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Basics of Teaching **Electrochemical Impedance Spectroscopy** of Electrolytes for Ion-rechargeable Batteries

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Outline

1. **Background**
   - Electrolytes and batteries
   - Basics – Electrolytes
   - Basics – Electrochemical impedance spectroscopy (EIS)
2. **Estimation of bulk resistance (R_b) from Nyquist plot**
   - 2-component (polymer + salt) systems
3. **Basics – Electrochemical terms**
4. **Impedance spectra**
   - 2-component (polymer + salt) systems
   - 2-component – electrolyte and non-electrolyte
5. **Conclusion**

Outline – Part 1: Estimation of Bulk Resistance of Solid Polymer Electrolytes

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   - ❑ Electrolytes and batteries
   - ❑ Basics – Electrolytes
   - ❑ Basics – Electrochemical impedance spectroscopy (EIS)
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5. **Conclusion**

Electrolytes and Batteries

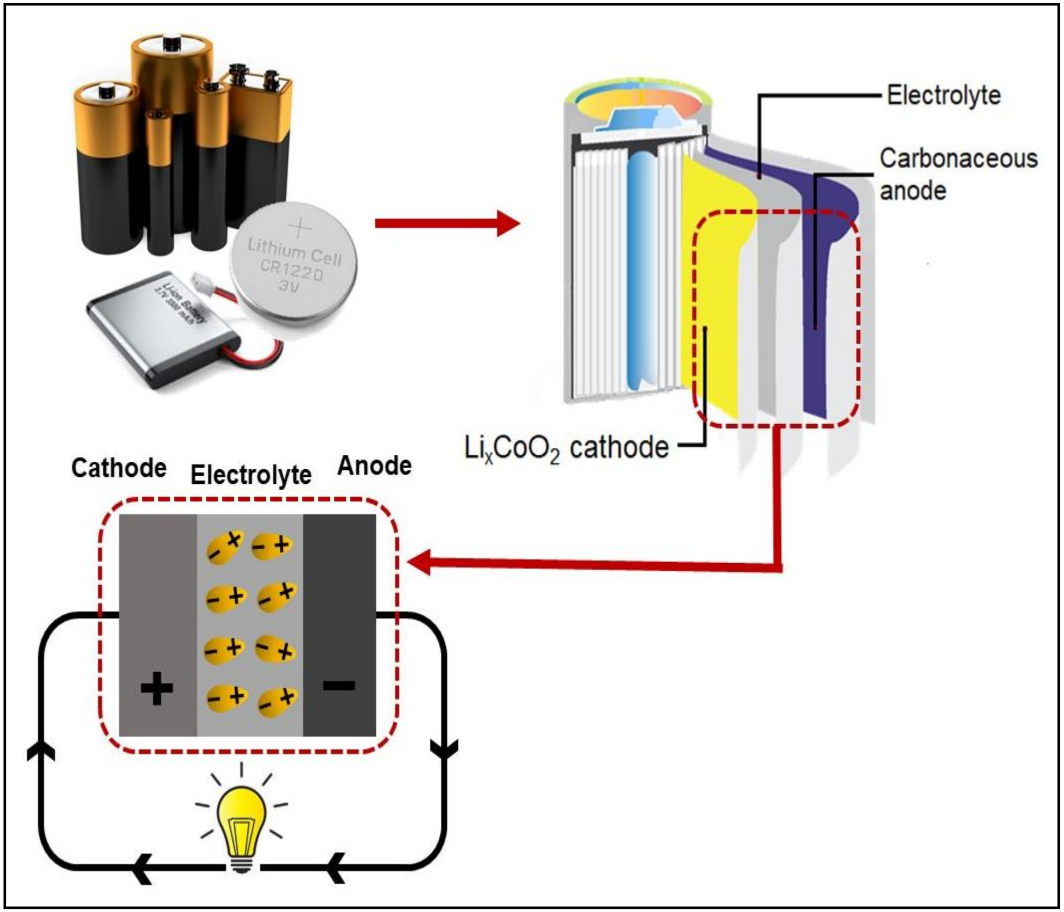


Figure 1.1 Illustration of basic configuration of a lithium ion (rechargeable) battery (Li-ion battery) in the discharged form

Basic concept of Lithium ion (rechargeable) batteries:

- All batteries are composed of two electrodes connected by an ionically conductive material called an electrolyte.
- Electrolyte is a medium that allows flow of charge entities (electrons) from one electrode to another electrode.
- Electrons flow through the circuit as a result of the spontaneous redox reaction at the respective electrodes (in the discharged form).
- Under an action of external electric potential, reverse redox reaction occur (in the charged state).

Solid Polymer Electrolyte (SPE)

(Solvent free polymer-salt complex)

- ☐ A thin film consisting of ionic salts dissolve in appropriate polymer which allows ionic conduction.
- ☐ SPE is considered as a highly potential material for the next generation high-energy rechargeable batteries.
- ☐ SPE is a dielectric material – it is capable to store electrical charges and be polarized when it is imposed under electric field.
- ☐ Effort for improvement of polymer-salt solutions pointed preferably towards two closely related directions, enhancement of:
  1. both carrier density and
  2. mobility.

Electrolytes and Batteries

The in-future revolution of flexible and powerful SPE in (rechargeable) batteries for soft electronics

Figure 1.2 Several prototypes of flexible or soft electronics

Basics – Electrolytes

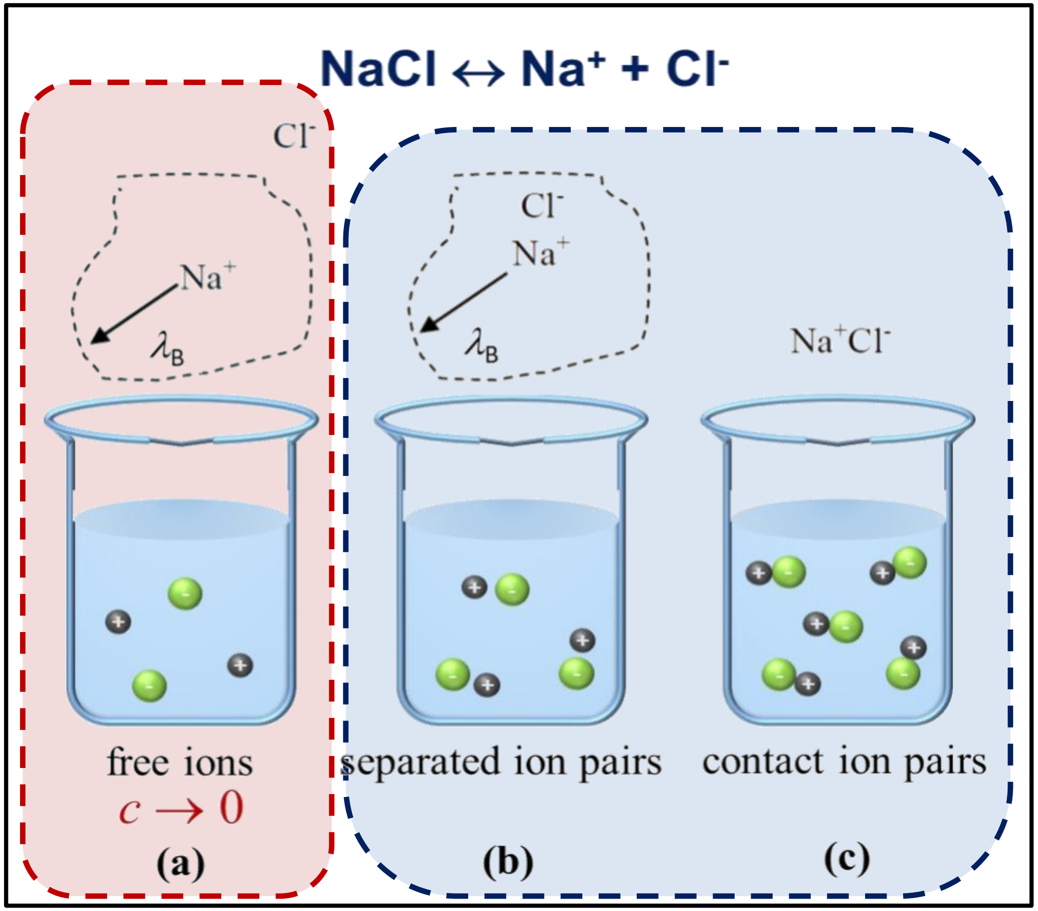


Figure 1.3 Possible ion configurations using aqueous sodium chloride solution (NaCl) (Fuoss, 1965).

Strong electrolyte – ionic compounds dissociate into free ions in the matrix completely

Weak electrolyte – small amount of ionic compounds dissociate into free ions in the matrix (separated or contact ion pairs)

Degree of ion dissociation depends on:

- ✓ Electrostatic interaction (λ_B)
- ✓ Electrolyte concentration (c)

A medium with higher dielectric constant will have shorter λ_B and have significant volume of free ions.

Basics – Electrochemical impedance spectroscopy (EIS)

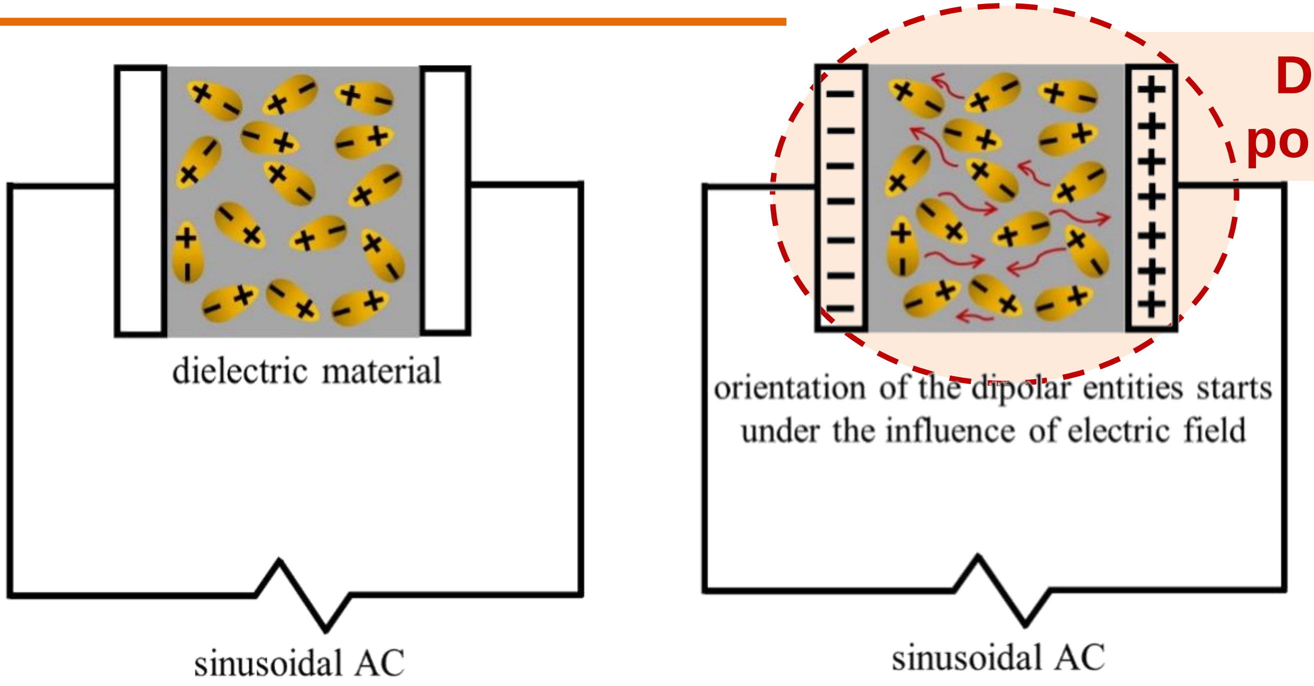
Impedance spectroscopy (IS):

- ❑ A technique involving oscillating (AC) electric signals to study conductivity of ionic conductors (solid or liquid), mixed conductors having electronic & ionic conductivity, electrode-electrolyte interfacial effects and related phenomena (*e.g.* dielectric behavior of materials *etc*).

- ❑ IS is also known as
  - AC Impedance Spectroscopy
  - Complex Impedance Spectroscopy
  - **Electrochemical Impedance Spectroscopy (EIS) (when applied to electrochemical systems)**

- ❑ For polymer electrolytes, conductance originates from IS, the sample forms usually a parallel plate capacitor.

Basics – Electrochemical impedance spectroscopy (EIS)

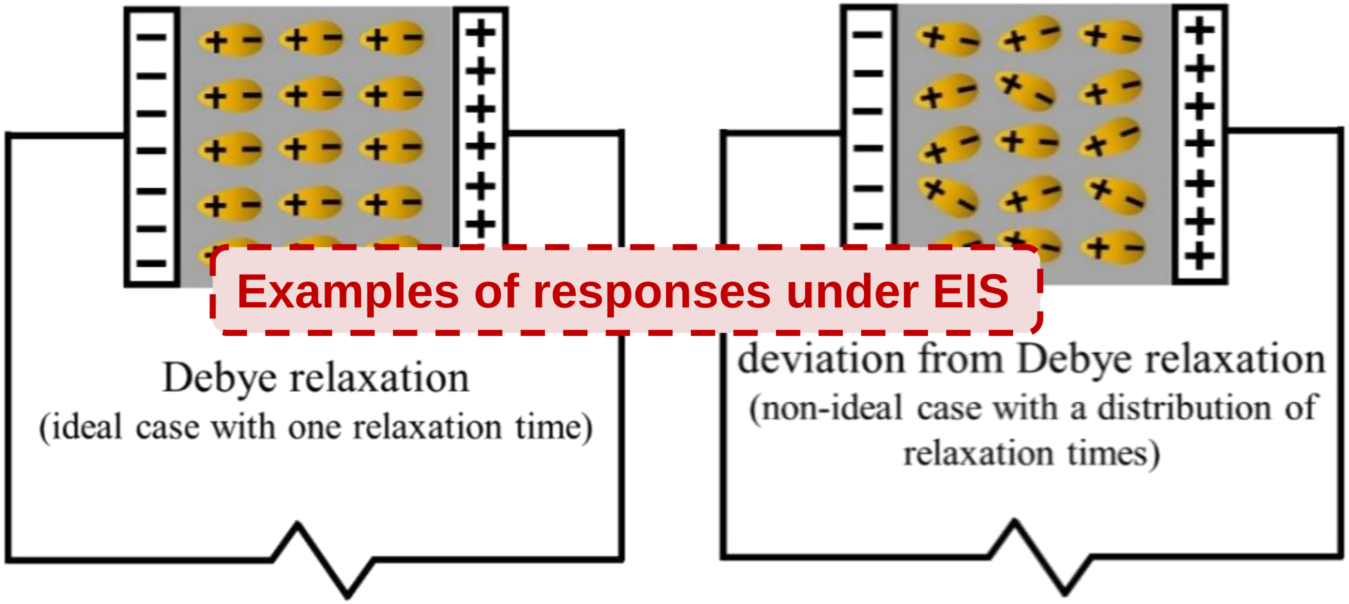


Dielectric polarization

Figure 1.4 Orientation of dipolar entities of dielectric material in between the blocking electrodes

- ❑ **Impedance measurement** or the response of a SPE using EIS is estimated by applying a low amplitude sinusoidal potential (AC voltage) over a range of frequencies to the sample.
- ❑ EIS measures the time response or the dielectric relaxation time of a dielectric.
- ❑ **Dielectric polarization** arises from a finite displacement of dipoles in a steady and flowing electric field.
- ❑ The **randomly oriented dipolar entities will start to align** towards the direction of the oppositely charged electrodes.

Basics – Electrochemical impedance spectroscopy (EIS)



Examples of responses under EIS

Figure 1.5 Orientation of dipolar entities of dielectric material in between the blocking electrodes

- **Dielectric relaxation** can be seen as the alignment of dipolar entities facing the oppositely charged electrodes at a certain frequency.
- **Ideally**, if a SPE has one dielectric relaxation time constant the system is known to follow Debye relaxation.
- However, most of the systems show **deviation from ideal Debye relaxation**, due to heterogeneity of the systems, which leads to the distribution of dielectric relaxation times.

Characteristics of the polymer electrolytes

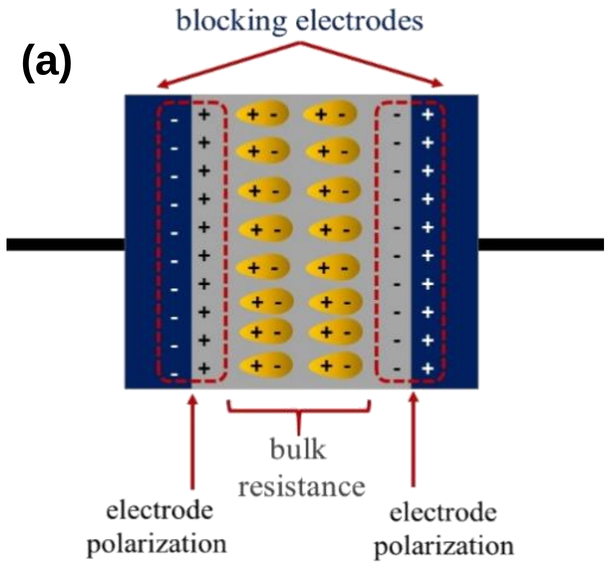
	Poly(ethylene oxide)	Poly(methyl acrylate)
Characteristics	**PEO**	**PMA**
M_w / kg mol^{-1}	300	40
T_g / °C	-53	13
T_m / °C	65	-
Salt content W_S	0.005 – 0.11	

2-component (polymer + salt) systems

(1) PEO + salt

(2) PMA + salt

Estimation of R_b from Nyquist plot



Dielectric modeled by conducting domains embedded in an insulating matrix

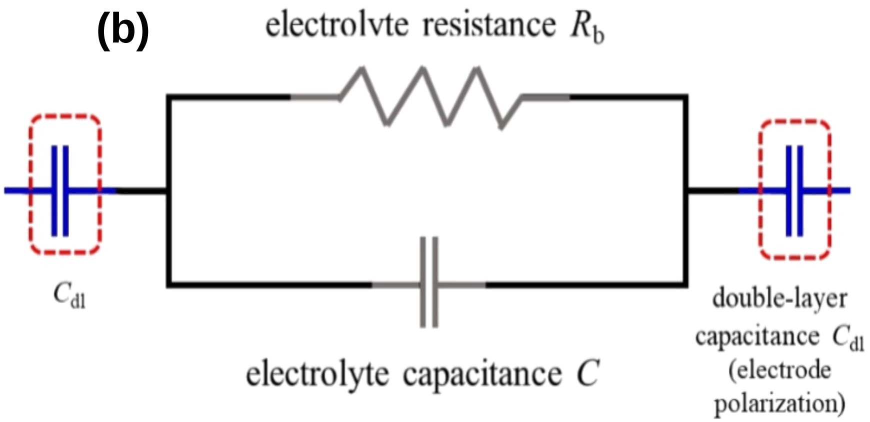
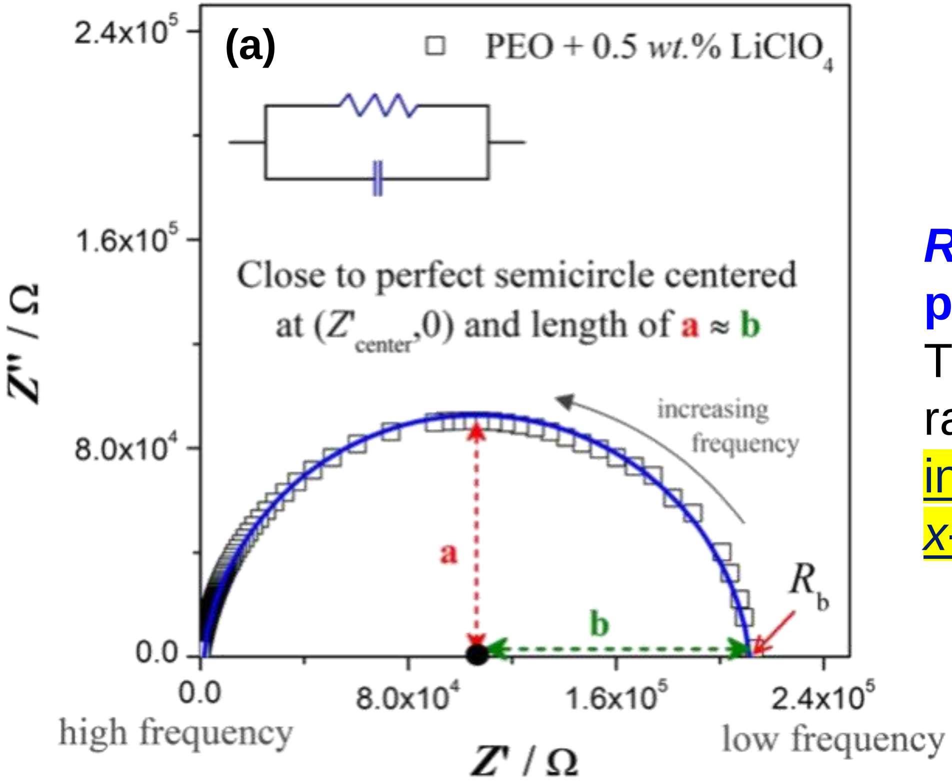


Figure 1.6 (a) Schematic drawing of SPE in between two blocking electrodes following Debye response. (b) Equivalent circuit (model) of SPE in between two blocking electrodes (Randles, 1947)

Estimation of R_b from Nyquist plot

Note: Kindly refer to supplementary files of Part 1 for step-by-step guides to estimate R_b

Frequency is hidden in Nyquist plot!



R_b of Nyquist plot with a close to perfect semicircle:

The $\underline{R_b}$ of the SPE can be estimated rather straight forward by finding the intersection point of the semicircle and *x*-axis at low frequency region.

Figure 1.7 (a) Example of a close to perfect semicircle that following Debye response; The solid blue curve is the semicircle fitting of the impedance data estimated from **Equation (1.1)**

$$(Z')^2 + (Z'')^2 = \left(\frac{R}{2}\right)^2 \quad \textbf{(1.1)}$$

Estimation of R_b from Nyquist plot

Note: Kindly refer to supplementary files of Part 1 for step-by-step guides to estimate R_b

R_b of Nyquist plot with a depressed semicircle:

The R_b of the SPE should be estimated from the intersection point of the corrected centered semicircle at Z' axis.

Important: The center of the depressed semicircle should lies somewhere below $Z'' = 0$. If not, it will point to imprecise R_b' and eventually to imprecise ionic conductivity σ_{DC}'.

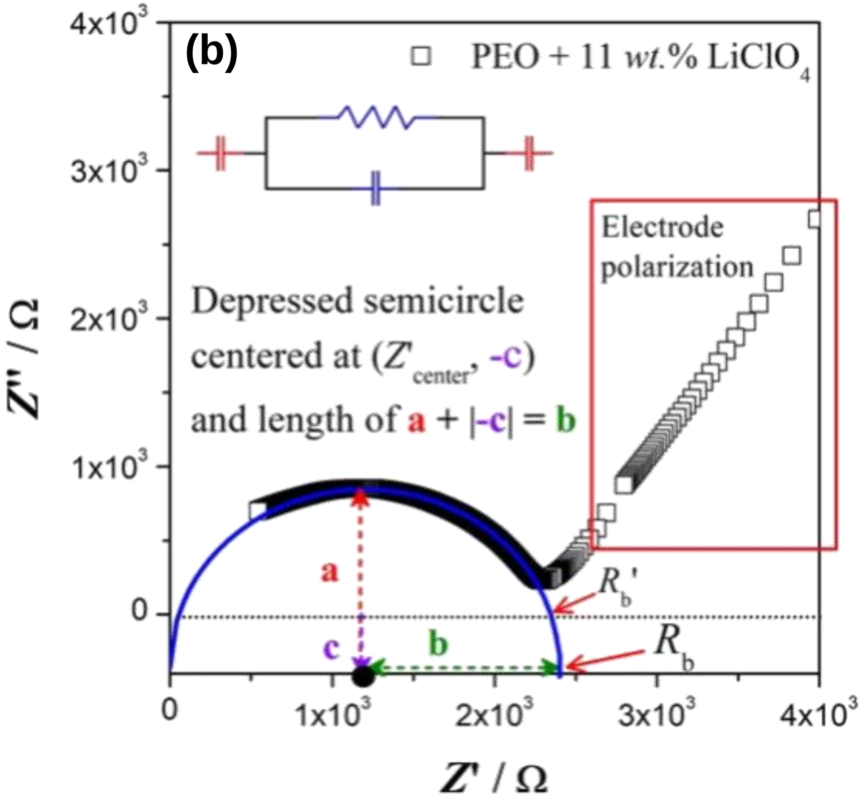


Figure 1.7 (b) Example of a depressed semicircle that deviates from Debye response; The solid blue curve is the semicircle fitting of the impedance data estimated from **Equation (1.1)**

$$(Z')^2 + (Z'')^2 = \left(\frac{R}{2}\right)^2 \quad \textbf{(1.1)}$$

Estimation of R_b from Nyquist plot

$x\ (R_b) < x\ (R_b')$

R_b' will lead to imprecise data interpretation

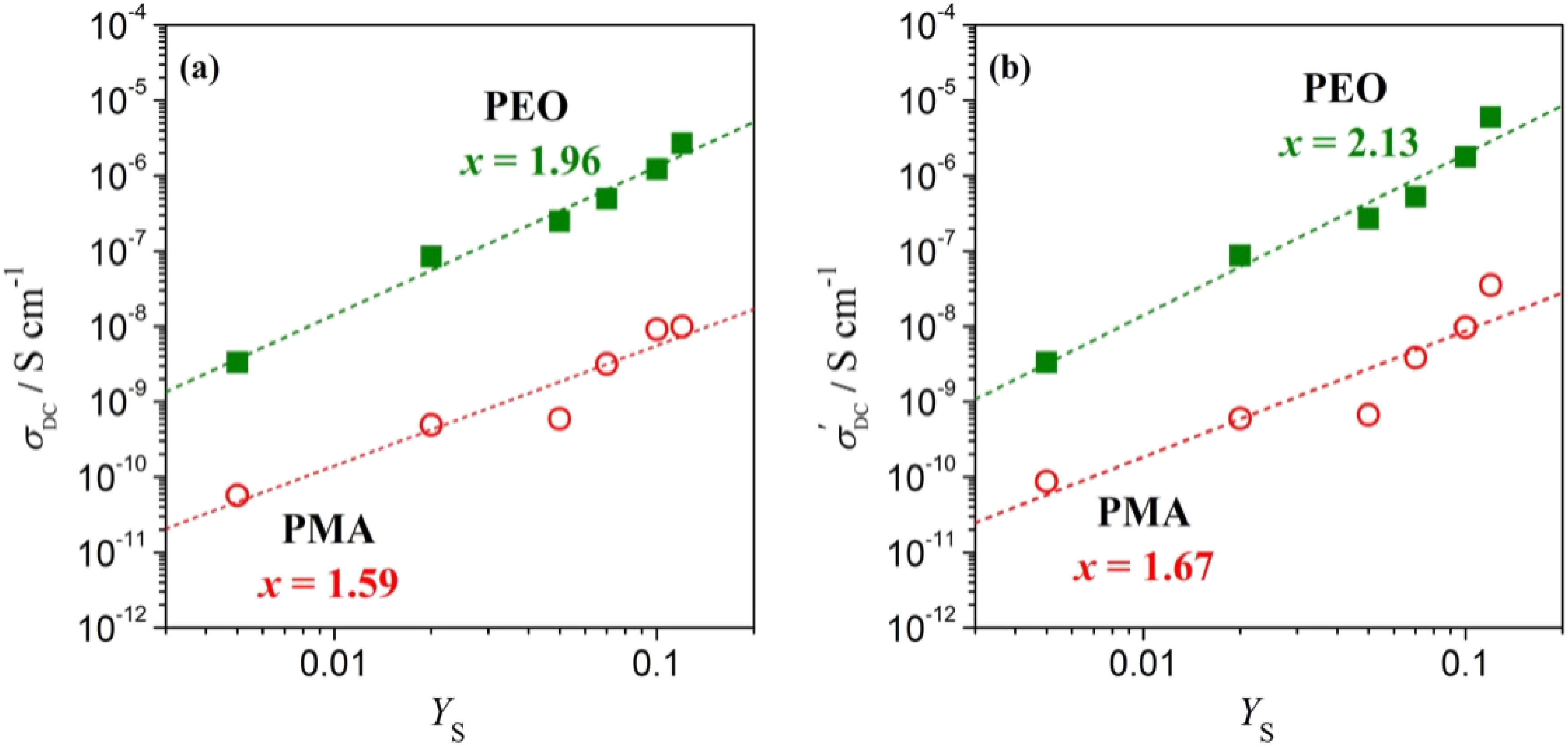


Figure 1.8 (a) σ_{DC} values estimated from R_b values and (b) imprecise σ_{DC}' values estimated from R_b' values for (■) PEO-salt and (○) PMA-salt systems. The dotted line – linear regressions after **Equation (1.3)**.

$\sigma_{DC} = L/(A\cdot R_b)$, where L and A denote the thickness and surface area of the sample **(1.2)**

$\sigma_{DC} = \sigma_o Y_S^x$, where Y_S = mass of salt/mass of polymer **(1.3)**

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Basics – Electrochemical terms

For periodic changes in electric field, electrochemical AC data are as follows:

In impedance spectroscopy, the sample forms usually a parallel plate capacitor with area *A* and thickness ϑ.

$$\text{Impedance } Z^* = Z' + iZ'' = \frac{1}{i\omega C_o \varepsilon^*}$$

$$\text{Permittivity } \varepsilon^* = \varepsilon' - i\varepsilon'' \qquad \textbf{(2.1)}$$

$$\text{Electric modulus } M^* = M' + iM'' = \frac{1}{\varepsilon^*}$$

$$M' = C_o\omega Z'' \qquad M'' = C_o\omega Z'$$

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z'}{Z''}$$

where, *X*' and *X*" denote real and imaginary parts of quantities *X*, *ω* and *f* represent angular frequency and frequency, respectively ($\omega = 2\pi f$).

Basics – Electrochemical terms

All of the quantities in Eq. (2.1) are closely related to complex conductivity:

$$\sigma^* = i\omega\varepsilon_o\varepsilon^* \qquad M^* = i\omega C_o Z^*$$

$$\sigma' = \frac{\vartheta}{A}\frac{Z'}{|Z|^2}$$

$$\sigma'' = \frac{\vartheta}{A}\frac{Z''}{|Z|^2}$$

(2.2)

$$\sigma_{DC} \propto \varepsilon''\omega$$

Basics – Electrochemical terms

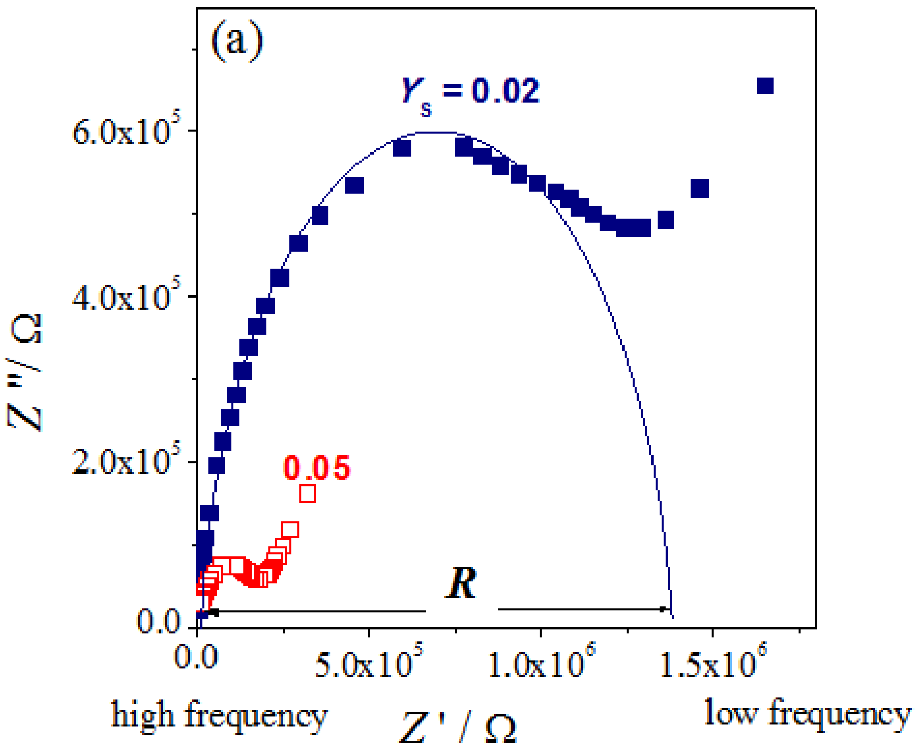
Interpretation of the quantities

- Z' represents Ohmic resistance
- Z'' can be seen as non-Ohmic resistance (*e.g.* capacity resistance as the consequence of sample acts as capacitor in EIS). It displays characteristic frequencies especially for dipole (or dielectric) relaxation resulting from local motions of charged entities
- ε' gives the stored energy (dielectric constant) and ε'' gives the dissipated energy for conductivity (dielectric loss)
- M'' (due to its proportionality to Z') gives "electric" relaxation of flowing charged entities (dipoles) that is it is coined by non-local motion. Resonance occurs when externally imposed frequency agrees with dipole relaxation frequency.
- σ' is coined by flow of charges (dissipation of charges)
- σ'' reflects storage of charges

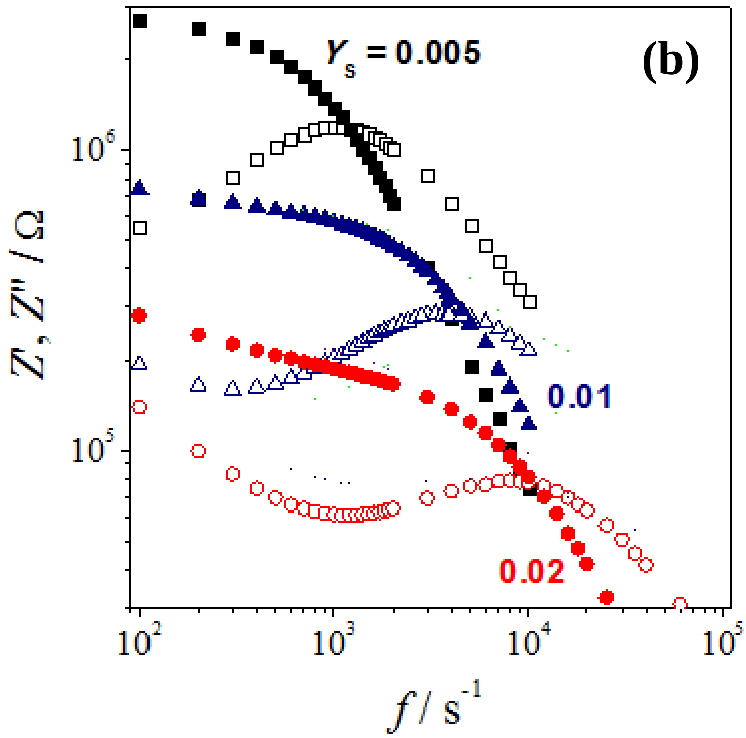
Bode plots shows frequency information explicitly

$$Y_S = \frac{\text{mass of salt}}{\text{mass of PEO}}$$

PEO + LiClO$_4$



Nyquist plot



Bode plot:

Impedance *versus* frequency

Z′ - solid markers

Z″ - open markers

Frequency-dependant impedance spectra are the **key quantities** of the interest for determination of electric properties of materials and their interfaces with conducting electrodes.

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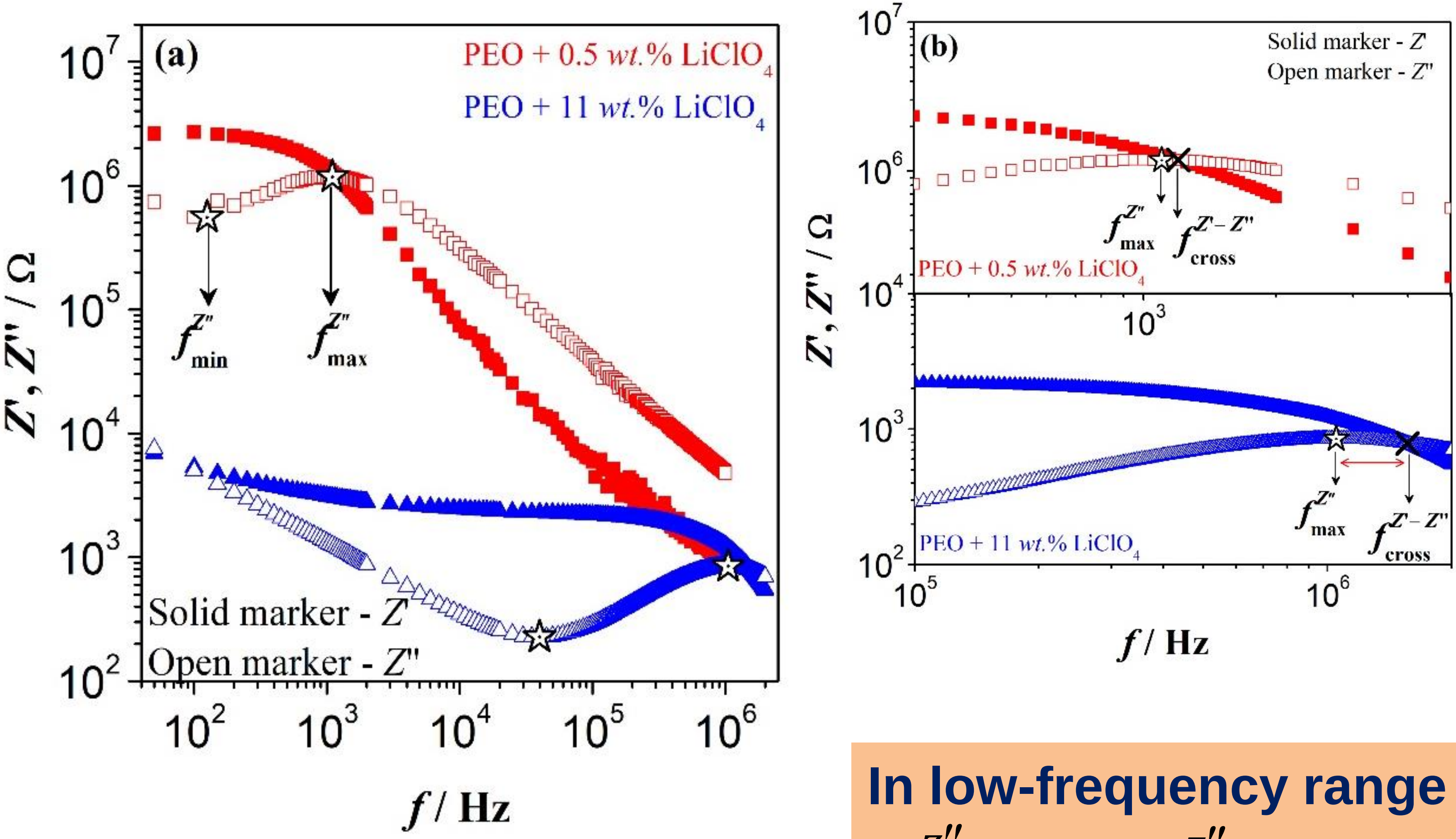

Figure 2.1 Frequency-dependent impedance spectra of (a) PEO-LiClO$_4$ and (b) zoom-in of PEO-LiClO$_4$,

In low-frequency range

$(f_{\min}^{Z''} < f < f_{\max}^{Z''})$:

- $Z' \approx const$
- $Z'' < Z'$
- $f_{\min}^{Z''} < f_{\max}^{Z''} < f_{\mathrm{cross}}^{Z'-Z''}$

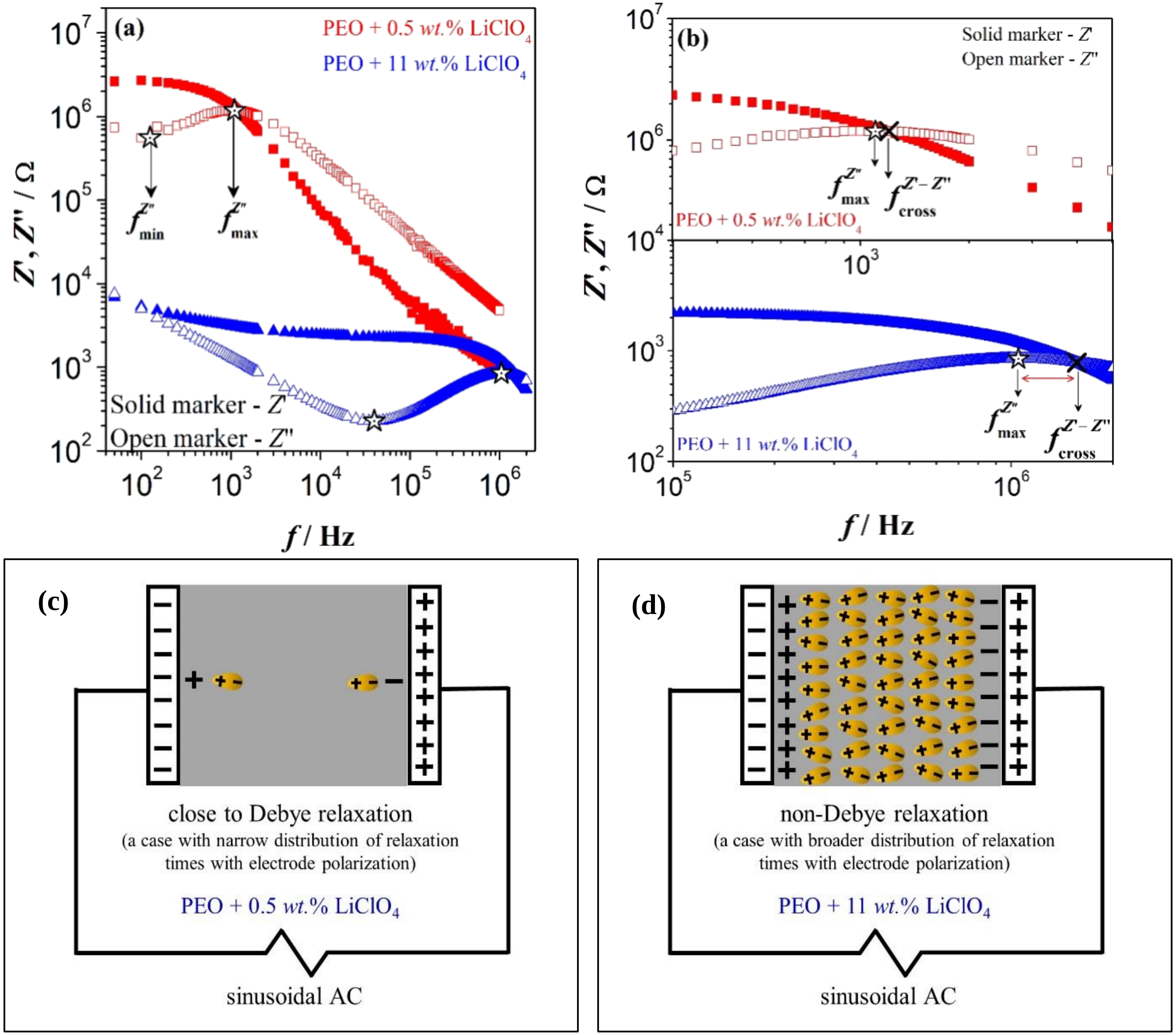

Figure 2.1 Frequency-dependent impedance spectra of (a) PEO-LiClO$_4$, (b) zoom-in of PEO-LiClO$_4$, and schematic illustration of dipolar entities orientation of the respective systems, where (c) close to Debye response and (d) deviation from Debye response under the experimental condition.

Interpretation:

- Increase in $f_{\min}^{Z''}$ and $f_{\max}^{Z''}$ with added salt content (at *T* = *const.*)
- The systems possess one intersection point of *Z′* and *Z″* spectrum at frequency region noted as $f_{\text{cross}}^{Z'-Z''}$. The distance of $f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$ is seen to broaden with elevating salt content.
- The **maximal resonance for *Z″* describes Debye relaxation** (*i.e.* under ideal conditions where no interactions between dipoles, only one relaxation time τ and $f_{\max}^{Z''}$ = $f_{\text{cross}}^{Z'-Z''}$). It results from reorientation of dipoles. **Interaction between dipoles leads to dispersion of relaxation times** which is indicated by $f_{\max}^{Z''} < f_{\text{cross}}^{Z''}$.
- The **minimum at $f_{\min}^{Z''}$** normally reflects to the accumulation of dipoles at the electrode-electrolyte interface (**electrode polarization or double-layer capacitance**). This phenomenon will normally result in distribution of relaxation times in the SPE.
- The three characteristic frequencies individually *i.e.* $f_{\min}^{Z''}, f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$ increase to higher frequency range, alongside with distancing of $f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$ are noted with increasing of salt content.

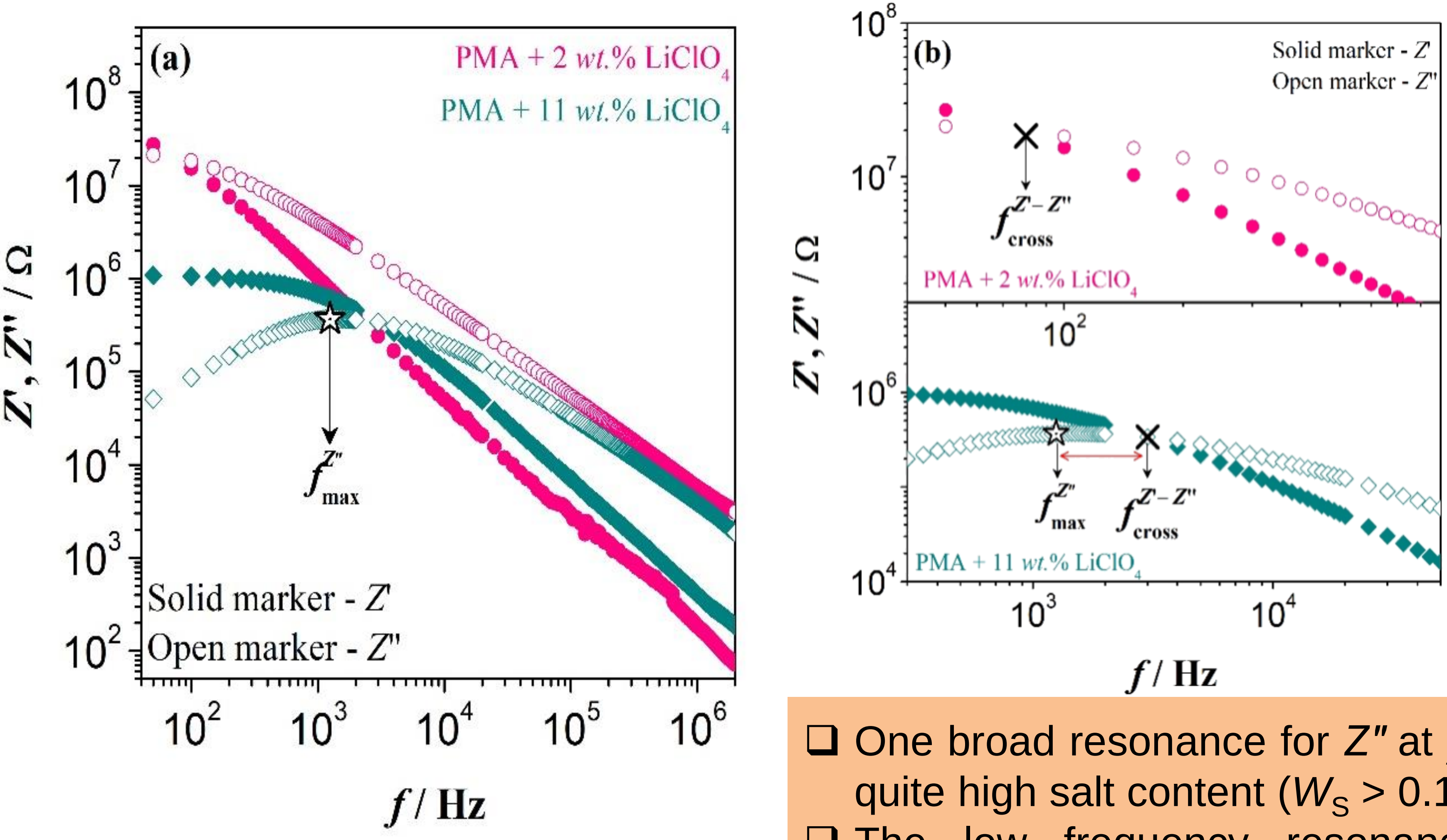

Figure 2.2 Frequency-dependent impedance spectra of (a) PMA-$LiClO_4$ and (b) zoom-in of PMA-$LiClO_4$,

- ☐ One broad resonance for Z'' at $f^{Z''}_{\text{max}}$ at quite high salt content ($W_S > 0.11$).
- ☐ The low frequency resonance for $f^{Z''}_{\text{min}}$ exists at very low frequency and is not accessible under the experimental condition.
- ☐ $f^{Z''}_{\text{max}} < f^{Z'-Z''}_{\text{cross}}$

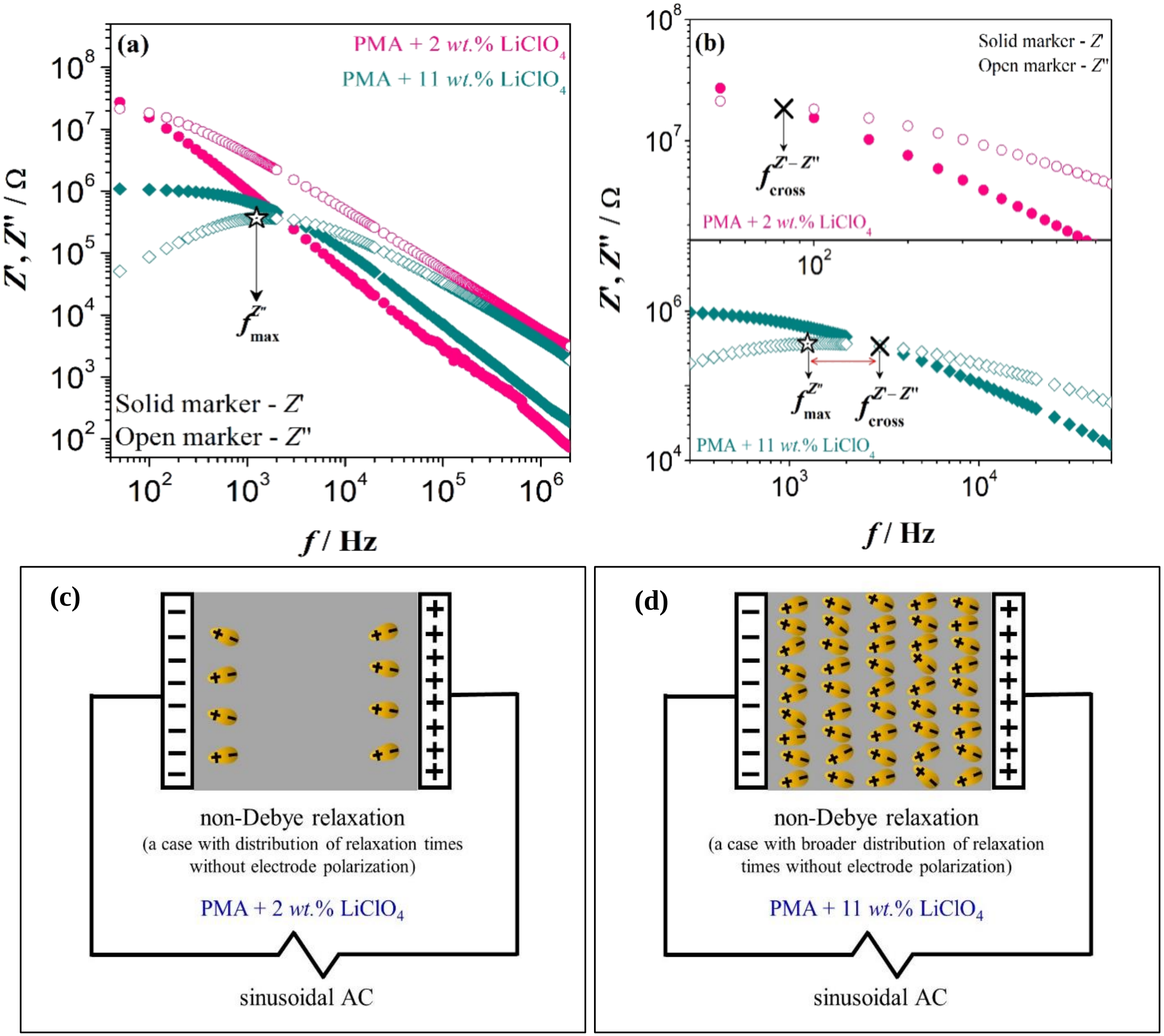

Figure 2.2 Frequency-dependent impedance spectra of (a) PMA-LiClO$_4$, (b) zoom-in of PMA-LiClO$_4$, and schematic illustration of dipolar entities orientation of the respective systems, where (c) deviation from Debye response and (d) large deviation from Debye response under the experimental condition.

Interpretation:

- ☐ One broad maximum resonance is only observed in Z'' spectrum of system with high salt content noted as $f_{\max}^{Z''}$ which indicates to the non-existence of dipolar entities in PMA at low salt content and only exist after adding higher salt content.
- ☐ Both systems at low and high salt content possess **one intersection point at Z' and Z'' spectrum** noted as $f_{\text{cross}}^{Z'-Z''}$. The distancing of $f_{\max}^{Z''}$ and $f_{\text{cross}}^{Z'-Z''}$ for system with high salt is seen to be wider than PEO at the same composition.
- ☐ Unlike PEO, **no $f_{\min}^{Z''}$ is noted** for both low and high salt systems for PMA. It seems the $f_{\min}^{Z''}$ of both compositions, most likely at zero frequency, and **exist at much lower frequency range,** it cannot be retrieved under this experimental condition.
- ☐ The interesting finding in PMA-Li salt system is the existence of distribution of relaxation times after addition of high composition of salt by $f_{\max}^{Z''} < f_{\text{cross}}^{Z'-Z''}$. This indicates to **large deviation from Debye response** and that may conclude the **orientation of dipolar entities of PMA-Li are mainly restricted only to local motions**.

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     - a. Impedance spectra
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     - c. Loss tangent spectra
     - d. Electric modulus
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5. **Conclusion**

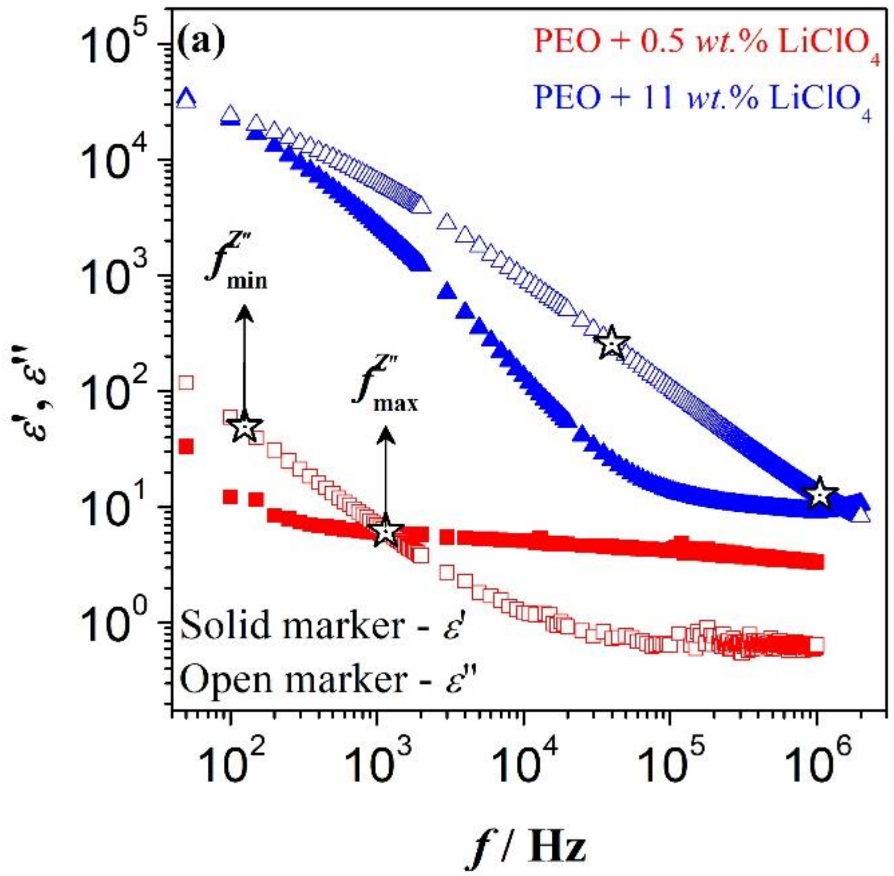

Figure 2.3 Frequency-dependent permittivity spectra of (a) PEO-LiClO$_4$

Interpretation:

In low-frequency range ($f^{Z''}_{\mathrm{min}} < f < f^{Z''}_{\mathrm{max}}$):

- $\varepsilon'' \propto \omega^{-n}$ with $n < 1$
  $n = 0.95$ for $W_S = 0.005$
  $n = 0.92$ for $W_S = 0.11$

- $n \sim 1$ [*i.e.* close to Debye relaxation for system with low content of salt (with $n = 1$)].

- $\omega_{\mathrm{cross}}^{\varepsilon' - \varepsilon''} = \omega_{\mathrm{cross}}^{Z' - Z''}$

Interpretation:

In low-frequency range ($f_{\min}^{Z''} < f < f_{\max}^{Z''}$):

- $\varepsilon'' \propto \omega^{-n}$ with $n < 1$
  $n = 0.90$ for $W_S = 0.11$

- $n < 1$ [*i.e.* deviate from Debye relaxation which indicates to dispersion of relaxation time].

- $\omega_{\min}^{Z''}$ is very small and not accessible under experimental condition

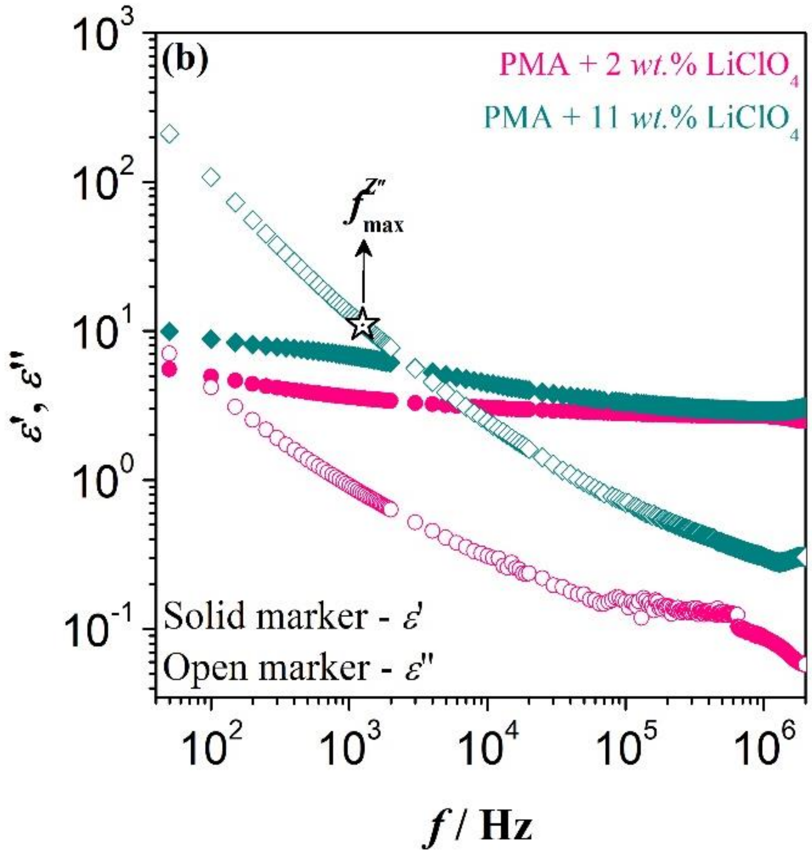

Figure 2.3 Frequency-dependent permittivity spectra of (b) PMA-$LiClO_4$

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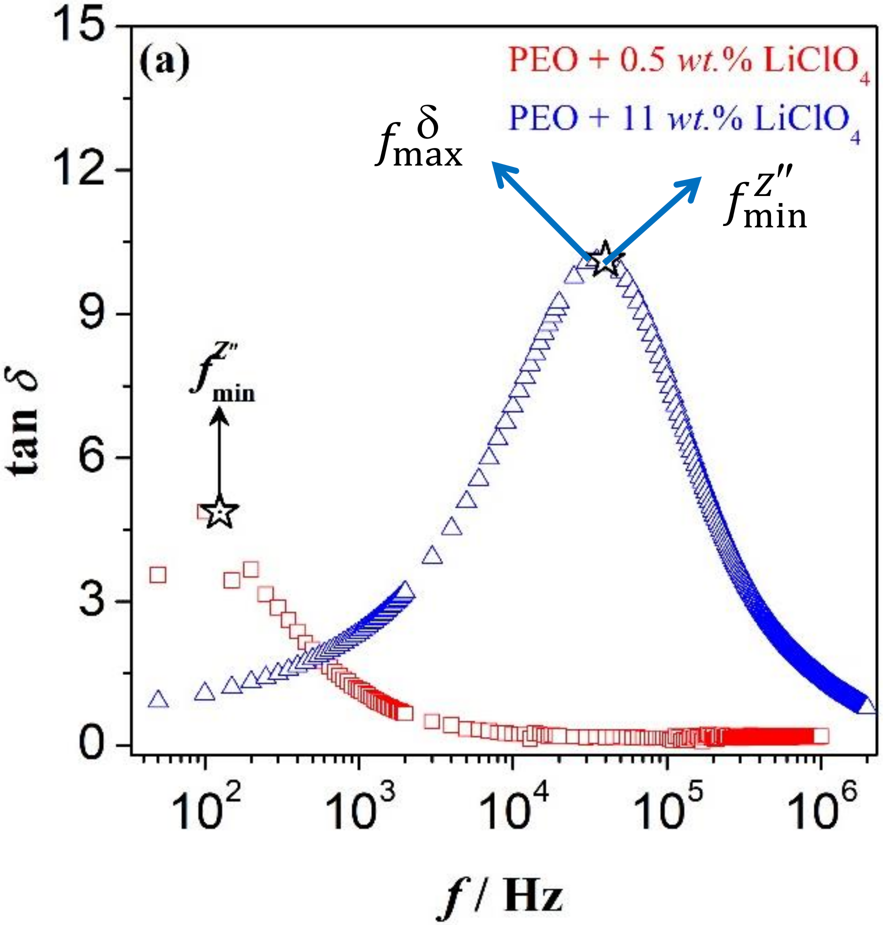

Figure 2.4 Frequency-dependent loss tangent spectra of (a) PEO-LiClO$_4$ loss tangent

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z'}{Z''}$$

- **ratio of mobile and stored dipoles.**
- should be maximum $f_{\max}^{\delta}$ near characteristic frequency $f_{\min}^{Z''}$ due to piling up of charges near interfacial region ($f_{\max}^{\delta} \approx f_{\min}^{Z''}$) [denotes as electrode polarization].
- for Debye approximation, one would have equality of the two frequencies ($f_{\max}^{\delta} = f_{\min}^{Z''}$).
- dispersion of the relaxation times cause ($f_{\max}^{\delta} < f_{\min}^{Z''}$).

$$\tan\delta = \frac{\varepsilon''}{\varepsilon'} = \frac{M''}{M'} = \frac{Z'}{Z''}$$

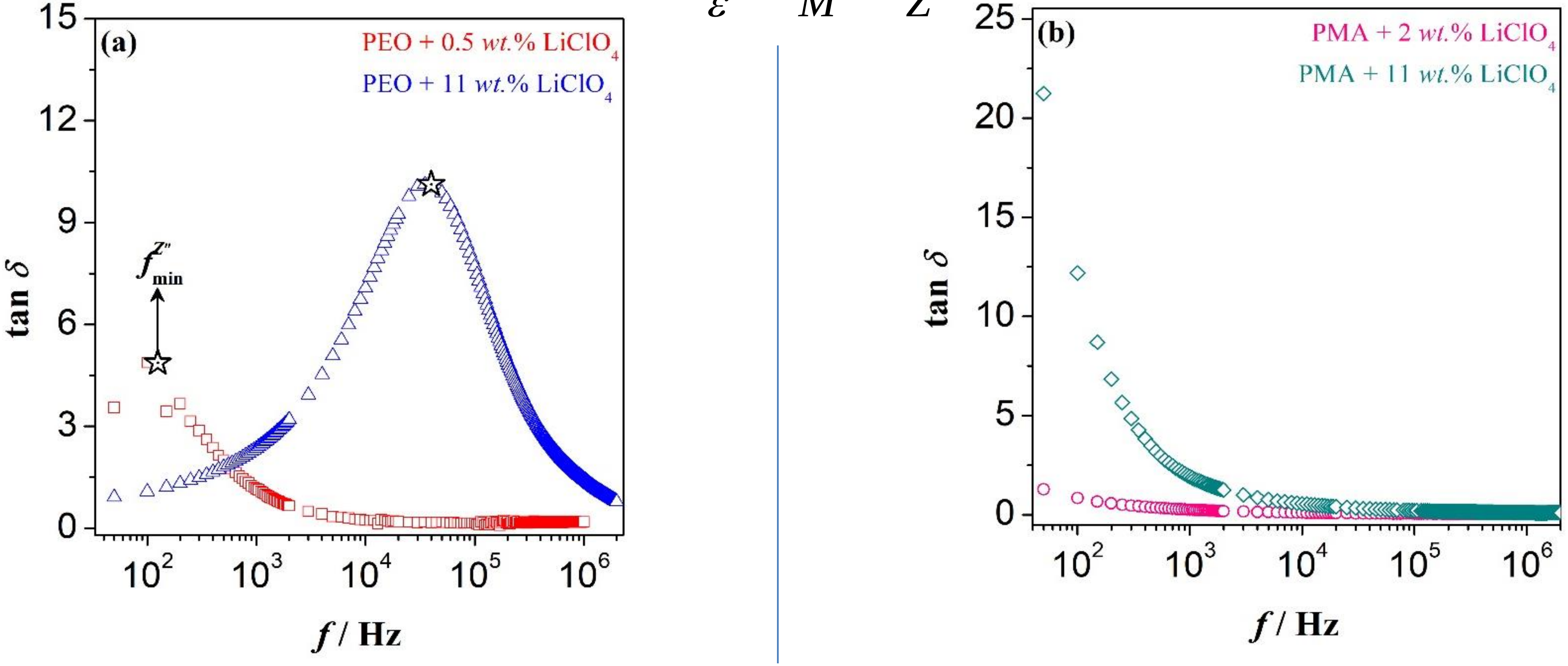

Figure 2.4 Frequency-dependent loss tangent spectra of (a) PEO-$LiClO_4$ and (b) PMA-$LiClO_4$

- With increasing salt content, tanδ appears at higher level and shifts to higher frequency (f^{δ}_{max}). This means increasing strength of relaxation.

- Monotonic decrease in tanδ that is no dipolar relaxation illuminates.
- No electrode-polarization relaxation as no visible maximal resonance in tan δ.

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General versions of modulus and impedance

Impedance $Z^* = Z' + iZ'' = \dfrac{1}{i\omega C_o \varepsilon^*}$

Permittivity $\varepsilon^* = \varepsilon' - i\varepsilon''$

(2.1)

Electric modulus $M^* = M' + iM'' = \dfrac{1}{\varepsilon^*}$

$M' = C_o \omega Z''$ $M'' = C_o \omega Z'$

Dynamically we see electric modulus after **Equation (2.1)** as dynamic quantity, where M'' is directly proportional to $\dot{Z}'$ where $\dot{Z}'$ is the time derivative of Z'. Hence, after several manipulations of **Equation (2.1)**, we see the symmetric formulations that are the central points of the discussion:

$$M'' \propto \omega Z' \qquad \textbf{(2.3)}$$

$$\frac{Z''}{R} \propto \omega \varepsilon' \qquad \textbf{(2.4)}$$

- **Equation (2.3)** manifests, imaginary part of modulus points towards electric relaxation or non-local transport of charged entities in the low-frequency range $(f_{\mathrm{min}}^{Z''} < f < f_{\mathrm{max}}^{Z''})$.

- It indicates to long-range motions of chains in the low-frequency range.

- Hence, it is a complement to imaginary part of impedance, **Equation (2.4)**, which reflects as dielectric relaxation bound to short-range irregular motion of charges.

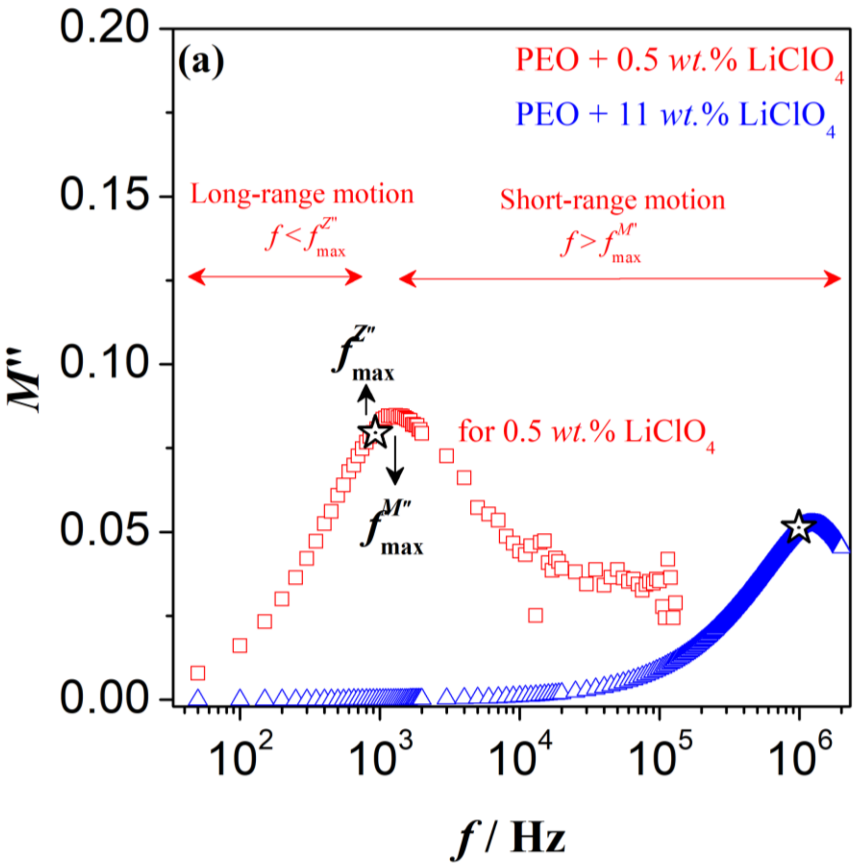

Figure 2.5 Frequency-dependent electric modulus spectra of (a) PEO-LiClO$_4$

- The **existence of maximum (relaxation)** denotes the **transition of long-range motion** in the range of frequency $f < f_{\max}^{Z''}$ to short-range motion at higher frequency range ($f > f_{\max}^{M''}$).
- The **charge transport for PEO is mainly governed by short-range** irregular (localized) motion as the dielectric relaxation **is more dominant.**
- We may conclude the conductance activity PEO-salt is dominated by local motions of dipoles and long-range motions only have minor influence on the system.

- ☐ Unlike PEO, PMA-Li system only shows conducting behaviour only after addition of sufficiently high salt content.

- ☐ The systems possess a **large deviation from Debye response**, as observed in $f_{\max}^{Z''} < f_{\text{cross}}^{Z' - Z''} < f_{\max}^{M''}$.

- ☐ The $f_{\max}^{M''}$ does not moves to lower value like PEO even added with same composition of salt. **The system is seen to be bounded to short-range irregular motions of dipoles only.**

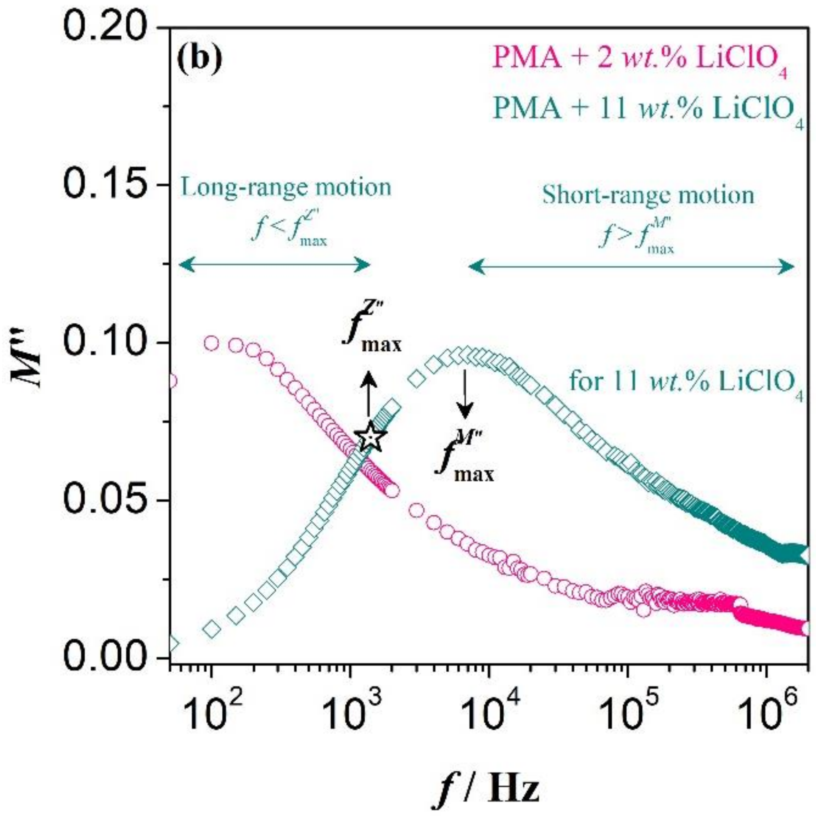

Figure 2.5 Frequency-dependent electric modulus spectra of (b) PMA-$LiClO_4$

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4. **Impedance spectra**
   - ☐ 2-component (polymer + salt) systems
   - ☐ 2-component – electrolyte and non-electrolyte
     1. a. Impedance spectra
     2. b. Permittivity spectra
     3. c. Loss tangent spectra
     4. d. Electric modulus
     5. e. Conductivity spectra
5. **Conclusion**

Conductivity $\boldsymbol{\sigma}$ is related to dynamic permittivity in the linear range

$$\sigma^{*} = \varepsilon_{0}\dot{\varepsilon}^{*} \qquad \textbf{(2.5)}$$

For periodic changes, Eq. (5) turns into $\sigma^{*} = i\omega\varepsilon_{0}\varepsilon^{*}$. Real and imaginary parts of conductivity are related to permittivity as in Eq. (6)

$$\sigma' \propto \omega\varepsilon'' \qquad \sigma'' \propto \omega\varepsilon' \qquad \textbf{(2.6)}$$

$\varepsilon'' \propto \dfrac{1}{\omega^{\mathrm{n}}}$ with exponent $n < 1$, but close to unity.

Imaginary part of permittivity is related to dissipation of energy by conduction. After Eq. (6) and $\varepsilon'' \propto \dfrac{1}{\omega^{\mathrm{n}}}$,

we expect $\sigma' \approx$ *const* in the low-frequency limit.

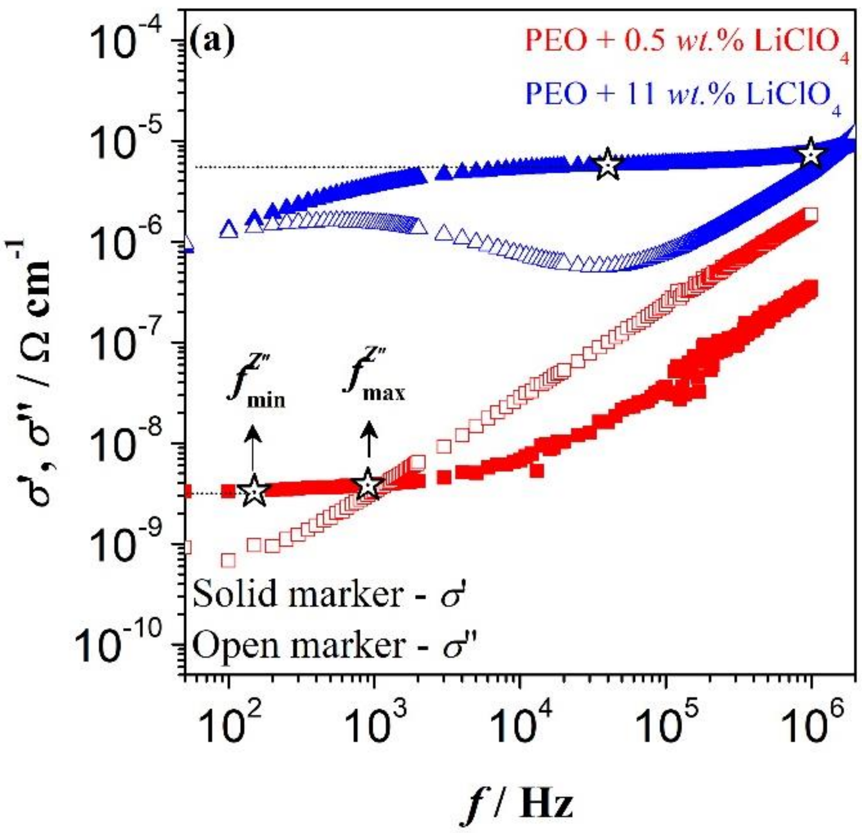

Figure 2.6 Frequency-dependent conductivity spectra of (a) PEO-LiClO$_4$. The dotted line marks as DC conductivity in the range of $f_{\min}^{Z''} < f < f_{\max}^{Z''}$.

- slight increase in conductivity σ' in the range of low-frequency, $f_{\min}^{Z''} < f < f_{\max}^{Z''}$, indicating slight deviation from Debye relaxation.
- Extrapolation to frequencies beyond $f_{\min}^{Z''}$ yields $\sigma'(f \rightarrow 0) = \sigma_{DC}$ (DC conductivity).
- For frequencies $f < f_{\min}^{Z''}$, electrode polarization appears, conductivity decreases (*i.e.* σ' decreases whereas σ'' increases).
- Imaginary part σ'' is related to stored energy from the electric field. Therefore, it loses energy during electrode polarization and conductance process

- The low frequency resonance of PMA is not accessible under the experimental procedure because it lies at very low frequency region.
- Thus, we may see the $\sigma' \approx const$ and σ'' in the range of f approaching zero ($f \rightarrow 0$) as there is no storage of charges in the interfacial region.
- Conductivity of PMA-Li system exhibits very low conductivity as compared to PEO-Li system (at the same content).
- Conductivity of PMA at high salt content mostly acts comparatively same as PEO at low salt content.

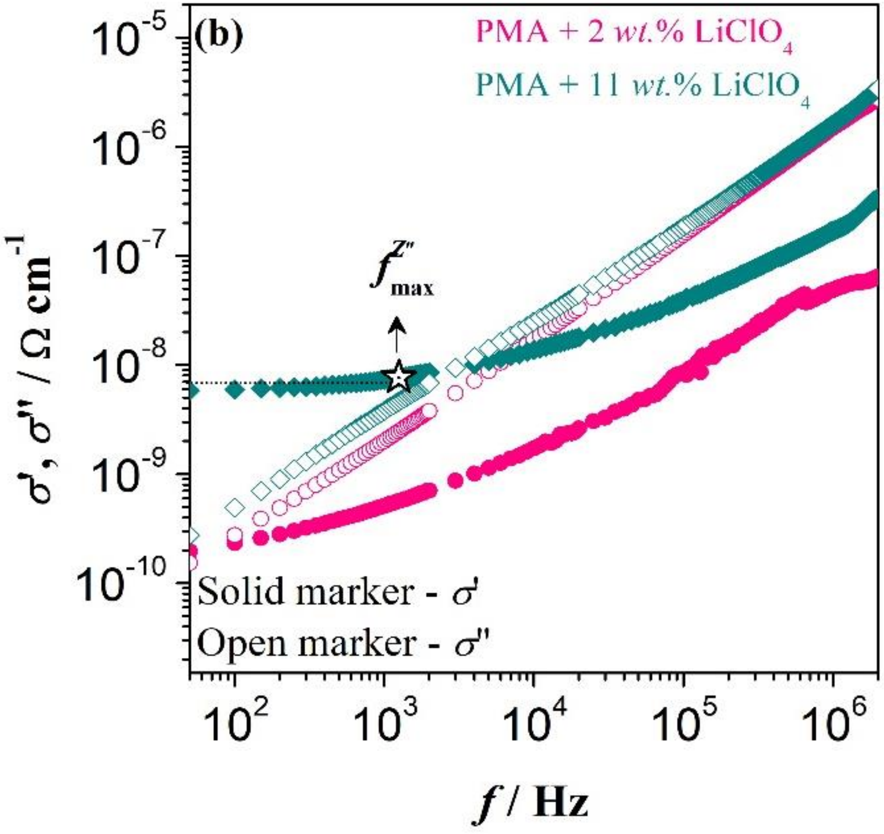

Figure 2.6 Frequency-dependent conductivity spectra of (b) PMA-LiClO$_4$. The dotted line marks as DC conductivity in the range of $f_{\mathrm{min}}^{Z''} < f < f_{\mathrm{max}}^{Z''}$.

Conclusion

- Two **different classes of systems**, *i.e.* high molar mass semi-crystalline **PEO and low molar mass amorphous PMA with addition of LiClO$_4$,** were employed for discussion on the phenomenological response of imaginary part of impedance spectrum (Z''), imaginary part of permittivity (ε''), tan δ (imaginary/real of permittivity), the imaginary part of electric modulus (M''), and the real part of conductivity (σ').

- We observe **there are interactions between the salt molecules and PEO chains leading to dipolar entities**, but they relaxed in random manner. Therefore, under the effect of external electric field, we **see PEO-salt system as a polymer electrolyte** because even with a tiny fraction of salt molecules dissolved in, the system **becomes electrically conductive**.

- **PMA-salt system only become slightly conductive after addition of high salt content**; however, it still **cannot display electrode polarization** or electric relaxation because the **dipoles are immobilized** (restricted to local motion only). Hence, in the classic sense, PMA-salt does not form a good polymer electrolyte.