CONDUCTIVITY OF GEL POLYMER ELECTROLYTES

Ing. Ondřej KREJZA, Doctoral Degree Programme (1)
Dept. of Electrical and Electronic Technology, FEEC, BUT
E-mail: xkrejz01@stud.feec.vutbr.cz

Supervised by: Dr. Jiří Vondrák

ABSTRACT

This article deals with liquid and gel polymer electrolytes, their polymerization and basic outlines of electrolytic conduction. The electrolytic conductivity of percholrates of Li dissolved in propylene carbonate was measured and compared to the PMMA based gels prepared from mentioned solution. The conductivity was measured between +90 and -70 ^{o}C.

1 INTRODUCTION

During the last years there was a lot of effort done on the electrochemical preparation of polymer gel electrolytes. These materials are often used as electrolytes in lithium batteries, super capacitors and elektrochromic components. Even when these materials are known for a longer time already, studies of their properties are being accomplished as late as in the recent years.

2 POLYMER GEL AND LIQUID ELECTROLYTES

In the common language is "electrolyte" oftenused in meaning of "liquid electrolyte". Under the category electrolyte we include those conducting systems where electric current is joined with material transporting.

2.1 LIQUD ELECTROLYTES

Materials conducting electric current are divided into two groups – ionofors and ionogens. Ionofor is a material compact from ions only. Conductivity of ionofor depends on concentration, dielectric constant and viscosity of dissolver. Ionogen is a material which crystals are compounded from molecules creating ions while being affected by dissolver.

2.2 GEL POLYMER ELECTROLYTES

Gel electrolytes are electrolytes with polymer addition with balanced ratio so polymeration will produce gel structure. Electrolyte is usually created from alcalic salts, often used is lithium perchlorate ($LiClO_4$).

Polymer electrolytes are defined as solid ion conductors formed with dissolving salt in polymer having fitting high molecular weight. Based on the method of holding ions in the polymer they can be divided into two groups: polyelectrolytes and gel electrolytes.

2.3 PROPERTIES AND USUABILITY OF GEL POLYMER ELECTROLYTES

Polymer gel electrolytes are very progressive materials. They can be prepared in semisolid or solid form, which is a cheap and reliable process when they are manufactured. Between requests for wide-usability of gel electrolytes is high conductancy. Polymer electrolytes and in recent days especially gel polymer electrolytes can be used in several different cases. In accumulators and supercapacitors they can replace liquid electrolytes, as they are more stable in the meaning of chemical and electric stability and also in electrochromic displays and devices as it is very handful to prevent devices from drying out or leaking electrolyte.

3 PREPARATION SAMPLES OF GEL POLYMER ELECTROLYTE

Samples that have contained solution of Li salt with different molar concentration in propylencarbonate were investigated They were mixed with solid oligomeric (polymerization precursor) SUPERACRYL (SPOFA DENTAL, a.s., Prague) and than added to the monomer (methylmethacrylate), after that we have obtained an elastic and homogenous polymer with good optical properties.

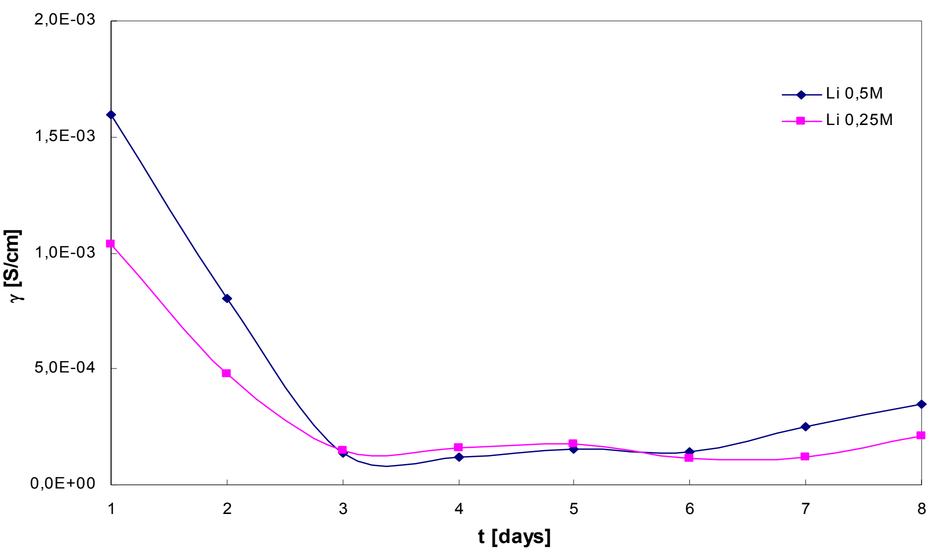
Gel polymer electrolytes –ratios of their individual ingredients:

1 ml $LiClO_4$ v PC + 700 mg solid oligomer + 1,5 ml liquid monomer

4 AGEING OF GEL POLYMER ELECTROLYTES

Specific el. conductivity was measured with the aid of four point method using special measuring head. This method is particulary useful for semiconductor measuring.

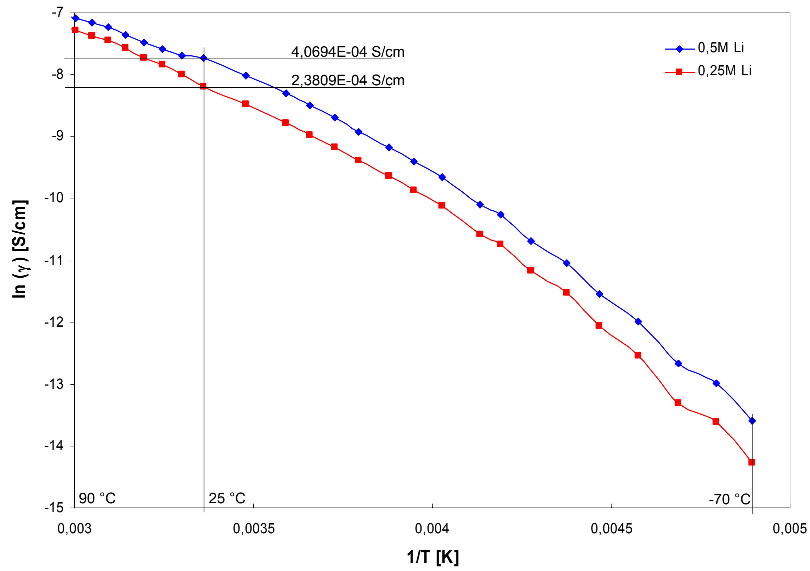
Fig. 1: *Ageing of gel polymer electrolytes; 1 kHz frequency range*



5 TEMPERATURE AND CYCLIC MEASUREMENTS

Measuring of specific el. conductivity had 10 kHz frequency range and temperature range was from +90 to -70 °C. Samples were fixed between two stainless steel sheets with accurately defined proportion. This electrode system was situated into the heat chamber and than into the liquid nitrogen cooled vessel with ethanol bath.

Fig. 2: *The influence temperature on specific conductivity of gel electrolytes; 10 kHz*

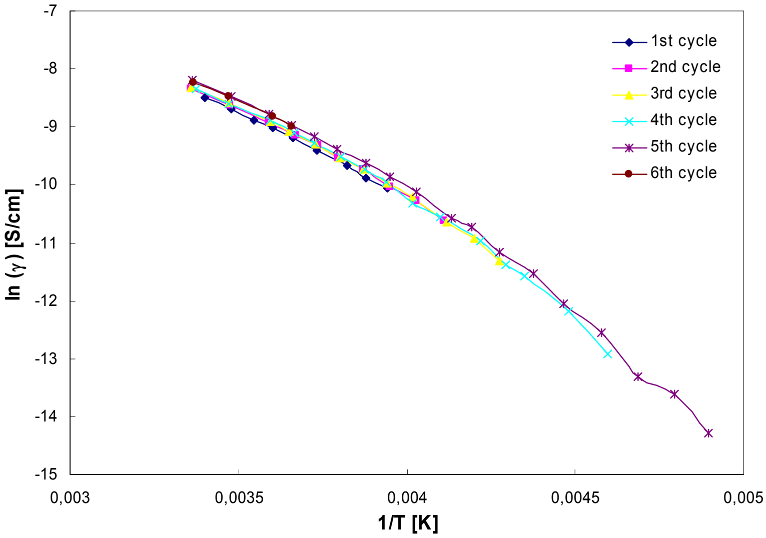


Tab. 1: *Specific el. Conductivity of gel polymer electrolytes –maximum and minimum values*

T [°C]	g [S/cm]	
	0,5M Li	0,25M Li
90	1,18E-03	1,01E-03
-70	1,25E-06	6,31E-07

In the area of negative temperature was measured 6 cycles (25 to -20; 25 to -30; 25 to -40; 25 to -55; 25 to -70; 25 to 0 °C). It was very important for checking reproducibility specific conductivity of samples see Fig.3, which was achieved in 1st cycle at temperature 25 °C. There was observed 25 minutes long interval for smooth transition undercooling electrode system on 25 °C.

Fig. 3: *The influence temperature on specific conductivity of gel electrolytes; 0,25M Li, 10 kHz*



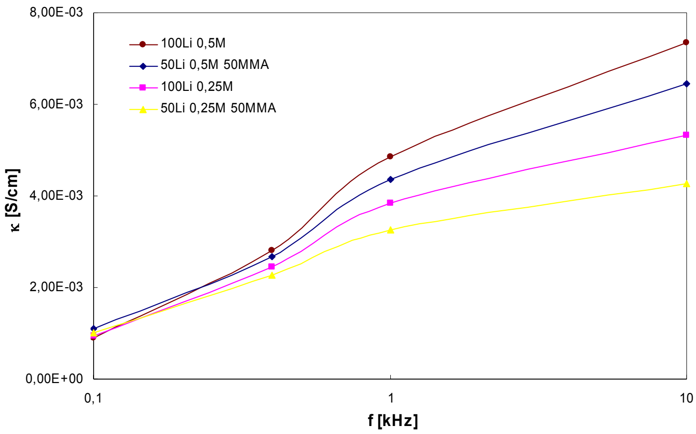
Tab. 2: *Reversibility/reproducibility of specific conductivity during past six cycles*

T = 25 °C f = 10 kHz γ [S/cm]		
	0,5M Li	0,25M Li
1st cycle	3,4203E-04	2,0320E-04
2nd cycle	4,0694E-04	2,3809E-04
3rd cycle	4,1789E-04	2,4470E-04
4th cycle	4,0474E-04	2,3665E-04
5th cycle	4,3744E-04	2,7616E-04
6th cycle	4,1073E-04	2,6762E-04
max. deviation [%]	7,5	16

6 LIQUID ELECTROLYTES

Measuring was surveyed with liquid electrolytes containing lithium salts dissolved in propylencarbonate and methylmetacrylate. The frequency range was from 0,1 to 10 kHz.

Fig. 4: *The influence frequency on specific conductivity of liquid electrolytes; T=25°C*



Tab. 3: *Specific el. conductivity of gel and liquid electrolytes, 25 °C, 10 kHz*

composition [%]	gel electrolytes γ [S/cm]	liquid electrolytes κ [S/cm]
100 Li 0,5M	4,0694E-04	7,3511E-03
50 Li 0,5M + 50 MMA		6,44E-03
100 Li 0,25M	2,3809E-04	5,3251E-03
50 Li 0,25M + 50 MMA		4,27E-03

7 CONCLUSION

The evolution of resistivity in time (see Fig. 1) has shown that there was a pronounced change of specific conductivity during first two days. From that time, specific conductivity became stable. The diference was probably caused by imperfect polymerization of the samples.

Speaking on temperature and cyclic measurement, between 4th and 5th cycle there was 14 hours pause. In the 5th cycle after regeneration the specific el. conductivity of the gel with composition of 0,25M $LiClO_4$ increased up to 16 % with respect to its original value. The lowest increase 7,5 % had the gel with composition 0,5M $LiClO_4$ (see Tab.2). No apparent visual change of the samples after the cycles was observed.

The specific electric conductivity of gel polymer electrolytes was lower than that of liquid electrolytes. We can see it in Tab.3. The sample with composition of 100 % 0,5M $LiClO_4$ liquid electrolyte had maximum value 7,3511E-03 S/cm opposite to value the sample with composition of 100 % 0,5M $LiClO_4$ gel electrolyte 4,0694E-04 S/cm. Conductivity of liquid electrolytes which contained monomeric methyl methacrylate was lower than the conductivity of liquid electrolytes which contained only lithium salts dissolved in propylencarbonate (see Tab.3).

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