



Study of the transport of alkali metal ions in a nonaqueous polymer electrolyte based on Nafion



E.A. Sanginov, R.R. Kayumov, L.V. Shmygleva, V.A. Lesnichaya, A.I. Karelin, Yu.A. Dobrovolsky *

Institute of Problems of Chemical Physics of RAS, 142432 Chernogolovka, Russia

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ABSTRACT

Single-ion conducting polymer electrolytes have received great attention due to their potential applications in electrochemical energy sources. In this work we have in detail studied features of ion transport of alkali metal ions in the polymer electrolytes based on Nafion plasticized with DMSO. The samples have been characterized by DSC, FTIR, and impedance spectroscopy. Based on the obtained results the speculations about the reasons for the presence of extremes in dependencies of both ion conductivity and activation energy on cation radius have been made. It is also suggested that solvate $\text{Li}^+(\text{DMSO})_4$ is the minimum transport unit in Nafion- Li^+ swollen in DMSO.

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1. Introduction

In connection with active development of electrochemical power sources, great attention is paid to the designing of new liquid, gel, polymer, and inorganic materials possessing high lithium-ion conductivity [1–7]. Among them the works on creation of solid polymer electrolytes single ion conductivity is of prior interest due to their high mechanical and structural characteristics, wide operating temperature range, and wide window of electrochemical stability [8,9]. The development of solid polymer electrolytes is of most particular interest when applied to creation of power-consuming devices with the use of reactive electrode materials (Li, Na, Mg, etc.).

Different single-ion conducting polymer electrolytes such as lithium polyacrylates [10–13], lithium salt of sulfonated polymers based on polyethylene oxides and polyethylene glycols [14–17], polyacrylates [18–22], aromatic polymers [23–28], etc. have been prepared and studied.

The polymer electrolytes based on ionomers with perfluorinated ionizable groups ($-\text{CF}_2\text{SO}_3^-$, $-\text{SO}_2\text{N}^-\text{SO}_2\text{CF}_3$, etc.) [17,18,22,24–38] are high-potential materials among the electrolytes with single cation conductivity, due to the presence of the weakest coordinating anions providing a high concentration of counter ions in nonaqueous media, which in turn favors the ion transport, especially at a high electrolyte concentration. Currently, most of the published works in this area are devoted to the study of lithium-ion transport in Nafion, which is a promising electrolyte for the lithium-ion batteries. Influence of the

nature of different organic plasticizer, whose primary function is providing the medium for ion transport, on the transport properties of Nafion membranes is detailed in the works [29–34]. It was demonstrated that the main determinants of ionic conductivity are the electrolyte swelling degree and some solvent properties such as molar volume, coordination number, and viscosity. High conductivity values were obtained using *N*-methylformamide, *N,N*-dimethylformamide, and DMSO due to high swelling degree of Nafion membrane (>100 wt.%). Ionic conductivity of these materials exceeds $10^{-3} \text{ S cm}^{-1}$ at room temperature in comparison to the conductivity of electrolytes swollen in organic carbonates (10^{-5} – $10^{-4} \text{ S cm}^{-1}$) used in commercial liquid electrolytes. The electrolytes based on lithiated Nafion were tested in the lithium and lithium-ion batteries and showed good performance [35–38]. The perspective of these polymer electrolytes is determined by their increased stability at prolonged tests compared with a commercial liquid electrolyte based on LiPF_6 .

There are few works on the polymer electrolytes with other cations in aqueous and aprotic media. In particular, the ionic conductivity of the Nafion membrane in different ionic forms was studied at room temperature [29,30,39,40]. It was demonstrated that the ionic conductivity of the polymer electrolyte based on DMSO increases in the series $\text{Na}^+ - \text{Cs}^+$, and the conductivity of Li^+ is comparable with that of Cs^+ . However, there was no detailed study of the influence of the cation nature on the transport properties.

The aim of the study was to study the effect of the nature of singly charged alkali metal ions on transport properties of the polymer electrolyte based on the Nafion and DMSO as a plasticizer. In this regard IR and DSC investigation as well as temperature dependence of conductivity of the electrolytes have been carried out.

* Corresponding author.

E-mail address: dobr@icp.ac.ru (Y.A. Dobrovolsky).

2. Experimental

Samples of Nafion-115 membrane were pretreated in a 3% solution of H₂O₂ at 60–80 °C for 2 h, washed with water, then aged in 0.1 M HCl at 60–80 °C for 1 h and thoroughly washed with water. Mobile protons were replaced by the alkali metal cations by aging the samples in an aqueous alcoholic alkali liquor 2 M (1:1 by volume) at 60–80 °C for 2 h, followed by thorough washing with water. To remove water, the samples were first dried at 110 °C for 1 h, and then in the desiccator over P₂O₅ for a week.

Before using, DMSO was distilled over desiccants under reduced pressure and stored over activated molecular sieves.

To prepare the swollen samples, the dried electrolytes were aged in a solvent in the presence of activated molecular sieves for 2 days at room temperature. To prepare the lithiated Nafion samples containing less DMSO, the dried samples were placed briefly in a solvent, blotted with a filter paper and held for two days for equilibration. The membrane swelling degree *W* was defined as the weight ratio of absorbed solvent to dry membrane.

The thermal stability was studied by differential scanning calorimetry (DSC) on the device STA 409PC Luxx (NETZSH, Germany) in alundum crucibles under the argon atmosphere. The heating rate of the samples was 10 K min⁻¹. Phase transitions in the low temperature range were studied on the device Mettler Toledo DSC 822e/200. The membranes were blotted with a filter paper and sealed in aluminum DSC pans. They were analyzed on thermal cycles of cooling from 20 to -70 °C and successive heating up with heating rate of 10 K min⁻¹.

The ionic conductivity of the samples was determined by the impedance spectroscopy. The impedance measurements were performed on the device Z-3000 (“Elins” LLC) in the frequency range of 1 Hz to 3 MHz on symmetric cells Ti/Nafion-M⁺/Ti with an active area of 0.2 cm². The amplitude of the external variable signal was 50 mV. The resistance of the membrane samples (*R_m*) was determined by the impedance hodograph by the high frequency cut-off on the axis of the active resistances. The specific conductivity of membranes σ [S cm⁻¹] was calculated as $\sigma = d/(R_m \times S)$, where *d* is the thickness of the membrane, *R_m* is the resistance of the membrane, and *S* is the electric contact area.

ATR IR spectra of the prepared samples were recorded under vacuum (<1 hPa) on spectrometer Vertex 70 V at room temperature using a Bruker diamond attachment in the 50–4500 cm⁻¹ (resolution 4 cm⁻¹, 50 scans). The spectra are presented in ATR units. At this scale, the spectra are normalized by the fixed depth of light penetration into the sample, thus ATR spectra in the far IR region up to 50 cm⁻¹ may be analyzed. The time of sample staying in the air required to transfer it into the attachment prior to evacuation of the cell was not exceed 0.5–1 min.

All operations with the polymer electrolytes were held in a box in the argon atmosphere, the content of O₂ and H₂O in the box atmosphere was <1 ppm.

3. Results and discussion

To study the influence of the cation nature on the properties of the polymer electrolyte the membrane samples of Nafion-M⁺ plasticized

by DMSO were obtained, where M⁺ = Li⁺, Na⁺, K⁺, Rb⁺ and Cs⁺. The main characteristics of the samples are presented in Table 1.

It is well known that the transport properties of polymer electrolytes are mainly determined by their swelling degree values due to participation of plasticizer in the formation of a network of transport channels as was shown for aqueous Nafion systems [41,42]. In our case the highest swelling degree was achieved for the sample in the Li⁺-form (about 130 wt.% of DMSO) which is well agree with earlier results [30]. The swelling degree of other electrolytes is much smaller and amounts to 61–72 wt.%. No apparent correlation of this parameter with the radius of cation has observed. The anomalously high swelling value of Nafion-Li⁺ is probably the result of high interaction of DMSO with lithium ion due to its small size and its charge. To eliminate the effect of the high content of DMSO, we have prepared the sample of Nafion-Li⁺ electrolyte with DMSO content comparable with swelling degree of other electrolytes.

TGA curves for the studied membranes are given in Fig. 1a. DMSO evaporation begins at a temperature above 50 °C under the argon stream with main weight loss up to 160 °C. The total weight losses are in good agreement with the results obtained from the gravimetric measurements. According to DSC (Fig. 1b), the maximum endothermic peak is in the range of 130–150 °C, depending on the cation (Table 1). The heat of DMSO desorption (ΔH_{vap} , Table 1), which includes both the heat of ion desolvation and DMSO evaporation, decreases with the increasing radius of the cation and approaches the evaporation heat of pure DMSO (~648 J g⁻¹ [43]). So, DMSO-cation interaction decreases with the increasing of the radius of cation.

Low temperature DSC data are summarized in Table 2. According to the obtained results, phase transition associated with DMSO melting within the polymer matrix occurs at the temperature of about 0 °C (Fig. 2) which is 15–25 °C lower than that for bulk DMSO. A marked decrease in melting point of DMSO contained within the polymer matrix is due to both salt and the capillary effects (pore size in the membranes of the Nafion type is at a nanometer level). These data are in good agreement with phase diagram for similar liquid LiSO₃CF₃-DMSO system [44]. As follows from the diagram, for this system containing 0.05–0.1 mol fraction of the salt DMSO crystallization temperature drops by about 5–15 °C.

The phase transition temperature of the studied electrolytes, except for the lithiated membrane, practically does not depend on the cation nature and is about -6 °C (Table 2). Phase transition for the lithiated sample occurs at a higher temperature (+3 °C), which is due to a higher content of DMSO. The latter also leads to a larger size of the ionic clusters. In accordance with the well-known Gibbs-Thompson equation, the melting point depression of a confined liquid is inversely as the pore diameter.

It should be noted that the specific melting heat of DMSO for the studied electrolytes ΔH_{melt} is significantly lower than that of bulk DMSO ($\Delta H_{\text{melt}}(\text{DMSO}) = 184 \text{ J g}^{-1}$ [45]). The lower values of the melting heat may be connected with the fact that some part of DMSO does not freeze due to solvation being in the “bound” state with the ion. The phenomenon is known for water-saturated Nafion [46,47]. The bound DMSO remains unfrozen down to -70 °C. The heat of phase transition increases in the series Na⁺–Cs⁺ but has the highest value

Table 1
The main characteristics of Nafion-M⁺/DMSO electrolytes.

M ⁺	Radius M ⁺ , Å	DMSO/M ⁺ , mol/mol	Swelling degree, wt.%	ΔH_{vap}^a , J g _{DMSO} ⁻¹	T_{vap}^b , °C	<i>E_a</i> , kJ mol ⁻¹	σ , S cm ⁻¹ 30 °C
Li ⁺	0.78	18.6	131.4	770	145.7	22.6 ± 0.5	2.0 × 10 ⁻³
		8.9	63.0	—	—	26.0 ± 0.6	6.8 × 10 ⁻⁴
Na ⁺	0.98	9.1	63.5	742	132.8	38.3 ± 0.3	3.5 × 10 ⁻⁴
K ⁺	1.33	9.9	68.1	731	131.1	36.6 ± 1.3	3.3 × 10 ⁻⁴
Rb ⁺	1.49	9.3	61.3	733	146.6	26.7 ± 2.2	6.9 × 10 ⁻⁴
Cs ⁺	1.65	11.3	71.6	720	139.6	19.1 ± 2.0	1.3 × 10 ⁻³

^a $\Delta H_{\text{vap}}(\text{DMSO}) = 648 \text{ J g}^{-1}$.

^b $T_{\text{boil}}(\text{DMSO}) = 189 \text{ °C}$.

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