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# IR SPECTRA STUDY: ADVANTAGES OF METHANOL VAPOR FEEDING FOR NAFION® MEMBRANE STRUCTURE

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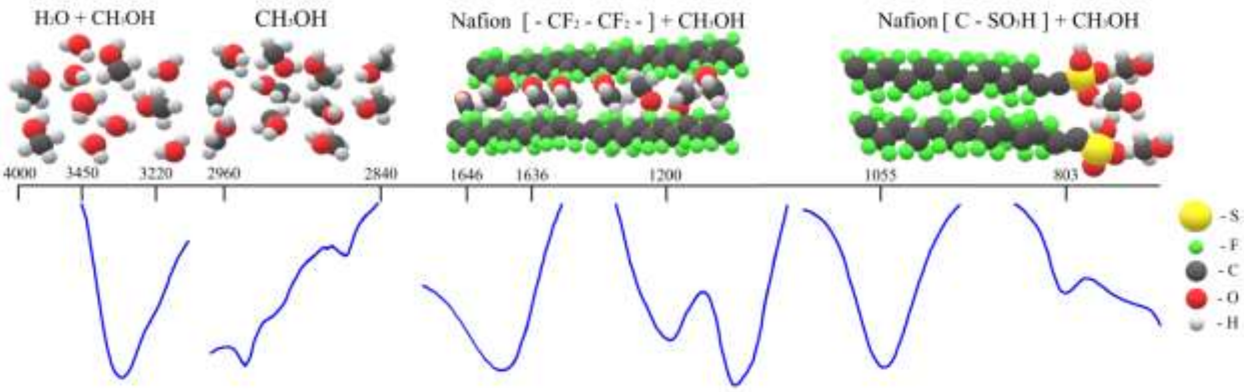
***Abstract:*** *This paper presents the IR-spectroscopy investigation of interaction between polymer proton-conducting membranes (Nafion® brand) and various solvents. The solvent effect on the formed membrane structure is determined. The advantages of saturating membranes with methanol vapors over dipping into water/water-methanol mixture for membrane properties as a solid polymer electrolyte in the fuel cell are shown. An original method of feeding methanol vapors to a fuel cell by a hydrogen flow is proposed.*



***Keywords****: membrane, solid polymer electrolyte, methanol vapor, IR spectroscopy, hydrogen*
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## Introduction

One of the major components of electrochemical devices with a solid polymer electrolyte is a proton exchange membrane (PEM). The DuPont's Nafion® membrane is most in demand as a polymer electrolyte. By its nature, this membrane is a perfluorinated polymeric sulfonic acid. It has a low ionic resistance, high mechanical strength and high chemical resistance. However, this type of membrane also has a number of disadvantages.

The membrane is most effective as a solid polymer electrolyte only if it is highly saturated with a solvent (water or water-alcohol mixture), which ensures the formation of proton-conducting channels inside its structure. Some of the publications consider the effects of water [1-3] and methanol [4] on the structure of membranes. Note that the standard method of dipping in a liquid solution is used to saturate the membranes. However, the effect of the solvent on the formed channels structure (the efficiency of proton conduction) in the case of using the solvent vapor to saturate membranes has not been properly studied. For fuel cells (FC) with direct alcohols (methanol) oxidation, a cross-over effect is also observed. This is associated with methanol diffusion to the cathode side of the device. The methanol flow through the membrane leads to a significant decrease in the performance of the electrochemical device. Also, attempts are being made to optimize the content of methanol in the fuel mixture to reduce this effect. The advantages of using 10 wt. % methanol solutions are shown in [5]. A partial strength reduction and dissolution of Nafion® membranes used as an electrolyte in FC with direct alcohols oxidation are investigated in water-methanol mixtures at various temperatures (up to 80 °C) [6].

From the perspective of the development of hydrogen energy and expansion of the scope of application of electrochemical devices, it appears important to improve reliability of their operation at subzero temperatures. In this case preference is given to FC with direct methanol oxidation (DMFC), which are more resistant to solvent solidification in the membrane volume at subzero temperatures. Studies of DMFC have shown advantages for the electrochemical performance of the devices when methanol is fed into the membrane electrode assembly (MEA) in vapor form as compared to liquid form. In the former case the performance of the device rises and that of the cross-over effect reduces [7, 8]. When methanol vapor is used, these processes can be significantly reduced or even prevented. Recently, researchers have been actively considering a new strategy for the use of hydrogen-air fuel cells at subzero temperatures, wherein resistance of the MEA to subzero temperatures is ensured by feeding alcohol vapor into the MEA volume as antifreeze [9, 10] as against standard methods of drying the MEA [11–25]. The addition of the antifreeze doubles the service life under conditions of subzero temperatures [9]. However, causes and mechanisms of these effects in regard to the membrane structure and properties are not currently reported.

In this work we study an interaction between various solvents (water/water-methanol mixture) and a Nafion® polymer proton conductive membrane. A comparative study of the interaction between membrane structure and methanol in the liquid and vapor phase is conducted. The advantages of feeding methanol vapor to the MEA are shown. IR spectroscopy is chosen as the main research method.

## Material and methods

### *Preparation of samples*

The paper considers the effect of solvents on the Nafion® membrane structure (two brands: Nafion®115 with a thickness of 127 μm and Nafion®212 with a thickness of 50 μm). The membranes are saturated with a solvent from the vapor/liquid phase.

The saturation time of the membranes immersed in liquid (water/water-methanol mixture) was 20 minutes, which is sufficient to stabilize the membrane structure [4]. Further saturation did not have a significant effect on changes in the membrane structure. A 10 wt. % methanol water solution was used.

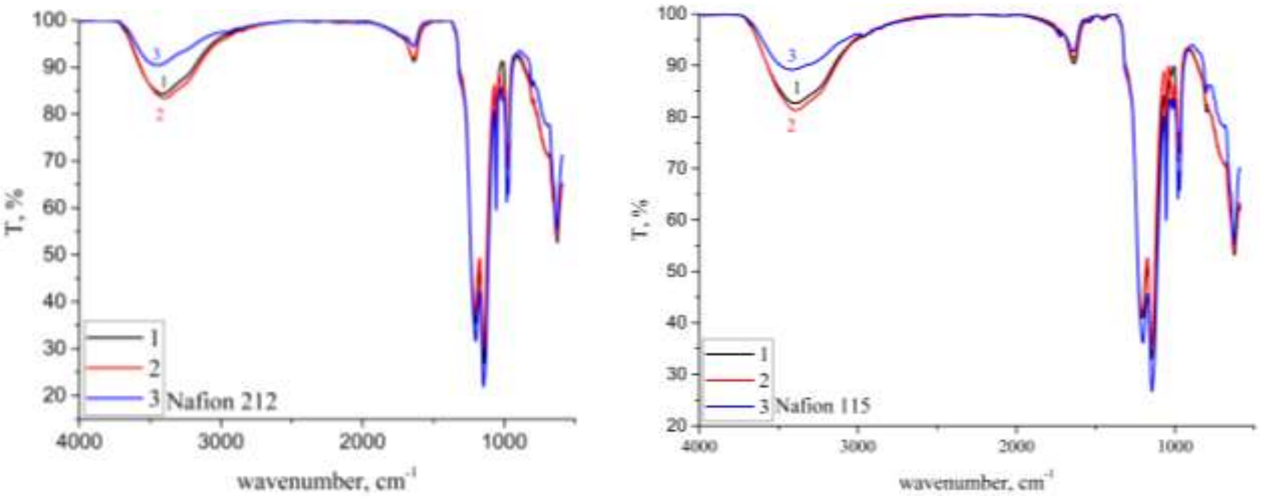
The membranes were saturated with methanol vapor in a closed cell. Hydrogen was used as a carrier gas. The carrier gas was humidified by passing through the volume of water-methanol mixture at 50º. The saturation time was 1 hour, which ensured stability of the methanol content in the volume of saturated membranes. A 10 wt. % methanol water solution was used.

### *Research*

The Nicolet iS5 FTIR spectroscopy complex was used. The effect of methanol on the membrane structure is associated with the IR spectral lines listed below. 3220 – 3450 cm$^{-1}$ lines correspond to the stretching of the O-H water and methanol group. 2840 – 2960 cm$^{-1}$ lines correspond to the stretching of the C-H methanol group. The peak at 1636 – 1646 cm$^{-1}$ lines corresponds to the vibration of the O-H methanol group. The shift of the peaks towards higher wave numbers shows that a greater number of methanol molecules interact with the hydrophobic domain in the Nafion® membrane structure. The peak at 1200 cm$^{-1}$ line for the dry membrane corresponds to vibrations of the -$SO_3^-$ and -$CF_2$ groups. When methanol is added, the peak shifts towards higher wavenumbers, indicating the interaction of methanol and the hydrophilic/hydrophobic domains. The peak at 1056 cm$^{-1}$ line corresponds to the vibrations of the -$SO_3^-$ group. The shift of the peaks towards lower wavenumbers (line 1055 cm$^{-1}$) indicates the interaction of the hydrophilic groups and methanol molecules. The peak size at 1015 cm$^{-1}$ line increases with increasing methanol concentration. The peak at 803 cm$^{-1}$ line corresponds to the stretching of the C-S bond due to the interaction of the structure with methanol.

## Results and discussion

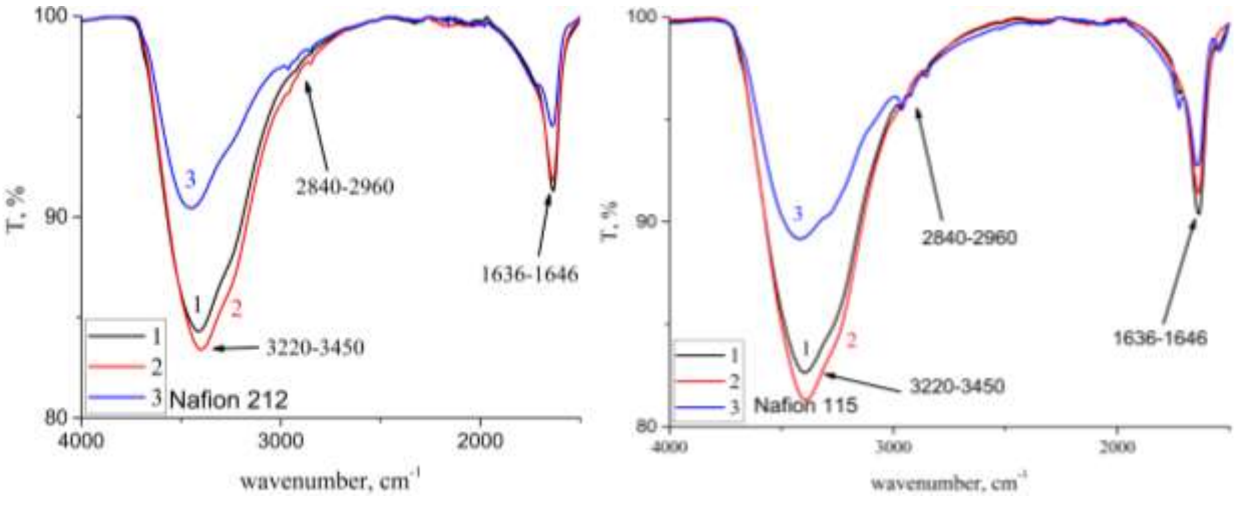
Fig. 1 (A and B) shows the IR-spectra of the investigated membrane samples. No effect of the membrane thickness on the results was observed. The free-state moisture content in the membranes saturated from the liquid phase (Fig. **2**: lines 3220-3450 cm$^{-1}$) is identical to both water and water-methanol mixtures, and higher than in the membranes saturated from the gas phase. Thus the use of a water-methanol mixture increases the total moisture capacity of the membrane by no greater than 15%, which was shown earlier [5]. The moisture capacity of a membrane saturated in a 10 wt. % water-methanol mixture is 25.6 wt. % versus 22.4 wt. % for saturation in water. The characteristic peaks of free methanol are reflected by 2840–2960 cm$^{-1}$ lines (Fig. **2**) and 1015 cm$^{-1}$ line (Fig**. 3**) of the spectrum. The content of free methanol in the membrane is maximal for membranes saturated with a water-methanol mixture from the liquid phase. There are no characteristic methanol peaks (2840–2960 cm$^{-1}$ and 1015 cm$^{-1}$) in the spectrum of the membrane saturated with water (Figs. 2 and 3). A reduction in the amount of free moisture in the membranes volume has a positive effect on their integrity at solidification under subzero temperatures [5].



A

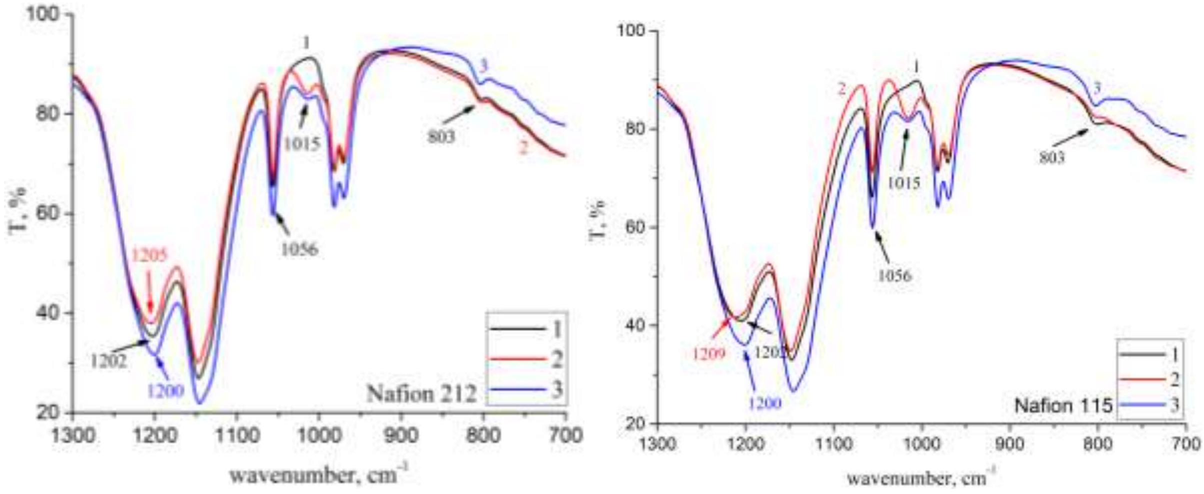
B

**Fig. 1.** IR-spectra of Nafion® 212 (A) and 115 (B) membranes saturated in different conditions: 1 – dipping in water, 2 – dipping in water-methanol mixture, 3 – saturation with methanol vapor.



A B

**Fig. 2.** IR-spectra fragments in the range from line 1500 to 4000 cm$^{-1}$ for Nafion® 212 (A) and 115 (B) membranes saturated in different conditions: 1 – dipping in water, 2 – dipping in water-methanol mixture, 3 – saturation with methanol vapor.



A B

**Fig. 3**. IR-spectra fragments in the range from line 700 to 1300 cm$^{-1}$ for Nafion® 212 (A) and 115 (B) membranes saturated in different conditions: 1 – dipping in water, 2 – dipping in water-methanol mixture, 3 – saturation with methanol vapor.

When considering the peaks characterizing the interaction between methanol and hydrophilic domain of the membranes (Fig.3: 1056 cm$^{-1}$ and 803 cm$^{-1}$ lines), there is observed an increase in the peak intensity for membranes saturated with water-methanol mixture from the vapor phase compared to saturation from the liquid phase, as well as their greater displacement relative to the peaks corresponding to the membrane saturated with water. This point to a greater amount of methanol associated with the membrane structure in hydrophilic domains upon saturation with methanol vapor, which leads to domain stretching and growth of proton conductive channels size. This effect reduces the ohmic and polarization resistance of the membrane as a part of an electrochemical device [26].

In the region characterized by the interaction between methanol and hydrophobic structure of Nafion® membranes (Fig. 2: 1636–1646 cm$^{-1}$ lines and Fig. 3: 1200 cm$^{-1}$ line), a greater peak shift is observed for membranes saturated by dipping into the liquid phase. The predominant distribution of methanol over the hydrophobic domain leads to its flow across the membrane and the cross-over effect, which adversely affects the performance of the FC [5]. When water-methanol mixture vapor is used for saturating the membrane, this process is not observed. In this way, the cross-over effect is reduced. Our results are confirmed by earlier studies of FCs with direct methanol oxidation [7, 8] where the authors conclude that the methanol cross-over effect across the membrane is reduced when methanol vapor is used.

The use of the method of saturating the membrane with water-methanol mixture from vapor phase with a hydrogen flow reduces the amount of free water/methanol in the pores and increases the binding of water/methanol in the hydrophilic domains of the membrane, which contributes to the stretching of the S-C chains in the membrane structure. This leads to an increase in the size of the channels, an increase in the proton conduction efficiency, and a decrease in the ohmic resistance of the membrane. Methanol redistributes between the hydrophobic matrix of the membranes and hydrophilic domains, evenly distributing throughout their volume without accumulating in pores. Also, the presence of methanol associated with the hydrophobic domain leads to the membrane swelling and an increase in the distance between polymer chains compared to the aqueous phase, which makes the polymer material more elastic. This has a positive effect on the spatial arrangement of chains of the hydrophobic matrix of the membrane at the solidification temperatures of the solvent, providing a high degree of polymer relaxation and preservation of its integrity under subzero temperatures, in particular during freeze-thaw cycling [5].

## Conclusions

In this work, the effect of the solvent on the membrane structure is determined by the IR spectroscopy. The advantages of using methanol vapor as compared to dipping into water/water-methanol mixture for the properties of the membrane as a solid polymer electrolyte in the fuel cell are shown. There is observed a decrease in free solvent capable of solidifying under subzero temperatures. The amount of methanol associated with the membrane hydrophobic domain reduces. This reduces the cross-over effect of methanol across the membrane to the cathode region. The methanol content in the hydrophilic domains of the membrane increases, providing for the growth of the size of proton conductive channels. An original method for supplying methanol vapor to a fuel cell with a hydrogen flow is proposed.

### CRediT authorship contribution statement

**D.D. Spasov:** Conceptualization, Methodology, Investigation, Writing. **R.M. Mensharapov:** Conceptualization, Methodology, Investigation, Writing. **N.A. Ivanova:** Conceptualization, Supervision, Investigation, Writing.

### Declaration of competing interest

The authors declare that they have pursued no competing financial interests or personal relationships that could have appeared to influence the work as shown in this article.

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# ИК-СПЕКТРОМЕТРИЯ: ПРЕИМУЩЕСТВА ПОДАЧИ ПАРОВ МЕТАНОЛА ДЛЯ СТРУКТУРЫ МЕМБРАН NAFION®

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***Аннотация:*** В работе методом ИК-спектроскопии исследовано взаимодействие различных растворителей с полимерной протонпроводящей мембраной марки Nafion®. Установлено влияние растворителя на структуру мембраны. Показаны преимущества использования паров метанола по сравнению с водой/метанолом в жидкой фазе для свойств мембраны в качестве твердого полимерного электролита в составе ячейки топливного элемента. Предложен оригинальный способ подачи паров метанола в ячейку с потоком водорода.

***Ключевые слова:*** *мембрана, твердый полимерный электролит, пары метанола, ИК-спектроскопия, водород*

## İQ-SPEKTROMETRİYA: NAFİON® MEMBRAN STRUKTURU ÜÇÜN METANOL BUXARININ VERİLMƏSİNİN ÜSTÜNLÜKLƏRİ

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***Xülasə:*** Bu işdə müxtəlif həllediсilərin Nafion® markalı polimer proton keçirici membranı ilə qarşılıqlı təsiri İQ spektroskopiya metodu ilə tədqiq edilmişdir. Həllediсinin membran quruluşuna təsiri müəyyən edilmişdir. Yanacaq hücrəsinin tərkibində bərk polimer elektrolit kimi membranın xassələri üçün maye fazada su/metanol ilə müqayisədə metanol buxarının istifadəsinin üstünlükləri göstərilmişdir. Hidrogen axını olan hücrəyə metanol buxarının verilməsi üçün orijinal üsul təklif olunur.

***Açar sözlər:*** *membran, bərk polimer elektrolit, metanol buxarı, İQ-spektroskopiya, hidrogen*