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Effect of Polarization on the O_2(g), Au/YSZ Electrode System

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The oxygen electrode reaction at the interface gold/yttria stabilized zirconia (YSZ) was investigated at moderate temperatures of 500 and 600℃ under ambient air condition, with emphasis put on the comparative analysis for effect of anodic and cathodic polarization on the electrode. Generally, at the temperature of 500℃, slow monotonous alterations of the absolute currents or potentials result from polarizations were observed, but the response curves exihibited obvious fluctuations at 600℃, which may be ascribed to the progressive transportation processes of the electro-active species in the electrode system. Due to the relatively weak adsorption ability of Au electrode interfaced with YSZ, the oxygen atoms induced by anodic polarization left toward the ambient air rapidly, which consequently led to the improved activity for oxidation reactions. However, while the electrode was under cathodic bias, the oxygen reduced mainly originated from the ambient air, and had to reach the reaction sites located at the two or three boundary interfaces through series of successive processes such as disassociation, adsorption and diffusion, which result in the low transporting efficiency of the active agencies beyond all doubt and consequently decreased activity for reduction reactions at the electrode system. The remarkable enhancement of electrode catalytic activity was only observed from the potentiostatic polarization experiments at 600℃ and with anodic polarization, perhaps due to the short polarization times and relatively low experiment temperatures.

Keywords: Au/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℃ 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 gold is one of the most attractive catalysts for many oxidation reactions and a candidate electrode for use in YSZ cells [15-24].

Since the pioneering work of Vayenas and coworkers [25-27], the phenomenon of NEMCA (non-Faradaic electrochemical modification of catalytic activity) or termed in situ electrochemical modification of catalytic activity has been investigated extensively to activate and precisely tune the rate and product selectivity of oxidation or partial oxidation on Pt, Ag and Pd electrodes interfaced with YSZ, dramatic changes in catalytic activity and selectivity were observed with all these reactions [28-31]. It was proposed that the NEMCA effect is due to changes in catalyst work function caused by the interaction of the catalyst surface with excess O^{2-} pumped electrochemically through the solid electrolytes [32-37].

Similar with other noble metals like Pt, Pd, and Ag, the enhancement of catalytic activity was also observed for gold electrodes on YSZ at long-lasting high bias, to explain this behavior Mar'ina et al. [38] suggested the increase of the coverage of reactive oxygen species such as O^{2-}_{ads} and O^{-}_{ads}. The authors of ref. [39, 40] ascribed to the stoichiometric changes of electrolyte induced by the high applied voltages. Tomczyk et al. [41] proposed that the oxygen electrode oxidation at the Au/YSZ interface is under mixed control of charge transfer and phenomenon induced by DC bias. More recently, the detailed experimental investigation by Raźniak et al. proved that the common patterns for increase of the three phase boundary length like deposition and subsequent reduction of metal oxides were not found in the vicinity of gold electrode interfaced with YSZ, and the occurrence of autocatalytic electrode reaction was suggested to explain the phenomenon of remarkable activity enhancement with over-potential down to -0.3V [42].

In the current work, short-lasting polarization of Au electrode deposited on YSZ electrolyte was extensively studied in ambient air condition and at moderate temperatures of 500 and 600℃ respectively, the emphasis was put on comparison between the effect of anodic and cathodic polarization on the electrode performance, which was considered to help understanding the electrochemical processes taking place on an Au 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℃, which were discs shaped of 10mm diameter and 2mm thickness. Its surfaces were polished with a 3000 waterproof alumina abrasive paper and afterwards 1μm diamond paste and cleaned by successive rinsing with hydrochloric acid, warm n-pentane, acetone, and demineralized water in an ultrasonic bath. During the 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 (Fluxless gold and platinum pastes were purchased from Institute of Rare Metals in Kunming, China) and afterwards sintered at 1100℃ in air, working electrode was prepared by the same technique with gold paste and sintered at 800℃ in air. The electrical contacts were made by using gold wires (d=0.1mm) glued onto the electrode surfaces with a tiny dot of gold paste fired at 550℃.

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 of 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 temperatures were 500 and 600℃, which were given by a K-type (NiCr-Ni) thermocouple placed in proximity of the surface of the working electrode and was led out of the furnace through a two-hole alumina tube. All of the chronoamperometry and chronopotentiometry measurements and data acquisition were made using a PAR 2263 advanced electrochemical system (Princeton Applied Research).

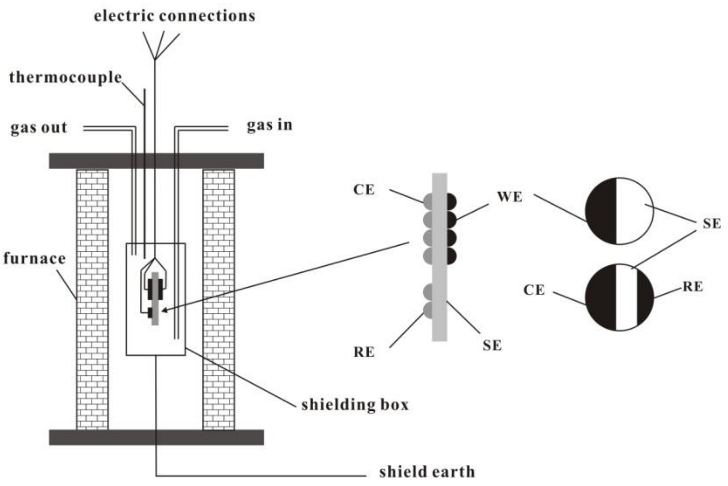

Figure 1. Schematic diagram outlining the electrochemical measurement assembly

3. RESULTS AND DISCUSSION

3.1. Chronoamperometric measurements

The following two types of potentiostatic polarization experiments have been carried out at 500 and 600℃ respectively: ① pretreatment by applying a voltage of -0.6V for 1000 seconds and subsequent polarization at a constant positive potential for 500 seconds; ② pretreatment by applying a voltage of 0.6V for 1000 seconds and subsequent polarization at a constant negative potential for 500 seconds. The pretreatment step was proposed to guarantee the Au/YSZ electrodes had identical reproducible initial states. Fig. 2 shows chronoamperometric curves obtained for experimental series of ①(red lines) and ②(blue lines) at different polarization potentials performed at 500°C. 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. The similar dependences obtained at 600°C are presented in Fig. 3.

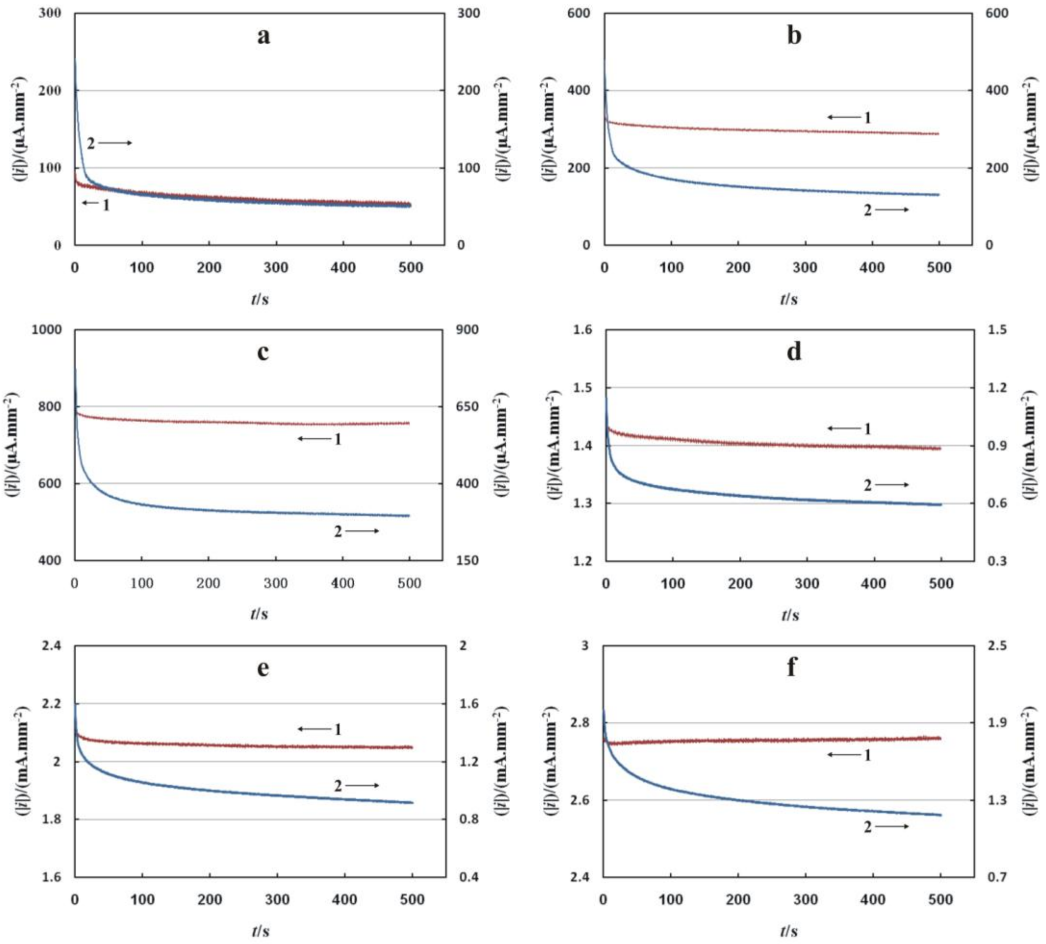

Figure 2. Chronoamperometric curves obtained for experimental series of ①(red lines) and ②(blue lines) (termed 1 and 2 respectively) at different polarization potentials, increasing the absolute potential step of 0.1V from open circuit to 0.6V (termed a, b, c, d, e, f respectively), ambient atmosphere, T=500°C.

As shown in Fig. 2, in the very early stage, near t=0, the absolute currents have an abrupt increase attributed to the ohmic polarization of electrolyte. As the polarization time extended, the absolute currents monotonically decreased because of the lowering charging current of the $O_{2(g)}$, Au/YSZ system. At longer times, the limiting currents were reached, which evidenced the steady-state of the electrochemical reaction achieved. At the same absolute over-potentials, the currents for the considered experimental series of ①approached stable values much faster than that of experimental series of ②, and the absolute limiting current values of the former experimental series were always larger than that of experimental series of ②, besides at 500°C, with the polarization over-potential

±0.1V the two experiments had the approximately equal stable values of absolute current. Among all of the response current curves, only at the over-potential 0.6V, after fast approach of stable state the current value gradually increased.

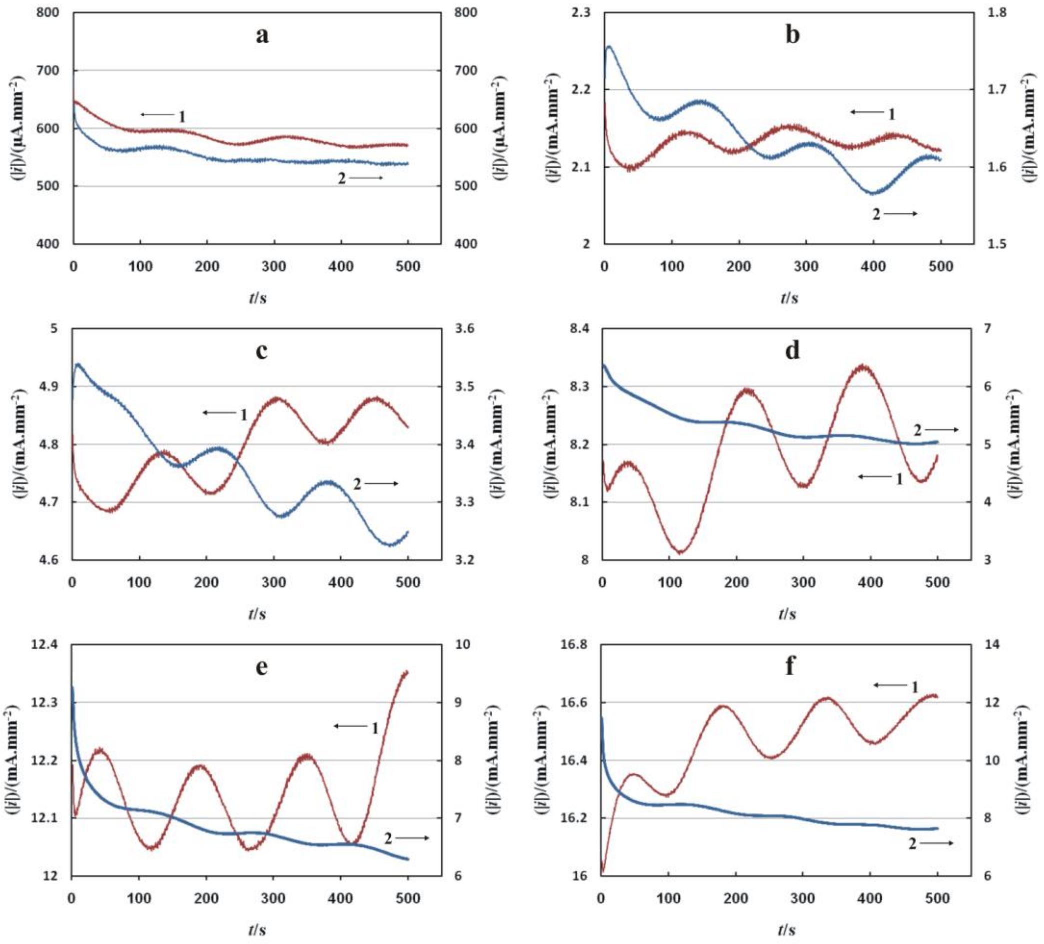

Figure 3. Chronoamperometric curves obtained for experimental series of ①(red lines) and ②(blue lines) (termed 1 and 2 respectively) at different polarization potentials, increasing the absolute potential step of 0.1V from open circuit to 0.6V (termed a, b, c, d, e, f respectively), ambient atmosphere, T=600℃.

Fig. 3 shows the following characteristics:

(a). similar with Fig. 2, longer time was necessary for the currents to stabilize when the electrode was polarized by negative over-potentials compared with that by positive over-potentials. And with the polarization over-potential ±0.1V, the absolute limiting current values of experimental series of ①approximately equaled that of experimental series of ②.

(b). all of the dependences exhibited fluctuations, and the kinetic steady-states were approached more slowly than that at 500℃, especially at the absolute over-potentials higher than 0.2V. When the electrodes were polarized upon the positive over-potentials ranging from 0.3V to 0.6V, the current curves had a tendency to re-increase at longer time, and this abnormal phenomenon was more obvious at the over-potential of 0.6V.

(c). while the electrodes were polarized at negative over-potentials, the absolute current curves rapidly reached to the maxmum values initially, and as the polarization going on, the curves decreased to a kinetic steady-states. It is noteworthy that the curves exhibited no tendency to re-increase during the whole polarization processes.

Under anodic polarization, the oxygen anions originating from the electrolyte lattice termed $O^{2-}_{(YSZ)}$ get to the YSZ/air, Au/YSZ, and Au/YSZ/air (three phase boundary, TPB) interfaces to oxidize by releasing two electrons. And similarly, the adsorbed oxygen atoms originating from the ambient air termed O_{atm} reduce at the three interfaces and leave toward the electrolyte when the electrode is polarized at negative over-potentials, it seems reasonable to schematize the electrochemical polarization mechanism in Fig. 4.

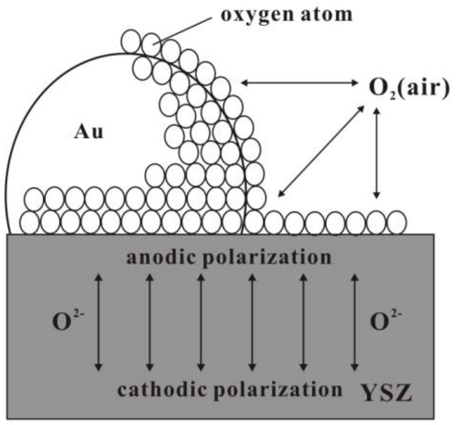

Figure 4. Schematic draw of the polarization mechanism of Au/YSZ.

According to the mechanism shown in Fig. 4, at YSZ/air binary interface, $O^{2-}_{(YSZ)}$ release two electrons and convert to oxygen atoms and afterwards desorb from the interface toward air under anodic polarization:

$O^{2-}_{(YSZ)}\text{-}2e_{(YSZ)} \rightarrow O_{atm}(YSZ/air) \rightarrow 1/2O_{2(air)}$ (1)

At Au/YSZ binary interface, the oxygen atoms pumped by anodic polarization adsorb on the interface, while the coverage come to the saturated extent, the oxygen atoms may have site-exchange reactions with Au atoms, and subsequently diffuse toward bulk Au and further evolved to the steady Au oxides.

$O^{2-}_{(YSZ)}\text{-}2e_{(Au)} \rightarrow O_{atm}(Au/YSZ) \rightarrow Au\text{-}O(Au/YSZ) \rightarrow Au\text{-}O_{(Au\ bulk)}$ (2)

At TPB, the adsorbed oxygen atoms induced by anodic polarization have three means to transport: desorbing toward air imediately; diffusing to the Au/air binary interface and afterwards desorbing toward air, or having site-exchange reactions with gold atoms.

$O^{2-}_{(YSZ)}\text{-}2e_{(Au)} \rightarrow O_{atm}(Au/YSZ/air) \rightarrow 1/2O_{2(air)}$ (3)

$O^{2-}_{(YSZ)}-2e_{(Au)}\rightarrow O_{atm}(Au/YSZ/air)\rightarrow O_{atm}(Au/air)\rightarrow 1/2O_{2(air)}$ (4)

$O^{2-}_{(YSZ)}-2e_{(Au)}\rightarrow O_{atm}(Au/YSZ/air)\rightarrow O_{atm}(Au/air)\rightarrow Au\text{-}O(Au/air)\rightarrow Au\text{-}O_{(Au\ bulk)}$ (5)

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 binary interface, then convert to oxygen anions by getting two electrons and further diffuse toward the electrolyte YSZ; at Au/air binary 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 reactions with gold atoms and diffuse into bulk Au, 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 imediately; diffusing to Au/YSZ interface and afterwards reducing.

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

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

(b). in the considered experimental series of ②, the oxygen atoms reduced at YSZ/air, Au/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, Au/YSZ, Au/air and TPB interfaces; (2) desorbing from the YSZ/air, Au/air and TPB interfaces toward air; (3) transporting into bulk Au from Au/YSZ binary interface and stored in the form of Au oxides. When the polarization started, the oxygen stored in the electrode system attributed to the pre-oxidation in the forms of adsorbed oxygen atoms and Au oxides reduced immediately, and result 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, 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). as we know, the adsorption ability of oxygen atoms on gold electrode interfaced with YSZ is relatively weak compared with other noble metals [35-36, 42], in other words, the adsorbed oxygen atoms are very easy to desorb from the Au/YSZ electrode system. While the electrode was under anodic polarization, the oxygen atoms induced by the oxidation of $O^{2-}_{(YSZ)}$ at Au/YSZ, YSZ/air and TPB interfaces mainly transported by desorption. During the experimental series of ②, only a small amount of oxygen may be stored in the forms of adsorbed atoms or metal oxides induced by the pre-oxidation, so the oxygen atoms reduced at each interface were mainly supplied by oxygen molecules in the ambient air through series of processes such as disassociation, adsorption and diffusion, which beyond all doubt results in the low oxygen transport efficiency, consequently leads to the lower absolute limiting currents for the experimental series of ②compared with that of experimental series of ①. Breiter [43] and Hansen [44] also reported on the Au electrode interfaced with YSZ was more active towards oxidation than towards reduction, that is evolution of oxygen was more pronounced than the reduction reactions.

3.2. Chronopotentiometric measurements

In the amperostatic polarization mode the following two types of experiments have been carried out at 500 and 600℃: ③pretreatment by applying a current of -0.6mA for 1000 seconds and subsuquent polarization at a constant anodic currents of 0.1, 0.2, 0.3, 0.4, 0.5 and 0.6mA for 500 seconds respectively; ④pretreatment by applying a current of 0.6mA for 1000 seconds and subsequent polarization at a constant cathodic currents of -0.1, -0.2, -0.3, -0.4, -0.5 and -0.6mA for 500 seconds respectively.

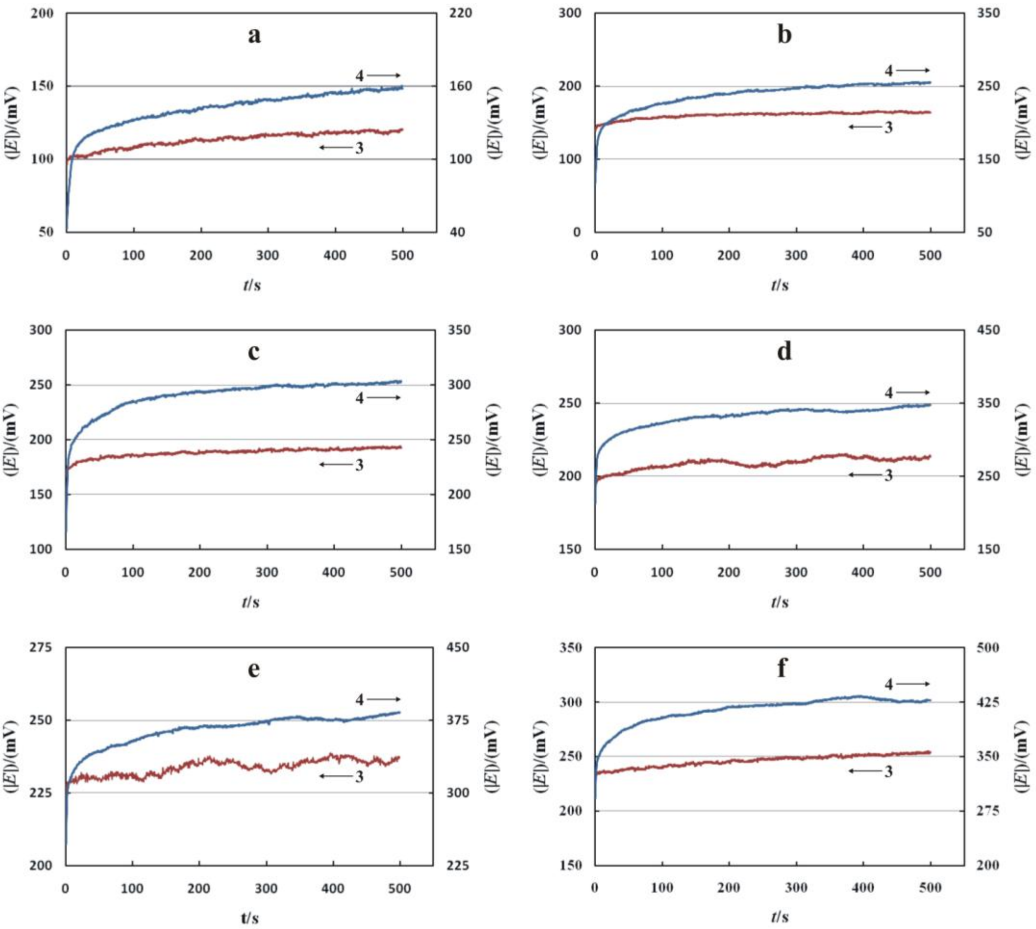

Figure 5. Chronopotentiometric curves obtained for experimental series of ③(red lines) and ④(blue lines) (termed 3 and 4 respectively) at different polarization currents, increasing the absolute currents step of 0.1A to 0.6A (termed a, b, c, d, e, f respectively), ambient atmosphere, T=500℃.

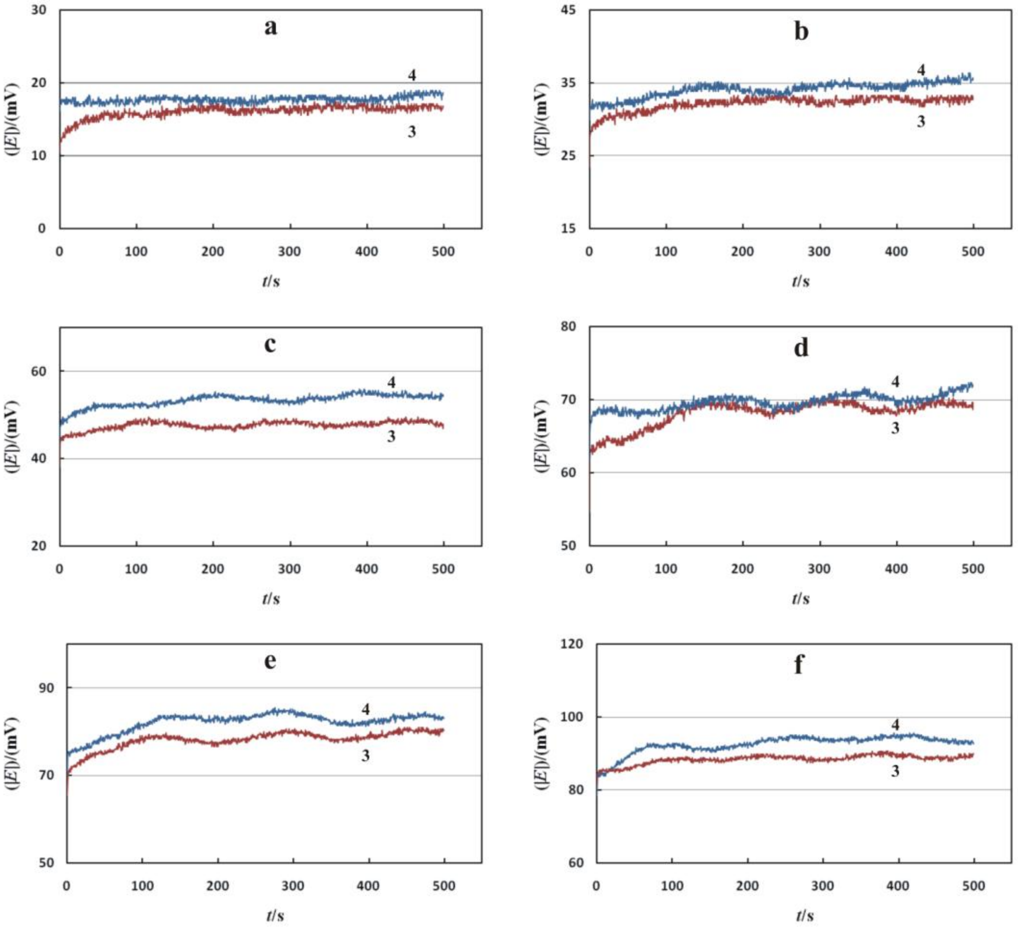

Figure 6. Chronopotentiometric curves obtained for experimental series of ③(red lines) and ④(blue lines) (termed 3 and 4 respectively) at different polarization currents, increasing the absolute currents step of 0.1A to 0.6A (termed a, b, c, d, e, f respectively), ambient atmosphere, T=600℃.

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 Au/YSZ electrodes had identical reproducible initial states. Fig. 5 shows the chronopotentiometric curves obtained for experimental series of ③(red lines) and ④(blue lines) (termed 3 and 4 respectively) at different polarization currents at 500℃. 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 obtained at 600℃ are shown in Fig. 6.

As shown in Fig. 5 and Fig. 6, for all applied currents the absolute potential curves increased abruptly initially due to the ohmic polarization, subsequently further increased because of the charging of the $O_{2(g)}$, Au/YSZ system and transporting of electro-active agencies in this system, at longer times, the steady-state potentials were achieved. The higher steady-state potentials of experimental series of ④than that of experimental series of ③strongly evidenced that the over-potentials result from the electrochemical polarization and the mass transport of electro-active agencies was higher than that of experimental series of ③. And the proposed causing was that oxygen atoms pumped by anodic polarization were very easy to leave toward air due to the weak adsorption ability of the electrode, which led to the higher activity for oxidation reactions on the electrode. But with cathodic polarization currents, the electro-active species needed for the reductions were difficult to reach the sites for the electrochemical reactions, because the agencies were mainly supplied by the ambient air and had to reach the reactions sites located at the two or three boundary interfaces through series of successive processes such as disassociation, adsorption and diffusion.

As shown in Fig. 6, the response curves also fluctuated during the amperostatic polarization at 600℃, which perhaps may be caused by the progressive transportation processes of the electro-active species in the electrode system, such as disassociation of oxygen molecules, adsorption or diffusion of oxygen agencies, desorption of oxygen atoms, generation or decompose of metal oxides.

Among the absolute potential curves in Fig. 5 and Fig. 6, the tendency to enhance the catalytic activity during anodic polarization like the experimental series of ①has not been found, which implied that the amperostatic polarization mode is less sensible to enclose the mechanism of polarization than potentiostatic polarization method.

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 relative high external current or potential for accumulation, which can be corroborated by our potentiostatic polarization experiments with positive potentials 0.6V at 500℃ and higher than 0.2V at 600℃. The remarkable enhancement of electrode catalytic activity was not observed with the cathodic polarization, perhaps due to the short polarization times and relatively low experiment temperatures. In ref. [40], Tomczyk et al. reported the enhanced catalytic activity of Au electrode interfaced with YSZ after polarizing with long-lasting (15hours) negative over-potentials at 800℃. Raźniak et al. [41] also evidenced the visible increase of absolute current when the Au electrode was polarized with negative over-potentials at least after 18 hours at 700℃.

4. CONCLUSIONS

In this work, we studied the polarization behavior of Au electrode deposited on YSZ electrolyte, using chronoamperometric and chronopotentiometric methods in the ambient air condition. Generally, at the temperature of 500℃, slow monotonous alterations of the absolute currents or potentials result from polarizations were observed, but the response curves exihibited obvious fluctuations at 600℃, which may be ascribed to the progressive transportation processes of the electro-active species in the electrode system. Due to the relatively weak adsorption ability of Au electrode interfaced with YSZ, the oxygen atoms induced by anodic polarization left toward the ambient air rapidly, which consequently led to the improved activity for oxidation reactions. However, while the electrode was under cathodic bias, the oxygen reduced mainly originated from the ambient air, and had to reach the reaction sites located at the two or three boundary interfaces through series of successive processes such as disassociation, adsorption and diffusion, which result in the low transporting efficiency of the active agencies beyond all doubt and consequently decreased activity for reduction reactions at the electrode system. The remarkable enhancement of electrode catalytic activity was only observed from the potentiostatic polarization experiments at 600℃ and with anodic polarization, perhaps due to the short polarization times and relatively low experiment temperatures.

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