

**Fractional Calculus applied for Derivation of Impedance of Porous  
Electrolyte System having Anomalous Diffusion-Drift and Complex  
Adsorption and Desorption as Surface Phenomenon**

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# **Fractional Calculus applied for Derivation of Impedance of Porous Electrolyte System having Anomalous Diffusion-Drift and Complex Adsorption and Desorption as Surface Phenomenon**

**Annexure to the Invited Talk Anomalous diffusion and its electrical response in impedance spectroscopy of polymer electrolytes-via-generalized fractional calculus for calculation details**

## **Abstract**

Here we do detailed derivation of impedance dispersion function, where electrolyte is porous, and electrodes considered as smooth. This impedance description arise due to transport of ions in a porous system and the process is split into two parts, one with anomalous diffusion-drift having fractional time derivatives and the other is integer order Fickian diffusion i.e. normal diffusion drift. The second process is Poisson's equation giving potential (Electric field) profile of the bulk electrolyte, and then application Gauss law to get charge density and then its derivative giving current density at the surface. The third process is taken at surface i.e. boundary condition considering the kinetics of adsorption-desorption which provides current density at electrode boundary, related to convolution of the memory-kernel with adsorption-desorption kinetics with fractional rate of change of ion density. This is different from blocking electrodes at the boundary. These new phenomenological expressions give finally impedance response dispersive function with frequency. This technique may be useful also for researchers observing the impedance dispersions in batteries and super-capacitors, and other electro-chemical analysis. This note is an annexure to the Invited Talk at Symposium CTTC-2013, at BARC, titled- "Anomalous diffusion and its electrical response in impedance spectroscopy of polymer electrolytes-via-generalized fractional calculus" for calculation details.

## Introduction

The impedance dispersion obtained in the experiments is due to the fact that the way ions participate in the process. The process is divided into three basic phenomena; the first one is diffusion-drift phenomena, which can be Fickian and non Fickian process governed by integer order time derivative and fractional order time derivative of the diffusing ions respectively. The non-integer order derivatives (fractional derivatives) in the rate of diffusing species tells the fact that the process is non-Markovian, and with memory. The non-Fickian nature of diffusion is first stated by Cattaneo in 1948. The anomalous impedance spectroscopy data as obtained in these experiments may be related to anomalous diffusion happening in the bulk material (electrolyte) due to spatial disorder in the solid electrolyte matrix. The spatial disorder also manifests as temporal fractional derivatives. This is one of the plausible reasons of ions in the bulk electrolyte (in this case solid polymer) obeying fractional diffusion equation at the small time scales and normal integer order diffusion equation at larger time scale. The process of mixed transport i.e. governed by fractional order and integer order taking place simultaneously is one of the plausible causes for anomalous response in electrical impedance-observed. The second process that is the local charge separation giving rise to potential and we write the Poisson's expression to get the potential profile in the bulk electrolyte and thus the Electric field function. We then apply (at the boundary electrodes) the Gauss's law to get the surface charge density and thereby the total charges at the surface; from there we derive the rate of change of the total charge, giving current function. The potential at the electrode and the current at the electrodes give the impedance function. The third phenomena which is very important is at the surfaces (the two electrodes), the kinetics of adsorption-desorption which gives the current density at the boundary-related to convolution of 'memory kernel' with the adsorption-desorption kinetics having fractional rate of change of ion density. With memory kernel as zero we get the blocking electrode case –i.e. the current at the boundary is zero- a classical case.

The anomalous response is at low frequencies, where it is observed that the real part of the impedance increases with decrease in frequency. This can be explained by adding fractional order impedance in the calculations. By taking the electrode (brass metal) electrolyte impedance as

$$Z_i(\omega) = C_q (i\omega)^{-q} \quad C_q > 0; \quad 0 < q < 1$$

We can explain the growing impedance as frequency decreases. This interfacial impedance contributes to total resistance of cell with term

$$\text{Re}\{Z_i\} = \text{Re}\{C_q (i\omega)^{-q}\} = C_q \omega^{-q} \cos\left(q \frac{\pi}{2}\right)$$

which is frequency dependent and particularly as  $\omega \rightarrow 0$  it diverges, that is one way to explain the anomalous impedance observed. But in the interface impedance the manifestation of fractional order ( $q$ ) comes about due to roughness in electrode surface (as observed in the super-capacitors); whereas in our case the brass electrodes are smooth, without noticeable roughness. The other way to explain this anomalous behavior to have different mobility for anions and cations and therefore different diffusion constants,

$$D_+ = 10D_-$$

But we are dealing with ions having same mobility and the diffusion constants those are  $H_3O^+$ ;  $OH^-$ .

We modify the theory on the basis of the fact that some fraction of the charge carriers ( $h$ ) diffuse through normal admittance and rest  $(1-h)$  with anomalous admittance. The material consists of a uniform “solvent” with, equally charged positive and negative ions moving with same mobility. The solvent is assumed to have an effective dielectric constant  $\varepsilon$  for particular plasticizer content. The sample has surface area  $S$  and thickness  $d$  is placed between the brass electrodes. The anomalous response is at low frequencies, where it is observed that the real part of the impedance increases with decrease in frequency.

This phenomena does not get reflected by usual (integer order) Poisson-Nernst-Plank (PNP) theory with boundary condition of blocking electrodes. The PNP theory visualizes constant and flat real impedance at low frequency, with a high frequency cut-off like a true low pass filter; fails to catch experimentally observed real part of impedance function rising with decrease of frequency.

The PNP is integer order differential equation theory-perhaps is inadequate to imbibe the complex mechanism if memorized relaxation (a non-Debye process), and complex adsorption-desorption processes at the electrodes (complex surface effects) are reckoned to play important role in observed impedance spectra.

## Theoretical Model

### Constitutive equation for bulk electrolyte with generalized calculus

We write the constitutive for bulk electrolyte as follows

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t) \quad q \in (0, 1) \dots\dots\dots(1)$$

This (1) is fractional diffusion equation with distributed order where  $n_\alpha(z, t)$  represents the bulk number density of diffusing and drifting species  $\alpha = +$  for positive species and  $\alpha = -$  for negative species, and  $j_\alpha(z, t)$  is current flux .The (1) is generalization of normal integer order constitutive equation of Diffusion, which is the following

$$\frac{\partial}{\partial t} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t)$$

Which we get if we have in (1) the kernel  $k(q) = \delta(q - 1)$ , demonstrated below

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = \int_0^1 dq (\delta(q - 1)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = \frac{\partial^1}{\partial t^1} n_\alpha(z, t) = \frac{\partial}{\partial t} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t)$$

We have used property of delta function that is

$$\int_b^d dx (\delta(x - c)) f(x) = f(c) \quad b \leq c \leq d$$

The kernel  $k(q)$  is a distribution function in general a continuous function of the fractional order  $q$  between zero and one, in our diffusion case we are having spread of fractional order between zero and one, thus we limit our integration in such a way.

The fractional order derivatives imbibe memory in relaxation of  $n_\alpha(z, t)$ . The second constitutive equation is current density is given by

$$j_\alpha(z, t) = -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz} \dots\dots\dots(2)$$

$\mathbb{D}$  is diffusion coefficient,  $V$  is the excitation voltage,  $T$  is the ambient temperature,  $k_B$  is Boltzmann constant,  $q_e$  is the electronic charge.

The fractional derivative of the order  $q$  is Caputo's derivative. This definition of fractional derivative is requiring that  $n_\alpha(z, t)$  be a differentiable function in the interval of interest at all points. The definition of Caputo derivative is

$${}^C D_t^q n_\alpha(z, t) = \frac{\partial^q}{\partial t^q} n_\alpha(z, t) \triangleq \frac{1}{\Gamma(k-q)} \int_{t_0}^t dt' (t-t')^{-q+k-1} n_\alpha^{(k)}(z, t') \dots\dots\dots(3)$$

$$k-1 < q < k, \quad k \in \mathbb{Z}^+, \quad q \in \mathbb{R}^+$$

The  $n_\alpha^{(k)} \equiv \frac{\partial^k}{\partial t^k} n_\alpha(z, t)$ , is the  $k$ -th integer order derivative (just greater than real order  $q$ ).

We use Caputo's fractional derivative instead of classical Riemann-Liouville (RL), for ease. The Caputo derivative requires differentiability condition where as the RL derivative requires function to be continuous need not be differentiable. RL derivative of a constant is not zero, but a decaying power function. If the process of differentiation is starting at start point of minus infinity the RL derivative of constant is zero. We use the property of Caputo derivative in the derivation with perturbation i.e.  ${}^C D_t^q(N) = 0$ , where  $N$  is constant number; as demonstrated in detail in subsequent sections for impedance calculations.

Taking  $k(q) = a\delta(q-1) + b\delta(q-q_0)$  in (1) and with (2) we obtain the fractional diffusion-drift equation as follows.

$$a \frac{\partial}{\partial t} n_\alpha(z, t) + b \frac{\partial^{q_0}}{\partial t^{q_0}} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t) = \mathbb{D} \frac{\partial^2 n_\alpha(z, t)}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{d^2 V}{dz^2}$$

The above is a diffusion-drift equation with order one with weight  $a$  and also with fractional order  $q_0 \in (0,1)$ , with weight  $b$

The dimension of  $a$  is nil i.e. dimensionless, and  $b$  has the dimension of  $[\text{sec}]^{q_0-1}$ . If we have small a perturbation of harmonic nature for voltage excitation say  $V(z,t) = \phi(z)e^{i\omega t}$  then the ion density too will have perturbation as  $n_\alpha(z,t) = N + \delta n_\alpha(z,t)$ ; where  $N$  is constant, and  $\delta n_\alpha(z,t) = n_\alpha(z)e^{i\omega t}$  for ions we can write the above diffusion-drift equation as follows:

$$\left[ a(i\omega) + b(i\omega)^{q_0} \right] n_\alpha(z) = \mathbb{D} \left[ n_\alpha''(z) \pm \frac{q_e N}{k_B T} \phi''(z) \right]$$

The double prime at RHS is double derivative w.r.t.  $z$ . With  $a=1$  and  $b=0$  we have normal integer order diffusion equation, and putting perturbed values we obtain:

$$i\omega n_\alpha(z) = \mathbb{D}_e \left[ n_\alpha''(z) \pm \frac{q_e N}{k_B T} \phi''(z) \right]$$

Clearly if, in the integer order system, we replace  $\mathbb{D}_e \equiv \mathbb{D} / \left[ a + b(i\omega)^{q_0-1} \right]$ , we obtain the generalized diffusion-drift equation with kernel  $k(q) = a\delta(q-1) + b\delta(q-q_0)$ . The diffusion constant has a property of frequency dependency. For integer order diffusion equation with  $a=1$  and  $b=0$ , we have the case where  $\mathbb{D}_e = \mathbb{D}$  frequency independent case, but for a pure fractional order case with fractional order  $q_0$  we get a frequency dependent diffusion constant. Put  $a=0$  and  $b=1$ , we get  $\mathbb{D}_e = \mathbb{D} / (i\omega)^{q_0-1}$  for a pure fractional order diffusion-drift equation. This  $\mathbb{D}_e$  takes its form as the case may be with the diffusion-drift equation in the overall impedance function.

### **Memory Integral & Fractional Derivative and generalization of Diffusion-Drift equation with memory integral**

We write the time evolution of a dynamic system as

$$\frac{\partial}{\partial t} n_{\alpha}(t) = -\int_0^t d\bar{t} K_D(t-\bar{t}) n_{\alpha}(\bar{t}) = -K_D(t) * n_{\alpha}(t)$$

Above represents memory integral i.e. all instances for  $\bar{t} = 0$  to  $\bar{t} = t$  contribute to situation at present time. This above is convolution, represented by (\*) of memory kernel  $K_D(t)$  and the relaxing quantity i.e.  $n_{\alpha}(t)$ . A Markovian case is relaxation without memory. Say we have kernel  $K_D(t) = \delta(t) / \tau_D$ , then we will have differential equation of the relaxing species as

$$\frac{\partial}{\partial t} n_{\alpha}(t) + \frac{1}{\tau_D} n_{\alpha}(t) = 0$$

The relaxation will be of type  $n_{\alpha}(t) = n_{\alpha}(0)e^{-t/\tau_D}$ ; that is solution of the homogeneous equation.

With a power law memory kernel  $K_D(t) = K_0 t^{q-2}$ ;  $0 < q \leq 2$  we have the following:

$$\begin{aligned} \frac{\partial}{\partial t} n_{\alpha}(t) &= -\int_0^t d\bar{t} K_D(t-\bar{t}) n_{\alpha}(\bar{t}) = -\int_0^t d\bar{t} K_0 (t-\bar{t})^{q-2} n_{\alpha}(\bar{t}) \\ &= -\frac{K_0 \Gamma(q-1)}{\Gamma(q-1)} \int_0^t d\bar{t} (t-\bar{t})^{(q-1)-1} n_{\alpha}(\bar{t}) \\ &= -\frac{1}{\tau_D^q} \times \frac{1}{\Gamma(q-1)} \int_0^t d\bar{t} (t-\bar{t})^{(q-1)-1} n_{\alpha}(\bar{t}) \end{aligned}$$

In above we have  $\tau_D^q = [K_0 \Gamma(q-1)]^{-1}$ . The fractional integration of order  $\alpha \in \mathfrak{R}^+$  is defined as follows

$${}_a D_t^{-\alpha} f(t) \triangleq \frac{1}{\Gamma(\alpha)} \int_a^t d\bar{t} (t-\bar{t})^{\alpha-1} f(\bar{t})$$

Using this definition we can write above expression in compact form i.e.

$$\frac{\partial}{\partial t} n_{\alpha}(t) = -\frac{1}{\tau_D^q} [{}_0 D_t^{-(q-1)} n_{\alpha}(t)] = -\frac{1}{\tau_D^q} [{}_0 D_t^{1-q} n_{\alpha}(t)]$$

Integrating both sides once we get



$$\begin{aligned}\int_0^t d\bar{t} \frac{\partial}{\partial \bar{t}} n_\alpha(\bar{t}) &= -\frac{1}{\tau^q} \left[ \int_0^t d\bar{t} {}_0 D_{\bar{t}}^{1-q} n_\alpha(\bar{t}) \right] \\ &= -\frac{1}{\tau_D^q} \left[ {}_0 D_t^{-1} {}_0 D_t^{1-q} n_\alpha(t) \right]\end{aligned}$$

$$n_\alpha(t) - n_\alpha(0) = -\tau_D^{-q} {}_0 D_t^{-q} n_\alpha(t)$$

Now we take Caputo derivative of order  $q$  on the both sides recognizing  $n_\alpha(0)$  is constant, and its Caputo derivative is zero we get fractional relaxation equation as

$${}_0^C D_t^q n_\alpha(t) + \frac{1}{\tau_D^q} n_\alpha(t) = 0$$

We got fractional order differential equation of relaxation, when the memory kernel is a slowly decaying power law.

We have the integer order diffusion-drift equation with its frequency domain expression as follows, with  $n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$  and  $V(z, t) = \phi(z) e^{i\omega t}$ .

$$\frac{\partial}{\partial t} n_\alpha(z, t) = \mathbb{D}_e \frac{\partial}{\partial z} \left[ \frac{\partial n_\alpha(z, t)}{\partial z} \pm \frac{q_e N}{k_B T} \frac{dV}{dz} \right] \quad (i\omega) n_\alpha(z) = \mathbb{D}_e \left[ n_\alpha''(z) \pm \frac{q_e N}{k_B T} \phi''(z) \right]$$

We used  $\frac{\partial}{\partial t} \equiv i\omega$ , in above frequency domain representation. If we add memory kernel for a relaxation of following type

$$\frac{\partial}{\partial t} n_\alpha(t) = -\int_{-\infty}^t d\bar{t} K_D(t-\bar{t}) n_\alpha(\bar{t})$$

we then have consolidated expression with memory integral as memory based diffusion-drift equation as:

$$\frac{\partial}{\partial t} n_\alpha(z, t) = \mathbb{D}_e \frac{\partial}{\partial z} \left[ \frac{\partial n_\alpha(z, t)}{\partial z} \pm \frac{q_e N}{k_B T} \frac{dV}{dz} \right] - \int_{-\infty}^t d\bar{t} K_D(t-\bar{t}) n_\alpha(z, \bar{t})$$

Note that we have purposely used  $\mathbb{D}$  instead of  $\mathbb{D}_e$ . The above has frequency domain expression as noted below with  $n_\alpha(z, t) = n_\alpha(z)e^{i\omega t}$  and  $V(z, t) = \phi(z)e^{i\omega t}$ .

$$(i\omega)n_\alpha(z) = \mathbb{D} \left[ n_\alpha''(z) \pm \frac{q_e N}{k_B T} \phi''(z) \right] - \{\bar{K}_D(i\omega)\} n_\alpha(z)$$

$$(i\omega)n_\alpha(z) \left[ 1 + \frac{\{\bar{K}_D(i\omega)\}}{(i\omega)} \right] = \mathbb{D} \left[ n_\alpha''(z) \pm \frac{q_e N}{k_B T} \phi''(z) \right]$$

Where  $\{\bar{K}_D(i\omega)\}$  is frequency Fourier transformed of the time domain memory kernel  $K_D(t)$ . With this memory kernel we are getting a frequency dependent diffusion constant as

$$\mathbb{D}_e = \frac{\mathbb{D}}{\left[ 1 + \frac{\bar{K}_D(i\omega)}{i\omega} \right]}$$

Here to we note that the diffusion constant which needs to be frequency dependent when we invoke memory kernel, as it were in the cases of presence of fractional time derivative in diffusion-drift equation. We had earlier obtained  $\mathbb{D}_e \equiv \mathbb{D} / [a + b(i\omega)^{q_0-1}] = \mathbb{D} / [1 + \{(i\omega)^{q_0}\} / (i\omega)]$  in case of  $a = b = 1$ , a similar result as obtained with memory convolution for

$$\frac{\partial}{\partial t} n_\alpha(z, t) + \frac{\partial^{q_0}}{\partial t^{q_0}} n_\alpha(z, t) = \mathbb{D} \frac{\partial^2 n_\alpha(z, t)}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{d^2 V}{dz^2}$$

Thus for cases with fractional order time derivative we have relaxation with memory and is a non-Markovian case in diffusion-drift equation. Indeed the usual diffusion-drift equation is an approximation only valid in time scales that are large when compared with the time scales in which diffusion-causing collision takes place. With fractional derivative part absent in the diffusion-drift equation with only integer order time derivative present, gives a situation of infinite phase velocity of information propagation, with zero collision time, which is rather non-physical, the fractional derivatives presence with  $q_0 < 1$  introduces some kind of damping, making finite phase velocity, implying finite collision time a physical scenario.

## The simple adsorption-desorption at the boundary interface and Langmuir approximation

Adsorption-desorption are surface dynamics where the electrolyte's ions get attached and de-attached while in contact with the surface electrode. We will consider physisorption, the species adsorbing retains its identity unlike chemisorption where bond is formed. Adsorption requires a particle to lose energy during collision with the surface. Some of the particles bombarding the surface will bounce back off the surface but at any particular density a certain fraction will remain giving rise to coverage of the surface. The covering ratio or coverage is defined as

$$\sigma_R = \frac{\text{Number of surface sites occupied}}{\text{Total number of surface sites}} = \frac{\sigma}{\sigma_0}$$

The coverage of the surface when dynamic equilibrium is reached depends on the density of phase. The variation of  $\sigma_R$  with density at given temperature is called adsorption isotherm. The simplest isotherm is Langmuir's isotherm that gives the relation between the coverage of the first layer and the density at a particular temperature; with three basic assumptions.

1. The adsorption occurs only on the first layer (monolayer coverage)
2. All adsorption sites are equivalent, and the adsorption process is uniform (it is perfectly flat at on a microscopic scale).
3. The adsorption energy of one site is independent of occupancy of neighboring sites.

The adsorbed particles are assumed to be in dynamic equilibrium with the molecules in the surroundings and the process can be treated as chemical reaction



The rate of adsorption is proportional to the density of  $A$  and the number of adsorbing sites at the surface i.e.

$$\frac{d\sigma}{dt} = k_a \rho (\sigma_0 - \sigma)$$

Where,  $k_a$  [ $\equiv$  cm/s] is the rate constant for adsorption;  $\rho$  [number/cm] is the bulk density (in one dimension) of adsorbate just in front of adsorbing surface, and  $\sigma_0 - \sigma$  [ $\equiv$  number] is the total number of the free sites at the surface. The dimension of  $\sigma$  and  $\sigma_0$  is just a number (i.e. dimensionless). The rate of desorption is proportional to number of adsorbed species, that is

$$\frac{d\sigma}{dt} = -k_d \sigma$$

Where the term  $k_d$  [ $(s)^{-1}$ ] is the rate constant for desorption. Introduce reduced quantities as  $\sigma_R = \sigma / \sigma_0$  and  $\rho_R = \rho / \rho_0$ . At the equilibrium “net rate of adsorption” i.e. adsorption rate plus desorption rate is zero that is

$$\text{Net rate of adsorption} = k_a \rho (\sigma_0 - \sigma) + (-k_d \sigma) = 0$$

From above we get Langmuir isotherm as  $\sigma_R = (\alpha \rho_R) / (1 + \alpha \rho_R)$ . The term  $\alpha$  governs steady state and is  $\alpha = \kappa \tau \rho_0 / \sigma_0$  with  $\tau = 1 / k_d$  and  $\kappa = k_a \sigma_0$ . The  $\tau$  characteristic time constant for desorption and  $\kappa$  is associated with adsorption phenomena. Notice that  $\kappa \tau$  has dimension of length. Also we have from the balance equation  $\rho_R = (\sigma_R) / [\alpha (1 - \sigma_R)]$ . Here we are considering the boundary electrodes is  $x - y$  plane are in situated at  $z = -d / 2$  and at  $z = +d / 2$ , a one dimensional case. We indicate  $\rho(z, t)$  the density of the particles of the medium in the position  $z$  at a given time  $t$ , and  $\sigma(t)$  are the surface density. The equilibrium values of these are

$$\lim_{t \rightarrow \infty} \rho(z, t) = \rho(z) = \rho \quad \lim_{t \rightarrow \infty} \sigma(t) = \sigma$$

The net rate of adsorption (adsorption rate + desorption rate) is as follows

$$\begin{aligned} \frac{d\sigma}{dt} &= k_a \rho (\sigma_0 - \sigma) - k_d \sigma \\ \frac{d\sigma}{dt} &= \kappa \rho \left( 1 - \frac{\sigma}{\sigma_0} \right) - \frac{1}{\tau} \sigma \\ \frac{d\sigma_R}{dt} &= \kappa \frac{\rho_0}{\sigma_0} \rho_R (1 - \sigma_R) - \frac{1}{\tau} \sigma_R \end{aligned}$$

At the equilibrium  $\frac{d\sigma_R}{dt} = 0$ , one gets the Langmuir isotherm, which can be shown to be thickness dependence. In fact, since  $\rho_0 d$  is the initial number of particles per unit area, the conservation of number of particles at any time requires following

$$2\sigma(t) + \int_{-d/2}^{d/2} \rho(z,t) dz = \rho_0 d$$

At the equilibrium  $t \rightarrow \infty$  thus we have  $2\sigma + \rho d = \rho_0 d$ . From this equilibrium relation we obtain  $\sigma_R + \alpha\delta(\rho_R - 1) = 0$ ; with  $\delta = d / 2\kappa\tau$  as dimensionless thickness, where  $\alpha = \kappa\tau\rho_0 / \sigma_0$ .

We have adsorption dynamics as derived just above as

$$\frac{d\sigma}{dt} = \kappa\rho \left(1 - \frac{\sigma}{\sigma_0}\right) - \frac{1}{\tau}\sigma$$

in the limit in which  $\sigma \ll \sigma_0$  i.e. the adsorbed sites are very small compared to total number of sites we get the adsorption dynamics as following (along with its dimensionless representation)

$$\frac{d\sigma}{dt} + \frac{1}{\tau}\sigma = \kappa\rho \qquad \frac{d\sigma_R}{dt} + \frac{1}{\tau}\sigma_R = \frac{\kappa\rho_0}{\sigma_0}\rho_R$$

The Green's function if we choose as  $\sigma_g(t) = \kappa e^{-t/\tau}$  is solution to the above (homogeneous) differential equation, and this we call Langmuir approximation which we will subsequently use. The Langmuir method has given a dynamic expression relating surface adsorbed species to the species density of bulk. The particular solution to this will be convolution of the Green's function with  $\rho(z,t)$  appearing at RHS of the Langmuir dynamic equation. So we can write the solution as

$$\sigma(z,t) = \int_{-\infty}^t d\bar{t} \left( \kappa e^{-(t-\bar{t})/\tau} \right) (\rho(z,\bar{t}))$$

The above is rather similar to memory integral where memory kernel  $K_m(t) = \kappa e^{-t/\tau}$ . The LHS of the above equation is proportional to the surface current density  $\sigma(z,t)|_{z=\pm d/2} \sim j_\alpha(z,t)|_{z=\pm d/2}$  while the bulk density of diffusing ions  $\rho(z,t)|_{z=\pm d/2} \sim n_\alpha(z,t)|_{z=\pm d/2}$ , with this we may write boundary condition (of a particular type as) as:

$$j_\alpha(z,t)|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa e^{-(t-\bar{t})/\tau} n_\alpha(z,\bar{t})|_{z=\pm d/2}$$

The frequency domain translation of the above is

$$j_\alpha(z,s)|_{z=\pm \frac{d}{2}} = \pm \kappa \left( \frac{\tau}{1+s\tau} \right) (n_\alpha(z,s))|_{z=\pm d/2}$$

The following are Laplace transformed relations used :

$$\mathcal{L}\{j_\alpha(z,t)\} = j_\alpha(z,s) = j_\alpha(z); \quad \mathcal{L}\{j_\alpha(z,t)\} = j_\alpha(z,s) = j_\alpha(z); \quad \mathcal{L}\{e^{-at}\} = (s+a)^{-1}$$

For steady state frequency response put complex Laplace frequency  $s = \text{Re}\{s\} + i\omega = i\omega$ ; put  $\text{Re}\{s\} = 0$  to get

$$j_\alpha(z,i\omega)|_{z=\pm \frac{d}{2}} = \pm \kappa \left( \frac{\tau}{1+i\omega\tau} \right) (n_\alpha(z,i\omega))|_{z=\pm d/2} \quad j_\alpha(z)|_{z=\pm \frac{d}{2}} = \pm \left( \frac{\kappa\tau}{1+i\omega\tau} \right) (n_\alpha(z))|_{z=\pm d/2}$$

The next section further generalizes the boundary condition by involving fractional time derivative in the rate for number density.

### Unusual boundary condition at the electrodes

For the influence of the surface, on the ions, we have to consider the boundary conditions subjected to the expression of current density at the electrode boundary  $z = \pm d/2$

$$j_\alpha(z,t)|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z,\bar{t})|_{z=\pm \frac{d}{2}}; \quad \bar{q} \in (0,1] \dots \dots \dots (4a)$$

This (4a) is an unusual process of dynamics of adsorption-desorption happening at the boundary, a much generalized way to write the process with the help of generalized calculus.

For a blocking electrode case the memory kernel of the convolution at RHS of equation (4a) is,  $K_m(t) = 0$  gives boundary condition as  $j_\alpha(z, t)|_{z=\pm d/2} = 0$ . For the fractional order distribution function as  $\bar{k}(\bar{q}) = \delta(\bar{q} - 1)$  and the memory kernel as at RHS as delta function i.e.  $K_m(t) = \delta(t)$  we return to a very simple case of adsorption-desorption at the boundary without any memory (Markovian-case), namely

$$j_\alpha(z, t)|_{z=\pm d/2} = \pm \frac{\partial}{\partial t} n_\alpha(z, t)|_{z=\pm d/2}$$

The above derivation is explained below, where we used the property of delta function, that is

$$\int_b^d \delta(x-c) f(x) dx = f(c) \quad \int_{-\infty}^t \delta(t-\bar{t}) f(\bar{t}) d\bar{t} = f(t)$$

And the derivation is following

$$\begin{aligned} j_\alpha(z, t)|_{z=\pm \frac{d}{2}} &= \pm \int_0^1 d\bar{q} (\delta(\bar{q} - 1)) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}} ; \quad \bar{q} \in (0, 1] \\ &= \pm \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial}{\partial \bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}} \\ &= \pm \int_{-\infty}^t d\bar{t} (\delta(t-\bar{t})) \frac{\partial}{\partial \bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}} \\ &= \pm \frac{\partial}{\partial t} n_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} \end{aligned}$$

The surface effect given by above integer order differential equation is true if the process at the electrodes is taking place as if, at all conditions the  $n_\alpha$ 's (the ions) ejecting or attaching to the surface uniformly, and with memory-less dynamics-in an homogeneous and smooth background. In reality the adsorption (energy) of one site may not be independent of neighboring one's

occupational state with adsorption happening at inner layers too. The relaxation times of adsorption & desorption may not have any set average-may be diverging as power-law statistics. This uncertain wait-time statistics may be another cause of anomalous adsorption-desorption at the boundary. Also all the adsorbing sites at boundary may not be equivalent. These are the anomalous conditions at the boundary, and thus a generalized way to express boundary condition is expressed in 4a. There can be several manifestations (from 4a) of boundary conditions as listed below along with different order distribution and respective memory Kernel.

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \frac{\partial}{\partial t} n_\alpha(z, t) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 1), \quad K_m(t) = \delta(t)$$

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \frac{\partial^{0.5}}{\partial t^{0.5}} n_\alpha(z, t) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 0.5), \quad K_m(t) = \delta(t)$$

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa_0 e^{-(t-\bar{t})/\tau_0} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q}), \quad K_m(t) = \kappa_0 e^{-t/\tau_0}$$

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa_1 e^{-(t-\bar{t})/\tau_1} \frac{\partial}{\partial \bar{t}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 1), \quad K_m(t) = \kappa_1 e^{-t/\tau_1}$$

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{-\infty}^t d\bar{t} \kappa_2 e^{-(t-\bar{t})/\tau_2} \frac{\partial^{0.5}}{\partial \bar{t}^{0.5}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \delta(\bar{q} - 0.5), \quad K_m(t) = \kappa_2 e^{-t/\tau_2}$$

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_{0.5}^{0.7} d\bar{q} \left( \frac{1}{2} \right) \times \int_{-\infty}^t d\bar{t} \kappa_3 (t-\bar{t})^{-\beta} \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm d/2} \quad \bar{k}(\bar{q}) = \frac{1}{2}, \quad 0.5 \leq \bar{q} \leq 0.7, \quad K_m(t) = \kappa_3 t^{-\beta}$$

In the third fourth and fifth expression in above list we have used Langmuir approximation as kernel  $K_m(t) = \kappa e^{-t/\tau}$ , which we have derived in previous section. The adsorption and desorption process at the surface with Langmuir approximation is employed for this unusual dynamics. The memory kernel with Langmuir approximation i.e.  $K_m(t) = \kappa_1 e^{-t/\tau_1}$  gives short range correlation (short time decaying memory) whereas in case, Delta function as  $K_m(t) = \delta(t)$ , there is no memory effect.



Therefore, including this memory kernel the boundary condition can be modified more precisely including both  $h$  fraction for normal and  $(1-h)$  fraction for anomalous situations, as described below:

$$h: \quad j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_N e^{-(t-\bar{t})/\tau_N} \frac{\partial n_{\alpha}(z, \bar{t})}{\partial \bar{t}} \Big|_{z=\pm \frac{d}{2}} \dots\dots\dots(4b)$$

$$(1-h): \quad j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_A e^{-(t-\bar{t})/\tau_A} \frac{\partial^{\bar{q}} n_{\alpha}(z, \bar{t})}{\partial \bar{t}^{\bar{q}}} \Big|_{z=\pm \frac{d}{2}} \dots\dots\dots(4c)$$

The precise nature and the origin of anchoring and ‘anchoring energy’ at surface due to adsorption in these electrolyte cells of impedance spectroscopy are: “Still subject of many fundamental and experimental studies and cannot be considered as solved problem”.

**The boundary operator  $\Phi$  for normal & anomalous cases**

From the above boundary condition we can obtain the boundary operator in frequency domain ( $i\omega$ ), for both normal and anomalous situations using (4b) and (4c)

$$\begin{aligned} j_{\alpha}(z, t) \Big|_{z=\pm \frac{d}{2}} &= \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}} n_{\alpha}(z, \bar{t})}{\partial \bar{t}^{\bar{q}}} \Big|_{z=\pm \frac{d}{2}} & n_{\alpha}(z, t) &= n_{\alpha}(z) e^{i\omega t} \\ &= \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) (i\omega)^{\bar{q}} e^{i\omega \bar{t}} n_{\alpha}(z) \Big|_{z=\pm \frac{d}{2}} \\ &= \pm \Phi(i\omega) n_{\alpha}(z) e^{i\omega t} \end{aligned}$$

Here we have used Caputo derivative  ${}^C D_t^q e^{\beta t} = \beta^q e^{\beta t}$  for  $\beta > 0$ ;  $0 < q < 1$ , thus we write in above  ${}^C D_t^{\bar{q}} n_{\alpha}(z) e^{i\omega t} = n_{\alpha}(z) (i\omega)^{\bar{q}} e^{i\omega t}$

Define boundary operator as

$$\Phi(i\omega) = \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) (i\omega)^{\bar{q}} e^{i\omega \bar{t}}$$

Take Langmuir kernel  $K_m = \kappa e^{-t/\tau}$  i.e.  $K_m(t-\bar{t}) = \kappa e^{-(t-\bar{t})/\tau}$  & place it above carry out following steps.

$$\begin{aligned}\Phi(i\omega) &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (\kappa e^{-(t-\bar{t})/\tau}) (i\omega)^{\bar{q}} e^{i\omega\bar{t}} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^t d\bar{t} \kappa e^{-\frac{t-\bar{t}}{\tau} + i\omega\bar{t}} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^t d\bar{t} \kappa e^{\bar{t} \left( i\omega + \frac{1}{\tau} \right) - \frac{t}{\tau}}\end{aligned}$$

Put  $x = \bar{t} \left( i\omega + \frac{1}{\tau} \right) - \frac{t}{\tau}$   $\frac{dx}{d\bar{t}} = \left( i\omega + \frac{1}{\tau} \right)$   $d\bar{t} = \frac{dx}{\left( i\omega + \frac{1}{\tau} \right)}$  to get the operator as following, with

limits of integration for  $\bar{t}$  as from  $-\infty$  to  $t$  gets new limits for  $x$  from  $-\infty$  to  $i\omega t$

$$\begin{aligned}\Phi(i\omega) &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \int_{-\infty}^{i\omega t} dx \frac{\kappa e^x}{\left( i\omega + \frac{1}{\tau} \right)} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \frac{\kappa}{\left( i\omega + \frac{1}{\tau} \right)} e^x \Big|_{x=-\infty}^{x=i\omega t} \\ &= \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}} \frac{\kappa e^{i\omega t}}{\left( i\omega + \frac{1}{\tau} \right)} \\ &= \pm \kappa \tau \left( \frac{1}{1+i\omega\tau} \right) \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}}\end{aligned}$$

Therefore we have boundary operator as:

$$\Phi(i\omega) = \pm \kappa \tau \left( \frac{1}{1+i\omega\tau} \right) \int_0^1 d\bar{q} (\bar{k}(\bar{q})) (i\omega)^{\bar{q}}$$

For normal case the order distribution function  $\bar{k}(\bar{q}) = m\delta(\bar{q}-1)$  with Langmuir kernel as

$$K_{mN} = \kappa_N e^{-t/\tau_N}$$

$$\Phi_N(i\omega) = \pm \kappa_N \tau_N \left( m \frac{i\omega}{1+i\omega\tau_N} \right)$$

For anomalous case the order distribution function  $\bar{k}(\bar{q}) = n\delta(\bar{q} - \bar{q}_0)$   $0 < \bar{q}_0 < 1$  and Langmuir relaxation kernel as  $K_{mA} = \kappa_A e^{-t/\tau_A}$

$$\Phi_A(i\omega) = \pm \kappa_{\bar{q}_0} \tau_A \left( n \frac{(i\omega)^{\bar{q}_0}}{1 + i\omega\tau_A} \right)$$

Here  $\tau_N$  and  $\tau_A$  signifies desorption relaxation time for normal and anomalous diffusions. Thus we have here the two different length scales for adsorption-desorption at the boundary, namely  $(\kappa_N \tau_N)$  and  $(\kappa_{\bar{q}_0} \tau_A)$ .

### The Poisson's equation and its solution

The potential gradient is determined via Poisson's equation that is (5)

$$\frac{\partial^2}{\partial z^2} V(z, t) = -\frac{q_e}{\epsilon} [n_+(z, t) - n_-(z, t)] \dots\dots\dots(5)$$

Time dependent potential exciting the cell is  $V(z, t) = \phi(z)e^{i\omega t}$  and at the boundary electrodes the potential is  $V(z, t) \Big|_{z=\frac{d}{2}} = \pm \left(\frac{V_0}{2}\right)e^{i\omega t}$ . Let there be a small perturbation in number density by application of a small oscillating with voltage  $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$  with  $\delta n_\alpha(z, t) \ll N$ , is a good linear approx, with perturbed density varying as,  $\delta n_\alpha(z, t) = n_\alpha(z)e^{i\omega t}$  Again let  $\psi_+(z) = n_+(z) + n_-(z)$  &  $\psi_-(z) = n_+(z) - n_-(z)$

From (1) and (2) we have

$$\int_0^1 dq(k(q)) \frac{\partial^q}{\partial t^q} n_\alpha = -\frac{\partial}{\partial z} \left[ -\mathbb{D} \frac{\partial n_\alpha}{\partial z} \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{d^2 V}{dz^2} \right]$$

$$= \mathbb{D} \frac{\partial^2 n_\alpha}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} n_\alpha \frac{d^2 V}{dz^2}$$

Substitute  $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$  recognize  $\frac{\partial n_\alpha(z, t)}{\partial t} = \frac{\partial[\delta n_\alpha(z, t)]}{\partial t}$  and Caputo's fractional derivative of constant, i.e.  ${}^C D_t^q [N] = {}^C \frac{\partial^q N}{\partial t^q} = 0$  Put  $n_\alpha(z, t) = N + \delta n_\alpha(z, t)$  and the perturbed density as  $\delta n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$  to get following

$$\int_0^1 dq(k(q)) \frac{\partial^q [N + \delta n_\alpha(z, t)]}{\partial t^q} = \mathbb{D} \frac{\partial^2 [N + \delta n_\alpha(z, t)]}{\partial z^2} \pm \frac{q_e \mathbb{D}}{k_B T} [N + \delta n_\alpha(z, t)] \frac{d^2 V}{dz^2}$$

$$\int_0^1 dq(k(q)) \frac{\partial^q [\delta n_\alpha(z, t)]}{\partial t^q} = \mathbb{D} \frac{\partial^2 [\delta n_\alpha(z, t)]}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2 V}{dz^2} \pm \frac{q_e \mathbb{D} \delta n_\alpha(z, t)}{k_B T} \frac{d^2 V}{dz^2}$$

Put in above  $\delta n_\alpha(z, t) = n_\alpha(z) e^{i\omega t}$  and  $V(z, t) = \phi(z) e^{i\omega t}$  to get the following, by neglecting the last term of RHS, which is very small as  $\delta n_\alpha(z, t) \ll N$ , we get:

$$\int_0^1 dq(k(q)) \frac{\partial^q n_\alpha(z) e^{i\omega t}}{\partial t^q} = \mathbb{D} \frac{\partial^2 n_\alpha(z) e^{i\omega t}}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d}{dz} \phi(z) e^{i\omega t}$$

use  ${}^C D_t^q [e^{i\omega t}] = \left( \frac{d}{dt} e^{i\omega t} \right) \Big|_{-\infty}^t = (i\omega)^q e^{i\omega t}$  to get

$$\int_0^1 dq(k(q)) (i\omega)^q n_\alpha(z) e^{i\omega t} = \mathbb{D} \frac{\partial^2 n_\alpha(z) e^{i\omega t}}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2}{dz^2} \phi(z) e^{i\omega t}$$

$$\int_0^1 dq(k(q)) (i\omega)^q n_\alpha(z) = \mathbb{D} \frac{\partial^2 n_\alpha(z)}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2}{dz^2} \phi(z)$$

We mention here that  ${}^C D_t^q e^{\beta t} \neq \beta^q e^{\beta t}$ , but  ${}^C D_t^q e^{\beta t} = \beta^q e^{\beta t}$  for  $\beta > 0$ ;  $0 < q < 1$ , thus

$$\int_0^1 dq(k(q)) \frac{\partial^q n_\alpha(z) e^{i\omega t}}{\partial t^q} = \int_0^1 dq(k(q)) \left\{ \frac{n_\alpha(z)}{\Gamma(1-q)} \int_{-\infty}^t dt' (t-t')^{-q} \frac{d}{dt} e^{i\omega t} \right\}$$

$$= \int_0^1 dq(k(q)) n_\alpha(z) \left\{ {}^C D_t^q e^{i\omega t} \right\} = \int_0^1 dq(k(q)) n_\alpha(z) \left\{ (i\omega)^q e^{i\omega t} \right\}$$

Here  ${}^C D_t^q e^{i\omega t} = \frac{1}{\Gamma(1-q)} \int_{-\infty}^t dt' (t-t')^{-q} \frac{d}{dt} e^{i\omega t}$

In our study we are dealing with steady state response, thus the lower terminal in the integral transformed representation is at minus infinity. Also at the minus infinity the function  $e^{\beta t}$ ,  $\beta > 0$  is zero. In this study thus we aren't concerned with the initial conditions-at minus infinity all initial conditions related to differential equations are at rest (zero).

We derived

$$\int_0^1 dq(k(q))(i\omega)^q n_\alpha(z) = \mathbb{D} \frac{\partial^2 n_\alpha(z)}{\partial z^2} \pm \frac{q_e \mathbb{D} N}{k_B T} \frac{d^2 \phi(z)}{dz^2} \dots\dots\dots(6)$$

Let us write the operator on LHS of above  $\int_0^1 dq(k(q))(i\omega)^q \equiv \Lambda(i\omega)$ , and write (6) as

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_\alpha(z) = \frac{\partial^2}{\partial z^2} n_\alpha(z) \pm \frac{q_e N}{k_B T} \frac{d^2 \phi(z)}{dz^2}$$

Use Poisson's expression:

$$\begin{aligned} \frac{\partial^2}{\partial z^2} V(z,t) &= -\frac{q_e}{\epsilon} [n_+(z,t) - n_-(z,t)] \\ \frac{\partial^2}{\partial z^2} \phi(z)e^{i\omega t} &= -\frac{q_e}{\epsilon} [n_+(z)e^{i\omega t} - n_-(z)e^{i\omega t}] \\ \frac{d^2 \phi(z)}{dz^2} &= -\frac{q_e}{\epsilon} [n_+(z) - n_-(z)] \end{aligned}$$

substitute in (6) to get

$$\frac{\Lambda(i\omega)}{\mathbb{D}} n_\alpha(z) = \frac{\partial^2 n_\alpha(z)}{\partial z^2} \mp \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \dots\dots\dots(7)$$

From (7) we segregate the equation for + and - charges as follows:

$$\begin{aligned} \frac{\Lambda(i\omega)}{\mathbb{D}} n_+(z) &= \frac{\partial^2 n_+(z)}{\partial z^2} - \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \\ \frac{\Lambda(i\omega)}{\mathbb{D}} n_-(z) &= \frac{\partial^2 n_-(z)}{\partial z^2} + \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \end{aligned}$$

Rearranging above we get two differential equations

$$\frac{\partial^2 n_+(z)}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} n_+(z) + \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \dots\dots\dots(8)$$

$$\frac{\partial^2 n_-(z)}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} n_-(z) - \frac{q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \dots\dots\dots(9)$$

Adding (8) and (9) we have

$$\frac{\partial^2 [n_+(z) + n_-(z)]}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} [n_+(z) + n_-(z)] \dots\dots\dots(10)$$

$$\frac{d^2}{dz^2} \psi_+(z) = \alpha_+^2 \psi_+(z) \quad \alpha_+^2 = \frac{\Lambda(i\omega)}{\mathbb{D}}$$

Subtracting (9) from (8) we have

$$\frac{\partial^2 [n_+(z) - n_-(z)]}{\partial z^2} = \frac{\Lambda(i\omega)}{\mathbb{D}} [n_+(z) - n_-(z)] + \frac{2q_e^2 N}{\epsilon k_B T} [n_+(z) - n_-(z)] \dots\dots\dots(11)$$

$$\frac{d^2}{dz^2} \psi_-(z) = \alpha_-^2 \psi_-(z) \quad \alpha_-^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{2q_e^2 N}{\epsilon k_B T} = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2}$$

Consolidating (10) and (11) we obtain 2<sup>nd</sup> order linear differential equation (not Fractional Differential Equation), as following

$$\frac{d^2}{dz^2} \psi_{\pm} = \alpha_{\pm}^2 \psi_{\pm} \dots\dots\dots(12)$$

$$\alpha_-^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2} \dots\dots\dots(13)$$

$$\alpha_+^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} \dots\dots\dots(14)$$

Remember  $\lambda^2 = (\epsilon k_B T) / (2q_e^2 N)$  gives Debye screening length  $\lambda$ . This is surface effect of bare sample, in contact with a substrate; where we have selective adsorbed charges on the surface screened by opposite charge giving a charge separation of a distance  $\lambda$ , distance from the surface. This is basic phenomena of formation of Electric Double Layer Capacity ELDC. This bare screening length gets altered when we have potential in the electrolyte cell. The solution of

the ordinary differential equation (12) is  $\psi_{\pm}(z) = c_{\pm 1}e^{\alpha_{\pm}z} + c_{\pm 2}e^{-\alpha_{\pm}z}$ . We have symmetry in potential distribution about centre as  $V(z,t) = -V(-z,t)$ . Applying this observation we get:

$$\begin{aligned} \psi_-(z) &= c_{-1}e^{\alpha_-z} + c_{-2}e^{-\alpha_-z} & \psi_-(-z) &= c_{-1}e^{\alpha_-(-z)} + c_{-2}e^{-\alpha_-(-z)} & \psi_-(z) &= -\psi_-(-z) \\ c_{-1}e^{\alpha_-z} + c_{-2}e^{-\alpha_-z} &= -\left(c_{-1}e^{\alpha_-(-z)} + c_{-2}e^{-\alpha_-(-z)}\right) & &= -c_{-1}e^{\alpha_-(-z)} - c_{-2}e^{-\alpha_-(-z)} \\ (c_{-1} + c_{-2})e^{\alpha_-z} &= -(c_{-1} + c_{-2})e^{\alpha_-(-z)} & (c_{-1} + c_{-2})(e^{\alpha_-z} + e^{-\alpha_-z}) &= 0 \end{aligned}$$

Implying that

$$c_{-1} + c_{-2} = 0 \quad c_{-1} = -c_{-2} \quad \psi_-(z) = c_{-1}e^{\alpha_-z} - c_{-1}e^{-\alpha_-z} = c_{-1}(e^{\alpha_-z} - e^{-\alpha_-z})$$

$$\psi_-(z) = n_+(z) - n_-(z) = 2c_{-1} \left( \frac{e^{\alpha_-z} - e^{-\alpha_-z}}{2} \right) = 2c_{-1} \sinh(\alpha_-z)$$

$$\psi_-(z) = 2c_{-1} \left( \frac{e^{\alpha_-z} - e^{-\alpha_-z}}{2} \right) = 2c_{-1} \sinh(\alpha_-z) \dots\dots\dots(15)$$

From Poisson's expression we have

$$\frac{d^2V(z,t)}{dz^2} = -\frac{q_e}{\epsilon} [n_+(z,t) - n_-(z,t)] \quad V(z,t) = \phi(z)e^{i\omega t} \quad n_{\alpha}(z,t) = n_{\alpha}(z)e^{i\omega t}$$

$$\frac{d^2}{dz^2} \phi(z) = -\frac{q_e}{\epsilon} [n_+(z) - n_-(z)] = -\frac{q_e}{\epsilon} \psi_-(z) = -\frac{q_e}{\epsilon} [2c_{-1} \sinh(\alpha_-z)] \dots\dots\dots(16)$$

Integrating (16) we get gradient of potential i.e. proportional to electric field in the cell

$$\frac{d\phi(z)}{dz} = -\frac{q_e}{\epsilon\alpha_-} [2c_{-1} \cosh(\alpha_-z)] + c_1 \dots\dots\dots(17)$$

Integrating (17) we get potential as a function in electrolyte cell

$$\phi(z) = -\frac{2q_e}{\epsilon\alpha_-^2} [c_{-1} \sinh(\alpha_-z)] + c_1z + c_0$$

At origin the center of cell we have  $\phi(z)|_{z=0} = \phi(0) = 0$  so from above  $c_0 = 0$

$$\phi(z) = -\frac{2q_e}{\varepsilon\alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z$$

### Calculation of Electric field charge density and current at the boundary electrodes and the cell impedance function:

The electric field is the negative gradient of potential function

$$E(z, t) = -\frac{d}{dz} V(z, t) = -\frac{d}{dt} \phi(z) e^{i\omega t} = -\phi'(z) e^{i\omega t} \quad E(z, t)|_{z=d/2} = -\phi'(z)|_{z=d/2} e^{i\omega t}$$

We apply Gauss law at the electrode at  $z = +d/2$  connected to potential  $+V/2$ . By this there will be preferential negative charges at the electrode adsorbed. The Gauss law at  $z = +d/2$  states that  $\oint_S E(z, t)|_{z=d/2} \cdot ds = Q_{total} / \varepsilon$ . Where  $Q_{total}$  is total charge enclosed in volume as  $-\sigma_s \cdot S$ . The

LHS of Gauss law is flux through a closed surface of area  $S$  at any time  $t$  at  $z = +d/2$  that is  $E(z, t)|_{z=d/2} \cdot S$ , therefore  $E(z, t)|_{z=d/2} = -\frac{\sigma_s}{\varepsilon}$  where  $-\sigma_s$  is total surface charge density. Implying

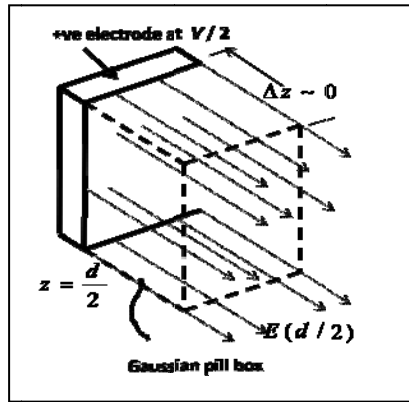
that  $\sigma_s = -\varepsilon E(z, t)|_{z=d/2} = \varepsilon \phi'(z)|_{z=d/2} e^{i\omega t}$ . Therefore total charge at  $z = d/2$  is,

$Q_{total} = \sigma_s S = \varepsilon S \phi'(z)|_{z=d/2} e^{i\omega t}$ . See the figure-1 of the pill box.

The current is, rate of change of total charge

$$I(z, t) |_{z=d/2} = \frac{d}{dt} Q_{total} = i\omega \varepsilon S \phi'(z)|_{z=d/2} e^{i\omega t}$$





**Figure-1: Gaussian pill box at the surface**

Impedance is

$$Z = \frac{V}{I} \Big|_{z=d/2} = \frac{\phi(z) \Big|_{z=d/2} e^{i\omega t}}{i\omega \epsilon S \phi'(z) \Big|_{z=d/2} e^{i\omega t}} = \frac{\phi(z) \Big|_{z=d/2}}{i\omega \epsilon S \phi'(z) \Big|_{z=d/2}} \dots\dots\dots(18)$$

From (2) we have

$$j_\alpha(z, t) = -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$$

using  $\Phi(i\omega) = \pm e^{-i\omega t} \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) (i\omega)^{\bar{q}} e^{i\omega \bar{t}}$  as obtained earlier we get the

following

$$j_\alpha(z, t) = -\mathbb{D} \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}}{k_B T} n_\alpha(z, t) \frac{dV}{dz} \quad n_\alpha(z, t) = N + n_\alpha(z) e^{i\omega t} \quad V = \phi(z) e^{i\omega t}$$

$$= -\mathbb{D} \frac{d}{dz} n_\alpha(z) e^{i\omega t} \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} e^{i\omega t} \quad \text{as } n_\alpha(z) \ll N$$

$$-\mathbb{D} \frac{d}{dz} n_\alpha(z) e^{i\omega t} \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} e^{i\omega t} \Big|_{z=\pm \frac{d}{2}} = \pm \Phi(i\omega) n_\alpha(z) e^{i\omega t} \Big|_{z=\pm \frac{d}{2}}$$

$$-\mathbb{D} \frac{d}{dz} n_\alpha(z) \mp \frac{q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} \Big|_{z=\pm \frac{d}{2}} = \pm \Phi(i\omega) n_\alpha(z) \Big|_{z=\pm \frac{d}{2}}$$

As we segregated the +ve and -ve species earlier for Drift-Diffusion equation (1) and (2) and then adding and subtracting the obtained expression from above we can get;

$$\mathbb{D} \frac{d}{dz} \psi_-(z) + \frac{2q_e \mathbb{D} N}{k_B T} \frac{d\phi(z)}{dz} \Big|_{z=\pm \frac{d}{2}} = \mp \Phi(i\omega) \psi_-(z) \Big|_{z=\pm \frac{d}{2}} \dots \dots \dots (20)$$

$$\mathbb{D} \frac{d}{dz} \psi_+(z) \Big|_{z=\pm \frac{d}{2}} = \mp \Phi(i\omega) \psi_+(z) \Big|_{z=\pm \frac{d}{2}} \dots \dots \dots (21)$$

We have from (15) & (17)

$$\psi_-(z) = 2c_{-1} \sinh(\alpha_- z) \quad \text{and} \quad \frac{d\phi(z)}{dz} = -\frac{q_e}{\varepsilon \alpha_-} [2c_{-1} \cosh(\alpha_- z)] + c_1$$

using them in (20) we get the following

$$2\mathbb{D}c_{-1} \cosh(\alpha_- z) + \frac{2q_e N \mathbb{D}}{k_B T} \left\{ -\frac{2q_e c_{-1} \alpha_- \cosh(\alpha_- z)}{\varepsilon \alpha_-^2} + c_1 \right\} \Big|_{z=\pm \frac{d}{2}} = \mp \Phi(i\omega) 2c_{-1} \sinh(\alpha_- z) \Big|_{z=\pm \frac{d}{2}}$$

$$\left[ \mathbb{D} \alpha_- \cosh(\alpha_- z) + \frac{q_e N \mathbb{D}}{k_B T} \left( -\frac{2q_e \alpha_-}{\varepsilon \alpha_-^2} \right) \cosh(\alpha_- z) \pm \Phi(i\omega) \sinh(\alpha_- z) \right] c_{-1} + \frac{q_e N \mathbb{D}}{k_B T} c_1 \Big|_{z=\pm \frac{d}{2}} = 0$$

$$\left[ \mathbb{D} \alpha_- \cosh(\alpha_- z) \left( 1 - \frac{2q_e N}{k_B T \varepsilon \alpha_-^2} \right) \pm \Phi(i\omega) \sinh(\alpha_- z) \right] c_{-1} + \frac{q_e N \mathbb{D}}{k_B T} c_1 \Big|_{z=\pm \frac{d}{2}} = 0$$

The parameters are

$$\alpha_-^2 = \frac{\Lambda(i\omega)}{\mathbb{D}} + \frac{1}{\lambda^2} \quad \text{or} \quad \frac{1}{\lambda^2} = \alpha_-^2 - \frac{\Lambda(i\omega)}{\mathbb{D}}$$

Thus we get

$$1 - \frac{1}{\lambda^2 \alpha_-^2} = 1 - \left( \alpha_-^2 - \frac{\Lambda(i\omega)}{\mathbb{D}} \right) \frac{1}{\alpha_-^2} = \frac{\Lambda(i\omega)}{\mathbb{D} \alpha_-^2}$$

using this in above we obtain (22)

$$\left[ \Lambda(i\omega) \frac{\cosh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right)}{\alpha_-} \pm \Phi(i\omega) \sinh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right) \right] c_{-1} + \frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} c_1 = 0$$

.....(22)

$$\frac{\cosh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right)}{\alpha_-} \left[ \Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right) \right] c_{-1} + \frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} c_1 = 0$$

We define

$$\Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right) = E$$

that is a new Fourier operator at  $z = d/2$  using this E we get in (22), we get (23)

$$\frac{E \cosh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right)}{\alpha_-} c_{-1} + \frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} c_1 = 0 \quad \text{.....(23)}$$

At  $z = d/2$  we have  $V = V_0/2$  and from (17) we have the potential function as

$$\phi(z) = -\frac{2q_e}{\varepsilon \alpha_-^2} \left[ c_{-1} \sinh(\alpha_- z) \right] + c_1 z + c_0$$

put  $z = \frac{d}{2}$ ,  $\phi(z)|_{z=\frac{d}{2}} = \frac{V_0}{2}$  to get

$$\frac{V_0}{2} = -\frac{2q_e}{\varepsilon \alpha_-^2} \left[ \sinh\left(\alpha_- \left\{ \frac{d}{2} \right\}\right) \right] c_{-1} + \left( \frac{d}{2} \right) c_1$$

From (23) we got

$$\frac{E \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\alpha_-} c_{-1} + \frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} c_1 = 0$$

From these we can get the values of  $c_{-1}$  and  $c_1$  to get the ratio of these two as:

$$\frac{c_1}{c_{-1}} = - \frac{\left[ \frac{2\mathbb{D}}{\lambda^2 \alpha_-^2} \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) + \frac{Ed}{\alpha_-} \right] E \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\frac{\varepsilon \mathbb{D}}{2\lambda^2 q_e} \left[ \frac{2\mathbb{D}}{\lambda^2 \alpha_-} \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) + Ed \right]} = - \frac{2\lambda^2 q_e E}{\alpha_- \varepsilon \mathbb{D}} \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)$$

.....(24)

$$Z = \frac{\phi(z)}{i\omega\varepsilon S \frac{d\phi(z)}{dz}} = \frac{-\frac{2q_e}{\varepsilon\alpha_-^2} [c_{-1} \sinh(\alpha_- z)] + c_1 z}{i\omega\varepsilon S \left[ -\frac{q_e}{\varepsilon\alpha_-} [2c_{-1} \cosh(\alpha_- z)] + c_1 \right]}$$

$$= \frac{1}{i\omega\varepsilon S \alpha_-^2} \left[ \frac{\sinh(\alpha_- z) - \frac{\alpha_-^2 \varepsilon z c_1}{2q_e c_{-1}}}{\frac{1}{\alpha_-} \cosh(\alpha_- z) - \frac{\varepsilon c_1}{2q_e c_{-1}}} \right]$$

.....(25)

Putting the ratio of constants of integration obtained as in (24) into impedance relation of (25) we have the following

$$\begin{aligned}
Z &= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\sinh(\alpha_- z) - \frac{\alpha_-^2 \varepsilon z}{2q_e} \frac{c_1}{c_{-1}}}{\frac{1}{\alpha_-} \cosh(\alpha_- z) - \frac{\varepsilon}{2q_e} \frac{c_1}{c_{-1}}} \right] \\
Z &= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\sinh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) - \frac{\alpha_-^2 \varepsilon \left(\frac{d}{2}\right)}{2q_e} \left(-\frac{2q_e \lambda^2 E}{\varepsilon \mathbb{D} \alpha_-}\right) \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\frac{1}{\alpha_-} \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) - \frac{\varepsilon}{2q_e} \left(-\frac{2q_e \lambda^2 E}{\varepsilon \mathbb{D} \alpha_-}\right) \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)} \right] \\
&= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\sinh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) + \frac{\alpha_- \left(\frac{d}{2}\right) \lambda^2 E}{\mathbb{D}} \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\frac{1}{\alpha_-} \cosh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right] \\
&= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) + \frac{\alpha_- \lambda^2 E}{\mathbb{D}} \frac{d}{2}}{\frac{1}{\alpha_-} \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right]
\end{aligned}$$

The impedance dispersion in terms of basic derived operators, use the following

$$E = \Lambda(i\omega) \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) = \left(\alpha_-^2 - \frac{1}{\lambda^2}\right) \mathbb{D} \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)$$

to get

$$\begin{aligned}
Z(i\omega) &= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) + \frac{\alpha_- \lambda^2 E d}{\mathbb{D}}}{\frac{1}{\alpha_-} \left[1 + \frac{\lambda^2 E}{\mathbb{D}}\right]} \right] \\
&= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\frac{\tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\lambda^2 \alpha_-} + \frac{Ed}{2\mathbb{D}}}{\frac{1}{\lambda^2 \alpha_-^2} + \frac{\left(\alpha_-^2 - \frac{1}{\lambda^2}\right) \mathbb{D} \pm \alpha_- \Phi(i\omega) \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\alpha_-^2 \mathbb{D}}} \right] \dots\dots\dots(26) \\
&= \frac{1}{i\omega\varepsilon S\alpha_-^2} \left[ \frac{\frac{\tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right)}{\lambda^2 \alpha_-} + \frac{Ed}{2\mathbb{D}}}{1 + \frac{\Phi(i\omega) \tanh\left(\alpha_- \left\{\frac{d}{2}\right\}\right) \left(\frac{i\omega \lambda^2}{\mathbb{D}}\right)}{\alpha_- i\omega \lambda^2}} \right]
\end{aligned}$$

We divide the process by assuming some species follow normal integer order laws and rest follow the fractional order laws, denoted by fraction  $h$  and  $(1-h)$  respectively, through admittances  $Y_N$  and  $Y_A$  to get  $Z_{final}$  as

$$\frac{1}{Z_{final}} = hY_N + (1-h)Y_A = \frac{h}{Z_N} + \frac{1-h}{Z_A} \dots\dots\dots(27)$$

$$Z_N = \frac{1}{i\omega S\varepsilon\alpha_{N-}^2} \frac{\frac{\tanh\left(\alpha_{N-} \left\{\frac{d}{2}\right\}\right)}{\lambda^2 \alpha_{N-}} + \frac{E_N d}{2\mathbb{D}_N}}{1 + \frac{\Phi_N(i\omega) \tanh\left(\alpha_{N-} \left\{\frac{d}{2}\right\}\right) \left(\frac{i\omega \lambda^2}{\mathbb{D}_N}\right)}{\alpha_{N-} i\omega \lambda^2}} \dots\dots\dots(28)$$

$$Z_A = \frac{1}{i\omega S\varepsilon\alpha_{A-}^2} \frac{\frac{\tanh\left(\alpha_{A-} \left\{\frac{d}{2}\right\}\right)}{\lambda^2 \alpha_{A-}} + \frac{E_A d}{2\mathbb{D}_A}}{1 + \frac{\Phi_A(i\omega) \tanh\left(\alpha_{A-} \left\{\frac{d}{2}\right\}\right) \left(\frac{i\omega \lambda^2}{\mathbb{D}_A}\right)}{\alpha_{A-} i\omega \lambda^2}} \dots\dots\dots(29)$$

$\mathbb{D}_N$  is the normal diffusion coefficient,  $\mathbb{D}_A$  is anomalous diffusion coefficient

$\int_0^1 dq(k(q))(i\omega)^q \equiv \Lambda(i\omega)$  is generalized fractional order differential operator in frequency

domain for  $\int_0^1 dq(k(q)) \frac{\partial^q}{\partial t^q}$

$\Lambda_N(i\omega) = a(i\omega)$  is integer order operator in frequency domain corresponds to  $a\left(\frac{\partial}{\partial t}\right)$

$\Lambda_A(i\omega) = b^q(i\omega)^q$  is fractional order operator in frequency domain corresponds to

$b^q\left(\frac{\partial^q}{\partial t^q}\right)$ ,  $0 < q < 1$

The normal and anomalous impedance are

$$Z_N = \frac{1}{i\omega S \varepsilon \alpha_{N-}^2} \frac{\frac{\tanh(\alpha_{N-} \{\frac{d}{2}\})}{\lambda^2 \alpha_{N-}} + \frac{E_N d}{2 \mathbb{D}_N}}{1 + \frac{\Phi_N(i\omega) \tanh(\alpha_{N-} \{\frac{d}{2}\})}{\alpha_{N-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_N}\right)}$$

$$Z_A = \frac{1}{i\omega S \varepsilon \alpha_{A-}^2} \frac{\frac{\tanh(\alpha_{A-} \{\frac{d}{2}\})}{\lambda^2 \alpha_{A-}} + \frac{E_A d}{2 \mathbb{D}_A}}{1 + \frac{\Phi_A(i\omega) \tanh(\alpha_{A-} \{\frac{d}{2}\})}{\alpha_{A-} i\omega \lambda^2} \left(\frac{i\omega \lambda^2}{\mathbb{D}_A}\right)}$$

$$\alpha_{N-}^2 = \frac{\Lambda_N(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} = \frac{a(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} \quad \alpha_{A-}^2 = \frac{\Lambda_A(i\omega)}{\mathbb{D}_A} + \frac{1}{\lambda^2} = \frac{b^q(i\omega)^q}{\mathbb{D}_A} + \frac{1}{\lambda^2}$$

The operator E for normal and anomalous case is

$$E_N = \Lambda_N(i\omega) + \alpha_{N-} \Phi_N(i\omega) \tanh\left(\alpha_{N-} \left\{\frac{d}{2}\right\}\right) = a(i\omega) + \alpha_{N-} \Phi_N(i\omega) \tanh\left(\alpha_{N-} \left\{\frac{d}{2}\right\}\right)$$

$$E_A = \Lambda_A(i\omega) + \alpha_{A-} \Phi_A(i\omega) \tanh\left(\alpha_{A-} \left\{\frac{d}{2}\right\}\right) = b^q(i\omega)^q + \alpha_{A-} \Phi_A(i\omega) \tanh\left(\alpha_{A-} \left\{\frac{d}{2}\right\}\right)$$

## Conclusion

The new phenomenological expressions are the following:

The diffusion-drift:

$$\int_0^1 dq (k(q)) \frac{\partial^q}{\partial t^q} n_\alpha(z, t) = -\frac{\partial}{\partial z} j_\alpha(z, t), \quad q \in (0, 1]$$

$$h: \quad \frac{\partial n_\alpha(z, t)}{\partial t} = -\frac{\partial}{\partial z} j_\alpha(z, t)$$

$$(1-h): \quad \frac{\partial^q n_\alpha(z, t)}{\partial t^q} = -\frac{\partial}{\partial z} j_\alpha(z, t)$$

$$h: \quad j_\alpha(z, t) = -\mathbb{D}_N \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}_N}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$$

$$(1-h): \quad j_\alpha(z, t) = -\mathbb{D}_A \frac{\partial}{\partial z} n_\alpha(z, t) \mp \frac{q_e \mathbb{D}_A}{k_B T} n_\alpha(z, t) \frac{dV}{dz}$$

The boundary adsorption-desorption

$$j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \pm \int_0^1 d\bar{q} (\bar{k}(\bar{q})) \times \int_{-\infty}^t d\bar{t} (K_m(t-\bar{t})) \frac{\partial^{\bar{q}}}{\partial \bar{t}^{\bar{q}}} n_\alpha(z, \bar{t}) \Big|_{z=\pm \frac{d}{2}}; \quad \bar{q} \in (0, 1]$$

$$h: \quad j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_N e^{-(t-\bar{t})/\tau_N} \frac{\partial n_\alpha(z, \bar{t})}{\partial \bar{t}} \Big|_{z=\pm \frac{d}{2}}$$

$$(1-h): \quad j_\alpha(z, t) \Big|_{z=\pm \frac{d}{2}} = \int_{-\infty}^t d\bar{t} \kappa_A e^{-(t-\bar{t})/\tau_A} \frac{\partial^{\bar{q}} n_\alpha(z, \bar{t})}{\partial \bar{t}^{\bar{q}}} \Big|_{z=\pm \frac{d}{2}}$$

The Poisson equation:

$$\frac{\partial^2}{\partial z^2} V(z, t) = -\frac{q_e}{\varepsilon} [n_+(z, t) - n_-(z, t)]$$

With these we have got the impedance expressions as the following

$$Z_N = \frac{1}{i\omega S \varepsilon \alpha_{N-}^2} \frac{\frac{\tanh(\alpha_{N-} \{\frac{d}{2}\})}{\lambda^2 \alpha_{N-}} + \frac{E_N d}{2\mathbb{D}_N}}{1 + \frac{\Phi_N(i\omega) \tanh(\alpha_{N-} \{\frac{d}{2}\})}{\alpha_{N-} i\omega \lambda^2} \left( \frac{i\omega \lambda^2}{\mathbb{D}_N} \right)}$$



$$Z_A = \frac{1}{i\omega S \varepsilon \alpha_{A-}^2} \frac{\frac{\tanh(\alpha_{A-} \{\frac{d}{2}\})}{\lambda^2 \alpha_{A-}} + \frac{E_A d}{2\mathbb{D}_A}}{1 + \frac{\Phi_A(i\omega) \tanh(\alpha_{A-} \{\frac{d}{2}\})}{\alpha_{A-} i\omega \lambda^2} \left( \frac{i\omega \lambda^2}{\mathbb{D}_A} \right)}$$

$$\alpha_{N-}^2 = \frac{\Lambda_N(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} = \frac{a(i\omega)}{\mathbb{D}_N} + \frac{1}{\lambda^2} \quad \alpha_{A-}^2 = \frac{\Lambda_A(i\omega)}{\mathbb{D}_A} + \frac{1}{\lambda^2} = \frac{b^q(i\omega)^q}{\mathbb{D}_A} + \frac{1}{\lambda^2}$$

With all the operators defined earlier. In a way we have derived these expressions which are suited in several electrochemical systems with anomalous transport and non-blocking boundary condition having memory based relaxation adsorption-desorption kinetics.

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