Ionic Conductivity and Dielectric Constant of a Solid Polymer Electrolyte Containing Salts $Litf_2$ and $Mgtf_2$

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Annotation

In this work, two samples of a solid polymer electrolyte have been prepared from a 20% concentrated solution of $LiTf_2$ and $MgTf_2$ salts.In this case, we obtained two different samples using as a polymer: PMMA as an active material $LiTf_2$, $MgTf_2$, and as a solvent ethylene carbonate and tetrahydroflun (THF).The technology of sample preparation and the parameters of active, reactive impedance, conductivity, dielectric constant have been determined. Compared to each other, the ionic conductivity of $LiTf_2$ was $3.07 \times 10^{-5}\ S/cm$, while that of $MgTf_2$ was $4.34 \times 10^{-5} S/cm$.
Key words: Solid polymer electrolyte, conductivity, dielectric constant, $LiTf_2$, $MgTf_2$.

Introduction

Recently, the need for environmentally friendly energy sources has increased, and new energy storage systems have emerged. Li-ion batteries are core components in electric cars as well as hybrid electric cars. As renewable energy sources proliferate globally, high-efficiency energy storage systems such as stand-alone power plants will be future batteries[1]. Today, Li-ion batteries serve millions of people in their day-to-day gadgets such as laptops, cell phones, digital cameras, video cameras. However, these batteries have brought disadvantages, such as the risk of explosion, difficulty charging at minus temperatures, and failure even when they are not in use. Research has discovered a new form of polymer-based Li-ion battery that is safer, lighter, and more compact than Li-ion batteries. These batteries differ from traditional Li-ion, lead-acid, nickel-cadmium batteries by high energy and power density, low cost, lightweight, small size, and long-term non-discharge even when not in use.

Polymer electrolytes are electro physically stable and have high ionic conductivity [2]. Various polymer electrolyte systems have been studied and applied in many electrophysical devices. When testing liquid electrolytes, we can observe the risk of solvent evaporation, electrochemical corrosion, and leakage. These conditions are significantly reduced in polymer electrolytes. In addition, polymer electrolytes exhibit properties that are very similar to liquid electrolytes and can maintain good electrode-electrolyte contact during battery operation. [3].

Polymer electrolytes are also divided into 3 types, respectively: solid polymer electrolyte (SPE)[4], Gel polymer electrolyte (GPE)[5], Liquid polymer electrolyte (LPE). Liquid polymer electrolytes consist of lithium salt in an organic solvent and a separator that prevents short circuits of the electrodes. Gel-polymer electrolytes are solvents, low-molecular-weight polymers, and lithium salts.

ISSN: 0010-8189

Polymethyl methacrylate (PMMA), polyacrylonitrile (PAN), propylin carbonate (PC), polyethylene oxide (PEO) [6], polyvinylidene fluoride (PVDF), polyvinyl butyl (PVB), polypropylene oxide are mainly used as compounds in polymer electrolytes. [7]. In addition, they eliminate the risk of flammability caused by normal liquid electrolytes. SPEs typically have a flexible, large electrochemical stability window, which is a much-needed feature for the development of high-voltage batteries. However, these benefits are costly. To obtain the best electrochemical performance of polymer electrolytes, several problems need to be solved, one of the biggest drawbacks being the relatively low ionic conductivity at room temperature (<10−4 S* sm -1) [8],[9]. PAN-based electrolytes are distinguished by high ionic conductivity and very good mechanical properties. However, these electrolytes do not come into good contact with the lithium electrode, which is a serious drawback [10]. In our study, PMMA-based polymer electrolytes were prepared using LiTf2 and LiMg2 salts.

Materials and Prepration

Materials used in the preparation of polymer electrolytes The following chemicals and solutions were used in the preparation of the electrolytes.Made in the USA (Sigma Aldrich firm): polymethylmethacrylate (PMMA), magnesium trifluoromethanesulfonate ($MgTf_2$), lithium trifluoromethanesulfonate ($LiTf_2$), ethylene carbonate (EC), tetrahydrofuran (THF).

Solid polymer electrolyte preparation: Firstly, 2 g of polymethyl methacrylate (PMMA, MW=996 ,000 g mol^{-1}), 1 g of ethylene carbonate (EC), 0.75 g of lithium trifluoroethanesulfonate ($LiTf_2$) were placed in a beaker and 40 ml of tetrahydrofuran (THF) was added as solvent [11]. Mixture was stirred for 24 hours at room temperature. On dissolution, the mixture was poured into an 8 cm petri dish, placed in the dark and dried for 24 hours [12]. Samples of 4 different thicknesses were taken.Using the above method, we can also prepare a second sample for the $MgTf_2$ salt.

Measurement method

A convenient way to obtain information about the electrochemical and physical properties of materials is to use the electrochemical impedance spectroscopy method. Typically, the frequency of the alternating electric field applied to the sample ranged from $10^{-6}$to 10^{12} Hz. In this range, one can study the bulk dielectric properties of the sample and the process of electrical conductivity [13],[14]. In our work, this method was mainly used to study the electrophysical parameters of the electrolytes. The efficiency of known polymer-based lithium-ion batteries is very much dependent on the electrophysical parameters of a solid polymer electrolyte [15]. Therefore, the ionic conductivity of the electrolyte was checked by electrochemical impedance spectroscopy under the influence of an electromagnetic field with a frequency from 50 Hz to 100 kHz using the Hi-Tester HIOKI 3531 Z [16],[17]. The experiments were carried out with electrolytes of different thicknesses and at different temperatures. Electrochemical impedance spectroscopy is one of the most reliable and effective methods for determining the ionic conductivity of liquid electrolytes, condensed salts, ion-conducting polymers and glass [11].

Nyquist plots are used in electrochemical impedance studies. In this method, the real impedance Z_r is plotted along the horizontal axis and the imaginary impedance Z_i along the vertical axis, the total resistance in complex form is expressed as follows [18].

ISSN: 0010-8189

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

where Z_o is impedance vector and θ is the angle between the vectors Z_r and Z_i The ionic conductivity s of the sample was calculated using the following formula:

$$\sigma = \frac{l}{RS} \quad (2)$$

where l is the thickness of the electrolyte, *R* is the bulk resistance of the electrolyte, *S* is the surface area of the electrolyte [19].

In addition, the dielectric constant of the polymer electrolyte is dependent on the frequency of the input signal. This was determined using equations 3 and 4.

$$\varepsilon_r = \frac{Z_i}{\omega C\,(Z_i^2+Z_r^2)} \quad (3)$$

$$\varepsilon_i = \frac{Z_r}{\omega C\,(Z_i^2+Z_r^2)} \quad (4)$$

Here$\omega = 2\pi\nu$ with ν as frequency, C is thethe electrical capacitance of the electrolyte[20].

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*10^{-5} 1/Ω*sm, PMMA-EC-$LiTf_2$sample conductivity is 3.07 1/Ω*sm (Figure 1,2).

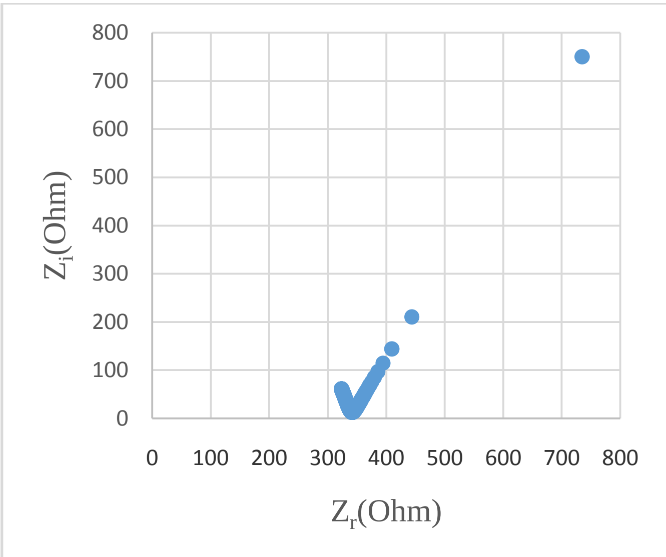

Figure 1. Graph of electrochemical impedance spectroscopy at room temperature of solid polymer electrolytes based on $LiTf_2$.

ISSN: 0010-8189

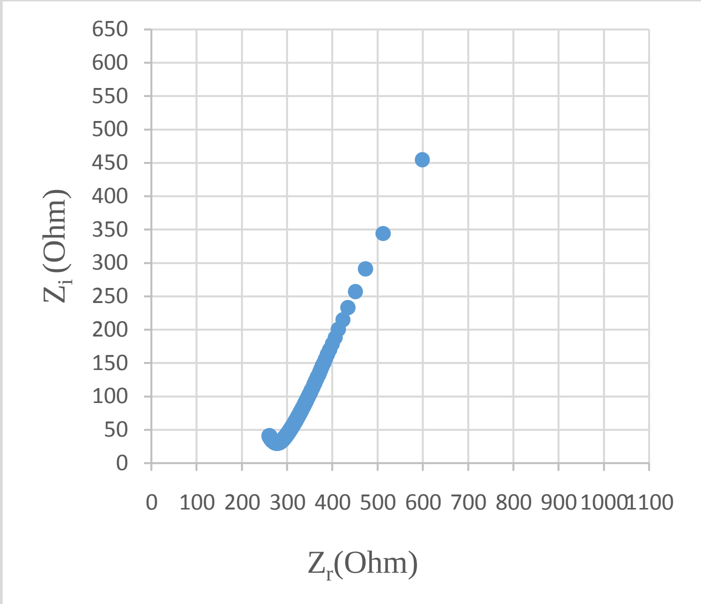

Figure 2. Graph of electrochemical impedance spectroscopy at room temperature of solid polymer electrolytes based on $MgTf_2$.

Based on the experiments described above, we determined some of the electrophysical parameters of the two types of electrolytes, which are shown in Table1.

Table1.Electrophysical parameters of the two types of electrolytes.

Electrolyte	σ (S/cm)	R_b (ohm)	ε
PMMA-EC-$LiTf_2$	3,07587E-05	521,46	1-6383
PMMA-EC-$MgTf_2$	4,34512E-05	260,61	0.4-8193

Conclusion

Samples $LiTf_2$ and $MgTf_2$ were compared with each other. The ionic conductivity of $LiTf_2$ was $3.07 \times 10^{-5} S/cm$, and $MgTf_2$ was $4.34 \cdot 10^{-5}\ S/cm$.The dielectric constant was higher at $MgTf_2$ and amounted to 8193.Therefore, it is advisable to use electrolytes containing a mixture of $MgTf_2$ salt in the manufacture of this type of battery.

ACKNOWLEDGMENTS

We are grateful to the IONIC Center of the University of Malaya, Republic of Malaysia, as well as to A.K Arof, Z. Osman, M.Z. Kufian, N. Hidayu for their close assistance in conducting the experiment.

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