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Ion exchange conversion of solid electrolyte, potassium sodiostannate, into isomorphous metastable sodium stannate

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Ionic conduction of layered potassium sodiostannate $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ was measured at various temperatures. It was converted into a new metastable sodium stannate $Na_{0.96}Sn_{0.76}O_2$ by ion exchange reaction using three different techniques.
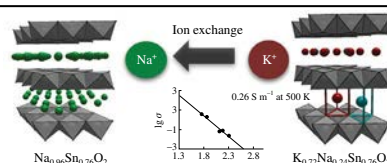
Layered complex oxides with alkali interlayer cations are a family of compounds currently used as solid electrolytes and electrode materials in chemical sources of electrical energy,[1–3] as parts of concentration sensors in gas and liquid media[4–8] *etc.* On the other hand, high cation mobility makes it possible to obtain new metastable phases using a soft chemistry route.[9–11]

Very high potassium ionic conduction was found in complex oxides with P2 (in Hagenmuller's definition[12]) structures. The letter P represents prismatic coordination of interlayer cations and figure '2' shows that there are two brucite-like layers per unit cell. The space group of non-distorted P2 structure is $P6_3/mmc$.[13]

The potassium indiostannate $K_{0.72}In_{0.72}Sn_{0.28}O_2$ with this structure has the highest known potassium-ionic conduction: 2.2 S m^{-1} at 500 K.[14] Recently, a high ionic conduction was revealed in isomorphous $K_{0.56}Ni_{0.52}Sb_{0.48}O_2$ (1.6 S m^{-1} at 573 K[15]) and $K_{0.72}Li_{0.24}Sn_{0.76}O_2$[16] (0.23 S m^{-1} at 500 K).

Previously,[17] we reported on the isomorphous potassium sodiostannate $K_{0.72}Na_{0.24}Sn_{0.76}O_2$, a perspective material for possible solid electrolyte application. In the present work we have measured ionic conduction of this compound and tried it for ion-exchange reactions.

Synthesis technique was described in detail.[17] Briefly, potassium sodiostannate was obtained from tin oxide SnO_2, sodium stannate Na_2SnO_3 and potassium hydroxide using two stage heating in argon atmosphere. The first heating was performed at 873 K for 30 min, the second one was at 1273 K for 2.5 h.

The ion conductivity measurements were carried out in the frequency range from 20 Hz to 20 kHz using virtual impedance analyzer developed in the Institute of Control Sciences of the RAS. We used the argon atmosphere and blocking indium electrodes for these purposes. Complex impedance plots recorded at different temperatures (298–571 K) were analyzed to extract the bulk resistance. A typical plot is presented in Figure 1. Conductivity of 64% dense ceramics at 500 K is 0.26 S m^{-1}. Frequency dispersion indicates a low electronic impact. Electronic resistance is about 5000 times greater than the ionic one in the equivalent circuit model and very large according to the polarization measurements under the DC voltage 1 V (more than 50 MΩ). Temperature dependence of conductivity is shown in Figure 1.

Note that the following factors could affect the conductivity measurement. On the one hand, dense ceramics synthesized using this method is quite a challenge. Measurements were performed for 64% density samples. This could result in low conductivity value. On the other hand, as the electrode material was indium melting at 430 K and capable of penetrating into the pores of the electrolyte, the effective interelectrode distance was reduced. This leads to an overestimation of conductivity.

Potassium ions of potassium sodiostannate can migrate from one prism to adjacent unoccupied prisms through rectangular faces. So there are no narrow bottlenecks in these conductivity pathways. Moreover, big potassium ions form rather wide channels – height of prisms is 4.7 Å. In consequence, ionic conductivity of obtained $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ is high.
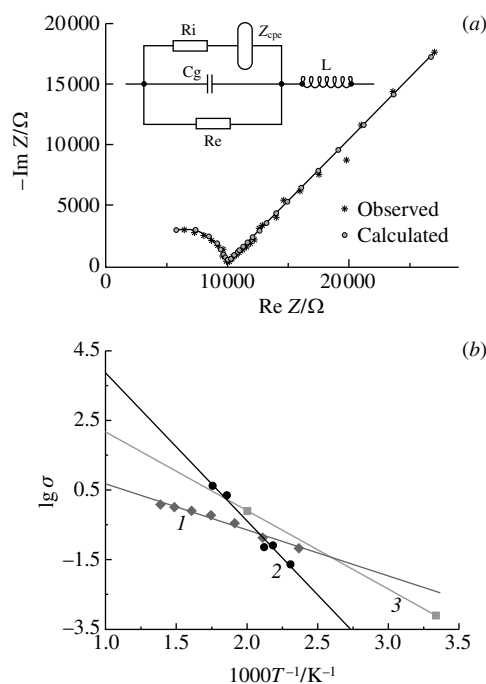
Figure 1 (*a*) Impedance plot of $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ (473 K). Parameters of impedance fit using the shown equivalent circuit: Ri = 9689(1) Ω, Re = 54.15(9) MΩ. (*b*) Temperature dependence followed the equation log $\sigma = f(1/T)$: (*1*) $K_{0.72}Li_{0.24}Sn_{0.76}O_2$,[16] (*2*) $K_{0.72}Na_{0.24}Sn_{0.76}O_2$ and (*3*) $K_{0.70}Zn_{0.35}Sn_{0.65}O_{2.3}$.[18]

This structure type is very attractive for ion exchange application due to the high mobility of interlayer cations.

Previously,[16] we exchanged interlayer potassium atoms of $K_{0.72}Li_{0.24}Sn_{0.76}O_2$ for sodium ones and have obtained a new sodium lithiostannate. So we used isomorphous potassium sodiostannate to obtain a layered sodium stannate by similar exchange reaction. Three techniques are known to perform this reaction. In all cases we used sodium nitrate, beforehand dried at 573 K for 2 h. Its excess for further experiments (procedures *1* and *3*) was 20% to increase equilibrium sodium concentration in solid phase.

In procedure *1* potassium sodiostannate and sodium nitrate were ground together and pressed into a pellet for highest possible contact of interacting substances. Then this pellet was heated at 573 K for 3 h. At this temperature, KNO_3 and $NaNO_3$ form the liquid phase,[19] which facilitates cations migration and increases the exchange rate. XRD† analysis showed the same structure type with decreased lattice constants.‡

To ensure that exchange was complete, the obtained sample (washed with DMF to remove admixture of nitrates) was heated at 1173 K for 2 h. After that XRD pattern showed a mixture of SnO_2 and Na_2SnO_3. There was no any compound with P2 structure in the obtained mixture, and Na_2SnO_3 has the same lattice constants as a pure compound. It proves the absence of the potassium ions in solid phase and therefore the completeness of ion exchange reaction. Moreover, it indicates that a new layered sodium stannate $Na_{0.96}Sn_{0.76}O_2$ is metastable and decomposes at elevated temperatures, and thus it cannot be obtained by conventional solid state technique, at least due to the kinetic difficulties at low temperatures or due to thermodynamic instability.

In procedure *2* the pellet of potassium sodiostannate was crushed into small pieces and put into the crucible with perforated bottom. Sodium nitrate was melted in the other big crucible. Then the first one was placed inside and kept in it for 15 min. This operation was repeated three times. XRD pattern of the product included reflections of a new sodium stannate and sodium nitrate. To remove nitrates, the pellet was ground and washed with dry methanol, then the product was air dried. XRD pattern showed a single-phase product, *i.e.* the successful exchange. Lattice parameters of obtained $Na_{0.96}Sn_{0.76}O_2$ were determined with an internal standard (BaF_2).§

In procedure *3* we used DMF dried with molecular sieves. Sodium nitrate and potassium sodiostannate were ground together and put into DMF. They were permanently blended for three days at gentle heating (313–318 K). Then the solvent was removed and evaporated. The XRD pattern exhibited a mixture of initial substances, in other words, potassium ions were not exchanged for sodium. Then this mixture was pressed into a pellet and kept for 1.5 h at 623 K, however, XRD analysis did not detect any changes. It was a much unexpected result. As shown above, the same substances reacted at this temperature (see procedures *1* and *2*). Apparently, DMF molecules formed complexes with sodium and potassium ions,[20] which were too large and therefore were unable to penetrate into the narrow interlayer space. They could be located in the grain boundaries thus blocking the cation transport. In order to activate ion exchange in DMF solution, we used microwave irradiation. The mixture of sodium nitrate and potassium sodiostannate with DMF was kept in the microwave oven (CEM, Discovery SP) in a closed glass vessel at 393 K for 1 h. Then the sample was washed with a new portion of DMF,

filtered and dried. By this means potassium ions were exchanged for sodium, XRD revealed the same structure as in two previous procedures.¶ However, slightly greater parameter *c* could indicate that ion exchange was not complete or a small portion of DMF molecules remained between the layers.

Thereby, in this work sodium stannate $Na_{0.96}Sn_{0.76}O_2$ (or $Na_{0.72}Sn_{0.76}Na_{0.24}O_2$) with the new unusual layered structure was obtained by the ion exchange technique. The part of sodium ions has octahedral coordination and the other part is located between layers in the trigonal prisms. The cell parameters for this compound are smaller than those in starting $K_{0.72}Na_{0.24}Sn_{0.76}O_2$, which is in agreement with the smaller radius of sodium ions. Parameter *c* in the obtained sodium stannate is similar to its value in isomorphous phases with sodium cations between the layers.[21,22]

One may conclude that a high mobility of the interlayer ions in the P2 phases gives great opportunities for obtaining new substances by ion exchange reactions. These methods can be used to prepare metastable phases that cannot be synthesized by solid state technique. Phases with potassium ions between the layers are of particular interest for ion exchange reactions. Due to the large radius of potassium such compounds have wide conduction pathways. Therefore, these channels can be filled with many individual ions, and even with some complex ones.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.mencom.2016.05.008.

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† The XRD scans were recorded using an ARL'Xtra diffractometer with monochromatic CuKα radiation.
‡ Lattice constants of $Na_{0.96}Sn_{0.76}O_2$ obtained using procedure *1*: $a = 3.151(3)$ Å, $c = 11.40(2)$ Å.
§ Lattice constants of $Na_{0.96}Sn_{0.76}O_2$ obtained using procedure *2*: $a = 3.1562(3)$ Å, $c = 11.3642(15)$ Å.

¶ Lattice constants of $Na_{0.96}Sn_{0.76}O_2$ obtained using procedure *3*: $a = 3.1641(13)$ Å, $c = 12.080(9)$ Å.