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Investigation of chemisorption properties of the PbO surface

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Chemisorption of O_2, Cl_2, and SO_2 on the orthorhombic and tetragonal PbO samples was studied in the 225—550 °C temperature range. The main features of chemisorption are independent of the crystal modification of the sample. The change in the type of conductivity of PbO during chemisorption of O_2 was found.

Key words: chemisorption, conductivity, semiconductor, surface, crystal modification.

The sorption and electrophysical properties of semiconducting oxides depend on many factors, namely, the method of preparation of the sample, its crystal structure, and the amount of admixtures. The influence of doping additives on the properties of oxide semiconductors have been studied fairly extensively.[1—5]. However, data on the influence of the type of the crystal structure of powdered oxides on their sorption properties are almost lacking in the literature. The purpose of this work was to study the chemisorption of O_2, Cl_2, and SO_2 on the surface of PbO in two crystal modifications, *viz.*, yellow orthorhombic and red tetragonal.

Experimental

According to the published data,[6] PbO is a semiconductor of the n type at low partial oxygen pressures and of the p type at high partial oxygen pressures. In particular, at temperatures of ~700 °C and an oxygen pressure of $1 \cdot 10^{-6}$—1 atm PbO is a p-semiconductor.[7]

The PbO sample in the yellow orthorhombic modification (analytically pure grade) with the specific surface (S_{sp}) 0.5 $m^2 g^{-1}$ (**1**) and two PbO samples in the red tetragonal modification, *viz.*, sample **2** (S_{sp} = 1.2 $m^2 g^{-1}$) obtained by the decomposition of freshly precipitated $Pb(OH)_2$[8] and sample **3**, which was received as a specially pure grade reagent (S_{sp} = 0.47 $m^2 g^{-1}$), were used. The specific surface was determined by the BET method from the low-temperature adsorption of Kr. The samples were identified using chemical and X-ray diffraction analyses.

Chemisorption was measured by the vacuum static method using a photoelectric pressure transducer based on a membrane gauge. The electric conductivity was determined by the probe method at a direct current.[9] A weighted sample (5.0 g) was pelleted under a pressure of 400 MPa. The pellet with the molded probes was placed into a reaction cell and trained *in vacuo* (residual pressure $1 \cdot 10^{-5}$ Torr) for 20 h until a constant value of electric conductivity was achieved. After such a treatment, the conductivity obeyed the Ohm law.

After the treatment of sample **1** *in vacuo* at 425 °C its conductivity at 350 °C was $1.5 \cdot 10^{-3}$ $Ohm^{-1} cm^{-1}$. Since the electroconductivity of samples **2** and **3** treated under the same conditions was by two—three orders of magnitude lower, they were treated at 550 °C to achieve comparable values of electroductivity. Measurements of the thermo-e.d.f. showed that after this treatment all samples had conductivity of the n type.

The activation energy of conductivity of sample **1** *in vacuo* in the temperature interval from 190 to 350 °C is 0.95 eV. The close values, *viz.*, 0.74 and 0.69 eV, were obtained for samples **2** and **3**, respectively, in the 350—550 °C temperature region.

Prior to experiment the samples were stored for 5 h in the reaction cell at a specified temperature and a pressure of $1 \cdot 10^{-5}$ Torr, and the gas to be sorbed was introduced at an initial pressure of 0.20—0.30 Torr. The instrumental error for pressure measurements was at most 3%, and that for conductivity measurements was 1%.

Chemisorption of O_2 was carried out at 225—350 °C for sample **1** and at 395—550 °C for samples **2** and **3**.

Chemisorption of O_2 on all samples occurs with a high rate, and the constant pressure 0.1—0.15 Torr is established in 1—3 min.

Results and Discussion

Preliminary studies showed that introducing the inert gas (Ar) into the cell at the temperature of experiment, did not change the electroconductivity of PbO. This indicates that the change in conductivity in the initial period of experiment cannot be caused by cooling of the sample.

The chemisorption properties of samples **1** and **2** are given in Table 1.

According to the estimate made from the geometric sizes of the molecule and an assumption of the complete filling of the surface, the surface coverage by chemisorbed O_2 is ~20% of the monolayer capacity. The chemisorption rate increases with temperature.

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Table 1. Chemisorption properties of the samples

Sample	Gas	T /°C	P_0[a] /Torr	Q[b] /μmol m^{-2}	σ_0[c] /Ohm^{-1} cm^{-1}	σ_1/σ_0[d]	σ_1/σ_0[e]
1	O_2	225	0.26	1.96	$1.71 \cdot 10^{-5}$	0.56	0.77
		275	0.28	1.84	$1.57 \cdot 10^{-4}$	0.64	1.07
		350	0.29	1.76	$1.56 \cdot 10^{-3}$	0.94	1.00
	Cl_2	225	0.33	3.04	$1.89 \cdot 10^{-5}$	0.96	1.00
		250	0.21	1.70	$6.06 \cdot 10^{-5}$	0.92	0.97
		275	0.30	2.64	$1.40 \cdot 10^{-4}$	0.93	0.97
		300	0.20	1.56	$2.69 \cdot 10^{-4}$	0.99	1.08
	SO_2	275	0.28	2.48	$1.30 \cdot 10^{-4}$	0.91	1.01
2	O_2	395	0.10	0.13	$3.50 \cdot 10^{-4}$	0.09	0.93
		550	0.27	0.45	$3.80 \cdot 10^{-3}$	0.29	1.14
	Cl_2	350	0.19	2.00	$6.24 \cdot 10^{-5}$	$<1 \cdot 10^{-4}$	$1.5 \cdot 10^{-3}$
	SO_2	395	0.30	0.50	$3.70 \cdot 10^{-4}$	0.79	1.20

[a] Initial pressure of the sorbed gas.

[b] Amount of the sorbed gas.

[c] Initial electroconductivity of the sample before sorption.

[d] Minimum relative electroconductivity.

[e] Relative electroconductivity of the sample after sorption.

The plots of the electroconductivity *vs.* chemisorption time are presented in Fig. 1 for sample **2**. The character of the electroconductivity changes during chemisorption is the same for all samples. A decrease in the conductivity corresponding to the uptake of O_2 is observed in the initial period followed by a conductivity increase at a constant gas pressure to nearly initial values. The chemisorption rate at each stage increases with temperature, and the initial decrease in the electroconductivity depends on the type of the sample and temperature. For sample **2** the initial decrease is one order of magnitude (see Fig. 1, Table 1), and for sample **1** it does not exceed 50%. Chemisorption on this sample was studied at lower temperatures (Fig. 2).

In experiments on the successive saturation of the PbO surface with dioxygen at 550 °C, the next portion of the gas was introduced to the cell after a constant pressure was established. It turned out that the pattern of the electroconductivity change during the sorption of each subsequent portion remains unchanged.

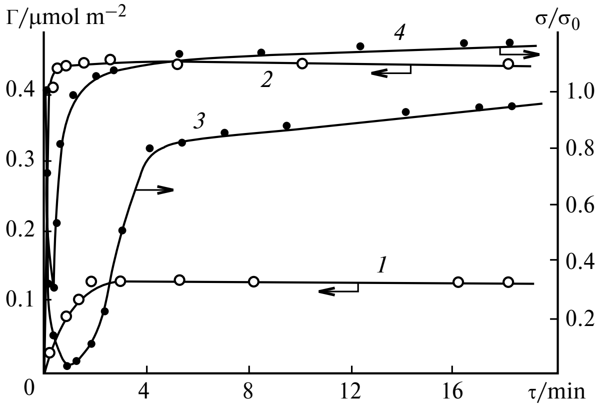

Fig. 1. Kinetics of chemisorption of O_2 (*1*, *2*) and the change in electroconductivity σ/σ_0 (*3*, *4*) of sample **2** at 395 °C (*1*, *3*) and 550 °C (*2*, *4*).

Pumping out O_2 from the cell at temperatures <400 °C did not change the electroconductivity of the samples. On removing O_2 from the gas phase at 550 °C, the conductivity decreased by 25—30%.

It is known that O_2 is the typical gas-acceptor, whose chemisorption is accompanied by the localization of free electrons of the surface layer of the sample in the vicinity of sorption sites on the metal surface. As a result, when the amount of chemisorbed dioxygen increases, the electroconductivity of semiconductors of the n type decreases and that of the p type increases. At the initial stage of O_2 chemisorption the samples of both PbO modifications exhibit the properties of a semiconductor of the n type. However, once the constant gas pressure ~$1 \cdot 10^{-1}$ Torr is established, the character of conductiv-

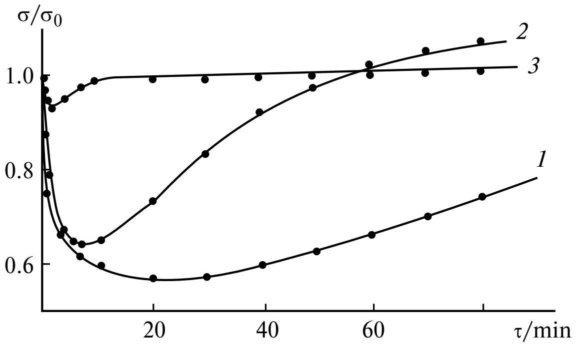

Fig. 2. Change in electroconductivity of sample **1** during chemisorption of O_2 at 225 (*1*), 275 (*2*), and 350 °C (*3*).

ity changes. The observed increase in the electroconductivity can be related[7] to the ability of PbO to gain the p type conductivity in the presence of O_2. It follows from the data obtained that at the sorption temperatures from 225 to 225—550 °C and the initial O_2 pressure $3 \cdot 10^{-1}$ Torr the type of conductivity of the oxide changes during O_2 chemisorption on PbO.

Chemisorption of Cl_2 was carried out at temperatures of 225—300 and 350 °C on samples **1** and **2**, respectively. The general character of Cl_2 sorption and the accompanying change in the conductivity for both modifications are similar to those observed for O_2 sorption; however, the rate of Cl_2 chemisorption is higher. The constant gas pressure in the cell is achieved already 1 min after the beginning of the experiment in the whole temperature region studied. The residual pressure of Cl_2 in the cell is somewhat lower than that for O_2 under comparable conditions, being 0.02—0.07 Torr (see Table 1).

The isothermal saturation of the sample **2** surface with dichlorine at 350 °C (Fig. 3) shows that the character of chemisorption is independent of the amount of sorbed Cl_2. When the monolayer coverage of the surface with sorbed Cl_2 is achieved, O_2 appears in the gas phase, which could not frozen out by liquid nitrogen and whose fraction was 2.5% of the amount of introduced Cl_2.

The initial decrease in the conductivity of sample **2** during chemisorption of Cl_2 exceeds four orders of magnitude (see Fig. 3, curve *2*). Then the electroconductivity increased by two orders of magnitude but with a lower rate. The change in the electroconductivity is much lower for sample **1** (see Table 1).

Freezing out Cl_2 from the cell at the temperature of experiment does not change the conductivity of the samples.

Dichlorine and dioxygen are chemisorbed only by the acceptor-type interactions with the PbO surface. The observed decrease in the electroconductivity of PbO shows that the oxide demonstrates the properties of the n type semiconductor in the moment of introducing Cl_2. The subsequent increase in the sample conductivity can be due to either a change in the type of conductivity of the sample or the restructurization of the surface sorption layer with the formation of the reaction products. The latter is favored by the fact that O_2 is evolved to the gas phase at surface coverages close to those corresponding to the monolayer capacity.

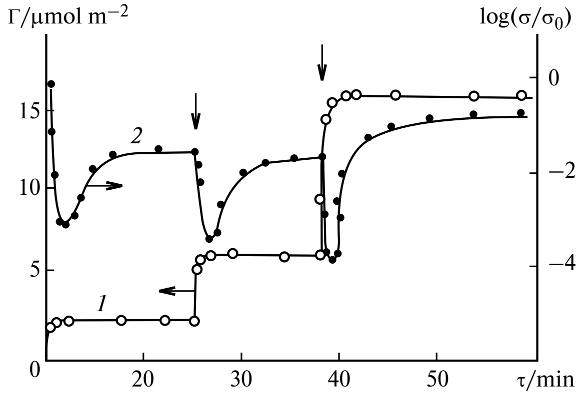

Fig. 3. Kinetics of chemisorption of Cl_2 (*1*) and the change in electroconductivity (*2*) of sample **2** at 350 °C.

The analogous character of the conductivity during Cl_2 chemisorption was observed earlier for several oxides, which are typical semiconductors of the n type (ZnO, CdO, In_2O_3). It was found by the method of temperature-programmed surface reactions that the increase in the conductivity of these oxides was due to the formation of metal chlorides and oxygen on the surface.[10—13] Evidently, the chemisorption interaction of PbO with Cl_2 is complicated by the occurrence of the chemical reaction.

The sorption of SO_2 was carried out at 275 and 395 °C on samples **1** and **2**. The same regularities of the sorption of the gases during chemisorption as for the sorption of O_2 were observed. The sorption of SO_2 occurs with a higher rate, and the surface coverage under comparable conditions is higher reaching 30% of the monolayer value. However, the decrease in the conductivity of the samples in the initial period is lower than that during O_2 sorption. The subsequent increase in the conductivity occurs with a lower rate. Freezing out SO_2 at the temperature of experiment was not accompanied by a change in the conductivity of PbO.

The character of the process did not change when SO_2 was chemisorbed on the surface containing presorbed O_2. No evolution of O_2 to the gas phase was observed.

Unlike Cl_2 and O_2, the character of interaction of SO_2 with the oxide surface can be either of acceptor- or donor-type, depending on the state of the surface. Correspondingly, the chemisorption complex can exist simultaneously in both forms on the surface of semiconducting oxides, and the character of the change in conductivity during chemisorption depends on their ratio.[4,5,14,15]

In the moment of the initial contact, the interaction of SO_2 with the PbO surface has an acceptor character, which is confirmed by the initial increase in the electroconductivity of the oxide. The subsequent increase in the electroconductivity can be caused by both a change in the type of conductivity of PbO and the appearance of a chemisorption complex formed by the donor-type interaction of SO_2 with the surface. The presence of this complex is supported by the following observation. Dioxygen was pre-adsorbed on PbO in such a way that the surface coverage was 25—30% of the monolayer capacity. During chemisorption on this surface, no competition for the active sites occurred on the surface: SO_2 adsorption did not decrease and O_2 was not displaced to the gas phase.

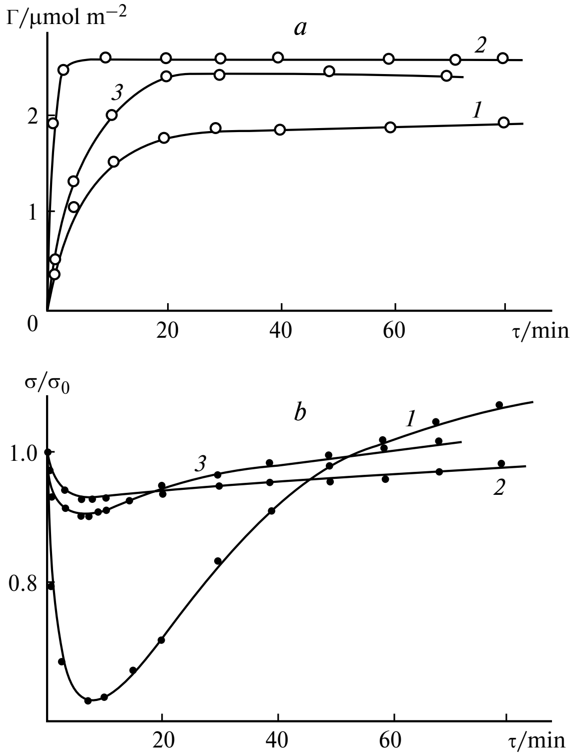

Fig. 4. Kinetics of chemisorption (*a*) and the change in electroconductivity (*b*) of sample **1** during sorption of O_2 (*1*), Cl_2 (*2*), and SO_2 (*3*) at 275 °C.

The kinetic curves of chemisorption of different gases on the sample **1** surface and changes in the electroconductivity of the sample accompanying chemisorption are presented in Fig. 4. Under conditions comparable with chemisorption of Cl_2 or SO_2, O_2 is sorbed with a lower rate and a lower surface coverage. However, the chemisorption of O_2 results in more substantial changes in the conductivity of the sample than the sorption of Cl_2 or SO_2.

Our studies showed that the features of chemisorption of O_2, Cl_2, and SO_2 on PbO and the character of the change in the oxide conductivity are independent of the type of the crystal modification of the samples and temperature of their treatment *in vacuo*. The chemisorption of all studied gases on the PbO samples with different crystal modifications is accompanied by the fast initial decrease in the conductivity followed by the relatively slow increase. In the moment of supply, PbO manifests the properties of the n type semiconductor, and the interaction with the surface has the acceptor character.

The increase in the electroconductivity of PbO observed after O_2 was completely sorbed by the sample, is due to a change in the type of the oxide conductivity. In the case of Cl_2 sorption, the chemisorption processes are complicated by the chemical reaction on the surface. The increase in the electroconductivity is a result, most likely, of the formation of chlorination products. For SO_2 chemisorption, the conductivity increase can be explained by the presence of the donor form of gas sorption on the PbO surface.

The crystal structure of the samples has an effect only on the numerical values of electroconductivity during sorption. Only the irreversible sorption of the gas is responsible for the change in the electroconductivity of the samples.

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