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Characterization of polymer electrolytes by dielectric response using **Electrochemical Impedance Spectroscopy**

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25th Short Course on
Polymer Characterization
in conjunction with 25th POLYCHAR 2017, Kuala Lumpur
Theme: **Polymer characterization**

Outline

1. **Background**
2. **Electrochemical Impedance Spectroscopy (EIS) for dielectric relaxation of polymer electrolytes**
3. **Impedance spectra**
   - ☐ 2-component (polymer + salt) systems
   - ☐ 2-component – electrolyte and non-electrolyte
4. **Conclusion**

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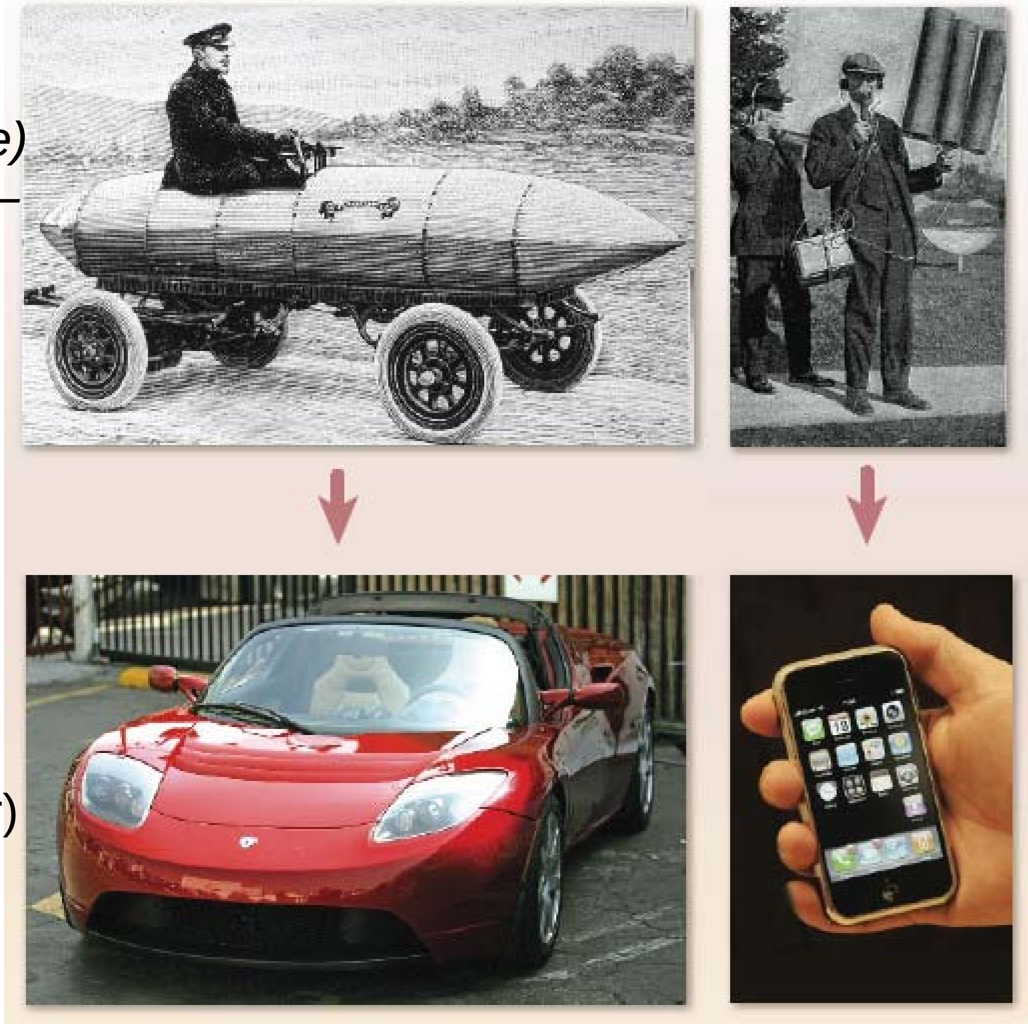
Building better batteries

1899
Belgian car
(*La jamais contente*)
equipped with lead–
acid batteries
(30 m s^{-1})

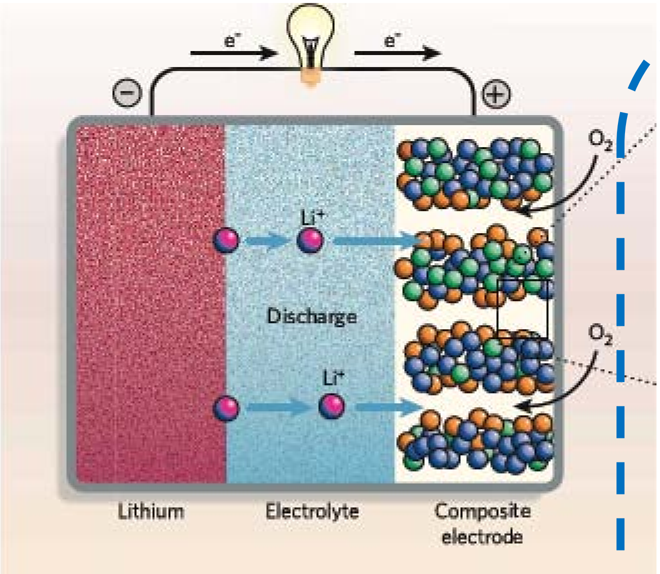
1920
first wireless
communication
took place in
Pennsylvania



~100 years later
fully electrical cars
(*e.g.* Tesla roadster)

~100 years later
the latest mobile
phones can
perform a wide
range of
functions

Armand M, Tarascon JM, Nature, 451, 652-657, 2008



Armand M, Tarascon JM,
Nature, 451, 652-657, 2008

Simple concept of batteries:

- ☐ All batteries are composed of two electrodes connected by an ionically conductive material called an electrolyte.
- ☐ When these electrodes are connected by means of an external device, electrons spontaneously flow from the more negative to the more positive potential.
- ☐ Ions are transported through the electrolyte, maintaining the charge balance, and electrical energy can be tapped by the external circuit.

Slow development:

- ☐ slowed down the deployment of electric cars and wireless communication
- ☐ **why?**
  1. lack of suitable electrode materials and electrolytes
  2. difficulties in mastering the interfaces between them.

Solid Polymer electrolyte

(Solvent free polymer-salt complex)

- ☐ thin film consisting of ionic salts dissolve in appropriate polymer which allows ionic conduction.
- ☐ Preferably used constituents are poly(ethylene oxide) (PEO) and lithium salts.
- ☐ The widely accepted idea is that lithium salts are molecularly dispersed in amorphous regions of the polymer.
- ☐ Efforts for improvements of polymer-salt solutions pointed preferably towards two closely related directions, enhancement of :
  1. both carrier density and
  2. mobility.

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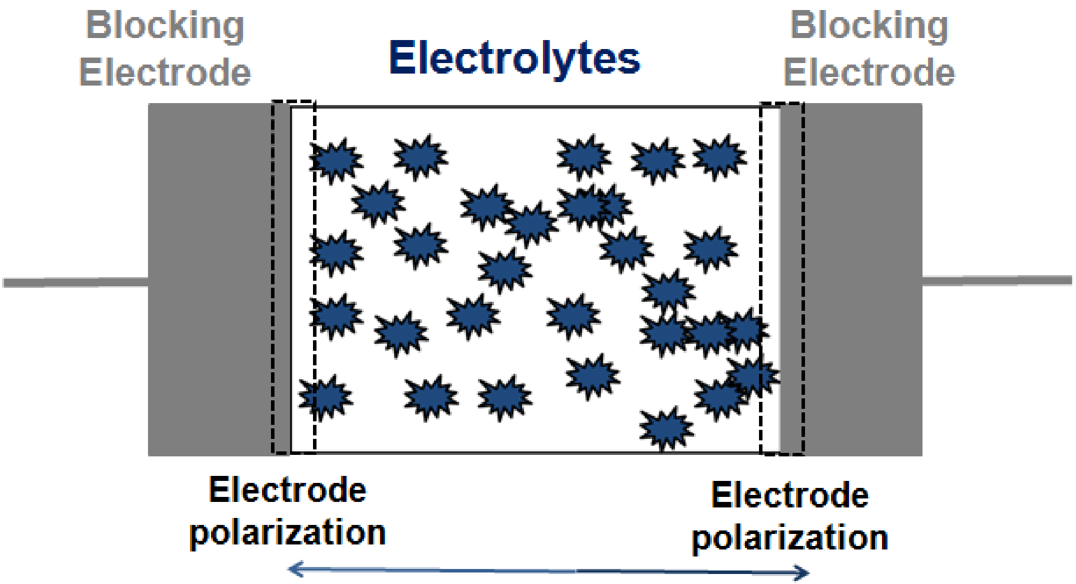
Impedance spectroscopy (IS)

- ☐ 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.



Blocking Electrode

Electrolytes

Blocking Electrode

Electrode polarization

Electrode polarization

Bulk impedance

Dielectric modeled by conducting domains embedded in an insulating matrix

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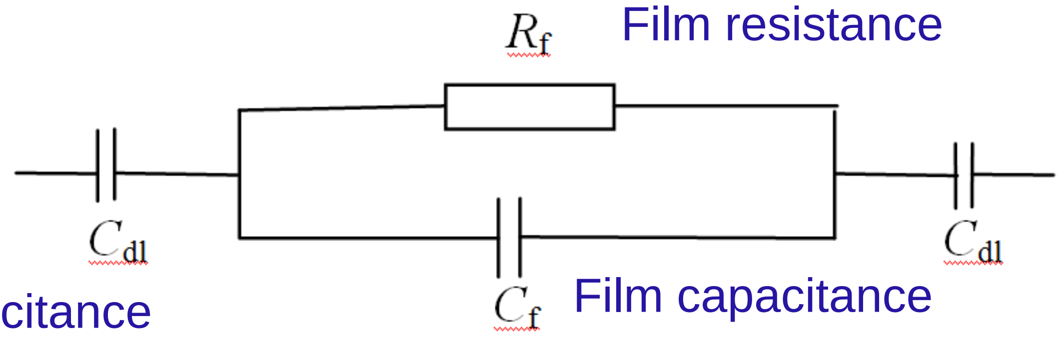


Film resistance

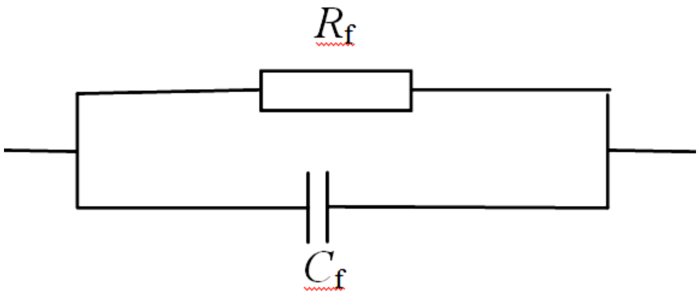
Double layer capacitance
electrolyte/electrode

Film capacitance

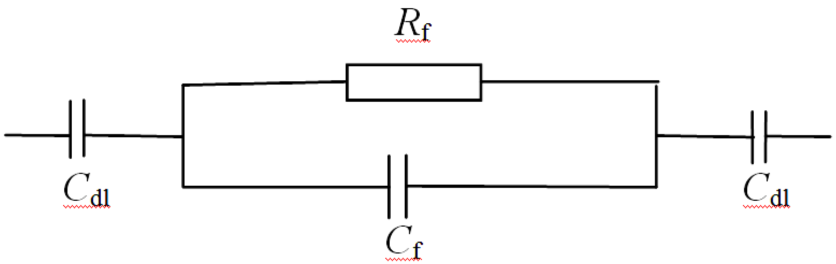
Polymer electrolyte film between
two blocking electrodes

Equivalent circuit for polymer electrolyte

Equivalent circuit for polymer electrolyte



Polymer electrolyte film between two blocking electrodes



Polymer electrolyte film between two blocking electrodes

Electrical circuits are not unique. A good fit to experimental data is not sufficient to validate a model.

Debye response

For a perfect semicircle centred at (R_b/2, 0), $Z' = Z''$

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

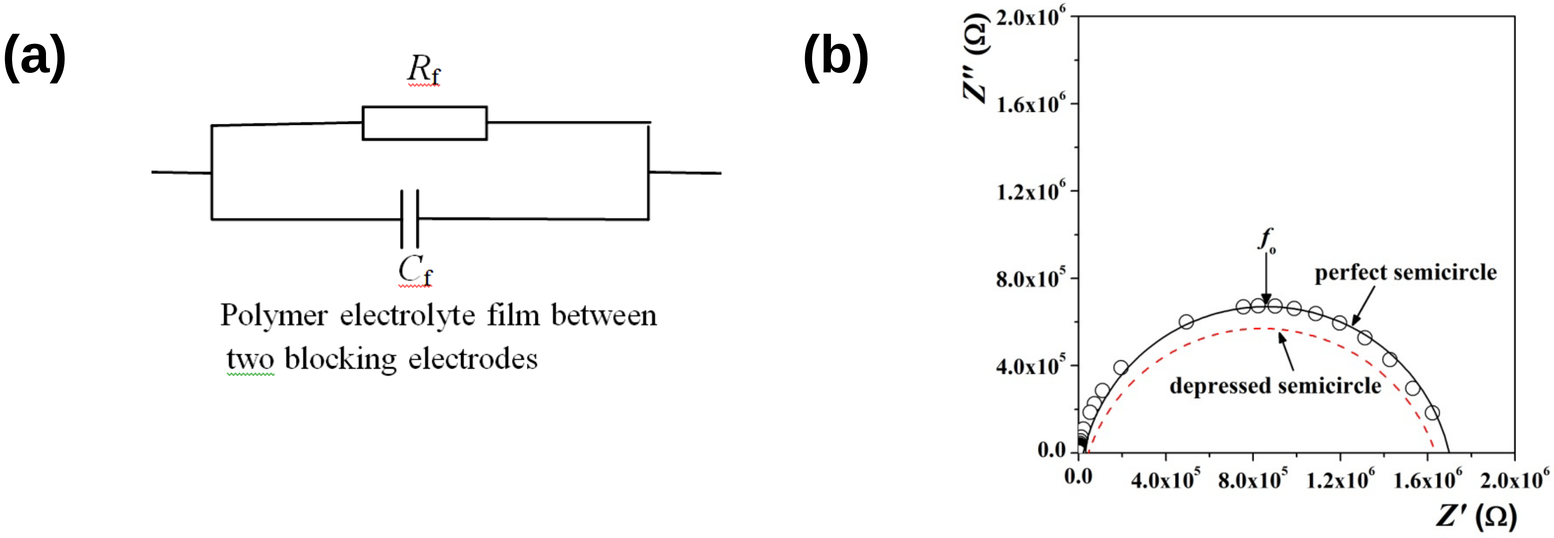
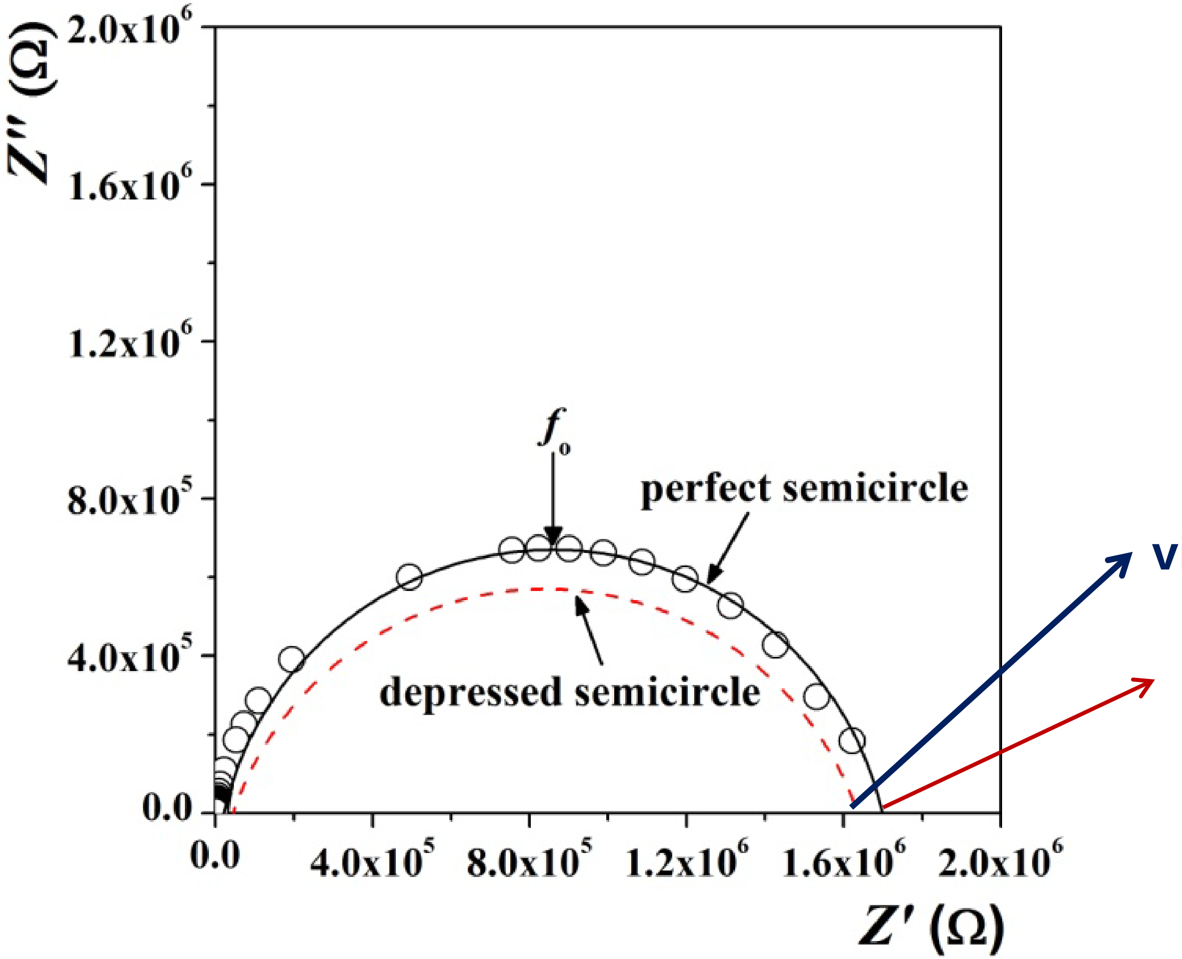


Illustration of a perfect semicircle of a Nyquist plot, where a pure resistor connected in parallel with a pure capacitor

Frequency is hidden for Nyquist plot!

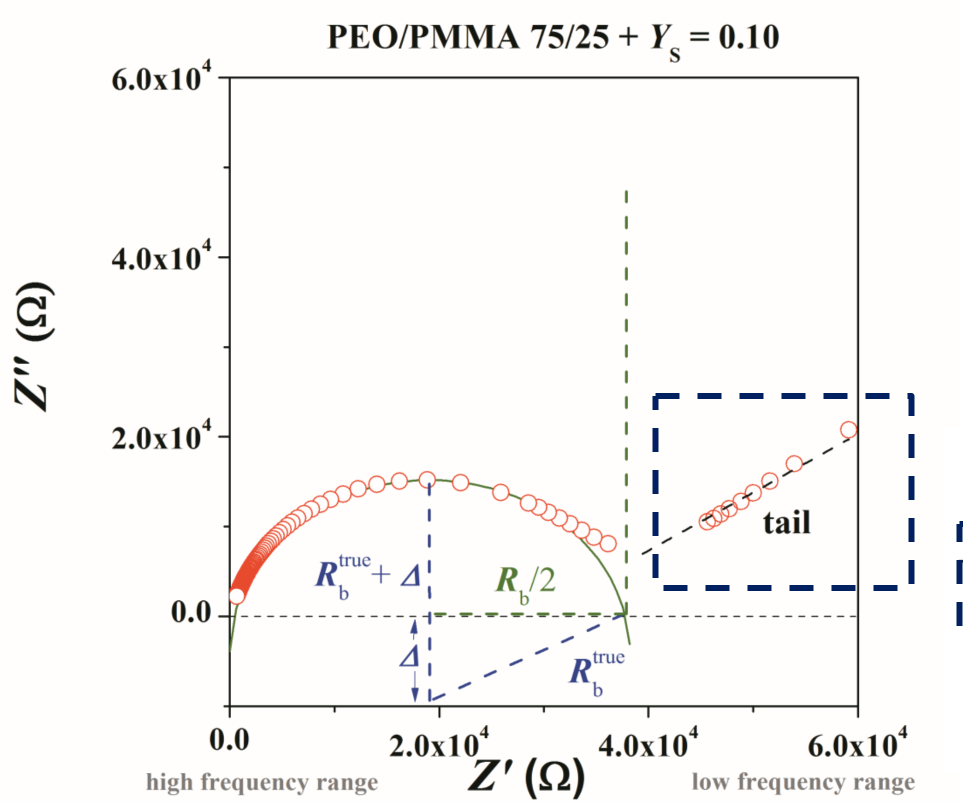


virtual R_b

True R_b

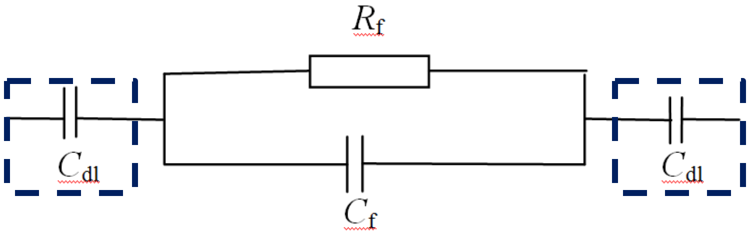
High frequency

Low frequency



$$|Z|^2 = (Z')^2 + (Z'')^2$$

$$|Z| = \frac{Z_o}{2} \equiv \frac{R_b}{2}$$



Polymer electrolyte film between
two blocking electrodes

Illustration of a depressed semicircle of a Nyquist plot

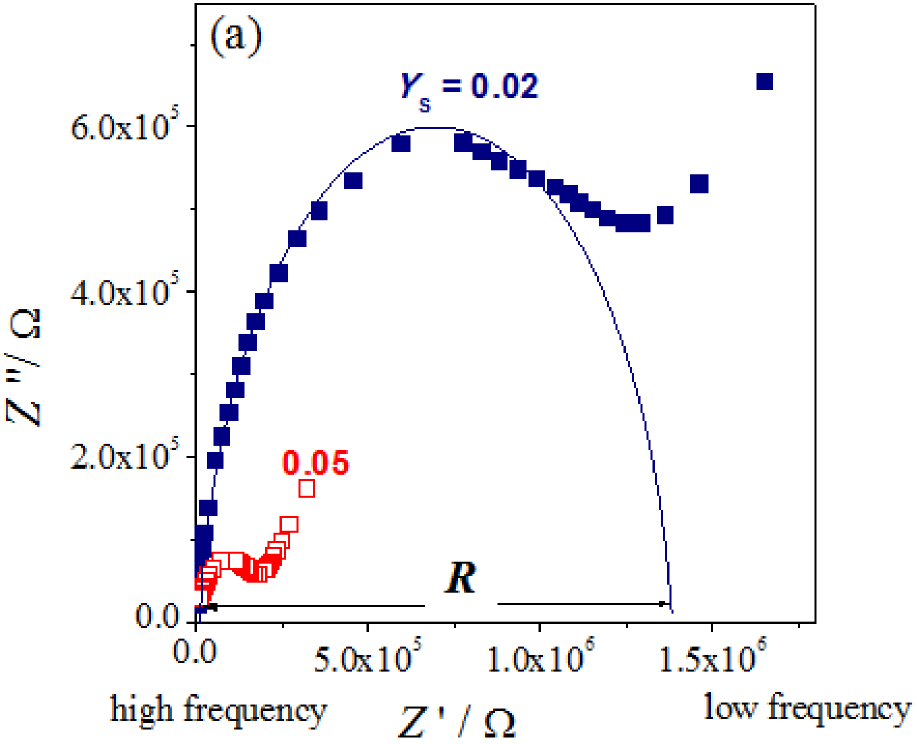
The coordinates of the centre of the depressed semicircle (below *x*-axis)

$$Z'_{\text{(centre)}} = \frac{R_b}{2} \quad \text{and} \quad Z''_{\text{(centre)}} = -\Delta$$

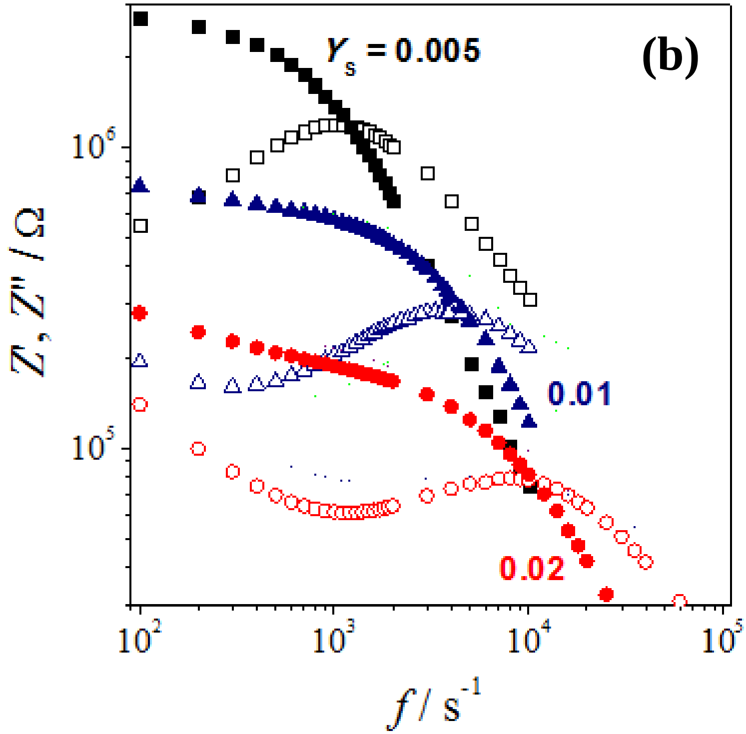
Bode plots shows frequency information explicitly

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

PEO + LiClO$_4$



Nyquist plot



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

Bode plot:

Impedance *versus* frequency

Z′ - solid markers

Z″ - open markers

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.

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

$$\text{Permittivity } \varepsilon^* = \varepsilon' - i\varepsilon''$$

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

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

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

where, *X*' and *X*" denote real and imaginary parts of quantity *X*, *ω* and *f* represent angular frequency and frequency, respectively (*ω* = 2π*f*).

All of the quantities in Eq. (1) are closely related to complex conductivity:

$\sigma'' =$

$$\sigma^* = i\omega\varepsilon_{\mathrm{o}}\varepsilon^* \qquad M^* = i\omega C_{\mathrm{o}} Z^*$$

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

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

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

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 and **ε''** gives the dissipated energy for conductivity
- **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

Permittivity related to dielectric behavior of materials and the interpretation of permittivity reads:-

- ☐ The real part of permittivity ε' [or dielectric constant when $\varepsilon'(f \rightarrow \infty)$; f denotes frequency] indicates the ability of the material (in this case, polymer is referred) to store energy reversibly from the applied electric field.

- ☐ The imaginary part of permittivity ε'' represents dielectric loss. Polarization (here alignment of dipoles) of a polymer electrolyte varies under an applied oscillating electric field. Some of the energy is dissipated due to dipole migration (or the flow of charged entities), conduction, or conversion into thermal energy (*via* molecular vibration).

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Characteristics of the polymers

	Poly(ethylene oxide) **PEO**	Epoxidized natural rubber **ENR-25**
M_w / kg mol^{-1}	300	300
T_g / °C	- 54	
T_m / °C	65	
salt content Y_S	0.005 – 0.12	0.01 – 0.30
Molecular structures		$p = 0.25$ $q = 0.75$

2-component (polymer + salt) systems

(1) PEO + salt

(2) ENR-25 + salt

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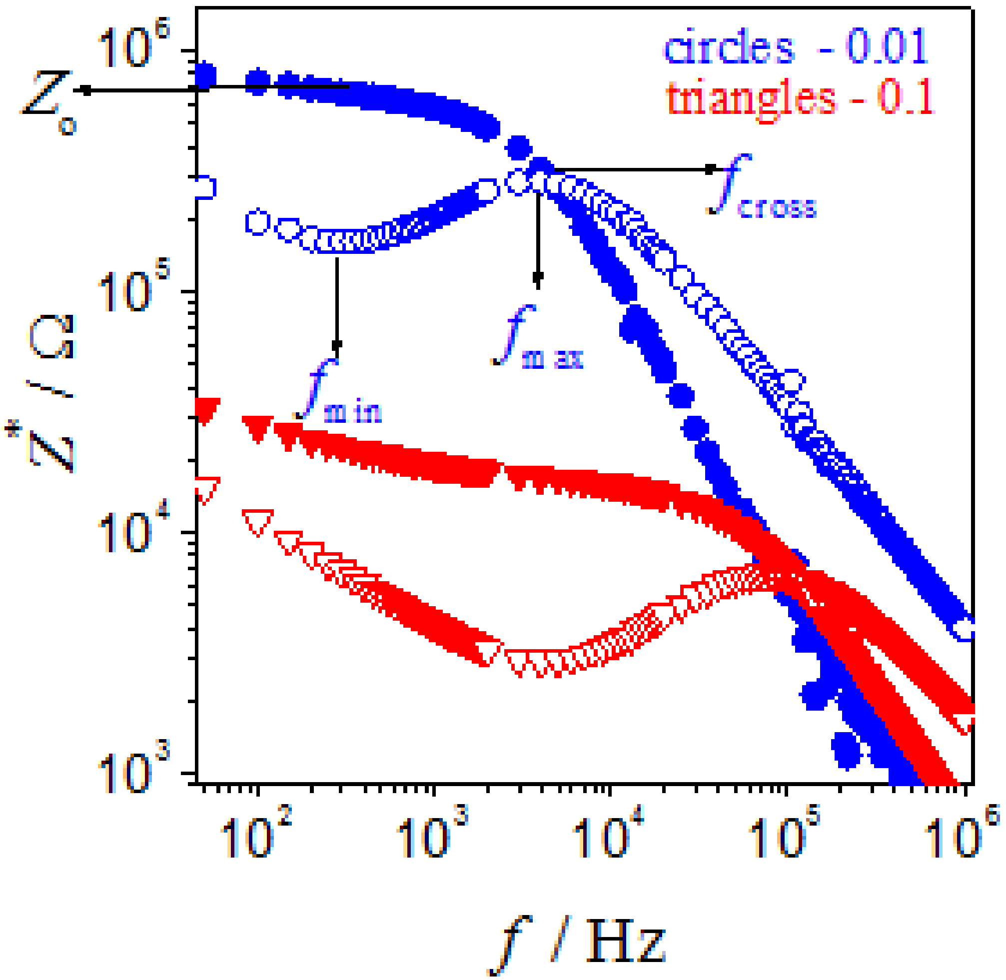


In low-frequency range

($\omega_{\min} \le \omega \le \omega_{\max}$):

❑ $Z' \approx const$

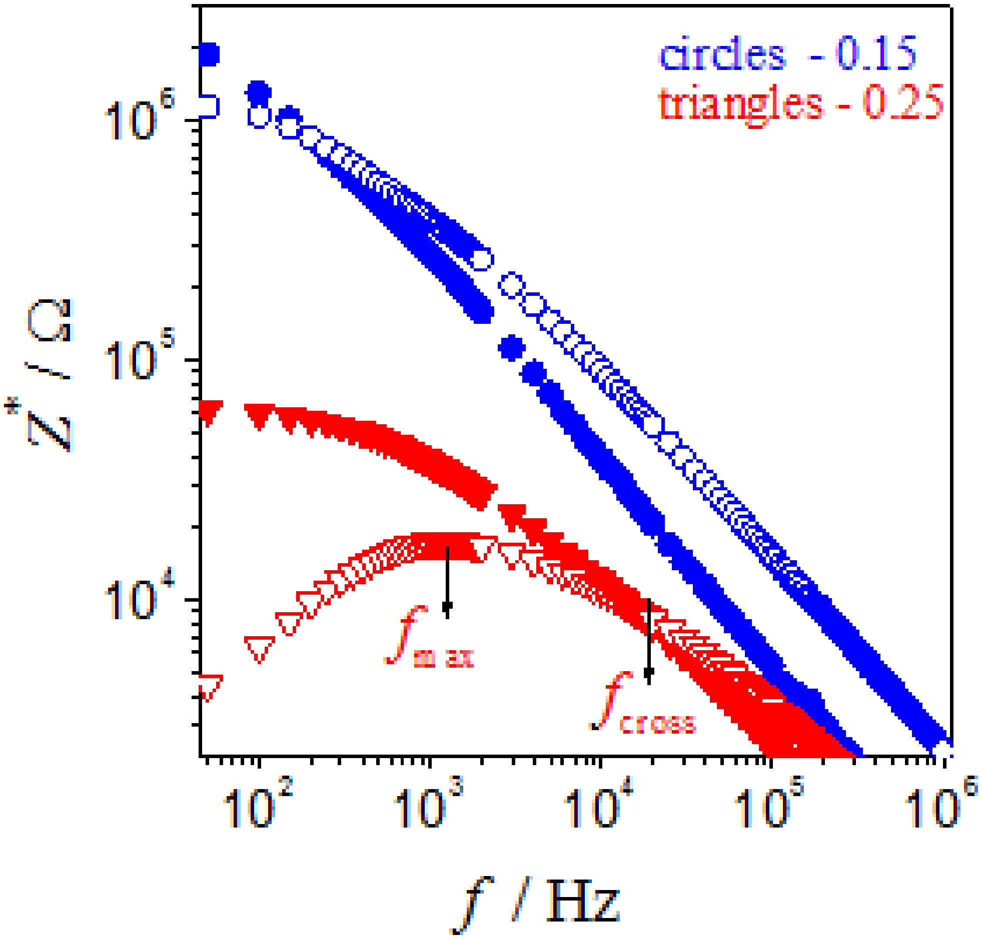
❑ $Z'' < Z'$

❑ $\omega_{\min} < \omega_{\max} < \omega_{cross}$

Impedance *versus* frequency for **PEO** for the indicated Y_S at room temperature
solid markers – real part
open markers – imaginary part

Interpretation:

- increase in ω_{min} and ω_{max} with added salt content (at T = *const*).
- the **maximal relaxation peak for Z''** ($Z''_{\max}$) describes **Debye relaxation** (*i.e.* under ideal conditions where no interactions between dipoles, only one relaxation time τ and $\omega_{\mathrm{max}} = \omega_{\mathrm{cross}}$). It results from reorientation of dipoles. **Interaction between dipoles leads to dispersion of relaxation times** which is indicated by $\omega_{\mathrm{max}} < \omega_{\mathrm{cross}}$.
- **Z' = *const* (abbreviated as Z_{o}) for $\omega \to 0$**. Z_{o} slightly depends on *f* especially at higher salt content. This is caused by greater deviation from Debye relaxation at higher salt content. Lower Z_{o} for higher electrode polarization is noted.
- Z' increases at ω = *const* (in the range $\omega \to 0$)) at lower Y_{S}.
- **both Z' and Z'' increase in the limit $\omega \to 0$** (for $\omega < \omega_{\mathrm{min}}$) **due to electrode polarization** (formation of double-layer or onset of electrode polarization). This leads to dispersion of relaxation times.



- ☐ Only one broad (dielectric) relaxation peak for Z'' at $\omega_{\max}$ at quite high salt content (Y_S > 0.2).
- ☐ The low frequency peak for Z'' at $\omega_{\min}$ shifts to very low frequency and is not accessible under the experimental condition.
- ☐ $\omega_{\max} < \omega_{\text{cross}}$

Impedance *versus* frequency for **ENR-25** for the indicated Y_S at room temperature
solid markers – real part
open markers – imaginary part

Interpretation:

- ❑ At $Y_S > 0.2$, $\omega \rightarrow 0$, $Z' = const$ and $Z'' \rightarrow 0$. Hence, no further relaxation in the ENR-25 systems is seen.

- ❑ Instead of $\omega_{max} \approx \omega_{cross}$ (for PEO systems), one recognizes $\boldsymbol{\omega_{max} < \omega_{cross}}$ for ENR-25 systems. This implies there is **no ideal (dipolar) Debye relaxation** (characterized by one relaxation time), we have always dispersion of relaxation times. Here, we see ω_{max} as average over the dispersion of relaxation times or the mean value.

- ❑ Merging of Z', belonging to different salt content, appears at much higher frequency as for PEO.

- ❑ No accumulation of dipoles in the interfacial region of the electrode-electrolyte is seen because ω_{min} is not observed or ω_{min} is very close to zero frequency. Consequently no electrode polarization.

Summary

1. **PEO** systems are polymers comprising dipoles of sufficient mobility (or drift) under the action of oscillating electric field. Relaxations in this system mean reorganization of dipoles in statistical distribution (not aligned). This reorganization is coined by some cooperative motions of the entities.

2. **ENR-25** at $Y_S > 0.2$ behaves like a macroscopic dipole or mobility of microscopic dipoles is restricted to localized motions.

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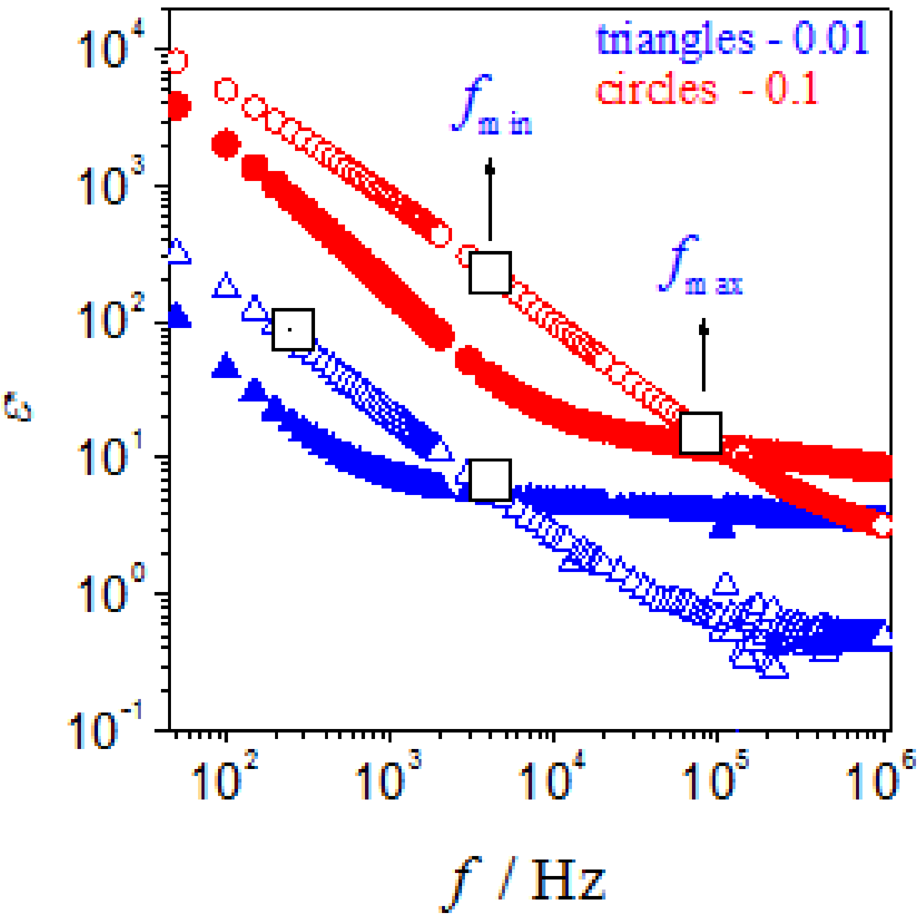
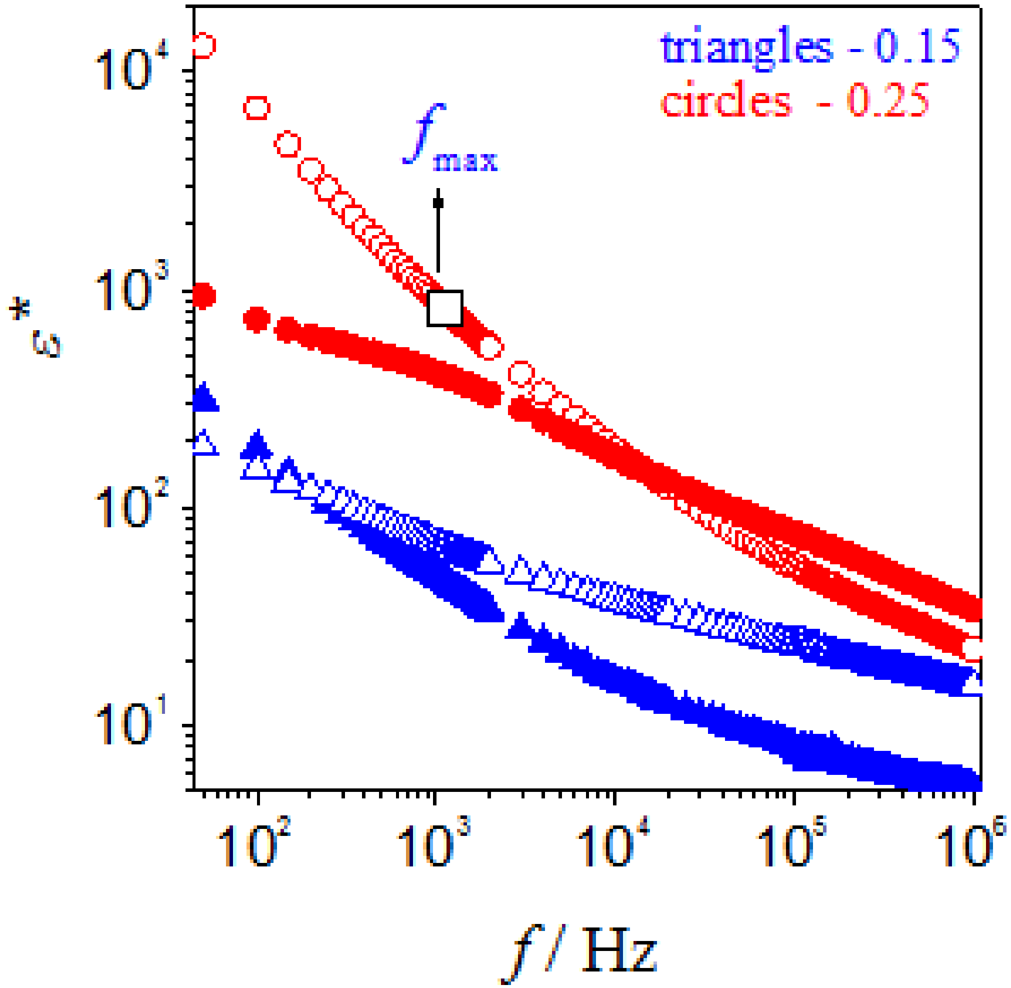


In low-frequency range

($\omega_{min} \le \omega \le \omega_{max}$):

- $\varepsilon'' \propto \omega^{-n}$ with $n < 1$
  $n = 0.94$ for $Y_S = 0.01$
  $n = 0.92$ for $Y_S = 0.1$
- $n \sim 1$ [*i.e.* close to Debye relaxation (with $n = 1$)]
- $\omega_{cross}^{\varepsilon} = \omega_{cross}^{Z}$

Permittivity *versus* frequency for **PEO** at room temperature for $Y_S = 0.01$ and 0.1
squares mark ω_{min} and ω_{max} of Z''
solid markers – ε'
open markers – ε''



Permittivity *versus* frequency for **ENR-25** at room temperature for $Y_S = 0.15$ and 0.25
square marks ω_{max} of Z''
solid markers – ε'
open markers – ε''

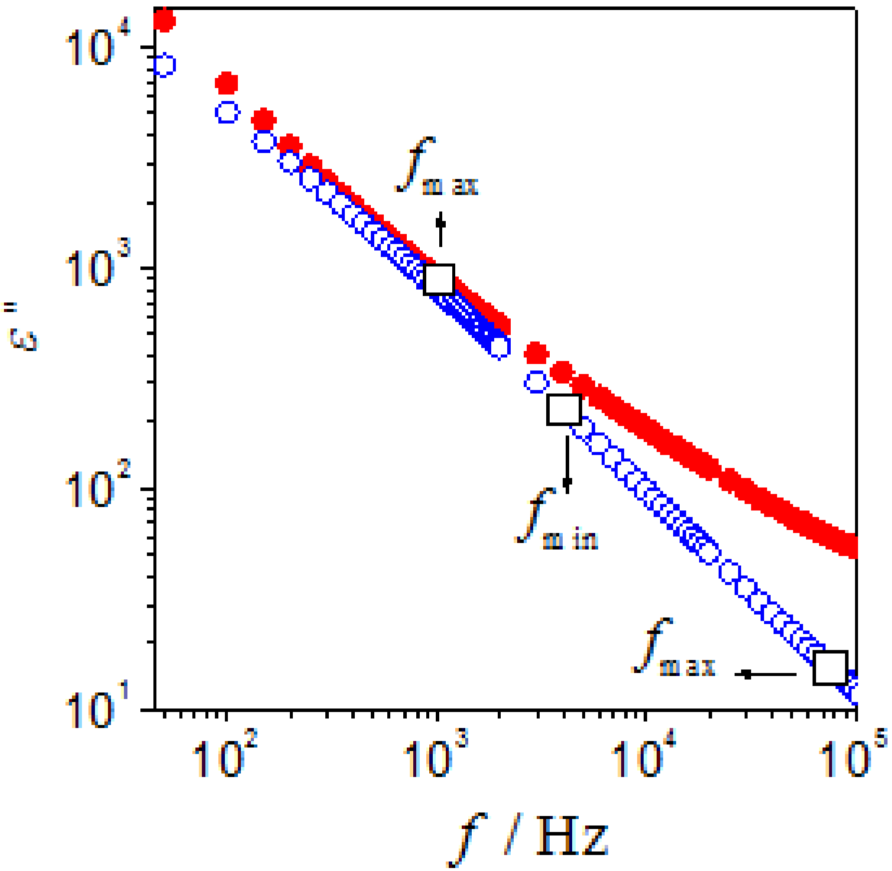
In low-frequency range

$(\omega_{min} \leq \omega \leq \omega_{max})$:

- ☐ ω_{min} is very small
- ☐ $\varepsilon'' \propto \omega^{-n}$ with $n < 1$
  $n = 0.89$ for $Y_S = 0.25$
- ☐ $n < 1$ [*i.e.* deviate from Debye relaxation and towards dispersion of relaxation time.

Summary

For frequencies $\omega < \omega_{max}$



Imaginary part of permittivity *versus* frequency at room temperature

solid markers – ENR-25 + $Y_S = 0.25$
open markers – PEO + $Y_S = 0.1$

- both systems that dispersion of relaxation times in the range of $\omega_{min} \ldots \omega_{max}$.

$$\varepsilon'' \propto \omega^{-n} \quad \text{with } n < 1$$

- $\varepsilon''_{ENR\text{-}25} \approx \varepsilon''_{PEO}$ in the limit $\omega \rightarrow 0$, hence, it leads to $\sigma_{DC,ENR\text{-}25} \approx \sigma_{DC,PEO}$ (~10^{-6} S cm^{-1}) for the two systems.

- the conductance process in the range $\omega_{min} \ldots \omega_{max}$ preferably depends on salt concentration and less dependence on the polymer.

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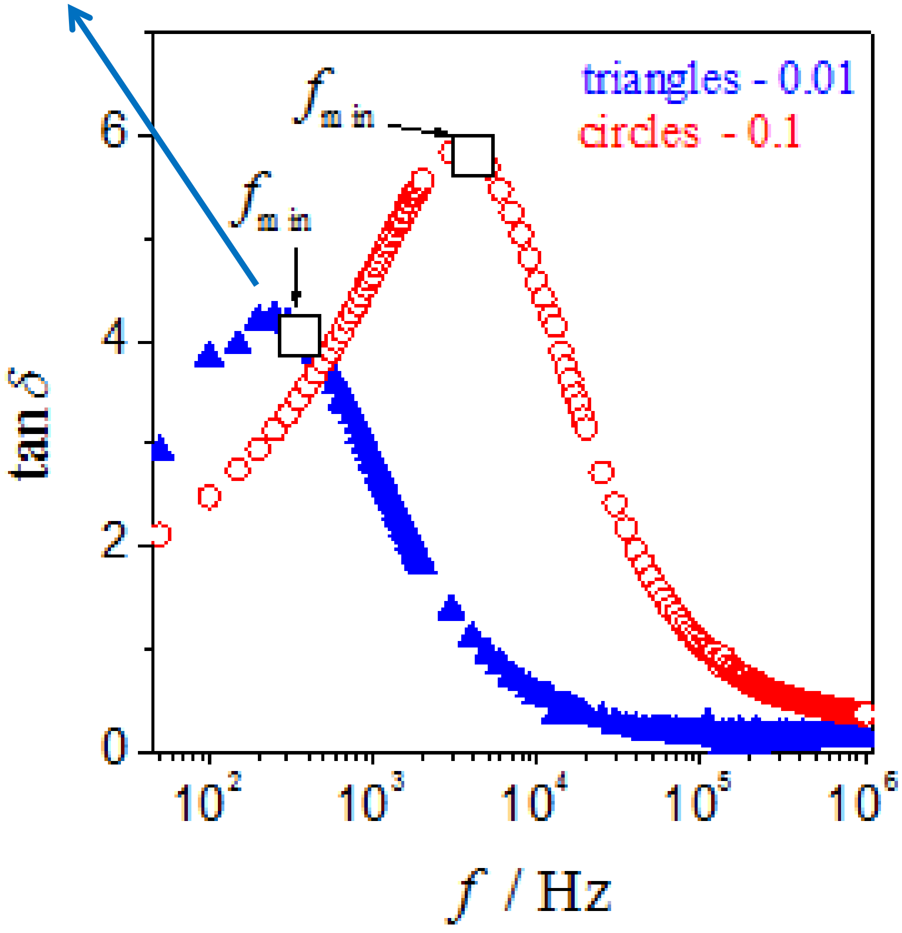
$\omega^{\delta}_{\max}$ - electrode-polarization relaxation



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

☐ ratio of mobile and stored dipoles.

☐ should be maximum $(\omega^{\delta}_{\max})$ near characteristic frequency $\omega_{\min}$ of $Z''(\omega^{Z''}_{\min})$ due to piling up of charges near interfacial region $(\omega^{Z''}_{\min} \approx \omega^{\delta}_{\max})$.

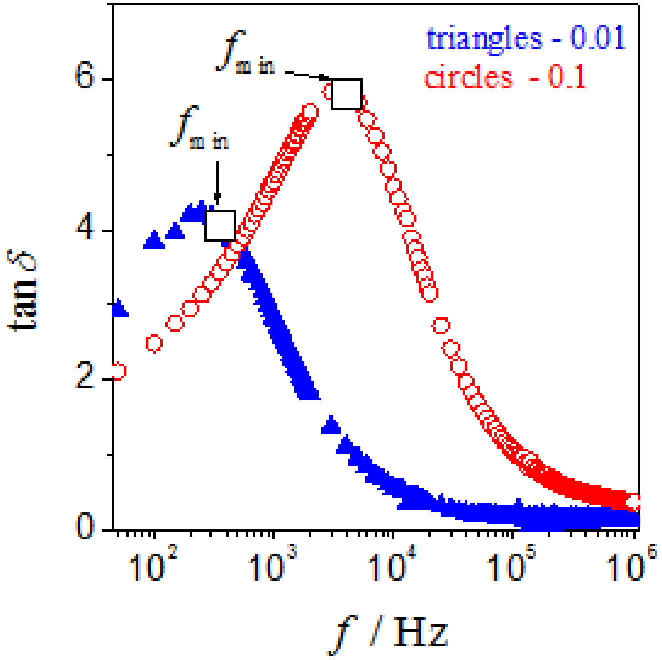
☐ for Debye approximation, one would have equality of the two frequencies $(\omega^{Z''}_{\min} = \omega^{\delta}_{\max})$

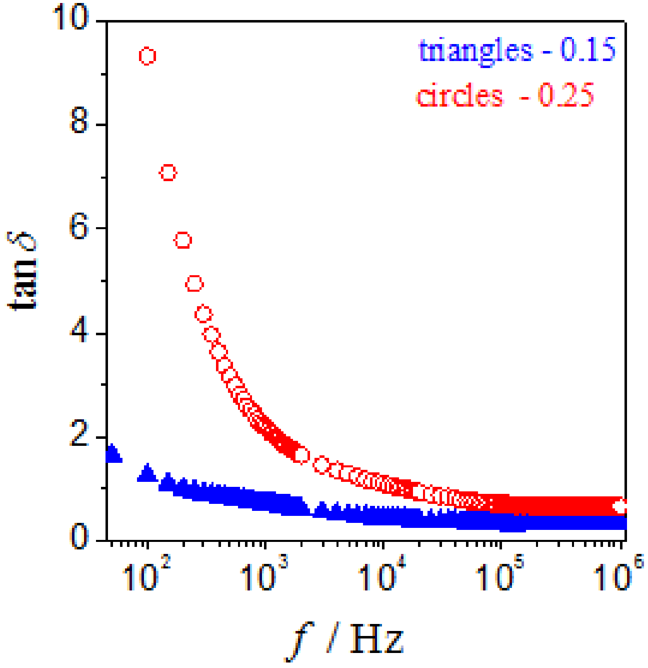
☐ dispersion of the relaxation times causes $(\omega^{Z''}_{\min} > \omega^{\delta}_{\max})$.

tanδ *versus* frequency for PEO systems at different Y_S

open squares mark $\omega^{\delta}_{\max} \underset{\approx}{<} \omega^{Z''}_{\min}$

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





tanδ *versus* frequency for **PEO** systems at different Y_S

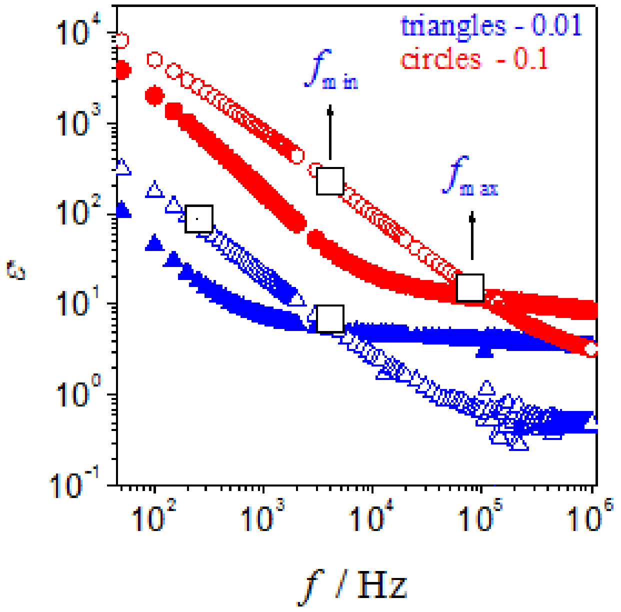
open squares mark $\omega^{\delta}_{\max} \underset{\approx}{<} \omega^{Z''}_{\min}$

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

tanδ *versus* frequency for **ENR-25** systems at different Y_S

- monotonic decrease in tanδ that is no dipolar relaxation emanates
- No electrode-polarization relaxation

Summary



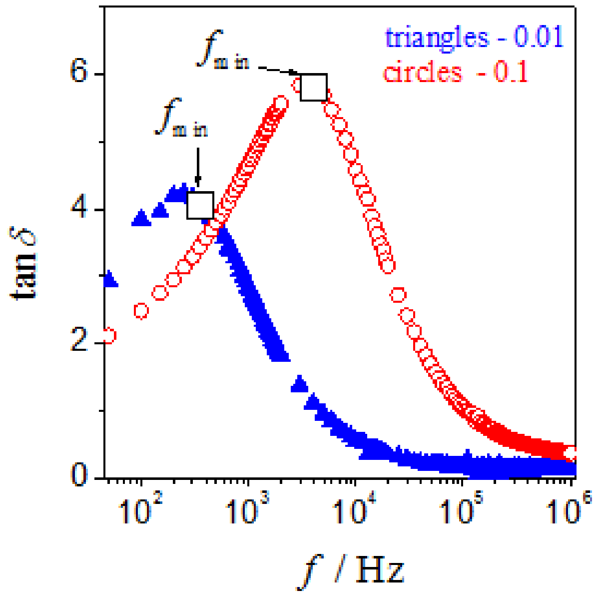
No relaxation peak

Permittivity *versus* frequency for **PEO** at room temperature for Y_S = 0.01 and 0.1

squares mark ω_{min} and ω_{max} of Z''

solid markers – ε'

open markers – ε''



relaxation peak

tanδ *versus* frequency for **PEO** systems at different Y_S

open squares mark $\omega^{\delta}_{\text{max}} \underset{\approx}{<} \omega^{Z''}_{\text{min}}$

- ☐ Dipolar relaxation in the electrode-polarization process (as strong coupling of dipole motion along polymer chains and segmental relaxation of polymer) displayed here by tanδ but no relaxation peak in ε''.
- ☐ **Electrode-polarization relaxation** as coined by localized dipolar motion restricted by surrounding polymer chains.

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General versions of modulus and impedance

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

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

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

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

Electric modulus might be given as dynamic quantity, $M'' \propto \dot{Z}'$ with $\dot{Z}'$ being time derivative of Z'. After a few manipulations, we get the symmetric version pointing towards the center of the problem:

$M'' \propto \omega Z'$ **(3)**

$\dfrac{Z''}{R} \propto \omega\varepsilon'$ **(4)**

- Eq. (3) manifests, imaginary part of modulus points towards electric relaxation or non-local transport of charged entities in the low-frequency range ($\omega_{\mathrm{min}} \leq \omega \leq \omega_{\mathrm{max}}$).
- It indicates long-range motion of dipoles coupled to segmental motions of chains in the low-frequency range.
- It is a complement to imaginary part of impedance, Eq. (4), which reflects dielectric relaxation bound to short-range irregular motion of charges.

For low-frequency range ($\omega_{\min} \le \omega \le \omega_{\max}$):

Neither Z' nor ε' display an extreme value, but $\omega Z'$ and $\omega\varepsilon'$ do. Eqs. (3) and (8) read in full

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

$$Z'' = C_o |Z|^2 \ \omega\varepsilon'$$

Hence,

$$M'' = \omega\tau \quad \text{with } C_o R = \tau$$

$$\frac{Z''}{R} = \varepsilon' \omega\tau$$

Thus, for **ideal Debye relaxation**, we have

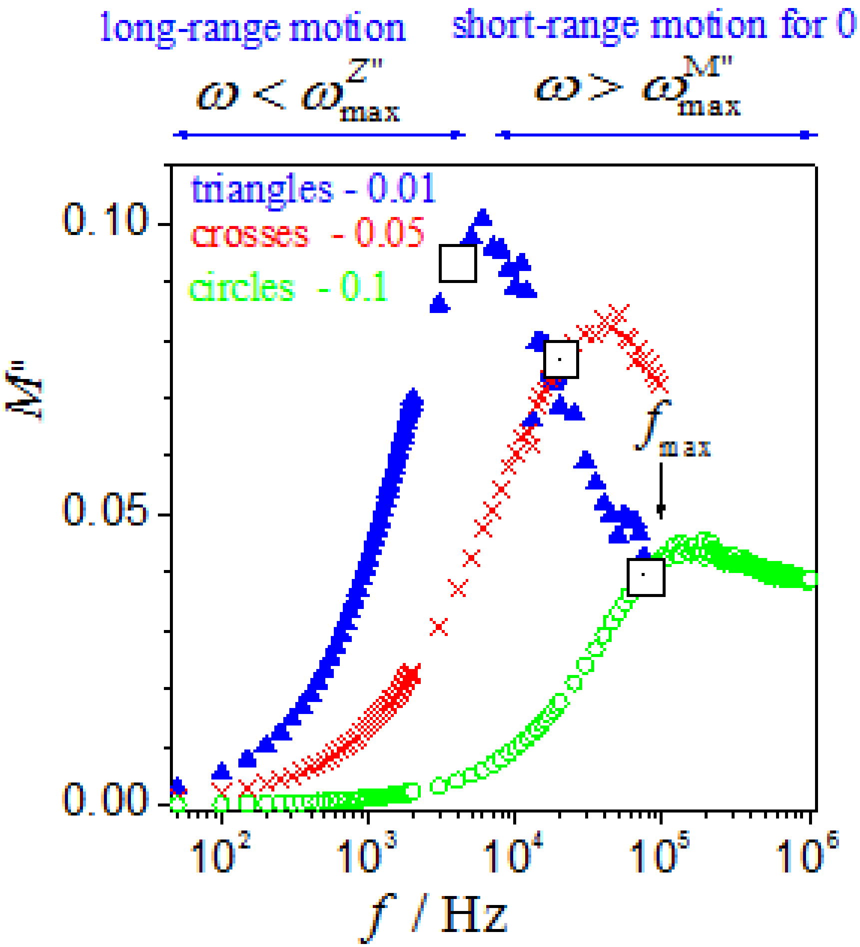
$$(M'')_{\max} = \left(\frac{Z''}{R}\right)_{\max}$$

since $\omega_{\max}\tau = 1$. Hence, we observe **collapse of the two functions in one master curve**.

$$(M'')_{\max} = \left(\frac{Z''}{R}\right)_{\max}$$

non-localized or long-range electric motion

localized dipolar motion



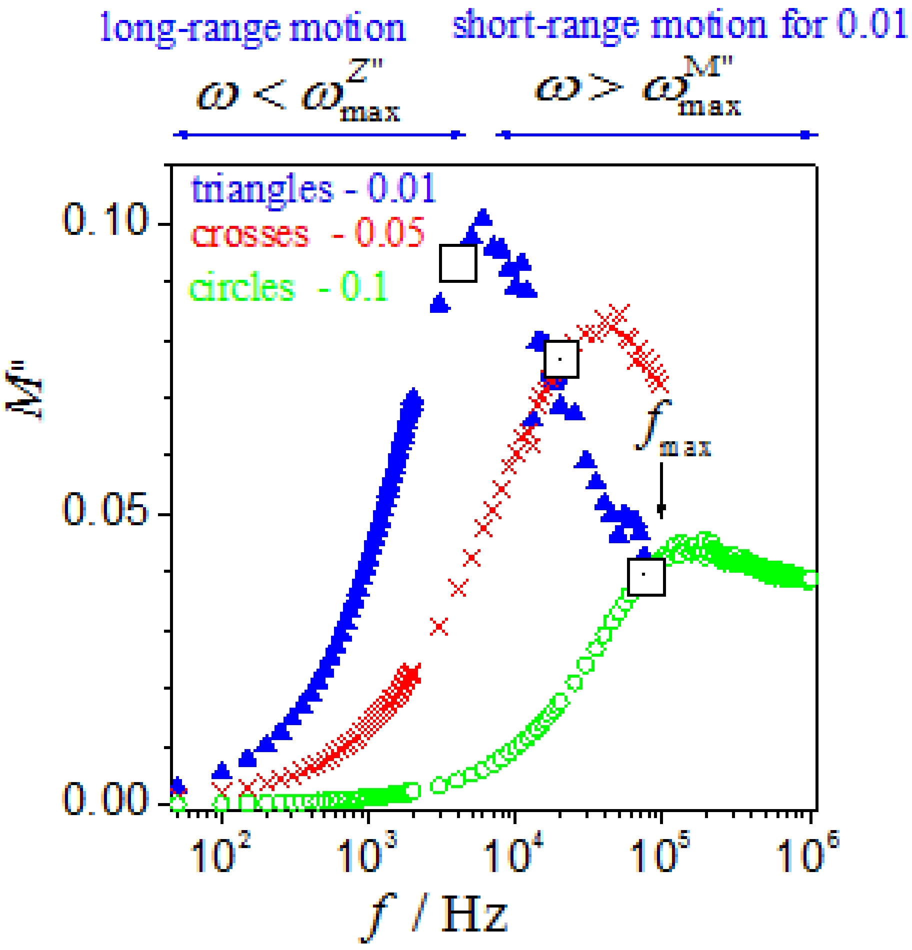
M'' versus frequency for **PEO** systems at indicated Y_S

squares give $\omega^{Z''}_{\max}$

$$\omega^{Z''}_{\max} < \omega^{Z'/Z''}_{\mathrm{cross}} < \omega^{M''}_{\max}$$

- reflects dispersion of relaxation times. Coincidence of the three characteristic frequencies provides information on the process ruling charge transport in the system.
- $\omega^{M''}_{\max}$ reflecting the transition from long-range motion for frequencies $\omega < \omega^{M''}_{\max}$ to local irregular motion in the range of high frequencies because charged entities cannot follow any more externally imposed rapid changes of electric field.

$$\omega_{\max}^{Z''} = \omega_{\text{cross}}^{Z'/Z''} = \omega_{\max}^{M''}$$



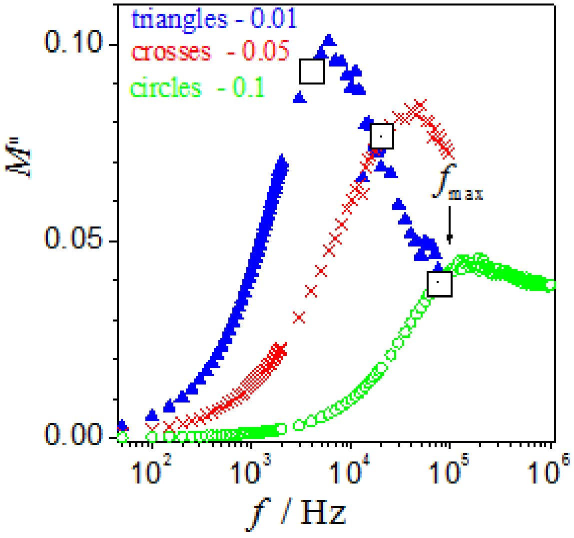
M″ versus frequency for **PEO** systems at indicated Y_S

squares give $\omega_{\max}^{Z''}$

- ❑ condensation of the two scaled functions $Z'/Z''_{\max}$ and appears $M''/M''_{\max}$ as natural consequence.
- ❑ Hence, dominance of electric relaxation or long-range motion of charged entities for frequencies $\omega < \omega_{\max}^{Z''}$ and short-range motions become dominant only for $\omega > \omega_{\max}^{M''}$.

PEO at Y_S

relaxation peak

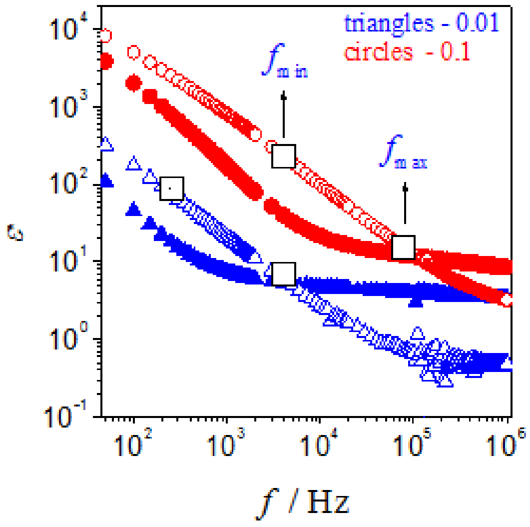


M'' versus frequency

squares give $\omega^{Z''}_{\max}$

$$\omega^{Z''}_{\max} = \omega^{Z'/Z''}_{\text{cross}} = \omega^{M''}_{\max}$$

No relaxation peak



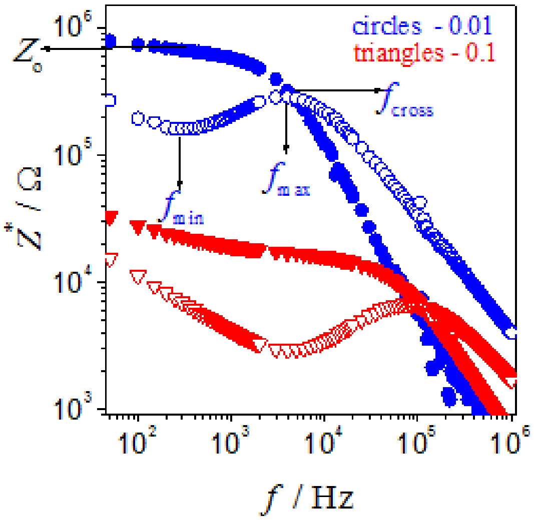
Permittivity *versus* frequency

squares mark $\omega_{\min}$ and $\omega_{\max}$ of *Z''*

solid markers – ε'

open markers – ε''

relaxation peak



Impedance *versus* frequency

solid markers – real part

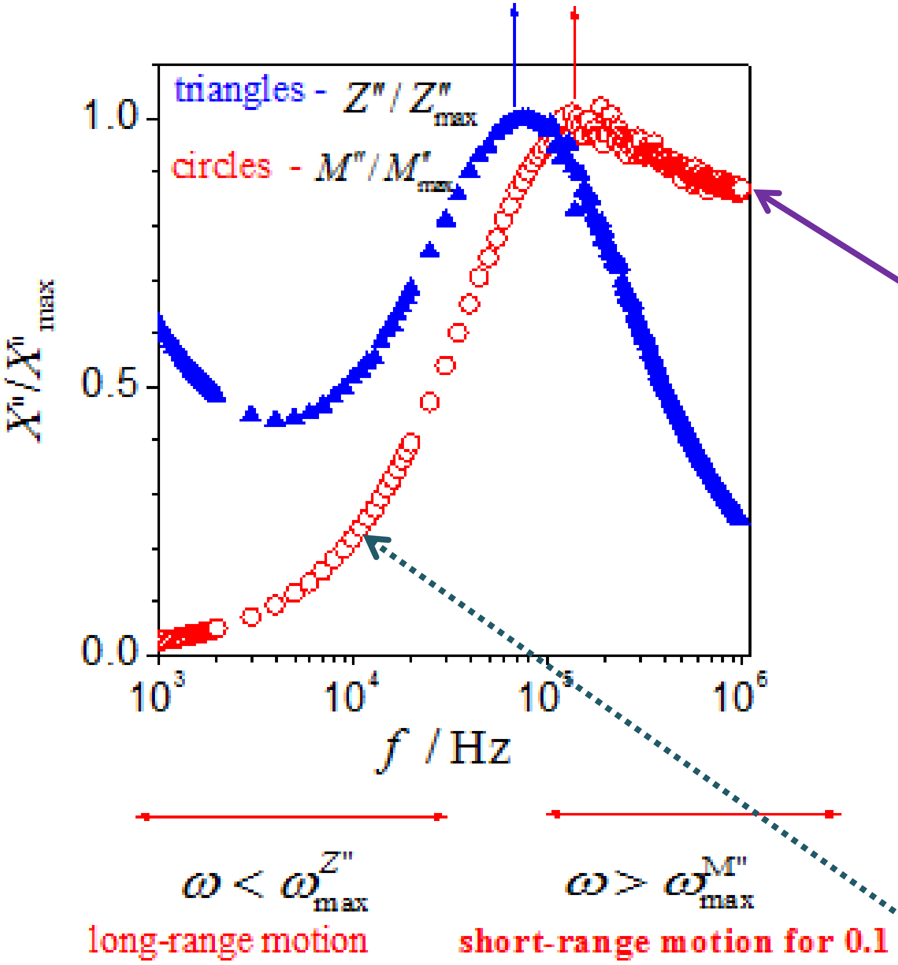
open markers – imaginary part

Generally, for **conduction based on long-range motion**:-

- a relaxation peak appears in spectrum $M''(\omega)$,
- no peak occurs in the corresponding $\varepsilon''(\omega)$-spectrum.
- a peak representing the dielectric relaxation process occurs in $Z''(\omega)$

Summary

$$\left(\frac{Z''}{Z''_{\max}}\right) \neq \left(\frac{M''}{M''_{\max}}\right)$$



Scaled representation $X' / X''_{\max}$ for **PEO** system at $Y_S = 0.1$

- This system is coined by mismatch of the two scaled functions.
- Addition of salt to PEO leads to reduced influence of crystallinity of PEO on the expense of long-range motion or dominance of dielectric relaxation.
- Charge transport is governed by short-range incessant random motions. In other words, it indicates conductivity is dominated by localized motion of dipolar structures in the PEO systems. Long-range motions / charge transports are of minor influence.

Outline

1. **Background**
2. **Electrochemical Impedance Spectroscopy (EIS) for dielectric relaxation of polymer electrolytes**
3. **Impedance spectra**
   - ☐ 2-component (polymer + salt) systems
   - ☐ 2-component – electrolyte and non-electrolyte
     1. a. Impedance spectra
     2. b. Permittivity spectra
     3. c. Tangent loss spectra
     4. d. Electric modulus
     5. e. Conductivity spectra
4. **Conclusion**

Conductivity σ is related to dynamic permittivity in the linear range

$$\sigma^{*} = \varepsilon_{o}\dot{\varepsilon}^{*} \qquad \textbf{(5)}$$

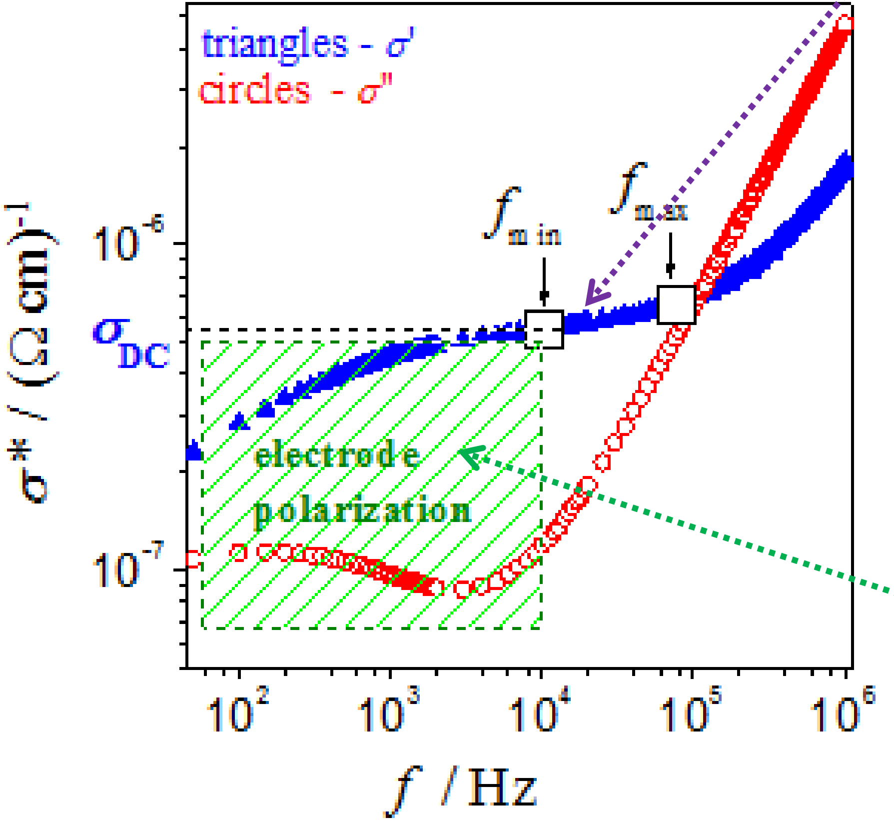
For periodic changes, Eq. (5) turns into $\sigma^{*} = i\omega\varepsilon_{0}\varepsilon^{*}$. Real and imaginary parts of conductivity are related to permittivity as in Eq. (6)

$$\sigma' \propto \omega\varepsilon'' \qquad \sigma'' \propto \omega\varepsilon' \qquad \textbf{(6)}$$

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

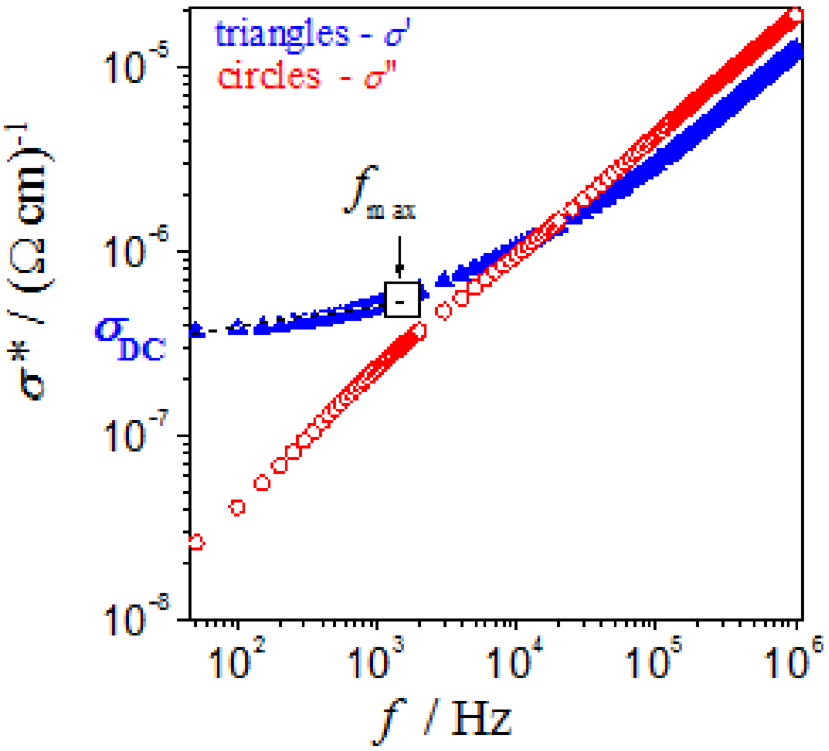
Imaginary part of permittivity is related to dissipation of energy by conduction. After Eq. (6) and $\varepsilon'' \propto \frac{1}{\omega^{n}}$,

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



Complex conductivity *versus* frequency for **PEO** system at $Y_S = 0.1$
squares symbolize ω_{min} and ω_{max}

- slight increase in conductivity σ' in the range between characteristic frequencies, ω_{min} and ω_{max}, indicating slight deviation from Debye relaxation.
- Extrapolation to frequencies beyond ω_{min} yields $\sigma'(\omega \rightarrow 0) = \sigma_{DC}$ (DC conductivity)
- For frequencies $\omega < \omega_{min}$, 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



Complex conductivity *versus* frequency for **ENR-25** system at $Y_S = 0.25$

square marks ω_{max}

- Conductivity of ENR-25 systems (with the higher salt content) exhibits approximately the same conductivity σ' (10^{-6} S cm^{-1}) in the low frequency range as PEO systems.
- Real part of conductivity of ENR-25 system decreases below ω_{max} and eventually turns into constancy due to negligible electrode polarization. Thus, we observe conductivity in the low-frequency range at same order of magnitude for PEO and ENR systems, which is independent of polymer and depends only on salt content.
- The ENR-25 systems at low salt content are insulator. In contrast to PEO systems, it exhibits conductivity only at high salt content.

Outline

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Summary (1/2)

PEO + salt systems

1. Dipoles are developing (even without electric field) under the action of osicilating electric field, they are able to make different motions or there are different modes of motion.
2. **Most of dipoles are partly immobilized**, imprisoned in cages formed by molecular potential walls. They can carry out only **localized motions** because they are unable to be at rest (due to quantum mechanics). This mode is especially existent at high frequencies. **At low frequencies a few of them** (having the correct position) **can carry out non-localized motions**, for example **hopping** along the chain molecules.
3. In short, PEO sytems have dominant dielectric relaxation, localized motion, and to minor extent electric flow (long-range motion) in the low-frequency regime. **There are interactions between dipoles, but they are relaxing individual**ly.
4. Hence, we observe, σ^*, ε^* and M^* *versus* frequency show that **both dielectric relaxation** (dominant) **and charge transport** are contributing to conductivity.
5. We regard **PEO sytems as a polymer electrolyte**.

Summary (2/2)

ENR-25 + salt systems

1. At high salt content show only **one dielectric relaxation** peak, no relaxation related to electrode polarization (which is visible in tanδ) and no relaxation of dipoles after long-range motion (which is visible in M'').
2. ENR-25 systems comprise of **macroscopic dipoles (due to immobile dipolar entities)**. These macroscopic dipoles are illustrated as relaxation in Z'' spectra. These systems are unable to generate myriads of molecular dipoles.
3. In strictest sense, this **(ENR-25 + salt) system is not polymer electrolyte** at room temperature.

The presentation of this work emphasizes on how to discuss this difficult matter in simpler manner. This work is a summary of our previous contribution to polymer electrolytes

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Thank you

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