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Proton mobility in the composites of iron acid sulfate monohydrate with silica

Valentina G. Ponomareva,[a] Elena B. Burgina,[b] Vasily A. Tarnopolsky[c] and Andrei B. Yaroslavtsev*[c]

[a] *Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, 630128 Novosibirsk, Russian Federation*
[b] *G. K. Boreskov Institute of Catalysis, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation*
[c] *N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 119991 Moscow, Russian Federation. Fax: +7 095 954 1279; e-mail: yaroslav@rfbr.ru*

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The protonic conductivity of the $(1-x)H_3OFe(SO_4)_2{\cdot}xSiO_2$ ($x = 0.1$–0.6) composites increased by 1.5–2.0 orders of magnitude and reached its maximal value at $x = 0.3$ for the samples calcined at 380 and 440 K.

After the observation of a sharp increase in the ion conductivity of a composite system of silver iodide with fine alumina by Liang,[1] the studies of transport processes in composite solid electrolytes are of considerable interest.[2–4] This study deals with protonic conductivity.[5,6] However, many attempts to increase protonic conductivity in composite systems were unsuccessful, except for protonic conductors based on alkali metal acid sulfates.[7–9] Acid sulfate monohydrates of trivalent elements $H_3OM^{III}(SO_4)_2$ are among the most stable compounds, which contain hydrated protons and have high protonic conductivity.[10,11]

The aim of this work was to study the protonic conductivity of the solid electrolytes $(1-x)H_3OFe(SO_4)_2{\cdot}xSiO_2$ ($x = 0.1$– 0.6).

Iron acid sulfate monohydrate was obtained from the corresponding tetrahydrate, which was precipitated from a solution of iron(III) chloride in sulfuric acid. The compound was identified using chemical and X-ray analysis. Silica with a specific surface area of 300 $m^2\,g^{-1}$ and uniform porosity (pore size of 7 nm and pore volume of 0.9 $cm^3\,g^{-1}$) was used in this work. Components were mixed in a certain ratio, ground in an agate mortar and pressed at 500 MPa. The pellets were calcined at 380–440 K in air for 20 min. The pellets were stored for two weeks under ambient conditions.

Ionic conductivity was measured using impedance spectroscopy by a double-electrode technique with silver or palladium electrodes in the frequency range 5 Hz–500 kHz. The measurements were carried out on cooling at a rate of 2 K min^{-1} in air. X-ray powder diffraction analysis was performed using a DRON-3 diffractometer with CuKα radiation. IR spectra were obtained with the use of a BOMEM MB-102 spectrometer in the frequency range 4000–400 cm^{-1} at room temperature.

X-ray diffraction data indicate the presence of the initial acid sulfate in the test composites. The samples calcined at 380 K are characterised by weak peak broadening with the growth of x, which can be due to a decrease in the particle size. The intensities of $H_3OFe(SO_4)_2$ reflections decreased at 440 K, and new peaks appeared as the molar fraction of SiO_2 increased. We assume that the presence of silica promotes iron acid sulfate decomposition at 440 K.

The formation of a composite leads to the loss of a surface OH^- stretching vibration mode (3660 cm^{-1}) in silica (Figure 1). A slight transformation was also observed in a wide peak (3500–2500 cm^{-1}), which corresponds to the stretching vibration of proton-containing groups of acid iron sulfate and silica forming H-bonds. The O–Si–O bending vibration (807 cm^{-1}) band disappeared in the composites or was shifted to higher frequencies. The above data suggest the interaction of composite components by the sorption of a part of $H_3OFe(SO_4)_2$ proton-containing groups with surface OH groups of highly dispersed silica.

The conductivity of $H_3OFe(SO_4)_2$ and its composites with silica as a function of temperature is shown in Figure 2. The conductivity of the initial acid salt and its activation energy (35 kJ mol^{-1}) are consistent with published data.[11] The conductivity of composites obtained at room temperature with highly dispersed silica slightly increased (twofold at $x = 0.1$) and decreased at $x > 0.2$ [Figure 2(*a*)] to the values significantly lower than that of the initial $H_3OFe(SO_4)_2$.

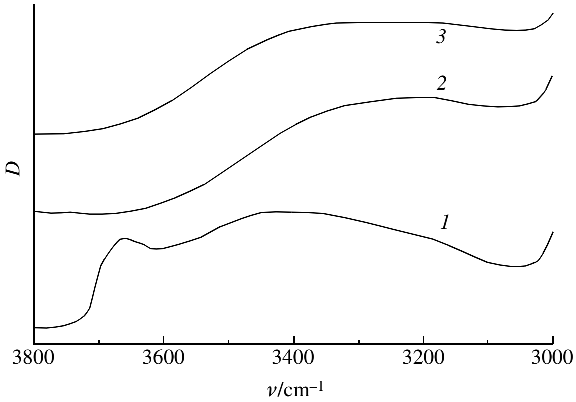

Figure 1 IR spectra in the frequency range 4000–1500 cm^{-1} for (*1*) silica ($S_{sp} = 300\ m^2\,g^{-1}$), (*2*) initial acid sulfate and (*3*) the composite $0.7H_3OFe(SO_4)_2{\cdot}0.3SiO_2$, obtained at 380 K.

The conductivity of composites obtained at 380 K with silica increased by 1.5 orders of magnitude at $x = 0.3$ and depended

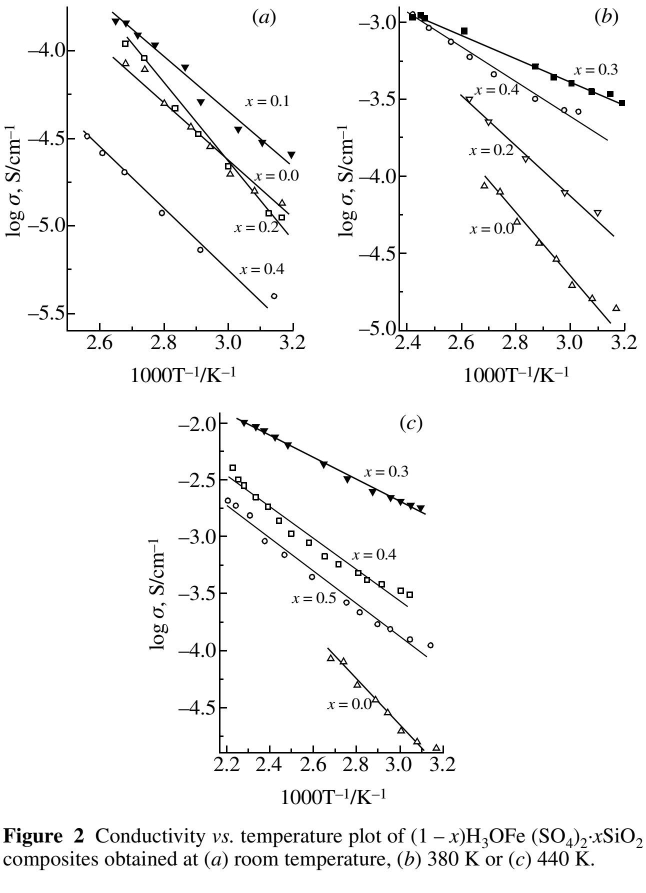

Figure 2 Conductivity *vs.* temperature plot of $(1-x)H_3OFe\,(SO_4)_2{\cdot}xSiO_2$ composites obtained at (*a*) room temperature, (*b*) 380 K or (*c*) 440 K.

on x [Figure 2(*b*)]. Similar dependence of the ionic conductivity on the sample composition remains after calcination at 440 K [Figure 2(*c*)]. Ionic conductivity increased by almost 2 orders of magnitude in comparison with the original $H_3OFe(SO_4)_2$ and sharply decreased at $x > 0.3$. However, partial decomposition of acid sulfate at these temperatures occured along with its dehydration. Therefore, the increase in the conductivity of samples calcined at 440 K can be explained by the presence of small amounts of decomposition products (such as sulfuric acid). A further increase in the molar fraction of silica in the composite (to $x = 0.5$) caused a decrease in the conductivity though the volume ratio of silica remained low (no higher than 14–20 vol%). Note that the conductivity of these composites remained high at elevated temperatures and reached $(1.1–1.2)\times10^{-3}$ S cm^{-1} at 400 K in the samples calcined at 380 K or 1.0×10^{-2} S cm^{-1} in the samples calcined at 440 K when partial decomposition of $H_3OFe(SO_4)_2$ takes place. The conductivity of the composite containing 0.3 mol of SiO_2 per formula unit was 1.8×10^{-3} S cm^{-1} at 315 K and was perfectly stable in an inert atmosphere at $T < 415$ K.

The conductivity increased in such materials due to sorption processes on the interface and to a decrease in the $H_3OFe(SO_4)_2$ particle size. According to the IR spectra, the sorption of protons of the acid sulfate with the surface OH groups of highly dispersed silica occurs in the composites. As the initial proton activity in iron acid sulfate is much higher than that in silica, we can assume that the main mechanism of this interaction is the transfer of hydrogen ions to the active surface groups of SiO_2, which is accompanied by the formation of proton vacancies in the surface layers of $H_3OFe(SO_4)_2$ lattice. A high concentration of vacancies near the interface caused by proton sorption on the OH groups of dispersed silica leads to the increase of the conductivity of the whole system. We believe that the contributions of both the deprotonated surface of acid iron sulfate and the protonated silica surface are important for increasing proton conductivity in this composite. The dependence of the conductivity on sample composition is consistent with published data for similar systems.[2,3,7] However, a conductivity drop was observed at low SiO_2 contents. Macrocrystalline particles of the initial $H_3OFe(SO_4)_2$ are effectively covered by fine silica, which leads to a percolation threshold drop and conductivity blocking even at low SiO_2 molar ratios.[12]

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