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TEMPERATURE DEPENDENCE OF ACTIVE AND REACTIVE IMPEDANCES OF PMMA-EC-LiTf / $MgTf_2$ Solid Polymer Electrolytes

UKTAMALIYEV BEKZOD

Doctoral student of Namangan Institute of Engineering and Technology
E-mail: uktamaliyevb@mail.ru, Phone.: (+99893) 670 03-33

M.KUFIAN

Centre for Ionics Universiti Malaya, Kuala Lumpur, Malaysia
E-mail.: mzkufian@um.edu.my

ABDUKARIMOV ABDULAZIZ

Associate professor of Namangan Institute of Engineering and Technology
Phone.: (+99897) 252 32-62

MAMATKARIMOV ODILJON

Professor of Namangan Institute of Engineering and Technology

Abstract. In this work, PMMA-EC-LiTf, PMMA-EC-$MgTf_2$ samples were prepared at a concentration of 20%. Using Nyquist coordinates, results were obtained for active and reactive impedances at temperatures from 243K to 283 K and at temperatures from 303 K to 373 K. R_b from $MgTf_2$ system are lower than LiTf in the room temperature. PMMA-EC-$MgTf_2$ sample conductivity is $4.34 \cdot 10^{-5} \frac{1}{Ом\cdotсм}$, PMMA-EC-$LiTf_2$ sample conductivity is $3{,}07 \cdot 10^{-4} \frac{1}{Ом\cdotсм}$

Keywords: Solid polymer electrolyte, impedance spectroscopy, active impedance, reactive impedance

Introduction. In recent years, high performance and environmentally friendly rechargeable batteries have been a major global interest due to their considerable attentions while lithium-ion-based batteries have been the best candidate in view of their specific capacity and cycle stability [1][2]. Polymer electrolytes usually refer to ion-conducting materials introduced by dissolving salt into the polymer matrix [3],[4]. Polymer electrolytes are promising materials for electrochemical device applications, namely, high energy density rechargeable batteries, fuel cells, supercapacitors, electrochromic displays [5][6]. Polymer electrolytes offer several advantages over liquid electrolytes and inorganic solid electrolytes, such as enhanced resistance to variations in the volume of the electrodes during the charge/discharge process, improved safety features, excellent flexibility and processability [7]. Solid polymer electrolytes are light-weight, flexible, nonflammable and provide a feasible solution to the safety issues facing lithium-ion batteries through the replacement of organic liquid electrolytes [8]. It is known from the literature that ion transport in polymer electrolytes does not occur in the crystalline phase, but mainly in the amorphous phase. [9][10][11][12]. It is desirable to choose a polymer matrix that is essentially amorphous, such as PMMA [13]. PMMA-based GPEs have been proposed for use in lithium batteries due to their beneficial effects on stabilizing the lithium-electrode interface. [14][15]. Therefore, it shows one of the important properties of a potential polymer electrolyte material. From previous works, this material showed acceptable conductivity value [16],[17],[18]. PMMA is a transparent amorphous polymer with good mechanical properties [19]. PMMA-based PEs exhibit low mechanical integrity and high brittleness.[20][21]. The potential of PMMA as a polymer host was reported by Iijima and Toyoguchi in 1985.[22]

Materials. Polymethyl methacrylate (PMMA), ethylene carbonate (EC), lithium trifluoromethanesulfonate (99.995%) [LiTf], magnesium trifluoromethanesulfonate (97%) [$MgTf_2$], tetrahydrofuran (THF)

Materials used in the preparation of polymer electrolytes. All materials were used as received unless stated otherwise. Sodium Poly (methyl methacrylate) (PMMA; ~MW: ~996,000), ethylene carbonate (EC), lithium trifluoromethanesulfonate (99.995%) [LiTf], magnesium trifluoromethanesulfonate (97%) [$MgTf_2$], were obtained from Aldrich and were stored in an argon atmosphere glove box.

It is a traditional method used due to its ease of fabrication which makes solid polymer electrolytes flexible. It can produce polymer film from various thicknesses (200–500 μm).

This process includes the following steps: 1. Addition of a specified amount of polymer to a solvent and kept stirring for homogenous mixing.

2. The addition of salt in the polymer matrix and again stirred at room temperature till the polymer–salt complexation is formed.

3. After this, addition of nanofiller/clay/plasticizer is added and stirring completed.

4. The viscous solution obtained is casted on glass or Teflon Petri dishes, and slowly evaporated by keeping at room temperature for few days.

5. A thin film of uniform thickness is obtained [23].

Method. Using Nyquist coordinates, this method takes a complex ohmic plane, in which the active impedance Z_r is placed on the x-axis and the reactive impedance Z_i is placed on the y-axis. [24].

$$Z = Z_r - j \cdot Z_i$$
$$Z_r = Z_0 \cdot \cos(\theta) \qquad (1)$$
$$Z_i = Z_0 \cdot \sin(\theta)$$

Here j = -1. Thus, to construct an impedance spectrum in Nyquist coordinates, the impedance curve for each point (ω, Z_0, θ) should be calculated from Z_r and Z_i; or the vector Z_0 is placed in the plane at an angle *th* to the x-axis and its endpoint determined so that the result obtained in both methods will be exactly the same.

Results and discussion. It can be observed that the values of R_b from $MgTf_2$ system are lower than $LiTf_2$ in the room temperature.PMMA-EC-$MgTf_2$ sample conductivity is $4.34 \cdot 10^{-5} \frac{1}{\text{Ом} \cdot \text{см}}$, PMMA-EC-LiTf sample conductivity is $3.07 \cdot 10^{-4} \frac{1}{\text{Ом} \cdot \text{см}}$ (Figure 1).

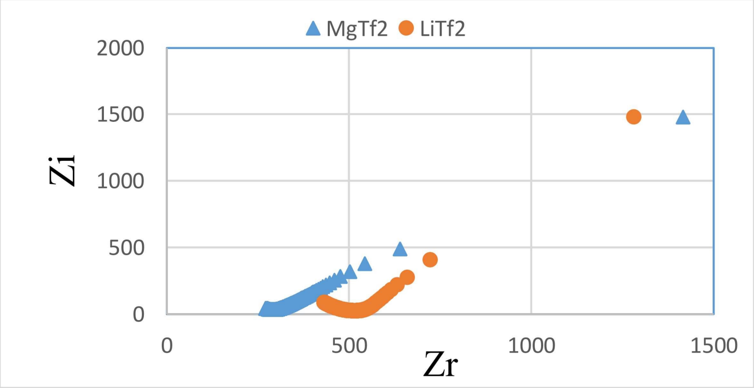

Figure 1. Graph of electrochemical impedance spectroscopy at room temperature of solid polymer electrolytes based on $MgTf_2$ and LiTf

It can be seen from the table that the highest conductivities obtained are $2.82 \cdot 10^{-7} \frac{1}{\text{Ом}\cdot\text{см}}$ and $1.93 \cdot 10^{-6} \frac{1}{\text{Ом}\cdot\text{см}}$ for GPE samples containing 30 wt% $MgTf_2$ and 15 wt% $Mg(TFSI)_2$, respectively [1]

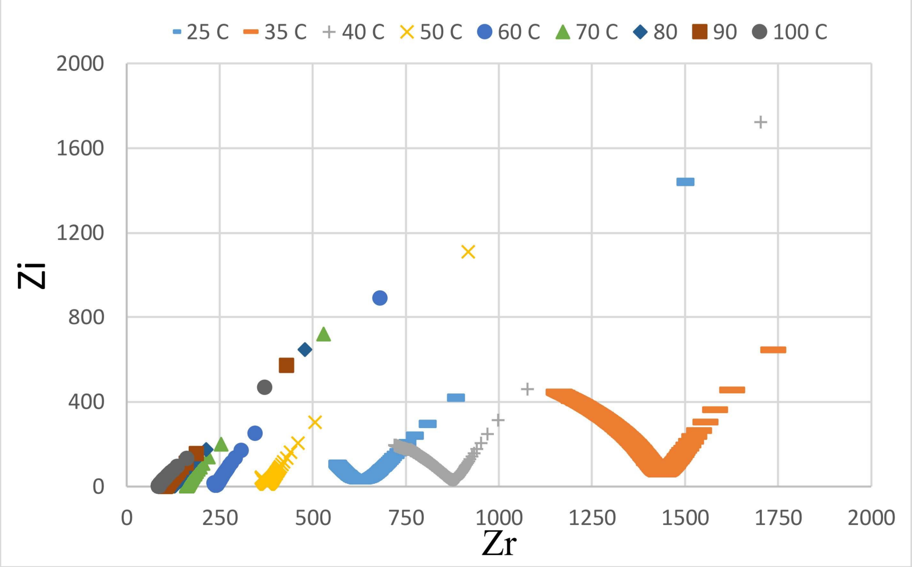

Figure 2. Graph of electrochemical impedance spectroscopy of LiTf-based solid polymer electrolyte in the temperature range 298-373K

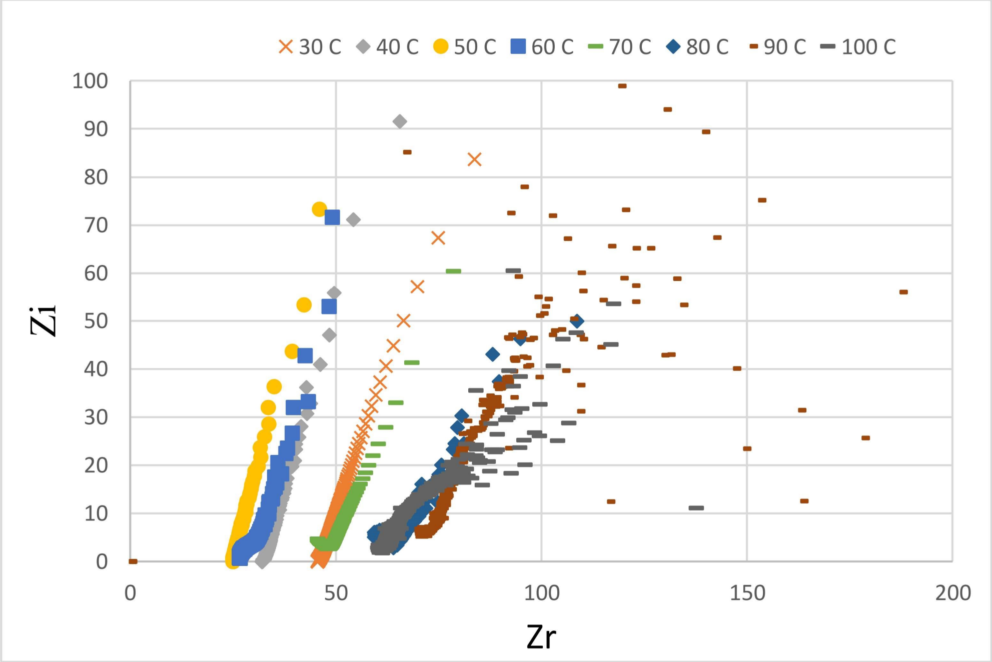

Figure 3. Graph of electrochemical impedance spectroscopy of a solid polymer electrolyte based on $MgTf_2$ in the temperature range 303-373K

PMMA-EC-LiTf measurements were taken over the temperature range 298 K to 373K. We found that the reactive impedance varied from 430 to 0.92 and the active impedance from 1180 to 86 in Nyquist coordinates. (Figure 2).

When the PMMA-EC-$MgTf_2$ sample was studied in the range of 298 K to 373 K, the initial value of the reactive impedance in Nyquist coordinates was almost unchanged, and that the active impedance varies from 70 to 25 (Figure 3).

PMMA-EC-$MgTf_2$ was sampled at temperature in the range 243K to 283 K with Zr impedance as well. The initial value of Zi was almost unchanged (Figure 4).

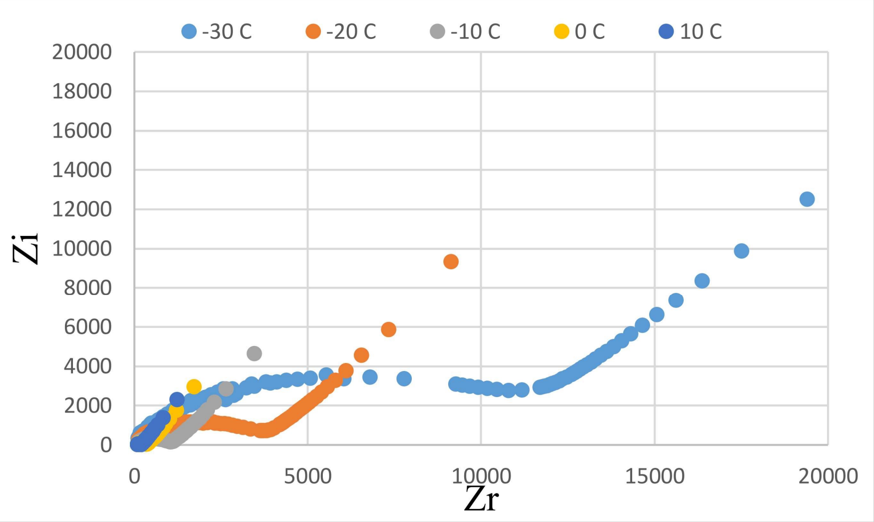

Figure 4. Graph of electrochemical impedance spectroscopy of a solid polymer electrolyte based on $MgTf_2$ in the temperature range 243-283K

Conclusion. In the experiment, it was observed that the impedances of the solid polymer electrolyte obtained at the same concentration containing the salts LiTf and $MgTf_2$ were not the same. We found that $MgTf_2$ has a better conductivity than LiTf due to the small active and reactive impedance of the sample.

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INNOVATIVE COMPLETELY SOLUBLE NPK GEL FERTILIZERS BASED ON BIOPOLYMERS WITH CONTROLLED RELEASE OF NUTRIENTS

IKRAMOV MUBOSHIR

Doctoral student of Institute of General and Inorganic Chemistry, AS Ruz
E-mail.: Ikramov.mx@mail.ru, phone.: (+99893) 914 00-98

ZAKIROV BAKHTIYOR

Institute of General and Inorganic Chemistry, AS Ruz
Phone.: (+99891) 162 26-80

Annotation. The aim of the present work was the preparation and properties evaluation of two innovative fertilizers based on multicomponent polymers characterized by a controlled release of nutrients. One method was based on a multicomponent liquid containing different amounts of microelements NPK 15-10-50 fertilizers with polyacrylamide hydrogel beads. The second method concerned the cross-linking of biodegradable polyvinyl alcohol with multicomponent NPK fertilizers.

Keywords: macro element, properties, fertilizers, polyvinyl alcohol, nutrients release.

Introduction. Fertilizers can be classified as single-component, multi-component or microelement fertilizers in solid (granulated), liquid or gel states [1-4]. Uncontrolled release of nutrients over time can lead to groundwater pollution and over-fertilization of soils. The pro-ecological and economic aspects of fertilization have forced the agrochemicals market to produce slow-acting fertilizers4. Slow action fertilizers include agrochemicals SRF (Slow Release Fertilizers) and/or interchangeably used CRF (Controlled Release Fertilizers). The distinction between both forms is not entirely unambiguous because both groups of fertilizers have similar functionalities and ultimately have analogous functions for plants.

The use of SRF/CRF positively influences the equal supply of nutrients to plants, decreases the degree of water pollution, reduces the amount of applied agrochemicals and consequently reduces the cost of the crops by complete use of all nutrients and substances supplied to plants [5-8]. According to the Association of American Plant Food Control Officials, the CRFs are coated products, whereas the SRFs are nitrous products decomposed by microorganisms. However, both terms are used interchangeably in various studies.

Coated fertilizers (CRF) are produced by coating traditional fertilizers with super-absorbents, waxes, resins, as well as polymers and hydrogels [9]. The nutrients release mechanism of CRF fertilizers is to infiltrate the solvents into the coat and dissolve the mineral salts. Due to the solvent absorption, an increase in osmotic pressure is observed inside the coat, leading to the diffusion of organic matter in the soil and the supply of medium to the plants. The release of nutrients from SRF occurs place as a result of decomposition of fertilizer coating due to microbiological processes in the soil.

During the last century, we observed the development of the fertilizers market and the appearance of innovative forms of fertilizers, in particular those with controlled release, which aroused great interest. Gel

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