochemical reactors [13-14] can be fabricated. In all of these applications metals are normally used as the catalytic active anodes and cathodes, and it has been shown that Pt is one of the most attractive catalysts for use in YSZ cells due to its high melting point, availability of stable structure, and minimized amount of impurities [15-18].

In YSZ cells, the two and three boundary interfaces (the main sites where the oxygen exchange occurs) are generated just by the deposition of electronic conductors on the electrolyte. And it is not difficult to imagine that any influencing factors of these interfaces might have a strong effect on the electrode kinetics under steady operating conditions. Polarization is closely related to the surfacial and bulk chemical states of porous Pt electrode deposited on YSZ, it strongly influences the electrochemical performance and its related research is crucial for the deeply understanding of electrode response mechanism and further improvement of the oxygen sensibility of the devices [19-20].

Experimentally at high oxygen partial pressure charge-transfer mechanism both for anodic and cathodic polarizations was implied while at low oxygen partial pressure limiting-current behavior for the cathodic polarization characterized a concentration polarization [21-22]. Yoon S P et al. [23] proposed that in the high temperature and low oxygen partial pressure region, the cathodic reactions mainly included gas phase diffusion and direct adsorption. While in the low temperature and high oxygen partial pressure region, the cathodic reaction was dominated by the disassociation of oxygen molecules. Sridhar S et al. [24-25] proved that the modification of the impedance response of Pt/YSZ electrode by the passage of direct current, and proposed the effect was complex functions of the direction and magnitude of the applied current. Kenjo T et al. [26] separated the polarization into consecutive one-electron transfer reactions as $O^{2-} \rightarrow O^- + e^-$ and $O^- \rightarrow O + e^-$, and found that the first electron transfer step was of a pure charge transfer while the second involved the concentration polarization due to the accumulation of O. The pulsed polarization of Pt/YSZ electrode was also employed for NO_x detection, and during the polarization the platinum oxide was formed at one electrode and reduced by the following pulse with opposite sign [27].

The EPOC (electrochemical promotion of catalysis) phenomenon of Pt/YSZ has made a strong impact on solid state electrochemistry, catalysis and surface science [28-33]. And various explanations have been suggested for the activation mechanism, in general assuming an increased number of active sites. On the one hand, the change of electrolyte property, or even more precisely the electrochemically-induced formation of additional metastable reaction sites on the YSZ surface [34-35]. On the other hand the change in the electrode interfaces was accounted. Suggested reason for this modification was a change of the three-phase boundary length due to the deposition and subsequent reduction of metal oxides in the vicinity of Pt electrodes [34-35]. And in earlier studies a change in work function of the Pt surface with excess O²⁻ pumped electrochemically through the solid electrolyte [36-41] was also proposed. More recently, it has been shown that the surface migration of electrode

material can take place [42]. In addition, it has been demonstrated that impurities such as oxygen-containing species induced by polarization participate in the oxygen transfer in Pt/YSZ electrode, which of course caused activation as well as degradation [43-48].

Due to the important role the electrode polarization play, in that the energy dissipation and therefore decreased efficiency of fuel cells, retarded response speed and weakened signal intensity of oxygen sensors, investigation on the correlation between polarization and performance of the devices are carried out extensively recently. However, no investigations about the influence of surface roughness of solid state electrolyte YSZ on the electrode polarization have been reported. In the present context, the influence of surface roughness of YSZ on polarization of Pt electrode deposited on the electrolyte was investigated in ambient air at 600°C, the emphasis was put on comparison between anodic and cathodic polarization influenced by the surface roughness of YSZ, which was considered to help understanding the electrochemical processes taking place on an Pt electrode in the YSZ cells.

2. EXPERIMENTAL

The YSZ electrolytes were prepared by slip casting method from powders of $ZrO_2+8mol\% Y_2O_3$ (TOSOH TZ 8Y) and sintering at 1500°C, which were discs shaped of 10mm diameter and 2mm thickness. Its surfaces were polished with 400, 1000, 3000 grade diamond pastes respectively, and afterwards cleaned by successive rinsing with hydrochloric acid, warm n-pentane, acetone, and demineralized water in an ultrasonic bath. During the polarization experiment, the working electrode and counter electrode are located in a symmetrical face-to-face arrangement on each side of the electrolyte discs, while the reference electrode is located nearby the counter electrode at a distance of 2mm to ensure a symmetrical current and potential distribution in the cell. Counter and reference electrodes were thin platinum films deposited by screen-printing platinum paste and subsequent sintered at 1100°C in air, working electrode was prepared by the same technique. The electrical contacts were made by using gold wires ($d=0.1mm$) glued onto the electrode surfaces with a tiny dot of gold paste (Fluxless platinum and gold pastes were purchased from Institute of Rare Metals in Kunming, China) subsequently fired at 550°C.

The test cell for electrochemical measurements, shown in Fig. 1, was of single-chamber type where all electrodes were exposed to the same atmosphere. To avoid the interference of electric field on the measurement system, it consisted of a closed tube (made up of stainless steel) of 100ml volume, and shield earth technique was used for this tube which act as a shielding box. The single pellet test cell was suspended in the box with three gold wires serving as electrical contacts to the electrodes. Gold wires were led out the box through a three-hole alumina tube. The stainless steel tube was put into a furnace equipped with a heat control system and has the same atmosphere with the outside air, the measuring temperature was given by a K-type (NiCr-Ni) thermocouple placed in proximity of the surface of the working electrode. All of the electrochemical measurements and data acquisition were made using a PAR 2263 advanced electrochemical system (Princeton Applied Research).

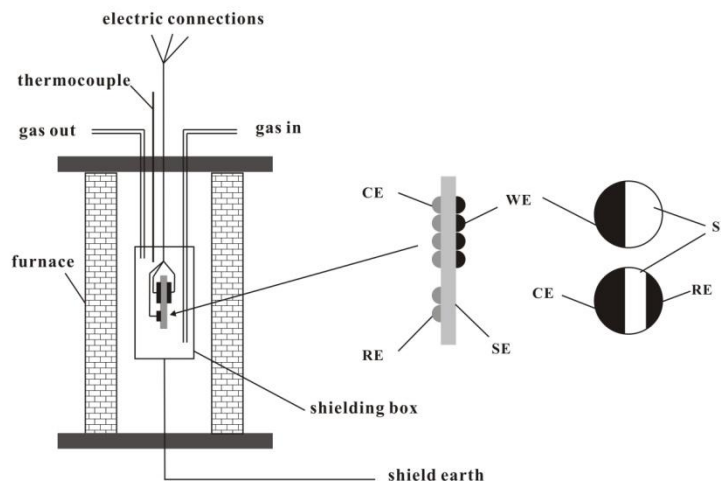
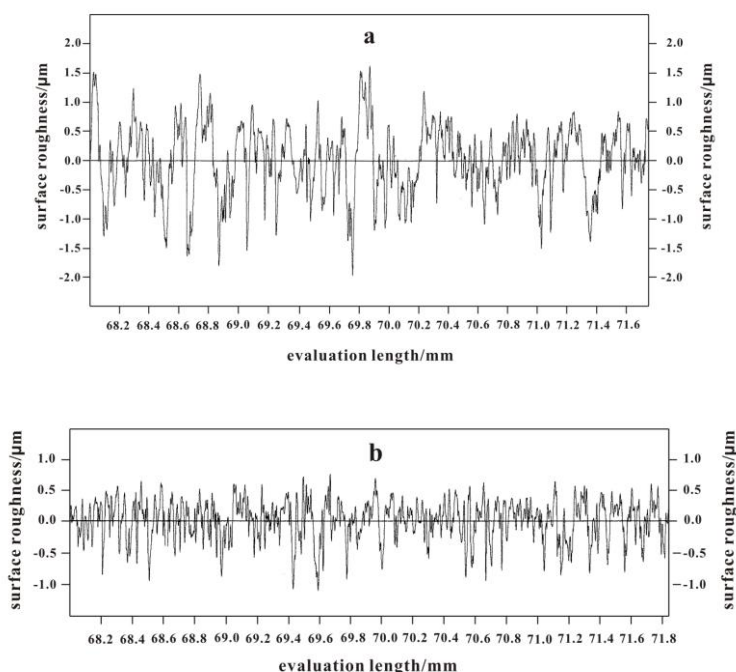


Figure 1. Schematic diagram outlining the electrochemical measurement assembly

3. RESULTS AND DISCUSSION

3.1 Surface roughness measurements

The surface profiles of the polished YSZ specimens obtained from Hommel-Werke T4000 are shown in Fig. 2, and the values of parameters are presented in Table 1. In which Ra (arithmetical mean surface roughness), Rt (total height of roughness profile) and Rz (ten-point mean roughness) characterized the height property of the surface profiles, while Rsm (mean value of the width of profile elements) evidenced the spacing property. As shown in Table 1, both height and spacing parameters are found to decrease with the increase of diamond paste grade.



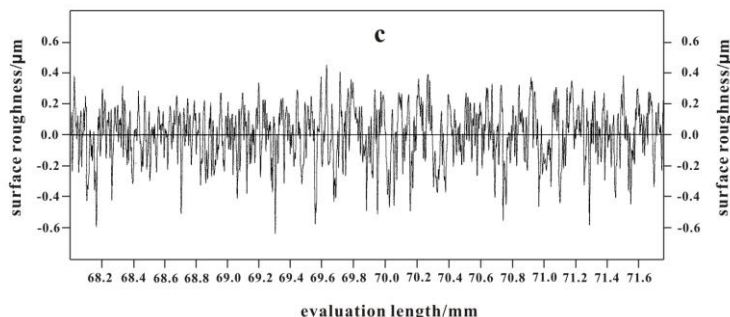


Figure 2. Surface profiles of YSZ specimens polished with 400, 1500, and 3000 grade diamond pastes (termed a, b, c respectively).

Table 1. Parameters of the YSZ surface roughness.

diamond paste grade	Ra/ μm	Rz/ μm	Rt/ μm	Rsm/ μm
400	0.29	2.76	1.68	110.37
1000	0.15	1.47	0.73	78.84
3000	0.09	0.85	0.42	45.21

3.2 Ac impedance measurements

The ac impedance spectra of the electrodes in the frequency ranges of 0.01 to 10^5 Hz, with an excitation voltage of 10 mV are shown in Fig. 3. As shown in Fig. 3, the electrode interfacial resistance was found to increase with the increase of diamond paste grade due to the influence of surface roughness of YSZ on the efficient contact area in the Pt/YSZ system.

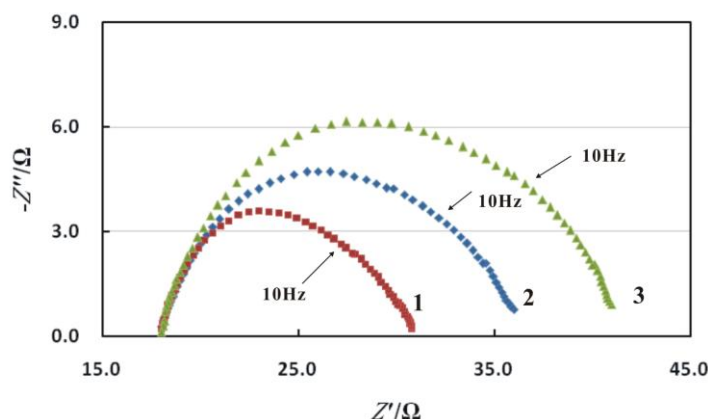


Figure 3. Comparison of spectra of electrode prepared by using 400, 1500, and 3000 grade diamond pastes (termed 1, 2, 3 respectively), ambient atmosphere, $T=600^\circ\text{C}$.

As we know, the good linkage of electrode material and YSZ is considered necessary for the transportation of oxygen-agencies across the electrode interface [32, 49-51]. In this work, the diameter range of platinum particles ($\leq 10\mu\text{m}$) in Pt paste is much larger than the size of profile valley of YSZ,

which result in the difficulty of well contactation between the platinum particles and YSZ surface. Furthermore, the poor fluidity of Pt paste induced by the addition of some organic matters also baffles the platinum particles linked with YSZ surface profile adequately. As a consequence, the maximum efficient contact area exists in the electrode prepared by using 400 grade diomand paste while minimum contact area exists in the electrode prepared by using 3000 grade paste. Wang T et al. [52] also found improved property of Pt electrode interfaced with YSZ result from the alteration of YSZ surface by treatment of HF.

3.3 Chronoamperometric measurements

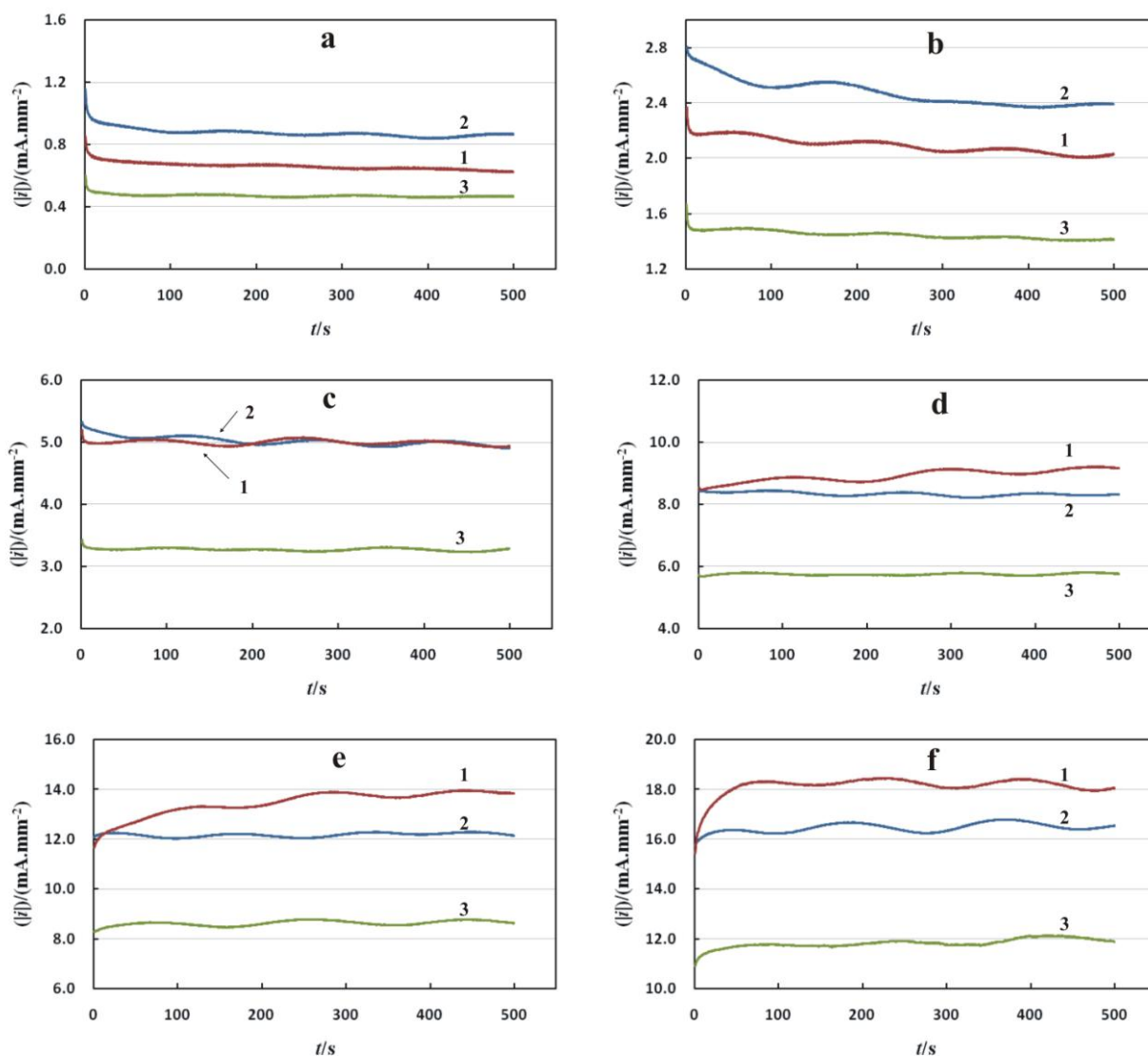


Figure 4. Chronoamperometric curves obtained for experimental series ① of electrode prepared by using 400, 1500, and 3000 grade diamond pastes (termed 1, 2, 3 respectively) at different polarization potentials, increasing the potential step of 0.1V from open circuit to 0.6V (termed a, b, c, d, e, f respectively), ambient atmosphere, T=600°C.

The following two types of potentiostatic polarization experiments have been carried out at 600°C: ① pretreatment by applying a voltage of -0.6V for 1000 seconds and afterwards polarization at a

constant positive potential for 500 seconds; ② pretreatment by applying a voltage of 0.6V for 1000 seconds and afterwards polarization at a constant negative potential for 500 seconds.

The pretreatment step was proposed to guarantee the Pt/YSZ electrodes had identical reproducible initial states. Fig. 4 shows chronoamperometric curves obtained for experimental series ① There are six groups of curves presented for the electrode, and the curves were recorded at over-potentials of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6V respectively. The similar dependences of experimental series ② are presented in Fig. 5, and the curves were recorded at over-potentials of -0.1, -0.2, -0.3, -0.4, -0.5, -0.6V respectively.

As shown in Fig. 4, in the very early stage, near $t=0$, the absolute currents had an abrupt increase attributed to the ohmic polarization of electrolyte. As the polarization time extended, the absolute currents further altered due to the charging of the $O_{2(g)}$, Pt/YSZ system and transporting of electro-active agencies in the system.

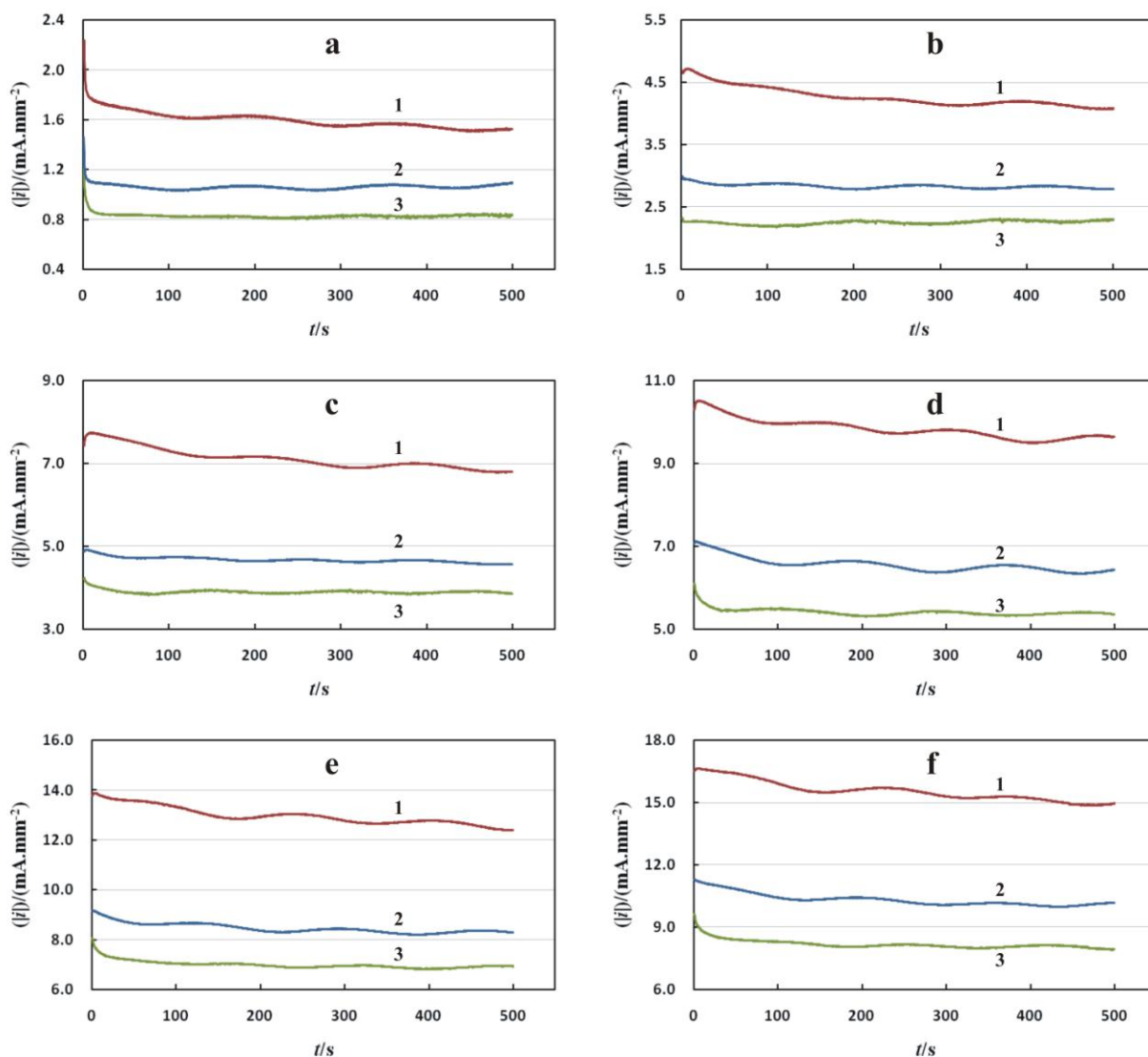


Figure 5. Chronoamperometric curves obtained for experimental series ② of electrode prepared by using 400, 1500, and 3000 grade diamond pastes (termed 1, 2, 3 respectively) at different polarization potentials, decreasing the potential step of -0.1V from open circuit to -0.6V (termed a, b, c, d, e, f respectively), ambient atmosphere, $T=600^{\circ}\text{C}$.

At longer times, the limiting currents were reached, which evidenced the steady-state of the electrochemical reaction achieved.

At the over-potentials up to 0.3V, the electrode prepared by using 1000 grade diamond paste had the maximum limiting currents. However, at the over-potentials larger than 0.3V, the electrode prepared by using 400 grade paste exhibited the best performance, and as the increase of diamond paste grade, the absolute limiting currents decreased.

As shown in Fig. 5, while the electrodes were polarized at negative over-potentials, the absolute current curves rapidly reached to the maximum values initially, and as the polarization going on, the curves decreased to kinetic steady-states. And in general, at the absolute over-potentials up to 0.3V, the results of higher absolute limiting currents of experimental series ② than that of experimental series ① were obtained by using the same polarization signals. However, at the over-potentials larger than 0.3V, experimental series ① exhibited better electro-catalytic activity than experimental series ② with the same polarization signals.

Under anodic polarization, the oxygen anions in the electrolyte termed $O^{2-}_{(YSZ)}$ will oxidize at the two or three boundary interfaces. And at YSZ/air interface, the $O^{2-}_{(YSZ)}$ release two electrons and convert to O_{atm} and afterwards desorb from the interface toward the ambient air. At Pt/YSZ interface, the oxygen atoms pumped by anodic polarization adsorb on the interface, while the coverage come to the saturated extent, the O_{atm} will have site-exchange reaction with Pt atoms, and afterwards diffuse toward bulk Pt and further evolve to the steady Pt oxides [44-48]. At TPB, the adsorbed oxygen atoms induced by anodic polarization have three means to transport: desorbing immediately; diffusing to the Pt/air interface and afterwards desorbing toward air, or having site-exchange reaction with platinum atoms.

While the electrode is polarized at cathodic over-potentials, the oxygen molecules in air termed $O_{2(air)}$ disassociate and adsorb on the YSZ/air interface, then get two electrons and convert to oxygen anions and further diffuse toward the electrolyte YSZ; at Pt/air interface, after the successive processes of disassociation and adsorption, the $O_{2(air)}$ convert to adsorbed atoms and on the one hand, have site-exchange reaction with platinum atoms and diffuse into bulk Pt, on the other hand, diffuse along the interface to TPB, and then get two electrons and transport into the electrolyte YSZ; at TPB, the adsorbed oxygen atoms have two reaction ways: reducing immediately; diffusing to Pt/YSZ interface and afterwards reducing.

With this model in mind we can now explain the previous results:

(a). during the experimental series ① $O^{2-}_{(YSZ)}$ rapidly oxidized at YSZ/air, Pt/YSZ, and TPB interfaces and resulted in the abrupt currents increase initially; as the polarization time extended, the adsorption of oxygen atoms on Pt/YSZ and TPB interfaces tended to be difficult attributed to the limited adsorbing sites, and the diffusion of oxygen atoms on Pt/air interface was also depressed due to the increased atoms on the interface, however, since the oxygen atoms might have site-exchange reaction with platinum atoms and were stored in bulk Pt, and especially the oxygen atoms would desorb at the YSZ/air, Pt/air and TPB interfaces toward air, which made the currents passing through the electrode system maintain the steady-state values.

(b). in the considered experimental series ② the oxygen atoms reduced at YSZ/air, Pt/YSZ and TPB interfaces mainly originated from the pre-oxidation processes and the ambient air. During the pre-

oxidation processes, the electrochemically pumped oxygen anions involved three processes: (1) adsorbing at the YSZ/air, Pt/YSZ, Pt/air and TPB interfaces; (2) desorbing from the YSZ/air, Pt/air and TPB interfaces toward air; (3) transporting into bulk Pt from Pt/YSZ interface and being stored in the form of Pt oxides. When the polarization started, the oxygen stored in the electrode system attributed to the pre-oxidation in forms of adsorbed oxygen atoms and Pt oxides will immediately reduced, and resulted in the abrupt increase of absolute current initially; as the polarization time extended, the quantity of oxygen originated from pre-oxidation processes decreased, and the timely supply from the ambient air was not in convenience, so led to the absolute current values decrease rapidly; at longer time, with successive processes of disassociation, adsorption and diffusion, the oxygen in the ambient air transported to the corresponding interfaces to reduction, which caused the currents passing through the electrode system stabilized at the steady-state values.

(c). during the anodic polarization at relatively low over-potentials, a small quantity of oxygen transported by the site-exchange reaction due to the depressed concentration differences at the Pt/YSZ interface, which made the transporting efficiency of oxygen species decreased and even lower than that of cathodic polarization with the same polarization signals. So we can found that experimental series ② exhibits better electro-catalytic activity than experimental series ① at the absolute over-potentials up to 0.3V. However, with the polarization at over-potentials larger than 0.3V, the more pronounced electro-activity for oxidation was found ascribed to the promotion of site-exchange reaction. Differently, in our previous study of gold/YSZ system, a better anodic electro-catalytic activity than reduction reaction always existed at the absolute polarization signal ranged from 0.1 to 0.6V [53].

(d). Although a relatively smaller quantity of oxygen anions oxidized at the limited two or three boundary interfaces of the electrode prepared by using 1000 grade diamond paste than that of the electrode prepared by using 400 grade paste, the site-exchange reaction might be actuated by the concentrated contact area in the former electrode, which made it exhibits the maximum electro-catalytic activity at the over-potentials lower than 0.4V. And as the polarization signal increased, the second electrode won and held the best electro-activity due to the saturation of site-exchange reaction.

3.4 Chronopotentiometric measurements

In the amperostatic polarization mode the following two types of experiments have been carried out at 600°C: ③ pretreatment by applying a current of -0.6A for 1000 seconds and afterwards polarization at a constant anodic currents of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6A for 500 seconds respectively; ④ pretreatment by applying a current of 0.6A for 1000 seconds and afterwards polarization at a constant cathodic currents of -0.1, -0.2, -0.3, -0.4, -0.5 and -0.6A for 500 seconds respectively. In this work, we defined the currents to be anodic when oxygen anions were pumped to the metal electrode and cathodic when oxygen anions were pumped to the solid state electrolyte YSZ. The pretreatment step was also proposed to guarantee the Pt/YSZ electrodes had identical reproducible initial states. Fig. 6 shows the chronopotentiometric curves obtained for experimental series ③ at different polarization currents. There are six groups of curves presented for the electrode, and the curves were recorded at different applied currents of 0.1, 0.2, 0.3, 0.4, 0.5, 0.6A. The similar

dependences of experimental series ④ are presented in Fig. 7, and the curves were recorded at currents of -0.1, -0.2, -0.3, -0.4, -0.5, -0.6A respectively.

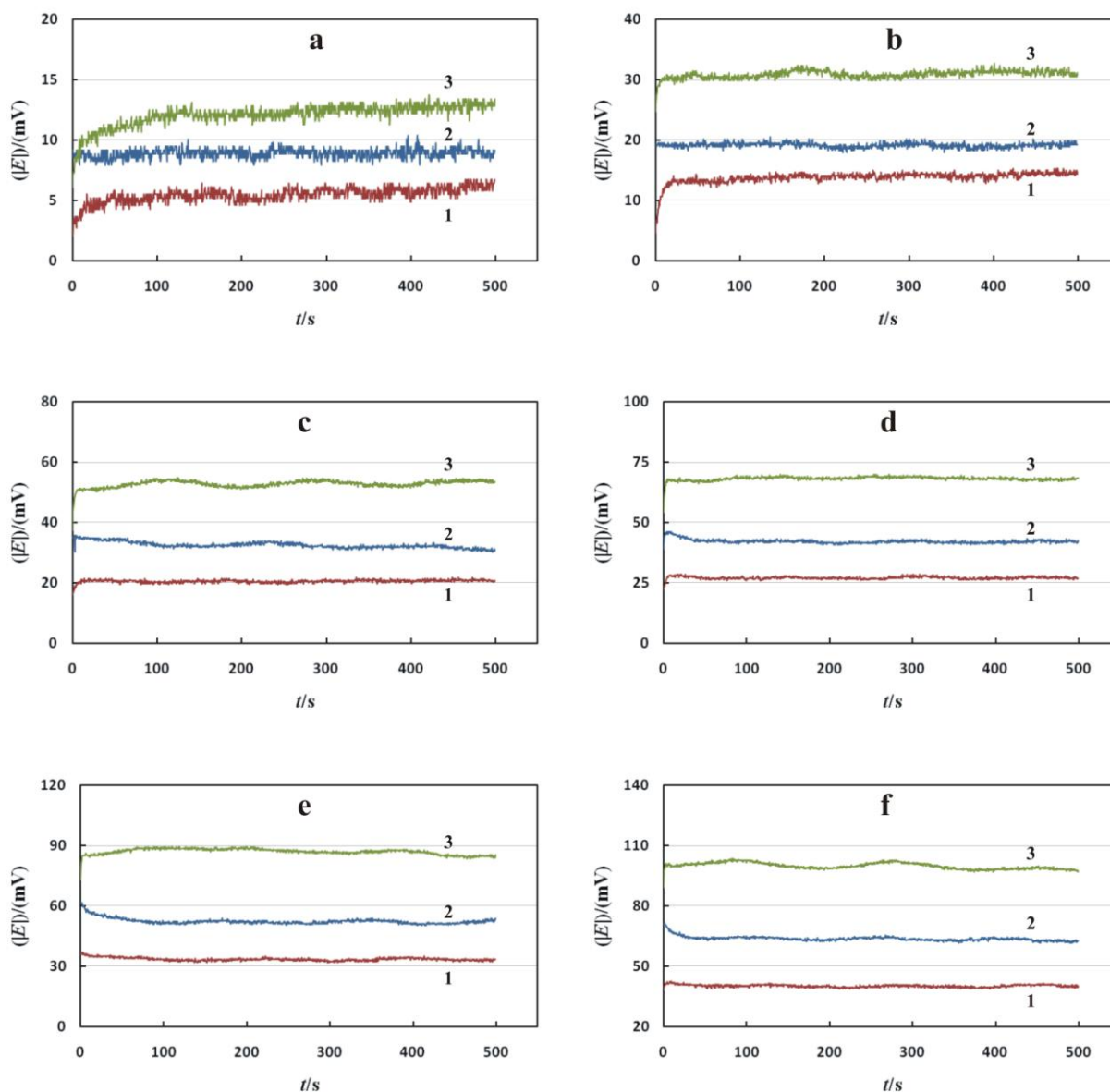


Figure 6. Chronopotentiometric curves obtained for experimental series ③ of electrode prepared by using 400, 1500, and 3000 grade diamond pastes (termed 1, 2, 3 respectively) at different polarization currents, increasing the currents step of 0.1A to 0.6A (termed a, b, c, d, e, f respectively), ambient atmosphere, $T=600^{\circ}\text{C}$.

As shown in Fig. 6 and Fig. 7, for the all applied currents the absolute potential curves increased abruptly initially due to the ohmic polarization, and then further altered because of the electrochemical and concentration polarizations in this system, at longer times, the steady-state potentials were achieved. In general, all of the response curves exhibited relatively smooth alterations during the amperostatic polarization mode, which perhaps caused by the larger polarization signals.

And the higher steady-state potentials of experimental series ④ than that of experimental series ③ strongly evidenced that under strong polarization, the electro-catalytic activity of anodic oxidation reactions are more pronounced than that of cathodic reduction reactions.

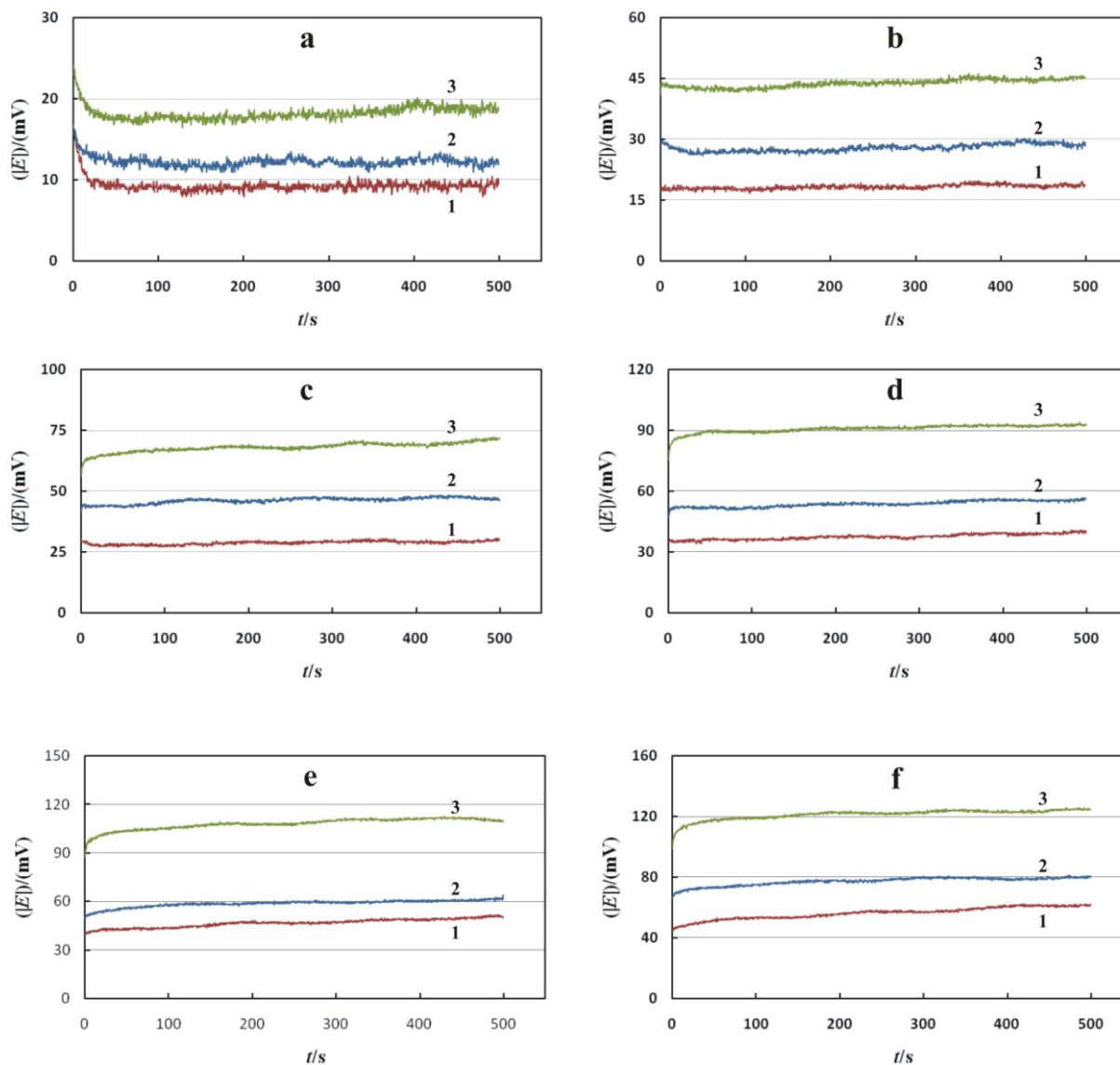


Figure 7. Chronopotentiometric curves obtained for experimental series ④ of electrode prepared by using 400, 1500, and 3000 grade diamond pastes (termed 1, 2, 3 respectively) at different polarization currents, decreasing the absolute currents step of -0.1A to -0.6A (termed a, b, c, d, e, f respectively), ambient atmosphere, T=600°C

It is noteworthy that during both potentiostatic and amperostatic polarization experiments, the remarkable enhancement of electro-catalytic activity was not observed, perhaps due to the short polarization time and relatively low temperature. From our point of view, the origin of the NEMCA effect may be attributed to the improvement of the electro-active agencies transportation in the electrode system either by prolonging the polarization time or applying relatively high external current

or potential for accumulation. In ref. [42], Raźniak et al. reported the enhanced catalytic activity of Pt electrode under polarization with long-lasting (18hours) negative over-potentials at 700°C, and the increase of three-phase boundary length due to the deposition and subsequent reduction of metal oxides in the vicinity of electrode was proposed to explain the unusual behavior. Mutoro et al. [16] also evidenced the electrode activation with the long-polarization (16 hours) at 0.5V, the enlargement of three phase boundary due to the formation of bubbles and their cracking under polarization was considered as the origin.

4. CONCLUSIONS

In this work, we studied the influence of surface roughness of YSZ on polarization of Pt electrode deposited on the electrolyte, using ac impedance spectroscopy, chronoamperometric and chronopotentiometric methods in ambient air at 600°C. The electrode properties were found to alter with the change of diamond paste grade due to the influence of surface roughness of YSZ on the efficient contact area in the Pt/YSZ system. In general, at the absolute over-potentials up to 0.3V, the limiting currents passing through the electrode during anodic polarization were lower than that under cathodic bias result from the depressed site-exchange reaction of oxygen and platinum atoms. However, while the electrode was polarized at the absolute over-potentials larger than 0.3V, the more pronounced electro-activity for oxidation was found ascribed to the promotion of site-exchange reaction. Although a relatively smaller quantity of oxygen anions oxidized at the limited interfaces of the electrode prepared by using 1000 grade diamond paste than that of the electrode prepared by using 400 grade paste, the site-exchange reaction might be actuated by the concentrated contact areas in the former electrode, which made it exhibits the maximum electro-catalytic activity at the over-potentials lower than 0.4V. As the polarization signal increased, the second electrode won and held the best performance due to the saturation of site-exchange reaction. The further chronopotentiometric experiments demonstrated that the electrode was more active towards oxidation than towards reduction reactions under strong polarization. It is noteworthy that the remarkable enhancement of electro-catalytic activity was not observed during both potentiostatic and amperostatic polarization experiments might be due to the short polarization time and relatively low experiment temperature.

ACKNOWLEDGEMENT

The authors gratefully acknowledge the National Natural Science Foundation of China (Grant No. 41203047), the National High-Tech Research and Development Program of China (Grant No. 2010AA09Z207), the “135” Program of Institute of Geochemistry (Chinese Academy of Sciences), and the Large-scale Scientific Apparatus Development Program of Chinese Academy of Sciences (Grant No. YZ200720) for the financial support of this work.

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