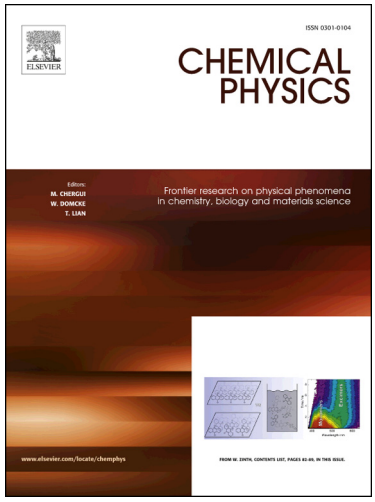

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Stretched-to-compressed-exponential crossover observed in the electrical degradation kinetics of some spinel-metallic screen-printed structures

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Abstract
Thermally-induced (170°C) degradation-relaxation kinetics is examined in screen-printed structures composed of spinel $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics with conductive Ag or Ag-Pd layered electrodes. Structural inhomogeneities due to Ag and Ag-Pd diffusants in spinel phase environment play a decisive role in non-exponential kinetics of negative relative resistance drift. If Ag migration in spinel is inhibited by Pd addition due to Ag-Pd alloy, the kinetics attains stretched exponential behaviour with ~0.58 exponent, typical for one-stage diffusion in structurally-dispersive media. Under deep Ag penetration into spinel ceramics, as for thick films with Ag-layered electrodes, the degradation kinetics drastically changes, attaining features of two-step diffusing process governed by compressed-exponential dependence with power index of ~1.68. Crossover from stretched- to compressed-exponential kinetics in spinel-metallic structures is mapped on free energy landscape of non-barrier multi-well system under strong perturbation from equilibrium, showing transition with a character downhill scenario resulting in faster than exponential decaying.

Keywords: Electrical Relaxation, Spinel, Ceramics, Kinetics, Stretched-exponential, Compressed-exponential.

1. Introduction

The stretched-exponential relaxation (SER) function (alternatively, nominated as *sub-exponential*) is most commonly used modelling curve to describe phenomenological response in degradation-relaxation (DR) kinetics in different substances prepared by freezing from a high-temperature out-of-equilibrium state [1-5]. In structurally-dispersive disordered solids, the tending towards equilibrium in the controlled parameter $\eta(t)$ occurs with increasingly slower DR rate, this process being known as physical ageing (PhA) [6]. Deviation from simple single-exponential dependence (i.e. *non-exponentionality*) is defined by the Kohlrausch-Williams-Watts (KWW) functional [1,2]

$$\eta(t) \sim exp\left[-\left(\frac{t}{\tau}\right)^{\beta}\right], \qquad (1)$$

where the time constant τ denotes *the relaxation time*, i.e. the characteristic time for the testing system to rearrange its structure towards an equilibrium, and *the dimensionless shape parameter* β (*non-exponentionality index* or *stretching exponent*) as an indicative of *wide distribution of diffusive relaxation times* attains positive less-unity values ($0<\beta<1$).

The KWW function (1) is not alone expression describing DR kinetics in different *out-of-equilibrium substances*. In a wide range of so-called *jammed systems* (including soft colloidal fractal gels, concentrated emulsions, surfactant phases, micellar polycrystals, lamellar gels, polymer