ISSN 1070-3632, Russian Journal of General Chemistry, 2013, Vol. 83, No. 4, pp. 633–635. © Pleiades Publishing, Ltd., 2013.
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Electric Conductivity of Porous Glass Modified by Oxides of Bivalent Cobalt, Nickel, and Copper

V. N. Pak, D. V. Formus, and S. M. Shilov

Herzen Russian State Pedagogical University, nab. r. Moiki 48, St. Petersburg, 191186 Russia
e-mail: pakviacheslav@mail.ru

Received September 25, 2012

Abstract—Multiply repeated operations of porous glass impregnation by aqueous solutions of bivalent cobalt, nickel, and copper nitrates followed by the thermal decomposition of the deposited salts provide a gradual accumulation of oxides in the carrying agent. In all cases, as the surface of glass open channels is filled with oxides, a section of substantial increase in conductance is detected, in which a tentative oxide monolayer is formed. Relations established between conductivity and its activation energy are treated on the basis of the conception of intervalence mechanism of electron transfer in the systems under consideration.

DOI: 10.1134/S1070363213040038

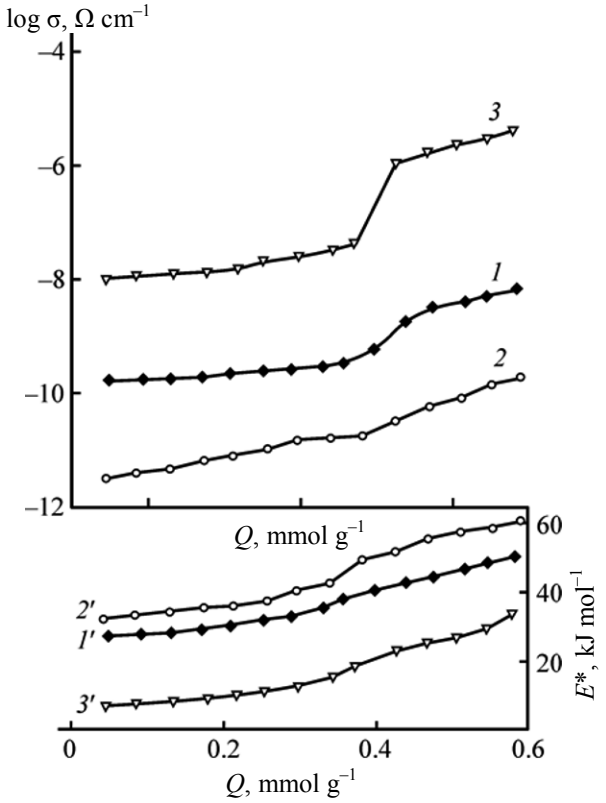
So far possibilities of application of porous glasses as media for the formation of nanostructures with preset electrical properties are known only scantily [1–6]. In particular, on the basis of measuring conductance it was found [6] that, as a content of copper(II) oxide is gradually increased, the surface of open channels in a porous glass is filled to form a preferentially two-dimensional deposit structure close to a monolayer. In this connection it is necessary to carry out a comparative study of the character and consequences of porous glass modification by bivalent copper, cobalt, and nickel oxides with the purpose of both confirming the earlier data [6] and determining the effect of the chemical nature of oxides on the value and nature of conductivity variation.

The structure of the modifying oxides monotonically "accumulated" on the surface of the carrying agent can be a combination of three-dimensional (island), two-dimensional (planar), and one-dimensional (chain) nanosize forms, their ratio (or the predominant presence of one of them) defining the mechanism and value of conductivity [6–10]. Gradual increase of the amount and size of particles of transition metal oxides fixed on the surface is accompanied by origination and progressing increase in the number of interparticle contacts. It results in the formation of rather extended ensembles with a conductivity, which is largely regulated by the extent of the electronic d_π–$2p_\pi$ conjugation in M–O–M metal-oxygen bridges [6, 10].

Following the procedure [6] applied previously, we deposited the oxides by impregnating plates of a wide-pore glass [11] with solutions of metal nitrates followed by removal of water from pore space and thermal decomposition of the salts distributed on the surface of the open channels of the carrying agent. Step-by-step buildup of the deposited mass was provided by a multiple repetition of the impregnating-decomposition operations. The retention of the linear shape of the relationships between the amount of accumulated oxide and the number of multiply (up to 15 times) repeated plotting cycles points to the insignificant effect of the contraction of the glass pore volume caused by this procedure [6].

The figure shows the dependences of the logarithm of the modified glass conductivity on the amount of oxide log $\sigma(Q)$ deposited at room temperature and also the variation of conductivity activation energies $E^*(Q)$ calculated from its temperature dependence for several samples with increasing amount of deposits. It is well seen that the systems under consideration show both close similarity and noticeable difference in their behavior.

The common feature of the log σ–Q relationships is the presence of three sections. At first the sequential accumulation of oxides on the walls of open channels is accompanied by a weak monotone raise. Then the section of the substantial conductivity growth follows,



Dependence of (1-3) the logarithm of conductivity and (*1′–3′*) energy of its activation on the relative amount of (*1, 1′*) cobalt, (*2, 2′*) nickel, and (*3, 3′*) copper oxides in porous glass.

and after its completion the raise again becomes slow. The clear likeness of the systems under consideration is also noticeable in $E^*(Q)$ dependences, the form of which reproduces to some extent the features of the conductivity variation.

To account for the data on the general properties of the systems under consideration, it is necessary to improve the earlier interpretation of the log σ–Q relationship for the modification of porous glass by copper(II) oxide [6]. As the conductivity of pure dry glass lies outside the measuring range, it is highly probable that the level of its values reached even on the first step of depositing oxides should be connected with a possibility of formation of primary current paths in the form of extended chains of conjugated metal-oxygen polyhedra on the walls of the carrying agent channels. The energy gain resulted from the elongation of conjugation chains can cause their preferential formation and lining along open channels of porous glass. The offered version of self-organization of oxides in pores of the carrying agent based on the results of measuring conductivity, in turn allows us to give a preliminary interpretation of the log σ–Q relationships. Low values of activation energies in the initial stage of filling a surface, most likely, characterize heat excitation of vibrations in the conductive chains promoting an increase in the $3d_\pi$–$2p_\pi$ conjugation in M–O–M bridges. During the subsequent monotone accumulation of oxides in the carrying agent the conductive chains gradually "become overgrown" with side M–O–M bonds that is accompanied by a raise in the structure rigidity, restrains the rate of conductivity growth, and results in small, but confidently logged increase in E^* values. The further evolution of the two-dimensional oxide structures results in the formation of multiple contacts between them and is completed by the formation of a distribution close to a monolayer [6]. Correspondingly, on the second section of filling the surface with oxides a consistent acceleration of the growth of the s and E^* values is observed. On the third section of the relationships under discussion a gradual supermonolayer build-up of the oxides defines the further stabilization of the structure as a whole and is accompanied by only negligible increase both in the conductivity and in its activation energy.

It was shown earlier [6] that the amount of copper oxide in porous glass in the region of formation of the tentative monolayer corresponds to the fixation of one copper(II)-oxygen polyhedron on the area of 10 Å^2. Not exaggerating a significance of this argument we can point out that it reasonably corresponds to the possibility of dense planar "packing" of oxide polyhedra on the walls of porous glass open channels.

When considering differences in the properties of the systems defined by the nature of the modifying oxides, we should first of all refine reasons of the significant decrease in the conductivity along the series: $\sigma_{CuO} >> \sigma_{CoO} > \sigma_{NiO}$. The mechanism of conductivity includes injection of electrons from an electrode and their transfer along M–O–M conjugated bonds. The conception of such processes of the activated migration (hopping) of electrons goes back to the classical works [12, 13]. In case of capsulated forms of copper oxide the specified mechanism is realized in essence due to "switching over" valence states typical for it: [–Cu^+(*e*)–O–Cu^{2+}–O–Cu^{2+}–] → [–Cu^{2+}(*e*)–O–Cu^+–O–Cu^{2+}–] → [–Cu^{2+}(*e*)–O–Cu^{2+}–O–Cu^+–].

The low value of the redox potential $E^0(Cu^+ – e \rightarrow Cu^{2+})$ of 0.153 V [14] corresponds to the relative ease

of the electron transfer. In the case of bivalent cobalt and nickel oxides the realization of conductivity by the above scheme meets essential difficulties, as it requires that the atoms should be "transferred" in the singly charged state unusual to them. The specified features are also clearly reflected in the succession of conductivity activation energies of the systems under consideration (see the figure) $E^*_{CuO} << E^*_{CoO} < E^*_{NiO}$ valid for all comparable values of the degree of filling a surface.

The sudden change in the conductivity, which is sharply expressed as copper oxide is accumulated, appeared stretched and smoothed in glasses with inclusions of nickel and cobalt oxides (see the figure). Obviously it is caused by a difference in the degree of electronic $3d_x$–$2p_\pi$ conjugation along the M–O–M bonds. The copper(II) oxide monolayer is formed in conditions of the increasing strengthening of collective electronic interactions in the system and appears as a sharp break of the log σ(Q) curve. The degree of π-binding in the Co–O–Co and Ni–O–Ni bridges seems to be not so significant, which shows itself in a decrease in conductivity, in the change of shape of its dependence on the content of oxides, and in the enhanced values of its activation energy.

EXPERIMENTAL

Porous glass was synthesized according to the procedure [11] in the form of thin (1 mm) plates, membranes penetrated by open channels with effective radius of ~70 nm. The plates were impregnated with 0.15 M solutions of the nitrates $Co(NO_3)_2$, $Ni(NO_3)_2$, and $Cu(NO_3)_2$. The dehydration and thermal decomposition of salts in the pore space were carried out in the mode of linear temperature rise (5 deg min^{-1}) up to 400°C with a subsequent calcination for 1 h [6]. Measurements of weight losses after the thermolysis completion reliably confirmed the formation of the oxides CoO, NiO, and CuO on the silica surface. The accumulation of the oxide mass in the carrier was provided by a multiple repetition of impregnation-decomposition operations. To decrease the contact resistance, we covered plates under study by a layer (of thickness ~1 mm) of graphite powder with the average particle size of 10–20 μm. Electric resistance was measured at the frequency of 1 kHz using a E7−11 universal measuring instrument (in some cases an R-5058 bridge) [6]. Recorded values were converted to the values of specific conductivity (σ) taking into account real sizes of samples.

REFERENCES

1. Enke, D., Janowski, F., and Schwieger, W., *Micropor. Mesopor. Mater*., 2003, vol. 60, no. 1, p. 19.
2. Charnaya, E.V., Tien, C., Wur, C.S., and Kumzerov, Yu.A., *Physica (C),* 1996, vol. 269, nos. 3–4, p. 313.
3. Pak, V.N., Verezhinskaya, R.L., and Burkat, T.M., *Zh. Fiz. Khim*., 2002, vol. 76, no 7, p. 1103.
4. Pak, V.N., Sukhanov, S.V., and Gavronskaya, Yu.Yu., *Zh. Prikl. Khim*., 2002, vol. 75, no. 10, p. 1651.
5. Lyubavin, M.V., Burkat, T.M., and Pak, V.N., *Zh. Prikl. Khim*., 2009, vol. 82, no. 7, p. 1143.
6. Pak, V.N., Formus, D.V., and Neshin, A.A., *Zh. Obshch. Khim*., 2012, vol. 82, no. 7, p. 1089.
7. Chopra, K. L., *Thin Film Phenomena*, New York: McGraw-Hill, 1969.
8. Kozhevin, V.M., Yavsin, D.A., Smirnova, I.P., Kulagina, M.M., and Gurevich, S.A., *Fiz. Tverd. Tela*, 2003, vol. 45, no. 10, p. 1895.
9. Das, D., Kundu, T.K., Dey, M.K., Chakraborty, S., and Chakravorty, D., *Proc. Ind. Acad. Sci. (Chem. Sci.),* 2003, vol. 115, nos. 5–6, p. 341.
10. Tur, T.M., Metelkina, Yu.S., and Pak, V.N., *Zh. Prikl. Khim*., 2000, vol. 73, no. 1, p. 48.
11. Lyubavin, M.V., Burkat, T.M., and Pak, V.N., *Neorg. Mater*., 2008, vol. 44, no. 2, p. 248.
12. Mott, N.F., Adv. Phys., 1967, vol. 16, no. 1, p. 49.
13. Mott, N.F. and Davis, E.A., *Electron Processes in Non-Crystalline Materials*, Oxford: Clarendon Press, 1971.
14. Rabinovich, V.A. and Khavin, Z.Ya., *Kratkii khimicheskii spravochnik* (Brief Chemical Handbook), Leningrad: Khimiya, 1977, p. 304.