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Abstract

Nafion Solvated by Ethylene Carbonate, Dimethyl Carbonate and Dimethylacetamide as Electrolyte for Lithium Metal Batteries †

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Abstract: Lithium metal batteries are a promising replacement for lithium-ion batteries due to their ability to achieve high energy densities. However, the unsafe operation of the lithium battery due to the formation and sprouting of dendrites through the separator limits their commercial application. We obtained a gel-polymer electrolyte based on a Nafion cation-exchange membrane solvated with a ternary mixture of ethylene carbonate - dimethyl carbonate - N,N-dimethylacetamide, which has an ionic conductivity of 1.8 mS/cm at 25°C and an electrochemical stability window of 4.1 V. The symmetrical Li/Li cell was shown to cycle stably at a current density of 0.1 mA·cm^2 for >350 h.

Keywords: polymer electrolyte; single-ion conductor; lithium metal battery; N,N-dimethylacetamide

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1. Introduction

Lithium metal batteries are considered as a promising replacement for lithium-ion batteries due to the high theoretical capacity of lithium (3,860 mAh·g^{-1}) [1]. The most important problem limiting their large-scale application is the dendrite growth through the separator [1], which is caused by low lithium cation transfer numbers according to space charge theory [2]. Thus, the use of single-ion conducting polymer electrolytes is one way to prevent dendrite formation [3]. Nafion membrane can be used as polymer electrolyte in such systems [4]. However, the solvation of these membranes by standard organic carbonates does not provide sufficient ionic conductivity [5]. However, the lithium conductivity of Nafion membrane solvated by N,N-dimethylacetamide (DMAc) are much higher than those of standard carbonate solvents [5]. However, there are reports of low chemical stability of DMAc in contact with alkali metals [6], and the use of mixtures of DMAc with ethylene carbonate increases the stability by creating a protective thin film that prevents the interaction of DMAc with the metal anode [7]. Thus, the purpose of this work was to obtain a polymeric electrolyte based on the Nafion membrane in Li$^+$ form solvated by mixture of ethylene carbonate (EC) – dimethyl carbonate (DMC) – N,N-dimethylacetamide (DMAc) and to characterize its properties for use in lithium metal batteries.

2. Materials and Methods

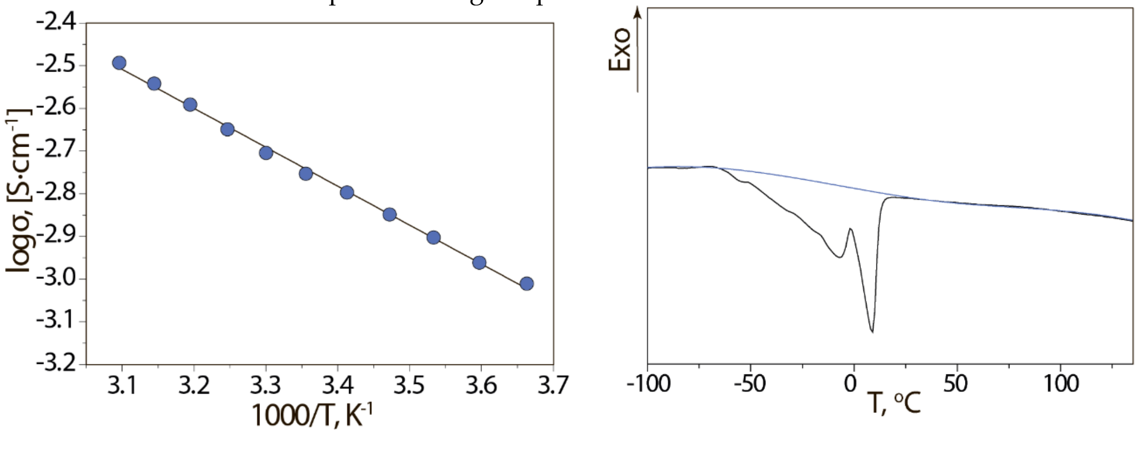
To obtain the gel-polymer electrolyte, dry Nafion-117 membrane was placed in the EC-DMC-DMAc solution (V:V:V=1:1:1) for 48 h. Anhydrous solvents with purity >99% were used to prepare the solution. The degree of solvation was calculated as the ratio of the number of solvent molecules to the total number of membrane functional groups, the first of which was determined by the weight gain after soaking membrane in solvents, assuming that the solvent composition was equal to the initial one. All work with the polymer electrolyte was performed in a dry Vilitek VBOX CHEM glovebox under argon atmosphere.

The ionic conductivity of the samples was studied by impedance spectroscopy in the temperature range 0 – +50°C under argon atmosphere using a symmetrical cell with stainless-steel electrodes (SS) in the frequency range 10 kHz - 3 MHz. The value of activation energy was determined by the slope of the temperature dependence of ionic conductivity. The electrochemical stability window of the membrane was determined by linear sweep voltammetry. The membrane sample was placed between a stainless-steel electrode (as a working electrode) and a lithium electrode (as a reference electrode) and assembled in a CR2032 coin-type cell. Li platting-stripping experiments were carried out at a current density of 0.1 mA·cm^{-2} in symmetrical CR2032 coin-type cell. The time per cycle was 1 h.

The differential scanning calorimetry of the solvated membrane was carried out using a NETZSCH STA 449F1 device in aluminum crucibles under helium atmosphere in the temperature range –130–+130 °C with the heating rate of 10 °C/min.

3. Results and Discussion

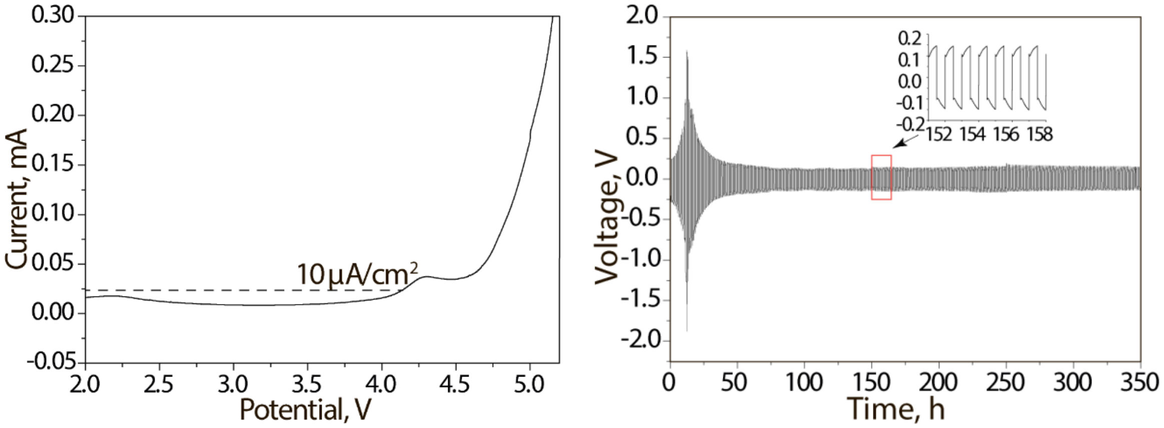
The polymer electrolyte was 154% swollen film with a thickness of ~160 μm. The degree of solvation of the obtained membrane was 19.4 solvent molecules per one sulfonic group. The temperature dependency of the ionic conductivity of the studied sample obey the Arrhenius equation and are linearized in log-1000/T plot (Figure 1a). At room temperature the ionic conductivity is 1.8 mSm·cm^{-1}, which exceeds the values typical for most polymer electrolytes and meets the requirements for electrolytes in lithium metal batteries [8]. The value of the activation energy of conductivity calculated from the slope of the straight line is 17.5±0.3 kJ·mol^{-1}. The DSC curve of the solvated membrane shows 2 endothermic peaks beginning at -57°C and -5°C (Figure 1b), which correspond to the glass transition and complete melting temperatures of the solvent mixture.



(**a**) (**b**)

Figure 1. **(a)** temperature dependence of ionic conductivity and **(b)** DSC curve of the obtained polymer electrolyte.

The electrochemical stability window of the obtained gel-polymer electrolyte was determined by linear sweep voltammetry (Figure 2a). No anodic peaks were observed on the curve, and a sharp increase in the current density corresponding to the electrolyte reduction [9] was detected only above 4.1 V vs. Li/Li$^+$. To further evaluate the stability of the resulting electrolyte with respect to the lithium electrodes, a symmetrical Li/Li cell was assembled and tested by Li platting-stripping experiments at a current density of 0.1 mA·cm^{-2} (Figure 2b). During the first cycles the voltage increases with a maximum of ~±1.5 V, which corresponds to electrolyte reduction with formation of SEI (Solid electrolyte interphase) layer at the interface of the electrode, after which the voltage uniformly decreases and reaches stable values of ~±140 mV at cycle 38, which remain stable for >300 h. This behavior of the cell during the initial cycles is associated with partial reduction of the solvent due to its interaction with lithium metal.



(**a**) (**b**)

Figure 2. (a) voltammetry of a SS/Li cell and **(b)** galvanostatic cycling of a symmetrical Li/Li cell at a current density of 0.1 mA·cm^{-2} for 350 h and selective cycles for about 150 h.

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