GEL POLYMER ELECTROLYTES COMPOSED OF ETHYL METHACRYLATE AND METHYL METHACRYLATE MEASURED AT HIGHER TEMPERATURE

Soňa Peterová

Doctoral Degree Programme (1), FEEC BUT

E-mail: xpeter18@stud.feec.vutbr.cz

Supervised by: Marie Sedlaříková

E-mail: sedlara@feec.vutbr.cz

Abstract: This paper is focused on the use of gel polymer electrolytes composed of copolymers of ethyl methacrylate and methyl methacrylate with positive NMC electrode ($LiNi_{0.33}Mn_{0.33}CO_{0.33}O_2$). This article describes the composition of gel polymer electrolyte, the method of preparation and description of the NMC electrode. The experiment is based on the measurement of capacity and impedance at the beginning and at the end of the experiment at room temperature and at higher temperature 40 °C.

Keywords: gel polymer electrolytes, copolymers, NMC electrode

1 INTRODUCTION

With the wider possibilities of using battery-powered devices, the diverse demands on these sources of electricity are growing also. The requirements for the number of cycles, capacity, electrochemical stability, safety, usage of ecological materials and ecological disposal of batteries are increasing. Nowadays, when lithium batteries are widely used, it is being considered to improve the electrolytes used in them too. Liquid electrolytes are used mostly in lithium batteries. The main reason is a high ionic conductivity. However, the problems of liquid electrolytes are for example safety, mainly flammability and toxicity. Gel polymer electrolytes consist of a polymer, an inorganic salt and an organic liquid. The polymer network prevents the liquid part from escaping from the matrix and gives the gel the properties of a solid. The organic liquid serves as a plasticizer and gives the matrix the properties of the liquid. The basic requirements for these electrolytes are high ionic conductivity in a wide range of heat, good mechanical properties, thermal and electrochemical stability and long life span. The conductivity of these electrolytes is in units of mS/cm. [1] [3]

2 EXPERIMENT

The experiment began with the preparation of gel polymer electrolytes (GPE). The gel polymer electrolytes consisted of salt, solvent, initiator of UV polymerization, crosslinking agent and monomers. Initially, the properties of GPE with single monomers like ethyl methacrylate (EMA), butyl methacrylate (BMA), isobutyl methacrylate (IBMA), lauryl methacrylate (LMA), trimetoxysilylpropyl methacrylate (TSPMA) and ethoxyethyl methacrylate (EOEMA) were measured. Combination of two GPE composed of monomers with the highest conductivity and electrochemical stability was chosen. After selecting the two monomers, the composition of the gel polymer electrolyte with a copolymer of EMA and MMA was calculated. The ratio of monomers EMA 20% and MMA 80% suited best to these conditions. Selection of the appropriate GPE composition was followed by the preparation of the Li/GPE/NMC cell. Firstly, it was necessary to mechanically clean the lithium plate from oxides on the surface, then to cut out a GPE of a certain size and transfer it to the cut-out part of the lithium and add an NMC electrode. Followed by setting the parameters of PEIS and GCPL measuring methods. Measurements at room and higher temperature can not be performed on one sample, therefore two samples with the same composition were prepared for the measurement.

2.1 CHEMICAL COMPOSITION

The method of preparing gel polymer electrolytes is based on mixing monomers with a polymerization initiator, a crosslinker and a salt in a solvent. During the preparation of gel polymer electrolytes, it is necessary to work in an inert atmosphere. Upon contact of the gel polymer electrolyte with the ambient air, the material degrades rapidly.

The GPE consists of the following materials:

- **Salt** Lithium hexafluorophosphate ($LiPF_6$)
- **Solvent** Ethyl Carbonate and Diethyl Carbonate (EC/DEC in weight 1:1)
- **Initiator of UV polymerization** Benzoin Ethyl Ether (BEE)
- **Crosslinking agent** Ethylene Glycol Dimethacrylate (EDMA)
- **Monomer** Ethyl Methacrylate (EMA) and Methyl Methacrylate (MMA)

The exact chemical composition of the gel polymer electrolyte is shown in table 1.

	Chemical substance	Quantity
EMA 20 % MMA 80 %	LiPF6	0.1519 ml
	EC/DEC	1.899 µl
	EMA	137.54 µl
	MMA	470.78 µl
	BEE	0.0139 g
	EDMA	38.2 µl

Table 1: Chemical composition of GPE

2.2 NMC ELECTRODE

NMC-based electrodes suitably combine the properties of nickel and manganese. Nickel has a high specific energy but poor stability. Manganese has a very low internal resistance but low specific energy. The NMC electrode excels in specific energy, specific power, safety, performance and life span. However, the price of these electrodes is also higher. It is used as a material for a positive electrode. There are several types of NMC electrodes, which are divided on the basis of the proportion of individual elements. The most common type is 111 NMC, which means that all elements are represented by the same proportion. For example, other basic elements ratios are 442 NMC or 622 NMC. Besides of the NMC electrodes, there are other materials used for the positive electrode, such as NCA (lithium-nickel-cobalt-aluminium) or LFP (lithium-iron-phosphate). The completed Li/GPE/NMC cell is shown in the figure 1 below. [2] [4]

Figure 1: Complete Li/GPE/NMC cell

2.3 RESULTS

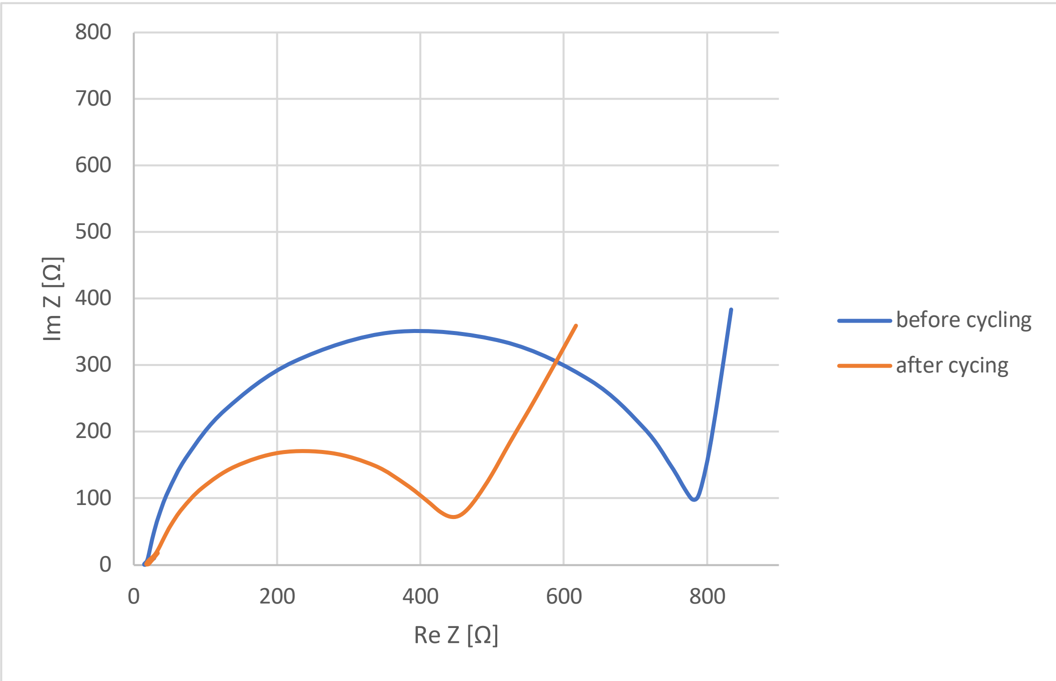

Figure 2: PEIS graph of Li/GPE/NMC cell at room temperature.

The PEIS method (Potentiostatic Electrochemical Impedance Spectroscopy) is an experimental method. The complex impedance is evaluated over a wide range of frequencies. The result of the measurement is the impedance spectrum and it is shown in figure 2. The method was used at the beginning and at the end of the measurement of the Li/GPE/NMC cell. At the beginning of all the measurement, the value of the real component of impedance is 779 Ω and after the measurement of capacity, the value of impedance is 452 Ω. This change can be evaluated as a decrease in impedance of 58%.

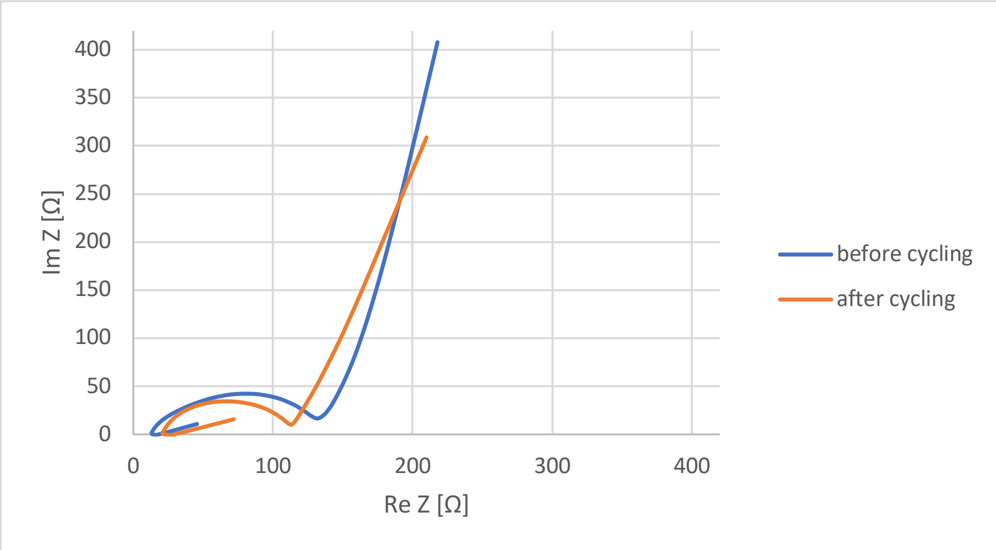

Figure 3: PEIS graph of Li/GPE/NMC cell at higher temperature 40 °C.

Measurement with higher temperatures were done with the same parameters only the temperature was 40 °C. There is graph of measured impedances before and after cycling shown in figure 3. The impedance value at the beginning of the measurement was 134.8 Ω and after the GCPL method measurement the impedance value was 112.6 Ω. The impedance decreased of 16.5 %. When measured with PEIS method at room temperature, the impedance decreased of 58%. This is significant difference from measurement at higher temperatures. Furthemore, it would be useful to detect differences in impedance at different temperatures.

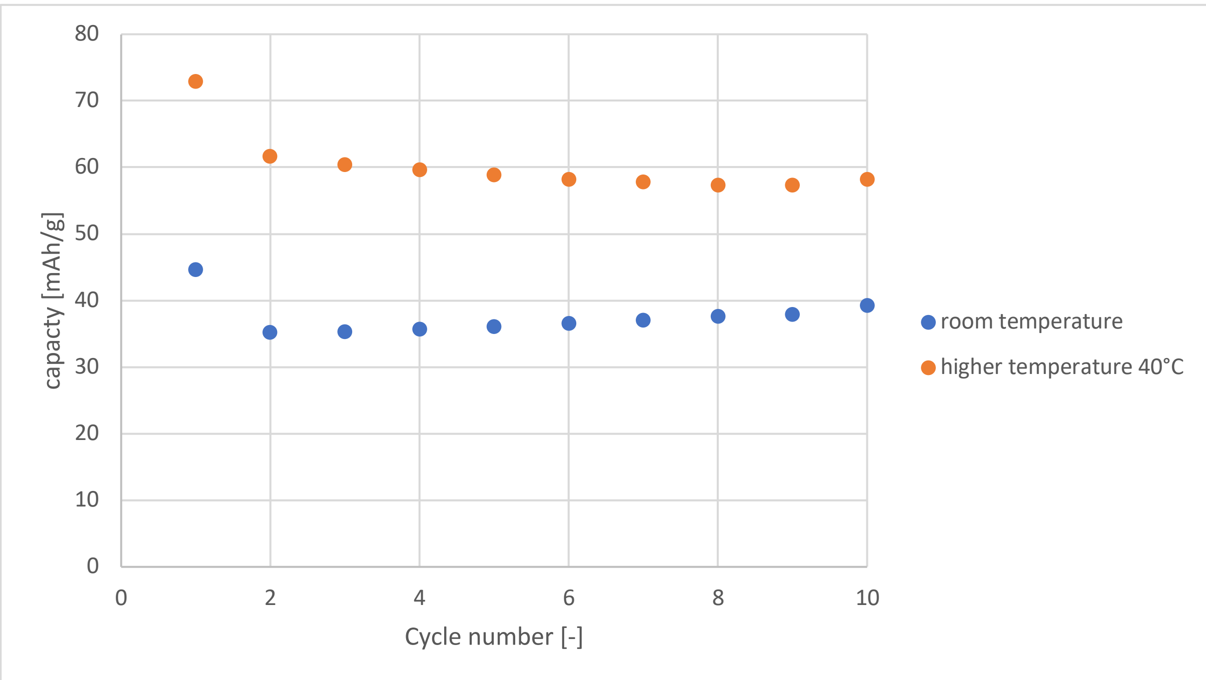

Figure 4: Capacity during cycling of Li/GPE/NMC cell.

Figure 4 shows the dependence of capacity on cycle number. The GCPL (Galvanostatic Cycling with Potential Limitation) was used for the measurement. This method allows cyclic charging and discharging within the required voltage limits. Ten cycles of charging and discharging with a current of 0.05 C up to 1.2 V were measured. At the beginning of the measurement, the capacity was 44.58 mAh/g, after that the value dropped to 35.15 mAh/g. From the third cycle, the capacity slowly raised again to 39.22 mAh/g. Due to this measurement the drop of capacity is 13.6 %. The average capacitance value is 37.51 mAh/g, while the theoretical value of capacity of the NMC electrode is 160 mAh/g.

As with room temperature and higher temperature measurements, we can see a significant decrease in capacity after the first charge and discharge cycle. Charging and discharging at room temperature took 91 hours, while at higher temperature the cycles took 141 hours. The average value of capacity at higher temperatures was 60.2 mAh/g.

3 CONCLUSION

The aim of this experiment was to determine behavior of a gel polymer electrolyte based on a copolymer of EMA and MMA with NMC electrode. The conductivity of the prepared gel polymer electrolyte was 5.52 mS/cm. Commercial electrodes from Customcell were used for the experiment. The measurement of gel polymer electrolyte and subsequent measurement of system Li/GPE/NMC were done at room temperature. The result of this measurement is that the prepared system of Li/GPE/NMC is stable at room temperature. After these experiments, it was necessary to investigate the behavior even at higher temperatures. The measurement was done at a temperature of 40 °C. The capacity of the cell is higher at higher temperatures and charging and discharging cycles take longer than at room temperature. Furthermore, it would be possible to continue research at higher and lower temperatures and study changes in capacity as a function of temperature. These measurements are important for follow-up research, which could explore the application of GPE in thin layers, because GPE applied in thin layers has a higher conductivity by volume.

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