STUDY OF ELECTROCHEMICAL PROPERTIES OF GEL POLYMER ELECTROLYTE BASED ON TETRAETHYL AMMONIUM SALT

Iuliia Veselkova

Doctoral Degree Programme (3), FEEC BUT

E-mail: xgrach00@vutbr.cz

Supervised by: Marie Sedlaříková

E-mail: sedlara@feec.vutbr.cz

Abstract: In this study, gel polymer electrolytes based on tetraethyl ammonium tetrafluoroborate salt (TEA BF_4) were prepared by UV-light polymerization technique. The effect of adding TEA BF_4 in different concentrations on electrochemical and mechanical properties were studied. Ionic conductivity and potential window were measured by impedance spectroscopy and linear voltammetry methods. The results indicate how salt concentration affects electrochemical properties of gel polymer electrolytes.

Keywords: gel electrolyte, polymer, lithium ion battery, conductivity, gel, methyl methacrylate.

1 ÚVOD

For the past decades, lithium ion batteries dominate the energy storage market for portable electronic devices, owing to high energy and power densities, high energy efficiency and long cycle life [1], [2].

In state-of-the-art lithium-ion batteries usually liquid electrolytes consisting of a lithium salt dissolved in a mixture of organic solvents are used, which display a low boiling point and flash point and are prone to leakage. To avoid the risk of electrolyte leakage solid polymer electrolytes, which consist of a lithium salt dissolved in a polymer matrix, have been developed. But solid polymer electrolytes in comparison with liquid electrolytes have lower ionic conductivity [2], [3].

To combine the advantages such as high ionic conductivity of liquid electrolytes and avoiding cell leakage of solid electrolytes gel polymer electrolytes have been introduced. In these systems a liquid electrolyte is immobilized into a polymer matrix. Gels possess both cohesive properties od solids and the diffusive property liquids [4]. This unique characteristic makes the gel to find various important applications including polymer electrolytes. Gel polymer electrolytes (GPEs) based on methacrylate have the advantage of wide availability, low toxicity and good electromechanical stability. In addition, the polymethacrylates can be synthesized by irradiation with UV-light, which as a fast and cheap synthesis method [1], [3], [4].

For successful applications, a gel polymer electrolyte must have a range of critical properties including the following: a high ionic conductivity, together with high electronic resistivity; high cation mobility; good mechanical properties; the ability to form good interfacial contacts between electrodes; a large electrochemical stability window; ease of processing; chemical and thermal stability and safety [2], [3].

2 PREPARATION OF GPE

Tetraethylammonuim tetrafluoroborate 99% (TEA BF_4), ethylene carbonate (EC), diethyl carbonate (DEC), methyl methacrylate (MMA), ethylene glycol dimethacrylate (EDMA), benzoin ethyl ether (BEE) were all purchased from Sigma-Aldrich.

Gel electrolyte solution was prepared as follows. TEA BF_4 was dissolved in solution EC:DEC (1:1 in weight). The monomer MMA, the cross-linking agent EDMA and the initiator of UV-light polymerization BEE were added to the solution. After stirring of 20 min, this solution was placed under UV-light in a special glass form to achieve gel structure. This form consists of several layers: a lower glass, a Teflone layer, a silicon layer and a cover glass with transparent foil.

3 METHODS OF CHARACTERIZATION

Electrochemical test cell El-Cell was used to measure electrochemical properties of gel polymer electrolyte. The GPE with diameter of 16 mm was sandwiched by two parallel stainless steels in test cell and connected to the potentiostat BioLogic [5], [6].

Ionic conductivity of GPE was determined by measuring the impedance spectroscopy measurement with a frequency range from 1 MHz to 0,1 Hz. There were 6 steps per decade and the amplitude sinusoidal signal was 10 mV. Ionic conductivity was determined using the following Eq. 1:

$$\gamma = \frac{1}{R} \cdot \frac{h}{S} \qquad (1)$$

where h (mm) is the thickness of GPE, S (cm^2) is the contact area of the gel sample and R is the bulk resistance of GPE [7], [8]. The thickness of gel polymer electrolyte was measured with a micrometer. Generally, the thickness of a GPE was 90 μm.

The electrochemical stability of GPE was conducted by linear voltammetry method in the potential range of 0,1 V to 5,1 V with sweep speed 0,5 mV/s. Values of potential window were calculated for 5 μA and 10 μA [7], [8].

4 RESULTS AND DISCUSSION

The gel polymer electrolytes with different concentration of TEA BF_4 were polymerized by irradiation with UV-light. All manipulation with GPE samples and their preparation was in glove box JACOMEX in argon atmosphere. The goal was the preparation of GPE with the high ionic conductivity and good electrochemical stability while maintaining the mechanical properties of the gel.

Table 1 shows values of ionic conductivity of gel polymer electrolytes, which were prepared. The concentration of salt TEA BF_4 was varied from 0,1 mol/l to 1,0 mol/l.

Concentration of TEA BF_4 [mol/l]	**γ [mS/cm]**
0,1	1,42
0,2	1,89
0,3	2,84
0,4	3,35
0,5	3,92
0,6	5,54
0,7	1,41
0,8	5,31
0,9	2,76
1,0	9,42

Table 1: Ionic conductivity of gel polymer electrolytes

From Table 1 can see, that the higher ionic conductivity has gel with concentration of TEA BF_4 of 1,0 mol/l. The least value of ionic conductivity has GPE with salt concentration of 0,1 mol/l.

In Figure 2 can see graph, which illustrated how ionic conductivity of GPEs changes with increasing of concentration of salt. Ionic conductivity of prepared gel electrolytes linear increase, because a value of ionic conductivity creates salt ions. It means that with higher salt concentration ionic conductivity will be increase. The ionic conductivity of gel with 0,7 mol/l of the salt and the gel with 0,9 mol/l of the salt have values of conductivity lesser. It can be caused by various factors. For example, a bag impermeability of glass form, residues of dirt on the surface of steel electrodes in testing cell, etc.

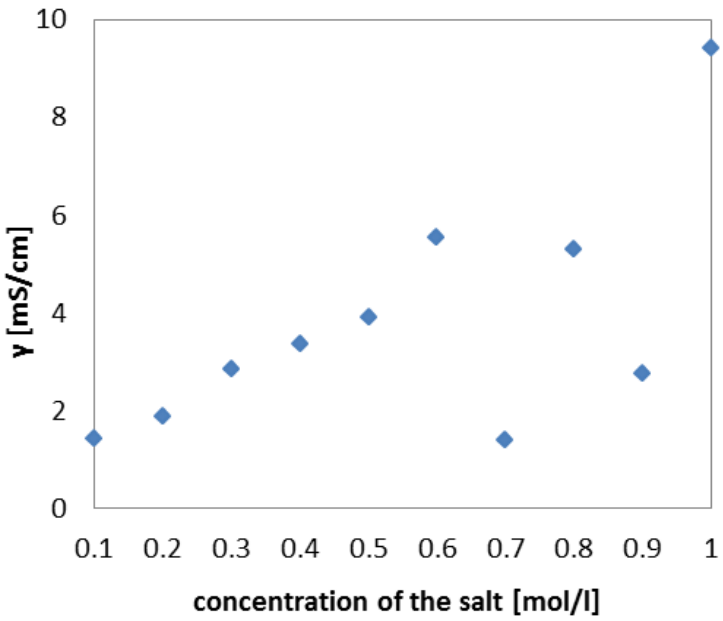

Figure 2: Ionic conductivity of GPEs depending on salt concentration

In Table 2 are values of potential windows of prepared gel polymer electrolytes.

Concentration of TEA BF_4 c [mol/l]	Potential window U [V]	
	5 µA	10 µA
0,1	3,89	4,44
0,2	3,83	4,30
0,3	3,90	4,30
0,4	3,97	4,40
0,5	4,08	4,51
0,6	3,59	4,24
0,7	3,81	4,47
0,8	3,94	4,44
0,9	3,57	4,09
1,0	2,89	3,53

Table 2: Values of potential windows of gel polymer electrolytes

The potential windows were calculated from curves of current densities. The curves of current densities of prepared gel polymer electrolytes illustrated in Figure 3 and Figure 4. From these curves can see, that GPEs was stable to 3 V, when the reaction of oxidation was not started in the testing cell. As can see in Fig. 4, the curve of GPE with salt concentration of 1,0 mol/l has some points, which are not on the line of curve. These peaks appear in part of potential window, where become an oxidation of surface of gel polymer electrolyte. It may be due to some particles, which are stay

in a liquid state, some chemical reactions on the electrolyte surface or due to imperfectly clean surface of electrodes of electrochemical cell.

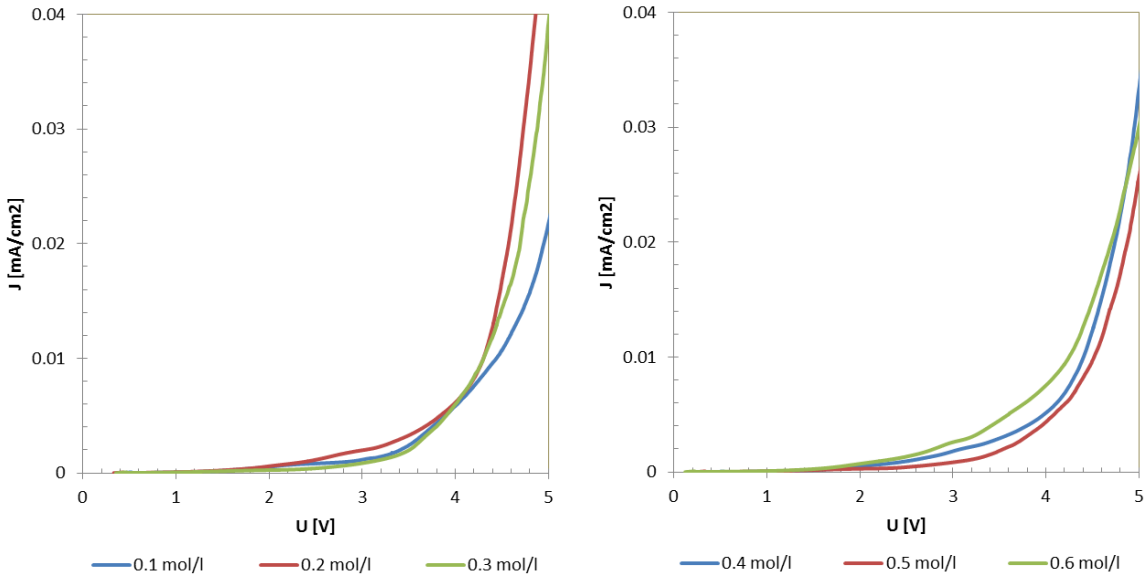

Figure 3: Curves of potential windows of gel polymer electrolytes (concentration of TEA BF_4 0,1 mol/l – 0,6 mol/l)

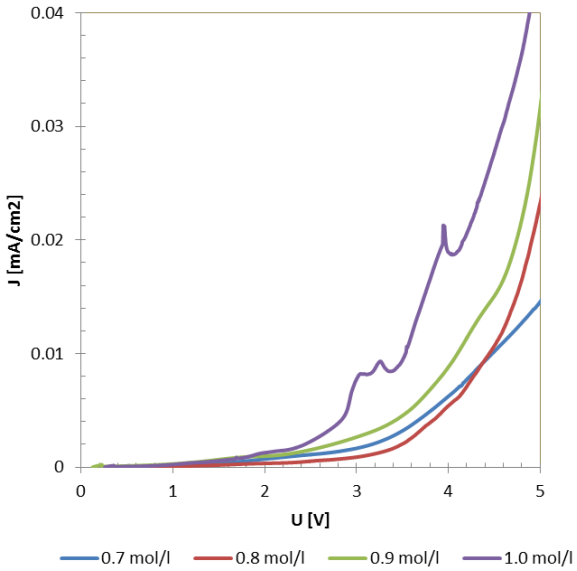

Figure 4: Curves of potential windows of gel polymer electrolytes (concentration of TEA BF_4 0,7 mol/l – 1,0 mol/l)

5 CONCLUSION

Due to the low cost, long chemical and mechanical stability and reasonably high conductivity, gel polymer electrolytes are suitable for various applications in the field of lithium batteries. Gel polymer electrolytes based on tetraethyl ammonium tetrafluoroborate salt have been prepared. Mechanical and electrochemical properties of prepared gel polymer electrolytes were studied.

Increasing the salt concentration had effect on increasing the ionic conductivity of the gel polymer electrolyte. The stability of the prepared GPEs was about the same. It means that salt does not a big influence on electrochemical stability in chemical composition, which was used in this paper. The effect on mechanical properties of GPEs was not fixed. All studied gels were elastic, non-adhesion, transparent and durable.

The results of this work could be used to future research, which will be focused on increasing ionic conductivity and stability by adding ionic liquids.

ACKNOWLEDGEMENT

This work was supported by the grant FEKT-S-17-4595 "Materiály a technologie pro elektrotechniku III"

REFERENCE

[1] Ding W., Chun Wei, Shiqi W.: Preparation and Properties of a High-Performance EOEOEA-Based Gel-Polymer-Electrolyte Lithium Battery. Polymers [online]. 2019, 11(8)

[2] Liang Sh., Wenqi Yan, Xu Wu: Gel polymer electrolytes for lithium ion batteries: Fabrication, characterization and performance. Solid State Ionics [online]. Elsevier B.V, 2018, 318, 2-18

[3] Zhu Ming, Jiaxin Wu, Yue Wang: Recent advances in gel polymer electrolyte for high-performance lithium batteries. Journal of Energy Chemistry [online]. Elsevier B.V, 2019, 37, 126-142

[4] Chojnacka J., Acosta J.L. a Morales E.: New gel electrolytes for batteries and supercapacitor applications. Journal of Power Sources [online]. Elsevier B.V, 2001, 97, 819-821

[5] Jahn M., Veselkova, I., Sedlaříková M., Bartušek K., Zatloukal M.: Gel polymer electrolytes modified nanoparticles or copolymers and polymerized in magnetic and electric fields. In ECS Transaction. ECS Transactions. 1. Pennington, New Jersey 08534-2839, USA: The electrochemical society, 2018. s. 83-91. ISBN: 978-1-60768-864-8. ISSN: 1938-5862.

[6] Veselkova, I., Peterová S., Sedlaříková M.: Gel electrolytes based on copolymers. In ECS Transaction. 1. The Electrochemical Society, 2019. s. 89-96. ISBN: 978-1-60768-864-8.

[7] Veselkova, I., Sedlaříková M., Fafilek G., Gierl-Mayer C.: Electrochemical and thermal properties of gel polymer electrolytes modified by flame retardants. In ECS Transaction. 1. Pennington, New Jersey 08534-2839, USA: The Electrochemical Society, 2019. s. 47-55. ISBN: 978-1-60768-864-8.

[8] Veselkova I., Jahn M., Sedlaříková M., Vondrák J.: Electrochemical properties of gel polymer electrolytes with flame retardant using as solvent. In ECS Transaction. ECS Transactions. 1. Pennington, New Jersey 08534-2839, USA: The Electrochemical Society, 2018. s. 15-21. ISBN: 978-1-60768-864-8. ISSN: 1938-5862.