

Measurement of Lithium Transference Number in PMMA Solid Polymer Electrolytes Doped with Micron-sized Fillers

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ABSTRACT

PMMA solid polymer electrolytes (SPEs) are much safer than gel polymer electrolytes (GPEs) due to their better mechanical and thermal stabilities. In this study, PMMA-LiCF₃SO₃-EC, PMMA-LiCF₃SO₃-EC-Al₂O₃ ($\leq 10\mu\text{m}$), and PMMA-LiCF₃SO₃-EC-SiO₂ ($\leq 10\mu\text{m}$) were prepared using solution cast method, their ionic conductivity and lithium transference number was investigated using electrochemical impedance spectroscopy (EIS) and Bruce-Vincent method, respectively. The experimental result shows that PMMA polymer electrolytes doped with SiO₂ ($\leq 10\mu\text{m}$) exhibits the highest ionic conductivity of 2.35×10^{-4} S/cm and lithium transference of 0.263 at room temperature. Linear sweep voltammetry (LSV) and Cyclic voltammetry (CV) analysis also shows that PMMA SPEs incorporated with SiO₂ ($\leq 10\mu\text{m}$) fillers can achieve electrochemical stability up to 3.2V, exhibits excellent reversibility, and good discharging performance.

KEYWORDS: ionic conductivity; solid polymer electrolyte; transference number; inorganic fillers.

1.0 INTRODUCTION

Increasing demand and advancement in electronic devices over the years had driven forward the development of high-capacity rechargeable batteries and fuel cells. Since the first industrial implementation by Sony Corporation in the 1990s, lithium-ion (Li-ion) battery has achieved tremendous technological advancement (Osinska, 2009). Their contributions, such as larger capacity, higher application voltage, longer lifespan, and lower weight, had made them an ideal power source for many applications. Lithium-ion batteries can be used in electric vehicles, portable power sources, and space exploration. An electrolyte is the heart of a lithium battery, and it acts as a medium for the charge to transfer between electrodes.

However, the liquid and gel electrolyte system in Lithium Batteries (LIB) has potential safety issues and poor electrochemical stabilities, which makes them not safe for certain applications (Yao, 2019). On the other hand, solid polymer electrolytes (SPEs) are a safer alternative. SPEs have better electrochemical stability, environmentally friendly, and safer for consumers (Song, 2015; Lim, 2018; Pitawala, 2007). Despite the potential advantages, SPEs usage in batteries is hindered due to their high degree of crystallinity and high interfacial resistance at ambient temperature, leading to low ionic conductivity and lithium transference number.

PMMA SPEs were a semi-amorphous polymer with improved mechanical and thermal properties over GPEs but can still exhibit respectable ionic conductivity and lithium

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transference number at room temperature (Sun, 2019; Faridi, 2018). However, most of the studies to date were focused on PMMA GPEs, and there are not many studies related to PMMA SPEs and their lithium transference number. Faridi *et al.* investigated the electrochemical properties in PMMA-LiClO₄ based GPEs for different salt concentrations (Faridi, 2018). They achieved an ionic conductivity and lithium transference number of $12.1 \times 10^{-3} \text{ S/cm}^{-1}$ and 0.42 respectively for 10% of PMMA and 0.75M of LiClO₄. They explained that the improvement in lithium transference number is associated with the higher polymer content. Higher PMMA concentration improves the degree of dissociation of lithium salts in the polymer complexes, frees up Li⁺ ions for ion conduction.

Musil *et al.* investigated the lithium transference number using the Bruce-Vincent method in PMMA-LiPF₆-EC: DMC GPEs with various salt concentrations (Musil, 2014). They obtained a lithium transference number of 0.24 and 0.69 for 0.005mol and 1mol of LiPF₆ salt concentration. Hosseinioun *et al.* also investigated the usage of crosslinked PMMA GPEs in Li-ion batteries (Hosseinioun, 2019). They reported that crosslinking increases the degree of dissociation of lithium salt in GPEs. The free anions or degree of dissociation of lithium salts are higher at 83% in PMMA GPEs than 71% of liquid electrolytes, which means PMMA GPEs have better ionic mobility than liquid electrolytes. This is evidenced by the obtained lithium transference number of 0.34 for PMMA GPEs and 0.24 for liquid electrolytes.

PMMA GPEs are capable of exhibiting high lithium transference number and ionic conductivity at room temperature, but they had poorer mechanical stability and thermal stability compared to SPEs. This makes SPEs better candidate for devices that are operating in high-temperature environments and require strict safety standards. Thus, in this study, PMMA in solid form, a safer alternative, was studied. The ionic conductivity and lithium transference number in inorganic filler enhanced PMMA SPEs were investigated and compared to results from several literature. Multiple studies have shown that PMMA SPEs can be manufactured into solid electrolytes used in supercapacitors and li-ion batteries requiring higher safety standards (Lim, 2018; Kurapati, 2019; Zakariya, 2020).

2.0 MATERIAL PREPARATION AND CHARACTERIZATION

2.1 SAMPLE PREPARATION

In this study, SPE films were prepared using solution cast method. Poly(methyl-methacrylate) (PMMA), Ethylene Carbonate (EC), Lithium Triflate (LiCF₃SO₃), Silicon Dioxide (SiO₂), and Alumina Oxide (Al₂O₃) in the experiment were obtained from Sigma Aldrich. In a typical synthesis, PMMA, EC, and LiCF₃SO₃ were dissolved in Tetrahydrofuran (THF) and stirred at room temperature for 24 hours until a homogenous solution is obtained. The homogenous solution was poured into a petri dish and kept in a desiccator until dry electrolytes film of PMMA-LiCF₃SO₃-EC (SPE1) was obtained. Similar steps were used to synthesis PMMA-LiCF₃SO₃-EC-Al₂O₃ (SPE2) and PMMA-LiCF₃SO₃-EC-SiO₂ (SPE3). The prepared sample composition and sample thickness are tabulated in Table 1.

Table 1. Composition ratio and thickness of PMMA SPE film prepared

ID	Weight Percentage wt%				
	PMMA	EC	LiCF ₃ SO ₃	Al ₂ O ₃	SiO ₂
SPE1	55	18	25	-	-
SPE2	55	18	25	2 (≤10μm)	-
SPE3	55	18	25	-	2 (≤10μm)

2.2 ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY (EIS)

Electrochemical Impedance Spectroscopy (EIS) was carried out using Gamry reference 600 series potentiostat for frequency ranging from 0.1Hz to 1MHz at room temperature with the sample sandwiched between two spring-loaded stainless-steel electrodes. The ionic conductivity is calculated by using the following equation:

$$\sigma = \frac{t}{R_B A} \quad (1)$$

, where t (cm) is the thickness of SPE film, R_B is the bulk resistance of electrolyte obtained from the Nyquist plot, and A (cm²) is the contact area between the film and the electrode, which equates to 2.56 cm² in this work. The results of PMMA SPE ionic conductivity were tabulated in Table 2.

2.3 TRANSFERENCE NUMBER CHARACTERISATION

The lithium transference number was defined as the number of moles of lithium-ion transferred for one Faraday of charge transferred. Ideally, the lithium transference number should be close to one in a high conductivity lithium polymer battery, and the lithium transference number, t^+ is calculated as:

$$t^+ = \frac{I_s}{I_o} \quad (2)$$

where I_o and I_s represent the initial and steady-state cell currents, respectively, however, the existing system is more complicated, with minute traces of contaminant of oxidation on the electrodes that can alter the experiment results. Hence Bruce *et al.* [12] introduced a correction factor to characterize the system before and after polarization, and the equation was rewritten as:

$$t^+ = \frac{I_s(\Delta V - I_o R_o)}{I_o(\Delta V - I_s R_s)} \quad (3)$$

ΔV is the polarization voltage of 20mV, R_o and R_s are the bulk resistance of electrolytes film taken into account interfacial resistance before and after the polarization, respectively (Bruce, 1987). Thus, the electrolyte film was characterized using EIS before and after dc polarization to determine the initial resistance, R_o , and the steady-state resistance, R_s of the sample (Pozyczka, 2017).

The Bruce-Vincent method is a reliable technique employed by multiple researchers to obtain lithium transference numbers in the polymer electrolytes system (Pozyczka, 2017; Yang, 2019; Xiao, 2018). High interfacial resistance was always the factor in limiting the performance of SPEs. Multiple researchers have reported that interfacial resistance was caused by the deposition of the oxide layer resulting from the diffusion of non-lithium ions during the chemical reaction. Besides, poor contact between the electrode and electrolytes interface, originating from the two different materials mismatched lattice and the volume changes occurring during cycling also increase the interfacial resistance (Ding, 2020; Jiang, 2019).

2.4 VOLTAMMETRY AND DISCHARGING TEST

Linear Sweep Voltammetry (LSV) was used to investigate the electrochemical stability window of SPEs. The potential window, representing the sample stability voltage, is a critical parameter that has to be evaluated to determine the application voltage used in electrochemical devices (Aziz, 2019). The voltage was swept from 0V (versus stainless steel electrode) at a scan rate of 5mVs^{-1} until the breakdown of electrolyte films (sharp increment of current) to determine the electrochemical stability voltage of the samples.

Then, five cycles of cyclic voltammetry (CV) were performed on the SPE film from 0V to 3V at a scan rate of 20mVs^{-1} , in which the SPE film was sandwiched between two stainless steel electrodes. Lastly, the SPE film was then assembled to evaluate its discharge performance. The cell was discharged with a current of 0.01mA at room temperature from 2V to 0.1V using stainless steel electrodes. All the measurements were carried out using a Gamry Reference 600 series potentiostat.

3.0 RESULTS AND DISCUSSION

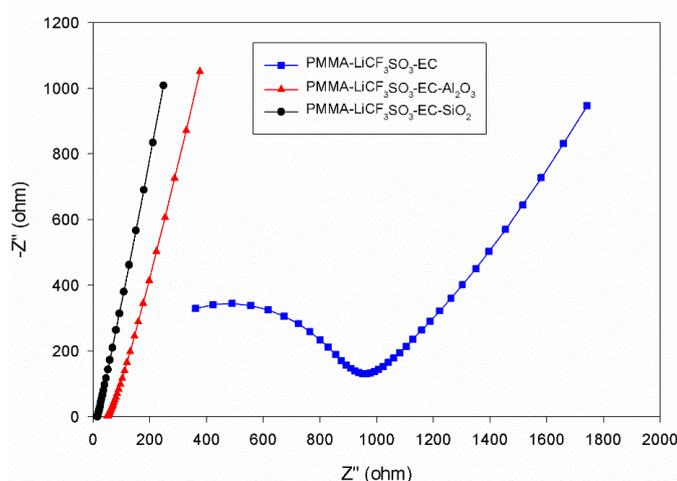


Figure 1. Nyquist plot of PMMA-LiCF₃SO₃-EC (Square), PMMA-LiCF₃SO₃-EC-Al₂O₃ (Triangle), and PMMA-LiCF₃SO₃-EC-SiO₂ (Circle).

Table 2. Ionic conductivity of PMMA-based solid polymer electrolytes.

Sample ID	Sample Composition	Filler	Filler Size	Ionic conductivity (S/cm)
SPE1	PMMA-LiCF ₃ SO ₃ -EC	-	-	1.22×10^{-5}
SPE2	PMMA-LiCF ₃ SO ₃ -EC-Al ₂ O ₃	Al ₂ O ₃	10 μ m	1.83×10^{-4}
SPE3	PMMA-LiCF ₃ SO ₃ -EC-SiO ₂	SiO ₂	10 μ m	2.35×10^{-4}

Figure 1. shows the Nyquist plot for SPE1, SPE2, and SPE3, respectively (see Figure 1). The appearance of semicircle for SPE1 suggests the presence of bulk capacitance in the system. Simultaneously, the linear line adjacent to the semicircle indicates the diffusion process resulting in electrode polarization effect (Saikia, 2008; Sivakumar, 2015). Furthermore, no semicircle is observed for SPE2, and SPE3 suggests only resistive components prevail.

The value of bulk resistance was determined at the interception point between the Nyquist curve and the x-axis, which corresponds to 964 Ω , and the obtained ionic conductivity is shown in Table 2. Ionic conductivity calculated for SPE1 was 1.22×10^{-5} S/cm. In comparison, Pal *et al.* obtained ionic conductivity of 3.52×10^{-5} S/cm for plasticized PMMA-LiClO₄ SPEs (Pal, 2018). Kurapati *et al.* also reported ionic conductivity values of 8.21×10^{-5} S/cm for her study on PMMA-CH₃COOLi SPEs (Kurapati, 2019). The obtained ionic conductivity for SPE1 was too low for electrochemical device applications (Chauvin, 2006). The low ionic conductivity of SPEs is the attribute of their crystalline nature, where the ionic mobility is low. Besides that, most of the Li⁺ ions already formed polymer-salt complexes with the polymer, reducing the fraction of ions available for ionic conduction.

Improvement in ionic conductivity was seen for SPE2 and SPE3 when inorganic fillers Al₂O₃ and SiO₂ of ($\leq 10 \mu$ m) were added, yielding an ionic conductivity of 1.83×10^{-4} S/cm and 2.35×10^{-4} S/cm, respectively. Chew *et al.* reported similar findings where they also observed improvement in ionic conductivity when they added Al₂O₃ into PMMA SPEs (Chew, 2011). They obtained an ionic conductivity of 2.05×10^{-4} S/cm for PMMA SPEs with Al₂O₃ fillers, an improvement from 1.36×10^{-5} S/cm without inorganic fillers. Marcinek *et al.* explained that the improvement in ionic conductivity was associated with the increases in conduction pathways for ionic conduction provided by inorganic filler due to their larger surface area (Marcinek, 2000).

Besides that, the presence of inorganic particles in the polymer matrix also lowers the fraction of polymer-salt complexes, which increases the fraction of Li⁺ ions free for ionic conduction. Saikia *et al.* (Saikia, 2008) reported that the glass transition temperature (T_g) and crystallinity of P(VDF-HFP)-PC-LiClO₄ decreases from -98°C to -104.6°C with the addition of 4 wt% SiO₂ aerogel particles. In Addition, Pitawala also reported decreases in T_g from -44°C to -49°C when they added 10 wt% of Al₂O₃ fillers into (PEO)₉LiTf. Furthermore, Dissanayake *et al.* also reported that the presence of inorganic fillers promotes amorphous region in the polymer matrix by lowering the transition temperature (Dissanayake, 2003). But they also informed that higher filler concentration above its optimal level would impose geometrical constriction, lowering the ion mobility. They reported 15 wt% of inorganic filler provided the maximum enhancement. Furthermore,

another study conducted by Yang *et al.* (Yang, 2010) show that decreases in conductivity with increasing filler content beyond 2.5 wt% attributed to an aggregation of fillers, strongly impeding polymer chain movement.

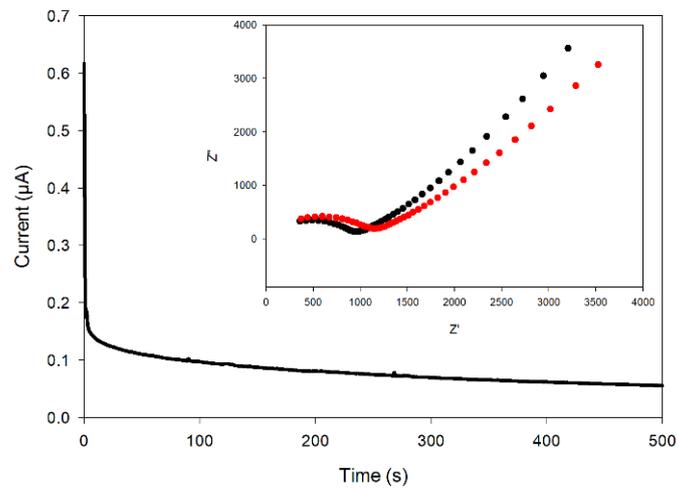


Figure 2. DC Polarization curve obtained via chronoamperometry for PMMA-LiCF₃SO₃-EC (SPE1) samples. (Inset Nyquist curve of SPE1 before and after dc polarization)

Table 3. Transference number of PMMA-based polymer electrolytes.

Sample ID	I_o (μA)	I_s (μA)	R_o (Ω)	R_s (Ω)	t^+
SPE1	0.617	0.055	964.1	1159	0.088
SPE2	0.834	0.180	69.42	75.31	0.215
SPE3	1.010	0.266	51.63	81.25	0.263

Figure 2. shows the current versus time plot obtained using the DC polarization technique, the resistance before and after polarization, and the obtained lithium transference number was tabulated in Table 3. The measured initial and steady-state currents were used to calculate the lithium transference number using Eqn (3) and included in Table 3. The lithium transference number obtained for SPE1 is 0.088, which is slightly lower than 0.16 reported by Xiao *et al.* for P(VDF-HFP)-LiPF₆-EC polymer electrolytes (Xiao, 2018). The low lithium transference number reported for SPE1 is associated with insufficient free Li⁺ ions available for ionic conduction due to the formation of polymer-salt complexes.

However, with micron-sized Al₂O₃ and SiO₂ fillers in the polymer matrix, the lithium transference number increases up to 0.215 and 0.263 for SPE2 and SPE3, respectively. Xiao *et al.* reported similar findings in their studies where the incorporation of nano-sized inorganic fillers enhances the lithium transference number (Xiao, 2018). They obtained a lithium transference number of 0.28 to 0.41 at room temperature for P(VDF-HFP) polymer electrolytes with 5-15 wt% of nano PMMA-ZrO₂ particles, which is an improvement from 0.16 without nano PMMA-ZrO₂ particles. The improvement in lithium transference number is associated with the distribution of inorganic filler in the polymer matrix.

Firstly, the presence of inorganic fillers reduces the fraction of polymer-salt complexes as inorganic fillers such as Al_2O_3 and SiO_2 fillers also forms polymer-ceramic complexes with the polymer host. This means that there is more Li^+ ions will be available for ionic conduction. Besides that, inorganic fillers also promote amorphous region in the polymer matrix as they reduced the degree of crystallinity of the polymer chain by lowering the glass transition temperature, T_g , which in turn enhances the ionic mobility, thus leading to improved lithium transference number.

Table 4. Lithium transference number obtained in this work compared to other researchers.

Composition	Type	Reference	t^+
PMMA-LiCF ₃ SO ₃ -EC	Solid	This work	0.088
PMMA-LiCF ₃ SO ₃ -EC-Al ₂ O ₃ ($\leq 10\mu\text{m}$)	Solid	This work	0.215
PMMA-LiCF ₃ SO ₃ -EC-SiO ₂ ($\leq 10\mu\text{m}$)	Solid	This work	0.263
PMMA-LiClO ₄ -EC	Gel	Faridi [7]	0.39-0.42
PMMA-LiPF ₆ -EC	Gel	Musil [8]	0.24-0.69
PMMA-LiClO ₄ -PC-EC	Gel	Appetecchi [26]	0.40
PMMA-LiBOB-EC	Gel	Hosseinioun [9]	0.34
PEO-LiCF ₃ SO ₃ EC-SiO ₂ ($\leq 12\text{nm}$)	Gel	Wang [27]	0.54
PEO-LiBF ₄ -EC-SiO ₂ ($\leq 12\text{nm}$)	Gel	Liu [28]	0.34-0.56
P(VDF-HFP)-LiPF ₆ -EC-PMMA-ZrO ₂	Solid	Xiao [15]	0.28

Table 4. shows the comparison for the lithium transference number obtained in this work to other literature. From the comparison, we can see that PMMA SPEs still have a lower lithium transference number compared to GPEs, as reported by (Faridi, 2018; Hosseinioun, 2019; Liu, 2004). This is acceptable because GPEs were much amorphous compared to SPEs due to their higher liquid solution. However, the higher liquid solution in GPEs results in a mechanically soft system and lower thermal stability. Although PMMA SPEs incorporated with inorganic fillers has lower lithium transference number compared to GPEs, but the presence of fillers in the polymer matrix served as a backbone for PMMA SPEs that ensure better mechanical and thermal stability compared to GPEs. Liang *et al.* show that the dispersion of nano- Al_2O_3 fillers into PEO-PMMA-LiTFSI polymer matrix enhances the tensile strength of SPEs up to 3.26 MPA compared to 2.78MPa for SPEs without inorganic filler (Liang, 2015).

Nevertheless, the lithium transference number in our study is comparable to the work from Xiao *et al.*. They reported lithium transference number ranging from 0.28 to 0.41 for P(VDF-HFP) polymer electrolytes doped with nano PMMA-ZrO₂ particles, close to 0.263 obtained for PMMA-LiCF₃SO₃-EC-SiO₂ in our study (Xiao, 2018). The lithium transference number in their study is higher than ours because they were using 5%-15% of nano PMMA-ZrO₂ particles while we only added 2% of SiO₂ fillers. Furthermore, the nano PMMA-ZrO₂ particles also have a greater effective surface area than micron-sized SiO₂ fillers, which also contributed to the higher lithium transference number obtained in their studies.

Figure 3. shows the LSV plot of the samples. The voltages were swept from 0V (versus stainless steel electrode) at a scan rate of 5 mVs^{-1} until a large increment of current was observed (see Figure 3). The large increment in current observed indicates the breakdown

of the electrolyte films. The stability voltage can be determined as the intersection of the extrapolated linear current in the high voltage region with the voltage axis.

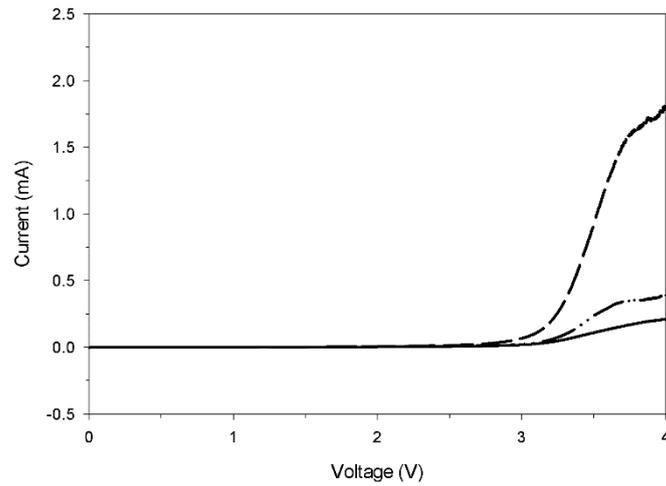


Figure 3. LSV curves with a scan rate of 5mVs^{-1} for PMMA-LiCF₃SO₃-EC (Solid line), (b) PMMA-LiCF₃SO₃-EC-Al₂O₃ (Dash dotted line), and PMMA-LiCF₃SO₃-EC-SiO₂ (Dash line).

LSV results revealed that the potential window of the blend is all above 3.0V; SPE1 (3.07V), SPE2 (3.13V), and SPE3 (3.2V). There was a notable improvement in the SPE voltage stability window containing inorganic filler compared to the polymer salts system. In comparison, Chandra *et al.* obtained an electrochemical stability voltage of 2.69V for PVC-PMMA-LiCl-TiO₂ polymer blend, an improvement from 1.69V without TiO₂ nanoparticles (Chandra, 2017). Dhatarwal *et al.* also reported stability of 3.0V for PEO-PMMA polymer blend doped with various nanoparticles (Dhatarwal, 2018).

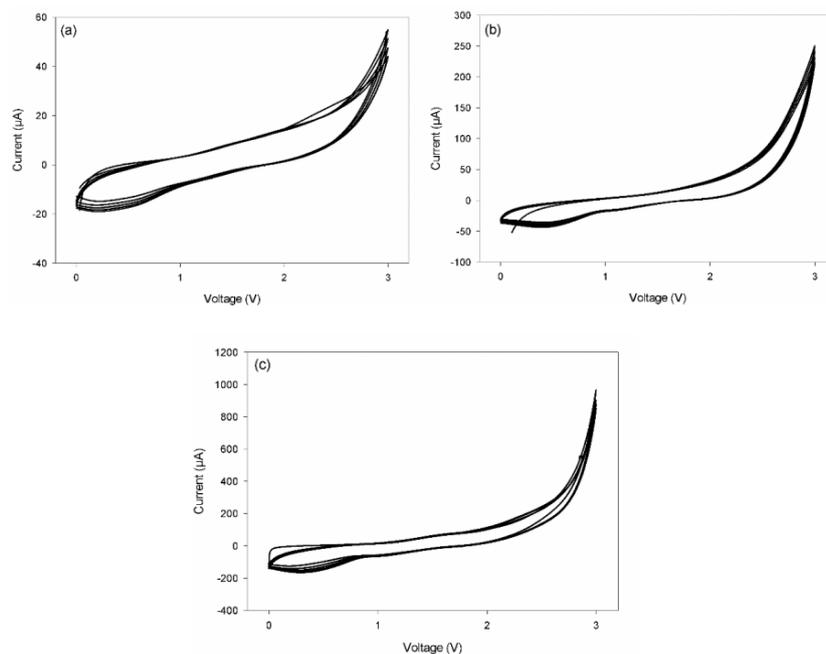


Figure 4. Five cycles of cyclic voltammetry curve versus stainless steel electrodes with a scan rate of 20mVs^{-1} for (a) PMMA-LiCF₃SO₃-EC, (b) PMMA-LiCF₃SO₃-EC-Al₂O₃ and (c) PMMA-LiCF₃SO₃-EC-SiO₂

The CV curve of the SPEs was shown in Figure 4. (see Figure 4). The absence of redox peak voltages and the overlapping of the subsequent sweeps indicates that the charging and discharging reaction at the interface between the electrolytes film and stainless-steel electrode is fully reversible for all the SPE films tested (Bandarayake, 2015). Jinisha *et al.* reported CV curve of a similar shape for PEO/PVP-LiNO₃ SPEs in their studies (Jinisha, 2017). They explained that the missing oxidation-reduction peaks in CV curves suggested that the SPE film has great reversibility within the voltage range. Furthermore, Bandarayake *et al.* also reported that CV curves with subsequent overlapping sweeps show that the SPE has good cycling capability and a longer lifetime. Their samples can retain 96% of its original specific capacity after 20 cycles (Bandarayake, 2016).

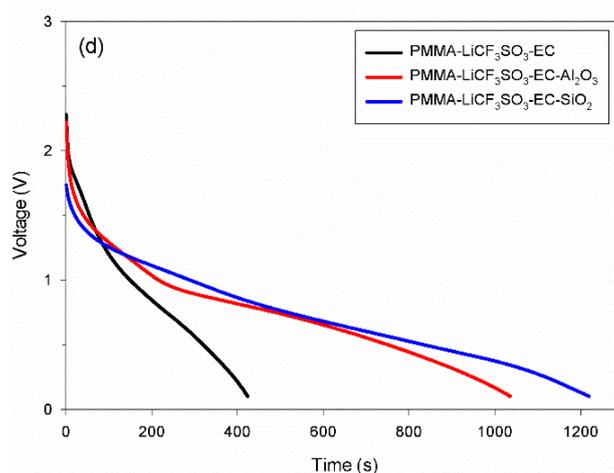


Figure 5. Discharge curve with a discharge current of 0.01mA for PMMA-LiCF₃SO₃-EC (black line), PMMA-LiCF₃SO₃-EC-Al₂O₃ (red line) and PMMA-LiCF₃SO₃-EC-SiO₂ (blue line) versus stainless steel electrodes

Furthermore, PMMA-LiCF₃SO₃-EC-SiO₂ that were doped with SiO₂ fillers samples has the highest energy density as evidenced by the discharging time as presented in Figure 5. (see Figure 5). It can be seen that PMMA-LiCF₃SO₃-EC-SiO₂ takes approximately 16% and 190% longer time to discharge compared to PMMA-LiCF₃SO₃-EC-Al₂O₃ and PMMA-LiCF₃SO₃-EC, respectively.

4.0 CONCLUSIONS

This work provided the ionic conductivity, lithium transference number, and electrochemical performance of PMMA SPEs. SiO₂ fillers enhanced PMMA SPEs can exhibit ionic conductivity of $2.35 \times 10^{-4} \text{ S/cm}$ and lithium transference number of 0.263 at room temperature. It is suggested that inorganic fillers promote amorphous region in PMMA SPEs, and the greater effective area of the fillers also provides pathways for ionic conduction. Besides, the presence of inorganic fillers reduces the fraction of polymer-salt complexes, freeing more Li⁺ ions for ionic conduction. The electrochemical studies also show that inorganic filler enhanced PMMA SPEs has great cycling capability and

reversibility within a voltage range of 3.0V. Inorganic filler enhanced SPEs may not exhibit superb ionic conductivity and lithium transference number like GPEs, but they had better mechanical and thermal properties than GPEs, which made SPEs much suitable for lower energy density but higher safety applications.

5.0 ACKNOWLEDGEMENT

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