AN INFLUENCE OF CONDUCTIVE COMPONENT COMPOSITION ON GEL POLYMER ELECTROLYTE PROPERTIES

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Abstract: This paper deals with searching of gel polymer electrolytes, which can be used as replacement of liquid electrolyte in lithium batteries and supercapacitors. The research reports how different salts and solvents affect mechanical, electrochemical and electrical properties of gel electrolytes. For measurement electrical and electrochemical properties were used methods such as impedance spectroscopy and cyclic voltammetry to calculate electrical conductivity and potential window respectively. Results indicate which chemical composition of gel polymer electrolyte theoretical can be work in electrochemical cell instead of liquid electrolyte.

Keywords: gel electrolyte, polymer, solvent, electrical conductivity, methyl methacrylate.

1 INTRODUCTION

In recent years the most widely used electrochemical power sources are lithium accumulators and supercapacitors. The development of current sources is focused on the research of new materials, which used in their manufacture and in the same time can be improve its safety, reliability, electrical and electrochemical properties, efficiency and flexibility [1,2].

In the field of chemical production prospective materials include gel polymer electrolytes, which now replace yet obsolete liquid electrolytes. These polymer gels, which based on conductive salt, have a number of advantages over the previous liquid electrolytes. The most important advantages are elimination of the risk of electrolyte spillage, high safety (no organic solvents with toxins are used), high shape flexibility, low reactivity due to solid component of gel, low density, resistance to mechanical stress, high temperatures and pressures, and vibrations. Also the advantages of gel polymer electrolyte include adhesion to the electrode surface, which limits the formation of aggregates and its surface and thus provides protection against internal short torsion and reduced power [1,2,3].

The main focus here is on improving polymer electrolyte parameters like increasing ion conductivity, expanding the potential window, improving the long-term chemical and electrochemical stability of both polymer and solvent docked. First section of this article presents basic chemical composition of gel polymer electrolyte, what salts and solvents were chosen and preparation process of gel electrolyte. In the previous section are all results, which were obtained in measurement process. And the final section will present some conclusions, which were made on the basis of measurements.

2 CHEMICAL COMPOSITION AND PREPARATION

The basic chemical composition of gel polymer electrolyte is composed of a conductivity component and a polymer component. The conductivity component usually contains conductive salt and solvent. There are lithium perchlorate ($LiClO_4$), lithium hexafluorophosphate ($LiPF_6$), lithium tetrafluoroborate ($LiBF_4$), sodium perchlorate ($NaClO_4$), sodium hexafluorophosphate ($NaPF_6$), sodium

tetrafluoroborate ($NaBF_4$) were used as a conductive salts. As solvents were chosen polyethylen carbonate (PC), ethylene carbonate/dimethyl carbonate (EC/DEC in weight 1:1) and ethylene carbonate/ dimethyl carbonate (EC/DMC in weight 1:1). The polymer component contains monomer, crosslinking agent and polymerization initiator. As monomer was used methyl methacrylate (MMA), as crosslinking agent was chosen ethylene glycol dimethacrylate (EDMA) and as initiator of polymerization was selected benzoin ethyl ether (BEE).

All gel polymer electrolytes were prepared in the same chemical composition with salt concentration 0.5 mol/l in selected solvent. The molar amount of monomer to conductivity component is 20 mol%. The molar amount of crosslinking agent to the monomer is 3.5 mol% and 1 mol% for initiator of polymerization [4,5]. The sample of gel polymer electrolyte can see in figure 1.

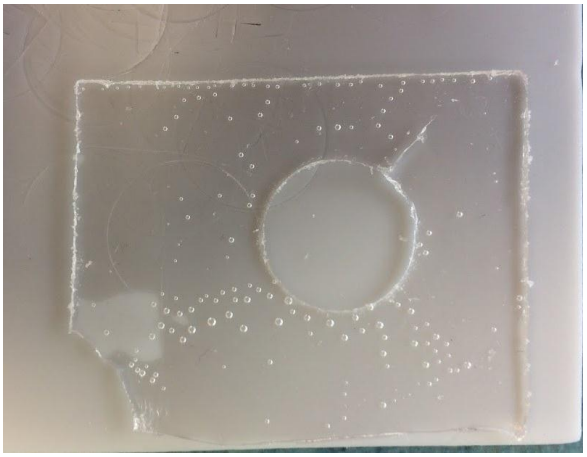

Figure 1: Sample of gel polymer electrolyte

Under the sample implied circular gel with diameter 16 mm with a defined thickness of 0.9 mm, which is cut out from the total area of formed (polymerized) gel. The development of gel samples consists of preparation of the solution, which injected into the form. The form has a square shape and consists of several layers: glass, Teflon, silicone, transparent foil and second glass. After that the form places into the polymerization chamber with UV light. The time of polymerization process in UV chamber is 60 min. All manipulation with gel polymer samples take place in glove box with argon atmosphere. Preparation of gel samples is focus on seeking for a gel polymer electrolyte with electrical conductivity 3-5 mS/cm and suitable potential window [3,4,5].

3 EXPERIMENTAL RESULTS

All gel samples analyze using two methods. There are electrochemical impedance spectroscopy and cyclic voltammetry. Impedance spectroscopy use to measure electrical conductivity. Cyclic voltammetry use to measure potential window of gel electrolytes. These methods have been used to evaluate and compare electrical and electrochemical properties. Measurement range of electrochemical impedance is from 1 MHz to 0.1 MHz and steps per decade is 6, amplitude sinusoidal signal is 10 mV.

The measurement results of gel samples, which were made with PC as solvent, are shown in table 1.

Gel samples, which were made with PC as solvent, have good mechanical properties. Most of them are clear, non-adhesive, without bubbles, have a good handing of the gel, flexible. The sample with $NaBF_4$ as salt in conductivity component is adhesive, poor handing of it.

Table 2 is shown the results of gel polymer samples, which were made with EC/DEC as solvent. Samples from this group of gel polymer electrolytes, which were made with EC/DEC as solvent, have different mechanical properties. The samples with $NaBF_4$, $LiClO_4$ and $LiBF_4$ are adhesive,

jerked, non-flexible and have a poor handing of them. The samples with the other salts have good mechanical properties.

Parameter	γ [mS/cm]	5 µA	10 µA
$LiClO_4$	2.75	-	-
$LiPF_6$	2.82	-	-
$LiBF_4$	1.75	1.58	3.05
$NaClO_4$	1.96	3.4	3.88
$NaPF_6$	2.2	-	-
$NaBF_4$	0.98	2.12	3.5

Table 1: Electrical conductivity and potential windows of gel polymer electrolytes with PC as solvent

Parameter	γ [mS/cm]	5 µA	10 µA
$LiClO_4$	1.47	0.83	1.09
$LiPF_6$	3.06	-	-
$LiBF_4$	1.98	-	2.93
$NaClO_4$	1.35	3.27	3.76
$NaPF_6$	6.46	-	-
$NaBF_4$	0.98	-	0.64

Table 2: Electrical conductivity and potential windows of gel polymer electrolytes with EC/DEC as solvent

Measured values of electrical conductivity and potential windows of gel samples, which were made with EC/DMC as solvent are shown is Table 3.

Parameter	γ [mS/cm]	5 µA	10 µA
$LiClO_4$	4.07	-	-
$LiPF_6$	5.18	-	-
$LiBF_4$	1.82	3.17	3.5
$NaClO_4$	3.45	1.0	1.2
$NaPF_6$	3.6	-	-
$NaBF_4$	0.63	2.6	3.7

Table 3: Electrical conductivity and potential windows of gel polymer electrolytes with EC/DMC as solvent

All gel samples with EC/DMC as solvent have bad properties. There are jerked, poor handing, non-flexible, adhesive and wrinkled.

Figure 2 shows how the electrical conductivity varies with the chosen lithium salt and solvent.

In salt comparison can be seen, that gel electrolytes based on $LiPF_6$ salt have higher conductivity in different solvents then other chosen lithium salts. The highest conductivity 5.18 mS/cm have gel

sample with EC/DMC as solvent, but mechanical properties of it are not good for next manipulation.

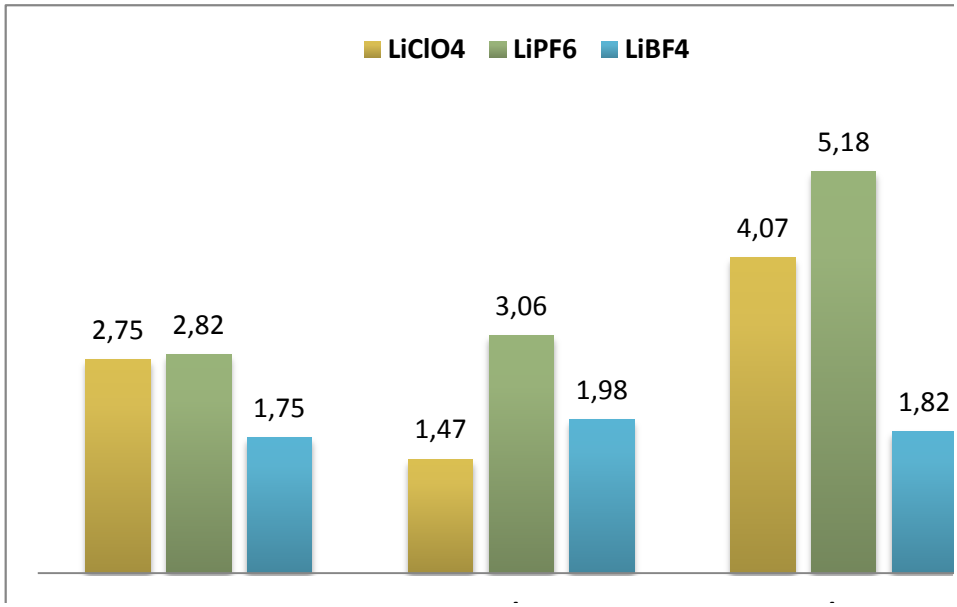

Figure 2: Electrical conductivity of lithium salts

Figure 3 shows how the electrical conductivity varies with the sodium salt in different chosen solvents. The higher conductivities have gel samples based on $NaPF_6$ salt. In the solvent EC/DEC gel polymer electrolyte with this salt has the highest conductivity 6.46 mS/cm.

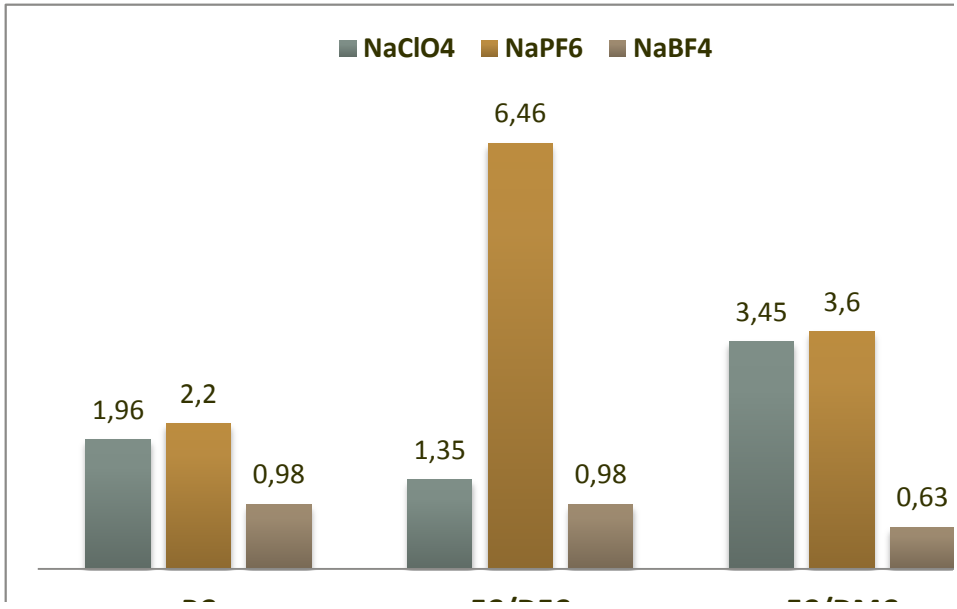

Figure 3: Electrical conductivity of sodium salts

4 CONCLUSIONS

This paper has shown that chemical composition in conductive component of gel polymer electrolytes have a considerable influence on electrical, electrochemical and mechanical properties. From the measured values of gel polymer electrolytes is evident that different salts and solvents have different effect on conductivity and electrochemical stability, may cause an increase or a decrease in the conductivity. Comparison of all properties gives, that fluorophosphates increase electrical con-

ductivity and electrochemical stability better than other conductive salts. Mechanical properties of these gel electrolytes are better too. The results of this work could be used to future research, which will be focused on increasing thermal stability of gel electrolytes and their further application in Li-ion batteries.

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