

## CHAPTER 6

### RESULTS OF EIS STUDIES

#### 6.1 Introduction

The Electrochemical Impedance Spectroscopy (EIS) is a good tool to characterize electrical properties of a polymer electrolyte. This chapter presents EIS based electrical properties of the prepared samples. The main purpose of EIS characterization is to determine the most suitable and the highest conducting polymer electrolyte composition for application in solar cells. The effect of salt and plasticizer variation on conductivity was investigated. The electrolyte with the highest conducting composition from the present study will be added with a small amount of iodine to create an iodide/triiodide redox couple in the electrolytes for DSSC fabrication.

Conductivity is defined as the product of number density of mobile ions ( $n$ ), electronic charge ( $e$ ) and mobility ( $\mu$ ). Thus, when studying ionic conductivity of a polymer electrolyte, it is useful and important to know the number density of charge carriers ( $n$ ), ionic mobility ( $\mu$ ) and diffusion coefficient ( $D$ ) to understand the conductivity behavior. Some authors have calculated the number density of charge carriers for gel polymer electrolytes using the total concentration of salt or acid (charge carrier suppliers) and the fraction of dissociated salt or acid obtained from vibrational spectroscopy (Ericson et al., 2000). Petrowsky et al., (2006) have also calculated the concentration of free ions in liquid electrolytes from vibrational spectroscopy. Majid and Arof (2005) have used the Rice and Roth model (Rice and Roth, 1972) to calculate the charge carrier density, but had to assume arbitrary *ion-jump distance* and *time to make-a-jump*. In order to measure

ionic mobility in polymer electrolytes, Chandra et al., (1998) and Shaju and Chandra, (1996) have devised the transient ionic current (TIC) experiment. However, it may be difficult to obtain reproducible TIC peaks over different cycles of sample polarization and depolarization. A new method to determine these parameters has been developed by Bandara and Mellander (2011) to simultaneously calculate the charge carrier number density  $n$ , ion mobility  $\mu$  and diffusion coefficient  $D$  for an electrolyte using broadband dielectric response. Unfortunately, in order to use the broadband dielectric response, the dissipative loss curve must exhibit a peak. It would be very difficult to calculate the three mentioned parameters if the dissipative loss curve does not show a maximum. A more universal method has been developed by Arof and his students which is reported in this thesis for the first time. Arof and students call this method the equivalent circuit model approach since it utilizes the equivalent circuit that represents the Nyquist plot of the samples. The approach has been used to calculate the ion mobility  $\mu$ , number density  $n$  and diffusion coefficient  $D$  of the mobile ions.

## 6.2 Conductivity Studies on NaI Based Electrolytes

### 6.2.1 Nyquist Plots of (PVDF-HFP) – NaI Electrolytes

Figure 6.1 (a) to (e) show the Nyquist plots for (PVDF-HFP)-NaI polymer electrolyte films having 10 to 50 wt.% NaI. The imaginary impedance ( $Z''$ ) versus real impedance ( $Z'$ ) was plotted to determine the value of bulk resistance,  $R_B$  in order to calculate the ionic conductivity of the polymer electrolyte using the equation  $\sigma = l/R_B A$ . Here,  $R_B$  is the bulk resistance,  $A$  is the surface area of contact between the electrode and electrolyte and  $l$  is the thickness of the polymer electrolyte. It is clearly seen that the Nyquist plots with the exception of Fig. 6.1 (a) and (d) show a semicircle and an inclined spike

respectively. The semicircle is related to ionic conduction in the bulk of the sample (Buraidah and Arof, 2010) and the spike can be attributed to the effect of blocking electrodes (Michael et al., 1997). The bulk resistance,  $R_B$  can be retrieved from the Nyquist plot as shown in Fig. 6.1 (a) to 6.1 (e).  $R_B$  value for electrolytes containing 10, 20, 30, 40 and 50 wt.% NaI concentrations is  $3.24 \times 10^6 \Omega$ ,  $6.65 \times 10^4 \Omega$ ,  $547 \Omega$ ,  $18 \Omega$  and  $323 \Omega$  respectively. The  $R_B$  for 10wt.% NaI was verified using the complex admittance plot in Fig. 6.1(a'). The admittance data can be obtained from impedance data using equations  $A' = Z' / [(Z')^2 + (Z'')^2]$  and  $A'' = Z'' / [(Z')^2 + (Z'')^2]$ .



**Fig. 6.1:** The Nyquist plots of (PVDF-HFP) - NaI polymer electrolyte with (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt.% NaI content

### 6.2.2 Ionic Conductivity of (PVDF-HFP) – NaI Electrolytes

The variation of ionic conductivity of the electrolytes with NaI salt concentration at room temperature is as shown in Fig. 6.2. From the graph, the ionic conductivity for pure PVDF-HFP is found to be  $6.20 \times 10^{-11} \text{ S cm}^{-1}$ . After the addition of 10 wt.% NaI into the polymer, the ionic conductivity has increased to  $2.14 \times 10^{-9} \text{ S cm}^{-1}$ . The ionic conductivity of polymer electrolyte increases with salt concentration until 40 wt. % NaI and decreases thereafter. The conductivity value at 40 wt.% NaI is  $5.21 \times 10^{-5} \text{ S cm}^{-1}$ .

**Fig. 6.2:** The room temperature ionic conductivity of (PVDF-HFP)-NaI electrolytes containing various wt.% of NaI

The low conductivity value at low salt content may be attributed to the small number density of charge carriers in the electrolytes. An increase in the concentration of NaI salt increases the number density of charge carriers which will enhance the conductivity. However, the conductivity decreases on further addition of (> 40 wt.%) salt. This has been attributed to the decrease in mobility of the charge carriers due to the increase in

viscosity of the electrolyte (Jiang et al., 1997) and/or the association of ions into neutral ion-pairs that do not contribute to conductivity (Buraidah and Arof, 2009). The formation of neutral ion aggregates at high salt concentrations has also been reported by Sequeira et al. (1994). In order to enhance the conductivity value of the (PVDF-HFP) - NaI electrolytes, a plasticizing agent comprising different amounts of equal weights of EC/PC mixture has been incorporated into the highest conducting composition. The results are discussed in section 6.2.3.

### **6.2.3 Determination of $n$ , $\mu$ , and $D$ by the Equivalent Circuit Model Approach for (PVDF- HFP) - NaI Electrolytes**

As mentioned above the increase and decrease of conductivity can be attributed to the number density of mobile ions. To verify these changes, the charge carrier concentration must be known. FTIR could not provide the charge carrier concentration as iodide salt in the spectrum may not be able to show free ion bands, ion-pair bands and heavier ion aggregate bands as for  $\text{LiCF}_3\text{SO}_3$  (Huang and Frech, 1992), LiBoB (Holomb et al., 2006) and thiocyanide salts (Zhang and Wang, 2009). So, in this work we make use of another approach i.e. the equivalent circuit model approach.

By using the Nyquist plots of (PVDF-HFP) – NaI electrolytes in Fig. 6.1 (a) to (e), the value of  $n$ ,  $\mu$ , and  $D$  were determined by the equivalent circuit model approach for samples containing 10 to 50 wt.% NaI.

#### **(a) Electrolyte with 10 wt.% NaI**

The Nyquist plot in Fig. 6.1 (a) takes the shape of a depressed semicircle. This implies that the polymer electrolyte membrane can be represented by a leaky capacitor (CPE)

connected in parallel to a resistor (R) (Linford, 1998). The equivalent circuit is shown in Fig. 6.3 (a).

**Fig. 6.3 (a):** Equivalent circuit for sample with 10 wt.% NaI

A leaky capacitor can be represented by a constant phase element (CPE) where the impedance of the CPE is given by the equation (Linford, 1998)

$$Z_{CPE} = \frac{1}{k(j\omega)^p}, \quad 0 \leq p \leq 1 \quad (6.1)$$

$$= \frac{k[\cos(\frac{\pi p}{2}) - j \sin(\frac{\pi p}{2})]}{\omega^p}$$

Here the inverse of  $k$  is the capacitance of the bulk sample,  $p$  is related to the deviation of the semicircle diameter from the vertical axis in the  $Z''$  vs  $Z'$  plot and of  $\omega$  is the angular frequency ( $\omega = 2\pi f$ ). The expressions for the real and imaginary parts of the impedance of this equivalent circuit are given below:

$$Z' = \frac{R + R^2 k^{-1} \omega^p \cos(\frac{\pi p}{2})}{1 + 2Rk^{-1} \omega^p \cos(\frac{\pi p}{2}) + R^2 k^{-2} \omega^{2p}} \quad (6.2)$$

$$Z'' = \frac{R^2 k^{-1} \omega^p \sin(\frac{\pi p}{2})}{1 + 2Rk^{-1} \omega^p \cos(\frac{\pi p}{2}) + R^2 k^{-2} \omega^{2p}} \quad (6.3)$$



The value of  $p$  and  $R$  can be determined from the plots in Fig. 6.1 (a) to (e). Here, the value of  $R$  is actually the bulk resistance,  $R_B$ .  $\omega = 2\pi f$  where  $f$  is the input frequency.  $k^{-1}$  represents the capacitance of the leaky capacitor obtained by taking the reciprocal of the value for  $k$  that can be obtained by trial and error or using some non-linear least squares software. By substituting the value of  $R$  and  $p$ , varying the frequency and selecting the most suitable value of  $k$  (trial and error) the fitting obtained for the Nyquist plot is as shown by the solid line in Fig. 6.3 (b).

**Fig. 6.3 (b):** The fitting obtained from equivalent circuit for 10 wt.% NaI sample

**(b) Electrolyte with 20 wt.% NaI**

The Nyquist plot in Fig. 6.1 (b), consists of a depressed semicircle and a tilted spike; the depressed semicircle can be represented by an equivalent circuit comprising a “leaky capacitor” and a resistor connected in parallel and the spike can be represented by another constant phase element (CPE 2) connected in series to equivalent circuit representing the semicircular part. The equivalent circuit for this sample is as shown in Fig. 6.4 (a).

**Fig. 6.4 (a):** Equivalent circuit for sample with 20 wt.% NaI

The expressions for the real and imaginary parts of the impedance of this equivalent circuit are given below:

$$Z' = \frac{R + R^2 k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right)}{1 + 2R k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2 p_1}} + \frac{\cos\left(\frac{\pi p_2}{2}\right)}{k_2^{-1} \omega^{p_2}} \quad (6.4)$$

$$Z'' = \frac{R^2 k_1^{-1} \omega^{p_1} \sin\left(\frac{\pi p_1}{2}\right)}{1 + 2R k_1^{-1} \omega^{p_1} \cos\left(\frac{\pi p_1}{2}\right) + R^2 k_1^{-2} \omega^{2 p_1}} + \frac{\sin\left(\frac{\pi p_2}{2}\right)}{k_2^{-1} \omega^{p_2}} \quad (6.5)$$

Here,  $p_1$  and  $p_2$  are determined from the Nyquist plot in Fig. 6.1 (b).  $R=R_B$  and  $k_1^{-1}$  and  $k_2^{-1}$  are the capacitance of CPE 1 and CPE 2 respectively.  $k_1^{-1}$  is the geometrical capacitance as in Fig. 6.1 (a).  $k_2^{-1}$  is the capacitance of the electrical double layer capacitor. The fitting curve is shown by the solid line in Fig. 6.4 (b).

**Fig. 6.4 (b):** The fitting obtained from equivalent circuit for 20 wt.% NaI sample

(c) **Electrolyte with 30 wt. % NaI**

The sample containing 30 wt.% NaI was analyzed using the same equivalent circuit used for the sample containing 20 wt.% NaI. The fitting shown in Fig. 6.5 is reasonably good except at 50 and 100 Hz.

**Fig. 6.5:** The fitting obtained from equivalent circuit for 30 wt.% NaI sample

**(d) Electrolyte with 40 wt.% NaI**

For sample containing 40 wt.% NaI, since the impedance plot has mainly the spike part, the equivalent circuit can be simplified to that shown in Fig. 6.6 (a)

**Fig. 6.6 (a):** Equivalent circuit for sample with 40 wt.% NaI

The expressions for the real and imaginary parts of the impedance of this equivalent circuit are given below:

$$Z' = R + \frac{k_2 \cos\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \quad (6.6)$$

$$Z'' = R + \frac{k_2 \sin\left(\frac{\pi p_2}{2}\right)}{\omega^{p_2}} \quad (6.7)$$

The fitting curve shown by the solid line in Fig. 6.6 (b) is reasonably good.

**Fig. 6.6 (b):** The fitting obtained from equivalent circuit for the 50 wt.% NaI sample

**(e) Electrolyte with 50 wt.% NaI**

For sample with 50 wt.% NaI, the equation for the impedance of the equivalent circuit are the same as sample with 20 and 30 wt.% NaI. The fitting is shown in Fig. 6.7.

**Fig. 6.7:** The fitting obtained from equivalent circuit for the 50 wt.% NaI sample  
The mobility ( $\mu$ ), number density ( $n$ ), and diffusion coefficient ( $D$ ) of mobile ions can be calculated using equations. These will be explained in the *Discussion* Chapter.

$$\mu = \frac{e(k_2 \varepsilon_r \varepsilon_o A)^2}{k_b T \tau_2}$$

$$n = \frac{\sigma k_b T \tau_2}{(ek_2 \varepsilon_r \varepsilon_o A)^2}$$

$$D = \frac{(k_2 \varepsilon_r \varepsilon_o A)^2}{\tau_2}$$

where  $k_b$  is Boltzmann constant ( $1.38 \times 10^{-23}$  J K<sup>-1</sup>),  $T$  is absolute temperature in Kelvin,  $e$  is the electron charge ( $1.602 \times 10^{-19}$  C),  $A$  is electrode-electrolyte contact area,  $\varepsilon_o$  is vacuum permittivity ( $8.85 \times 10^{-14}$  F cm<sup>-1</sup>),  $\tau_2 = \frac{1}{\omega_2}$  with  $\omega_2$  is angular frequency corresponding to minimum in imaginary parts of the impedance  $Z_i$  and  $\varepsilon_r$  is the dielectric constant of the material.

The calculated values of  $n$ ,  $\mu$  and  $D$  obtained from this method are summarized in Table 6.1. and the graphs of  $n$ ,  $\mu$  and  $D$  against NaI contents are shown in Fig. 6.9. It can be seen from Fig. 6.9, the mobility ( $\mu$ ), number density ( $n$ ), and diffusion coefficient ( $D$ ) of mobile ions vary with NaI content and the variations have the same trend as the variation of the conductivity with NaI concentration shown in Fig. 6.2. It may be inferred that the room temperature (RT) conductivity is influenced by all the three parameters.

**Table. 6.1:** Summary of  $n$ ,  $\mu$  and  $D$  obtained from the Equivalent Circuit Model and the respective  $R$ ,  $p_1$ ,  $p_2$ ,  $k_1^{-1}$  and  $k_2^{-1}$  value for (PVDF-HFP)-NaI

NaI (wt.%)	$R(\Omega)$ ( $\times 10^2$ )	$p_1$	$k_1^{-1}(F)$ ( $\times 10^{-10}$ )	$p_2$	$k_2^{-1}(F)$ ( $\times 10^{-5}$ )	$n$ ( $\text{cm}^{-3}$ ) ( $\times 10^{21}$ )	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) ( $\times 10^{-11}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ ) ( $\times 10^{-13}$ )
10	30000	0.85	2.9	-	-	0.68	1.94	4.99
20	650	0.90	20.0	0.44	0.88	1.43	531.0	1364
30	5.4	0.79	50.0	0.70	2.04	1.98	6872	1765
40	0.18	-	-	0.63	14.9	2.96	12300	31600
50	3.25	0.65	769	0.61	2.56	1.78	1134	2912

**Fig. 6.8:** Variation of (a)  $n$ , (b)  $\mu$  and (c)  $D$  obtained from equivalent circuit model Approach with different NaI contents for (PVDF-HFP)-NaI

#### **6.2.4 Nyquist Plots of (PVDF-HFP) – NaI- (EC/PC) Electrolytes**

Figure 6.9 (a) to (e) show the Nyquist plots for (PVDF-HFP)-NaI-(EC/PC) polymer electrolyte films having 10 to 50 wt.% (EC/PC) with the fixed wt. ratio of 60 wt.% (PVDF-HFP) - 40 wt.% NaI.  $R_B$  value for 10, 20, 30, 40 and 50 wt.% (EC/PC) concentrations are 12.0  $\Omega$ , 4.1  $\Omega$ , 16.1  $\Omega$ , 17.5  $\Omega$  and 24.7  $\Omega$  respectively.

**Fig. 6.9:** The Nyquist plots of (PVDF-HFP) - NaI polymer electrolyte with (a) 10, (b) 20, (c) 30, (d) 40 and (e) 50 wt.% EC/PC content

### ***6.2.5 Ionic Conductivity of Plasticized (PVDF-HFP) – NaI – (EC/PC) Electrolytes***

Fig. 6.10 shows the room temperature ionic conductivity of (PVDF-HFP) – NaI – EC/PC at various contents of EC/PC plasticizer. After the incorporation of 10 wt.% (EC/PC) into highest conducting composition of 60 wt. % (PVDF-HFP) – 40 wt. % NaI, the



conductivity value has increased from  $5.21 \times 10^{-5} \text{ S cm}^{-1}$  to  $7.77 \times 10^{-5} \text{ S cm}^{-1}$ . Further addition up to 20 wt.% (EC/PC) has increased the conductivity to  $1.53 \times 10^{-4} \text{ S cm}^{-1}$ . The conductivity value decreases after further addition of (> 20 wt.%) (EC/PC) binary plasticizer. These results indicate that, for (PVDF-HFP) – NaI – (EC/PC) electrolytes, the highest conductivity value has been found in the sample with 20 wt.% EC/PC and 80 wt.% of highest conducting (PVDF-HFP)-NaI composition. The composition of this electrolyte is 48 wt.% (PVDF-HFP) - 32 wt.% NaI – 20 wt.% (EC/PC). This composition will be used to fabricate the dye-sensitized solar cell.

**Fig. 6.10:** The room temperature ionic conductivity of (PVDF-HFP) – NaI – (EC/PC) electrolytes containing various wt.% of (EC/PC)

#### **6.2.6 Determination of $n$ , $\mu$ , and $D$ by the Equivalent Circuit Model Approach for (PVDF - HFP) – NaI – (EC/PC) Electrolytes**

The value of  $n$ ,  $\mu$ , and  $D$  for all (PVDF-HFP)-NaI-(EC/PC) samples were determined by the equivalent circuit model approach that has been used for (PVDF-HFP)-NaI samples in the previous sub-section. The fitting obtained for the Nyquist plot is shown by the solid line in Fig. 6.11 (a) to (e) for EC/PC concentration ranging from 10 to 50 wt.% respectively. The  $n$ ,  $\mu$  and  $D$  values obtained from the fitting are tabulated in Table 6.2 and their variations are shown graphically in Fig. 6.12.



**Fig. 6.11:** The fitting obtained for Nyquist plot of electrolytes having (a) 10 (b) 20 (c) 30 (d) 40 and (e) 50 wt.% (EC/PC)

**Table. 6.2:** Summary of  $n$ ,  $\mu$  and  $D$  obtained from the Equivalent Circuit Model and the respective  $R$ ,  $p_2$  and  $k_2^{-1}$  value for (PVDF-HFP)-NaI-(EC/PC)

(EC/PC) (wt.%)	$R(\Omega)$	$p_2$	$k_2^{-1}(F)$ ( $\times 10^{-5}$ )	$n$ ( $\text{cm}^{-3}$ ) ( $\times 10^{22}$ )	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) ( $\times 10^{-8}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ ) ( $\times 10^{-10}$ )
10	11.4	0.57	5.95	2.01	5.21	13.4
20	4.5	0.85	7.44	4.17	9.53	24.5
30	15	0.65	6.10	1.75	2.49	6.41
40	16.5	0.67	11.1	1.56	1.54	3.97
50	24	0.74	9.09	1.01	0.82	2.12

**Fig. 6.12:** Variation of (a)  $n$ , (b)  $\mu$  and (c)  $D$  obtained from equivalent circuit model approach with different (EC/PC) contents in (PVDF-HFP)-NaI-(EC/PC)

### 6.3 Conductivity Studies on KI Based Electrolytes

### 6.3.1 Nyquist Plots of (PVDF-HFP) – KI

Figure 6.13 (a) to (e) shows the Nyquist plots for (PVDF-HFP)-KI polymer electrolyte films with the variation of 5 to 30 wt.% KI.  $R_B$  value for 5, 10, 15, 20, 25 and 30 wt.% KI concentrations are  $2.75 \times 10^6 \Omega$ ,  $1.31 \times 10^3 \Omega$ ,  $337 \times 10^2 \Omega$ ,  $25.7 \Omega$ ,  $75.0 \Omega$  and  $843 \Omega$  respectively. The  $R_B$  for 5 wt.% KI was verified using the complex admittance plot in Fig. 6.13(a'). The admittance data can be obtained from impedance data using equations  $A' = Z' / [(Z')^2 + (Z'')^2]$  and  $A'' = Z'' / [(Z')^2 + (Z'')^2]$ .







**Fig. 6.13:** The Nyquist plots of (PVDF-HFP)-KI polymer electrolyte at (a) 5 (b) 10 (c) 20 (d) 25 and (e) 30 wt. % KI

### ***6.3.2 Ionic Conductivity of (PVDF-HFP) – KI system***

Fig. 6.14 shows that in the (PVDF-HFP) – KI electrolyte system, ionic conductivity increases with the salt content and reaches a maximum value at room temperature of  $1.20 \times 10^{-4} \text{ S cm}^{-1}$  when the salt content is 20 wt.%. The gradual decrease in conductivity at high salt concentrations after 20 wt.% may be due to ion association that had taken place between the dissociated ions.

**Fig. 6.14:** The room temperature ionic conductivity of (PVDF-HFP) – KI at various wt.% of KI

### ***6.3.3 Determination of $n$ , $\mu$ , and $D$ by The Equivalent Circuit Model Approach for (PVDF-HFP)-KI electrolyte***

By using the same method as in section 6.2.4, the value of  $n$ ,  $\mu$ , and  $D$  can be determined.

Fig. 6.15 (a) to (f) show the fitting (in solid line) results for Nyquist plots of (PVDF-HFP) – KI electrolytes at 5, 10, 15, 20, 25 and 30 wt.% KI contents respectively. The calculated values of  $n$ ,  $\mu$  and  $D$  obtained from this method are summarized in Table 6.2.

and the graphs of  $n$ ,  $\mu$  and  $D$  against NaI contents are shown in Fig. 6.16. It can be seen from Fig. 6.15, the mobility ( $\mu$ ), number density ( $n$ ), and diffusion coefficient ( $D$ ) of mobile ions vary with KI content and the variations have the same trend as the variation of the conductivity with NaI concentration shows in Fig. 6.14.





**Fig. 6.15:** The fitting obtained from equivalent circuit for (PVDF-HFP)-KI at different wt.% KI (a) 5, (b) 10, (c) 15, (d) 20, (e) 25 and (f) 30.

**Table. 6.3:** Summary of  $n$ ,  $\mu$  and  $D$  obtained from the Equivalent Circuit Model and the respective  $R_p$ ,  $k_1^{-1}$  and  $k_2^{-1}$  value for (PVDF-HFP)-KI

KI (wt.%)	$R(\Omega)$ ( $\times 10^2$ )	$p_1$	$k_1^{-1}(F)$ ( $\times 10^{-8}$ )	$p_2$	$k_2^{-1}(F)$ ( $\times 10^{-5}$ )	$n$ ( $\text{cm}^{-3}$ ) ( $\times 10^{21}$ )	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) ( $\times 10^{-10}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ ) ( $\times 10^{-12}$ )
5	30000	0.85	0.29	-	-	0.039	1.684	4.326
10	12.60	0.7	2.63	0.57	2.63	0.958	16.47	42.29
15	3.30	0.6	2.87	0.80	0.71	1.045	213.1	547.3
20	0.23	-	-	0.63	10.0	3.748	760.6	1953
25	0.80	0.2	0.0002	0.76	1.54	1.079	460.6	1183
30	8.0	0.9	0.07	0.60	0.65	0.236	86.19	221.4

**Figure 6.16:** The variation of (a)  $n$ , (b)  $\mu$  and (c)  $D$  obtained from Equivalent circuit model approach for (PVDF-HFP)-KI electrolyte with different KI contents.

#### **6.3.4 Nyquist Plots of (PVDF-HFP) - KI-(EC/PC) electrolytes**

Figure 6.17 (a) to (f) show the Nyquist plots for (PVDF-HFP)-KI-(EC/PC) polymer electrolyte films having different plasticizer contents varying from 10 to 60 wt.% (EC/PC).  $R_B$  value for 10, 20, 30, 40, 50 and 60 wt.% (EC/PC) concentrations are 81.5  $\Omega$ , 74.0  $\Omega$ , 71.5  $\Omega$ , 56.0 $\Omega$ , 15.0  $\Omega$  and 51.0  $\Omega$  respectively.





**Fig. 6.17:** The Nyquist plots of (PVDF-HFP)-KI-(EC/PC) polymer electrolyte at (a) 10 (b) 20 (c) 30 (d) 40 (e) 50 and (f) 60 wt.% (EC/PC)

### ***6.3.5 Ionic Conductivity of (EC/PC) Plasticized (PVDF-HFP) – KI system***

Fig. 6.18 exhibits the variation in conductivity with plasticizer content. Addition of 50 wt. % EC/PC as plasticizer enhanced the conductivity of the system to a maximum value of  $1.10 \times 10^{-3} \text{ S cm}^{-1}$  as shown. Higher conductivity of solid polymer electrolyte obtained through the addition of plasticizers may be attributed to plasticization process which lowers the viscosity of the ionic environment and thereby increases the ionic mobility in the system (Bandara et. al, 1998). This highest conducting sample will be used for solar cell fabrication.

**Fig. 6.18:** The room temperature ionic conductivity of (PVDF-HFP)–KI–(EC/PC) at various wt.% of (EC/PC)

### ***6.3.6 Determination of $n$ , $\mu$ , and $D$ by the Equivalent Circuit Model Approach for (PVDF - HFP) – KI – (EC/PC) Electrolytes***

By using the same method as in section 6.2.4, the value of  $n$ ,  $\mu$ , and  $D$  can be determined. Fig. 6.19 (a) to (f) show the fitting (in solid line) results for Nyquist plots of (PVDF-HFP) – KI-(EC/PC) electrolytes having 10, 20, 30, 40, 50 and 60 wt.% (EC/PC) contents respectively. The calculated values of  $n$ ,  $\mu$  and  $D$  obtained from this method are summarized in Table 6.4. and the graphs of  $n$ ,  $\mu$  and  $D$  against NaI contents are shown in Fig. 6.20.





**Fig. 6.19:** The fitting obtained from equivalent circuit for (PVDF-HFP)-KI-(EC/PC) having different wt.% (EC/PC) (a) 10, (b) 20, (c) 30, (d) 40, (e) 50 and (f) 60.

**Table. 6.4:** Summary of  $n$ ,  $\mu$  and  $D$  obtained from the Equivalent Circuit Model and the respective  $R$ ,  $p_2$  and  $k_2^{-1}$  values for (PVDF-HFP)-KI-(EC/PC) electrolytes

(EC/PC) (wt.%)	$R(\Omega)$	$p_2$	$k_2^{-1}(F)$ ( $\times 10^{-5}$ )	$n$ ( $\text{cm}^{-3}$ ) ( $\times 10^{21}$ )	$\mu$ ( $\text{cm}^2 \text{V}^{-1} \text{s}^{-1}$ ) ( $\times 10^{-9}$ )	$D$ ( $\text{cm}^2 \text{s}^{-1}$ ) ( $\times 10^{-10}$ )
10	85	0.77	1.36	2.56	3.21	8.24
20	80	0.77	1.39	6.53	45.7	11.7
30	74	0.77	1.50	15.5	60.4	15.5
40	55	0.65	2.28	45.5	71.3	18.3
50	18	0.80	3.40	54.6	80.0	20.6
60	51	0.63	7.30	20.7	43.0	11.1

**Figure 6.20:** The variation of (a)  $n$ , (b)  $\mu$  and (c)  $D$  obtained from Equivalent circuit Model approach for (PVDF-HFP)-KI-(EC/PC) electrolyte having different (EC/PC) content.

#### 6.4 Summary

The ionic conductivity of unplasticized and plasticized (PVDF-HFP) polymer electrolytes with NaI and KI as doping salts have been presented in this chapter. The incorporation of (EC/PC) plasticizer mixture helps in the enhancement of the conductivity values. The (PVDF-HFP) – NaI plasticized film with 20 wt.% (EC/PC) has the highest conductivity value of  $1.53 \times 10^{-4} \text{ S cm}^{-1}$  at room temperature. For the plasticized (PVDF-HFP) – KI, highest conductivity value is  $1.10 \times 10^{-3} \text{ S cm}^{-1}$  for the electrolyte with 50 wt. % (EC/PC). Parameters that include mobility of the ions ( $\mu$ ), density of charge carriers ( $n$ ) and diffusion coefficient ( $D$ ) obtained from the equivalent circuit model approach describe the conductivity behavior of the electrolytes investigated.