# Z-FIT Calculation for PVDF-HFP/PEMA Solid Polymer Electrolyte using Nyquist Impedance for Lithium Battery Application

**M. Gunasekaran[1], *P. Sivakumar[2]**

Department of Physics, Periyar E.V.R. College, Tiruchirappalli, TN, India.
[1]gunaphy6@gmail,[2]psivakumarevrc@gmail.com

## Abstract

Solid Polymer electrolyte prepared using PVDF-HFP/PEMA polymers as blending, silicon dioxide optimized and characterizing using Nyquist Impedance to carry out the a.c. conductivity with the Z-Fit value of bulk resistance (Rb). The parallel plate capacitance (Cp) and charge transfer resistance (Rct) is remaining parameter of Z-Fit. The higher conductivity attain by for 8 wt. % of $SiO_2$ with the complex of PVdF-HFP/PEMA (30%) + EC/DEC (62%) + $LiClO_4$ (8%).

**Keywords:** Capacitance, Conductivity, Electrolyte, Resistance.

## 1. Introduction

The fast development in size, thickness lessening of electronic strategy and growth of manufacturing in modern, insist has been raise to produce tiny sized transportable devices [1]. Nowadays it is more or less generally conventional that such amalgamation of size and thickness can only be getting hold off by using non conservative electrodes and electrolyte resources and that the mainly capable alternative are persons based on lithium functioning scheme. With this state of affairs, effort have been made in Bisphenol A ethaxyalate dimethacrylate (BEMA)/poly (ethylene glycol) methyl ether methacrylate (PEGMA) [2], poly (ethylene oxide) (PEO) [3-4] based polymer electrolytes to reach a considerable electrical conductivity at ambient temperature. Commonly solid polymer electrolytes have much compensation, such as high high specific energy, ionic conductivity, light and easy processibility, wide electrochemical stability windows. Polymer electrolyte studies have been carried out in poly (vinyl alcohol) (PVA) [5, 6], poly (vinyl chloride) (PVC) [7, 8], poly (vinylidene fluoride) (PVdF) [9, 10], poly (acrylonitrile) (PAN) [11, 12] and poly (methyl methacrylate) (PMMA) [13, 14]. Polymer host is doped with inorganic salt and one or more plasticizers in order to enhance the conductivity. Among these polymers, PVdF is of semi crystalline nature and the electrolytes based on PVdF are usual to have high anodic stabilities due to strong electron withdrawing efficient groups and also they have high permittivity, comparatively low dissipation aspect and high dielectric constant, which assist in higher ionization of lithium salts providing a higher concentration of charge carriers. In the present investigation, Bulk resistance (Rb), charge transfer resistance (Rct), parallel plate capacitance (Cp) and conductivity studies have been performed on poly (vinylidene fluoride-co-hexafluoropropylene) (PVdF-co-HFP) with poly (ethyl methacrylate) blend based polymer electrolytes with $LiClO_4$ as salts and ethylene carbonate (EC) and diethyl carbonate (DEC) as plasticizers.

## 2. Materials

The polymers Poly (vinyledene fluoride-co-hexafluropropylene) and Poly (ethyl methacrylate) were purchased from Sigma Aldrich. Ethylene carbonate and Diethyl carbonate were purchased from Alfa Aeser. Lithium perchlorate and Silicon dioxide were purchased from Sigma Aldrich. Acetone was purchased from Merck. All materials are used without any treatment.

## 3. Preparation of Electrolyte membrane

The polymers PVDF-HFP and PEMA mixed as 30% with the ratio of 3:2 based on literature review [15]. The plasticizer EC and DEC mixed as 62 % with the equal ratio of (1:1). Lithium perchlorate salt was taken as 8%. Silicon dioxide is varying from 0% to 10% increment step of 2%. All materials are dissolved in 100 ml acetone until swelling well for 8 hours. Before to casting on clean glass plate stirrer for 2 hour and solvent evaporated @ 60$^{o}$C. The prepared electrolyte membrane was dried before impedance analysis.

## 4. Characterization

The prepared electrolyte membranes subjected to impedance spectroscopy (PEIS) using Biologic SP-150 model and its EC-Lab version 11.02 used to Z-Fit Calculation to carry out the Bulk Resistance (Rb), Parallel Plate Capacitance (Cp), Charge Transfer Resistance (Rct) and A.C. Conductivity Calculated using Rb. In this present study frequency range used from 1Hz to 1MHz. Fig.1 shows equivalent circuit for Rb, Cp and Rct.

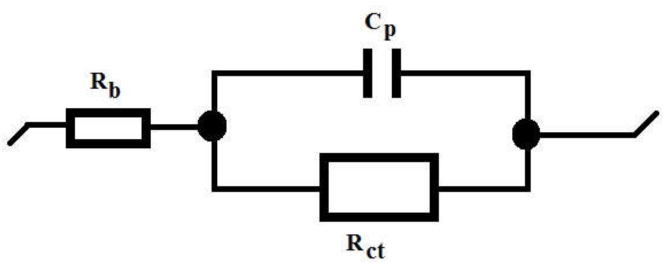


**Figure 1. Equivalent circuit for bulk resistance (Rb), parallel plate capacitance (Cp) and charge transfer resistance (Rct).**

## 5. Result and Discussion

To determine the electrochemical parameters (Resistance, Capacitance and Charge Transfer Resistance) Nyquist impedance is most significant method. This method supported by Potentiostat Electrochemical Impedance Spectroscopy (PEIS) technique. The main objective of the Nyquist Impedance issues the resistance of the material through the real (Z') and imaginary (Z") component of the axis, such as X-axis and Y-axis represented as Nyquist plot. Fig.2-7 shows the Nyquist Plot for prepared polymer electrolyte membrane. To calculate the a.c. conductivity is used the following equation $\sigma = t/Rb*A$, where $\sigma$ is a.c. conductivity of the prepared solid polymer electrolyte, t is thickness of the membrane, Rb is bulk resistance carried out from Z-Fit and A is area of the electrode.

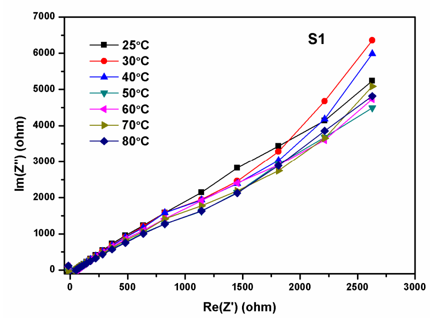


Figure 2. Nyquist Plot for S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$

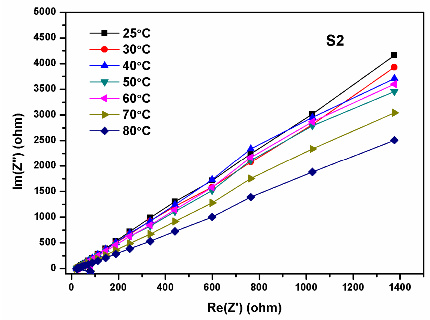


Figure 3. Nyquist Plot for S2 = S1+$SiO_2$ (2 wt. %)

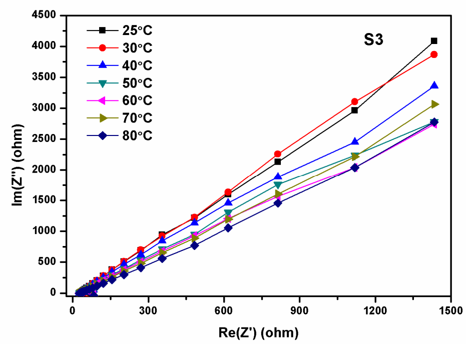


Figure 4. Nyquist Plot for S3 = S1+$SiO_2$ (4 wt. %)

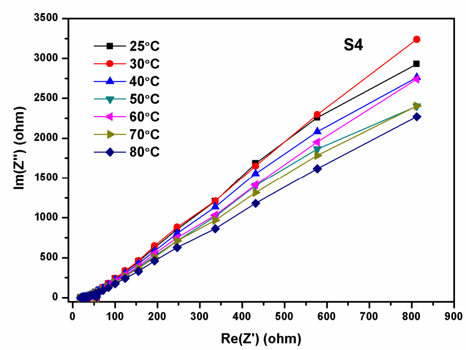


Figure 5. Nyquist Plot for S4 = S1+$SiO_2$ (6 wt. %)

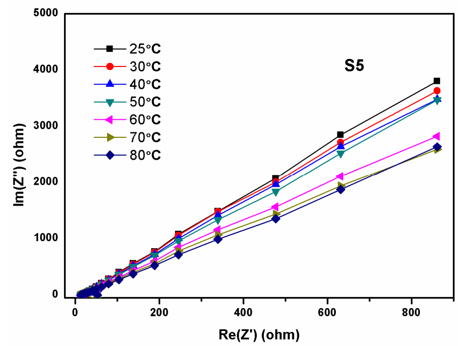


**Figure 6. Nyquist Plot for S5 = S1+$SiO_2$ (8 wt. %)**

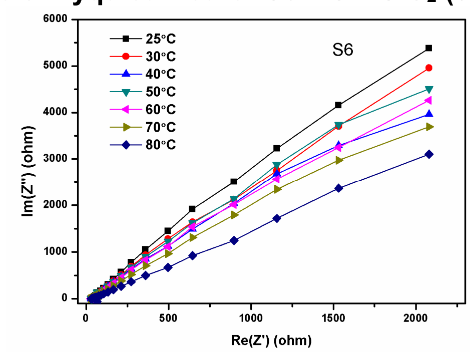


**Figure 7. Nyquist Plot for S6 = S1+$SiO_2$ (10 wt. %)**

### 5.1. Temperature vs. Bulk Resistance (Rb)

Table-1 Given for calculated bulk resistance (Rb) using Z-Fit for prepared polymer membranes (PMs) and Figure-8 shown correlation chart for temperature dependant bulk resistance of PMs following as S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2=S1+$SiO_2$ (2%), S3=S1+ $SiO_2$ (4%), S4=S1+ $SiO_2$ (6%), S5=S1+ $SiO_2$ (8%) and S6=S1+ $SiO_2$ (10%). The lowest bulk resistance of the prepared polymer membranes (PMs) achieved in S2 (2%) at room temperature and the higher bulk resistance of the PMs occurred for 6% of $SiO_2$. The Rb of all PMs is varying depending upon the various weight percentages with increasing the temperature. The high temperature (80°C) gives the lower Rb in S2 with the supporting of $SiO_2$ (2%) and the higher bulk resistance occur for 6% of ceramic material ($SiO_2$). Which is confirm the bulk resistance of prepared membrane variant depending upon the ceramic weight percentage and its reduction related with respect to the temperatures.

**Table 1. Temperature dependant Bulk Resistance (Rb)**

| SPEs | Rb (ohm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25°C | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C |
| S1 | 168.9567 | 185.0878 | 179.2722 | 152.3084 | 152.7629 | 155.2666 | 135.6045 |
| S2 | 166.5659 | 172.7136 | 156.0393 | 149.3677 | 135.0821 | 120.8919 | 97.37769 |
| S3 | 431.6889 | 411.6705 | 362.6466 | 332.4007 | 323.0447 | 258.828 | 305.3924 |
| S4 | 641.9751 | 627.1717 | 561.7201 | 519.892 | 464.7894 | 382.6827 | 321.0837 |
| S5 | 251.7089 | 233.7212 | 210.9331 | 204.5532 | 183.5687 | 160.3248 | 127.9937 |
| S6 | 471.833 | 452.0425 | 393.4565 | 407.2567 | 330.4765 | 307.1888 | 247.4296 |

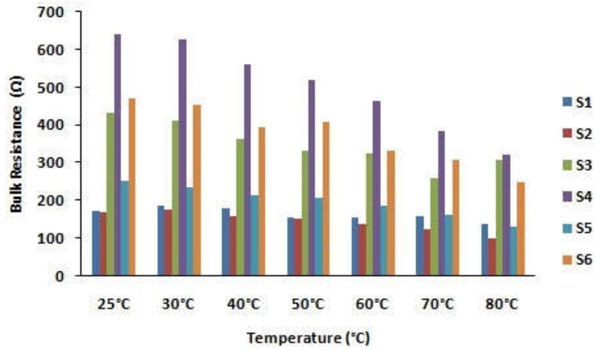


**Figure 8. Temperature dependant Bulk Resistance for S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2 = S1+$SiO_2$ (2 wt. %), S3 = S1+$SiO_2$ (4 wt. %), S4 = S1+$SiO_2$ (6 wt. %), S5 = S1+$SiO_2$ (8 wt. %) and S6 = S1+$SiO_2$ (10 wt. %)**

### 5.2. Temperature vs. Parallel Plate Capacitance

Table-2 Given for calculated parallel plate capacitance (Cp) using Z-Fit for prepared polymer membranes (PMs) and Figure-9 shown correlation chart for temperature dependant parallel plate capacitance (Cp) of PMs following as S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2=S1+$SiO_2$ (2%), S3=S1+ $SiO_2$ (4%), S4=S1+ $SiO_2$ (6%), S5=S1+ $SiO_2$ (8%) and S6=S1+ $SiO_2$ (10%). The lowest parallel plate capacitance (Cp) of the prepared polymer membranes (PMs) achieved in S6 (10%) at room temperature and the higher parallel plate capacitance (Cp) of the PMs occurred for 4% of $SiO_2$. The Cp of all PMs is varying depending upon the various weight percentages with increasing the temperature. The high temperature (80°C) gives the lower Cp in S6 with the supporting of $SiO_2$ (10%) and the higher parallel plate capacitance (Cp) occur for 6% of ceramic material ($SiO_2$). Which is confirm the parallel plate capacitance (Cp) of prepared membrane variant depending upon the ceramic weight percentage and its reduction related with respect to the temperatures.

**Table 2. Temperature dependant Parallel Plate Capacitance (Cp)**

| SPEs | Cp (F) x $10^{-5}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25°C | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C |
| S1 | 2.06 | 1.96 | 2.09 | 2.40 | 2.39 | 2.41 | 2.48 |
| S2 | 2.11 | 2.24 | 2.19 | 2.59 | 3.01 | 3.31 | 3.82 |
| S3 | 2.13 | 2.32 | 2.61 | 3.02 | 3.36 | 3.60 | 3.87 |
| S4 | 1.68 | 1.73 | 2.13 | 2.05 | 2.27 | 2.55 | 2.84 |
| S5 | 1.69 | 1.84 | 2.31 | 2.61 | 2.63 | 2.89 | 3.58 |
| S6 | 1.39 | 1.55 | 1.91 | 1.44 | 1.92 | 1.79 | 2.22 |

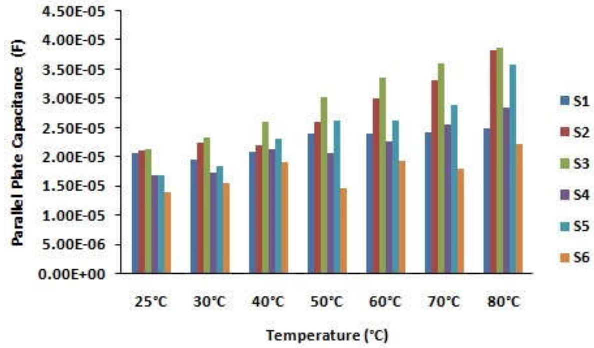


**Figure 9. Temperature dependant Parallel Plate Capacitance for S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2 = S1+$SiO_2$ (2 wt. %), S3 = S1+$SiO_2$ (4 wt. %), S4 = S1+$SiO_2$ (6 wt. %), S5 = S1+$SiO_2$ (8 wt. %) and S6 = S1+$SiO_2$ (10 wt. %).**

### 5.3. Temperature vs. Charge Transfer Resistance

Table-3 Given for calculated charge transfer resistance (Rct) using Z-Fit for prepared polymer membranes (PMs) and Figure-10 shown correlation chart for temperature dependant charge transfer resistance (Rct) of PMs following as S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2=S1+$SiO_2$ (2%), S3=S1+ $SiO_2$ (4%), S4=S1+ $SiO_2$ (6%), S5=S1+ $SiO_2$ (8%) and S6=S1+ $SiO_2$ (10%). The lowest charge transfer resistance (Rct) of the prepared polymer membranes (PMs) achieved in S3 (4%) at room temperature and the higher charge transfer resistance (Rct) of the PMs occurred for 10% of $SiO_2$. The Rct of all PMs is varying depending upon the various weight percentages with increasing the temperature. The high temperature (80°C) gives the lower Rct in S3 with the supporting of $SiO_2$ (4%) and the higher charge transfer resistance (Rct) occur for 10% of ceramic material ($SiO_2$). Which is confirm the charge transfer resistance (Rct) of prepared membrane variant depending upon the ceramic weight percentage and its reduction related with respect to the temperatures.

**Table 3. Temperature dependant Charge Transfer Resistance (Rct)**

| SPEs | Rct (ohm) | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25°C | 30°C | 40°C | 50°C | 60°C | 70°C | 80°C |
| S1 | 11449.92 | 14579.92 | 13533.19 | 9775.268 | 10611.2 | 11747.21 | 11820.21 |
| S2 | 10784.64 | 11130.26 | 11960.35 | 9990.142 | 8501.795 | 8280.121 | 7424.813 |
| S3 | 9295.041 | 10559.42 | 9815.325 | 8716.67 | 8116.058 | 7286.096 | 6253.217 |
| S4 | 10318.28 | 10355.3 | 8416.053 | 9941.007 | 9234.582 | 8173.533 | 8005.35 |
| S5 | 15842.02 | 12594.76 | 9492.287 | 8912.083 | 8966.708 | 9023.221 | 6630.896 |
| S6 | 19566.58 | 17702.13 | 11168.15 | 18400.54 | 11709.65 | 15437.77 | 12035.21 |

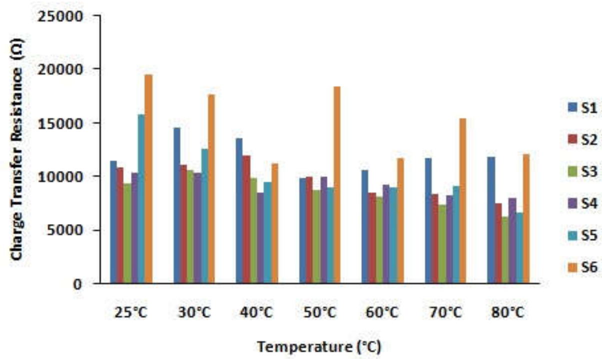


**Figure 10. Temperature dependant Charge Transfer Resistance for S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2 = S1+$SiO_2$ (2 wt. %), S3 = S1+$SiO_2$ (4 wt. %), S4 = S1+$SiO_2$ (6 wt. %), S5 = S1+$SiO_2$ (8 wt. %) and S6 = S1+$SiO_2$ (10 wt. %)**

### 5.4. Temperature vs. A.C. Conductivity

Table-4 Given for calculated a.c. conductivity (σ) using Z-Fit for prepared polymer membranes (PMs) and Figure-10 shown correlation chart for temperature dependant a.c. conductivity (σ) of PMs following as S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2=S1+$SiO_2$ (2%), S3=S1+ $SiO_2$ (4%), S4=S1+ $SiO_2$ (6%), S5=S1+ $SiO_2$ (8%) and S6=S1+ $SiO_2$ (10%). The lowest a.c. conductivity (σ) of the prepared polymer membranes (PMs) achieved in S5 (8%) at room temperature and the higher a.c. conductivity (σ) of the PMs occurred for 10% of $SiO_2$. The a.c. conductivity (σ) of all PMs is varying depending upon the various weight percentages with increasing the temperature. The high temperature (80$^o$C) gives the lower a.c. conductivity (σ) in S2 with the supporting of $SiO_2$ (2%) and the higher a.c. conductivity (σ) occur for 8% of ceramic material ($SiO_2$). Which is confirm the a.c. conductivity (σ) of prepared membrane variant depending upon the ceramic weight percentage and its reduction related with respect to the temperatures.

**Table 4. Temperature dependant A.C. Conductivity**

| SPEs | σ (S/cm) x $10^{-4}$ | | | | | | |
|---|---|---|---|---|---|---|---|
| | 25$^o$C | 30$^o$C | 40$^o$C | 50$^o$C | 60$^o$C | 70$^o$C | 80$^o$C |
| S1 | 2.10 | 2.15 | 2.27 | 2.45 | 2.63 | 2.90 | 3.35 |
| S2 | 1.97 | 2.03 | 2.18 | 2.36 | 2.52 | 2.88 | 3.34 |
| S3 | 3.58 | 3.76 | 4.04 | 4.27 | 4.38 | 5.68 | 4.61 |
| S4 | 2.25 | 2.33 | 2.55 | 2.85 | 3.29 | 4.06 | 5.06 |
| S5 | 1.14 | 1.39 | 1.65 | 8.29 | 8.57 | 9.22 | 9.97 |
| S6 | 3.80 | 3.90 | 4.15 | 4.55 | 5.45 | 6.79 | 8.56 |

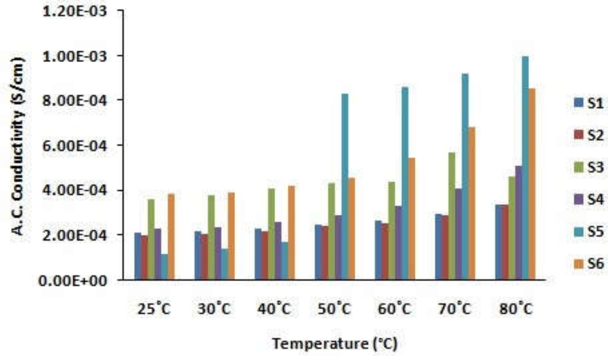


**Figure 11. Temperature Dependant A.C. Conductivity for S1=PVdF-HFP/PEMA+EC/DEC+$LiClO_4$, S2 = S1+$SiO_2$ (2 wt. %), S3 = S1+$SiO_2$ (4 wt. %), S4 = S1+$SiO_2$ (6 wt. %), S5 = S1+$SiO_2$ (8 wt. %) and S6 = S1+$SiO_2$ (10 wt. %)**

## 6. Conclusion

Solid polymer electrolyte membrane prepared by solvent casting technique. Impedance analysis was used to characterize the prepared solid polymer electrolyte with the supporting of Z-Fit calculation. The optimized $SiO_2$ gives the higher a.c. conductivity at 80ºC as $9.97x10^{-4}$ for eight percentage of weight. Charge transfer resistance (Rct), Parallel plate capacitance (Cp) and Bulk resistance (Rb) were calculated.

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