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Solvation and sodium conductivity of nonaqueous polymer electrolytes based on Nafion-117 membranes and polar aprotic solvents

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ABSTRACT

Nafion-117 membranes in the Na^+-forms with pore-intercalated mixtures of aprotic organic solvents have been obtained. Dependences of solvent uptake of the membranes *versus* their pretreatment conditions and compositions of initial organic solvent mixtures are described. Ionic conductivity of the obtained membranes in the temperature range −20–50 °C is investigated using impedance spectroscopy. It is demonstrated that ionic conductivity increases with increasing solvent uptake. The highest conductivities at 30 °C (~4 mS/cm) are obtained for the membranes thermally treated in methanol and aged in ethylene carbonate-dimethylacetamide, ethylene carbonate-diethyl carbonate-dimethylacetamide and propylene carbonate-dimethylacetamide-tetrahydrofuran mixtures. Thermal stability is studied by differential scanning calorimetry. It is shown that the membrane with intercalated propylene carbonate-dimethylacetamide-tetrahydrofuran mixture is characterized by a constant phase composition in a broad temperature range (up to −100 °C) and retention of high conductivity at low temperatures (~1 mS/cm at −20 °C).

1. Introduction

LIBs are the most common portable energy sources due to their high capacity [1]. However lithium is a rare element, which limits the possibility of its application to fully meet the quickly growing demand in energy storage devices. SIBs can serve as a possible alternative to LIBs, due to the similarity of physical and chemical properties of sodium and lithium, as well as higher availability of sodium (ratio of the resources is Li:Na = $1:10^3$) [2–5]. Along with novel electrode materials for SIBs, development of novel electrolytes that should provide ionic transport is also crucial.

Important characteristics of an electrolyte are high ionic and low electronic conductivity. Furthermore, an electrolyte should possess mechanical strength, electrochemical stability, be inert to other components of an electrochemical cell and perform sustainably in a broad range of temperatures. It is generally known that LIBs lose the greater part of their power and capacity at temperatures below −10 °C [6]. The main reasons that limit the application of metal-ion batteries at low temperatures are lowering of the rates of electrochemical processes. In particular, conductivity of liquid electrolyte, diffusion rate in solid phases, rate of charge transfer in electrochemical processes decrease. Apart from that a more intensive formation of lithium dendrites is possible due to a low rate of intercalation [6, 7]. In order to overcome these limitations intensive research is carried out aimed at both improving the intercalation/deintercalation kinetics in the electrodes (reduction of particle size, doping, preparation of carbon-containing composites, replacement of a conductive additive) [8, 9] and modification of the electrolyte. In the case of liquid electrolytes the composition of the organic solvent mixture can be varied [6], most commonly used $LiPF_6$ can be substituted with other salts, such as $LiBF_4$ or $LiAsF_6$ [10], salt additives such as NaCl (1%) can be used with the electrolyte [11]. This results in the decrease in solvent freezing point, increase in conductivity of the electrolytes, and compatibility with electrodes improves as a result of a decreased interaction between the electrolyte and electrodes, which produces a poorly conductive film on the surface of electrodes [12]. In the field of SIBs major efforts of the researchers are focused on the possibility to operate at elevated temperatures and safety [2]. Meanwhile, there are virtually no investigations of conductivity of electrolytes with sodium conductivity at low temperatures. While a large number of applications require for batteries to operate under thermal extremes. For example, military-grade batteries are expected to operate from −40 °C to 60 °C. Electric vehicles

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Abbreviations: DEC, diethyl carbonate; DMA, dimethylacetamide; DME, dimethoxyethane; DSC, differential scanning calorimetry; EC, ethylene carbonate; IR spectroscopy, infrared spectroscopy; LIBs, lithium-ion batteries; PC, propylene carbonate; SIBs, sodium-ion batteries; TGA, thermogravimetric analysis; THF, tetrahydrofuran

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require battery systems capable of having stable performance in both hot and colder regions. Equipment for cold climates and high-altitude drones can experience temperatures as low as −60 °C [13].

Electrolytes most commonly used in SIBs are liquid electrolytes composed of a solution of a sodium salt with a bulky anion, for example $NaClO_4$, $NaPF_6$ or NaTFSI, in various polar aprotic solvents, such as linear (dialkyl carbonates) and cyclic (ethylene carbonate, propylene carbonate *etc.*) carbonates, as well as ethers (tetrahydrofuran, dimethoxyethane *etc.*) [14]. An advantage of liquid electrolytes is their high ionic conductivity (~10 mS/cm). A 1 M solution of $NaClO_4$ salt in a double solvent mixture of EC-DME (50:50 wt%) is notable for the highest ionic conductivity (12.55 mS/cm) [15]. The main drawbacks of liquid electrolytes are: possible electrolyte leakage, possible salt decomposition producing aggressive products, parallel transfer of cation and anion during charge/discharge, inflammability. This makes the use of a battery not safe [16].

Solid electrolytes based on polysulfides [17], phosphates with NASICON structure [18], ionic liquids [19], gel-polymer [20, 21] and solid polymer electrolytes [22] can serve as a promising alternative to liquid electrolytes. In the solid polymer electrolytes sodium salts are dissolved in a polymer matrix (PEO-NaX, $\sigma \sim 10^{-4}$ mS/cm) [23] or coupled with functional groups of a polymer ($-SO_3^-Na^+$, $-[SO_2NSO_2CF_3]^-Na^+$ *etc.*) [24–26]. Perfluorinated Nafion membranes, which contain functional sulfonic groups in the sodium form can be considered as promising candidates for a simultaneous use as an electrolyte and a separator in SIBs [24, 27]. Nafion membranes are characterized by high ionic conductivity in aqueous solutions, however, in aprotic solvents their conductivity drops sharply [24] and prevents their use as electrolytes. The reasons behind this are lower dielectric permittivity and higher viscosity of aprotic solvent solutions, as well as insufficient solvent uptake of the membranes. By varying the solvent composition and pretreating the membranes with polar solvents in order to increase the sizes of pores and channels, one can achieve an improvement of Li^+ conductivity [28]. At the same time the processes of Na^+ solvation in aqueous and nonaqueous media are quite different from the Li^+ solvation due to the difference in ionic radius [29, 30]. So the solvent uptake of polar aprotic solvents and conductivity of Nafion-117 membrane in Na^+-form need a special study.

The aim of the present work was to search for the optimum condition of pretreatment of Nafion-117 membrane in Na^+-form and for the composition of pore-intercalated anhydrous organic solvents for the preparation of electrolytes with high sodium conductivity, in particular at low temperatures. The composition of solvent mixtures to fill the membrane pores was chosen according to their physical properties, such as melting and boiling temperature, dielectric permittivity and dynamic viscosity (Table S1).

2. Experimental

Nafion-117 membranes manufactured by DuPont were conditioned by a standard procedure [31], and afterwards aged in 2 M water solution of sodium chloride and kept for 48 h at constant stirring. To remove Cl^--ions membranes were washed several times with deionized water. To remove water membranes were dried under vacuum at 70 °C for 12 h, and afterwards were placed either in methanol for ~24 h, or into a hermetically sealed cell filled with 40 ml methanol and kept for 6 h at 60 °C. To remove the alcohol from the membranes pores they were dried under vacuum at 70 °C for 12 h. Further in the text the membranes are denoted as follows: without any treatment: Nafion, treated with methanol: Nafion-MeOH, thermally treated with methanol: Nafion-therm.

In order to fill the pores of the membranes with aprotic solvents the obtained samples were placed in a dry argon-filled box (with a humidity level < 10 ppm) and aged in the following solvent mixtures: EC-DME (V:V = 1:1), EC-PC (V:V), EC-THF (V:V = 1:1), EC-DMA (V:V = 1:1), EC-DEC-DMA (V:V:V = 1:1:1) and PC-DMA-THF V:V:V = (1:1:1). The choice of solvents is based on their physical properties (Table S1). Membranes were kept in the mentioned solutions over activated molecular sieves (3 Å) for 7 days with a single replacement of solvents. Operations with the polymer electrolyte were performed in a glove box under argon atmosphere, contents of O_2 and H_2O in the box were < 1 ppm.

Solvent uptake of the membranes (n) was calculated as the number of solvent molecules divided by the number of sulfonic groups in the membranes, based on the swelling of the membranes (ω) (Eq. (1)), ion exchange capacity of 0.91 mmol/g and assumed that the composition of the sorbed mixture within the membrane pores is the same as the contacting solution.

$$\omega = \frac{m_s - m_d}{m_d} \tag{1}$$

where m_s and m_d are weights of solvated and dry membranes, respectively.

IR spectra were collected using IR spectrometer Nicolet iS5 with a SpecacQuest accessory in the attenuated total reflection mode with a diamond crystal in the frequency range 500–4000 cm^{-1}.

Ionic conductivity of the obtained samples was investigated by impedance spectroscopy at temperature range −20–50 °C under the argon atmosphere. A dynamic climate chamber Binder MKF115 was used to set the required temperature. The measurements were performed using an alternating-current bridge Elins Z-1500 J (frequency range 1 kHz–2 MHz) on symmetric cells carbon/membrane/carbon. Resistance was determined by an intercept with the active impedance axis in Nyquist coordinates. Temperature dependence of ionic conductivity of the studied samples follows Arrhenius equation and can be linearized in logσ - 1000/T coordinates. Activation energy values were determined as the inclination of the linear plot in logσ - 1000/T coordinates.

Dynamic viscosities of the pristine solutions were collected using a vibration viscometer SV-10 (A&D, Japan) at 21.5 °C. Calibration of the viscometer was carried out using *N,N*-dimethylacetamide.

Calculation of dielectric permittivity of pristine solutions was done using a Looyenga equation for homogenous mixtures (Eq. (2)) [32]:

$$\varepsilon^{1/3} - 1 = \sum_i (\varepsilon_i^{1/3} - 1)\varphi_i \tag{2}$$

where ε and ε_i are the dielectric permittivities of the mixture and the single component, respectively, φ_i is the volumetric fraction of the component.

DSC measurements of Nafion-therm membranes with intercalated solvents were performed on the NETZSCH STA 449F1 device in aluminum crucibles in the temperature range −130–150 °C with a heating rate 10 °C/min.

3. Results and discussion

3.1. Ionic conductivity

When dehydrated membranes are placed in organic solvents the sorption of the latter by the membrane occurs. The absence of OH group characteristic peaks in IR spectra of the membranes containing aprotic solvents and their mixtures proves that the obtained samples contain almost no water or methanol (Fig. S1).

The amount of organic solvents absorbed by the membranes increases as follows: Nafion < Nafion - MeOH < Nafion - therm. Influence of pretreatment on the sorption of organic solvents can be explained by the so-called "memory effect" of the membranes [28, 33, 34]. The most pronounced effect is achieved for membrane thermally treated in methanol. Increasing the temperature of treatment results in the pressure of methanol vapor increasing considerably, facilitating the sorption of additional amount of methanol and increase of pore and channel sizes in the membranes, which leads to better solvation in

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