GEL POLYMER ELECTROLYTES BASED ON MMA WITH IONIC LIQUIDS

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Abstract: Gel polymer electrolytes are perspective electrolytes for new types of Li-ion batteries today. The properties respectively advantages of these gels can be used also in other fields of electrochemistry. Very promising combination can be electrochemically stable polymers and ionic liquids, which are substances that consist of an organic cation and an inorganic or organic anion, with a melting point below 100 °C. Main advantages of ionic liquids are high ionic conductivity, inflammability and excellent electrochemical stability. These ionic liquids may be suitable for new lithium-ion batteries and supercapacitors, especially where the required higher thermal stability. In this paper, I will present fundamental characteristics of gel polymer electrolytes with ionic liquids.

Keywords: Gel, polymer, electrolytes, batteries, cell, methyl methacrylate, UV light, conductivity, ionic liquids, potential window.

1 INTRODUCTION

Gel polymer electrolyte materials separate anode and cathode and play the significant role of transmitting lithium ions during charging and discharging processes. Also, electrolyte is one of the key components that define the battery's performance: charging/discharging capacity, safety, cycling performance, and current density. The main advantages these electrolytes are the elimination leakage of electrolyte, better resistance to vibration and mechanical damage, or better resistance to volume changes of the electrodes. Another advantage is the adhesion of the gel to the electrode surface, this effect reduces the formation of aggregates on the surface and thus provides protection against internal short circuit and reduction capacity. Advanced gel polymer electrolytes having the same ionic conductivity as liquid electrolytes [3,5,7,8]. Subsequent research has focused on improving electrical, electrochemical and mechanical properties of these electrolytes by adding ionic liquids [6,8].

Ionic liquids are composed of an organic cation and an inorganic or organic anion. The characteristic melting point is lower than 100 °C. Some ionic liquids are liquid even at room temperature. Among the advantages, we can mention zero vapor pressure, high thermal stability, low toxicity, non-flammability, a broad temperature range at which the liquid and unique solvation properties. The ionic liquids can be used as a substitute for volatile organic solvents and a suitable environment for the preparation of chemical reactions. Compounds which would have ionic character and when the low melting point are salts in which there is no coordination between the cation and anion [6,8].

2 CHEMICAL COMPOSITION AND PREPARATION

The gel polymer electrolyte is composed of a conductive component and the polymer component. This conductive part forms a salt $LiPF_6$ and a solvent EC/DEC (1:1 weight). The polymeric part forms methyl methacrylate as a monomer, benzoin ethyl ether as a polymerization initiator (UV light) and ethylene glycol dimethacrylate as a networking agent [3,5]. The molar proportion of monomer to the conductive component (0,5 mol/l LiPF6 in EC/DEC) is 20 mol%. The molar proportion of polymerization initiator and networking agent to the monomer is for the polymerization initiator 1,0 mol% and for the networking agent 3,5 mol%. Ionic liquids are added to improve chemical, electrochemical and mechanical properties of the gel polymer electrolytes. Specific ionic conductivity of the gel polymer electrolyte without ionic liquid is 3,06 mS/cm. Selected ionic liquids, which are used in the experimental section [2,4]:

- 1-Ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide - EMIM TFSI,
- 1-Ethyl-3-methylimidazolium tetrafluoroborate - EMIM BF_4,
- 1-Ethyl-3-methylimidazolium hexafluorophosphate - EMIM PF_6,
- 1-Ethyl-3-methylimidazolium dicyanamide - EMIM DCA.

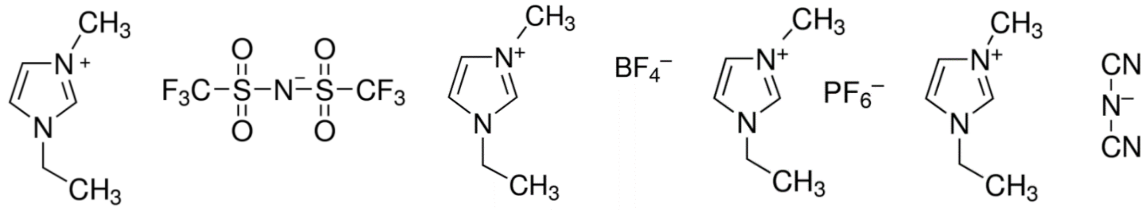

Figure 1: The structural formula of EMIM TFSI, EMIM BF_4, EMIM PF_6 and EMIM DCA (from left to right) [2,4]

Table 1 shows the basic characterization of the individual ionic liquids.

Ionic liquid	Molecural weight [g/mol]	Density [g/cm^3]	Melting point [°C]	Flash point [°C]
EMIM TFSI	391,31	1,53	-15	> 200
EMIM BF_4	197,97	1,29	15	> 350
EMIM PF_6	256,13	1,35	58-62	------
EMIM DCA	177,21	1,11	-21	------

Table 1: Characteristic properties of selected ionic liquids [2,4]

Sample resp. gel polymer electrolyte is disc with a diameter 16 mm and thickness 0,9 mm, which is cut out from the total area of formed (polymerized) gel. All handling of the gel is performed in a glove box with argon atmosphere. All chemicals are mixed in a vial with a magnetic stirrer in glove box. The time required for complete dissolution of all chemicals is about 20 minutes and time of polymerization in UV chamber is 1 hour. Samples are measured in metallic El-Cells using the potentiostat Bio-Logic (potentiostatic impedance atd linear sweep voltammetry) [1].

The Potentiostatic Impedance (PEIS) experiment performs impedance measurements into potentiostatic mode by applying a sinus around a potential E that can be set to a fixed value or relatively to the cell equilibrium potential [1].

Linear sweep voltammetry (LSV) is one half of one cycle of cyclic voltammetry. Cyclic Voltammetry (CV) is the most widely used technique for acquiring qualitative information about electrochemical reactions. CV provides information on redox processes, heterogenous electron-transfer reactions and adsorption processes. It offers a rapid location of redox potential of the electro active species. Plot of current to voltage is called polarization curve or potential window [1].

3 EXPERIMENTAL RESULTS

In the experimental part were measured four series of samples with different ionic liquids. Volume amounts of the ionic liquid is related to the volume of the conductive component (salt + solvent). Conductive component is one hundred percent. The total amount of conductive component and the ionic liquid is one hundred percent of the volume conductive component plus the volume of ionic liquid (percent). Measurement range of potentiostatic impedance is from 1 MHz to 0,1 Hz, steps per decade is 6 and amplitude sinusoidal signal is 10 mV. The measured results shown in Table 2 and Figure 2. Measurement range of linear sweep voltammetry is from 0,1 V to 5,1 V and sweep speed 0,5 mV/s. The measured results shown in Table 3 and Figures 3, 4, 5.

Conductivity												
EMIM TFSI												
V_{IL} [%]	1	5	10	25	50	75	90	100	125	150	175	200
γ [mS/cm]	3,32	9,08	11,7	7,02	8,89	5,75	7,57	6,27	4,90	6,87	7,75	6,40
EMIM BF_4												
V_{IL} [%]	1	2,5	5	10	15	20	25	30				
γ [mS/cm]	1,86	2,08	8,79	5,87	20,36	6,06	8,02	0,62				
EMIM PF_6												
V_{IL} [%]	1	1,5	2,5	3,5	5	7,5	10	15				
γ [mS/cm]	3,35	4,75	7,59	4,38	3,93	1,99	2,61	1,87				
EMIM DCA												
V_{IL} [%]	2,5	5	10	15	20	25	30					
γ [mS/cm]	3,10	5,70	2,71	31,3	4,05	6,67	3,60					

Table 2: Conductivity of gel polymer electrolytes with ionic liquids

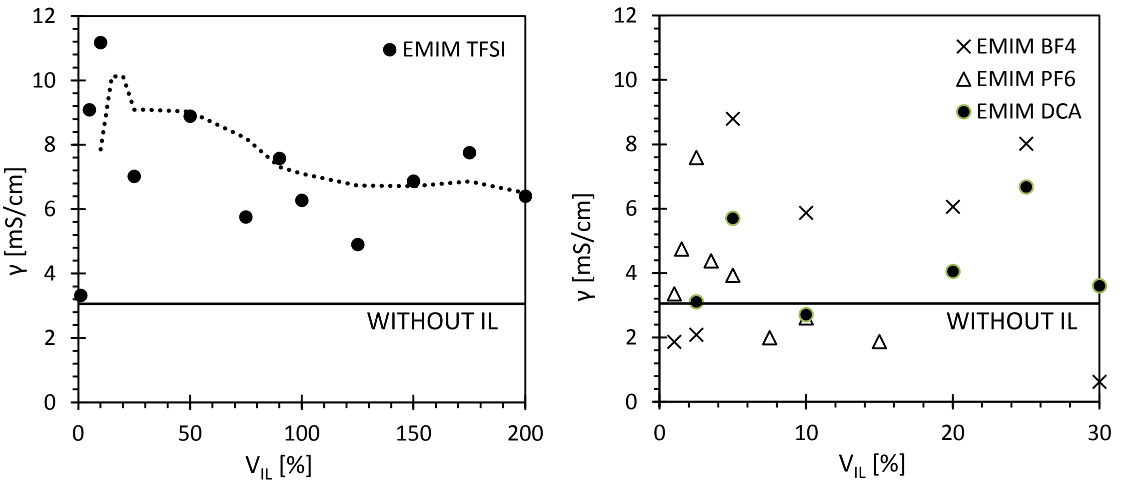

Figure 2: Graphs of conductivity for EMIM TFSI and EMIM BF_4 / PF_6 / DCA

Potential window												
EMIM TFSI												
V_{IL} [%]	1	5	10	25	50	75	90	100	125	150	175	200
5 µA [V]	2,84	4,39	4,22	3,13	4,72	2,56	4,48	2,97	2,82	5,03	-	4,73
10 µA [V]	4,69	4,60	4,48	3,49	-	2,95	4,97	3,28	3,25	-	-	-
EMIM BF_4												
V_{IL} [%]	1	2,5	5	10	15	20	25	30				
5 µA [V]	3,20	3,89	3,99	2,93	1,54	3,87	-	2,71				
10 µA [V]	4,28	-	4,39	3,69	3,91	4,62	0,2	3,09				
EMIM PF_6												
V_{IL} [%]	1	1,5	2,5	3,5	5	7,5	10	15				
5 µA [V]	4,89	4,58	-	-	0,92	5,07	-	-				
10 µA [V]	-	-	-	-	1,73	-	-	-				
EMIM DCA												
V_{IL} [%]	2,5	5	10	15	20	25	30					
5 µA [V]	3,93	-	4,00	-	3,76	4,18	3,13					
10 µA [V]	4,41	-	-	-	-	-	-					

Table 3: Potential windows of gel polymer electrolytes with ionic liquids

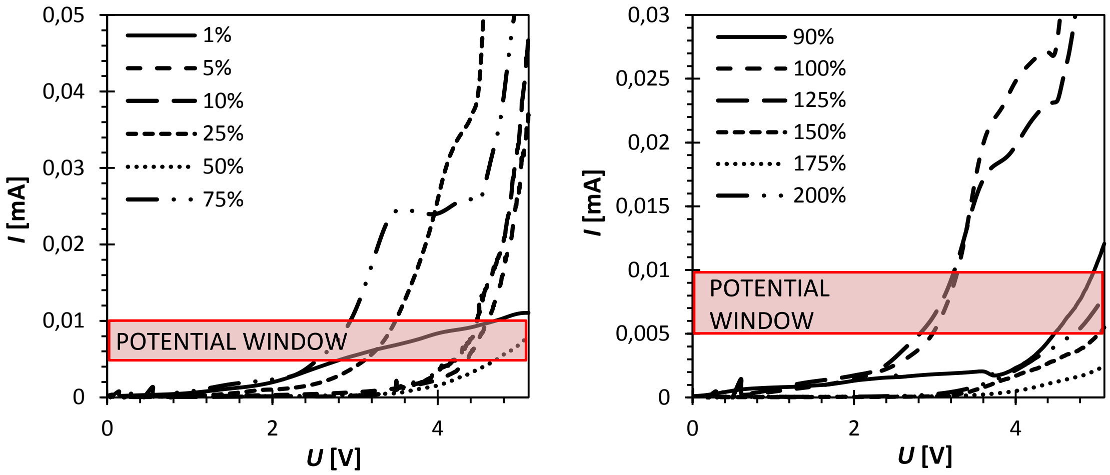

Figure 3: Potential windows for EMIM TFSI

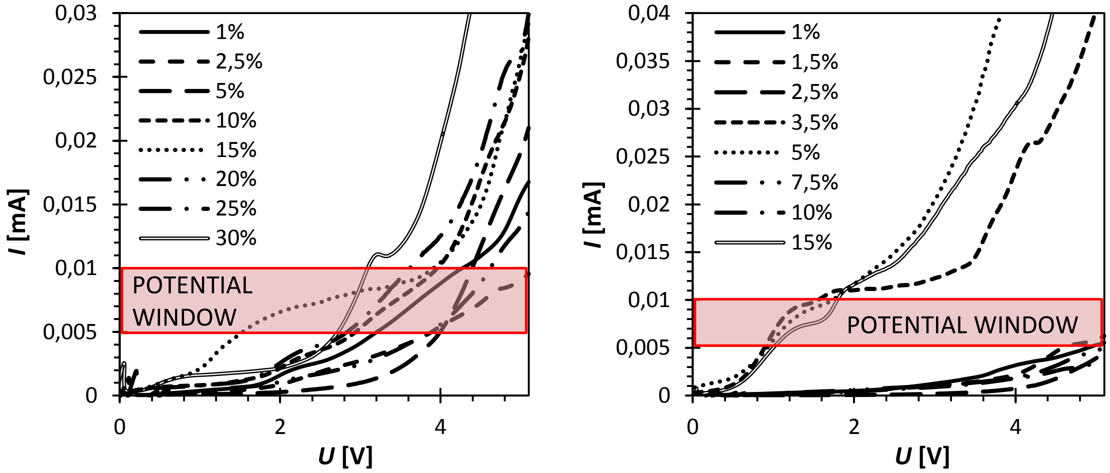

Figure 4: Potential windows for EMIM BF_4 and EMIM PF_6

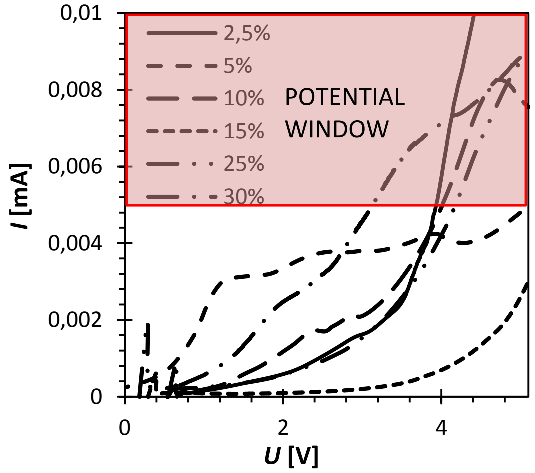

Figure 5: Potential window for EMIM DCA

4 CONCLUSION

These experimental measurements served as the initial studies on the gel polymer electrolytes with ionic liquids. From the measured values of gel polymer electrolytes is evident that the ionic liquid improves conductivity and electrochemical stability if the concentration of ionic liquid is not too high. On contrary, large quantities of ionic liquid conversely decrease the conductivity. It seems best to range from 1% to 25%, where the conductivity is comparable to the commercially used liquid electrolytes. The best properties for use in gel polymer electrolytes have ionic liquid - EMIM TFSI. Further research will be focused on the thermal properties using thermal analyzes – TGA (thermogravimetries), DTA (differential thermal analysis) and EGA (analysis of evolved gases). Also, the research will be focused on the various combinations of lithium salts ($LiCl_4$, $LiBF_4$, $LiPF_6$) and sodium salts ($NaClO_4$, $NaBF_4$, $NaPF_6$) with next solvents (propylene carbonate, dimethyl carbonate and dimethylformamide). The main goal is higher ionic conductivity (>25 mS/cm) with good electrochemical stability and to validate the use of Li-ion cells.

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REFERENCES

[1] BIOLOGIC SCIENCE INSTRUMENTS. *EC-Lab Software Techniques and Applications*. 10.1x. Bio-Logic SAS, 1, rue de I´Europe, F-38640 Claix, France, 2011. Available form: www.bio-logic.info

[2] *Chemical Book* [online]. Chemicalbook, 2016 [cit. 2017-03-05]. Dostupné z: http://www.chemicalbook.com/

[3] KREJZA, Ondřej. *Gel polymer electrolytes for electrochromic device*. Brno, 2009. Dizertační práce. Vysoké učení technické v Brně, Fakulta elektrotechniky a komunikačních technologií. Vedoucí práce Prof. Ing. Jiří Vondrák, DrSc.

[4] *SIGMA-ALDRICH: A part of Merck* [online]. 2017 [cit. 2017-03-05]. Dostupné z: http://www.sigmaaldrich.com/czech-republic.html

[5] SEDLAŘÍKOVÁ, Marie. *Polymerní gelové elektrolyty a jejich využití v elektrotechnice*. Brno, 2003. Habilitační práce. Vysoké učení technické v Brně, Fakulta elektrotechniky a komunikačních technologií.

[6] STENGER-SMITH, John D. a A. IRVIN. *Ionic Liquids for Energy Storage Applications* [online]. Texas State University, 2009 [cit. 2017-03-05]. Dostupné z: http://www.sigmaaldrich.com/technical-documents/articles/material-matters/ionic-liquids-for.html

[7] STEPHAN, A. Manuel. Review on gel polymer electrolytes for lithium batteries. *European Polymer Journal* [online]. Science Direct, 2006(42), 21-42 [cit. 2017-03-05]. Dostupné z: http://krc.cecri.res.in/ro_2006/034-2006.pdf

[8] ZHANG, Ruisi. *Advanced gel polymer electrolyte for lithium-ion polymer batteries*. Iowa, 2013. Graduate theses and Dissertations. Iowa State University. Vedoucí práce Professor Reza Montazami.