

POLYMERIC PROTON CONDUCTING MEMBRANE BASED ON POLY(VINYL ALCOHOL) AND AROMATIC ACIDS

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Introduction

Proton conducting polymeric electrolytes are widely used as proton conducting membranes in polymeric membrane fuel cells in recent years.

High thermal stability, mechanical strength, gas impermeability, high moisture adsorption stability and conductivity $\sim 10^{-3} - 10^{-1}$ S/cm at 298 K are the basic requirements for proton conducting polymeric electrolytes used as membranes in fuel cells.

The aim of this work was preparation of new generation of proton conducting membranes, which would keep high transport parameters in wide temperature and humidity range, and testing their in hydrogen-oxygen fuel cell.

Objects

As the objects of research were chosen the individual aromatic acids, which contain carboxylic, hydroxyl- and sulfonated groups; polymeric electrolytes based on poly (vinyl alcohol) (PVA) and aromatic acids, which were obtained by casting technique.

Experimental details

Thermal stability was determined by differential-thermal analysis (Q-1500D) and differential-scanning calorimetry (STA 409PC). Conductivity measurement were carried out by impedance spectroscopy (Elins Z-350M). Structure was investigated by IR-spectroscopy. To measure characteristics of fuel cells containing investigated membranes we used cyclic voltamperometry and EMF tests.

Results and discussion

The influence of composition and structure of crystalline aromatic benzenepolycarboxylic and sulfonic acids with different location and quantity of carboxylic, hydroxyl and sulfonate groups on proton transport parameters were investigated.

Aromatic carboxylic acids have low proton conductivity value that is caused by proton transport on crystal structure defects. The conductivity of aromatic benzene polycarboxylic acid does not exceed 10^{-12} S/cm at moisture absence in environment.

Visible proton conductivity was detected only at relative humidity > 40 % rel. Conductivity rises up to $10^{-5} - 10^{-6}$ S/cm when humidity increased up to 95 % rel. [1].

Crystalline aromatic compounds which contain SO_3H -groups keep high proton conductivity even at vacuum ($10^{-5} - 10^{-6}$ S/cm). It greatly increases when environment humidity increased. However they «become blurred» on air to form liquid phase already at ~ 30 % rel. humidity.

Introduction individual aromatic carboxylic and sulfonic acids in to organic polymeric matrix with its own continuous hydrogen bonds system may be the good way to overcome those own lacks. We used the PVA as polymeric matrix. Besides the presence of hydrogen bonds system the polymers based on PVA possess low gas impermeability and high adhesion to the most of materials that is determinant factor for fuel cell development.

PVA – benzenepolycarboxylic acid system membranes are gas-proofed and possess conductivity from 10^{-5} to 10^{-6} S/cm at 95 % relative humidity (table 1) and are dissolvable in water. Homogeneous films can be obtained only at PVA – acid molar ratio 10 : 1 and more. However, the conductivity of obtained polymeric materials greatly exceed conductivity of individual acid even at high dilution by PVA.

Homogeneous films with conductivity up to $10^{-3} - 10^{-2}$ S/cm at 95 % rel. humidity were obtained by sulfonic acid introduction in PVA in the investigated composition interval. The lack of membrane doped by aromatic sulfonic acid is its high hygroscopicity that results in decrease of membranes mechanical strength: transfer to gel-like state at PVA – acid molar ratio and more than 1 : 0.5.

PVA – phenol-2,4-disulfonic acid electrolyte possess the most high conductivity among investigated systems based on sulfonic acids. All synthesized films are optically transparent, homogeneous and roentgenamorphous. Quantity of water absorbed by film and its conductivity depend on environment humidity, temperature and composition (fig. 1).

Table 1. Polymer electrolyte proton conductivity depend on humidity

acid	σ_{298} , S/cm PVA : acid (10 : 1)	
	47 % RH	95 % RH
benzoic	$3.1 \cdot 10^{-8}$	$9.7 \cdot 10^{-8}$
1,4-benzenedicarboxylic	$1 \cdot 10^{-8}$	$3.7 \cdot 10^{-6}$
1,2,4-benzenetricarboxylic	$1.2 \cdot 10^{-8}$	$9.2 \cdot 10^{-6}$
4-hydroxybenzoic	$8 \cdot 10^{-9}$	$4.1 \cdot 10^{-6}$
2,5-dihydroxybenzoic	$1.7 \cdot 10^{-8}$	$2.4 \cdot 10^{-4}$
p-toluenesulfonic	$1.1 \cdot 10^{-4}$	$1.7 \cdot 10^{-2}$
p-phenolsulfonic	$3.6 \cdot 10^{-4}$	$2.4 \cdot 10^{-2}$
phenol-2,4-disulfonic	$1.5 \cdot 10^{-2}$	$4.3 \cdot 10^{-2}$
5-sulfosalicylic	$6.8 \cdot 10^{-5}$	$6.5 \cdot 10^{-3}$
flavianic	$6.2 \cdot 10^{-5}$	$3.4 \cdot 10^{-3}$

Synthesized films are stable up to 373 K. Conductivity temperature dependence is described better by VTF-equation at low humidity (< 30 % rel.) and by Arrhenius equation at higher humidity. It is caused by the change of conductivity mechanism from thermoactivation (at high humidity) to ion transport model at the movement of polymeric chain (at low humidity).

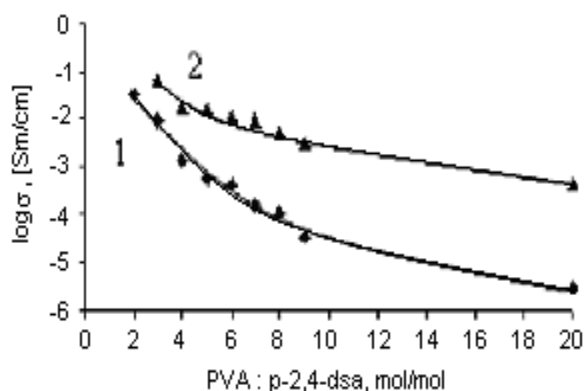


Fig. 1. Film conductivity dependence vs PVA- p-2,4-dsa molar ratio at different humidity (% rel.): 1 – 32, 2 – 44

Conductivity of obtained materials exceed Nafion (fig. 2). in considered temperature and humidity range.

The possibility of practical application membrane based on PVA and phenol-2,4-disulfonic acid in construction of single fuel cell that consist of membrane, Pt-black catalyst, gas diffusion layer from porous carbonic paper («Ballard®» AvCarbTMP50T) as current collector [2] was investigated.

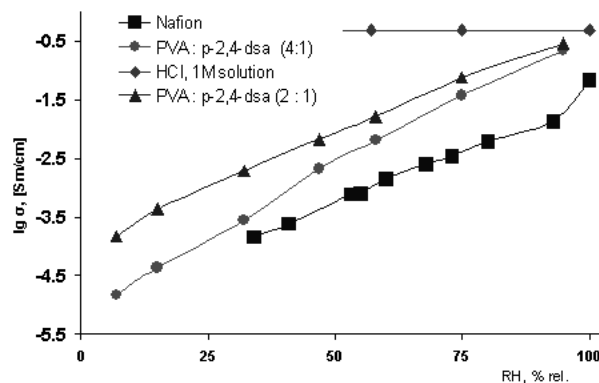


Fig. 2. Proton conductivity for different materials at 298 K

The EMF of investigated fuel cells is about 1 ± 0.03 V does not depend on membrane composition and environment humidity.

By impedance spectrum analysis it was shown that exchange current in H_2 media noticeably exceed exchange current in air media and does not depend on membrane composition and environment humidity.

The parameters of the fuel cells based on membranes with high concentration of phenol-2,4-disulfonic acid do not depend on environment humidity at electrochemical H_2 oxidation process because of presence of water in reaction products and its fast redistribution in proton conducting membrane volume.

An effective cell work can be realized at humidity > 32 % rel. Current density reaches 250 mA/cm^2 at 0.4 V in investigated cells and the maximum power of their is more than 100 mW/cm^2 .

Acknowledgement

This work was supported by RFBR project № 03-03-32422.

Literature

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