PAPER • OPEN ACCESS

Different approaches in sulfonated poly (ether ether ketone) conductivity measurements

To cite this article: D Fedorenko and G Vaivars 2019 *IOP Conf. Ser.: Mater. Sci. Eng.* **503** 012030

IOP Conf. Series: Materials Science and Engineering **503** (2019) 012030 doi:10.1088/1757-899X/503/1/012030

Different approaches in sulfonated poly (ether ether ketone) conductivity measurements

D Fedorenko[1,2] and G Vaivars[1,2]

[1]Faculty of Chemistry, University of Latvia, Jelgavas Street 1, Riga, LV-1004, Latvia
[2]Institute of Solid State Physics, University of Latvia, Kengaraga Street 8, Riga, LV-1063, Latvia

E-mail: deniss.fedorenko@gmail.com

Abstract. Ion conductivity of sulfonated poly (ether ether ketone) (SPEEK) membranes with various degree of sulfonation (DS) was investigated using impedance analysis with different measuring cell configuration and ion conductivity was calculated from resistances of polymer membranes. SPEEK was synthesized from poly (ether ether ketone) (PEEK) via sulfonation reaction in concentrated sulfuric acid (95–98%). Scanning electron microscopy (SEM) analysis of membrane surface was performed to determine possible mechanical damage to the membrane during resistance measurements.

1. Introduction

In modern society there is increasing interest towards innovative technology as well as transition to sustainable energy. Polymer electrolyte membrane is a key component in fuel cell technology, as it provides ion transport in fuel cell [1]. Sulfonated poly (ether ether ketone) (SPEEK) is promising material for application in direct methanol fuel cell [2]. And it was reported that the SPEEK membrane might be cross-linked to enhance its properties [3]. Ion conductivity of polymer electrolyte membrane is a key parameter for providing high efficiency and therefore correct conductivity measurements are very important. Impedance analysis is being used widely to determine membrane conductivity. The literature data on specific cell configuration is limited. At the same time the methods for measuring conductivity of polymer membrane were not described sufficiently by authors previously. The membrane contact with the electrode is important and the contact resistance is difficult to evaluate. That's why it is considered as a probable reason for decreased conductivity. It was also mentioned, that the conductivity of a membrane can be measured by two probe method and slight anisotropy of proton conductivity is observed and through-plane setup showed slightly higher proton conductivity than in-plane setup. Four probe method is limited for polymer membranes due to the low material hardness and strong dependence on relative humidity [4].

The aim of our study is to compare two different methods of measuring ion conductivity of polymer electrolyte membranes using impedance analysis and evaluating them as not being damaging for membranes. First, the standard method by pressing sample in-between two metal electrodes was used. Second, the membrane was pressed in-between two Nafion membranes with a known conductivity (differential method). In this paper two approaches of ion conductivity measurements have been applied for SPEEK membranes with different degrees of sulfonation (DS) using resistance data obtained by performing impedance analysis. It was revealed, that the differential method as compared to the single membrane method shows good correlation with a reference material, which was commercial Nafion N-117 membrane.

2. Experimental

SPEEK was synthesized from poly (ether ether ketone) (PEEK) via sulfonation with concentrated sulfuric acid (95–98%) at 60ºC. Degree of sulfonation was determined using titration method as described previously [3, 5]. Metrohm Autolab potenciostat/galvanostat with FRA was used to determine the membrane resistance in a frequency range from 100 Hz to 50 kHz and signal amplitude 10 mV. Measurements were taken at 22ºC temperature. The membranes were immersed in a deionized water for 24 h and maintained RH = 100% in a measuring chamber.

Conductivity measurements of SPEEK membranes as well as Nafion membranes were performed through-plane using impedance analysis with various cell configurations. In differential method, the SPEEK membrane was sandwiched between two Nafion membranes and pressed between two copper electrodes (1 cm in diameter). The resistance R_1 was obtained from Nyquist plot extrapolating to the high frequencies. Using the same method, resistance of two Nafion membranes (R_2) was determined and as a result, from the difference between two of these measurements, resistance $R_{membrane}$ and conductivity of SPEEK membrane was calculated using equation (1).

$$R_{membrane} = R_1 - R_2 \tag{1}$$

In case of the single membrane method the SPEEK membranes were pressed between two copper electrodes. Impedance analysis was performed, and the resistance was found from Nyquist plot. The Nafion membrane was used as a reference. The conductivity of polymer membrane using differential and single membrane configuration was calculated from the complex resistance data from Nyquist plot and the results were compared with the literature data.

Scanning electron microscopy (SEM) method was used to inspect the membrane surface and characterize the mechanical damage before and after conductivity measurements for both SPEEK and Nafion membranes.

3. Results and discussion

In our work two methods for measuring conductivity are assessed. Results were compared with a literature data. In both cases, the same membrane preparation method was used and *N,N*-dimethylformamide as a solvent. Membrane thickness ranged from 0.12 to 0.18 µm and was measured with digital micrometer. Electrode surface area was 0.785 cm^2. Figure 1 shows cell configuration for differential and single membrane method. The variation of data (Figure 2, Table 1 and 2) is significant.

The Nafion and SPEEK membrane conductivities that were obtained by using both methods are shown in Table 3. The Nafion conductivity according to the product information is 0.10 S/cm and the same value was reproduced using differential method. As we can see from the Figure 2, the SPEEK membrane conductivity as a function of DS might be plotted as a line, if the same method is used for measurements. However, the data from both methods vary significantly. We can conclude that the contact resistance between electrodes and membrane is quite high. The usage of differential method allows to exclude it efficiently. From such point of view evaluating the literature data, it is evident that the contact resistance was the reason also for high variation of literature data.

It is worth mentioning that the cell stability can be evaluated via Kramer–Kronig test and during our measurements, the function χ^2, χ^2_{re} and χ^2_{im} values were between 10^{-5} and 10^{-6} and that means that the cell was stable, and equilibrium was not disturbed during impedance analysis.

Figure 3 shows an example of data for SPEEK membrane with DS = 0.82 impedance analysis with differential method. Nyquist and Bode plot were presented for cell configuration that consists of two Nafion membrane and one SPEEK membrane between them. Resistance is obtained from extrapolation to the high frequencies where imaginary impedance is equal to zero.

Extrapolation with semicircle method cannot be used in this case because full semicircle is not obtainable and therefore linear regression method is being used. Bode plot shows that the contact resistance is significant. Consequently, this explains higher resistance and lower conductivity for single membrane method and it shows that the differential method excludes contact resistance more efficiently.

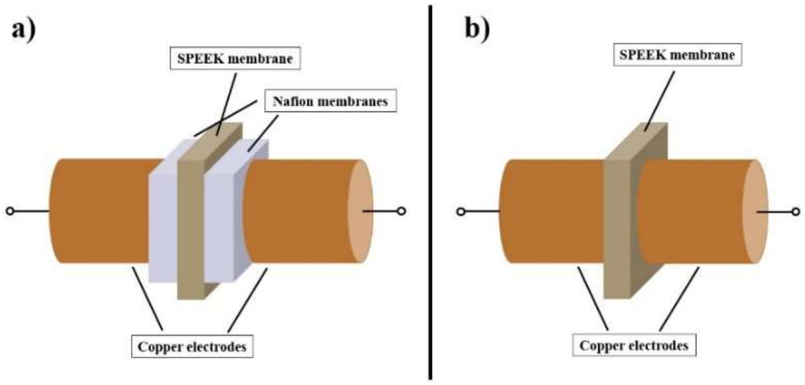

Figure 1. Representation of cell configuration: a) differential method, b) single membrane method

Table 1. Ion conductivities of SPEEK membranes as measured by differential method.

DS	σ. S/cm
0.34	0.0036
0.57	0.0071
0.71	0.0112
0.82	0.0146
0.89	0.0156

Table 2. The differential method as compared with a single membrane method.

Method	Ion conductivity σ, S/cm	
	SPEEK (DS = 0.82)	Nafion
Differential	0.015	0.095
Single membrane	0.0028	0.04

Table 3. Ion conductivity of SPEEK membranes from literature data.

DS	σ, S/cm	Reference	DS	σ, S/cm	Reference	DS	σ, S/cm	Reference
0.30	0.0060	[6]	0.67	0.0022	[8]	0.80	0.0114	[9]
0.36	0.0015	[7]	0.67	0.0075	[9]	0.81	0.0250	[6]
0.48	0.0020	[8]	0.69	0.0038	[10]	0.83	0.0072	[7]
0.48	0.0025	[7]	0.70	0.0013	[11]	0.84	0.0123	[9]
0.57	0.0039	[7]	0.74	0.0021	[11]	0.87	0.0134	[9]
0.57	0.0042	[9]	0.74	0.0091	[9]	0.88	0.0033	[10]
0.59	0.0009	[10]	0.78	0.0130	[6]	0.90	0.0095	[7]
0.63	0.0090	[6]	0.79	0.0160	[8]			
0.65	0.0059	[7]	0.80	0.0180	[6]			
0.67	0.0020	[10]	0.80	0.0080	[11]			

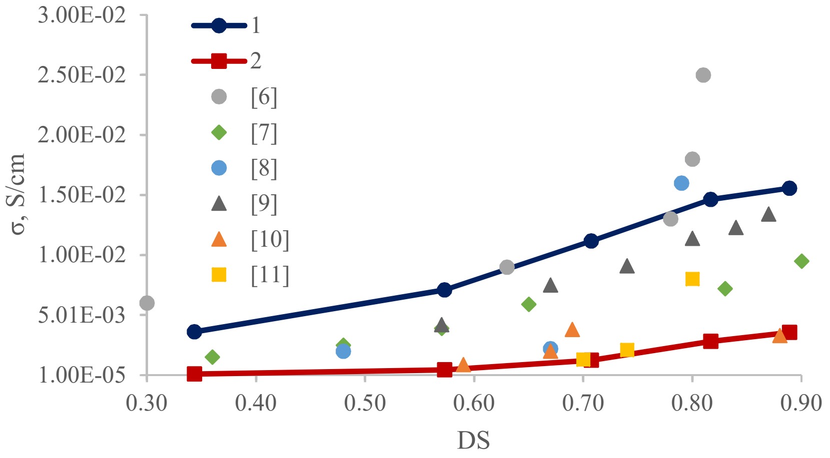

Figure 2. Ion conductivities of SPEEK membrane from literature data and by using two measuring methods: differential (1) and single membrane (2) method.

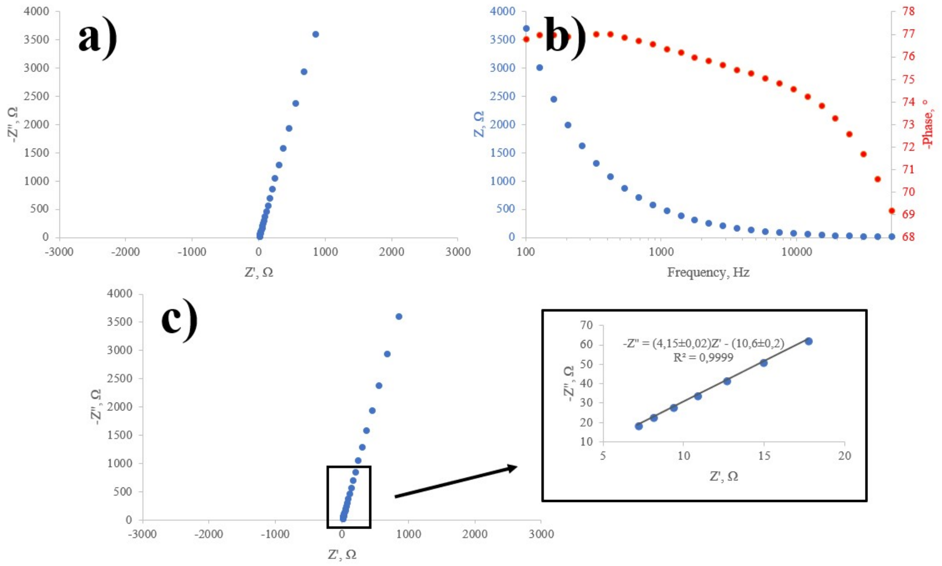

Figure 3. Impedance analysis for SPEEK membrane with a DS = 0.82 by applying differential method with two Nafion membranes: a) Nyquist plot, b) Bode plot, c) obtaining the resistance from Nyquist plot by extrapolating to the high frequencies.

SEM analysis was used to inspect the membrane surfaces. As an example, the SPEEK membrane with DS = 0.82 is presented. Figure 4 reveals some characteristic surface defects, which were produced during synthesis process. After impedance analysis with a differential method no additional defects were observed, but after measuring with a single membrane method, it is obvious, that there are significant scratches. Similar pattern was observed by inspecting Nafion membranes. After impedance analysis the increasing mechanical damage of the Nafion membrane surface could be observed. SPEEK membranes are less elastic, so the mechanical damage is also more pronounced.

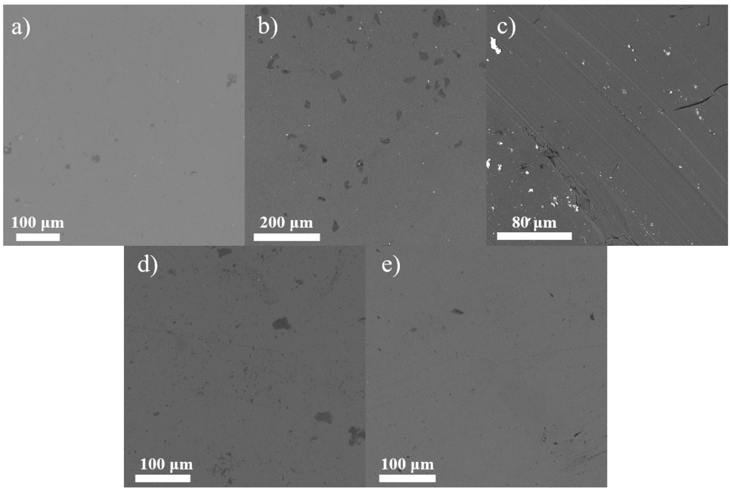

Figure 4. Scanning electron microscope images of SPEEK membrane with DS = 0.82: a) before impedance analysis, b) after impedance analysis with a differential method, c) after impedance analysis with a single membrane method, d) Nafion membrane before impedance analysis and e) Nafion membrane after impedance analysis with a differential method.

4. Conclusion

In this study sulfonated poly (ether ether ketone) membranes were studied using impedance analysis. Differential method proved to be more accurate in conductivity measurements as compared to the single membrane method. Commercial Nafion membrane was used as a reference. SEM analysis revealed also that the differential method is less damaging to the membrane surface. Therefore, the differential method in impedance analysis proved to be more efficient. The membranes are typically used in different solid state ionic devices and the same membrane might be used in a device also after conductivity measurements. The variety of distribution of literature data might be explained by variety of the contact resistance between membrane and measuring electrodes.

Acknowledgement

Authors of this work acknowledge funding from European Union`s Horizon 2020 Research and Innovation Program project under grant agreement No 768789.

References

[1] Hinds G 2017 *Curr. Opin. Electrochem.* **5** 11–9
[2] Luo H, Vaivars G and Mathe M 2010 *J. Power Sources* **195** 5197–200
[3] Luo H, Vaivars G and Mathe M 2012 *Int. J. Hydrogen Energy* **37** 6148–52
[4] Soboleva T, Xie Z, Shi Z, Tsang E, Navessin E and Holdcroft S 2008 *J. Electroanal. Chem.* **622** 145–52
[5] Boaretti C, Roso M, Lorenzetti A and Modesti M 2015 *Material* **8** 4096–117
[6] Luo H Proton conducting polymer composite membrane development for Direct Methanol Fuel Cell applications PhD Thesis 2008 University of the Western Cape Cape Town
[7] Yu F and Hu J 2016 *Int. J. Electrochem. Sci.* **11** 724–37
[8] Xing P, Robertson G P, Guiver M D, Mikhailenko S D, Wang K and Kaliaguine S 2004 *J. Membr. Sci*. **229** 95–106
[9] Xi J, Li Z, Yu L, Yin B, Wang L, Liu L, Qiu X and Chen L 2015 *J. Power Sources* **285** 195–204
[10] Kaliaguine S, Mikhailenko S D, Wang K P, Xing P, Robertson G and Guiver M 2003 *Catal. Today* **82** 213–22
[11] Zaidi S M J, Mikhailenko S D, Robertson G, Guiver M and Kaliaguine S 2000 *J. Membr. Sci.* **173** 17–34

Institute of Solid State Physics, University of Latvia as the Center of Excellence has received funding from the European Union's Horizon 2020 Framework Programme H2020-WIDESPREAD-01-2016-2017-TeamingPhase2 under grant agreement No. 739508, project CAMART²