Supplementary File 1 (S1)

A step-by-step guideline to estimate characteristic frequency in impedance using mathematical regression with commercial graphical software

Introduction

This step-by-step practical guideline is for estimation of characteristic frequency in impedance spectra of solid polymer electrolyte (SPE) by employing mathematical regression approach using the commercial graphical software named Origin® software (version Pro 8.1). The characteristic frequencies under discussion are, *i.e.* $f_{\min}^{Z''}$, $f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$. Hence, this guide is divided into three sub-topics for estimation the respective characteristic frequency in impedance spectra using mathematical approach with commercial graphical software:

1. Estimation of characteristic frequency $f_{\min}^{Z''}$
2. Estimation of characteristic frequency $f_{\max}^{Z''}$
3. Estimation of characteristic frequency $f_{\text{cross}}^{Z'-Z''}$

This mathematical approach is one of the approaches, which may be employed for extraction of reproducible data before data interpretation. Besides, it is not limited for impedance, it may be adopted for other electrochemical terms for instance the tangent loss, electric modulus *etc.* It applies to any quantity that exhibits characteristic frequency as in impedance (refer to **Figure S1.1**), where similar procedures can be applied. The mathematical operations, regression as well as presentation the figures were performed by using Origin® software. The step-by-step guidelines for estimation of each characteristic frequency (*i.e.* $f_{\min}^{Z''}$, $f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$) are shown using poly(ethylene oxide) (PEO) added with 2 *wt.*% of lithium perchlorate ($LiClO_4$). The first step, which applies to all quantities, is to import data points of real (Z') and imaginary (Z'') parts of impedance as a function of frequency (f) from other format data file (*i.e.* excel or txt) into the workbook of Origin® software. Afterwards, plot the imported data set by employing the "scatter" function with the values of f in *x*-axis and the values of $Z'$and Z'' in the *y*-axis. Then, convert the plot from linear scales to logarithmic scales (log to the base of 10) for the both axes as shown in **Figure S1.1**. This plot is known as Bode plot, where the frequency is distinctive. This logarithmic plot is very useful to determine and inspect the significant characteristic visually. **Figure S1.1** displays several characteristic frequencies that are significant for data interpretation from impedance spectroscopy. Each characteristic frequency displays in **Figure S1.1** is outlined and further described in the main text of Part 2 of this article.

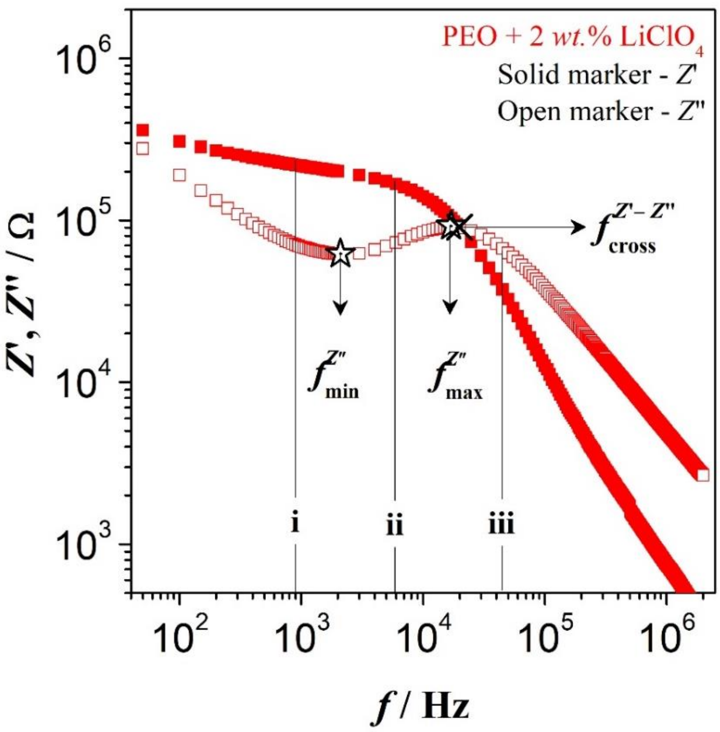

Figure S1.1 Frequency-dependent impedance spectra of PEO added with 2*wt.*% of $LiClO_4$. The star and cross markers represent the respective characteristic frequencies.

Estimation of characteristic frequency $f_{\mathrm{min}}^{Z''}$

1. To estimate $f_{\mathrm{min}}^{Z''}$, re-plot the frequency-dependent Z'' against f by selecting data points lie between region of **i** and **ii** (around 20 – 30 data points) using linear scales, which apply to both axes (see **Figure S1.2**). The values of f in x-axis and the values of Z'' in the y-axis.
2. Next, fit the curve using the polynomial fitting function by fourth order of polynomial function. It is important to note that different of polynomial orders may be applied for curve fitting using polynomial function on condition that the selected data points are well-fitted. The fitting can be done by selecting the command of “polynomial fit” available in the “analysis” toolbar (the polynomial order can be amended in the “polynomial fit” dialog window as demonstrated in **Figure S1.2**).

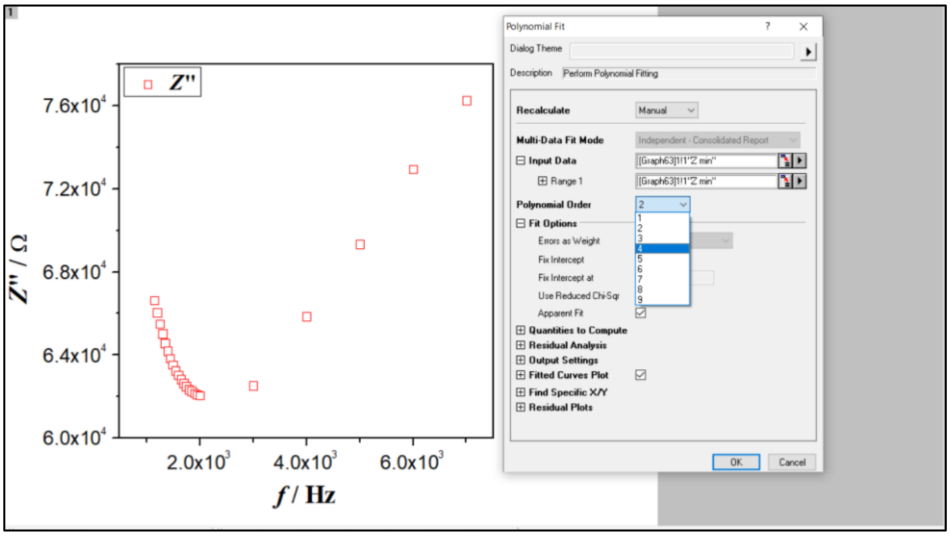

Figure S1.2 Plot of Z'' against f for PEO added with 2 *wt.*% of $LiClO_4$ with curve fitting using Origin software

3. The result of the polynomial fitting is normally tabulated as presented in **Figure S1.3**. The table include the equation of the polynomial function, the square of correlation coefficient (r^2), the y-intercept and the coefficients of variable x displayed at different powers depending on the degree order of the polynomial function. A good curve fitting between the selected data points and the order of the polynomial function can be reflected in the r^2, where the value should be positioned in the range of 0.970 – 0.999.

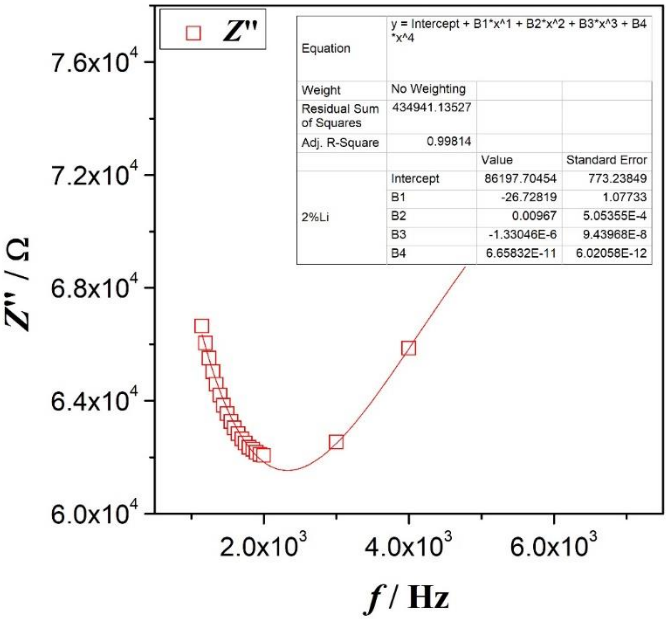

Figure S1.3 Curve fitting with results for plot of Z'' against f using fourth order polynomial fit function for PEO added with 2 *wt.*% of $LiClO_4$

4. Then, the estimation of $f_{\mathrm{min}}^{Z''}$ can be performed by extracting the equation of the fourth order polynomial equation obtained from the table in **Figure S1.3**. The equation is listed in **Equations (S1.1)** below:

$$Z'' = 86197.7 - 26.73f + 0.0097f^2 - 1.33\times10^{-6}f^3 + 6.66\times10^{-11}f^4 \quad \textbf{(S1.1)}$$

The maximal of Z'' can be obtained by differentiating the **Equation (S1.1)** into

$$\frac{\mathrm{d}(Z'')}{\mathrm{d}f} = -26.7 + 0.0193f - 3.99\times10^{-6}f^2 + 2.66\times10^{-10}f^3 \quad (\mathbf{S1.2})$$

where the **Equation (S1.2)** shall be equalled to zero $\left[\frac{d(Z'')}{df} = 0\right]$. The cubic equation of **Equation (S1.2)** can be solved using Origin® software for extraction of $f_{\mathrm{min}}^{Z''}$value. It can be done by adding the new graph sheet and click “Add graph function” at the “Graph” toolbar section to insert the cubic equation in a computer language [refer to **Equation (S1.3)**] in the “Plot Details” window as shown in **Figure S1.4**.

–26.7 + (0.0193**x*) – (3.99*e*-6**x*^2) + (2.66*e*-10**x*^3) **(S1.3)**

Lastly, click “OK” to display the curve of the written **Equation (S1.3)** in the dialog window of Origin®.

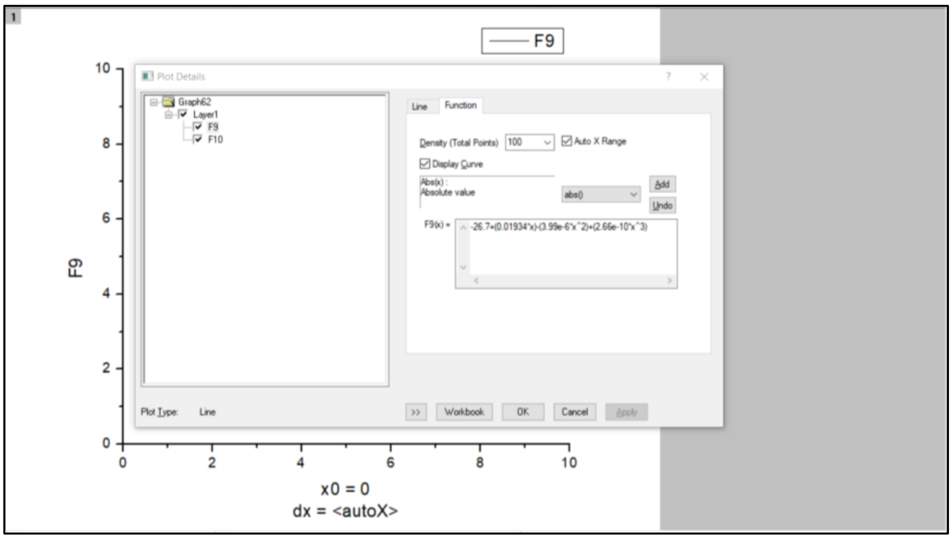

Figure S1.4 Insertion of the **Equation (S1.3)** in the new graph using the add graph function in the Origin software

5. One horizontal curve parallel to the *x*-axis will be displayed upon the insertion of the cubic equation into the dialog window as illustrated in **Figure S1.5**. The value of $f_{\mathrm{min}}^{Z''}$ can be determined by re-scaling the *x*- and *y*-axes in a way that the horizontal line forming into a upwards curve that will intersects with the *x*-axis at *y* = 0 (refer to **Figure S1.6**). The plot can be enlarged nearly at the intersection point $f_{\mathrm{min}}^{Z''}$ at *y* = 0 in order to elucidate the $f_{\mathrm{min}}^{Z''}$ value correctly. Note: Please ensure the *x*- and *y*-axes of the plot start

from zero in order to extract $f^{Z''}_{\min}$ at $y = 0$ correctly. As displayed in **Figure S1.6**, the $f^{Z''}_{\min}$ = 2295 Hz (or s^{-1}).

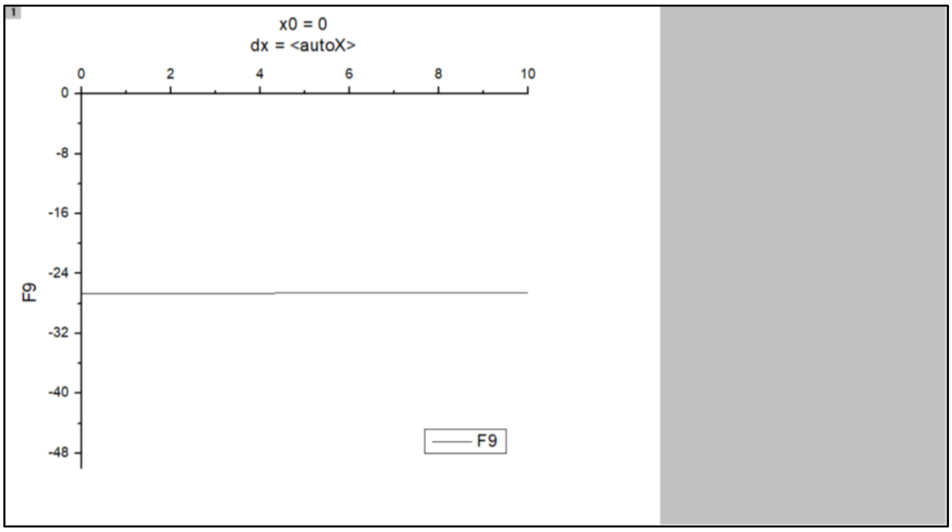

Figure S1.5 The appearance of horizontal line after insertion of **Equation (S1.3)** in the new graph

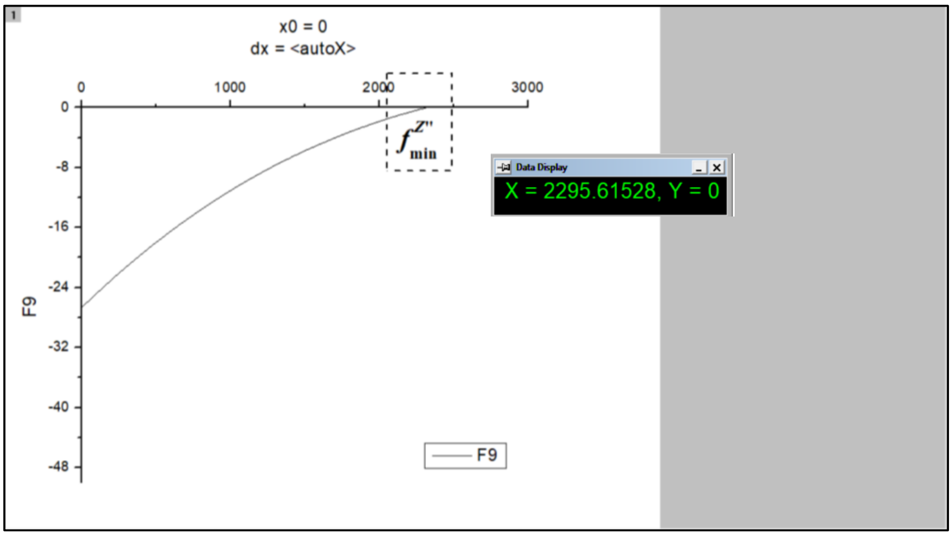

Figure S1.6 Scales adjustment for the two axes in order to locate the $f^{Z''}_{\min}$

Estimation of characteristic frequency $f^{Z''}_{\max}$

1. To estimate $f^{Z''}_{\max}$, re-plot the frequency-dependent Z'' against f by selecting data points lie between region of **ii** and **iii** (around 20 – 30 data points) using linear scales, which apply to both axes (see **Figure S1.7**). The values of f in x-axis and the values of Z'' in the y-axis.

2. Similarly, repeat the same steps, that were applied to $f^{Z''}_{\mathrm{min}}$, from step number 2 until number 5 in order to retrieve the value of $f^{Z''}_{\mathrm{max}}$.

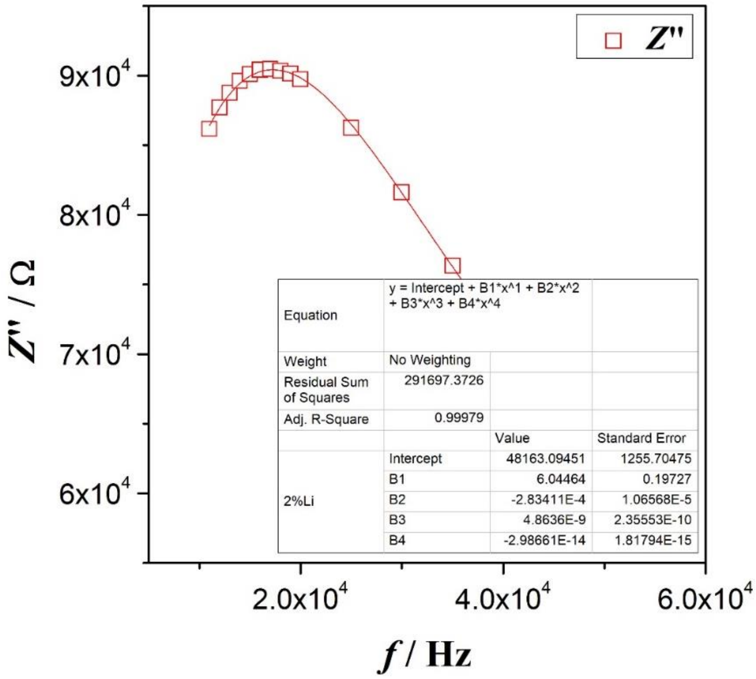

Figure S1.7 Curve fitting with results for plot of Z'' against f using fourth order polynomial fit function for PEO added with 2 *wt.*% of $LiClO_4$

3. The equation obtained from the fourth order of the polynomial fitting for Z'' at region **ii** to **iii**, is listed in **Equations (S1.4)** below:

$$Z'' = 48163 + 6.05f - 2.83\times10^{-4}f^2 + 4.86\times10^{-9}f^3 - 2.98\times10^{-14}f^4 \quad \textbf{(S1.4)}$$

The maximal of Z'' can be obtained by differentiating the **Equation (S1.4)** into

$$\frac{\mathrm{d}(Z'')}{\mathrm{d}f} = 6.05 - 5.66\times10^{-4}f + 1.46\times10^{-8}f^2 - 1.19\times10^{-13}f^3 \quad \textbf{(S1.5)}$$

where the **Equation (S1.5)** shall be equalled to zero $\left[\frac{d(Z'')}{df} = 0\right]$. The cubic equation of **Equation (S1.5)** can be solved using Origin® software for extraction of $f^{Z''}_{\mathrm{max}}$value. It can be done by adding the new graph sheet and click "Add graph function" at the "Graph" toolbar section to insert the cubic equation in a computer language [refer to **Equation (S1.6)**] in the "Plot Details" window as shown in **Figure S1.8**.

6.05 – (5.66*e*-4**x*) + (1.46*e*-8**x*^2) – (1.19*e*-13**x*^3) **(S1.6)**

Lastly, click "OK" to display the curve of the written **Equation (S1.6)** in the dialog window of Origin®.

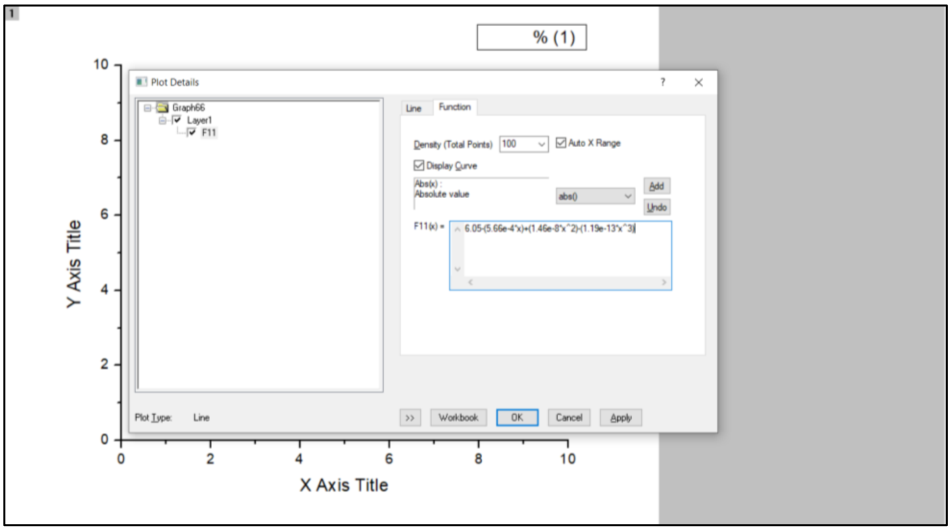

Figure S1.8 Insertion of the **Equation (S1.6)** in the new graph using the add graph function in the Origin software

4. Both x- and y-axes of the horizontal plot can be rescaled until the intersection point of x-axis at y = 0 appears. The $f_{\text{max}}^{Z''}$ is identified exactly at x-axis with y = 0. As shown in **Figure S1.9**, the $f_{\text{max}}^{Z''}$ = 17256 Hz (or s^{-1}).

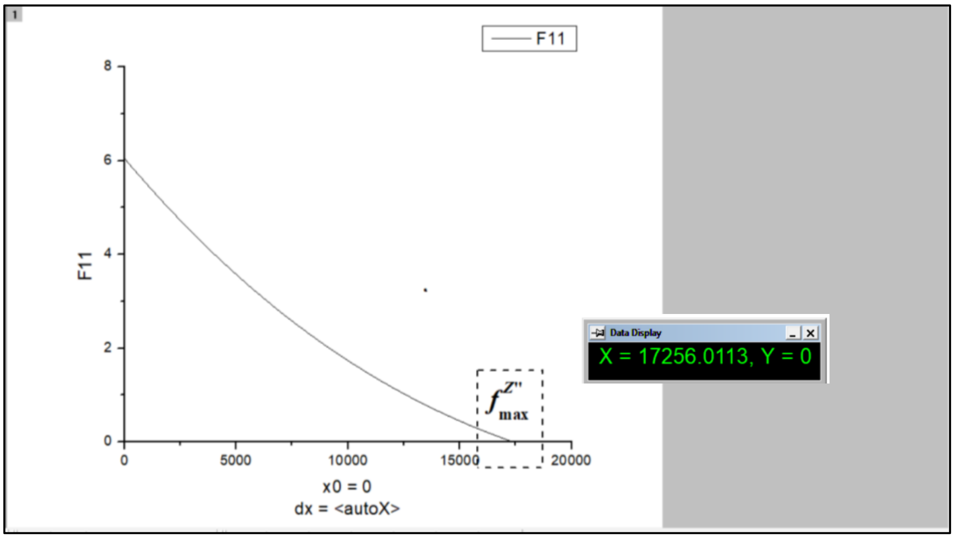

Figure S1.9 Scales adjustment for the two axes in order to locate the $f_{\text{max}}^{Z''}$

Estimation of characteristic frequency $f_{\text{cross}}^{Z'-Z''}$

1. To estimate $f_{\text{cross}}^{Z'-Z''}$, firstly, is to determine and select the data points that can have a linear curve which normally falls closely to $f_{\text{max}}^{Z''}$ and lie in region of **ii** and **iii** (around 5 – 10 data points). Then, re-plot the selected data points with frequency-dependent Z' and Z'' against f using linear scales, that apply to both axes (see **Figure S1.10**). The values of f in x-axis and the values of $Z'$and Z'' in the y-axis.
2. After plotting the graph, fit the selected data points for both quantities Z' and Z'' as a function of f with linear fit function in order to determine the intersection that points

towards $f_{\mathrm{cross}}^{Z'-Z''}$. The linear fitting can be done by selecting the command of "linear fit" available in the "analysis" toolbar (as demonstrated in **Figure S1.10**).

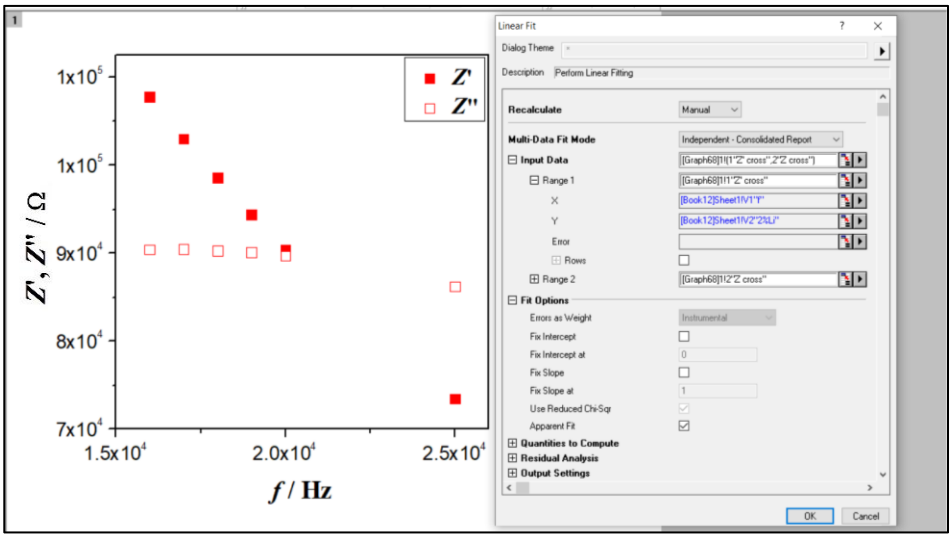

Figure S1.10 Plot of Z', Z'' against f for PEO added with 2 *wt.*% of $LiClO_4$ with linear fitting using Origin software

3. The results of the linear fitting for Z' and Z'' are tabulated as presented in **Figure S1.11**. The tables include the equation of the linear function, the square of correlation coefficient (r^2), the y-intercept and the coefficients of variable x. A good curve fitting between the selected data points and the linear function can be reflected in the r^2, where the value should be lying in the range of 0.970 – 0.999.

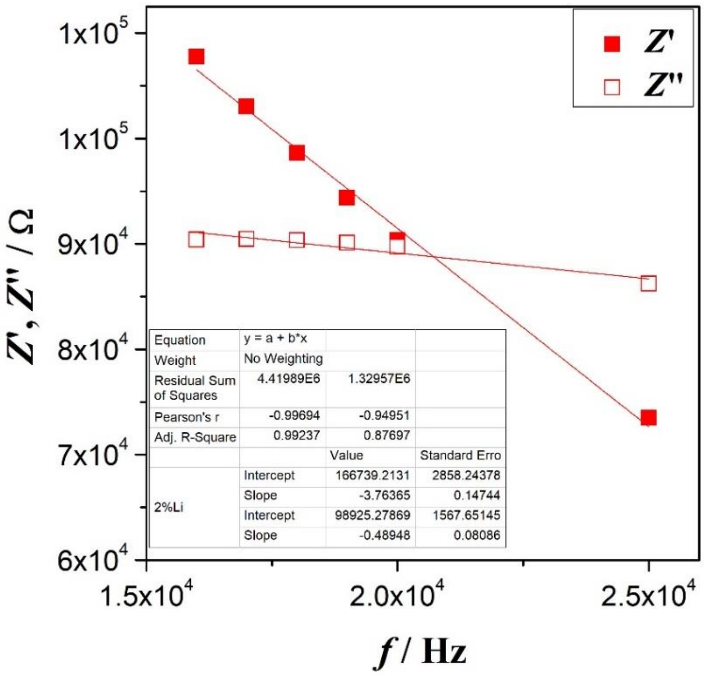

Figure S1.11 Linear regression results for plot of Z', Z'' against f using linear fit function for PEO added with 2 *wt.*% of $LiClO_4$

4. The linear regression of Z' and Z'' against f are listed as follow:

$$Z': y1 = 166739.2 - 3.76f \quad \textbf{(S1.7)}$$

$$Z'': y2 = 98925.3 - 0.49f \quad \textbf{(S1.8)}$$

5. In order to extract the value of $f_{\mathrm{cross}}^{Z'-Z''}$, one need to solve the linear equations of $y1$ and $y2$ by equating to each other. We note here, the f in the linear equation for both $y1$ and $y2$ is $f_{\mathrm{cross}}^{Z'-Z''}$, only when both linear equations are equalled to each other. To find the frequency of the cross of Z' and Z'', are noted as below:

$$y1 = y2$$

$$166739.2 - 3.76f = 98925.3 - 0.49f$$

$$-3.76f + 0.49f = 98925.3 - 166739.2$$

$$-3.27f = -67813.9$$

$$\underline{f = 20738.2}$$

We note here, the $f_{\mathrm{cross}}^{Z'-Z''}$ = 20738.2 Hz (or s^{-1}) at $y1$ (Z') = $y2$ (Z'').