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On the origin of the non-Faradaic electrochemical modification of catalytic activity (NEMCA) phenomena. Oxygen isotope exchange on Pt electrode in cell with solid oxide electrolyte

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Homomolecular oxygen exchange on Pt electrode in a zirconia electrochemical cell was studied. It was found that the current passing through the cell (O^{2-} pumping through the electrolyte) does not change the rate of oxygen exchange on the Pt electrode with respect to its open circuit value, a fact that indicates that the strength of the chemisorptive bond of oxygen on the Pt electrode is invariant under open and closed circuit conditions.

Keywords: Oxygen isotope exchange; Pt electrode; solid oxide electrolyte; oxygen pumping; NEMCA phenomena

1. Introduction

Much attention has recently been given to the study of the oxidative transformations of gases (CO, CH_4, C_2H_4, CH_3OH) on electrode-catalysts, including Pt, in electrochemical cells operating with yttria-stabilized zirconia (YSZ) electrolytes:

$$\text{gas} + O_2, \text{metal catalyst}|ZrO_2\ (8\text{–}10\ \text{mol\%}\ Y_2O_3)|\text{metal}, O_2 .$$

Numerous experimental studies in this field have been carried out and recently reviewed by Vayenas et al. [1]. Our experimental results have also been reported [2–7].

The passing of an electric current through the cell (a flow of O^{2-} anions through the electrolyte) can considerably increase or decrease the catalytic activity of the electrode-catalyst with respect to its open circuit value. It was essential that the induced changes in the catalytic reaction rate were reversible (upon current interruption the rate returned to its open circuit value) and were one to two orders of magnitude higher than the rate of O^{2-} pumping through the electrolyte. This effect is known as the non-Faradaic electrochemical modification of catalytic activity (NEMCA) [1].

The NEMCA effect is of interest for heterogeneous catalysis, since current passing through the cell or electrode potential is an additional parameter that, together with the temperature and composition of the gas phase, can be applied to control catalytic properties of metal electrode-catalysts. According to the concept of Vayenas et al. [1], the essence of the NEMCA effect consists in the fact, that during polarization of the metal electrode, i.e. when current is passing through the cell, the electrode work function changes. The authors suggest that it leads to changes in the strength of the chemisorptive bond of adsorbed oxygen and hence in the catalytic properties of the electrode. But the question as to whether the bond strength of oxygen adsorbed on Pt electrode changes or remains unchanged when the electric current is passing through the cell, is still open for discussion.

One of the methods to determine adsorption–desorption characteristics of oxygen, including the strength of the chemisorptive bond, is by oxygen isotopic exchange. This method is used extensively in the fields of heterogeneous catalysis [8,9] and electrochemistry of solid electrolytes [10].

The present paper is devoted to the investigation of the influence of electrochemical pumping of oxygen on the oxygen isotope exchange on Pt electrode-catalyst in a cell with YSZ electrolyte:

$$^{16}O_2 + ^{18}O_2, \mathrm{Pt}|\mathrm{YSZ}|\mathrm{Pt}, \mathrm{air}.$$

2. Experimental

Experiments were carried out in a static vacuum system (fig. 1) equipped with a mass-spectrometer for gas phase analysis and provided a vacuum of up to 10^{-7} Torr [11]. By turning the head of piston rod 1, one can easily isolate the electrochemical cell ($V \approx 5$ cm^3) from the rest of the reaction volume ($V \approx 620$ cm^3). This provides the possibility to pump and substitute the gas phase without changing the pressure in the electrochemical cell.

The cell itself was a tube closed at one end made from gas-impervious YSZ electrolyte with Pt electrodes deposited on the inner (working Pt electrode-catalyst) and outer (counter and reference electrodes) surfaces of the tube. The tube was 70 mm in length, 10 mm in diameter and had 0.6 mm wall thickness. The geometrical area of working and counter electrodes was ≈ 3 cm^2 and that of the reference was 0.3 cm^2. According to the data obtained by scanning electron microscopy, deposited Pt electrodes were porous and had thicknesses on the order of 10 μm. A typical scanning electron micrograph of a section perpendicular to Pt electrode–electrolyte interface is shown in fig. 2.

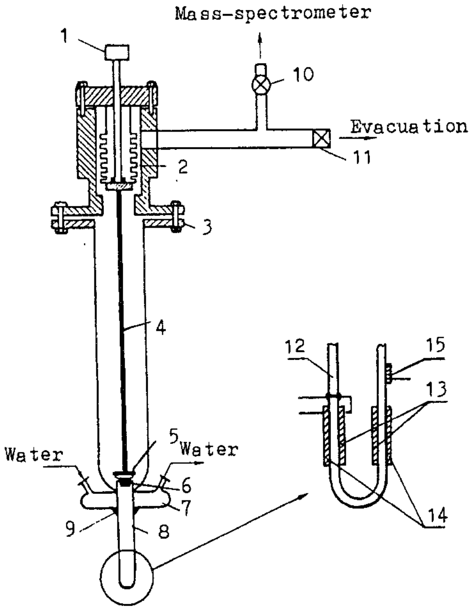

Fig. 1. Scheme of reaction unit. 1, head of piston rod; 2, bellows; 3, flange; 4, piston rod; 5, plug with a viton O-ring; 6, polished reactor butt-end; 7, chill; 8, electrochemical cell; 9, special glue; 10, leak valve; 11, cut-off valve; 12, YSZ electrolyte; 13, working electrode; 14, counter electrode; 15, reference electrode.

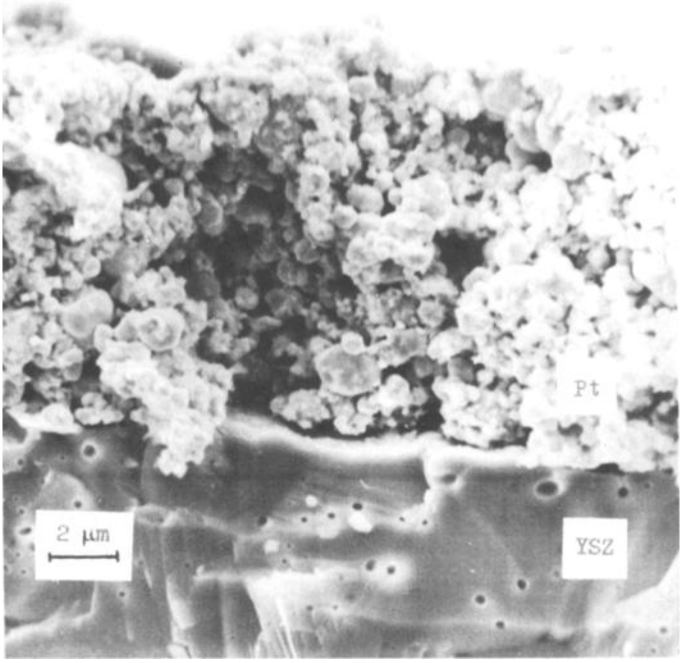

Fig. 2. Scanning electron micrograph of a section perpendicular to the Pt electrode–electrolyte interface.

The oxygen isotope exchange was studied over the temperature range from 713 to 795 K and oxygen pressure range from 0.1 to 0.8 Torr. In all experiments counter and reference electrodes were fed with air. It should be emphasized that, as shown by the experiments under these conditions, only a homomolecular exchange, i.e. isotope exchange in dioxygen, was observed. Heterogeneous exchange, i.e. the exchange of atoms between dioxygen and oxygen in the solid oxide electrolyte, was not observed. Note this type of exchange was observed at the temperature above 873 K. Moreover, in a blank test made in a cell without deposited Pt electrode no oxygen isotope exchange took place.

In our experiments, a non-equilibrium mixture of isotope molecules, prepared by mixing "heavy" oxygen (80% of ^{18}O) with natural oxygen in the ratio 1:1, was used. During operation the electrochemical cell was heated in a furnace, and the temperature was measured by a thermocouple pressed to the outer surface of the YSZ tube. The electric current flowing through the cell was controlled by a potentiostat which was also used to measure the electrode potential. The techniques used for electrochemical measurements have been presented in detail elsewhere [4].

The sequence of measurements of homomolecular exchange rate is described below. Prior to the experiments, the Pt electrode was heated in oxygen up to 973 K and treated by passing an electric current through the cell to remove carbon-containing impurities. During operation with an open circuit in the electrochemical cell (i.e. in this case the Pt electrode was an ordinary heterogeneous catalyst) the cell was heated and equilibrated in $^{16}O_2$. Then, by turning the head of piston rod 1 the electrochemical cell was closed and the rest of the reaction volume was outgassed to $\approx 10^{-7}$ Torr. After that, the reaction volume was filled with a non-equilibrium mixture of oxygen isotope molecules to achieve a given pressure. Then, the cell was opened by turning the head of piston rod 1 and the isotope exchange experiment was started.

The isotope exchange is followed by measuring the pressures of $^{16}O_2$, $^{18}O_2$, ^{16}O–^{18}O mass-spectrometrically. The typical variations of partial pressures of oxygen isotopes with time are illustrated in fig. 3.

The rate of homomolecular exchange (r) is expressed [10,12] as

$$r(t/N) = \ln(P_{34} - P_{34}^{*})/(P_{34}^{0} - P_{34}^{*}), \tag{1}$$

where N is the number of dioxygen molecules in the system, t is the time of exchange, P_{34}, P_{34}^{0} and P_{34}^{*} are the running, initial and equilibrium pressures of asymmetric ^{16}O–^{18}O molecules having mass 34, respectively. Eq. (1) is valid, independently of the exchange mechanism, provided that N and the fraction of ^{18}O in dioxygen does not change during the experiment. These conditions were maintained during the whole course of the experiments under open circuit conditions.

The sequence of oxygen isotope exchange measurements under closed circuit was similar to that under open circuit conditions. The difference was that an electric current was applied to the cell. With the current applied, the Pt electrode-catalyst, depending on the polarity of the applied current, can behave either as an

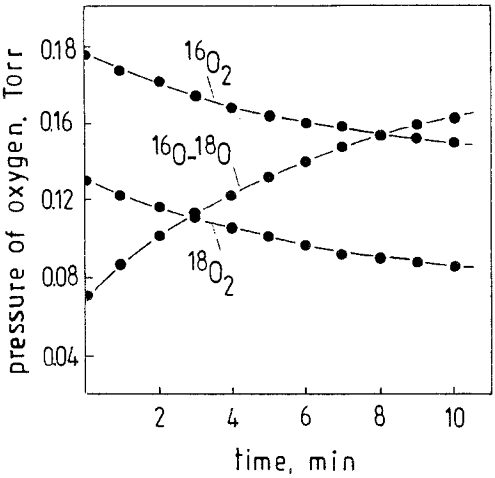

Fig. 3. Variations of partial pressures of oxygen isotopes ($^{16}O_2$,$^{18}O_2$,^{16}O–^{18}O) versus time during oxygen exchange under open circuit conditions at temperature of 783 K and overall pressure of oxygen 0.4 Torr.

anode or as a cathode. The former leads to electrochemical supply of oxygen into the reaction zone, while the latter leads to electrochemical removal of oxygen from the reaction zone. Thus, the current application leads to the changes in oxygen pressure, N and fraction of ^{18}O. These changes can be easily determined experimentally by mass-spectrometer and/ or calculated from

$$V_{O_2} = I/4F, \tag{2}$$

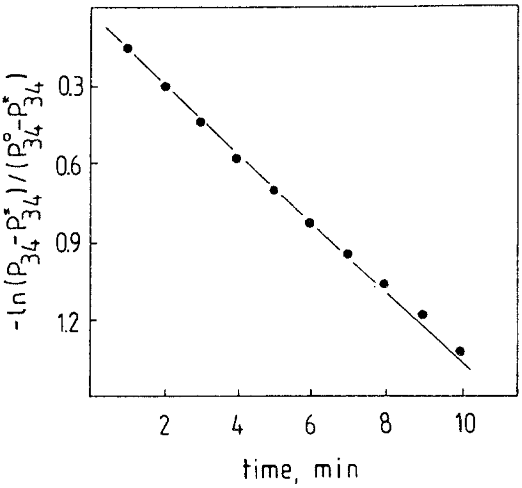

Fig. 4. Variation of $\ln(P_{34} - P^*_{34})/(P^0_{34} - P^*_{34})$ versus time during oxygen exchange under closed circuit conditions at temperature of 783 K and overall pressure of oxygen 0.4 Torr. The current passing through the cell is 2 mA. P^*_{34}, P^0_{34} and P_{34} are the equilibrium, initial and running pressure of ^{16}O–^{18}O.

where I is the applied current, F is Faraday's constant, V_{O_2} is the flow of oxygen through the electrolyte.

However, in the course of the study under the current application of current, the changes in oxygen pressure, N and fraction of ^{18}O were negligible. In particular even at the largest value of applied current used in our experiments ($I = 2$ mA), eq. (1) was valid. Indeed, as shown in fig. 4, the data obtained at $I = 2$ mA give a straight line in terms of $\ln(P_{34} - P^*_{34})/(P^0_{34} - P^*_{34})$ versus t (see eq. (1)).

Both under open and closed circuit conditions the accuracy of oxygen isotope exchange rate measurements was 10% of the measured value.

3. Results and discussion

3.1. OXYGEN ISOTOPE EXCHANGE UNDER OPEN CIRCUIT CONDITIONS

One could expect that the observed open circuit potential of the cell (E_{obs}) in the course of the isotope exchange experiments will coincide with the theoretical Nernst potential (E_{theor}):

$$E_{theor} = (RT/4F)\ln(P'_{O_2}/P^0_{O_2}), \tag{3}$$

where $P^0_{O_2}$ is the oxygen pressure in air above counter and reference electrodes, P'_{O_2} is the overall pressure of oxygen ($^{16}O_2$,$^{18}O_2$,^{16}O–^{18}O) above the working electrode-catalyst.

Experimental and theoretical values of potential at the typical reaction conditions are given in table 1. As is shown, E_{obs} are in good agreement with the corresponding theoretical values of the potential. This fact indicates that the

Table 1
Observed and experimental values of open circuit potential of the cell: O_2, Pt|YSZ|Pt, air

Experimental conditions		E_{obs} [a] (V)	E_{theor} (V)
T (K)	P_{O_2} (Torr)		
725	0.1	–0.114	–0.115
	0.2	–0.105	–0.104
	0.4	–0.090	–0.093
	0.8	–0.079	–0.082
783	0.1	–0.127	–0.125
	0.2	–0.111	–0.113
	0.3	–0.103	–0.106
	0.4	–0.101	–0.101
	0.6	–0.095	–0.094
	0.8	–0.088	–0.090

[a] E_{obs} reached the listed values during 0.5–1 min after changing of oxygen pressure above the working electrode. E_{obs} did not change during the whole course of the oxygen exchange study, which lasted usually 10–20 min.

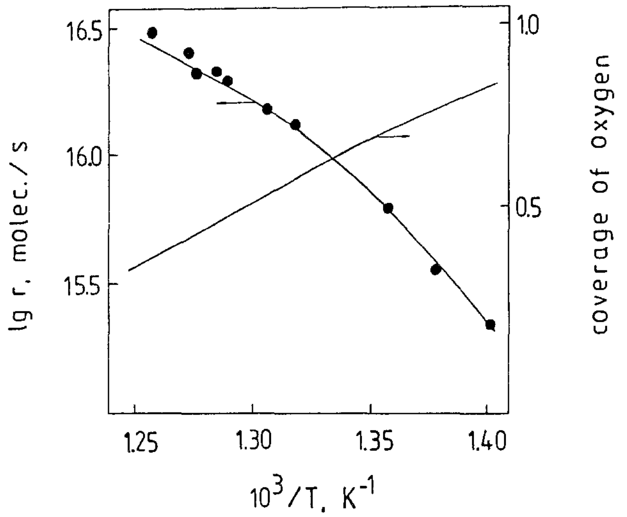

Fig. 5. Temperature dependences of the homomolecular oxygen exchange rate and oxygen coverage at oxygen pressure 0.4 Torr under open circuit conditions. Dots, experiment; solid line, theory.

thermodynamic activity of oxygen on Pt electrode-catalyst during the isotope exchange equals the gas phase oxygen activity, i.e. oxygen adsorption on the electrode-catalyst is in equilibrium.

The temperature dependence of homomolecular exchange rate, that has been measured over the temperature range from 713 to 795 K at oxygen pressure 0.4 Torr, is plotted in fig. 5. Clearly the activation energy of exchange (E) is not constant and decreases from 209 kJ/mol to 117 kJ/mol with increasing temperature.

Fig. 6 shows the dependence of the reaction rate on oxygen pressure at 723 and 783 K over the pressure range from 0.1 to 0.8 Torr. As is seen, the reaction order in oxygen (n) equals 0.1 at 723 K and $n = 0.6$ at 783 K.

By inspecting figs. 5 and 6, one sees that the kinetic parameters (E and n) of homomolecular oxygen isotope exchange depend on the temperature. On increasing the temperature from 713 to 795 K the reaction order in oxygen increases from 0.1 to 0.6 and the activation energy decreases from 209 to 117 kJ/mol.

Comparison of our results with those in refs. [13–15] on oxygen isotope exchange on Pt is given in table 2. The activation energy and reaction order of exchange on Pt monocrystals (111), (110), (100) in region I are in satisfactory agreement with the corresponding values for Pt electrode-catalyst (Pt/YSZ). However, the kinetic parameters of oxygen exchange on film, powder and Pt(100) in region II differ considerably from those on Pt/YSZ.

From our point of view this discrepancy is due to the different temperature range used during the course of the experiments on Pt/YSZ and on film, powder and Pt(100) in region II (see table 2). As follows from ref. [15], the mechanism of homomolecular oxygen exchange at high temperature may differ from that at low temperature. So, at low temperature, both a weakly and a strongly bound oxygen

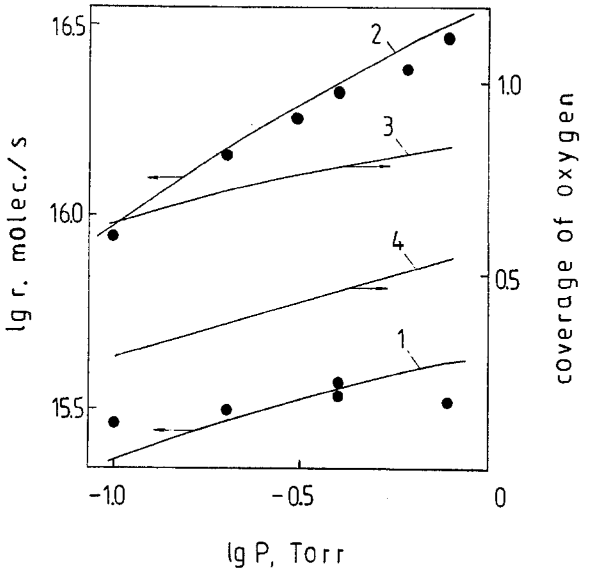

Fig. 6. Dependences of the homomolecular oxygen exchange rate (1, 2) and oxygen coverage (3, 4) on pressure of oxygen at 752 K (1, 3) and 783 K (2, 4) under open circuit conditions. Dots, experiment; solid lines, theory.

state participate in exchange, whereas at high temperature only a strongly bound oxygen state takes part in the exchange.

The obtained kinetic data permit some conclusions to be made about the mechanism of oxygen isotope exchange on Pt/YSZ. It seems reasonable to suppose that exchange follows the adsorption–desorption mechanism with the participation of a strongly bound oxygen state [O],

Table 2
Kinetic parameters of homomolecular oxygen isotope exchange on platinum

Sample of Pt	Experimental conditions		E^a (kJ/mol)	n^a	Ref.
	T(K)	P(Torr)			
film	473–523	0.15–0.5	69	0.5	[13]
powder	373–573	4.5–120	67	0.5–0.6	[14]
Pt(100)	653–800	1.5×10^{-2}–0.8			
	region I	(high T)	185	0	
	region II	(low T)	75	0.6	[15]
Pt(110)	730–790	4×10^{-2}–0.8	220	0	[15]
Pt(111)	750–915	4×10^{-2}–0.8	125	0.35 → 0.55	[15]
Pt/YSZ	723–793	0.1–0.8	209 → 117	0.1 → 0.6	this work

[a] E and n are activation energy of exchange and reaction order in oxygen, respectively; → notices the changes of E and n with increasing T.

$$O_2 + 2[\ ] \rightleftarrows 2[O],$$

where [ ] represents an adsorption site on the Pt electrode-catalyst surface. At lower temperatures (713–740 K) the oxygen surface coverage seems to be close to unity. In this case, in accordance with the experiment, the reaction order should be equal to zero, and activation energy of exchange (E) should be the same as the activation energy of oxygen desorption (E_{des}) and/or the heat of oxygen adsorption (q) on Pt. Indeed, in the region with $n = 0.1$ ($n \approx 0$) the value of E for Pt/YSZ is 209 kJ/mol and is close to the known values of E_{des} and q, which range from 180 to 240 kJ/mol for Pt [8,16,17].

When the temperature increases, the oxygen surface coverage decreases. In accordance with the experiment it should lead to the increase in reaction order in oxygen and to the decrease in the activation energy of exchange.

Let us check our qualitative considerations of homomolecular oxygen exchange mechanism within a framework of classical Langmuir dissociative adsorption model. In this case the rate (r) of oxygen isotope exchange which follows the adsorption–desorption mechanism can be written as

$$r = k_{\mathrm{d}}\theta^2 = k_{\mathrm{a}}P(1-\theta)^2 = k_{\mathrm{a}}P[1 + (Pk_{\mathrm{a}}/k_{\mathrm{d}})^{1/2}]^{-2}, \tag{4}$$

where k_{a} and k_{d} are the kinetic constants of oxygen adsorption and desorption, θ is the atomic oxygen coverage of Pt electrode-catalyst and P is the oxygen pressure.

The kinetic expression (eq. (4)) with kinetic constants $k_{\mathrm{a}} = 1.9 \times 10^7$ molec./s Torr and $k_{\mathrm{d}} = 8.8 \times 10^{32} \exp(-28500/T)$ molec./s provides a quantitative description of the experimental data shown in figs. 5 and 6. It should be noted that activation energy of kinetic constant of oxygen desorption is 237 kJ/mol. This value is close to the activation energy of exchange (209 kJ/mol in the region with $n = 0.1$) and is in reasonable agreement with known values of E_{des} and q on Pt [8,16,17]. The activation energy of kinetic constant of oxygen adsorbtion k_{a} is zero. This is reasonable from the known fact that the oxygen adsorption on Pt is practically a non-activated process.

Using eq. (4) we also calculated the dependences of oxygen surface coverage on the temperature and the pressure of oxygen. These dependences are plotted in figs. 5 and 6. By inspecting figs. 5 and 6, one can easily see that the decrease of oxygen coverage with increasing temperature leads to a decrease in activation energy and an increase in reaction order. As is seen, with increasing temperature, the surface coverage of oxygen decreases from 0.8 to 0.35. It is in agreement with the above qualitative considerations.

Thus, a very good agreement between experimental results and above theoretical considerations permits us to conclude that the homomolecular oxygen exchange on Pt/YSZ follows the adsorption–desorption mechanism. In other words, the oxygen isotope exchange occurs at the oxygen adsorption–desorption equilibrium and the exchange rate is equal to the rate of the dissociative adsorption and/

Table 3
Homomolecular oxygen isotope exchange rates on Pt electrode-catalyst under open and closed circuit conditions

Experimental conditions [a]				Exchange rate (molec./s)
T (K)	P (Torr)	I (mA)	E (V)	
725	0.4	0	−0.090	$(3.6 \pm 0.3) \times 10^{15}$
		0.2	0.188	$(3.5 \pm 0.3) \times 10^{15}$
		0.5	0.200	$(3.6 \pm 0.3) \times 10^{15}$
		−0.1	−1.06	$(3.3 \pm 0.3) \times 10^{15}$
783	0.4	0	−0.101	$(2.0 \pm 0.2) \times 10^{16}$
		0.5	0.205	$(2.0 \pm 0.2) \times 10^{16}$
		1.0	0.220	$(1.9 \pm 0.2) \times 10^{16}$
		2.0	0.240	$(2.0 \pm 0.2) \times 10^{16}$
		−0.3	−1.00	$(2.0 \pm 0.2) \times 10^{16}$
783	0.8	0	−0.088	$(2.8 \pm 0.3) \times 10^{16}$
		1.0	0.210	$(2.7 \pm 0.3) \times 10^{16}$
		1.0	0.230	$(2.7 \pm 0.3) \times 10^{16}$
		−0.3	−0.40	$(2.6 \pm 0.3) \times 10^{16}$

[a] T is the temperature; P is the overall pressure of oxygen ($^{16}O_2$,$^{18}O_2$,^{16}O–^{18}O); I is the electric current passing through the cell; E is the potential of Pt electrode-catalyst with respect to reference electrode. The current is positive when O^{2-} is pumped to the Pt electrode-catalyst (anodic polarization of electrode). The current is negative when O^{2-} is pumped from the Pt electrode-catalyst (cathodic polarization of electrode).

or associative desorption of oxygen. The activation energy of isotope exchange is either equal to the activation energy of oxygen desorption (at $n \approx 0$) or is a constituent part of that (at $1 > n > 0$) and thereby can be directly related to the strength of chemisorptive bond of oxygen on Pt electrode.

3.2. OXYGEN ISOTOPE EXCHANGE UNDER CLOSED CIRCUIT CONDITIONS

Taking into account the above results it seems evident that, if the electric current flowing through the cell changes the bond strength of chemisorbed oxygen on Pt electrode, the rate of homomolecular exchange under closed circuit must differ from that under open circuit conditions. In accordance with the present concept of the NEMCA phenomenon [1], the anodic polarization (O^{2-} pumping to Pt electrode-catalyst) should decrease the bond strength of chemisorbed oxygen, whereas the cathodic polarization (O^{2-} pumping from Pt electrode) should increase it.

Therefore, we expected that the exchange rate under anodic and cathodic polarization of electrode-catalyst would be, respectively, higher and lower than its open circuit value.

Table 3 shows the homomolecular oxygen exchange rates both under open and closed circuit conditions. As is seen, neither anodic nor cathodic polarizations of the Pt electrode change the rate of oxygen homomolecular exchange with respect to its open circuit value.

This fact firmly indicates that the strength of chemisorptive bond of oxygen on Pt electrode remains unchanged during polarization. Thus, the non-Faradaic modification of the oxidation reaction rate [1] can hardly be attributed to the changes in the strength of chemisorptive bond of oxygen when Pt electrode is polarized.

Further investigations are clearly needed to clarify the origin of the NEMCA phenomenon. It is important to obtain the data on the state and concentration of adsorbed species on electrode during catalytic reaction and passing of electric current through the cell by in situ surface science techniques. Note that, under closed circuit conditions, both the concentration and the nature not only of oxygen species but the other intermediate surface species taking part in catalytic reaction may be changed.

It would be of interest to elucidate the effect of the changes in solid oxide electrolyte on a catalytic activity of electrode during its polarization. According to refs. [18,19], these changes may be essential and are due to the formation of electronic defects in the solid electrolyte.

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