Physicochem. Probl. Miner. Process. 49(1), 2013, 287−300

www.minproc.pwr.wroc.pl/journal/

Physicochemical Problems
of Mineral Processing

ISSN 1643-1049 (print)
ISSN 2084-4735 (online)

Received June 24, 2012; reviewed; accepted July 22, 2012

PREPARATION AND PHYSICOCHEMICAL CHARACTERISATION OF CERAMIC SUPPORTS FOR SUPORTED LIQUID MEMBRANES

Iwona CICHOWSKA-KOPCZYNSKA, Monika JOSKOWSKA,
Anna WOJCIECHOWSKA, Robert ARANOWSKI

Department of Chemical Technology, Chemical Faculty, Gdansk University of Technology,
80-952 Gdansk, Poland, aran@pg.gda.pl

Abstract: Supported liquids membranes are very promising products. They have been intensively investigated in last two decades and widely used in many technologies especially in gas separation and purification processes. A key aspect in obtaining satisfying effectiveness and long membrane lifetime is a proper choice of ionic liquid and polymeric or ceramic support. Properties of both affect the processes of obtaining useful supported ionic liquid membranes. In comparison to polymeric membranes, ceramic ones are slightly thicker, however they are thermally and mechanically more stable. Our research was aimed at sintering fine glass particles of 500 to 45 μm in size in order to prepare porous membranes which can be used as supports for liquid membranes. Dextrin and borax were used as pore-making agents. The membranes, as disks 35 mm in diameter and 3 mm of thickness, were prepared. The porosity was determined using absorption method. It was found, that the porosity could be controlled by changing the applied pressure from 1 to 5 MPa, particle size distribution, sintering temperature, type and amount of pore-enhancing agents.

Keywords: *glass cullet, recycling, porous material, membranes*

Introduction

Supported liquids membranes (SLMs) are very promising for separation and purification of gaseous streams because of their very small demand for the membrane phase. This feature is very important particularly in supported ionic liquid membranes (SILMs) due to a high cost of ionic liquids (ILs). The SLM is a two phase system of porous support and liquid phase kept in the membrane pores by capillary forces (Walczyk, 2006). However, one of the major obstacles to industrial applications is a limited lifetime (poor stability) of the membrane due to the loss of the organic solvent from the support pores.

http://dx.doi.org/10.5277/ppmp130126

The most popular materials for supported liquid membrane supports preparation are polymer and ceramic membranes. The latter are widely used in filtration and separation technologies. Microstructure, porosity, pore size and wettability have a great influence on their permeability (Weixing, 2006). Moreover, inorganic membranes gained a significant attention due to their high stability in organic solvents and high temperatures (Kuraoka, 2000). In comparison to polymeric membranes, ceramic supports have higher mechanical, chemical and thermal stability. Operational temperature for polymeric supports cannot exceed 100ºC, whereas for ceramic ones it is nearly 700ºC. They are also resistant for concentrated acids and can be used in contact with a broad spectrum of organic solvents without any changes in their structure and mechanical properties. Ceramic supports reveal the ability of long-term work and the cost of their preparation is relatively low. Usually, they are made of waste glass cullet. Glass has been also widely used to produce hollow fiber membranes (Kuraoka, 1998) and some of them present high selectivity for different gases (Sehelekhin, 1992; Way, 1992).

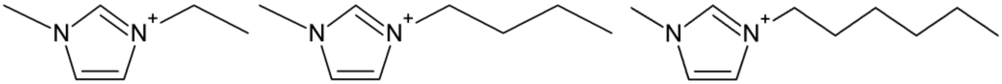
This work has been focused on the use of glass cullet to produce porous membranes, that can be applied in the supported ionic liquid membrane technology (SILMs). However, such application requires determination of products properties. The aim of this study was to investigate the factors influencing sinterability to improve the mechanical properties of ceramic bodies made from soda-lime glass cullet. Furthermore, the effect of the amount of pore-making organic and inorganic components was examined.

Properties mentioned above, give the SILMs predominance over traditional SLMs (Gamer, 2008, Hernandez-Fernandez, 2009, Letcher, 2007), as ionic liquids (ILs) have negligible vapor pressure, are non-flammable, liquid in a wide range of temperatures and solubilize many organic and inorganic species (Kittel, 2009, Pernak, 2000, Schaffer, 2011).

Experimental

Materials

Silicate-soda-lime colorless glass was used in this investigation. Pure dextrin and borax were obtained from POCH, Poland, with a purity of ≥ 95%. Five ionic liquids were used in this study: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [EMIM][Tf_2N], 1-ethyl-3 methylimidazolium trifluoromethanesulfone [EMIM][TfO], 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [BMIM][Tf_2N], 1-butyl-3-methylimidazolium trifluoromethanesulfone [BMIM][TfO], 1-hexyl-3-methylimida-zolium bis(trifluoromethylsulfonyl)imide [HMIM][Tf_2N]. All chemicals were supplied by Merck Chemicals Company, Darmstadt, Germany, with purity higher than 99%. The molecular structures of ILs cations and anions used in this study are shown in Figs 1 and 2.

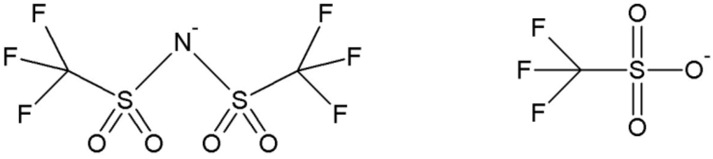


1-ethyl-3-methylimidazolium [EMIM]

1-butyl-3-methylimidazolium [BMIM]

1-hexyl-3-methylimidazolium [HMIM]

Fig. 1. Structure of ionic liquids cations used in the experiments



bis(trifluoromethylsulfonyl)imide [Tf_2N]

trifluoromethanesulfone [TfO]

Fig. 2. Structure of ionic liquids anions used in the experiments

Preparation of glass matrix

The technology of producing glass porous materials requires the use of glass in the form of powder (Ciecińska, 2007). Glass samples were crushed in a jaw crusher and then ground using a disc mill and ball mill, for 2 hours, respectively. The maximum particle size of 500 μm was obtained. Particle-size distributions were determined with standard sieve analysis and the orbiting laboratory shaker (OS 10 basic, IKA) with frequency vibration of 450 rpm. Glass particles with the grain size distribution of: 250–500; 106–250; 63–106; 45–63 μm were used for preparation of porous discs, by sintering with pore-enhancing compound. The chemical composition of glass cullet used in the experiments was determined using an X-ray fluorescence spectrophotometer, according to the procedure described in PN-EN ISO 12677:2005 and is presented in Table 1. Into a disc shaped form, ceramic powder was pressed using a hydraulic

Table 1. Chemical composition of glass used for sintering

Compound	Weight percent [%]
SiO_2	73.20
Na_2O	12.50
CaO	9.87
Al_2O_3	2.62
MgO	0.96
K_2O	0.59
Fe_2O_3	0.10
TiO_2	0.07
SO_3	0.06
MnO	0.02

press under pressure of 1 MPa to 5 MPa. The discs were then sintered at 700°C for 60 minutes in air atmosphere. A linear increase of temperature with 10°C/min rate was applied to obtain 700°C. Selected properties of membranes (specific density, apparent density, total porosity) were examined according to standard test method PN-EN 1389:2005 (Komitet, 2005). The structures of obtained porous membranes were observed with a scanning electron microscope (SEM).

Morphological characterization

Philips-FEI XL 30 ESEM (Environmental Scanning Electron Microscope) was used to determine morphological properties and the average pore size of ceramic supports. Before SEM observation, obtained samples of supports were coated with ultrathin gold layer.

Wetting of ceramic supports with ionic liquids

In order to determine the effect of chemical structure of the ionic liquids on ceramic supports wetting, cations differing in alkyl chain lengths and different anions were selected. In order to determine the wettability of various supports by ionic liquids, capillary rise method based on Washburn equation was used (Joskowska, 2012, Siebold, 2000, Studenbacker, 1955, Trong, 2006, Washburn, 1921, Wolfrom, 2002). Ceramic membrane samples sized 5×3×10 mm were used in the experiments. The time of penetration, increase in height of liquid penetrating into ceramic membrane and the decrease in mass of the liquid in a container was recorded every second using an electronic balance, attached to a computer. The time *t* = 0 approximately corresponded to the moment of membrane submersion in the wetting liquid. The experiments were repeated eight times and the mean value was calculated. On the basis of the Washburn equation, angle values were calculated. The results are shown in Table 7.

Results and discussion

Granular composition of glass powder obtained by milling is presented in Table 2.

Table 2. Granular composition of glass powder

Size of glass grains [μm]	Sifting [%]
>500	90.20
250–500	7.57
106–250	1.06
63–106	0.23
45–63	0.07
<45	0.88

During thermal analysis, the glass powder becomes soft at 700ºC and melts at 810ºC, whereas at 1020ºC the samples flow. On the basis of thermal analysis, the optimal temperature of sintering was selected. It was found that addition of dextrin and borax slightly decreases the softening temperature, to 698ºC and 695ºC, respectively. However it can be roughly assumed that such amounts of compounds do not affect the softening temperature. To obtain the highest possible porosity, the samples were sintered at 700ºC.

Tables 3–5 present the results obtained using different types of binder: 50% aqueous solution of dextrin, dry dextrin, 50% aqueous solution of borax and using various glass powder granulation, different amounts of binder and pressures in a range from 1 to 5 MPa.

Table 3. Properties of ceramic supports obtained using 50% aqueous solution of dextrin (15% m/m), at 700ºC

Granulation [μm]	Pressure [MPa]	Bulk density [g/cm^3]	Effective porosity [%]	Total porosity [%]
250–500	1	1.75	23.2	30.3
250–500	3	1.81	23.7	27.9
106–250	1	1.85	20.6	26.3
106–250	3	1.89	21.0	24.7
63–106	1	1.96	14.8	21.6
63–106	3	1.97	17.4	21.3
45–63	1	2.06	15.9	17.8
45–63	3	2.07	14.7	17.3
<45	1	2.07	13.7	17.5
<45	3	2.07	13.3	17.1

Supports prepared using 50% aqueous solution of dextrin had a total porosity of 30.3% (granulation 250–500 μm). Still, the lower granulation of glass powder, the lower porosity of supports. Glass powder granulation of size less than 45 μm (in comparison to 250–500 μm grain size) decreases the total porosity from 30.3% to 17.5%. An increase in press pressure from 1 to 3 MPa decreases the total porosity from 30.3% to 27.9% (for grain size 250–500 μm). However, when using 5% m/m and 10% m/m of 50% aqueous solution of dextrin the total porosity is lower than for 15% m/m for each granulation used. For 250–500 μm granulation, the porosity is reduced from 30.3% (15% m/m of binder) to 27.8% (10% m/m of binder) and 25.3% (5% m/m of binder). Formulation of ceramic support occurred to be impossible when adding 50% aqueous solution of dextrin above 15% m/m. However, the porosity obtained using aqueous solutions of dextrin was not sufficient to obtain satisfying support for the liquid membrane. In order to increase the total porosity, the solution was substituted with dry dextrin in amounts of 10, 15 and 20% m/m. However, preliminary experiments revealed that 10 and 15% m/m is not enough for obtaining satisfying porosity.

Moreover, using more than 20% m/m prevented from obtaining stable discs. Table 4 presents characteristics of supports obtained using 20% m/m of dry dextrin.

Table 4. Properties of ceramic supports obtained using 20% m/m of dry dextrin

Granulation [μm]	Pressure [MPa]	Sintering temperature [ºC]	Bulk density [g/cm^3]	Effective porosity [%]	Total porosity [%]
250–500	1	700	0.86	65.4	65.7
250–500	3	700	0.87	64.6	65.2
250–500	5	700	1.32	45.6	47.3
250–500	1	810	1.28	44.8	48.5
106–250	1	700	0.92	62.7	63.2
106–250	3	700	0.94	61.8	62.6
63–106	1	700	0.95	61.1	61.9
63–106	3	700	1.02	58.3	59.4
45–63	1	700	0.99	59.3	60.6
45–63	3	700	1.06	56.1	57.6
<45	1	700	1.12	56.7	58.4
<45	3	700	1.20	50.2	52.9

For granulation of 250–500 μm usage of dry dextrin gives supports with 65.7% total porosity. As mentioned in the case of dextrin water solution, the porosity is lower when using fine glass powder. An increase in press pressure from 1 to 3 MPa slightly decreases the porosity for the 250–500 μm grain size. It decreases from 65.7% to 65.2%. Further pressure increase to 5 MPa reduces porosity to 47.3%.Moreover sintering at 810ºC also reduces the total pores volume to 48.5% (for granulation of 250–500 μm).

Experiments have been also conducted using borax as a binder. Table 5 presents characteristics of ceramic supports obtained using 10% m/m of 50% aqueous solution of borax for different grain sizes at 700ºC.

Table 5. Characteristics of ceramic supports obtained using 50% aqueous solution of borax (10% m/m)

Granulation [μm]	Pressure [MPa]	Bulk density [g/cm^3]	Effective porosity [%]	Total porosity [%]
250–500	1	1.82	22.0	27.4
250–500	3	2.01	16.3	19.6
106–250	1	1.88	20.3	24.8
106–250	3	2.03	15.5	19.1
63–106	1	2.78	11.3	13.1
63–106	3	1.97	10.2	12.5
45–63	1	2.19	11.2	14.7
45–63	3	2.14	10.4	12.7
<45	1	2.18	11.8	13.6
<45	3	1.97	10.7	12.5

The 50% aqueous solution of borax gives 27.4% porosity (granulation of 250–500 μm). Still, the lower grain size is, the lower porosity is obtained. Using powder granulation of size less than 45 μm leads to 50% lower porosity in comparison to the 250–500 μm grain size. Again, an increase in press pressure reduces the porosity. Application of 5% m/m of 50% aqueous solution of borax reduces porosity from 27.4% to 18.3% (granulation of 250–500 μm).

Dry borax has been also used in the experiments. However, 10% m/m and 5% m/m occurred to be too much to obtain stable supports. Application of dry borax is not possible for such purposes. Figure 3 shows the dependence of granulation on porosity using different binder types at 700ºC and press pressure of 1 MPa. It is clearly visible that the decrease in granulation causes the decrease in porosity for all the binders used in this study.

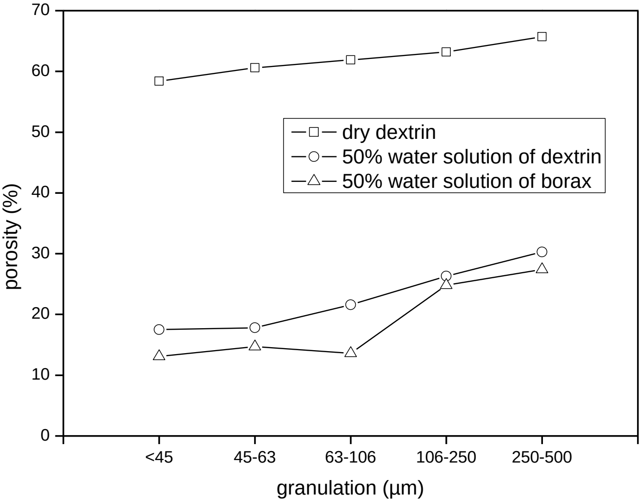


Fig. 3. Total porosity vs. granulation of glass powder

Press pressure of 1 MPa, sintering temperature of 700°C and addition of dextrin of 20% m/m gives the highest porosity for different grain sizes. Application of 50% aqueous solution of dextrin gives lower porosity than application of dry dextrin. Moreover, addition of dextrin water solution above 15% m/m prevents from obtaining stable support. The increase in pressure and sintering temperature also reduces the support porosity. Application of borax as binder does not improve properties of supports. Moreover, it is not possible to obtain any support using dry borax.

To summarize, the best properties of supports are obtained when using glass powder with granulation of 250–500 μm, 20% m/m of dextrin as binder and sintering temperature of 700°C. Porosity obtained using press pressure of 1 MPa and 3 MPa does not differ significantly, however, membranes prepared with 3 MPa of press pressure show higher mechanical stability.

The total porosity of obtained supports is at the level of 60% and it stays in correlation with values obtained by other authors that utilized saccharose as binder, sintering temperature of 1000^{o}C and granulation of 45–100 µm (Miecińska, 2007).

Kosmulski et al. (2009) used quartz sand, cryolite, glass cullet of 18% m/m and 40% water solution of dextrin to obtain 42% porosity (Kosmulskiet al., 2009). Porosity of 65% can be also obtained using water as a pore-forming agent. At 700^{o}C water evaporates forming pores (Yanagisawa, 2006). Figure 4 presents the surface of ceramic supports obtained using glass powder with granulation of 250–500 µm, press pressure of 1 MPa and either 10% m/m addition of borax or 20% m/m addition of dextrin.

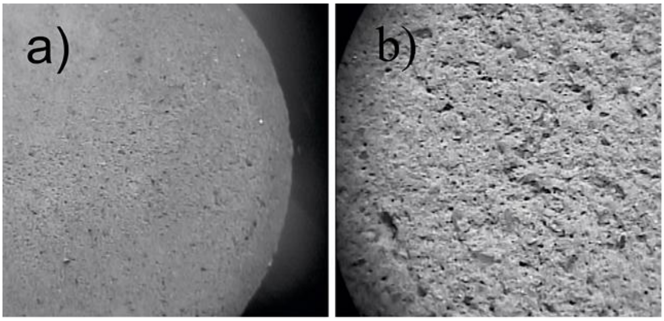


Fig. 4. Structure of ceramic supports obtained with a) 10% m/m of dry borax, b) 20% m/m of dry dextrin

Depending on the type of pore-forming agent used, supports demonstrate different textures. Surface of supports obtained using dextrin shows higher roughness. Figures 5-10 present SEM micrographs of ceramics formed using 500–250 µm glass particles.

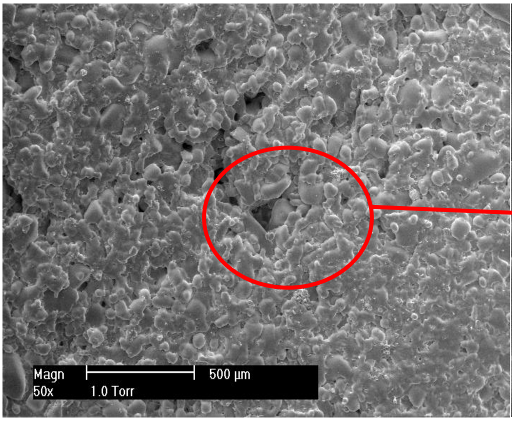


Fig. 5. SEM micrograph, 500–250 µm, 20% dry dextrin, 1 MPa, 700°C

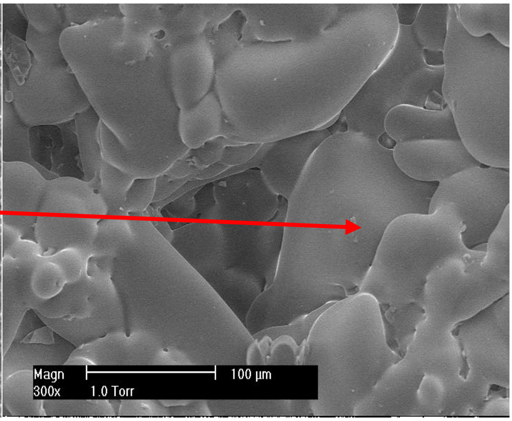
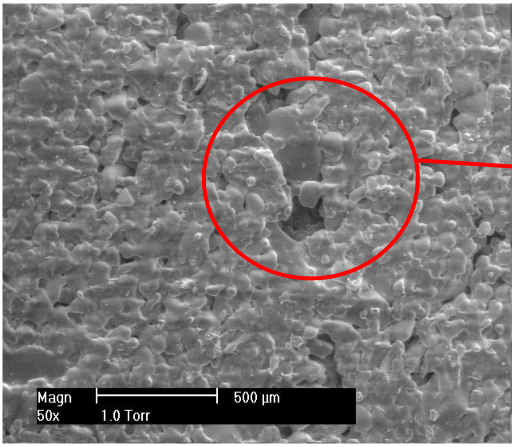


Fig. 6. SEM micrograph, 500–250 µm, 20% dry dextrin, MPa, 700°C



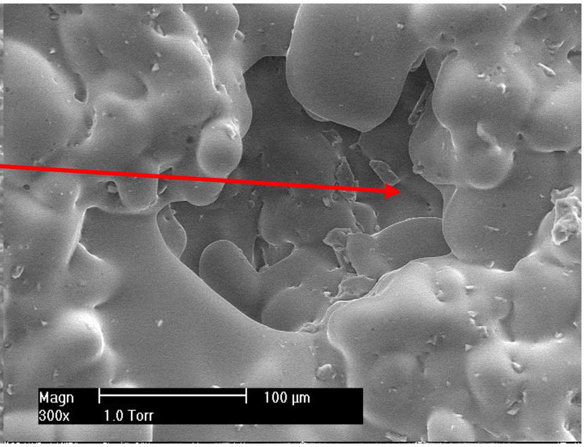
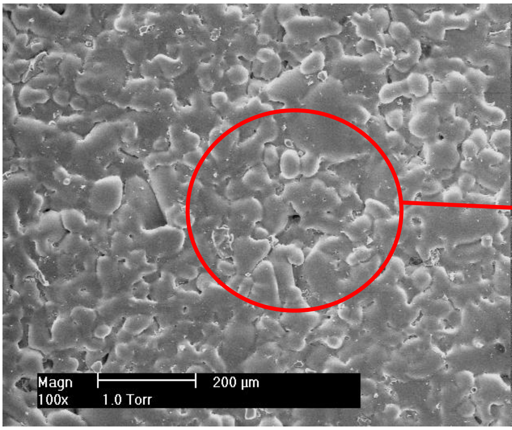


Fig. 7. SEM micrograph, 500–250 µm,
15% aqueous solution of dextrin, 1 MPa, 700°C

Fig. 8. SEM micrograph, 500–250 µm,
15% aqueous solution of dextrin, 1 MPa, 700°C



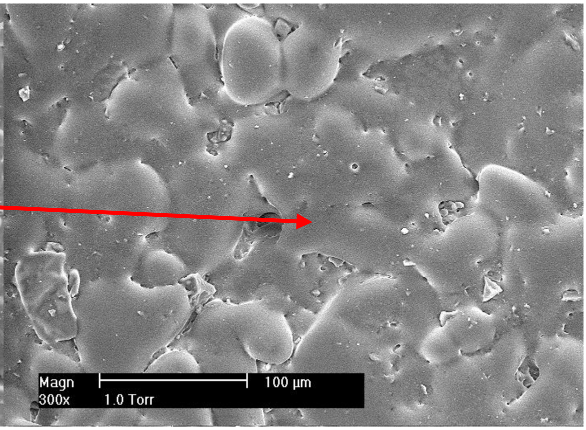


Fig. 9. SEM micrograph, 500–250 µm,
10% solution of borax, 1 MPa, 700°C

Fig. 10. SEM micrograph, 500–250 µm,
10% solution of borax, 1 MPa, 700°C

In both cases, using dextrin or borax, support structure is irregular and pores are heterogeneous. However, supports obtained using borax (Figs 9 and 10) are slightly more homogenousand the pores are rather closed. The matrix obtained using dextrin has larger amount of pores opened. This is confirmed by porosity experiments (Tables 3 and 4). The SEM micrographs allowed to calculate the average pores size which is 72 ± 27 µm using 20% of dry dextrin.

The method using dextrin as a pore-making agent occurred to be suitable to prepare ceramic supports with porosity over 60%. Both substrates are easily available, not expensive and the supports obtained have repetitive properties.

Wetting experiments have been based on the mass increase measurements. A graph of square of mass increase vs. time is presented in Fig. 11.

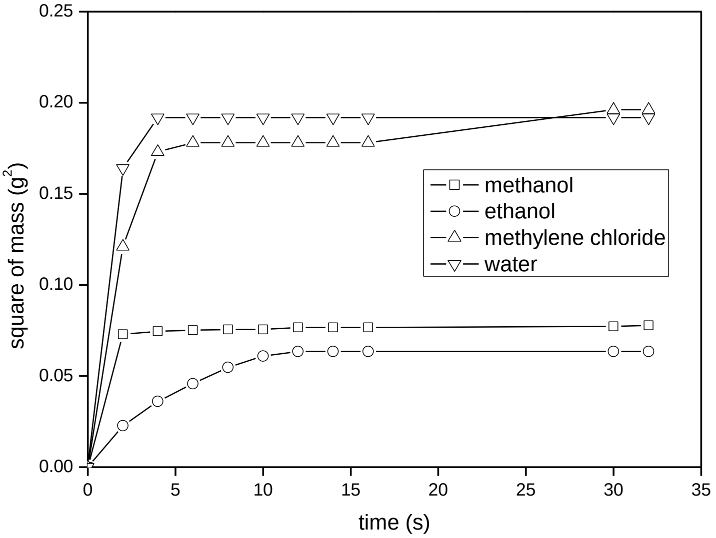


Fig. 11. Membrane wetting with reference liquids

Liquids wet ceramic materials in two steps. At first, liquid fills the pores rapidly, and afterward it moves in horizontal direction subsequently until the mass is constant. The rapidity of wetting is affected by liquid viscosity, density and surface tension. Table 6 presents physicochemical properties of reference liquids.

Table 6. Physicochemical properties, penetration time for reference liquids at 298K

Reference liquid	Density [kg/m^3]	Viscosity [mPa·s]	Surface tension [mN/m]	Penetration time [*s*]
Water	997	0.895	72.6	4
Methanol	793	0.584	23.0	1
Ethanol	789	1.190	22.0	10
Methylene chloride	1320	0.423	27.2	4

Among the examined liquids, methanol wets the ceramic matrix best, whereas ethanol penetrates the matrix the most slowly. In practice, the best wetting liquid is chosen on the basis of the highest value of $r\cos\theta$, so the ratio $m^2\eta/(t\rho^2\gamma)$ should be the highest among the examined liquids (Ayala, 1987).

Methanol has been chosen as the reference liquid for further experiments, and the contact angle was assumed as 0 degree ($\cos\theta = 1$). On this basis contact angles for ionic liquids were calculated (Table 7).

Table 7. Physicochemical properties and contact angles of ionic liquids at 298 K

Liquid	Viscosity [mPa·s]	Surface tension [mN/m]	Penetration time [s]	*K**	cosθ	θ [deg]
Metanol	0.58	23.0	1	reference liquid	1	–
[EMIM][Tf_2N]	32.6	32.6	45	40.1	0.892	27
[BMIM][Tf_2N]	48.1	30.8	70	61.4	0.878	29
[HMIM][Tf_2N]	70.0	32.6	99	84.6	0.854	31
[EMIM][TfO]	40.4	37.8	45	42.1	0.935	21
[BMIM][TfO]	74.3	34.7	94	84.3	0.897	26

* K is the quotient of surface tension of methanol and viscosity of ionic liquid ratio and surface tension of ionic liquid and viscosity of methanol ratio.

A graph of ceramic matrix wetting with [Tf_2N] based ionic liquids is presented in Fig. 12.

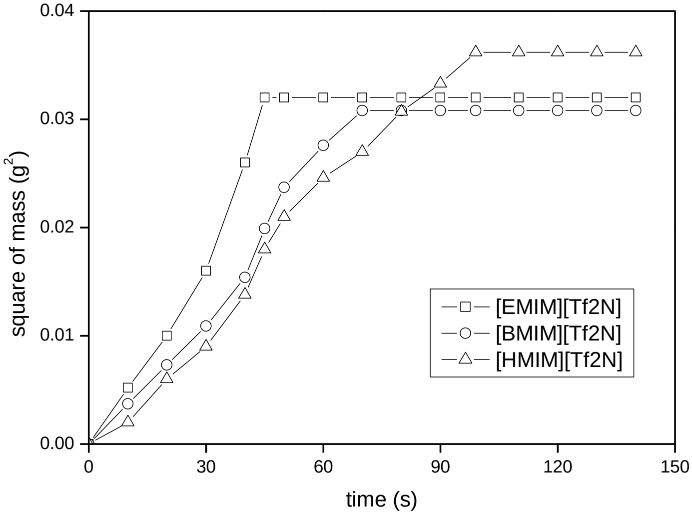


Fig. 12. Square of mass vs. penetration time for [Tf_2N] based ionic

It can be seen that the time of penetration increases as the numbers of carbon atoms in alkyl chain in imidazolium cation increases. It is also confirmed with data obtained for ionic liquids with [TfO] as anion (Fig. 13).

The best wetting is observed for [EMIM][TfO] and [BMIM][TfO] ~ [EMIM][Tf_2N] > [BMIM][Tf_2N] > [HMIM][Tf_2N] respectively. Wettability of [Tf_2N] based ionic liquids is as following: [EMIM] > [BMIM] > [HMIM]. Increasing numbers of carbon atoms in hydrocarbon chain of ILs leads to an increase of contact angle

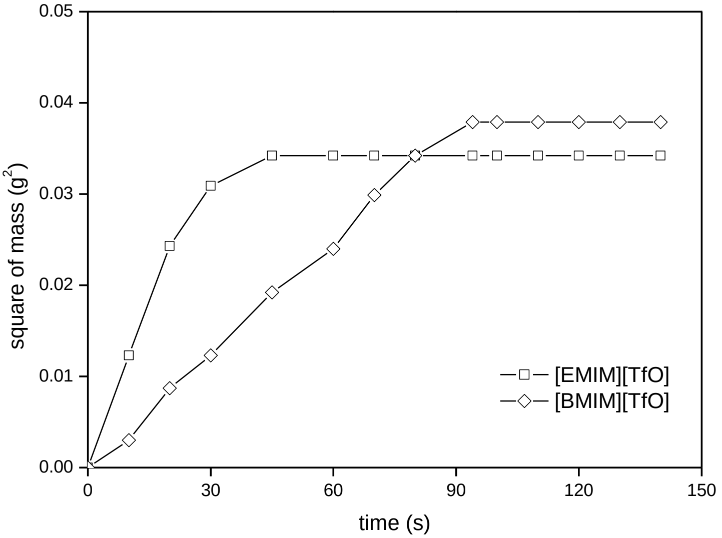


Fig. 13. Square of mass vs. penetration time for [TfO] based ionic

between ionic liquid and ceramic matrix, what is in correlation with the viscosity of ILs (the viscosity increases in the following order: [EMIM] < [BMIM] < [HMIM]). The dependence is observed for [TfO] based ionic liquids likewise. All of the values of contact angles are lower than 90 degree, so it can be concluded that the ceramic matrix is well wetted with examined ionic liquids and can be used as a membrane phase to obtain stable support for ionic liquid membranes.

Conclusions

In the present study, porous materials were prepared from glass powders by sintering at 700°C, with dextrin and borax as pore-making agents. The obtained porous materials had different bulk density and total porosity. The porosity could be controlled by changing the particle size distribution, kind and amount of pore-forming agents, applied pressure on preparation stage and sintering temperature. The glass porous materials obtained with pure dextrin exhibited higher porosity, comparing with sodium tetraborate. The maximum total porosity was obtained for the following parameters: 250–500 μm glass size fraction, the applied pressure 1 MPa, and sintering temperature 700°C (softening point for this glass cullet). As a result, porous materials of over 60% total porosity were obtained. Applying this method allows to prepare porous membranes which can be applied as supports for liquids. Moreover such supports are well wetted with commonly used ionic liquids. Due to this fact, formation of SILMs based on ceramic supports is reasonable by all means. Such membranes can be used in catalytic processes (where ionic liquids are used as catalysts), biological filtration (due to antiseptic properties of some ILs) or separation and purification processes (for example separation of carbon dioxide from biogas).

Acknowledgements

This research was supported by the National Science Centre, grant No. 7563/B/T02/2011/40, Removal of Volatile Organic Compounds from Gas Phase using Ionic Liquids. Financial support of this work was provided also by the National Centre for Research and Development of Poland, grant 04/strategic program/2010 on Advanced Technologies of Energy Generation, Pilot Agricultural Biogas Microstation and Fermentation and Separation of Carbone Dioxide from Biogas with Ionic Liquids Application. We are very grateful for financial support provided by the National Science Centre, grant No. 1815/B/H03/2009/36.

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