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Electrochemical Impedance Spectroscopy Analysis of Ethylene Carbonate Sustained PVDF-HFP/PEMA Blend Based Polymer Membrane

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Abstract- **This paper presents the application of Solid Polymer Membrane toward the electrolyte purpose of electrochemical device fabrication to avoid the electrolyte leakage. PVDF-HFP and PEMA polymers are hosting to membrane formation and ethylene carbonate to give the support as flexible nature of membrane. PVDF HFP/PEMA/EC/Acetone based Complexes Polymer Solution (CPS) and PVDF-HFP/PEMA/EC based Solid Polymer Membrane (SPM). The resultant CPS and SPM are subjected to Electrochemical Impedance Spectroscopy and also analysed the electrochemical properties such as Resistance (R), Capacitance (C), Solution Resistance (Rs), Double Layer Capacitance (Cdl) and Charge Transfer Resistance (Rct). After the conversion of CPS to SPM solution resistance is reduced which is confirm the acetone completely removed from the solid polymer membrane. The charge transfer resistance also reduced from the order of 105 to 104 leads the electronic conduction when these type of SPM using the electrolyte preparation for electrochemical application.**

Index Terms- **CPS, SPM, EIS, Reistance, Capacitance, Cdl, Rct.**

I. INTRODUCTION

Polymers are having many classes like Acrylic polymer, Addition polymer, aliphatic polyamides, aliphatic polyesters and Aromatic polyamides. Most of the polymers are used for home appliances and technological view. From the recent decade's polymer are widely used in electrical and electronic applications, especially PVC, PAN have received special attention in the fabrication of battery, fuel cell, sensor and electrochromic devices using electrically conducting polymer classes [1-4]. PVC, PAN, PMMA, PVDF and PVAc those polymers are literature to use as polymer electrolyte preparation for lithium ion battery application [5-9]. In all kind of electrochemical application polymer are mostly used as binder and electrolyte membrane preparation as host materials. In this study chemical copolymer with poly (ethyl methacrylate) plasticized with the support of EC. Ethylene carbonate is a organic solvent which has 243^{o}C boiling point and its reaction occurred with CO_2 only[10] there is no reaction with poly(vinylideneflouride-co-hexaflouropropylene) and poly(ethyl methacrylate) even though the presence of EC on PVDF-HFP/PEMA polymer membrane becomes to flexible nature. Due to the requirement of polymer membrane for electrolyte purpose of electrochemical application, in this present study optimize of plasticizer with blended hosting polymer membrane characterised by electrochemical impedance spectroscopy to analyse the prepared polymer membrane.

II EXPERIMENTAL

PVDF-HFP/PEMA based polymer membrane prepared by solution casting techniques, 1:1 ratio of host polymer PVDF-HFP /PEMA deceased from 80% to 10% in the variation of 10% mean time addition of plasticizer EC increased from 0% to 80% in the interval of 10%. The ratio of the prepared polymer membrane shown in table.1 The prescribed weight ratio of the PVDF-HFP and PEMA dissolved in 20ml of acetone stirred for one hour and swelling for 24 hours, after the swelling of polymer added ethylene carbonate as prescribed ratio. After the 12 hour PVDF-HFP/PEMA/EC complexes solutions continuously stirred @60oC and 700rpm. After the evaporation of acetone the resultant jelly solution casted on cleaned glass plate. The casted polymer membrane dried well before to electrochemical characterization. Plasticized PVDF-HFP/PEMA/EC/Acetone complexes polymer solution (CPS) and PVDF-HFP/PEMA/EC solid polymer membrane (SPM) are carried to electrochemical impedance spectroscopy analysis. Electrochemical impedance spectroscopy analysis carried out using EC-Lab Electrochemical work station, the frequency range 1Hz to 1MHz. Complexes Polymer Solution filled in beaker as 5ml, 10ml and 15ml and stainless steel (SS) used as blocking for the electrochemical analysis. Through the Z-Fit calculation measured the Resistance, Capacitance, Solution Resistance, Double Layer Capacitance and Charge Transfer Resistance is calculated. The Equivalent circuit diagram for Rs+Cdl/Rct shown in Figure 8.

Table 1: Ratio of complexes Polymer Solution (CPS) for volume of 5ml, 10ml, 15ml and Solid Polymer membrane (SPM)

Sample Code		PVdF-HFP %	PEMA %	EC %	Acetone (ml)
CPS	SPM				
CPS1	SPM1	50	50	0	20
CPS2	SPM2	40	40	20	20
CPS3	SPM3	36	30	40	20
CPS4	SPM4	20	20	60	20
CPS5	SPM5	10	10	80	20

III. MRESULT AND DISCUSSION

Electrochemical Impedance Spectroscopy (EIS) Analysis of CPS

Figure 1-3 are Niquist plot of Impedance spectroscopy studies which is plotted with the real part of resistance in X-axis and imaginary part of resistance in Y-axis. In this EIS resistance increases directly proportional to increasing the frequency range from 1Hz to 1MHz, Table.2 shows the resistance in ohm and capacitance in Farad for the prescribed ratio followed in Table.1. Figure.4 shows the correlation chart resistance for the 5ml, 10ml and 15ml volume of complexes polymer solutions (CPS). When increasing the plasticizer from zero percentage to eighty percentages the resistance becomes reduced, mean time volume dependant of complexes polymer solution increasing the volume of polymer solution the resistance also increases as well as the ethylene carbonate increased of all complexes polymer solutions.

Table 2a: The Specific Resistance of CPS (5ml, 10ml and 15ml)

Sample Code	Resistance (Ohm)		
	5ml	10ml	15ml
CPS1	3646.482	3902.087	10799.41
CPS2	***1198.714***	***1062.824***	4721.768
CPS3	1967.51	3268.319	3055.657
CPS4	2587.14	1467.657	5896.885
CPS5	1564.406	2739.933	***2333.666***

Table 3b: The Capacitance of CPS (5ml, 10ml and 15ml)

Sample Code	Capacitance (F)		
	5ml	10ml	15ml
CPS1	2.84E-10	5.22E-10	1.21E-09
CPS2	***3.38E-10***	***7.31E-10***	1.22E-09
CPS3	1.41E-10	2.98E-10	5.63E-10
CPS4	3.05E-10	1.34E-09	1.13E-09
CPS5	2.50E-10	4.78E-10	***7.26E-10***

The resistance increment calculated using the subtraction from higher frequency resistance by the value of lower frequency resistance, the resultant increment of résistance Figure.5 shows correlation chart for the resistance increment which is inversely proportional to the resistance in all complexes polymer solutions and various volume of CPS.

From the Z-Fit calculation capacitance also measures for the all complexes polymer solutions with the various volume of CPS. The capacitance values are shown in table.2 the capacitance of complexes polymer solutions increased directly proportional to the increasing the content of ethylene carbonate but which increment in non-linear even though the volume of solution increased the capacitance also increased as linearly. These are evident in the correlation chart of capacitance shows the figure.6.

The capacitance increment calculated using the subtraction from higher frequency capacitance by the value of lower frequency capacitance, the resultant increment of capacitance for the 5ml, 10ml and 15ml volumes and increased content of ethylene carbonate. Figure.7 shows correlation chart for the capacitance increment which is directly proportional to the capacitance in all complexes polymer solutions as non-linearly and various volume as linearly

Table 3: Solution Resistance (Rs) in Ohm for Complexes Polymer Solutions

Sample Code	Solution Resistance (R_s) in Ohm		
	5ml	10ml	15ml
CPS1	2898.047	2964.752	211.4599
CPS2	953.9181	744.2995	2390.516
CPS3	1876.784	2703.58	1739.386
CPS4	2288.838	1325.74	3098.042
CPS5	1497.765	2364.556	1815.505

Table 4: Double Layer Capacitance (Cdl) of Complexes Polymer Solutions

Sample Code	Double Layer Capacitance (C_{dl}) in Farad		
	5ml	10ml	15ml
CPS1	2.38E-11	2.78E-11	1.85E-11
CPS2	4.07E-11	4.68E-11	2.34E-11
CPS3	4.23E-11	2.88E-11	2.77E-11
CPS4	3.51E-11	7.45E-11	2.24E-11
CPS5	5.83E-11	3.73E-11	3.90E-11

Table 5: Charge Transfer Resistance (Rct) of Complexes Polymer Solutions

Sample Code	Charge Transfer Resistance (R_{ct}) in Ohm		
	5ml	10ml	15ml
CPS1	266445.5	198040.1	128996
CPS2	257489.3	168333.4	116616.3
CPS3	410985.5	265131.5	188879.5
CPS4	265966.7	115422.6	125378.9
CPS5	281938.8	196247.2	164127.6

Figure.8 shows the extended analysis of electrochemical characterization using this equivalent circuit with the element of solution resistance (Rs), double layer capacitance (Cdl) and the charge transfer resistance (Rct) in EC-lab V11.02 software. The result of Z-Fit calculation for the relevant equivalent circuit shows in table.3-5 followed as Rs, Cdl and Rct. Non-plasticizer of polymer solution having highly 2898.047 ohm of solution resistance, when increasing the volume of non-plasticized polymer solution lesser resistance. Figure.9 shows the plasticised complexes polymer solution increasing the ethylene carbonate content the solution resistance also increased linearly but increasing the volume of polymer solution non-linearly increased the solution resistance. Figure.10 shows the double layer capacitance of the complexes polymer solution increased when increasing the ethylene carbonate mean time lower volume of polymer solution having higher double layer capacitance and higher volume of CPS are having decreased double layer capacitance. Due to the increment of ethylene carbonate the charge transfer resistance are increased as non-significantly otherwise the higher volume of polymer solutions gives the increased charge transfer resistance and its opponent to increase the volume of polymer solution such charge transfer resistance are decreased as significantly which is evident in figure.11.

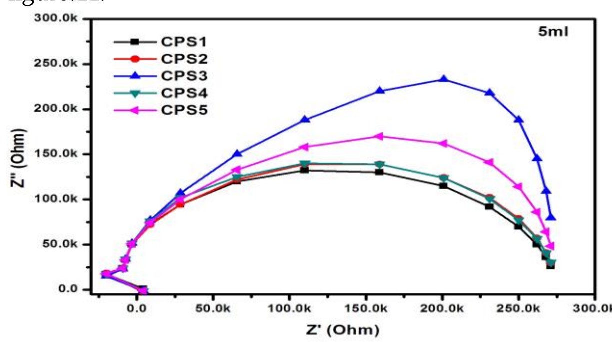

Figure 1: Nyquist Plot for 5ml PVDF-HFP/PEMA/EC/Acetone of CPS

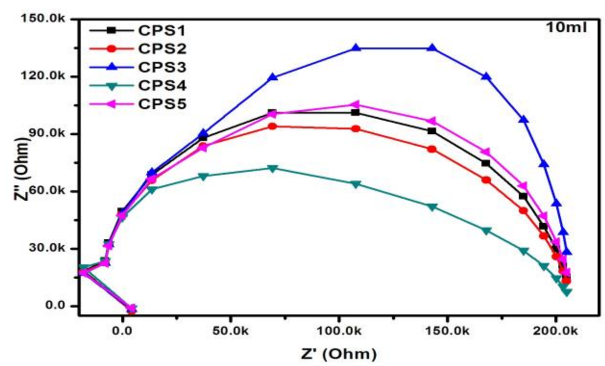

Figure 2: Nyquist Plot for 10ml PVDF-HFP/PEMA/EC/Acetone of CPS

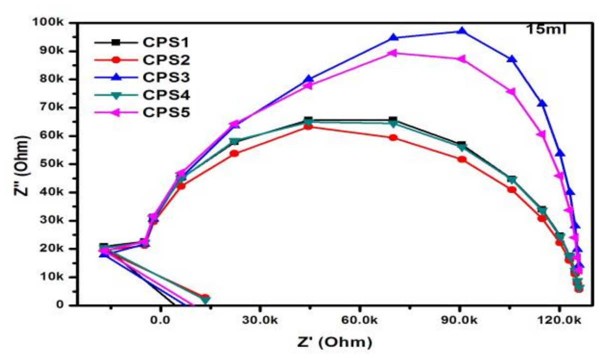

Figure 3: Nyquist Plot for 15ml PVDF-HFP/PEMA/EC/Acetone of CPS

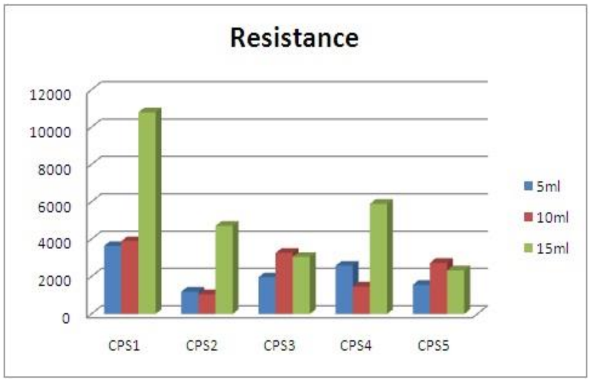

Figure 4: Correlation Chart for Resistance of the Complexes Polymer Solutions (CPS)

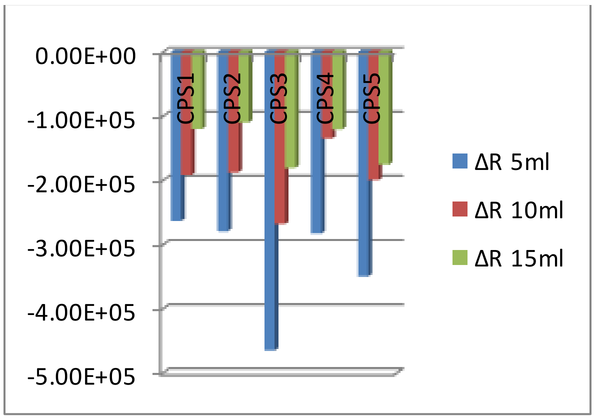

Figure 5: Correlation Chart for Resistance Increment of the Complexes Polymer Solution (CPS)

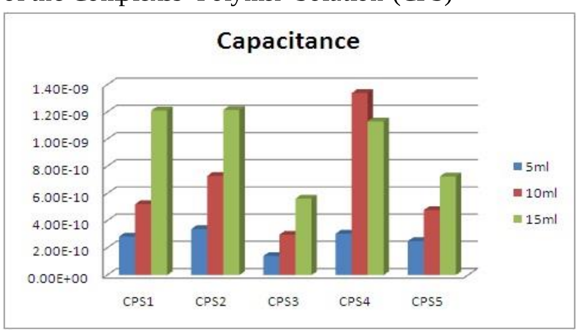

Figure 6: Correlation Chart for Capacitance of the Complexes Polymer Solutions (CPS)

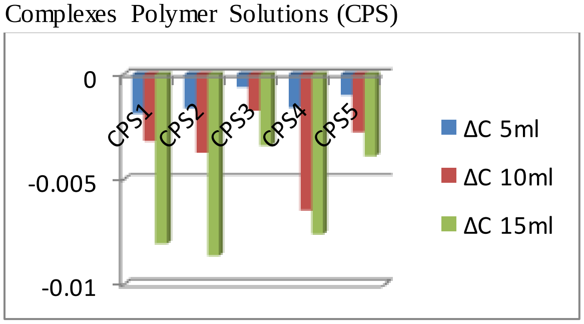

Figure 7: Correlation Chart for Capacitance Increment of Complexes Polymer Solutions (CPS)

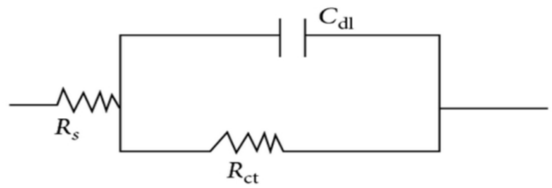

Figure 8: Equivalent circuit diagram of Solution Resistance (R_s), Double Layer Capacitance (C_{dl}) and Charge Transfer Resistance (R_{ct})

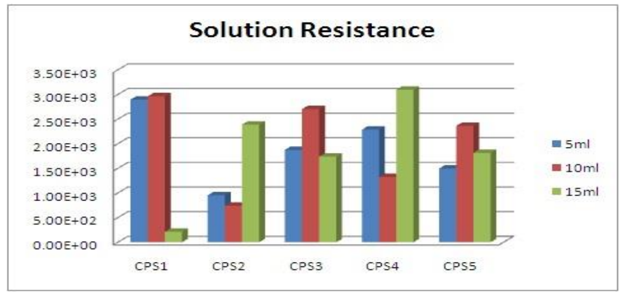

Figure 9: Correlation Chart for Solution Resistance of CPS

Sampl e Code	R (Ohm)	C (F)	Rs (Ohm)	Cdl (F)	Rct (Ohm)
SPM1	1.5E+03	8.4E-06	5.0E+02	3.1E-10	1.6E+04
SPM2	2.4E+03	7.3E-10	1.7E+03	9.1E-11	6.1E+04
SPM3	2.4E+03	7.3E-10	1.7E+03	9.1E-11	6.1E+04
SPM4	2.5E+03	1.3E-09	1.5E+03	9.5E-11	6.0E+04
SPM5	2.5E+03	1.3E-09	1.5E+03	9.5E-11	6.0E+04

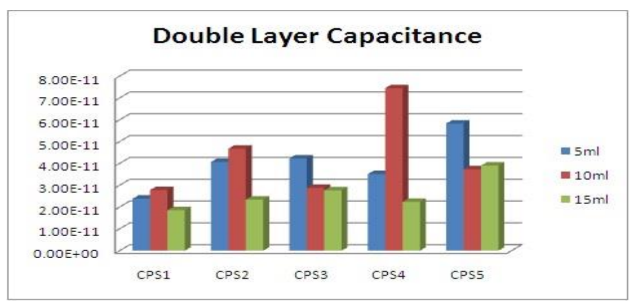

Figure 10: Correlation Chart for Double Layer Capacitance of CPS

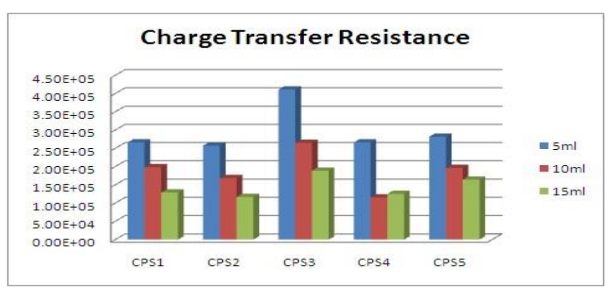

Figure 11: Correlation Chart for Chart Transfer Resistance of CPS

Electrochemical Impedance Spectroscopy (EIS) of Solid Polymer Membrane (SPM)

Figure.12 shows the Nyquist impedance plot for Solid Polymer Membrane (SPM) and Figure.13 shows resistance of Solid Polymer Membrane. Non-plasticized polymer membrane resistance occurred as 1.56 X 103, when increasing the plasticizer content increased to 2.54 X 103. The capacitance of SPM has 8.46 X 10-6 for non-plasticized polymer membrane, increasing the plasticizer content capacitance also decreased form 10% of EC to 80%EC its evident figure.14. Solution the resistance of SPM1 is lesser than the plasticized polymer membrane from SPM2-SPM5. Double Layer Capacitance has order of 10-10 for non-plasticized polymer membrane and also decreasing the Cdl when increases of ethylene carbonate. Charge transfer resistance (Rct) of solid polymer membrane of SPM proportional to the solution resistance. The lower Rct value increases when increasing the EC. Figure.15, 16 and 17 are correlation chart of solution resistance, double layer capacitance and charge transfer resistance. The Z-Fit calculation result for R+C/R shows in table.6.

Table 6: Resistance (R), Capacitance (C), Solution Resistance (Rs), Double Layer Capacitance (Cdl) and Charge Transfere Resistance (Rct) for SPM

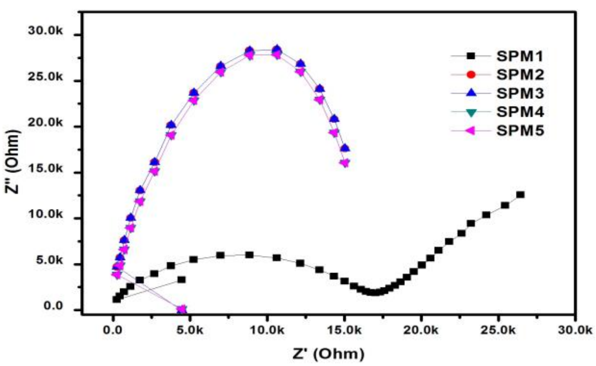

Figure 12: Nyquist Plot for Solid Polymer Membrane (SPM)

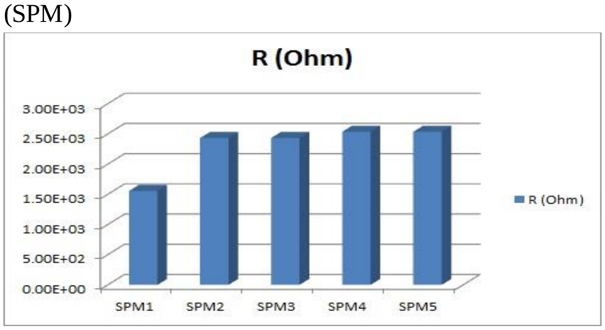

Figure 13: Correlation Chat for Resistance of Solid Polymer Membrane (SPM)

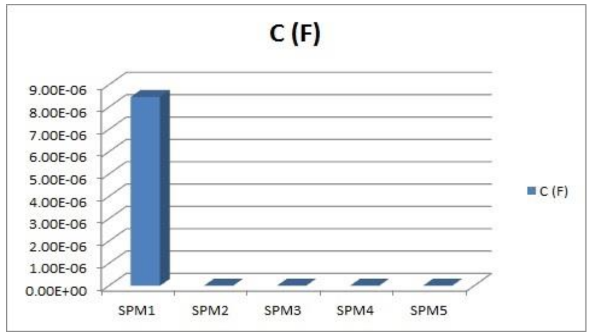

Figure 14: Correlation Chat for Capacitance of Solid Polymer Membrane (SPM)

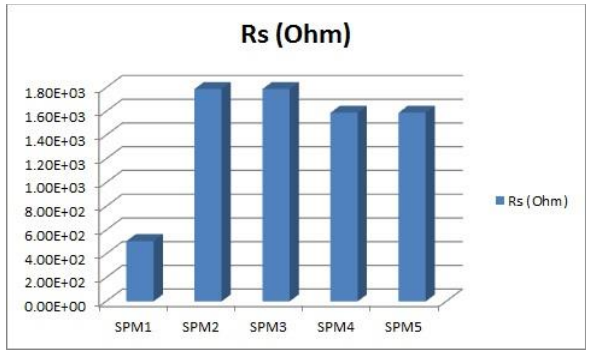

Figure 15: Correlation Chat for Solution Resistance of Solid Polymer Membrane (SPM)

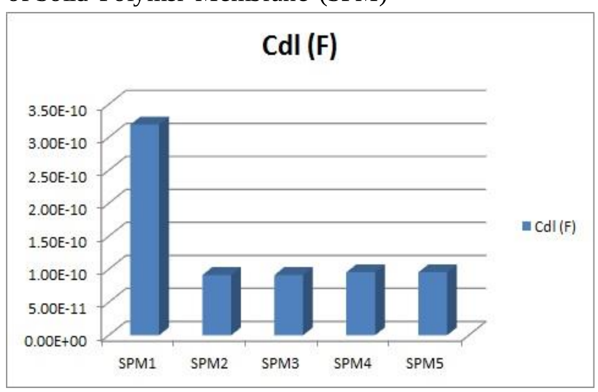

Figure 16: Correlation Chat for Double Layer Capacitance of Solid Polymer Membrane (SPM)

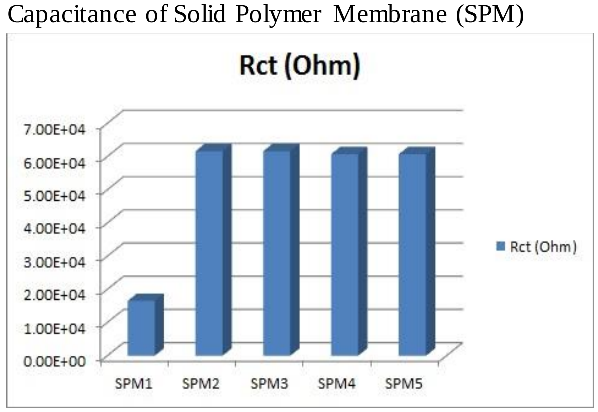

Figure 17: Correlation Chat for Charge Transfer Resistance of Solid Polymer Membrane (SPM)

IV. CONCLUSION

In this present study PVDF-HFP/PEMA/EC/Acetone based Complexes Polymer Solution (CPS) and PVDF-HFP/PEMA/EC based Solid Polymer Membrane (SPM) prepared with increasing of ethylene carbonate. The resultant CPS analysed by Electrochemical Impedance Spectroscopy (EIS), thereafter CPS converted to Solid Polymer Membrane (SPM) using the solution casting technique and its resultant membrane characterized by EIS. After the conversion of CPS to SPM solution resistance is reduced which is confirm the acetone completely removed from the solid polymer membrane. The charge transfer resistance also reduced from the order of 105 to 104 leads the electronic conduction when these type of SPM using the electrolyte preparation for electrochemical application.

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