

Fractional Time Derivatives, Anomalous Diffusion and Poisson – Nerst – Planck Model

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The very irregular state of motion observed for small pollen grains suspended in water by Robert Brown initiated one of the most fascinating field of the science, which is reported in several contexts of nature, the so-called diffusion process. Satisfactory explanations for this motion were proposed by Einstein, Smoluchowski and Langevin in their pioneering works. The main feature regarding this random motion is the linear growth with time manifested by mean square displacement, which is an important characteristic of a Markovian process. Contrasting with this scenario, several cases, for example, in living cells, crowding systems, and amorphous conductor, have pointed out that diffusion may exhibit a nonlinear time dependence for the mean square displacement typical of non-Markovian processes which, consequently, has implication on the physical properties of these systems, in particular on the electrochemical properties, which represents a relevant research field of material science.

Despite the deviations between experimental data and theoretical predictions, results from impedance spectroscopy are usually investigated in the framework of the Poisson - Nernst-Planck (PNP) diffusional model and/or equivalent circuits. These disagreements are especially remarkable in the low frequency limit, where the PNP and equivalent circuits with simple elements predict an asymptotic impedance Z characterized by a power-law dependence in the frequency ω with a unitary exponent (i.e., $Z: 1/(i\omega)$) but the experimental data usually exhibit a different power-law regime. These discrepancies consist, therefore, in strong motivation for investigating extensions/generalizations of the PNP model as well as of the equivalent circuits.

Here, we discuss for the PNP model possible extensions by using the well-established features of the fractional calculus, more specifically, fractional time derivatives expressed by the Caputo approach. We first consider changes on the bulk equation and after extending the boundary conditions to take into account the complexity inherent to the surface effects, which can be related to charge transfer, accumulation, and/or adsorption – desorption. We show that the extensions of the PNP model can be related to equivalent circuits and by means of electrical conductivity, the different diffusive regimes present in these systems may be evidenced. The results obtained from these extensions are also compared with experimental data, showing that the proposed fractional calculus based approach is able to describe the data behavior.