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XRD Measurement for Particle Size Analysis of PMMA Polymer Electrolytes with SiO_2

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Abstract. PMMA-based polymer electrolytes with $LiCF_3SO_3$ lithium salt, EC plasticizer, and SiO_2 filler are prepared using the solution cast method. SiO_2 filler sizes at 10 μm and 63 μm are used to estimate the particle size in the polymer electrolytes system. EIS analysis calculates ionic conductivity based on the Cole-Cole plot generated in frequency ranging from 0.1 Hz to 1 MHz. The calculation results in ionic conductivity at 1.44×10^{-4} S/cm and 8.1×10^{-5} S/cm for 10 μm and 63 μm SiO_2 filler, respectively. FWHM measurement is performed for each diffraction peak based on the XRD spectra. Debye-Scherrer equation is used to estimate the resultant particle size. Peak broadening effect caused by the instrument is considered for a more accurate estimation of particle size in the polymer electrolyte system. Linear regression is employed to determine the average particle size arising from these diffraction peaks. The results showed that larger filler size results in the formation of a larger particle size.

Keywords: Debye-scherrer equation; PMMA; Polymer electrolytes; SiO_2; XRD

1. Introduction

Over the decades, polymer electrolytes have been an attractive candidate in battery industries for replacing conventional liquid electrolytes in numerous applications (Tang et al., 2021; Zhou et al., 2019; Arya et al., 2017). The absence of liquid substances in polymer electrolytes eliminates leakage, which is a crucial drawback in liquid electrolyte batteries. However, the absence of liquid substances hinders the battery's performance. Researchers have employed numerous approaches to improve ionic conductivity, which is the most crucial measurement in determining the performance of a battery. Incorporating ceramic filler to form composite polymer electrolytes is proven capable of restraining polymer crystallization, which subsequently leads to drastic increase in ionic conductivity. Nonetheless, several attractive characteristics such as good compatibility with electrodes, superior mechanical properties, and high lithium transference number eventually pushed composite polymer electrolytes to be the most promising candidate in realizing batteries with high electrochemical performance capability (Priyono et al., 2019; Zhang et al., 2018; Mauger et al., 2017; Jodi et al., 2016). Various types of host polymers have been investigated particularly poly (ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA), poly(acrylo

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nitrile) (PAN), poly(vinylidene fluoride) (PVDF), poly(vinyl alcohol) (PVA), poly(vinyl pyrrolidone) (PVP), poly(propylene oxide) (PPO), and poly(vinyl chloride) (PVC).

Dhatarwal et al. (2018) investigated the electrochemical performance of PMMA/PEO polymer electrolyte dispersed with different types of fillers, including SiO_2. The reported ionic conductivity falls in the range of 10^{-5} to 10^{-6} S/cm at room temperature with stable voltage up to 3V. The PVC/PMMA– Li4Ti5O12 films prepared by Al-Muntaser et al. (2020). The polymer matrix reported electrical properties at 2.39×10^{-7} S/cm along with improved amorphous properties. The author applied the Scherrer equation and obtained a crystallite size of 40 nm through X-ray Diffraction (XRD) pattern analysis. Mallaiah et al. (2021) prepared PEO/PVDF–NaNO3 blended polymer electrolyte with constant wt% of salt and varying wt% of the host polymer. It is observed that maximum ionic conductivity is obtained at 9.334×10^{-5} S cm^{-1} with PEO:PVDF = 80:20. Addition of ionic liquid into PVDF/HFP polymer electrolyte prepared by Gupta et al. (2020) has increased ionic conductivity tremendously up to 2.05×10^{-2} S/cm. Debye-Scherrer equation is then used to analyze crystallite size, and the work reported particle size in the range of 4.4 Å. The PVP + $CH_3COONa:Al_2O_3$ nanocomposite polymer electrolyte prepared by Kumar et al. (2019) recorded the highest ionic conductivity up to 6.25×10^{-5} S/cm at room temperature with an average crystallite size of 18 nm.

In the present work, composite polymer electrolytes are prepared with PMMA host polymer, lithium trifluoromethanesulfonate ($LiCF_3SO_3$) salt, ethylene carbonate (EC) plasticizer, and silicon dioxide (SiO_2) filler. PMMA is selected as the host polymer owing to its good compatibility with the lithium electrode interface. The high dielectric constant of EC promotes lithium salt dissociation to form Li^+ cations, which move freely throughout the polymer matrix. Adding SiO_2 inert filler is mainly linked to dominant interfacial conductivity. The surface area of filler interacts with negatively charged anions through the Lewis-acid effect, thus creating more Li^+ cations, which enhance ionic conductivity and lithium transference number (Xu et al., 2020; Tominaga et al., 2013). Most of the XRD analysis retrieved from the literature do not focus on estimating crystallite size. Thus, this work is intended to perform an in-depth analysis of the XRD spectrum, particularly to investigate the effect of filler size and resultant crystallite size on the ionic conductivity of polymer electrolytes.

2. Methods

In the present work, PMMA host polymer, $LiCF_3SO_3$ lithium salt, EC plasticizer, and SiO_2 fillers are used as received from Sigma Aldrich without further purification process. Polymer electrolyte films are prepared by using the solution cast method (Tran et al., 2020). Each material is weighted according to the required wt% and mixed together. The mixture is dissolved in tetrahydrofuran (THF) with continuous stirring at room temperature for 24 hrs. The solution is then cast onto a petri dish and allowed for drying in a fume hood at room temperature until a thin film polymer electrolyte is formed. Figure 1 illustrates the polymer electrolyte film preparation by using the solution cast method. Electrochemical Impedance Spectroscopy (EIS) measurement is performed using Gamry Instrument with frequency between 0.1 Hz to 1 MHz. The polymer electrolyte film is trimmed into smaller samples of equal sizes and placed in between two metal electrodes to determine the ionic conductivity of the polymer electrolyte. X-ray spectroscopy is carried out on the polymer electrolyte membranes by using the XPERT-PRO diffractometer system, which uses 1.54 Å

CuKα radiation. The electrolyte membranes are scanned with and angle 2θ ranging from 10° to 90° to determine the crystallinity structure and estimation of crystallite size.

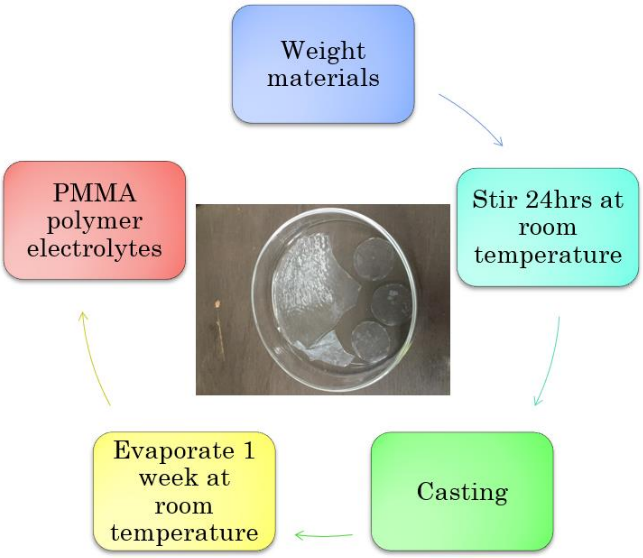


Figure 1 Polymer electrolytes sample preparation by using solution cast method

3. Results and Discussion

3.1. EIS Measurement

Ionic conductivity is the most important parameter determining polymer electrolyte performance. Figure 2 shows the Nyquist pole obtained from EIS measurement by using amry Instrument with frequency ranging from 0.1 Hz to 1 MHz. A small arc appears at high frequency region followed by a linear line extending towards low frequency region. This indicates the presence of bulk ionic conduction, where resistor and capacitor appear parallel. Bulk resistance (R_b) is read from the interception point between the line and the horizontal axis. Ionic conductivity is then calculated by using the expression shown in Equation (1)

$$\sigma = \frac{t}{R_B A} \tag{1}$$

where t is the sample's average thickness (cm), R_B is the bulk resistance (Ω) read from the Nyquist plot, and A is the contact area of the polymer electrolyte sample, fixed at 2.56 $cm^{2.}$

Ionic conductivity for 10 μm SiO_2 filler results in 1.44×10^{-4} S/cm, while 63 μm SiO_2 filler results in 8.1×10^{-5} S/cm. These results are in good agreement with PMMA–$LiCF_3SO_3$–EC–Al_2O_3 performed in earlier work (Eric-Koh et al., 2021a; 2021b; Sun et al., 2019; Yap et al., 2019; Sun et al., 2018). Pal et al. (2018) achieved 3.0×10^{-4} S/cm for PMMA–$LiClO_4$–PC with 1wt% TiO_2. On the other hand, Li et al. (2021) reported 1.13 mS/cm for PMMA gel polymer electrolyte added with 150 nm SiO_2. Incorporating a small filler size can reduce the porous structure of host polymer, creating new pathways for the transportation of Li^+ ions in the polymer matrix. Since it is easier for Li^+ ions to hop from one coordination site to the other, this faster movement of ions leads to the achievement of higher ionic conductivity.

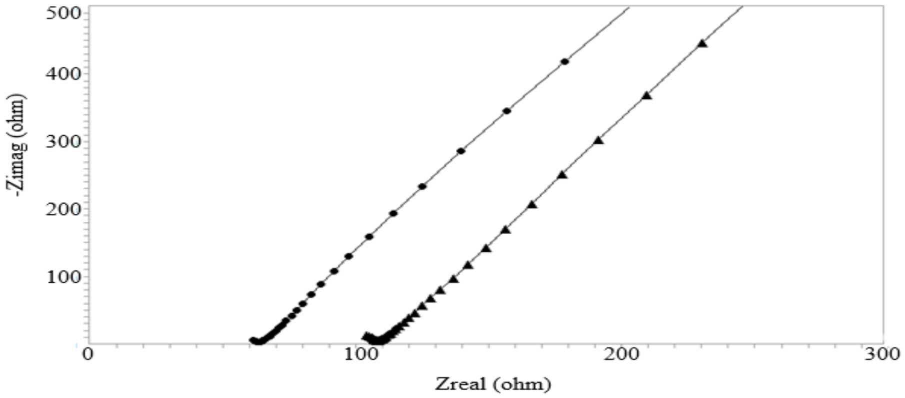


Figure 2 Nyquist plot for polymer electrolytes with 10 μm (●) and 63 μm (▲)

3.2. XRD Analysis

Composite polymer electrolytes are prepared by using SiO_2 as the filler. For this, two filler grain sizes used in this study are 10 μm and 63 μm, to study the relationship between filler size and crystallite size in the polymer matrix. Figure 3 shows the XRD patterns of these two types of filler sizes.

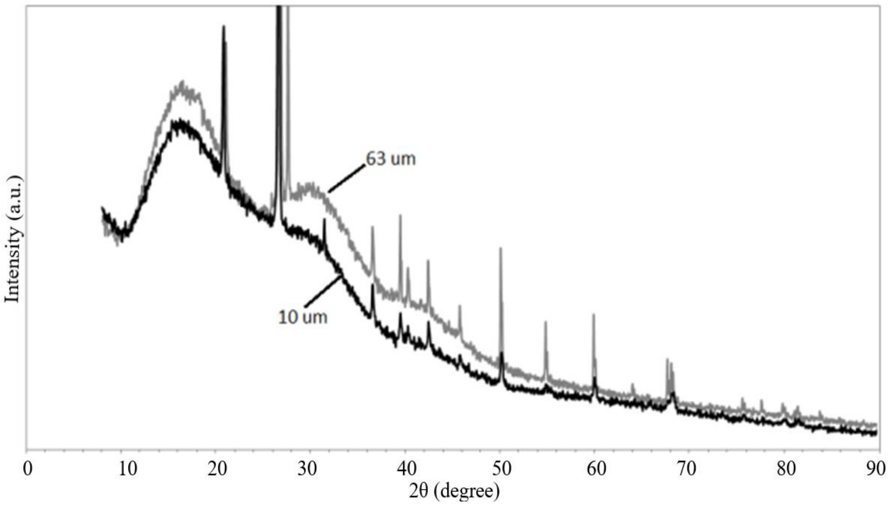


Figure 3 XRD patterns of PMMA-based composite polymer electrolytes with different SiO_2 filler grain sizes

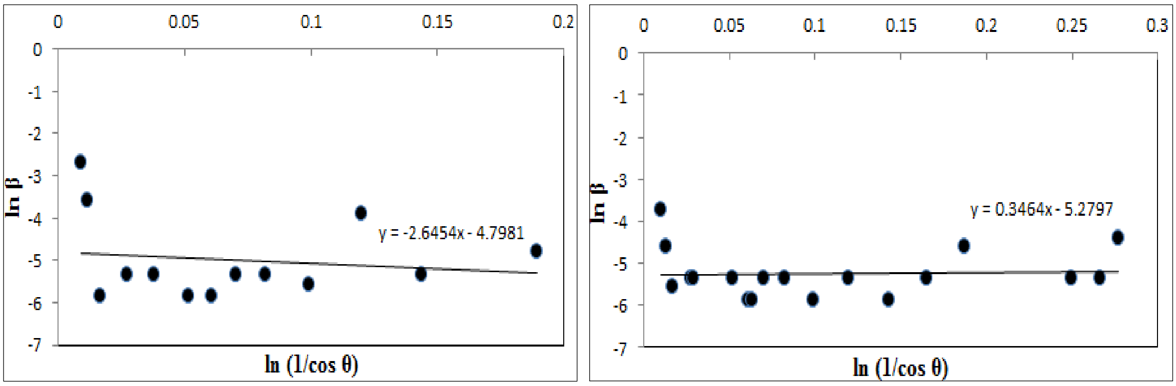
Although both filler sizes used are in the micron range, however, it is obvious that 63 μm SiO_2 gives diffraction peaks with higher intensity than 10 μm SiO_2. This conveys preliminary information on the existence of severe dissimilarities in the overall crystalline structure of these polymer electrolyte systems. Particle size is calculated by using Debye-Scherrer (Sengwa et al., 2014; Scherrer, 1918) equation, as shown in Equation (2).

$$d = \frac{K\lambda}{\beta \cos\theta} \tag{2}$$

Where K is set constant at 0.9, λ =1.54 Å for X-ray wavelength with CuK_α radiation, β is the particle broadening, and θ (degree)is the position at which the peak broadening occurs. Polymer electrolyte film broadening (β_{sample}) arising at each peak position is measured at full-width-half-maximum (FWHM) by the X-PERT PRO instrument (Saadiah et al., 2019). The effect of peak broadening due to the measurement instrument is also considered to further improve the accuracy of this calculation. The values of particle size (d) calculated from each diffraction peak are tabulated in Table 1.

Table 1 Particle size for SiO_2 at different diffraction peaks.

Filler Size	Peak Position (2θ)	FWHM β_{sample} (rad)	Particle size, d (nm)
10 µm	15.5508	0.0687	2.0379
	17.4953	0.0275	5.1176
	20.8451	0.0034	49.2916
	26.6432	0.0051	29.7576
	36.5805	0.0034	51.0578
	39.4965	0.0034	51.5077
	42.5067	0.0051	31.0701
	45.8233	0.0051	31.4371
	50.2149	0.0043	39.7798
	54.9635	0.0206	7.6162
	59.977	0.0051	33.4327
	68.2631	0.0084	20.5308
63 µm	16.2544	0.0240	5.8436
	18.2752	0.0103	13.8670
	21.0543	0.0043	36.6378
	26.7728	0.0052	29.7656
	36.5843	0.0051	30.4980
	39.5177	0.0034	51.5111
	42.4822	0.0051	31.0675
	45.7933	0.0051	31.4336
	50.1325	0.0034	53.5188
	54.86660	0.0051	32.6257
	59.9179	0.0034	55.9548
	68.0040	0.0103	16.5147



(a) (b)

Figure 4 Linear regression plots of improved Scherrer equation for SiO_2 filler size (a) 10 µm and (b) 63 µm.

Based on Table 1, averaging crystallite size is analysed using a linear regression method. Equation (2) is first rearranged, followed by natural logarithm to derive an equation resembling linear line expression, as shown in Equation (3).

$$\beta = \frac{K\lambda}{d\ \cos\theta}$$

$$\begin{aligned} \ln\beta &= ln\left(\frac{1}{cos\,\theta}\ \frac{K\lambda}{d}\right) \\ &= \ln\left(\frac{1}{cos\,\theta}\right) + ln\left(\frac{K\lambda}{d}\right) \end{aligned} \tag{3}$$

The regression equation obtained for each SiO_2 filler size is included in Figure 4. For the smaller size at 10 μm, the intercept value at the vertical axis is $ln(K\lambda/d) = -4.7981$. The average crystallite value is computed as $d = \frac{K\lambda}{e^{-4.7981}} = 16.8094 \quad nm$. Subsequently, the same method can also calculate the average crystallite value for 63 μm grain size. As such, the resultant average crystallite value is $d = \frac{K\lambda}{e^{-5.2797}} = 27.2087 \quad nm$. At this point, it is observed that a larger filler grain size leads to the formation of a larger particle size, which hinders the movement of Li^+ ions, thus reducing the resultant ionic conductivity. Nonetheless, the average crystallite size obtained in this work is in close agreement with those reported in the literature, which resides in the nano- size range (Gupta et al., 2020; Kumar et al., 2019; Lim et al., 2017).

4. Conclusions

PMMA–$LiCF_3SO_3$–EC–SiO_2 polymer electrolytes are prepared by using 10 μm and 63 μm SiO_2 filler, respectively. Particle size in a polymer electrolyte system is calculated by using the Debye-Scherrer equation. The peak broadening effect caused by instrument is considered in the equation for a more accurate estimation of particle size. Particle size for polymer electrolytes with 10 μm and 63 μm SiO_2 are estimated at 16.8094 nm and 27. 2087 nm respectively. Thus, it can be concluded that a smaller filler size results in a smaller particle size in the polymer electrolyte system. This reduces the porosity structure of polymer electrolytes and promotes the movement of Li^+ ions, thus leading to higher ionic conductivity.

Acknowledgements

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