Scientific article
UDC 546.722/723-44
DOI: 10.52957/2782-1900-2024-5-2-140-146

ELECTRICAL CONDUCTIVITY OF POTASSIUM POLYFERRITE DOPED WITH DOUBLY CHARGED CATIONS

A. N. Dvoretskaya, L. G. Anikanova, T. N. Sudzilovskaya, Z. G. Malysheva, N. V. Dvoretsky

Alexandra N. Dvoretskaya, Student**; Lyubov G. Anikanova**, Candidate of Chemical Sciences, Associate Professor; **Tatiana N. Sudzilovskaya**, Candidate of Chemical Sciences, Associate Professor**; Zoya G. Malysheva**, Candidate of Chemical Sciences, Associate Professor**; Nikolay V. Dvoretsky**, Doctor of Chemical Sciences, Professor**.**
Yaroslavl State Technical University, Yaroslavl, Russia
dvoretskayaaleksandra@mail.ru, anikanoval@mail.ru, sudzilovskayatn@mail.ru, malyshevazg@mail.ru, dvoretskiin@mail.ru

Keywords: *polyferrite, promoter, doubly charged cation, charge compensation, electronic conductivity, cationic conductivity, iron oxide catalyst*

Abstract*. To clarify the charge compensation mechanism and the way of alloying additives placement, the authors synthesised samples of potassium β″-polyferrites with a wide range of mole fraction of introduced doubly charged cations. For these samples, the authors measured the electronic conductivity, cationic conductivity, and performed X-ray diffraction (XRD) analysis. The authors identified the charge compensation mechanism in potassium β″-polyferrite when doped with divalent ions of calcium, strontium, magnesium, and zinc. The charge compensation mechanisms differ depending on the radius of the introduced doubly charged ion. The results of cationic conductivity measurements of potassium β″-polyferrites show the mobility reduction of large calcium and strontium cations of potassium ions. Such additives are quite promising for improving the mechanical strength and thermal stability of the catalyst granules. They also increase the chemical stability of the contact granules. Corrosion resistance of pellets is a critical parameter. It determines the period of effective functioning of the catalyst. The data on electronic conductivity allow one to conclude that the introduction of Mg^{2+}, Zn^{2+} cations sharply reduces the electron exchange in the structure of potassium β″-polyferrite. This should inevitably cause deactivation of the catalyst, while Ca^{2+} and Sr^{2+} ions do not reduce the electron transfer rate. Moreover, using the proposed approach will intensify the research process.*

For citation:
Dvoretskaya, A.N., Anikanova, L.G., Sudzilovskaya, T.N., Malysheva, Z.G. & Dvoretsky, N.V. (2024) Electrical conductivity of potassium polyferrite doped with doubly charged cations, *From Chemistry Towards Technology Step-By-Step,* 5(2), pp. 140-146 [online]. vailable at: https://chemintech.ru/ru/nauka/issue/5176/view

Introduction

Potassium polyferrite with β″-alumina type structure is the active phase of promoted iron oxide catalysts for dehydrogenation of alkylaromatic and olefinic hydrocarbons. The maximum concentration of active dehydrogenation centres is activated on the surface of potassium β″-polyferrite [1-3]. K-β″Fe_2O_3 has a set of unique properties. It is a solid electrolyte with high conductivity due to its electronic and cationic components. Cationic conductivity is due to the increased mobility of potassium ions in the so-called cationic conducting layers. These layers are characterised by loose oxygen packing (filling is 2/3 of the number of available positions) with free movement of alkali metal cations among them [2, 4]. Electronic conductivity is provided by the intense $Fe^{2+} \rightleftarrows Fe^{3+}$ electron exchange of the polyferrite structure. Moreover, this exchange is characteristic only for the structure of the catalytically active phase - potassium β″-polyferrite [3], i.e. K-β″Fe_2O_3.

Solid electrolytes are a class of solid-phase materials with a set of characteristics determining broad prospects for their use in science and industry. Polyferrite systems, as well as other types of solid electrolytes possessing adjustable cation mobility, are characterised by high thermostability and a wide range of variation of electronic conductivity. The mechanism of cationic conductivity is of great importance for the development of mass transfer theoretical provisions in catalytically active polyferritic systems and for the control of alkaline promoter migration through the volume of solid-phase catalyst. The presence of electron exchange is a necessary condition for this material to exhibit catalytic properties in redox processes. Italso includes the dehydrogenation reaction. The value of electronic conductivity can be used as a representative parameter of polyferritecatalytic activity. This can be used to predict the efficiency of the developed catalyst and optimise the amount of alloying additives. Moreover, the required information can be obtained without labour-intensive and costly catalytic tests. The cationic conductivity of polyferrite is directly related to the migration and emission of the alkaline promoter [5]. The cationic conductivity data of K-β″Fe_2O_3 can predict the corrosion resistance of the catalytically active phase and catalyst lifetime.

Additives introduced to improve any of the catalyst properties usually have a dual effect, i.e., they can adversely affect other contact performance characteristics [6-10].

Thus, definingof the distribution method and mechanism of the additives action introduced into a complex heterogeneous system isa relevant issue.

The purpose of this research is to determine the effect of doubly charged cations addition on the electronic and cationic conductivity of potassium polyferrite of the β″-alumina type.

Main body

We prepared mixtures of potassium monoferrite, haematite, additives, and metallic iron obtained by the carbonyl method by careful grinding in an agate mortar under a layer of diethyl ether in a box filled with dried air. We used hematite of special purity (mass fraction of the main substance α-Fe_2O_3 at least 99.98%) applied in microelectronics. We tableted the obtained mixtures without taking them out of the box using a laboratory press. We prepared initial monoferrite by calcination of a mixture of potassium carbonate with iron oxide in equimolar ratio at a temperature of 970 K for 4 hours. Then we took the starting substances for the preparation of tablets in ratios satisfying the following equations:

$$6KFeO_2 + (1 - q)Fe + (13 - q)Fe_2O_3 + 3qMO \rightarrow 3K_2Fe^{II}_{1-q}M_qFe^{III}_{10}O_{17},$$

where M is Mg, Zn;

$$(6-6q)KFeO_2 + Fe + (13+3q)Fe_2O_3 + 3qMeO \rightarrow 3K_{2-2q}Fe^{II}Me_qFe^{III}_{10}O_{17},$$

where Me is Ca, Sr.

The parameter q was varied in the range of 0-0.40.

We added magnesium and zinc to the initial mixtures in the form of oxides. We used calcium and strontium in the form of carbonates.

We placed the tablets in a crucible, filled the top with powder of the same composition as the tablets, and calcined at 1070 K in a muffle furnace in a nitrogen atmosphere for 6 hours.

After calcination, we transferred the samples to a sealed box and cooled them in an inert gas current. We performed X-ray phase analysis of polyferrite samples on a DRON-UM1 instrument; emission $Co_{K\alpha}$ (λ = 179.02 pm).

X-ray phase analysis confirmed that the tablet samples after calcination are single-phase polyferrite of β"-alumina type. No loss of alkali metals was observed according to atomic absorption spectroscopy.

We measured the electronic conductivity of the pellets at 570 K using a complex impedance setup based on the scheme presented in Nariki [11].

We synthesised samples of β″-polyferrites of potassium with a wide range of mole fraction of introduced doubly charged cations to elucidate the mechanism of charge compensation, the way of placement of alloying additives. We measured the electronic conductivity, cationic conductivity, and performed X-ray diffraction analysis for these samples.

As a result, with increasing the proportion of doping doubly charged ions Mg, Zn, there is a drop in the electronic conductivity of potassium polyferrite of the β″-alumina type (Fig. 1).

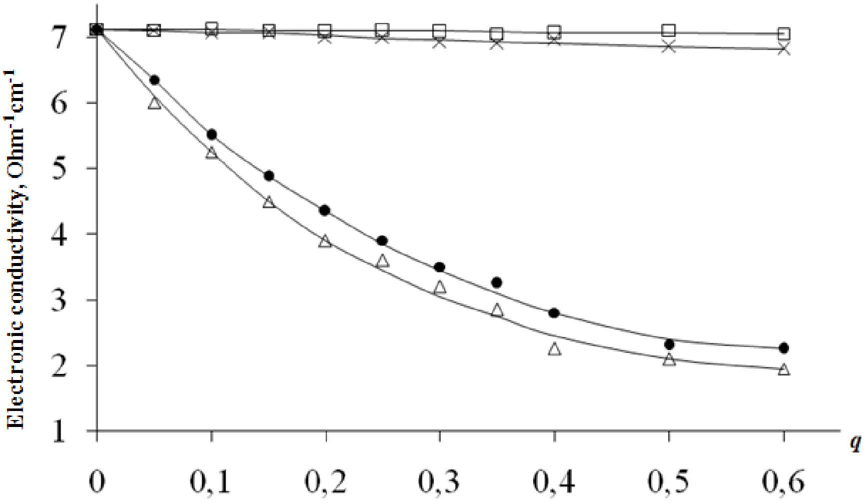

Fig. 1. Electronic conductivity of polyferrites depending on the content of doping ion as follows: □ – Sr; x – Ca; • – Zn; Δ – Mg

This effect is related to a decrease in the concentration of doubly charged iron in the polyferritic system. It increases the distance between the doubly and triply charged iron ions, and leads to a fall in the intensity of electron exchange between $Fe^{2+} \rightleftarrows Fe^{3+}$.

The obtained data can be explained considering the upper limit of isomorphic substitutability in the octahedral voids of the oxygen ion lattice is 99 pm [8]. The radii of doping doubly charged ions Mg, Zn are smaller than this limit. Therefore, the ions can enter the spinel-like block and replace doubly charged iron in it. Indeed, Mg and Zn ions, which are comparable in size to the Fe^{2+} radius (Table 1), can enter the spinel-like block and substitute doubly charged iron at these positions.

Table 1. Effective radii of doubly charged ions included in the structure of potassium β″-polyferrite [13]

Ions	Ca^{2+}	Sr^{2+}	Mg^{2+}	Zn^{2+}	Fe^{2+}	Fe^{3+}
Radius, pm	104	112	66	74	80	67

The decrease in the intensity of electron exchange in the K-β″Fe_2O_3 structure as a result of doping with magnesium and zinc cations negatively affects the catalytic activity of polyferrite [12]: the concentration of selective active centres on the surface decreases, and the selectivity of the catalyst action decreases as well.

The introduction of doubly charged Ca and Sr cations into the polyferrite structure had almost no effect on the electronic conductivity (see Fig. 1). Consequently, these doping ions are not able to replace the doubly charged iron. Hence, we assumed that Ca^{2+} and Sr^{2+} ions are not included in the spinel block, but are located in the interblock space or create a separate phase.

A single-phase system is implemented if the ratio of components satisfies the formula $K_{2-2q}Me_qFe^{II}Fe^{III}_{10}O_{17}$.

Therefore, another mechanism of charge compensation was proposed. This mechanism considered the assumption that Ca^{2+} and Sr^{2+} ions enter the interblock space replacing potassium ions.

According to the obtained results, the charge compensation mechanism of potassium polyferrite doped with small-radius divalent charges can be represented as follows:

$$K_2Me_qFe^{II}_{1-q}Fe^{III}_{10}O_{17}.$$

The formulae we have established reflect the different charge compensation mechanisms in potassium polyferrite, as well as the different ways in which the dopant is placed in the K-β″Fe_2O_3 structure (Fig. 2).

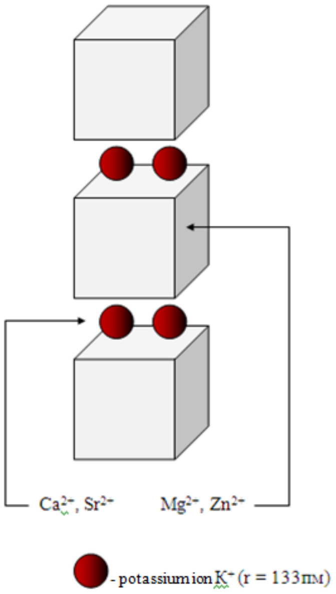

Fig. 2. Placement of doping doubly charged ions in the unit cell of potassium polyferrite

Thus, the placement of these ions, at which the integrity of the structure will be preserved, is possible only in the interblock space (see Table 1, Fig. 2). In contrast to magnesium and zinc ions, calcium and strontium cations do not reduce the intensity of electron exchange in the polyferrite structure. The doping with Ca^{2+} and Sr^{2+} cations should not affect the catalytic activity of K-β″Fe_2O_3.

Based on the results of cationic conductivity measurements, the samples containing calcium and strontium ions decreased the cationic conductivity, in contrast to the samples with magnesium and zinc additives, with no effect on the cationic conductivity (Fig. 3). The greatest decrease is observed in samples containing strontium ions. The obtained data on cationic conductivity can be explained by different placement of ions in the structure of polyferrite (see Fig. 2).

Any introduced doubly charged ions with radii less than 99 pm will be accommodated in the spinel-like block in the same manner as magnesium and zinc, replacing doubly charged iron and not reducing the cationic conductivity. Calcium and strontium cations with radii greater than 99 pm are located in the interblock space and reduce the cationic conductivity of polyferrite (see Fig. 3).

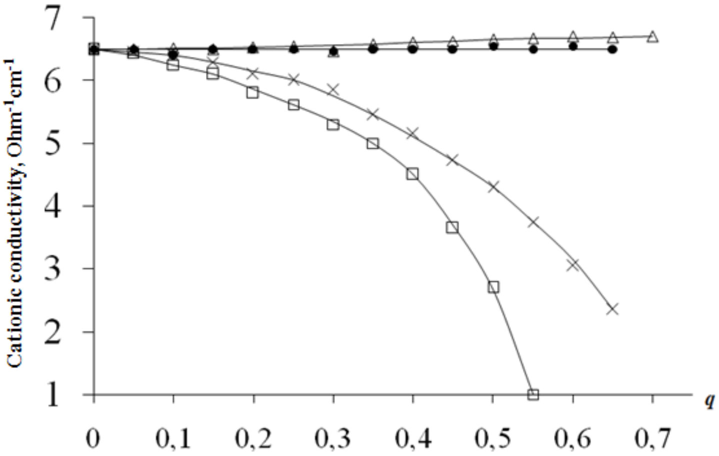

Fig. 3. Cationic conductivity of β″-polyferrites of composition $K_2Me_qFe^{II}_{1-q}Fe^{III}_{10}O_{17}$ and $K_{2-2q}Me_qFe^{II}Fe^{III}_{10}O_{17}$ depending on the content of the alloying ion (Me): □ – Sr; x – Ca; • – Zn; Δ – Mg

The decrease of cationic conductivity for polyferrites doped with calcium and strontium is due to decrease in the number of charge carriers and decrease in their mobility. Formula representing the charge compensation mechanism of $K_{2-2q}Me_qFe^{II}Fe^{III}_{10}O_{17}$provides the introduction of calcium or strontium ions accompanied by a rapid decrease in the amount of potassium ions. The number of charge transferring ions drops, replacing an alkali metal ion with an alkaline earth ion, reduces the cationic conductivity.

Apparently, the doubly charged alkaline earth metal ions do not have sufficient mobility to compensate decrease in potassium concentration and provide a high level of cationic conductivity.

Moreover, when some critical concentration of alkaline-earth ions in the interblock space is reached, there begin the preparation for the rearrangement of the β″-alumina-type polyferrite structure into a hexagonal structure of the magnetoplumbite type. This process apparently leads to a decrease in the width of the cation-conducting layer and the subsequent unification of spinel-like blocks. The structural features of the formed magnetoplumbite do not suggest the presence of appreciable cationic conductivity. This explains the acute drop in the cationic conductivity of β″-proliferrites doped with calcium and especially strontium when the q coefficient passes the 0.4 mark.

The cationic conductivity of β″-polyferrite is a representative parameter to estimate the mobility of potassium ions within the cation-conducting layer. Moreover, the mobility of potassium cations is related to the ease of alkaline promoter emission. It also concerns with the corrosion resistance of β″-polyferrite - the ability of the catalyst to function despite unfavourable effects of the reaction medium and the presence of catalytic poisons [5]. Ca^{2+} or Sr^{2+} ions entering the interblock space reduce the mobility of alkali promoter ions and prevent its emission during catalyst operation. Thus, the introduction of Ca^{2+} or Sr^{2+} ions into the structure is useful not only for increasing the mechanical strength and thermal stability of the catalyst granules [14]. Nevertheless, italso increases the chemical stability of the contact granules [12].

The level of electronic conductivity is used as a representative parameter to predict the catalytic performance of the synthesised material. The use of such measurements will significantly reduce the labour intensity of experiments to evaluate the efficiency of new promoters and modify catalysts. It makes the process more operative by eliminating long-term catalytic tests.

Conclusions and recommendations

We have identified a charge compensation mechanism in potassium β″-polyferrite upon doping with doubly charged calcium, strontium, magnesium, and zinc ions. The charge compensation mechanisms differ depending on the radius of the introduced doubly charged ion and are described by the following formulas: $K_2Me_qFe^{II}_{1-q}Fe^{III}_{10}O_{17}$ – for cations Mg^{2+}, Zn^{2+}, comparable in size to the Fe^{2+} ion, and $K_{2-2q}Me_qFe^{II}Fe^{III}_{10}O_{17}$ – for large Ca^{2+} and Sr^{2+} ions, which size exceeds 99 pm – the upper limit of isomorphic substitutability in the oxygen ion crystal lattice. The above effect is related to the different way of placing additives in the β″-polyferrite structure. We found that large doping ions are distributed in the interblock space, while cations comparable in size to the doubly charged iron replace it in the spinel-like block. The results of cationic conductivity measurements of potassium β″-polyferrites showed the mobility reduction of large calcium and strontium cations of potassium ions. Therefore, the above additives are promising for increasing the mechanical strength and thermal stability of the catalyst granules. Hence, they increase the chemical stability of the contact granules. Corrosion resistance of pellets is a critical parameter. It determines the period of catalyst effective functioning.

The data on electronic conductivity allow one to conclude that the introduction of Mg^{2+}, Zn^{2+} cations sharply reduces the electron exchange in the structure of potassium β″-polyferrite. This should inevitably lead to deactivation of the catalyst, while Ca^{2+} and Sr^{2+} ions do not reduce the electron transfer rate. The use of the proposed approach will intensify the research process because materials with low electronic conductivity are unpromising as catalysts for redox processes, i.e., dehydrogenation.

References

1. **Joseph, Y., Ketteler, G., Kuhrs, C., Ranke, W., Weiss, W. & Schlögl, R.** (2001) On the Preparation and Composition of Potassium Promoted Iron Oxide Model Catalyst Films, *Phys. Chem. Chem. Phys.*, 18(3), pp. 4141-4153. DOI: 10.1039/B104263G.
2. **Ketteler, G., Ranke, W. & Schlögl, R.** (2002) Potassium-Promoted Iron Oxide Model Catalyst Films for the Dehydrogenation of Ethylbenzene: An Example for Complex Model Systems, *Journal of Catalysis,* 212(1), pp. 104-111 [online]. Available at: https://doi.org/10.1006/jcat.2002.3785
3. **Dvoretskii, N.V., Anikanova, L.G. & Malysheva, Z.G.** (2018) Types of active centers on surface of promoted iron oxide catalyst, *Izv. vuzov. Khimiya i khim. tekhnologiya*, 61(6), pp. 61-68 [online]. Available at: http://dx.doi.org/10.6060/tcct.20186106.5658 (in Russian).
4. **Kotarba, A., Kruk, I. & Sojka, Z.** (2002) Energetics of Potassium Loss from Styrene Catalyst Model Components: Reassignment of K Storage and Release Phases, *Journal of Catalysis*, 211(1), pp. 265-272 [online]. Available at: https://doi.org/10.1006/jcat.2002.3725
5. **Anikanova, L.G. & Dvoretskii, N.V.** (2016) Stabilization of Alkali Promoters in Structure of the Iron Oxide Dehydrogenation Catalysts, *Kataliz v promyshlennosti,* 8(2), pp. 145-151 [online]. Available at: http://dx.doi.org/10.18412/1816-0387-2016-1-29-36 (in Russian).
6. **Kotarba, A., Rożek, W., Serafin, I. & Sojka, Z.** (2007) Reverse Effect of Doping on Stability of Principal Components of Styrene Catalyst: $KFeO_2$ and $K_2Fe_{22}O_{34}$, *Journal of Catalysis*, 247(2), pp. 238-244 [online]. Available at: https://doi.org/10.1016/j.jcat.2007.02.009 (accessed 11.02.2024).
7. **Meima, G.R. & Menon, P.G.** (2001) Catalyst Deactivation Phenomena in Styrene Production, *Applied Catalysis A: General,* 212, pp. 239-245 [online]. Available at: https://ru.scribd.com/document/342010350/Catalyst-Deactivation-Phenomena-in-Styrene (accessed 11.02.2024).
8. **Anikanova, L.G. & Dvoretskii, N.V.** (2012) Distribution of Alkaline Promoters within the Structure of Iron Oxide Catalyst for Dehydrogenation, *Kataliz v promyshlennosti*, 4(4), pp. 307-312. DOI: 10.1134/S2070050412040022 (in Russian).
9. **Abe, K., Ohshima, M., Kurokawa, H. & Miura, H.** (2010) Effect of addition of Ce to Fe-K mixed oxide catalyst in dehydrogenation of ethylbenzene, *Journal of the Japan Petroleum Institute,* 53(2), pp. 89-94. DOI: 10.1627/jpi.53.89.
10. **Abe, K., Kano, Yu., Ohshima, M., Kurokawa, H. & Miura, H.** (2011) Effect of adding Mo to Fe-Ce-K mixed oxide catalyst on ethylbenzene dehydrogenation, *Journal of the Japan Petroleum Institute*, 54(5), pp. 338-343. DOI: 10.1627/jpi.54.338.
11. **Nariki, S., Ito, S., Uchinokura, K. & Yoneda**, **N.** (1988) Formation of β-, β″-and β‴-Alumina Type Ferrites in Rb_2O-Fe_2O_3 and Cs_2O-Fe_2O_3 Systems and Ionic Conduction of β- and β″- Phases, *Journal of the Ceramic Society of Japan*, 96(1110), pp. 186-192 [online]. Available at: https://doi.org/10.2109/jcersj.96.186 (accessed 10.02.2024).
12. **Anikanova, L.G. & Dvoretsky, N.V.** (2020) Effect of Doubly Charged Ion Additives on the Activity and Chemical Stability of Catalytically Active Potassium Ferrites, *Kataliz v promyshlennosti,* 12(3), pp. 201-206. DOI: 10.1134/s2070050420030022(in Russian).
13. **Bugaenko, L.T., Ryabykh, S.M. & Bugaenko, A.L.** (2008) Almost complete system of average ionic crystallographic radii and its use for determining ionization potentials, *Vestn. mosk. un-ta. Ser. 2. Khimiya***,** 49(6), pp. 363-384 [online]. Available at: https://cyberleninka.ru/article/n/pochti-polnaya-sistema-srednih-ionnyh-kristallograficheskih-radiusov-i-ee-ispolzovanie-dlya-opredeleniya-potentsialov-ionizatsii/viewer (accessed 12.02.2024) (in Russian).
14. **Dvoretskaya, A.N., Anikanova, L.G., Sudzilovskaya, T.N., Malysheva, Z.G. & Dvoretskiy, N.V.** (2023) Formation of a ceramic structure of promoted iron oxide catalyst, *From Chemistry Toward Technology Step-By-Step,* 4(3), pp. 60-68 [online]. Available at: https://doi.org/10.52957/2782-1900-2024-4-3-60-68 (accessed 21.02.2024) (in Russian).

Received 13.05.2024
Approved 21.05.2024
Accepted 22.05.2024