

Electrode Polarization and the Macdonald/Coelho Model

Electrode polarization occurs at low frequencies, where the transporting ions have sufficient time to polarize at the blocking electrodes during the cycle. That polarization manifests itself in (1) an increase in the effective capacitance of the cell (increasing the dielectric constant) and (2) a decrease in the in-phase part of the conductivity, as the polarizing ions reduce the field experienced by the transporting ions. The natural time scale for conduction is the time scale where ion motion becomes diffusive

$$\tau_{\sigma} \equiv \frac{\varepsilon_s \varepsilon_0}{\sigma_{DC}} \quad (1)$$

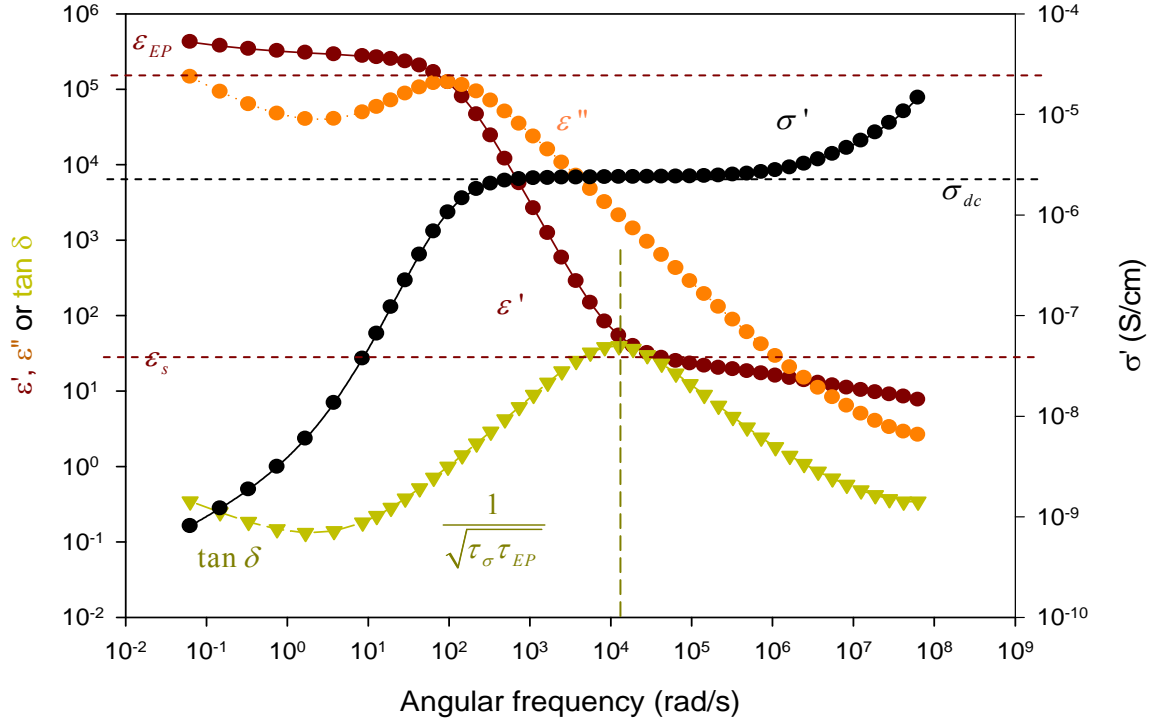
where ε_s is the static relative permittivity of the sample, ε_0 is the permittivity of vacuum and σ_{DC} is the DC conductivity, evaluated from a roughly 3-decade frequency range where the in-phase part of the conductivity $\sigma'(\omega) = \varepsilon''(\omega) \varepsilon_0 \omega$ is independent of frequency. At frequencies below $1/\tau_{\sigma}$ all ions participate equally in conduction and the in-phase part of the conductivity σ' becomes independent of frequency. At frequencies far below $1/\tau_{\sigma}$ the conducting ions start to polarize at the electrodes and fully polarize at the electrode polarization time scale

$$\tau_{EP} \equiv \frac{\varepsilon_{EP} \varepsilon_0}{\sigma_{DC}} \quad (2)$$

where ε_{EP} is the (considerably larger) effective permittivity after the electrode polarization is complete. The Macdonald/Coelho model treats electrode polarization as a simple Debye relaxation with loss tangent

$$\tan \delta = \frac{\omega \tau_{EP}}{1 + \omega^2 \tau_{\sigma} \tau_{EP}} \quad (3)$$

In practice, the conduction time scale τ_{σ} and electrode polarization time scale τ_{EP} are calculated from fitting the measured loss tangent associated with electrode polarization to Eq. (3). The peak in $\tan \delta$ occurs at the geometric mean of τ_{σ} and τ_{EP} .



The Macdonald/Coelho model then determines the number density of conducting ions p and their mobility μ from τ_{EP}

$$p = \frac{1}{\pi l_B L^2} \left(\frac{\tau_{EP}}{\tau_\sigma} \right)^2 \quad (4)$$

$$\mu = \frac{eL^2 \tau_\sigma}{4\tau_{EP}^2 kT} \quad (5)$$

where $l_B \equiv e^2 / (4\pi\epsilon_s \epsilon_0 kT)$ is the Bjerrum length, L is the spacing between electrodes, e is the elementary charge, k is the Boltzmann constant and T is absolute temperature. The time scale for electrode polarization τ_{EP} is proportional to the electrode spacing L in the Macdonald/Coelho model, making the number density of conducting ions p and their mobility μ material properties that are independent of L . A material property relevant for actuation is τ_{EP} / L , obtained from Eq. (5).

$$\frac{\tau_{EP}}{L} = \sqrt{\frac{e\tau_\sigma}{4\mu kT}} = \frac{1}{\mu} \sqrt{\frac{\epsilon_s \epsilon_0}{4pkT}} \quad (6)$$

Here we used Eq. (1) and the relation $\sigma_{DC} = e\mu p$, where e is the elementary ionic charge. For fast actuation, ion-conducting membranes need to be thin (small L) have high mobility μ of conducting ions, and a high conducting ion content p .

Actuation can be modeled as an equivalent resistor-capacitor circuit, with the time scale for polarization (or charging) $\tau_{EP} = RC$, where R is the resistance and C the capacitance of the equivalent circuit. The actuation is created on time scale τ_{EP} by a build-up of conducting ions in the Stern layer (within the Debye length of the electrode). The charge Q built up in the Stern layer is directly proportional to the applied voltage V , as $Q = CV = \tau_{EP}V/R$. With the resistance $R = L/(\sigma_{DC}A)$, where A is the electrode surface area, we have a simple relation for the charge accumulation per unit of electrode surface area (charge density).

$$\frac{Q}{A} = \frac{\tau_{EP}}{L} V \sigma_{DC} \quad (7)$$

Hence, the material property τ_{EP}/L multiplied by the conductivity σ_{DC} determines the charge density at the electrode. Combining Eqs. (6) and (7) writes the charge density in terms of the number density of conducting ions and the dielectric constant.

$$\frac{Q}{A} = Ve \sqrt{\frac{\epsilon_s \epsilon_0 p}{4kT}} \quad (8)$$

To increase the charge density of polarizing ions (and hence the strain in the actuator) we need membranes with large dielectric constant ϵ_s and large number density of conducting ions p .

The above is based on linear response theory. The Macdonald/Coelho model assumes that the build-up of ions near the electrode is sufficiently small that they do not interact with other ions near the electrode. Nonlinear electrode polarization will occur when the polarizing ions start to interact with each other – when they are separated by the Bjerrum length on the electrode surface (where their Coulomb repulsion is the thermal energy).

$$l_B = \frac{e^2}{4\pi\epsilon_0\epsilon_s kT} \quad (9)$$

The relevant dimensionless parameter is (from Eq. 7) ions per square Bjerrum length.

$$\frac{Ql_B^2}{Ae} = \frac{\tau_{EP}V\sigma_{DC}l_B^2}{Le} = \frac{\tau_{EP}eV\sigma_{DC}l_B}{4\pi\epsilon_0\epsilon_s kTL} < 1 \quad (10)$$

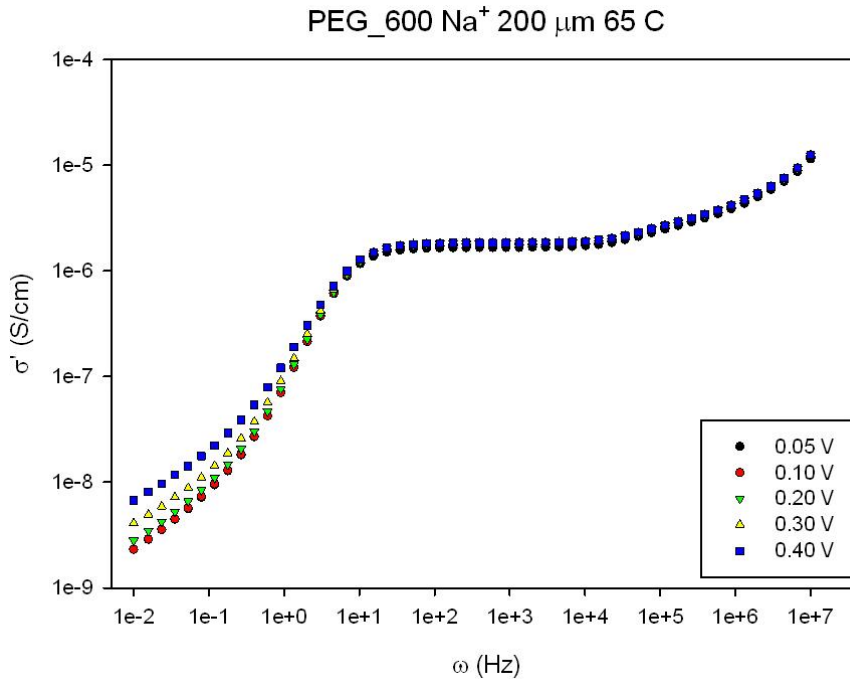
Or from Eq. 8

$$\frac{Ql_B^2}{Ae} = Vl_B^2 \sqrt{\frac{\epsilon_s \epsilon_0 p}{4kT}} = \frac{eV}{kT} \sqrt{\frac{pl_B^3}{16\pi}} < 1 \quad (11)$$

Since our typical ionomeric single-ion conductor, 100% sulfonated PEG600-Na at 65 °C has $\epsilon_s = 88$, $l_B = 0.6$ nm and $p = 0.0002$ nm⁻³, we expect

$$\sqrt{\frac{pl_B^3}{16\pi}} = 0.001$$

And nonlinearities should start when the applied voltage is of order 0.1 volt. The data at



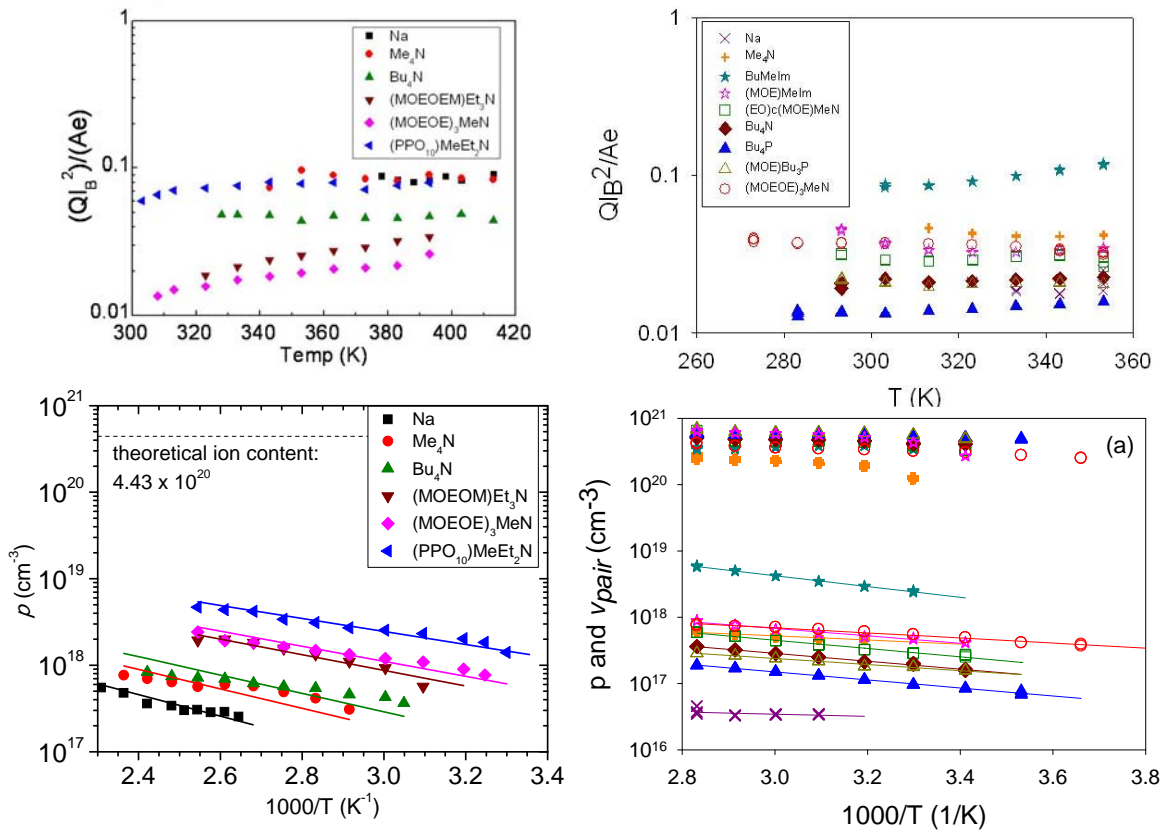
left suggest that nonlinear effects are first seen between 0.1 and 0.2 V, for a 200 μm thick sample. The DC conductivity is independent of voltage to at least

2V but EP is nonlinear (the low frequency drop in σ' is the consequence of EP).

The dimensionless parameter of Eqs. 10 and 11 is shown, along with conducting ion content p from Eq. 4, for two other ionomer systems with various counterions below.

Polyurethane carboxylate PEG600- ionomers

Aldrich Polyester Sulfonated Phthalate Ionomer



All the above data were taken at 0.1 V amplitude with 100 μm sample thickness. The data at left are for a sulfonated polyester ionomer sold by Aldrich as the Na-salt and ion exchanged with a variety of larger counterions. The data at right are for a polyurethane carboxylate ionomer based on PEG600, made in the acid form and titrated with the appropriate base. All of these data show $0.01 < Ql_B^2/(Ae) < 0.1$, with the trend that larger counterions usually have higher conducting ion content and larger $Ql_B^2/(Ae)$ but of course there are also differences in dielectric constant for these ionomers with different counterions and that changes the Bjerrum length in Eq. 11. Collectively this suggests that 0.1 V is safely linear response for all of these ions but that the onset voltage for nonlinear effects in electrode polarization will depend on the particular ionomer and counterion, through the conducting ion content and dielectric constant (Bjerrum length).