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Composite Membranes of Sulfonated Poly(ether ether ketone) with Active Carbon: Composite Preparation and Investigation of their Properties for Potential Application for CO_2 Electrochemical Reduction

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In this study, synthesis of sulfonated poly(ether ether ketone) (SPEEK) was performed using sulfonation method with concentrated sulfuric acid. Polymer with three degrees of sulfonation was obtained: 0.87; 0.82 and 0.74. Composite membranes were synthesized with an activated carbon. Ultrasonication method was used in order to achieve homogeneity of distribution of the additive in polymer solution and then in polymer membranes. Membranes with various content of the additive were made: 0; 0.15; 0.3; 0.5; 0.6; 0.8; 1.0; 2.0 and 3.0 %. Swelling degree, water uptake, proton conductivity, isoelectric point, thermal properties and surface morphology of the membranes were analyzed. Proton conductivity was determined using impedance analysis with two electrode system and through-plane configuration. Two methods were used: differential and single membrane method. Differential method is proposed to have significant advantage as it reduces contact resistance, which otherwise is difficult to control and evaluate. Surface zeta potential of membrane surface was investigated, and membranes have shown variation of the potential. Isoelectric point was determined for the membranes with DS 0.82 and carbon content 0 % and 0.5 %, and it was found to be at pH 4. Water uptake and swelling degree of the membranes was studied, and active carbon content was found to not have major influence on those properties, but higher content of sulfonic groups leads to increased water uptake and swelling degree. Thermogravimetric analysis showed slightly better thermal properties of membranes with the additive, compared to the blank membranes, which can be related to differences in the water uptake. Surface of the membrane was investigated using scanning electron microscopy, and no considerable defects were observed.

Keywords: sulfonated poly(ether ether ketone), impedance analysis, surface zeta potential, CO_2 reduction.

1. INTRODUCTION

Polymer electrolyte membrane (PEM) is a key component in fuel cell technology, as it provides proton transfer and separates anode and cathode space [1]. Sulfonated poly(ether ether ketone) is an example of PEM, and it is a promising material for application in hydrogen fuel cell [1], direct flow methanol fuel cell (DMFC) [2], for water desalination by electrodialysis [3] and it can also be used in CO_2 converters for CO_2 electrochemical reduction into hydrocarbons [4].

One of the most important parameters of PEM is proton conductivity, because of the proton motion to cathode [5]. For application in electrochemical cells it is also important for the membrane to have appropriate thermal and mechanical properties, because in PEM fuel cells the membrane is being exposed to elevated temperature and mechanical stress [6]. One of the challenges determining proton conductivity is contact resistance. Impedance analysis is usually used to determine membrane conductivity. Two electrode system is commonly used for this purpose, and it is possible to make a measurement by through-plane and in-plane configuration, however anisotropy is observed, and through-plane configuration provides slightly higher results [6, 7]. Therefore, differential method is proposed for effective reduction of the influence of contact resistance. In our work, a two electrode system was used, through-plane configuration, and two measuring methods: differential and single membrane method.

Composite membrane fabrication containing organic and inorganic additives can lead to improvements in properties [8]. One way to modify the properties is to use graphene oxide [9] or carbon nanotubes [10] for SPEEK composite preparation. Cross-linking and blending with other polymer are also considered as efficient modification methods [11]. Inorganic additives can be montmorillonite (MMT), zeolites, SiO_2, TiO_2. It is that these reported to decrease methanol permeability, swelling degree, increase thermal stability, but also decrease proton conductivity [8].

SPEEK membranes are a promising material for application in CO_2 electrochemical reduction. Consequently, it is necessary to investigate properties of the membranes. Generally, in literature SPEEK membranes are being investigated with only one relatively high degree of sulfonation (DS) and different content of additives. In this work, membranes with three different DS and various additive content were prepared and studied. Surface zeta potential of SPEEK membranes or composite membranes was not reported previously.

CO_2 conversion is being widely studied nowadays. CO_2 non-controlled emissions have led to economical, sociological and climate consequences. One of the methods

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of decreasing CO_2 levels is CO_2 conversion to useful chemical compounds, such as formic acid, formaldehyde, methanol, oxalic acid, methane, ethylene and ethanol [12]. One of the main challenges of CO_2 electrochemical reduction is the development of catalyst, which will be both effective and selective and lead to the desired product [12, 13].

In this study, active carbon as an additive was investigated, as it provides high surface area and it is used in catalysis, also it is cheaper than graphene and has a similar nature. The aim of our study is to investigate proton conductivity, thermal properties, swelling degree and water uptake and evaluate surface zeta potential for composite membranes with wide range of content of the additive for application in CO_2 reduction cells. There are difficulties in evaluation and quantification of contact resistance, therefore differential method is proposed as it excludes contact resistance more efficiently [14].

2. EXPERIMENTAL DETAILS

2.1. SPEEK sulfonation and preparation of composite membranes

SPEEK was synthesized from poly(ether ether ketone) (PEEK), obtained from Sigma Aldrich (number average molecular weight Mn ~10300, weight average molecular weight Mw ~20800) using sulfonation method with sulfuric acid (Sigma Aldrich, 95 – 97 %) described before [15]. Sulfonation of PEEK was carried out at 60 °C for 8; 6 and 4 h. SPEEK with various DS was obtained: 0.87; 0.82 and 0.74. A previously described titration method was used for determination of DS [16].

Composite membranes were prepared by dissolving SPEEK in *N,N*-dimethylformamide (DMF) and adding different content of activated carbon (REAHIM, OY mark A, particle size (diameter) distribution about 2 μm). Total number of membranes was 27, and for each of the DS it was 9, and carbon content was: 0; 0.15; 0.3; 0.5; 0.6; 0.8; 1.0; 2.0 and 3.0 %. Homogeneity of particle distribution in the membranes was obtained by using ultrasonication method of polymer solution with carbon. Selecta Ultrasons bath was used for 30 minutes of ultrasonication and polymer membranes were made by using a solvent cast method. Polymer solutions were poured into Petri dishes and dried for 48 h at 80 °C.

2.2. Water uptake and swelling degree of the SPEEK composite membranes

Water uptake and swelling degree were determined for each of the prepared membranes. Dry membranes were weighted, length and thickness were measured. After that, membranes were immersed in deionised water for 24 h, weighted and measured again. Water uptake was calculated by Eq. 1 [8, 15] and swelling degree was calculated by Eq. 2 [17].

$$\text{Water uptake} = \frac{G_w - G_d}{G_d} \cdot 100\%, \quad (1)$$

where G_w is mass of the wet membrane, g; G_d is mass of the dry membrane, g.

$$\text{Swelling degree} = \frac{L_w - L_d}{L_d} \cdot 100\%, \quad (2)$$

where L_w is length of the wet membrane, g; L_d is length of the dry membrane, g. Swelling degree was also measured and calculated for membrane thickness, and it was calculated similarly to Eq. 2.

2.3. Impedance analysis of the SPEEK composite membranes

Impedance analysis of the membranes was performed by two methods, described in our previous work [14]. Measurements were performed in two electrode through-plane configuration (electrode diameter was 1 cm). Metrohm Autolab potentiostat/galvanostat PGSTAT204 was used, and measuring parameters were: frequency range was 50 kHz to 100 Hz; 10 frequencies per decade; signal amplitude 10 mV. In the differential method the SPEEK membrane was sandwiched between two Nafion membranes and pressed between two copper electrodes. Impedance analysis was performed, and the resistance was obtained from Nyquist plot extrapolating to the high frequencies. After that two Nafion membranes were put into the measuring cell and impedance analysis was performed similarly and resistance of two Nafion membranes was determined. From the difference between two of these measurements, resistance R and conductivity σ of SPEEK membrane was calculated, using the equation (3) [15].

$$\sigma = \frac{l}{R \cdot S} \quad (3)$$

where σ is conductivity, $S \cdot cm^{-1}$; l is membrane thickness, cm; R is SPEEK membrane resistance, Ω; S is electrode surface area, cm^2. Impedance analysis was performed at 22 °C temperature for both methods.

2.4. Electrokinetic analysis of the SPEEK composite membranes

Surface zeta potential was investigated using Anton Paar SurPASS 3 electrokintic analyser. 0.001 M KCl solution was used as an electrolyte solution and for corrections of pH of the solution for determination of isoelectric point 0.05 M solutions of NaOH and HCl were used for pH corrections in interval from pH 4 to pH 9. Clamping cell was used to measure surface zeta potential of the membranes.

2.5. Thermal properties of the SPEEK composite membranes

Thermal properties were investigated using thermal analysis apparatus SETARAM LABSYS Evo with water circulator JULABO FL1203 for cooling. Ceramics crucibles (Al_2O_3) were used without lid and empty crucible was used as a reference. Thermal analysis was carried out in TG/DSC mode from 40 °C to 450 °C with heating rate 10 $K \cdot min^{-1}$ and argon flow 20 $mL \cdot min^{-1}$. Sample mass was about 10 mg and was measured on analytical balance.

2.6. Morphology analysis of the SPEEK composite membranes

Scanning electron microscopy (SEM) method was used to investigate the morphology. Phenom Pro Table Top SEM was used and both sides of the membranes were investigated. Acceleration voltage was 5 kV, and detector mode was set to BSD full mode.

3. RESULTS AND DISCUSSION

3.1. Obtaining SPEEK composite membranes

SPEEK composite membranes were synthesized with different degrees of sulfonation as well as with different content of active carbon. Fig. 1 shows the membranes, fabricated in this work.

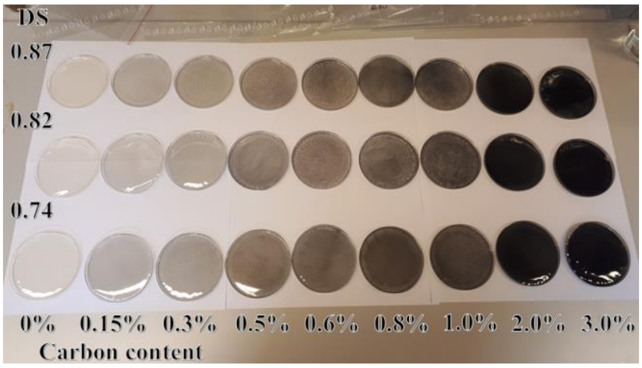

Fig. 1. SPEEK composite membranes with three various degree of sulfonation and nine various carbon contents from 0 to 3.0 %

The membranes with the same percent between various DS from the outside look similar. The membranes look homogeneous, and ultrasonication method proved to provide a good distribution of the particles in the volume of the membranes. Additionally, no layering was observed, and, while keeping the membranes in deionized water, no particle migration into the water was observed.

3.2. Water uptake and swelling degree properties of the SPEEK composite membranes

Fig. 2 shows the results of the water uptake test and determination of swelling degree. SPEEK polymer contains hydrofilic $-SO_3H$ groups, and water has high affinity to these groups. This results in higher water uptake for the membranes with higher DS, which is beneficial in application for fuel cell, because water facilitates proton tranfer according to Grothuss mechanism [18]. Water absorption in polymers is related to increase in mass and spacial dimensions (length, width, thickness). Therefore, it is important to evaluate these properties for application in electrochemical devices, where ususally the membrane is being exposed to water.

From Fig. 2 one can observe, that SPEEK membranes can absorb relatively large amount of water, and mainly this results in an increase of mass, thickness. Length increase found to be smaller in comparison with thickenss and mass increase. Mass increased approximitely by 25 – 25 %, thickness by 20 – 25 % and length only by 5 – 10 %. Comparing the membranes with the same DS and various carbon content, no correlation was observed between carbon content and the increase in spacial dimensions. Comparing the membranes with various DS, membranes with lower level of DS show less increase in percent than the membranes with higher DS. Also, it was observed, that increase of length and thickness was not equal.

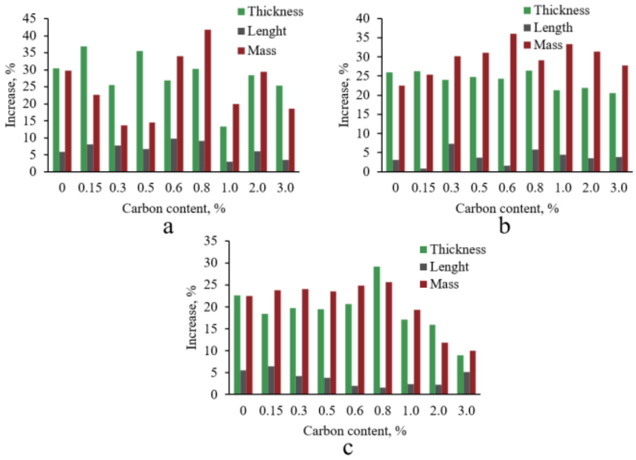

Fig. 2. Water uptake and swelling degree of SPEEK composite membranes with various carbon content and DS: a – 0.87; b – 0.82; c – 0.74

3.3. Impedance analysis

Differential method and single membrane method were used to study membrane conductivity. Fig. 3 shows cell configuration for both methods.

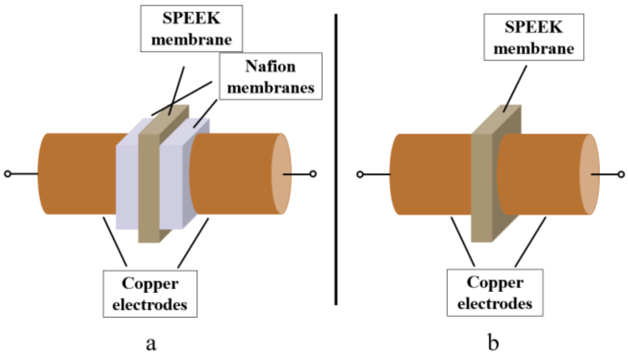

Fig. 3. a – cell configuration of two methods used for impedance analysis: differential method; b – single membrane method [14]

Results of determination of proton conductivity are shown on Fig. 4 and confidence interval was calculated from three parallel measurements ($p = 0.95$ un $t_{p,n} = 4.303$). Typical Nyquist plot was also shown for SPEEK membrane with DS 0.87 and carbon content 2.0 % respectively. An example of extrapolation to the high frequencies was also provided. Simplified Randles equivalent circuit was used (without Warburg element). We compared Nyquist plots for the membranes with various DS and carbon content and we concluded that among all the membranes there were no significant changes that would have a dependence on the DS or carbon content. The results have shown, that the resistance changes between the membranes which can be observed on the Nyquist plots, which results in changes of conductivity. The results have shown, that the membranes with higher DS also have higher conductivity, than the membranes with lower DS. Possible explanation may be as the membranes not only contain higher amount of SO_3H groups, but also can absorb more water which facilitates proton transfer via Grothuss mechanism [19].

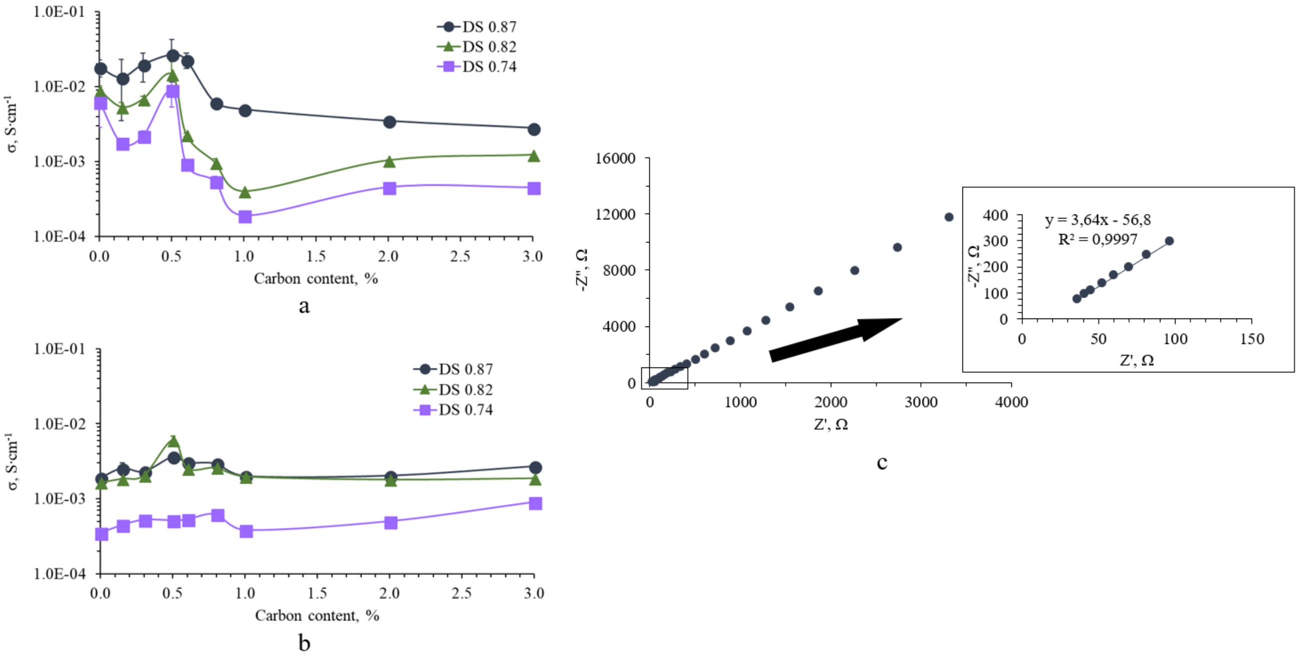

Fig. 4. Proton conductivity by impedance analysis of SPEEK composite membranes with three DS and various carbon content by two methods: a – differential method; b – single membrane method; c – Nyquist plot for SPEEK composite membrane with DS 0.87 and carbon content 2.0 % (c) by differential method

This correlation is also observed in our work and is confirmed by two methods.

The single membrane method have shown systematic bias of the conductivity results and provide lower conductivity than the differential method. Similar observations were made in our previous work [14], and are explained based on the influence of contact resistance.

The differential method excluded contact resistance more efficiently [14]. The results with differential method have shown, that the membranes with active carbon provide lower conductivity in comparison with blank membranes and starting with 2.0 % of carbon content conductivity does not change significantly. The decrease of the conductivity can be interpreted as particles of the active carbon suppress proton conductivity through the Grothuss mechanism in proton channels, containing water. The membranes with carbon content of 0.5 % were an exception, because they have shown slightly higher conductivity. It is also important to notice, that the deviation of data is high, and unambiguous conclusion regarding the results cannot be made.

3.4. Electrokinetic analysis

Determination of isoelectric point was made for the membranes with DS 0.82 and carbon content 0 % and 0.5 %. Fig. 5 shows dependence of surface zeta potential on pH of the solution.

Isoelectric point determination results have shown, that the membranes with carbon content 0 % and 0.5 % were similar. The values of zeta potential are close to 0 mV and the interval of changes was only about 1 mV. Therefore, the variation of the data was high, and the surface zeta potential could not be evaluated correctly. The results have shown, that adding active carbon to the membrane changes its surface properties. Zeta potential of the surface is dependent on many factors, such as surface morphology, chemical composition of the material and polarity of the surface [20], as well as electrolyte concentration [21].

Isoelectric point was at pH 3.9 for 0 % active carbon and at 4.0 for 0.5 %. Isoelectric point was relatively close between two of these membranes. The results appeared to be trustworthy, because sulfonic groups are acidic groups, and therefore isoelectric point also should be in weak acidic region. Further studies are required in order to investigate the processes at the surface of the membrane.

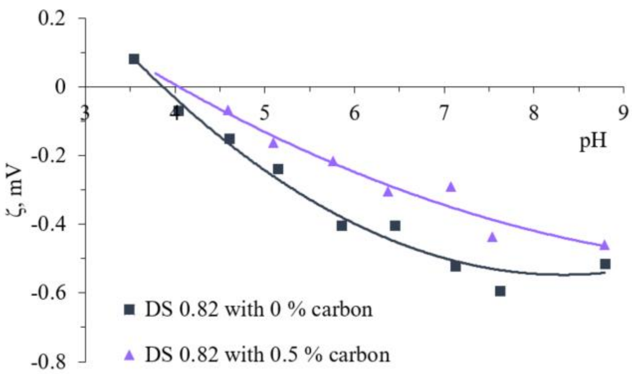

Fig. 5. Determination of surface zeta potential of SPEEK composite membranes with DS 0.82 and 0 % carbon as well as 0.5 % carbon

3.5. Thermogravimetric analysis

Thermal properties of the SPEEK membranes and processes at elevated temperature were investigated. Fig. 6 shows the mass losses of the SPEEK composite membranes. Nafion membrane was investigated for comparison.

Due to inability to determine the products of decomposition because of absence of MS or FTIR detector connected to the apparatus, identification of the processes at elevated temperature was limited.

Therefore, evaluation of thermal processes was compared with the study of other authors. Three main regions were observed for the SPEEK membranes. The first region was up to 150 °C, and in this region, water evaporates as well as the solvent DMF. The second region was after 200 °C, and desulfonation of the membranes occur with liberation of SO_2 and CO_2. The third region was at about 450 °C, and pyrolysis of the main polymer chain occurred with liberation of CO_2 and H_2O [22].

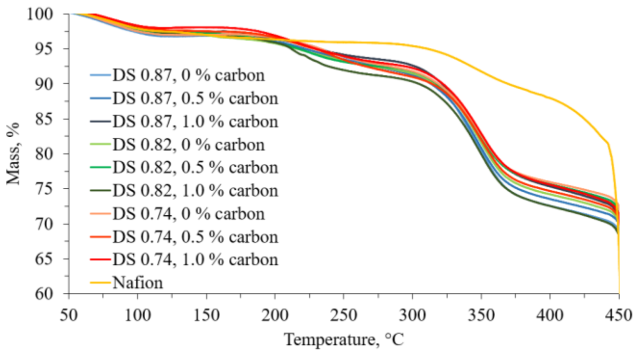

Fig. 6. Thermogravimetric analysis of the SPEEK membranes with DS 0.87; 0.82; 0.74 and carbon content 0; 0.5; 1.0 % as well as Nafion membrane

Thermal analysis of Nafion membrane have shown similar stages of decomposition. In the first stage water evaporated, in the second stage polymer desulfonation occurred and in the third stage the main chain of the polymer decomposed [23]. Also, rapid mass loss was observed at 450 °C for Nafion membrane, but for the SPEEK membrane no such observation was made.

It was found, that Nafion and SPEEK composite membranes have comparable thermal properties, as both was able to withstand elevated temperature up to 200 °C. Thermal properties of PEEK was found significantly better than of the SPEEK membranes, and the beginning of decomposition was reported to be at 550 – 600 °C [24, 25].

Thermogravimetric analysis of the SPEEK membranes has shown the analogous results comparing membranes with various DS and carbon content. All the investigated membranes had three distinct regions with comparable mass losses and no additional processes that would lead to different decomposition stages or significantly different mass losses. The membranes with carbon have shown slightly better thermal properties, as the stages of decomposition contain less mass loss than membranes without the additive. One of the possible explanations of increased thermal stability besides possible interactions between active carbon and polymer chains can be, that SPEEK membranes with carbon content of 0.5 % and 1.0 % have shown slightly less increase in mass in water uptake investigation.

Carbon content in the composite membranes was found to have an important impact on the investigated properties. In our work FTIR analysis was also performed for all the membranes. We were able to find signals for the bonds of the polymer chain; however, it was found that carbon content does not have significant impact on the spectra and significant changes were not observed. The only change in the spectra was decreased intensity of the signals when compared between the membranes with lower and higher carbon content with membranes with higher carbon content having decreased intensity. Also, there were no significant changes in the spectra compared with blank membranes. We can assume, that Raman spectra could provide more information regarding new bonds in the composite.

3.6. SEM analysis of the SPEEK composite membranes

Fig. 7 shows the results of the SEM analysis. From the SEM analysis it was possible to observe, that the surface of the membranes appeared to be the same despite various degree of sulfonation and active carbon content. Also, both sides of the membranes were rather similar and contained no significant differences.

Some defects were observed on the surface of the membranes, which could be related to the membrane fabrication method. Also, electron conductive particles were found on the surface of the membranes, and they could not be identified, but most likely membrane surface was contaminated with dust particles from surrounding air. In our previous work similar analysis was performed for the membranes, and the results are analogous [14].

4. CONCLUSIONS

In this study, SPEEK composite membranes with various DS and active carbon content were fabricated and investigated. The results from impedance analysis have shown that the membranes with high degree of sulfonation also have higher conductivity, and this correlation was observed both for blank and composite membranes and was confirmed by both differential and single membrane methods. The single membrane method had a systematic bias compared to the differential method, and the difference between the methods was explained by the contact resistance. Composite membranes with active carbon proved to have lower conductivity than blank membranes. Data deviations did not allow to undoubtedly evaluate increasing conductivity of the membranes with carbon content 0.5 %. Both composite membranes and blank membranes absorb significant amount of water and the mass increase was 25 – 35 %, thickness increase was 20 – 35 % and length increase was 5 – 10 %. Determination of surface zeta potential have shown isoelectric point to be at pH 4, which corresponds to acidic nature of the sulfonic groups. And with addition of active carbon the surface zeta potential values at different pH also changes. Thermal analysis has shown that SPEEK and Nafion thermal properties are comparable. Addition of active carbon to the membrane provides slightly increased thermal stability. In conclusion, SPEEK composite membranes as PEM have acceptable properties in order to use them as functional material in CO_2 electrochemical reduction cell.

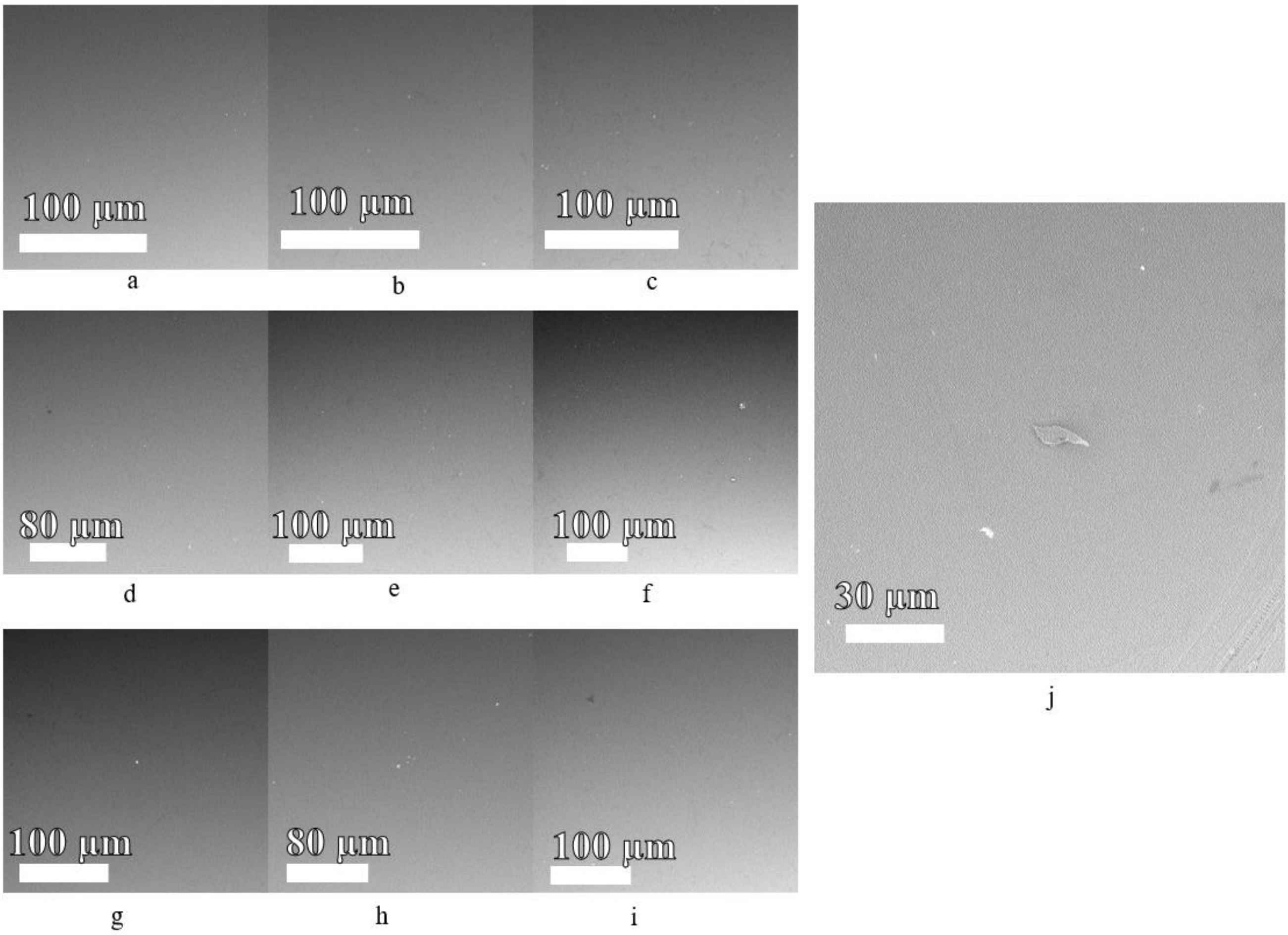

Fig. 7. Results of SEM analysis of SPEEK composite membranes with DS 0.87 and carbon content: a – 0 %; b – 0.5 %; c – 1.0 %; with DS 0.82 un carbon content: d – 0 %; e – 0.5 %; f – 1.0 %; with DS 0.74 un carbon content: g – 0 %; h – 0.5 %; i – 1.0 %; and SPEEK composite membrane with DS 0.87 and carbon content: j – 0 % with higher magnification

Acknowledgments

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