

Lithium-Ion Conductivity of Polymers Based on Sulfonated Polystyrene and Polymethylpentene Intercalated by Organic Solvents

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Abstract—Ion-exchange membranes based on polymethylpentene and sulfonated polystyrene with different grafting degrees were obtained. Solvation and mobility of lithium ions depending on the composition of initial organic solvents were studied. The highest ionic conductivity at room temperature (30°C) are obtained for the membranes containing dimethylsulfoxide ($\sigma = 1.31 \times 10^{-4}$ S/cm for membrane with $GD = 78\%$). Membranes containing dimethylformamide are characterized by a constant phase composition in a broad temperature range and the highest ionic conductivity at low temperature ($\sigma = 9 \times 10^{-6}$ S/cm at -20°C for a polymer with $GD = 78\%$).

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INTRODUCTION

Despite the relatively short time which has elapsed after the creation of lithium-ion batteries (LIBs), they have become the most widely used rechargeable portable energy sources. The most important characteristics of the electrolyte of LIBs are high ionic and low electronic conductivity, as well as a wide window of electrochemical stability. The most commonly used liquid electrolytes are characterized by an ionic conductivity of $\sim 10^{-2}$ S/cm at room temperature. Such electrolytes are the solution of a lithium salt (perchlorate LiClO_4 , hexafluoroarsenate LiAsF_6 , hexafluoroborate LiBF_6 , trifluoromethanesulfonate LiTf , hexafluorophosphate LiPF_6 , etc.) in various mixtures of polar aprotic organic solvents. The disadvantages of liquid electrolytes are the hygroscopy and aggressive decomposition products of the salts being used, the parallel transport of the cation and anion in the process of charge/discharge, low thermal stability, and inflammability, as well as the possible dendrite formation in the course of operation of a battery, which makes it unsafe [1].

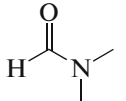

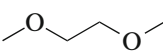
Solid electrolytes [2, 3], e.g., on the basis of phosphates with the structure of Nasicon [4, 5], oxides with the structure of garnet [6], and polysulfides [7], as well as gel-polymer [8, 9] and solid polymer electrolytes [10, 11], can serve as an alternative for liquid electrolytes.

Polymer electrolytes are also characterized by flexibility, which provides a convenient design for a battery.

Materials constructed on the basis of polymer matrices with lithium salts with a bulky anion (ClO_4^- , PF_6^- , BF_4^- , etc.) dissolved in them are the most commonly used class of solid polymer electrolytes for LIBs [12]. The essential condition for the provision of the solubility of these salts is the presence of electronegative ions capable of coordinating lithium ions in the polymer matrix. Poly(ethylene oxide), various polycarbonates, polysiloxanes, etc., are such polymers [13]. Ionic transport is mainly fulfilled in the amorphous region of the polymer of such electrolytes and is due to the local segmental mobility [14].

Polymeric membranes containing ionogenic groups (SO_3^- , COO^- , $[\text{SO}_2\text{NSO}_2\text{CF}_3]^-$, etc.) in the lithium form can be considered promising electrolytes for LIBs [15, 16]. Perfluorinated Nafion-type membranes where lithium ion ionically connects to functional group were the most widely studied for the use in LIBs [17–19]. Such membranes have high conductivity only in the solvated form. To make their use in LIBs possible, they are intercalated with anhydrous organic solvents such as linear and/or cyclic organic carbonates, ethers, dimethylsulfoxide, and dimethylformamide [18, 20–24]. The disadvantage of perfluorinated membranes is their high cost.

Table 1. Physical properties of the solvents: dynamic viscosity at 25°C (μ), dielectric permeability (ϵ), dipole moment (d), and crystallization and boiling points (T_{cr} and T_b)

Solvent	Chemical structure	μ , mPa s	ϵ	T_b , °C	T_{cr} , °C	d , D
DMF		0.92	36.7	153	-61	3.8
DMSO		2.00	45.0	189	18	4.0
DME		0.46	7.2	85	-71	1.1

Because of this, an important direction is the study of the properties of materials obtained, e.g., with the use of graft polymerization of monomers onto an inert polymer [25–28]. The active centers for grafting are generally formed under the action of high-energy radiation or via plasma treatment [25, 27, 29]. Various polymers, e.g., on the basis of hydrocarbons [25, 27, 28] or perfluorinated polymers [25, 30], are used as the matrix for grafting. Monomers containing ionogenic groups [30] or styrene with subsequent sulfonation [31, 32] are used as the reagents for polymerization grafting. Here, properties of membranes such as ionic conductivity, moisture content, and mechanical strength strongly depend on the degree of grafting [27].

The aim of this work was to synthesize and study the lithium-ion conductivity of a polymer electrolyte made of an ion-exchange membrane based on polymethylpentene and sulfonated polystyrene with the addition of anhydrous low-molecular-weight organic solvents.

EXPERIMENTAL

The membranes were obtained according to a procedure described in [33]. A film of polymethylpentene of the TPX®MX-002 (Mitsui, Japan) was irradiated with ultraviolet light in air. Graft polymerization was carried out in a mixture of styrene and methanol at a boiling point of the solution of 68°C. The grafting solution contained iron(II) sulfate as the homopolymerization inhibitor and coinitiator. The grafting degree (GD) of polystyrene was determined by the change in the weight of the film after graft polymerization.

The films were sulfonated in a 1.5 vol % solution of chlorosulfonic acid in dichloroethane at room temperature. The reaction was terminated by adding methanol. To transform the films into the lithium form, they were placed into a 1M solution of LiOH in methanol and conditioned at 60°C. To remove the alcohol from the membrane, the samples were dried under vacuum at 40°C.

The ion-exchange capacity (IEC) of the membranes was determined via acid–base titration related to the dry cationite.

The choice of solvents for filling the pores of the membranes was determined by the wide range of temperatures in which their existence in the liquid state is possible, high dielectric permeability, low dynamic viscosity, and high value of the dipole moment favoring the solvation of ions. In connection with this, the following solvents were chosen: dimethylformamide (DMF) and dimethylsulfoxide (DMSO). To decrease the viscosity and crystallization point of the liquid in the intrapore space, mixtures of solvents on the basis of DMF and DMSO containing an equal volume of dimethoxyethane (DME) were used. The properties of this solvents being used are listed in Table 1.

To obtain polymer electrolytes, the membranes were conditioned in these solvents over activated molecular sieves (3 Å) for 7 days with a single replacement of the solvents for new solvents. The works with the polymer electrolyte were carried out in a dry argon box (concentration of O_2 of <1 ppm and level of humidity of <10 ppm).

Degree of solvation n (the number of solvent molecules accounting for one sulfo group of the membrane) was determined on the basis of the values of IEC and the weight solvent content. In the case of binary mixtures, the molecular weight of the mixture was calculated from the assumption of the equality of the volumes of the components of the mixture.

The ionic conductivity of the samples was studied via impedance spectroscopy in a range of temperatures of –20 to 50°C in an airtight cell filled with argon. To set the required temperature, a Binder MKF115 climate chamber with stationary conditions was used. The measurements were performed using an Elins Z-1500J alternating current bridge (a range of frequencies of 10 kHz–2 MHz) on carbon/membrane/carbon symmetrical cells. The value of the resistance was found by the interception on the axis of active resistances in the Nyquist coordinates.

RESULTS AND DISCUSSION

With the increase of grafting degree of the membranes under study from 41 to 78%, IEC increases from 1.8 to 2.4 mmol/g (Table 2). When a dry membrane is placed into a liquid, the sorption of the solvent by the membrane occurs. In generally, solvation degree of membranes increases with increasing GD (Table 2). Hereinafter, the membranes are denoted as ($GD = 41\%$) and ($GD = 78\%$).

A clear dependence of the degree of solvation on the nature of the intercalated solvent is observed for the studied membranes. The degree of solvation of the membranes increases in the following series: DMF–DME < DMSO–DME < DMF < DMSO (Fig. 1, Table 2). The highest conductivity of the membranes

Table 2. Grafting degree, ion-exchange capacity, and degree of solvation of the studied membranes

	<i>GD</i> , wt %	<i>IEC</i> , mmol/g	Degree of solvation			
			DMSO	DMF	DMSO–DME	DMF–DME
<i>I</i>	41	1.8	7.8 ± 0.3	4.8 ± 0.2	4.4 ± 0.1	2.0 ± 0.1
<i>II</i>	78	2.4	8.8 ± 0.1	5.4 ± 0.1	4.5 ± 0.1	2.5 ± 0.1

containing DMSO is explained by its high solvating capability [34, 35], which is due to the high dipole moment. Membranes containing DMF are also characterized by a quite high degree of solvation. Adding DME to these solvents in order to decrease the viscosity and crystallization point of a solvent leads to a decrease in the degree of solvation. Thus, the degree of solvation of polymer *I* in the case of a transition from DMSO to the DMSO–DME mixture decreases from $n = 7.8$ to $n = 4.4$, while, in the case of a transition from DMF to the DMF–DME mixture, it decreases from $n = 4.8$ to $n = 2.0$ (Table 2).

Figure 1 presents the values of conductivity of the membranes under study at 30°C depending on the degree of solvation.

In general, the ionic conductivity increases with the increase in the degree of solvation among the studied polymers, i.e., in the case of transition from membranes containing DMF–DME to membranes containing DMSO. With the growth in the solvation from 2.0 to 8.8, the ionic conductivity of the membranes (σ) increases from 3×10^{-6} to 1.31×10^{-4} S/cm (at 30°C). In the case of membranes with the same *IEC*, the concentration of charge carriers in a solvated membrane is determined by the concentration of functional groups, which only decreases in the process of sorption of a solvent. The effect of an increase in the conductivity with the increase in the solvent content in the pores is determined by the increase in the size of the pores and channels of the membrane and, consequently, the mobility of charge carriers.

Among the studied polymers with different *GD* containing the same solvent, a membrane with higher *GD* is characterized by higher conductivity. This is explained by the higher concentration of charge carriers. With the growth in the degree of solvation, the fraction of lithium ions coordinated by solvent molecules increases, which corresponds to a higher degree of dissociation of the functional groups and leads to an increase in the lithium-ion mobility. Such regularities are noted in works [36–38] for perfluorinated sulfocationite and carboxyl membranes in the lithium form. With the increase in the degree of solvation, the number of counterion–ionogenic group contact ion pairs in the membranes decreases, while the number of separated ion pairs increases.

One of the most important characteristics of the electrolyte is the constancy of the phase composition in a wide range of temperatures. The linear section of

the temperature dependence of conductivity in the $\log \sigma - 1000/T$ coordinates means the absence of phase transitions of the samples under study in the temperature region under consideration. Given that the samples under study contain two phases, a liquid and a solid polymer, they can have phase transitions which are characteristic for both phases. For the polymer, these are glass transition and melting points which are above the temperatures under study; for the liquid they are crystallization and boiling points which can be in the range of temperatures under study (Table 1).

The deviation of the temperature dependence of conductivity from a linear dependence is observed for the membranes containing DMSO (Figs. 2a, 2b). Thus, for the membranes containing individual DMSO, kinks are observed at $\sim 15^\circ\text{C}$, which is associated with the gradual melting of DMSO in the membrane. Adding an equal volume of DME to DMSO decreases the crystallization point of the liquid, which is evidenced by the linear temperature dependence of ionic conductivity in a range of temperatures of -20 to $\sim 35^\circ\text{C}$ (Fig. 2b). Above $\sim 35^\circ\text{C}$, the evaporation of highly volatile DME from the pores of the membrane occurs, which leads to the deviation of the temperature dependences of conductivity from linear dependences.

For membranes containing DMF, which is characterized by a low melting point and a high boiling point

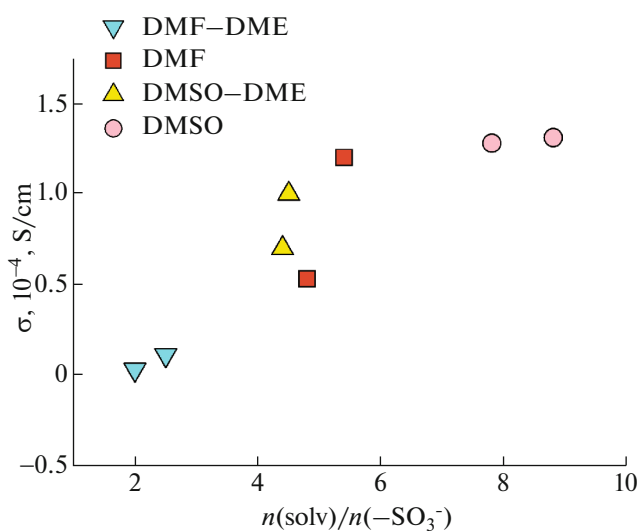


Fig. 1. (Color online) Dependence of the ionic conductivity (at 30°C) on the degree of solvation of the samples under study conditioned in different solvents.

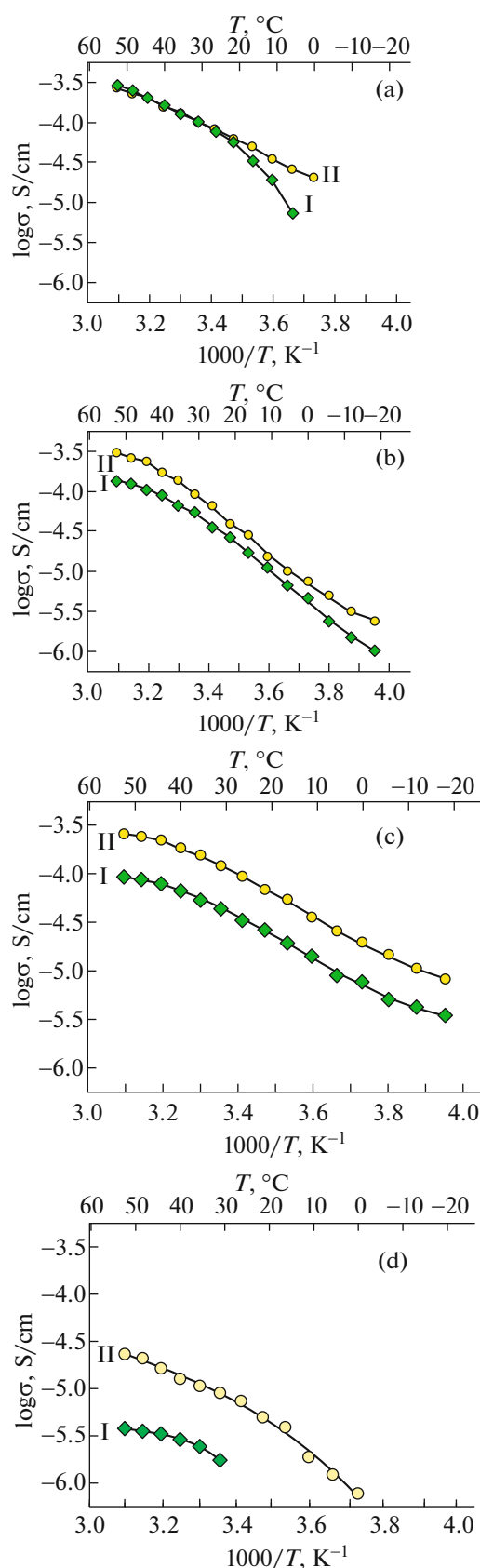


Fig. 2. (Color online) Temperature dependences of the ionic conductivity of membranes *I* and *II* conditioned in (a) DMSO, (b) DMSO–DME, (c) DMF, and (d) DMF–DME.

(Table 1), a linear dependence of the logarithm of ionic conductivity on temperature is observed in the studied range of temperatures (Figs. 2c, 2d). The conductivity of the membranes containing individual DMF retains relatively high values at negative temperatures ($\sigma = 9 \times 10^{-6}$ S/cm at -20°C for membrane *II*).

CONCLUSIONS

Membranes in the lithium form based on polymethylpentene and sulfonated polystyrene with different grafting degrees of polystyrene with aprotic organic solvents intercalated into the pores have been obtained. It has been found that membranes conditioned in DMSO-containing solvents are distinguished by the highest degree of solvation. A membrane with a grafting degree of 78% conditioned in DMSO ($\sigma = 1.31 \times 10^{-4}$ S/cm) is characterized by the highest ionic conductivity at 30°C . DMF-containing membranes are characterized by the constancy of the phase composition in a wide range of temperatures and the highest ionic conductivity at negative temperatures ($\sigma = 9 \times 10^{-6}$ S/cm at -20°C for the polymer with $GD = 78\%$).

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REFERENCES

1. E. Quartarone and P. Mustarelli, "Electrolytes for solid-state lithium rechargeable batteries: recent advances and perspectives," *Chem. Soc. Rev.* **40**, 2525–2540 (2011).
2. A. B. Yaroslavtsev, "Solid electrolytes: main prospects of research and development," *Russ. Chem. Rev.* **85**, 1255–1276 (2016).
3. Z. Gao, H. Sun, L. Fu, F. Ye, Y. Zhang, W. Luo, and Y. Huang, "Promises, challenges and recent progress of inorganic solid-state electrolytes for all-solid-state lithium batteries," *Adv. Mater.* **30**, 1705702 (2018).
4. I. A. Stenina, I. Y. Pinus, A. I. Rebrov, and A. B. Yaroslavtsev, "Lithium and hydrogen ions transport in materials with NASICON structure," *Solid State Ionics* **175**, 445–449 (2004).
5. Z. Jian, Y. S. Hu, X. Ji, and W. Chen, "NASICON-structured materials for energy storage," *Adv. Mater.* **29**, 1601925 (2017).
6. J. F. Nonemacher, C. Hüter, H. Zheng, J. Malzbender, M. Krüger, R. Spatschek, and M. Finsterbusch, "Microstructure and properties investigation of garnet structured $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ as electrolyte for all-solid-state batteries," *Solid State Ionics* **321**, 126–134 (2018).
7. C. Li, Z. Xi, D. Guo, X. Chen, L. Yin, "Chemical immobilization effect on lithium polysulfides for lithium-sulfur batteries," *Small* **14**, 1701986 (2018).
8. Y. Xue and D. J. Quesnel, "Synthesis and electrochemical study of sodium ion transport polymer gel electrolytes," *RSC Adv.* **6**, 7504–7510 (2016).

9. H. Gao, W. Zhou, K. Park, and J. B. Goodenough, "A sodium-ion battery with a low-cost cross-linked gel-polymer electrolyte," *Adv. Energy Mater.* **6**, 1600467 (2016).
10. L. Yue, J. Ma, J. Zhang, J. Zhao, S. Dong, Z. Liu, G. Cui, and L. Chen, "All solid-state polymer electrolytes for high-performance lithium ion batteries," *Energy Storage Mater.* **5**, 139–164 (2016).
11. B. Sun, J. Mindemark, K. Edstrom, and D. Brandell, "Polycarbonate-based solid polymer electrolytes for Li-ion batteries," *Solid State Ionics* **262**, 738–742 (2014).
12. M. Armand, "Polymer electrolytes—an overview," *Solid State Ionics* **9–10**, 745–754 (1983).
13. V. di Noto, S. Lavina, G. A. Giffin, E. Negro, and B. Scrosati, "Polymer electrolytes: present, past and future," *Electrochim. Acta* **57**, 4–13 (2011).
14. K. Xu, "Nonaqueous liquid electrolytes for lithium-based rechargeable batteries," *Chem. Rev.* **104**, 4303–4417 (2005).
15. A. Ghosh and P. Kofinas, "Nanostructured block copolymer dry electrolyte," *J. Electrochem. Soc.* **151**, A428–A431 (2008).
16. J. F. Snyder, M. A. Ratner, and D. F. Shriver, "Ion conductivity of comb polysiloxane polyelectrolytes containing oligoether and perfluoroether sidechains," *J. Electrochem. Soc.* **150**, A1090–A1094 (2003).
17. P. Han, Y. Zhu, and J. Liu, "An all-solid-state lithium ion battery electrolyte membrane fabricated by hot-pressing method," *J. Power Sources* **284**, 459–465 (2015).
18. Y. Liu, Z. Cai, L. Tan, and L. Li, "Ion exchange membranes as electrolyte for high performance li-ion batteries," *Energy Environ. Sci.* **5**, 9007–9013 (2012).
19. Z. Cai, Y. Liu, S. Liu, L. Li, and Y. Zhang, "High performance of lithium-ion polymer battery based on non-aqueous lithiated perfluorinated sulfonic ion-exchange membranes," *Energy Environ. Sci.* **5**, 5690–5693 (2012).
20. P. Aldebert, M. Guglieimi, and M. Pineri, "Ionic conductivity of bulk, gels and solutions of perfluorinated ionomer membranes," *Polym. J.* **23**, 399–406 (1991).
21. M. Doyle, M. E. Lewittes, M. G. Roelofs, S. A. Perusich, and R. E. Lowrey, "Relationship between ionic conductivity of perfluorinated ionomeric membranes and nonaqueous solvent properties," *J. Membr. Sci.* **184**, 257–273 (2001).
22. J. Gao, C. Sun, L. Xu, J. Chen, C. Wang, D. Guo, and H. Chen, "Lithiated nafion as polymer electrolyte for solid-state lithium sulfur batteries using carbon-sulfur composite cathode," *J. Power Sources* **382**, 179–189 (2018).
23. E. A. Sanginov, E. Yu. Evshchik, R. R. Kayumov, and Yu. A. Dobrovolskii, "Lithium-ion conductivity of the nafion membrane swollen in organic solvents," *Russ. J. Electrochem.* **51**, 986–990 (2015).
24. A. I. Karelin, R. R. Kayumov, and Yu. A. Dobrovolskii, "Structure of lithium ion-conducting polymer membranes based on nafion plasticized with dimethyl-sulfoxide," *Pet. Chem.* **56**, 1020–1026 (2017).
25. M. Nasef, "Preparation and applications of ion exchange membranes by radiation-induced graft copolymerization of polar monomers onto non-polar films," *Prog. Polym. Sci.* **29**, 499–561 (2004).
26. T. Zhou, R. Shao, S. Chen, X. He, J. Qiao, and J. Zhang, "A review of radiation-grafted polymer electrolyte membranes for alkaline polymer electrolyte membrane fuel cells," *J. Power Sources* **293**, 946–975 (2015).
27. E. Y. Safronova, D. V. Golubenko, N. V. Shevlyakova, M. G. D'yakova, V. A. Tverskoi, L. Dammak, D. Grande, and A. B. Yaroslavtsev, "New cation-exchange membranes based on cross-linked sulfonated polystyrene and polyethylene for power generation systems," *J. Membr. Sci.* **515**, 196–203 (2016).
28. D. V. Golubenko, E. Y. Safronova, A. B. Ilyin, N. V. Shevlyakova, V. A. Tverskoi, G. Pourcelly, and A. B. Yaroslavtsev, "Water state and ionic conductivity of grafted ion exchange membranes based on polyethylene and sulfonated polystyrene," *Mendeleev Commun.* **27**, 380–381 (2017).
29. Z. Xu, J. Wang, L. Shen, D. Men, and Y. Xu, "Microporous polypropylene hollow fiber membrane. Part I. Surface modification by the graft polymerization of acrylic acid," *J. Membr. Sci.* **196**, 221–229 (2002).
30. Y. Ding, X. Shen, J. Zeng, X. Wang, L. Peng, P. Zhang, and J. Zhao, "Pre-irradiation grafted single lithium-ion conducting polymer electrolyte based on poly(vinylidene fluoride)," *Solid State Ionics* **323**, 16–24 (2018).
31. N. Walsby, F. Sundholm, T. Kallio, and G. Sundholm, "Radiation-grafted ion-exchange membranes: influence of the initial matrix on the synthesis and structure," *J. Polym. Sci., Part A* **39**, 3008–3017 (2001).
32. J. A. Horsfall and K. V. Lovell, "Synthesis and characterization of sulfonic acid-containing ion exchange membranes based on hydrocarbon and fluorocarbon polymers," *Eur. Polym. J.* **38**, 1671–1682 (2002).
33. D. V. Golubenko and A. B. Yaroslavtsev, "New approach to the preparation of grafted ion exchange membranes based on UV-oxidized polymer films and sulfonated polystyrene," *Mendeleev Commun.* **27**, 572–573 (2017).
34. V. Gutmann, "Empirical parameters for donor and acceptor properties of solvents," *Electrochim. Acta* **21**, 661–670 (1976).
35. E. Pasgreta, R. Puchta, M. Galle, N. van Eikema Hommes, A. Zahl, and R. van Eldik, "Ligand-exchange processes on solvated lithium cations: DMSO and water/DMSO mixtures," *ChemPhysChem* **8**, 1315–1320 (2007).
36. V. I. Volkov, E. V. Volkov, S. V. Timofeev, E. A. Sanginov, A. A. Pavlov, E. Yu. Safronova, I. A. Stenina, and A. B. Yaroslavtsev, "Diffusion mobility of alkali metals in perfluorinated sulfocationic and carboxylic membranes as probed by ^1H , ^7Li , ^{23}Na , and ^{133}Cs NMR spectroscopy," *Russ. J. Inorg. Chem.* **55**, 318–324 (2010).
37. D. Yu. Voropaeva, S. A. Novikova, T. L. Kulova, and A. B. Yaroslavtsev, "Conductivity of Nafion-117 membranes intercalated by polar aprotic solvents," *Ionics* **24**, 1685–1692 (2018).
38. V. I. Volkov and A. A. Marinin, "NMR methods for studying ion and molecular transport in polymer electrolytes," *Russ. Chem. Rev.* **82**, 248–272 (2013).

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