GEL POLYMER ELECTROLYTES BASED ON ETHYLENE GLYCOL DIMETHACRYLATE AND THEIR ELECTRO-CHEMICAL CHARACTERIZATION

Iuliia Veselkova

Doctoral Degree Programme (4), FEEC BUT

E-mail: xgrach00@vutbr.cz

Supervised by: Marie Sedlaříková

E-mail: sedlara@feec.vutbr.cz

Abstract: The electrochemical properties of cross-linked gel polymer electrolyte based on ethylene glycol dimethacrylate are investigated. Impedance spectroscopy was used for studying the mode of electrical conductivity in prepared gel electrolytes. A study of electrochemical stability was provided using linear sweep voltammetry. The increasing amount of ethylene glycol dimethacrylate shows the decreasing of electrical conductivity. The presence of cross-linking agent affects not only the electrochemical properties but also the mechanical properties.

Keywords: gel electrolyte, polymer, methyl methacrylate, cross linking.

1   INTRODUCTION

Gel polymer electrolytes (GPEs) have attracted a big interest in the field of lithium-ion batteries due to their good features. It is one of the most desirable alternatives among various electrolytes for electrochemical devices [1]. In comparison with liquid electrolytes, GPEs have high ionic conductivity and wettability, which is unique [2]. Also, gel electrolytes eliminate the problem with leakage of electrolytes due to cohesive properties and a problem with fire hazards due to the high flammability of organic solvents [3], [4]. To reach high mobility close to that of the liquid fraction and to reach mechanical cohesion, a cross-linking strategy was used [4].

Crosslinking is a strategy for improving a gel polymer electrolyte with good mechanical strength. The network structure of cross-linked polymers is characterized by the higher density of cross-linking points and the consequently reduced deformability of the chain segments. The cross-linking is formed by covalent chemical bonds or by physical interaction [5], [6].

The main goal of the research was to determine the impact of cross-linker on the electrochemical properties of GPEs. Gel polymer electrolytes based on methyl methacrylate were polymerized by UV irradiation with varying concentrations of ethylene glycol dimethacrylate as a cross-linking agent. Results indicated the temperature dependence of electrical conductivity and electrochemical stability of gel polymer electrolytes, which were prepared.

2   PREPARATION OF GEL POLYMER ELECTROLYTE

Lithium hexafluorophosphate-98% (LiPF$_6$), ethylene carbonate (EC), diethyl carbonate (DEC), ethylene glycol dimethacrylate (EDMA), methyl methacrylate (MMA) and benzoin ethyl ether (BEE) were chosen for preparation of gel polymer electrolytes. All these materials were purchased from Sigma-Aldrich (Merck) [7].

The preparation of gel polymer electrolytes can be divided into two phases. The first phase is the preparation of a conductive solution (liquid electrolyte) and the second phase is the formation of the gel structure of the prepared solution.

The preparation of the solution involves mixing chemicals. The conductive salt LiPF$_6$ must be dissolved in an organic solvent EC/DEC (1:1 by weight) along with the monomer MMA, the cross-linking agent EDMA and the initiator of polymerization BEE. After being stirred for 20 minutes all materials were dissolved, and the prepared solution can be a move to a second phase. The second phase can be described as the conversion of the liquid state of a conductive solution into a gel structure. It means that the prepared and mixed solution then be poured into a form, which is placed in a chamber with UV-light and a radiation intensity of 1250 µW/cm^2 [7], [8], [9].

3 MEASUREMENT TECHNIQUES

The gel samples were sandwiched between two stainless steel electrodes in the electrochemical testing cell for measurement of electrochemical properties.

Electrical conductivity was measured by electrochemical impedance spectroscopy with a frequency range between 1 MHz and 0.1 Hz. There were 6 steps per decade and the amplitude sinusoidal signal was 10 mV. The value of electrical conductivity γ was calculated from Eq. (1) [7]:

$$\gamma = \frac{1}{R} \cdot \frac{h}{S} \tag{1}$$

where R is the bulk resistance, h is the thickness and S is the surface area of the gel sample.

The electrochemical interface stability of gel samples was performed using linear sweep voltammetry in the voltage range between 0.1 V and 5.1 V with sweep speed 0.5 mV/s. Values of the potential window were calculated for 5 µA/cm^2 of limiting current density [7], [8], [9]. The measurements have been provided at room temperature 23 °C.

4 RESULTS AND DISCUSSION

Gel polymer electrolytes with EDMA were prepared during the experiment. The amount of EDMA was changed between 0.35 mol% and 3.5 mol%. Samples for electrochemical characterization were prepared in an argon-filled glove box JACOMEX and measurements taken using a Biologic potentiostat [7].

Electrical conductivity is one of the important factors in the gel polymer electrolyte. Table 1 presents values of electrical conductivity of GPE at room temperature 23 °C.

Amount of EDMA [mol%]	Electrical conductivity γ [mS/cm]
0.35	3.16
0.75	4.27
1.0	3.21
1.35	3.05
1.75	3.51
2.0	1.81
2.35	2.32
2.75	1.96
3.0	1.95
3.5	1.74

Table 1: Electrical conductivity of gel polymer electrolytes at room temperature

From Table 1 can see that the electrical conductivity generally decreases with an increase in the amount of cross-linking agent EDMA. The cross-linking reaction causes an increase in the resistance for ion transport, which decreases the electrical conductivity with increasing cross-linking density [10]. The highest electrical conductivity has a gel sample with a 0.75 mol% amount of EDMA.

Figure 1 shows the temperature dependence of the electrical conductivity of GPE based on EDMA. The temperature was changed from 30 °C to 60 °C. The Arrhenius plots illustrated an increase of electrical conductivity with increasing temperature due to enhancement of the ionic mobility.
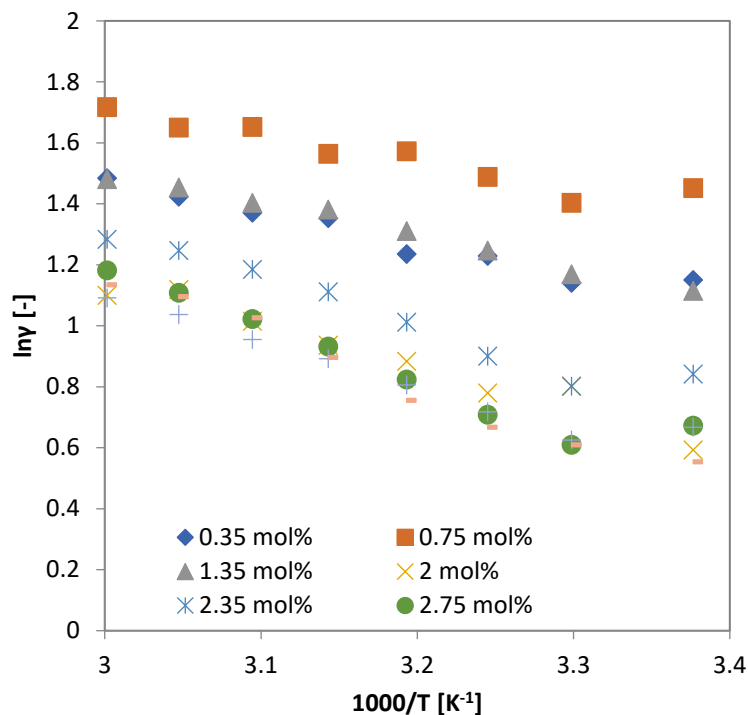

Figure 1:   Arrhenius plots of electrical conductivity of GPEs

Values of the potential window were presented in Tab.2. These values describe the electrochemical stability of prepared gel samples.

Amount of EDMA [mol%]	Potential window U [V]
0.35	4.07
0.75	3.61
1.0	2.06
1.35	3.11
1.75	3.48
2.0	3.86
2.35	3.77
2.75	2.80
3.0	3.89
3.5	3.70

Table 2:   Potential windows of gel polymer electrolytes based on EDMA

The gel polymer electrolytes with an amount of EDMA of 0.35 mol% has a wider potential window in comparison with other prepared samples. It means that this sample more stable.

Fig. 2 and 3 presents curves of current densities of prepared gel samples. The curves have some peaks, which appear as a potential window, where become oxidation of the surface of gel polymer electrolyte. It may be due to some particles, which stay in a liquid state, some chemical reactions on the electrolyte surface.
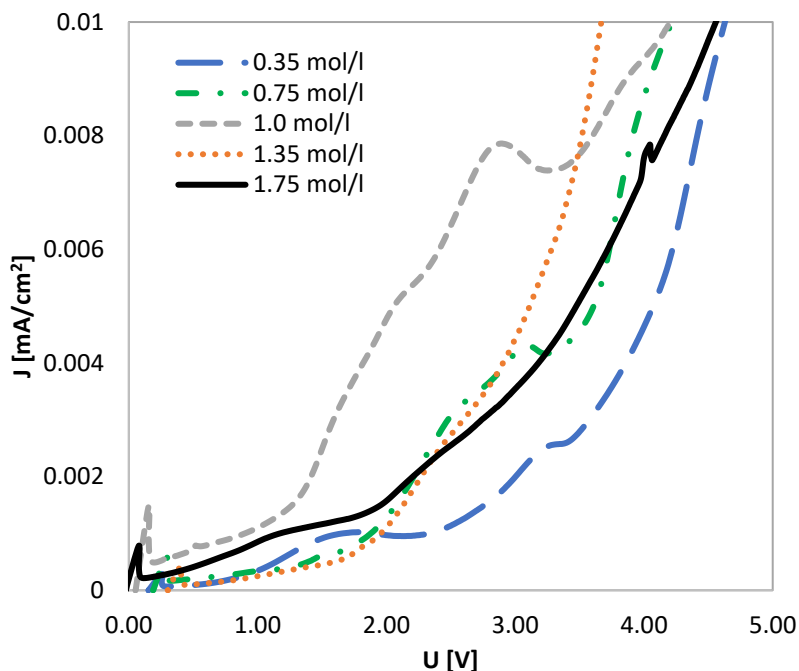

Figure 2: Linear sweep voltammograms of gel polymer electrolytes
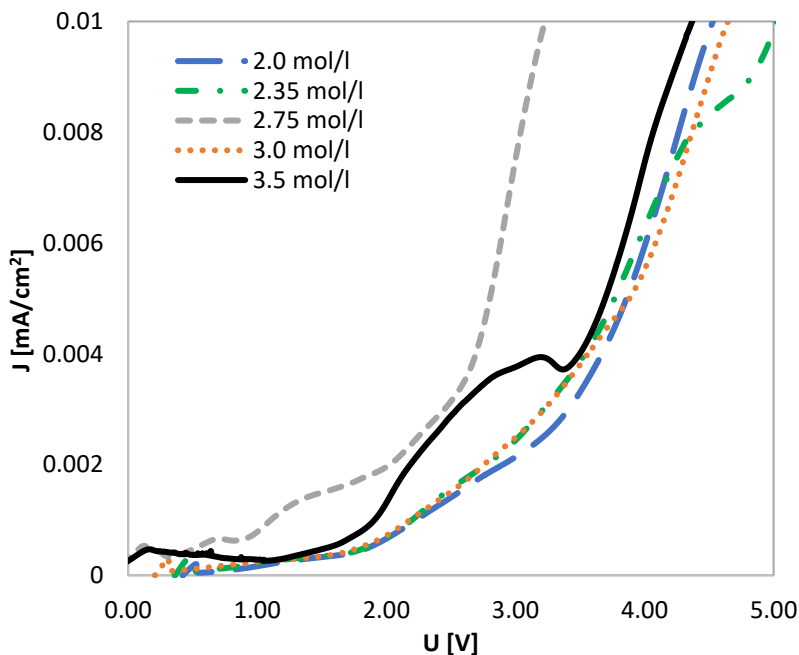(amount of EDMA 0.35 mol% - 1.75 mol%)

Figure 3: Linear sweep voltammograms of gel polymer electrolytes
(amount of EDMA 2.0 mol% - 3.5 mol%)

5 CONCLUSION

Cross-linked gel polymer electrolytes were introduced. The electrochemical properties such as electrical conductivity and electrochemical stability were measured of prepared gel polymer electrolytes. The highest electric conductivity has GPE with the concentration of EDMA of 0.75 mol%. The electrochemical stability of this gel sample was 3.61 V. Comparison of all samples show the decreasing tendency of electrical conductivity with the increasing EDMA concentration. However, electrical conductivity increases with the temperature increase. In contrast with electrochemical properties, the mechanical properties are improved with the increase of a concentration of the crosslinking agent.

ACKNOWLEDGEMENT

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