Electronic Supplementary Material (ESI) for CrystEngComm.

Enhancing Lithium-Ion Conductivity in NASICON Glass-Ceramics by Adding Yttria

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Electronic Supplementary Information

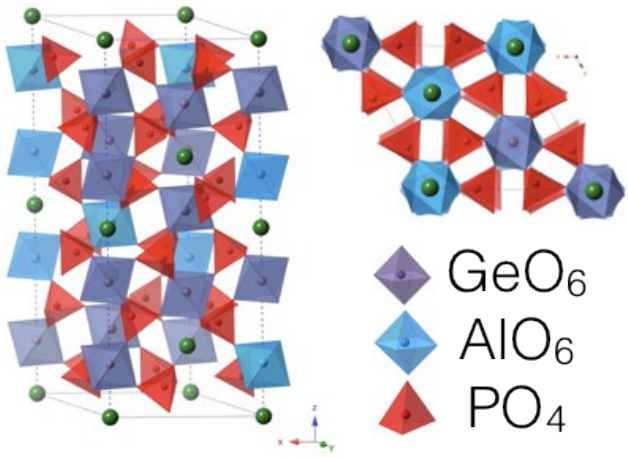

Fig. S1. LAGP crystal structure.

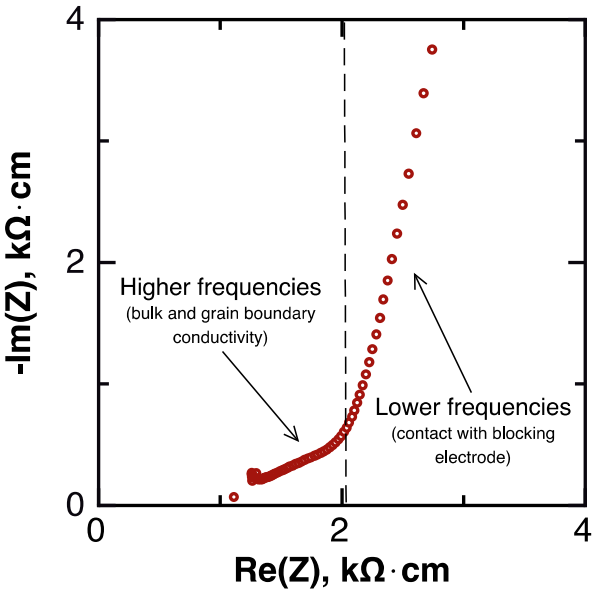

Fig. S2. Typical Niquist plot obtained for LAGP glass-ceramic solid electrolyte.

Impedance spectra were obtained with Biologic SP-300 potentiostat with EIS analyzer capability. Test cell - Au/LAGP/Au. Gold contacts (XX nm) were prepared by magnetron sputtering. The plot in fig. S1 shows the data for Y-containing LAGP glass-ceramics, obtained by aneealing the

glass at 600°C for 30 min and further at 750°C for 2 hours. 7 MHz - 1 Hz frequency range and 10 mV potential amplitude were used.

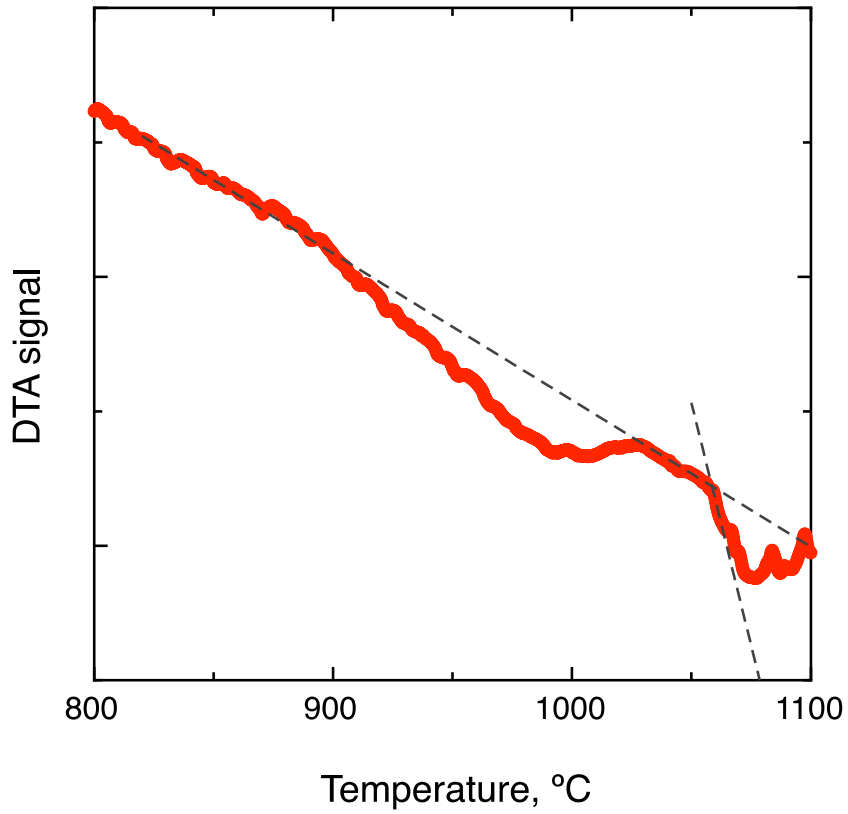

Fig. S3. Melting point determination from DTA data for LAGP glass.

Melting point for LAGP glass has been determined using analysis of DTA patterns. In order to do so glass pieces have been heated up to 1100°C at 3°C/min rate. Melting point was calculated as interception point of lines as shown in fig. S2.

Fig. S4. Non-homogeneous crystallization of pure LAGP glass-ceramics.

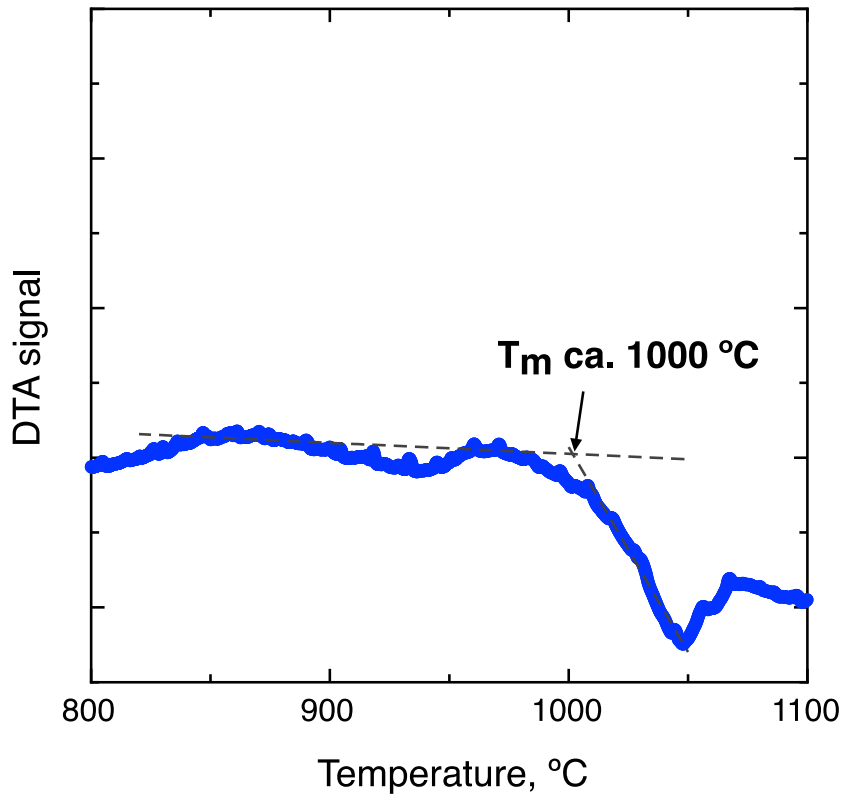

Fig. S5. Melting point determination from DTA data for LAGP glass with yttria additive.

Same approach as described for LAGP glass has been used to determine melting point in yttria modified glass.

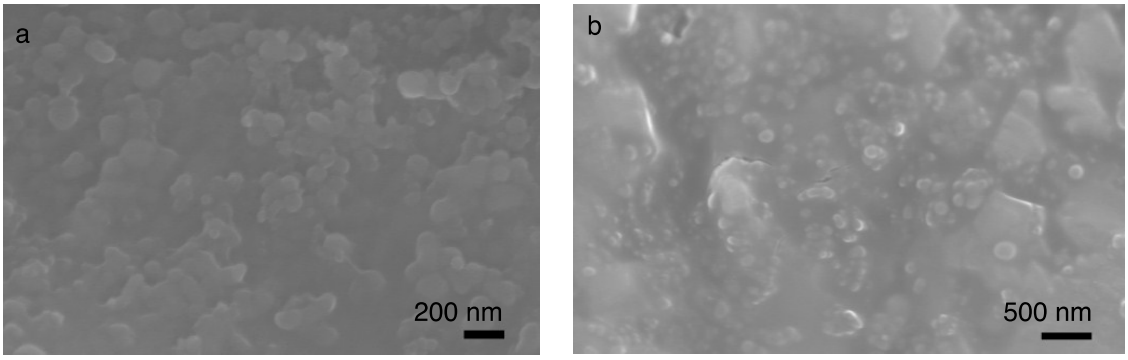

Fig. S6. SEM images of the polished cross-sections of Y-free (a) and Y-containg (b) glass ceramics, obtained by 30 min annealing at 600°C and further 2-hours crystallization at 750°C.

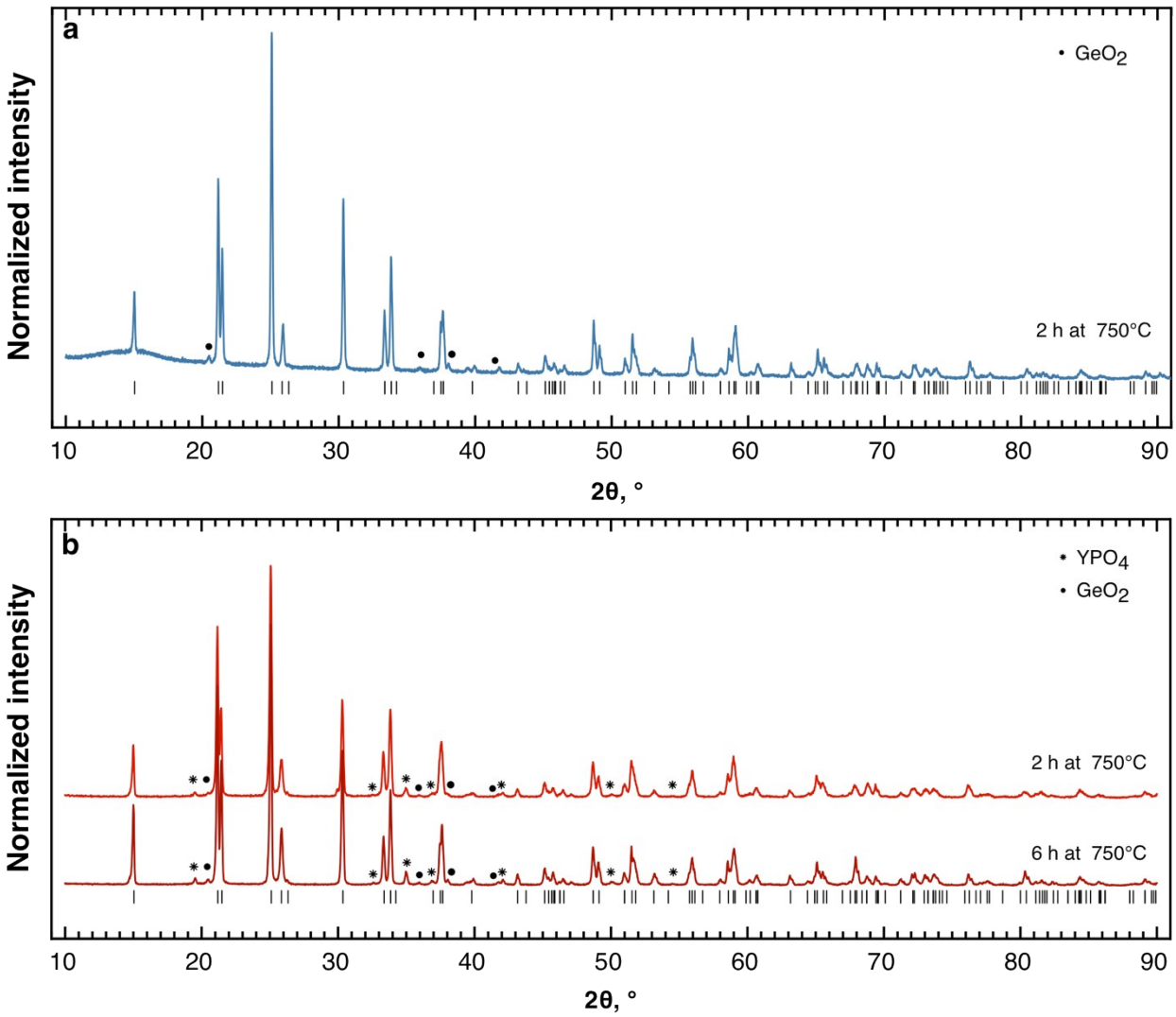

Fig. S7. XRD patterns of the Y-free (a) and Y-containing (b) samples. All the samples were preliminary annealed at 600°C for 30 min.

Detected impurities are YPO_4 with xenotyme structure (PDF card [900-1654]), and GeO_2 (PDF card [36-1463])

Table S1. Results of Rietveld refinement of NPD data for glass ceramic samples with and without Y_2O_3 additive.

Sample	*Y-free*	*Y-containing*
Symmetry Group	R-3c	R-3c
a, b, Å	8.2617(9)	8.2605(3)
c, Å	20.6895(10)	20.6819(10)
alpha, beta, °	90	90
gamma, °	120	120
cell volume, Å	1222.99(10)	1222.18(9)
Secondary phases	GeO_2	GeO_2
		YPO_4
R_p	7.42	8.95
wR_p	6.02	5.8
Chi^2	3.57	1.47

Y-free	atomic coordinates			occupancy	B_{iso}
	x	y	z		
Li1	0	0	0	1	2.5
Li3	0.07	0.34	0.07	0.14259	2
Al1	0	0	0.14238	0.14259	0.54
Ge1	0	0	0.14238	1.85741	0.54
P1	0.28381	0	0.25	3	0.62
O1	0.17513	0.97668	0.18903	6	1.14
O2	0.18654	0.15994	0.08392	6	1.32

Y-containing	atomic coordinates			occupancy	B_{iso}
	x	y	z		
Li1	0	0	0	1	2.5
Li3	0.07	0.34	0.07	0.30157	2
Al1	0	0	0.14292	0.30157	0.54
Ge1	0	0	0.14292	1.69843	0.54
P1	0.28324	0	0.25	3	0. 62
O1	0.17642	0.97561	0.18859	6	1. 14
O2	0.18657	0.16057	0.08386	6	1.32

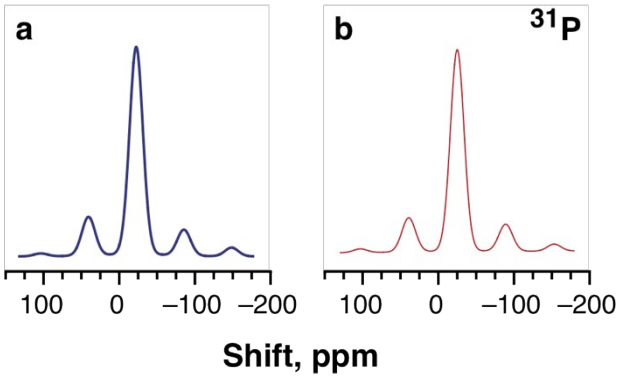

Fig. S8. ^{31}P MAS NMR spectra of LAGP glasses without (a) and with (b) yttria additive.

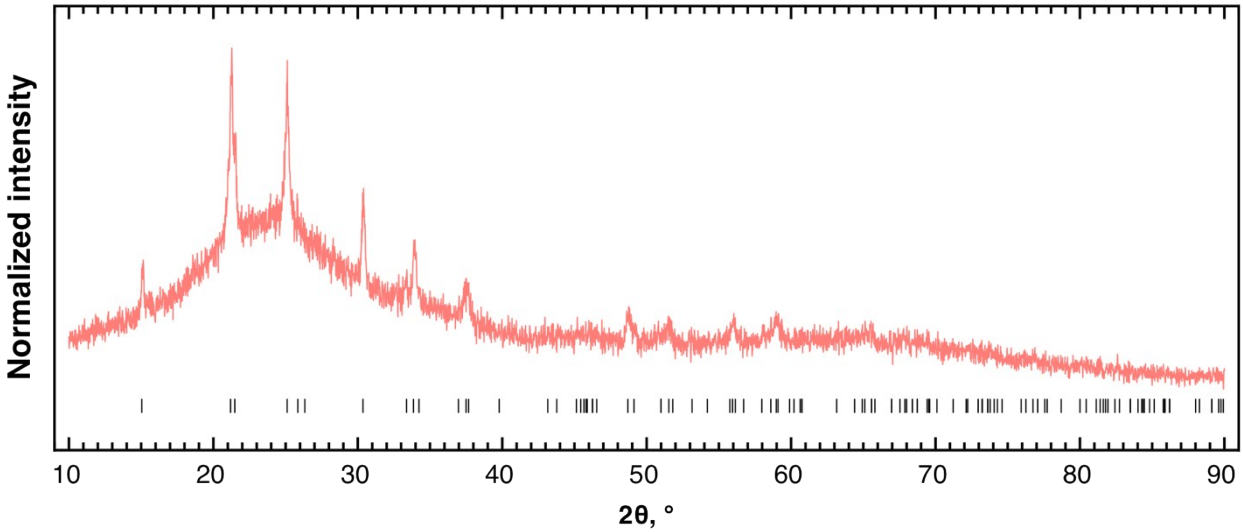

Fig. S9. XRD pattern of the Y-containing sample after first annealing at 600^{o}C for 30 min.

To further demonstrate the absence of open porosity in ceramics the gas permitivitty was also evaluated.

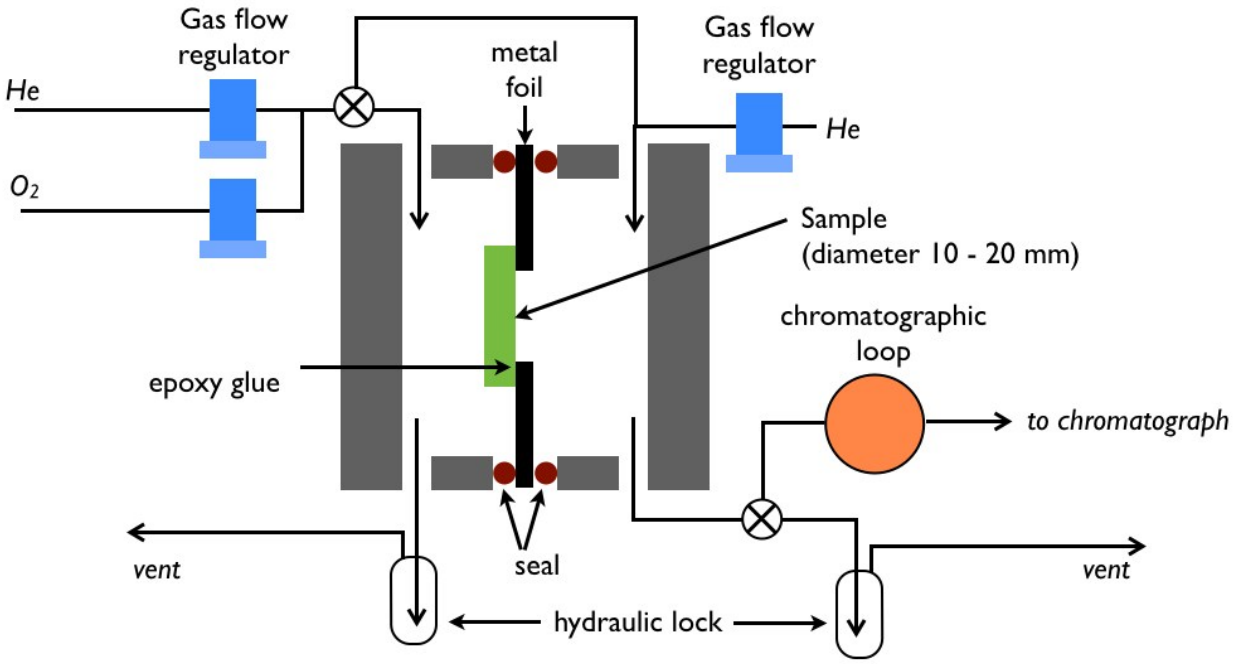

Fig. S10. Schematics of the setup for gas permeability measurements.

Tested membranes were tightly attached with epoxy glue to the holder, which was sealed with viton O-rings into the experimental cell. One side of the cell was purged with He (99.9999%), while the other side was purged with oxygen (99.999%). Helium and oxygen flow values were selected in such a way that no presure difference was observed between two sides of tested membrane. Oxygen and helium flow was 300 ml/min. In such condition, driving force for oxygen permeability through membrane was difference in O_2 partial pressure between two chambers. Oxygen permeability was measured with Perkin Elmer Clarus 600 gas chromatograph equiped with thermal conductivity and mass-spectrometer detectors. The cell was flushed with He and O_2 for 1 hour before sampling the probe into a chromotographic loop.

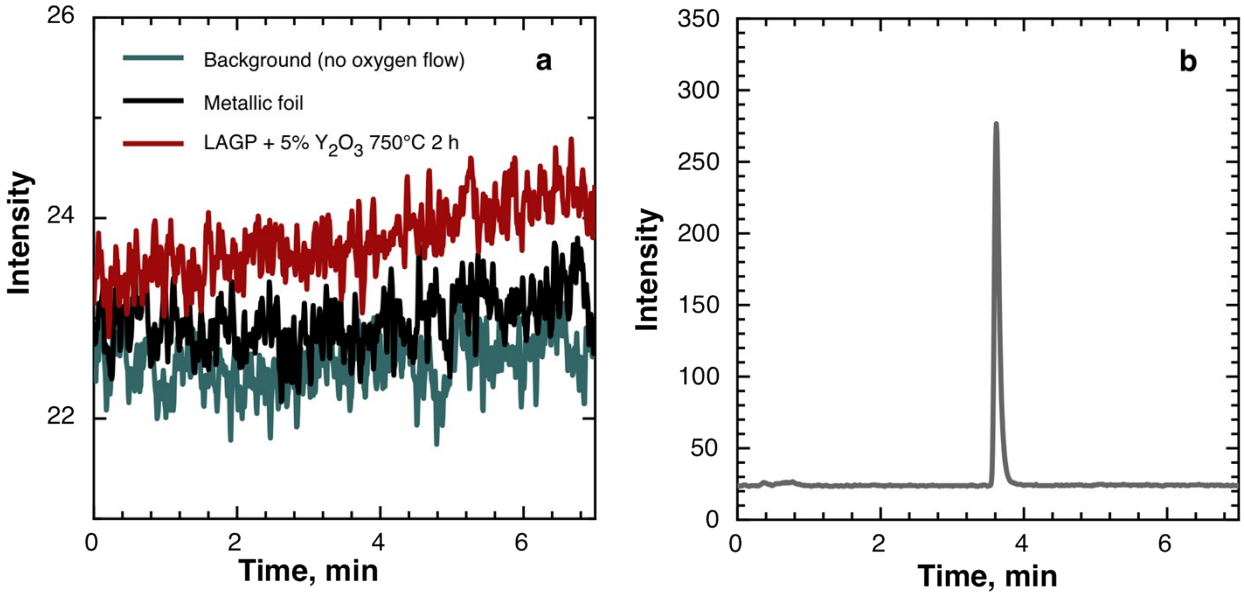

Fig. S11. (a) Chromatogramms obtained with thermal conductivity detector during gas permeability tests with 100 µm Al foil and 400 µm Y-containing LAGP memebrane; tests with the same glass-ceramic membrane with no oxygen flow (He on both sides of the membranes) were also perfomed. (b) Chromatogramm obtained in the same conditions but with porous anodic Al_2O_3 membrane, used a reference.

Gas mixture tested by the chromatograph contains He as a carrier gas and O_2 that passed through tested membrane. Chromatogramms obtained during metallic foil and glass-ceramic membrane testing do not show any signs of oxygen passed through. Since no O_2-related peak is observed on chromatogramm for solid electrolyte membrane, we have calculated detection threshold for our setup, which for O_2-He combination was $2.5 \cdot 10^{-6}$ %. Thereby estimated gas permeability for our glass-ceramic membranes is lower than 1.10^{-6} ml/(min·cm^2). Chromatogramm obtained with Al_2O_3 membrane contains intensive peak within 3.5 - 4 min interval corresponding to oxygen passed through porous membrane.