POLYTETRAPHENYLMETACYCLOPHANOCTOLS AS POLYELECTROLYTES OF FUEL CELL

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Introduction

The application of the new polymeric electrolytes with high ionic and low electronic conductivity in a wide temperature interval, chemical and electrochemical stability, and good physicomechanical properties is perspective direction of perfection of chemical sources of electric energy. Novel polymers based on metacyclophanoctols have properties of cation exchange materials [1−3] hence swelled ones have ionic electric conductivity.

The aim of this work was research of electric conductivity of polytetraphenyl-metacyclophanoctol (I) and sulphonated polytetraphenylmetacyclophanoctol (II)

I: R=Ph,

II: R=Ph-SO₃H   ,
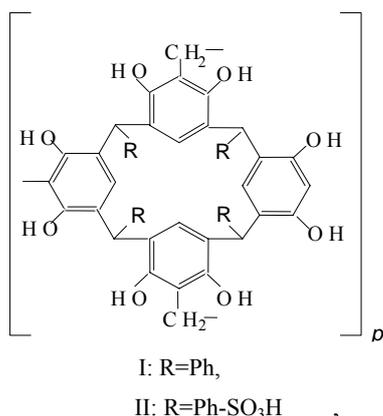
equilibrated with aqueous solutions of electrolytes.

Results and discussion

Electric conductivity of swelled cation exchangers to which belongs researched polymers has ionic character and essentially depends on type of mobile counter-ion [4]. Values of specific electric conductivity of network polymers based on cis-tetraphenylmetacyclophanoctol in the H^+, Na^+, Li^+, Ag^+, Cu^{2+}, Ni^{2+}, Ba^{2+} forms are presented in the table.

Values of specific electric conductivity of metal forms of sulphonated polymer (II) are a little bit above than the electric conductivity of appropriate forms of polymer I.

Essential distinction in electric conductivity of H-form of polymers is determined by the different

Table 1. The specific electric conductivity of polymers (χ); the diffusion activation's energies (E_a) and coefficients of self-diffusion ($\overline{D}_i$) of cations in polymer equilibrated with solutions of electrolytes at 298 K.

Electrolyte	$\chi \cdot 10^4$, S·cm^{-1}	$\overline{D}_i \cdot 10^6$, cm^{-2}·s^{-1}	E_a, kJ·mol^{-1}
Polymer I			
HCl	3.3± 0.5		
LiOH	99.5±0.8	5.3±0.7	19.1±2.1
NaOH	118.8±0.8	7.0±0.7	19.9±2.1
Ba(OH)₂	17.6± 0.8	0,2±0.1	25.7±2.1
Polymer II			
HCl	2080±0.5		
LiCl	120±0.5	5.2±0.5	14.0±1.6
NaCl	134.8±0.5	9.2±0.5	14.6±1.6
AgNO₃	117±0.5	6.9±0.4	15.0±1.5
BaCl₂	38.9±0.8	1.1±0.1	14.1±1.6
CuCl₂	43±0.5	0.56±0.03	16.6±1.6
NiCl₂	40±0.5	0.52±0.03	16.3±1.5
LiOH	131.7±0.8	4.2±0.7	14.2±2.1
NaOH	156.6±0.8	6.5±0.7	16.1±1.6
Ba(OH)₂	28.4±0.8	0.2±0.1	20.2±2.1

contents of mobile protons: ion migration in the polymer I are caused by presence of weak acid resorcinol OH−groups, the polymer II contains as phenolic OH−groups, and strong acid SO₃H−groups dissociating with formation of free protons in a wide pH range [2].

Electric conductivity of sulphonated polymer in the form of double-charged cations averages between 0.003 − 0.004 S·cm^{-1}. It increase till 0.01 − 0.02 S·cm^{-1} for single-charged metal cation forms and reaches 0.2 S·cm^{-1} in case of the H−form of polymer II. In the systems containing H^+ the relay race mechanism of the charge moving is the reason of the much greater electric conductivity of the H-form in comparison with salt forms of polymer II, probably. The increase of electric conductivity of polymer when double-charged cations are replaced by single-charged metal cations can be caused by the easing of electrostatic interaction of the immobilized ion with counter-ion.

It would appear reasonable that the easing coulombic interactions of cations with functional

groups of polymer will be accompanied by increase of self-diffusion coefficients and reduction of activation's energies of counter ion diffusion in the polymer phase. Really, the values of cation self-diffusion coefficients in polymers phase (table 1) calculated by Nernst-Einshtein equation increase with reduction of cation charges.

The diffusion activation's energy of metal cations in polymer is calculated according to Arrhenius equation on values of angular factors of an inclination of linear dependences $\ln \overline{D}_i$ from $1/T$ (Fig. 1). Ones remains constant in an interval of temperatures 298-333 K. Energy of activation of metal cation diffusion in the polymer II equilibrated with salt solutions averages between $14 - 15$ kJ·mol^{-1}, it has no expressed dependence on cation charges and does not reflect the cation position in the sequence of electric conductivity of the investigated polymer ionic forms. Hence, the probability of decrease of double-charged cation mobility in comparison with single-charged metal cation mobility because of additional interactions with a polymeric matrix at ionization only SO_3H-groups is insignificant. When the polymers equilibrated with alkaline solutions and not only strong acid, but also weak acid resorcinol OH-groups are ionized, the value E_a for Ba^{2+} is higher than energy of activation of Li^+, Na^+ diffusion. It is possible because of amplification of Ba^{2+} interaction with resorcinol OH−groups favorably grouped in $cis-$tetraphenylmetacyclophanoctol structure.

Conclusions

Electric conductivity of polytetraphenyl-metacyclophanoctols in the form of single-charged metal cations (0.01-0.015 S·cm^{-1}) is comparable with ionic conductivity of not aqueous electrolyte solutions in lithium sources of electric current and solid sodium aluminate offered as electrolytes in chemical sources of a electric current. Electric conductivity of H−form of sulphonated polytetraphenylmetacyclophanoctol (0.2 S·cm^{-1}) surpasses conductivity of electrolytes in fuel cells.
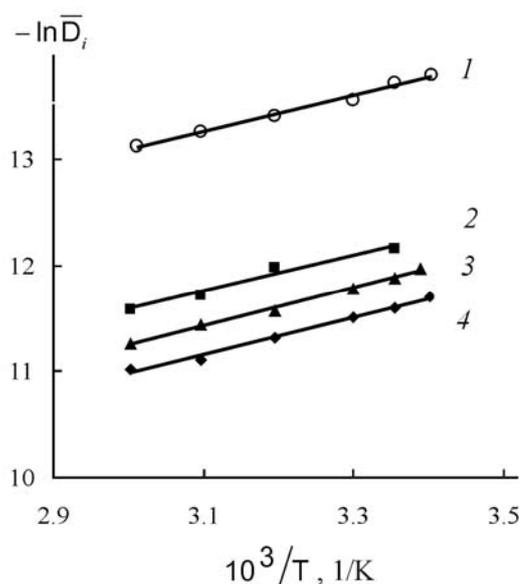
Fig. 1. Self-diffusion coefficients of Ba^{2+} (*1*), Li^+ (*2*), Ag^+ (*3*), Na^+ (*4*) cations in polymer II.

References

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