Entropic Restrictions Control the Electric Conductance of Superprotonic Ionic Solids

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1 Matrix entropy as a function of porosity.

The eqn (15) in the main text was proposed on the basis of experimental evidence.^{1,2} We first note that, in general, the dependence of the porosity on the applied pressure can be modeled by a relation of the form: $P(\phi) = P_0 \phi^{-\gamma}$, with P_0 a reference pressure and γ an exponent. Now, the eqn (15) can be derived from thermodynamic considerations by recasting that a phase transition between states 1 and 2 is described by the Clapeyron equation, which is given by

$$\frac{dP}{dT} = \frac{\Delta S_{12}}{V_0 \Delta \phi},\tag{1}$$

where we used the fact that the volume may be written as proportional to the porosity $V = V_0 \phi$, with V_0 a reference volume. Assuming that pressure depends on temperature through the porosity: $P(T) = P[\phi(T)]$ and using the chain rule, the last equation can be written in the form

$$\frac{\Delta S_{12}}{\Delta \phi} = V_0 \frac{dP}{d\phi} \frac{d\phi}{dT}.$$
(2)

Using the definition of the thermal expansion coefficient and the relation for ϕ , we have $\alpha = (1/\phi)d\phi/dT$. Assuming in addition that the dependence of the pressure on ϕ is $\gamma \simeq 1$, then eq 2 can be written in the differential form $dS_{21} = -dS_{12} = -\alpha k_B T d\phi/\phi$, where $V_0 P_0 \sim k_B T$. Integration of this equation gives

$$\Delta S_{12} = -\alpha k_B T \ln \left| \frac{\phi}{\phi_0} \right|,\tag{3}$$

where ϕ_0 is a reference volume fraction. For instance, in the transition from monoclinic (mn) to cubic (cub) phases ϕ_0 , corresponds to ϕ_{mn} . The eq 3 coincides with the referred eq 15.

2 General formula for the effective conductivity

The most simple dependence of the local properties for the electrical current inside confined ionic channels or pores of the material can be analyzed in analogy with the migration of particles in presence of a concentration gradient.^{3,4} Following this analogy, the total number of electrons crossing a membrane is proportional to its width W and to the gradient of the electrochemical potential which can be approximated as $\Delta \mu/L$ with L the total length of the membrane. However, in the local scale, since the electrons only pass through the void spaces, the number of electrons crossing per unit of time has to be the same when only the void space is considered, and therefore, it has to be proportional to the average width of the pore $\langle \omega(x) \rangle$ and to the local gradient which can be written as $\Delta \mu_x/L_x$ where L_x is the average real length that the electrons have to travel inside the pore. In general, this distance L_x is greater than the length of the membrane L accounting for the tortuosity factor of the membrane. Therefore, charge conservation in the stationary state implies

$$\hat{\sigma}_{\nu}W\frac{\Delta\mu}{L} = \sigma_{\nu,0} \langle w \rangle \frac{\Delta\mu_x}{L_x}.$$
(4)

where $\sigma_{\nu,0}$ is the local conductivity, that is, the one being measured when the pores are very wide and the effects of the geometry of the pore can be neglected. In contrast, $\hat{\sigma}_{\nu}$ is the effective electrical conductivity of the membrane which takes into account the diminution of the flux due to the presence of inaccessible space in the material.

Taking into account that the electrochemical potential is measured by unit of volume, it can be proven that $\Delta \mu_x L_x = \delta L \Delta \mu$ where δ measures the constriction factor of the porous material and whose precise mathematical form at first order is⁵

$$\delta = \left\langle \frac{1}{w(x)} \right\rangle \langle w(x) \rangle. \tag{5}$$

Substituting the last two equations in eqn (4), we find that the effective conductivity is

$$\hat{\sigma}_{\nu} = \sigma_{\nu,0} \frac{\phi}{\tau} \delta. \tag{6}$$

The three geometrical parameters are the porosity $\phi = \langle w(x) \rangle / W$ which measures the diminution of the available space, the tortuosity $\tau = (L_x/L)^2$ which measures the elongation of the path effective distance that charged particles have to travel inside the pores and finally, the constriction factor δ given before, which takes into account the geometrical aspects of the corrugation of the pore and the effects of surface reactions in the pore.^{3–5} The formula deduced here analytically coincides with the macroscopic reduction of the flux encountered in experiments.^{6,7}

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