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# Charge and mass transport in the phenol-2,4-disulfonic acid-polyvinyl alcohol ion exchange membranes studied by pulsed field gradient NMR and impedance spectroscopy

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## Abstract

The self-diffusion of water molecules, $H^+$ and phenol-2,4-disulfonic acid molecules in phenol-2,4-disulfonic acid–polyvinyl alcohol membranes was investigated. The acid molecules are formed in clusters, therefore, the acid self-diffusion is restricted. The restriction size, which is about $10^{-7}$ m, and degree of cluster connection are controlled by the membrane compound. The behaviour of protonic conductivity is very similar to the water molecule self-diffusion. The conductivity mechanism is vehicle type at high water content and relay-race type at low water content.

*Keywords:* Fuel cell; Phenol-2,4-disulfonic acid–polyvinyl alcohol membranes; Self-diffusion; Protonic conductivity; Pulsed field gradient NMR; Impedance spectroscopy

## 1. Introduction

The low temperature fuel cell efficiency is determined by the polymeric membrane protonic conductivity, which is controlled by the proton and water molecule translational mobilities. Therefore, the comparison of mass and charge transport parameters is necessary to interpret the membrane transfer mechanism.

Pulsed field gradient NMR (PFG NMR) is an established method of the direct self-diffusion coefficients measurements of solvate molecules and counter ions in ion-exchange systems.

The self-diffusion of water molecules, $H^+$ and $Li^+$ in sulfonation perfluorinated Nafion [1], MF-4SK [2,3], polystyrene [3] and aromatic polyamide membranes [4] was investigated. Microscopic ionic and water molecule mobilities in perfluorinated MF-4SK membranes were determined by $^1H$ and $^7Li$ NMR relaxation techniques. The self-diffusion coefficients of $Li^+$ ions and water molecules from Einstein equation were calculated [3,5]. The calculated self-diffusion coefficients are in good agreement with the self-diffusion coefficients measured directly by PFG NMR. Therefore, it was concluded, that the macroscopic charge and mass transfer is controlled by the local ion and molecule jumps between adjacent sulfo groups. The dependences of $Li^+$ and $H_2O$ self-diffusion coefficients on membrane humidity are similar, so ionic and water molecules translation motion is correlated [2]. This correlation is especially important for the $H^+$ transfer. The proton transport occurs along a hydrogen bond network formed by water molecules (relay race mechanism). Proton translational motion is also possible together with water molecules during water self-diffusion (vehicular mechanism). The humidity threshold exists below which the water and proton mobility is very low. Decrease in this critical water content is very important for the fuel cell membranes. The value of the threshold is determined by the concentration of sulfonate group, the mode of sulfonate group distribution, ionic transport channel structure and the existence of charge groups forming additional H-bonds in polymeric matrices [2,4]. The quantitative relations of structural and motion parameters were derived from the percolation theory [2,6]. The values of critical threshold water content for the polystyrene and perfluorinated membranes are about 5 water molecules per sulfonate group [2,3]. For the aromatic

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polyamide membranes humidity threshold is lower (2–3 water molecules per sulfonate group) because carbonyl polymeric groups are also involved in hydrogen bond forming [4]. From the point of view of the humidity threshold reducing, the composite membranes on the basic of phenol-2,4-disulfonic acid–polyvinyl alcohol are very attractive [7]. At low water content the protonic conductivity in these membranes is one order of magnitude higher than that of the classical fuel-cell membrane Nafion.

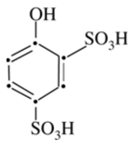
The investigation of proton conductive mechanism is necessary in further improve most of this type of membranes. The conductive mechanism may be understood on basis of mutual diffusivity and conductivity investigations. These kind of measurements were realized in polymer electrolytes [8–10], polyphosphate composite [11] and gel electrolyte [12]. The comparison of ionic conductivity obtained from the NMR diffusivities using Nernst–Einstein equation with those from the direct measurement enables to estimate the ionic associations [8–10] and to understand the type of conductivity mechanism [11]. The correlation between plasticizer mobility and ion diffusion in gel electrolyte was found [12].

This research concentrates on dependence of the main features of proton conduction and self-diffusion in phenol-2,4-disulfonic acid–polyvinyl alcohol membranes as function of composition. The pulsed field gradient NMR and impedance spectroscopy techniques are applied for this investigation.

## 2. Materials and methods

Self-diffusion and protonic conductivity of the phenol-2,4-disulfonic acid and composite phenol-2,4-disulfonic acid polyvinyl alcohol (PSA–PVA) membranes were measured.

Phenol-2,4-disulfonic acid polyvinyl alcohol membranes were prepared from the mixture of aqueous (2.5% by weight) polyvinyl alcohol (–(–$CH_2$–CH(OH)) $_n$–) solution and phenol-2,4-disulfonic acid solution by the way of sprinkling on the teflon substrate. The ratio of molar ratios of polyvinyl alcohol monomeric units to acid component was 4/1, 6/1, 8/1 and 10/1 [7]. In order to prepare cross linked membranes, the glutaraldehyde ($CHO(CH_2)_3CHO$) (0.5, 1.0, 1.5, 2.0, 3.0 molar fraction) were added in phenol-2,4-disulfonic acid–polyvinyl alcohol solution, containing the molar fraction of phenol-2,4-disulfonic acid equal 4/1. The amount of glutaraldehyde is in percent ratio of molar fraction to amount of polyvinyl alcohol units.



The given value of relative humidity was achieved by the sample equilibration in desiccator during 1 week.

The self-diffusion measurements were carried out on home-made set up machine, the NMR frequency for protons was 100 MHz, stimulated spin-echo pulsed sequence was used, maximum value of magnetic field gradient amplitude was 40 T/m. The experimental details have been described previously in [13].

The dependence of spin echo amplitude $A(g)$ on gradient amplitude g (diffusion decay) was analyzed. The diffusion decay decomposed on the exponential components.

$$A(g) = A(0)\sum_{i}^{m} p_i \ \exp\left(-\gamma^2 g^2 \delta^2 t_d D_{\mathrm{si}}\right) \qquad (1)$$

$$\sum_{i}^{m} p_i = 1 \qquad (2)$$

where $\gamma$ — gyromagnetic ratio for protons, $\delta$ — is duration of the magnetic field gradient pulse, $t_d = \Delta - \delta/3$ is diffusion time, $\Delta$ is interval between magnetic gradient pulses, $D_{\mathrm{si}}$, $p_i$ — are the self-diffusion coefficient and population, accordingly, in $i$-th diffusion state (or phase). The Eq. (1) is applied for multi phased systems containing $i$ different phases where the self-diffusion coefficients $D_{si}$ and the relative amount of diffusate (or populations) $p_i$ are differ. The details are given in [13,14].

The self-diffusion was characterized by two or three self-diffusion coefficients for PSA–PVA system (m is equal 2 or 3 in Eq. (1)) and three self-diffusion coefficients for PSA–PVA cross-linked films (m are equal 3 in Eq. (1)).

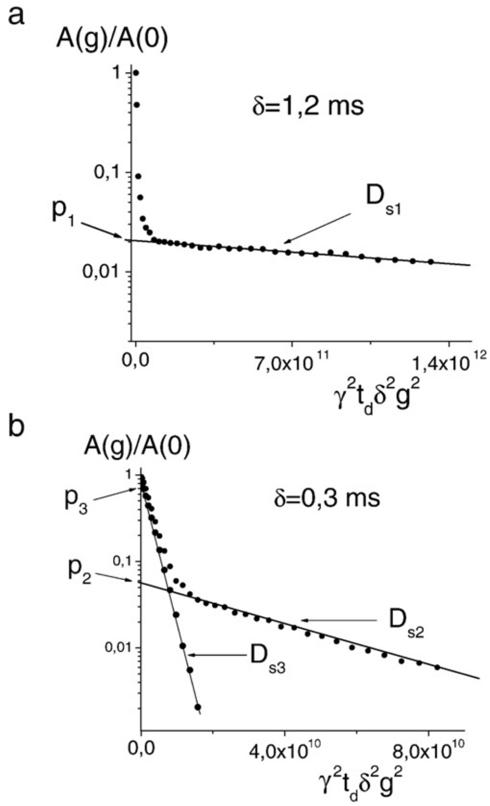


Fig. 1. Dependence of the stimulated spin-echo attenuation on the pulsed field gradient amplitude in the phenol-2,4-disulfonic acid polyvinyl alcohol membrane. The amount of cross linked glutaraldehyde is 1%. The sample was equilibrated at the 75% relative humidity. The gradient pulse durations are 1.2 ms (a) and 0.3 ms (b). The experimental dots in b are the result of subtraction the straight line with parameters $p_1$, $D_{s1}$ (a) from the initial experimental curve.