Exploring the dynamics and consequences of ageing phenomena in thick-film nanostructures

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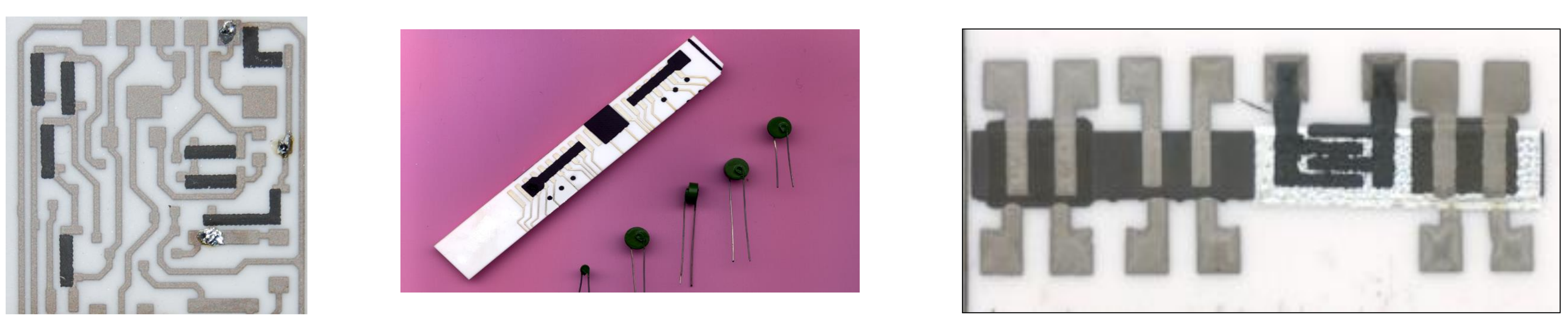
Oxymanganospinel ceramics are one of the most perspective materials for device application as negative temperature coefficient thermistors. To eliminate the degradation, the method of chemical modification of ceramics at the initial technological stages is used. In this investigation of ageing processes in the single as well as two- and three-layered thick-film elements based on $NiMn_2O_4$-$CuMn_2O_4$-$MnCo_2O_4$ ceramics was performed. The ageing test was carried out at long-term isothermal treatment at 170 °C to study the thermal stability of the obtained thick films. General duration of ageing test was 250 h, measurements electrical resistance *R* was performed at 25 °C after 6, 12, 18, 24, 30, 48, 64, 104, 144, 208 and 250 hours.

OBJECT



Semiconductor thick films: $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ and $Cu_{0.1}Ni_{0.8}Co_{1.2}Mn_{1.9}O_4$, etc.)

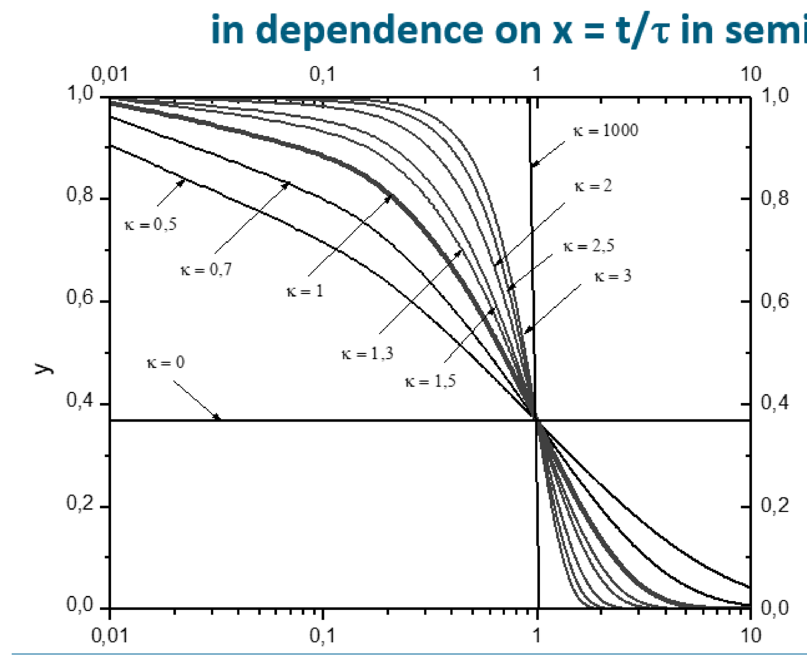
Kinetics models

Relaxation function for analytical description of degradation kinetic

RF1 **Monomolecular RF** (α=1, β=0)	$\eta \approx \exp\left(-\frac{t}{\tau}\right)$	$\tau = \frac{1}{\lambda}$	$\lambda \neq 0$
RF2 **Bimolecular RF** (α=2, β=0)	$\eta \approx \left(1+\frac{t}{\tau}\right)^{-1}$	$\tau = \frac{1}{\lambda}$	$\lambda \neq 0$
RF3 **Partly-generalized RF** ($\alpha \neq 0$, β=0)	$\eta \approx \left(1+\frac{t}{\tau}\right)^{-\kappa}$	$\tau = \frac{1}{\lambda \cdot (\alpha - 1)}$	$k = \frac{1}{\alpha - 1}, \alpha \neq 1$ $\lambda \neq 0$
RF4 **DeBast-Gillard or Williams-Watts RF** (α=1, $\beta \neq 0$)	$\eta \approx \exp\left[-\left(\frac{t}{\tau}\right)^{\kappa}\right]$	$\tau = \frac{1+\beta}{\lambda}$	$k = 1+\beta, \beta \neq -1$ $\lambda \neq 0$
RF5 **Fully-generalized RF** ($\alpha \neq 0$, $\beta \neq 0$)	$\eta \approx \left(1+\left(\frac{t}{\tau}\right)^{\kappa}\right)^{-r}$	$\tau = \left(\frac{1+\beta}{\lambda \cdot (\alpha - 1)}\right)^{\frac{1}{1+\beta}}$	$\kappa = 1+\beta,$ $\lambda \neq 0$ $r = \frac{1}{\alpha - 1}$

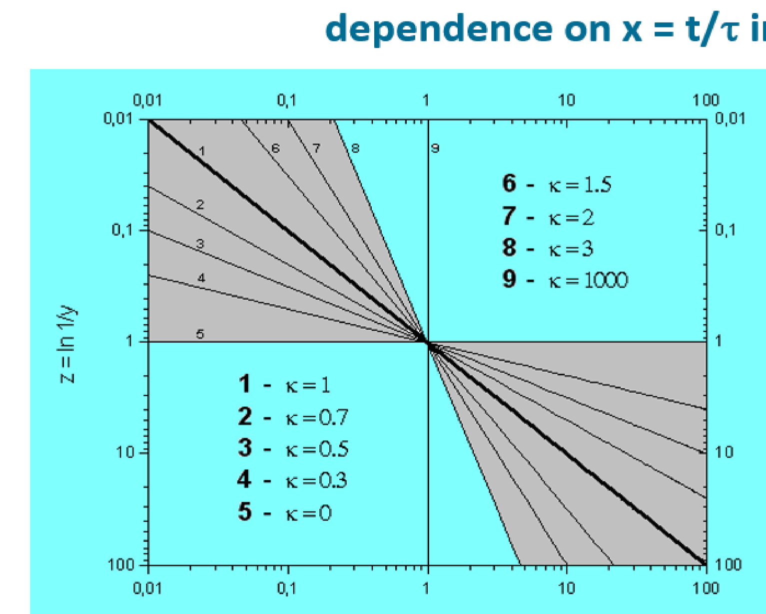
Kinetics models

Stretched (0 < κ < 1) and suppressed (κ > 1) character of exponential-power-like RF y = η(t) = exp[(-x)^κ] in dependence on x = t/τ in semi-logarithmic scale



The power-like index *κ* in the functional determines the deviation from ideal exponential-like kinetics, obtained at *κ* = 1, but not the approaching to this kinetics. That is why, sometimes, they call it the non-exponentionelity index. In other words, all exponential-power-like RFs corresponding to *κ* values more or less than 1,0 are non-exponential ones.

Linearization form of stretched (0 < κ < 1) and suppressed (κ > 1) exponential-power-like RF y = η(t) = exp[(-x)^κ] in dependence on x = t/τ in logarithmic scale

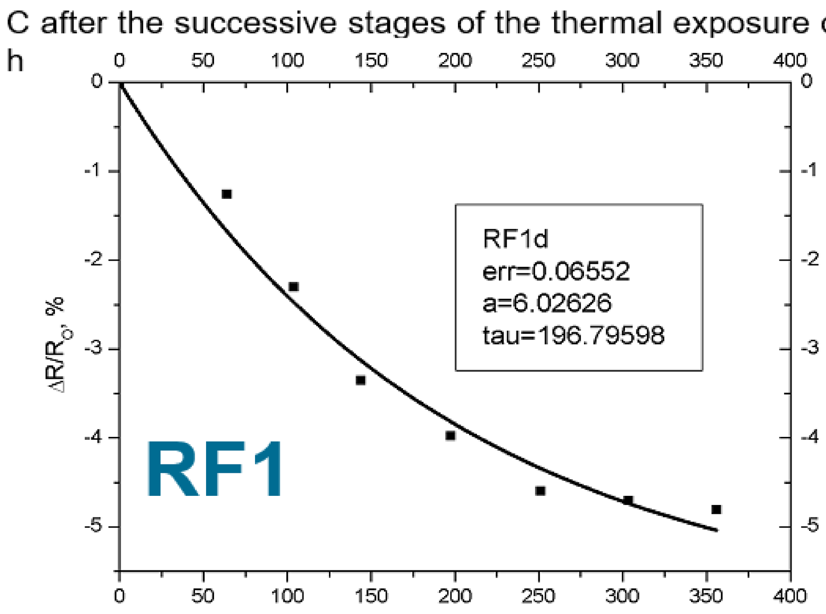


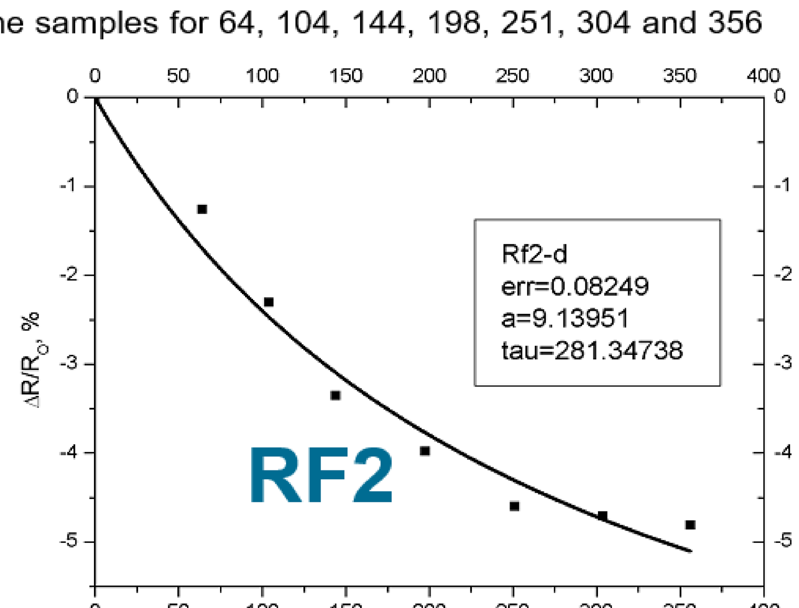
The ideal exponential curve by transforming into stretched-exponential one extends in time, tending asymptotically to straight line *y=e* with *κ* = 0.

RESULTS

Degradation kinetics in $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$-based thick films

To study thermally-induced processes in thick films based on $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$ ceramics, degradation tests were carried out under conditions of long-term isothermal exposure (356 hours) at a temperature of 170 C in a HPS 222 heat chamber. The measurement of the nominal electrical resistance *R* was carried out at 25 C after the successive stages of the thermal exposure of the samples for 64, 104, 144, 198, 251, 304 and 356 h

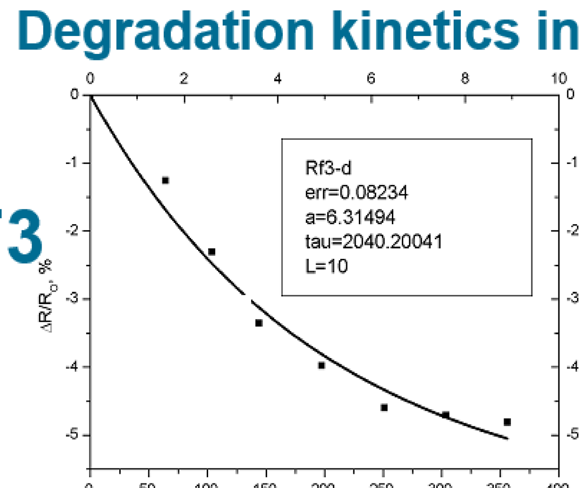




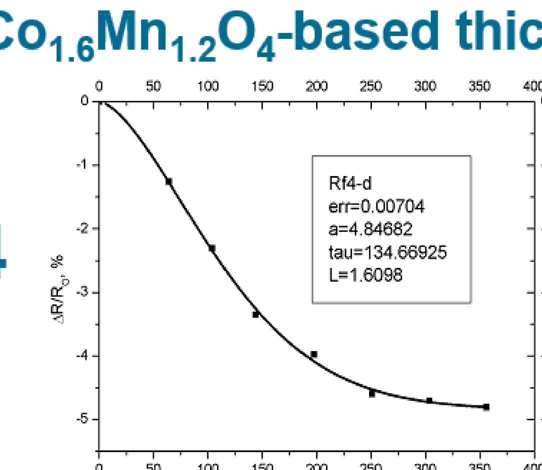
As a controlled parameter, the value of the relative change (drift) of the electric resistance $\Delta R/R_0$ (R_0 - the initial value of the electric resistance, ΔR - absolute change in the electrical resistance caused by the degradation test) was chosen

Degradation kinetics in $Cu_{0.1}Ni_{0.1}Co_{1.6}Mn_{1.2}O_4$-based thick films

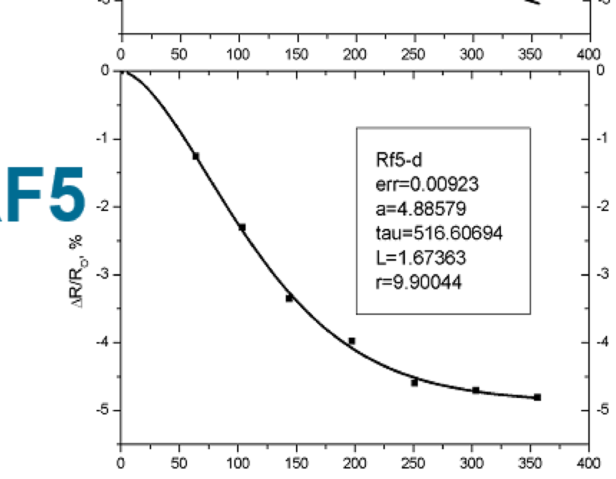
RF3



RF4

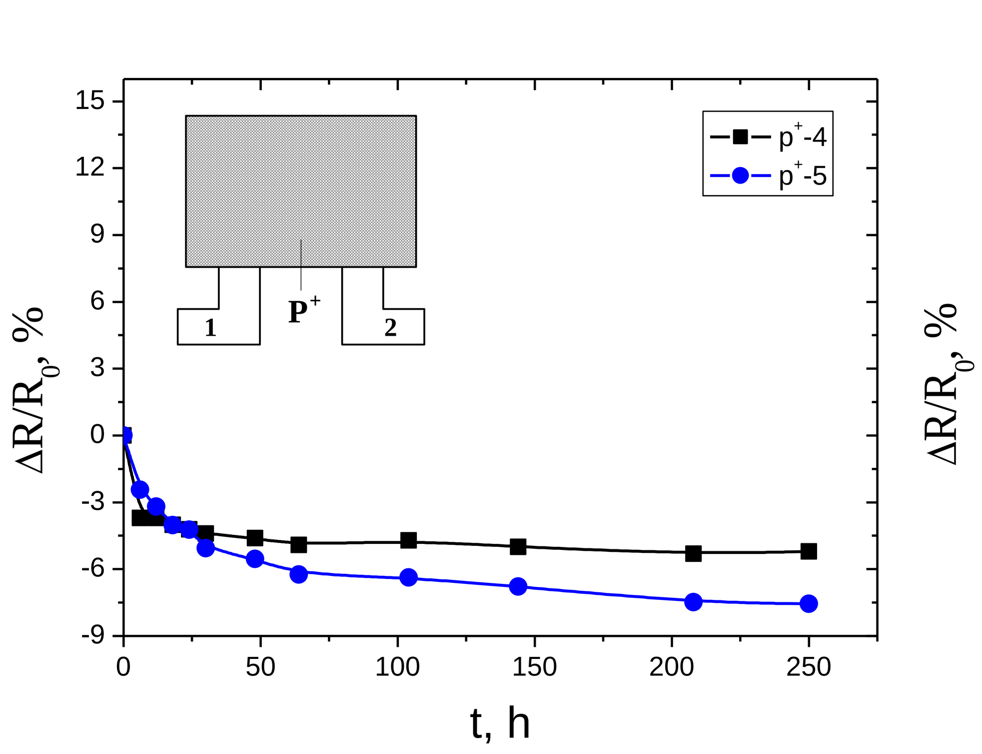


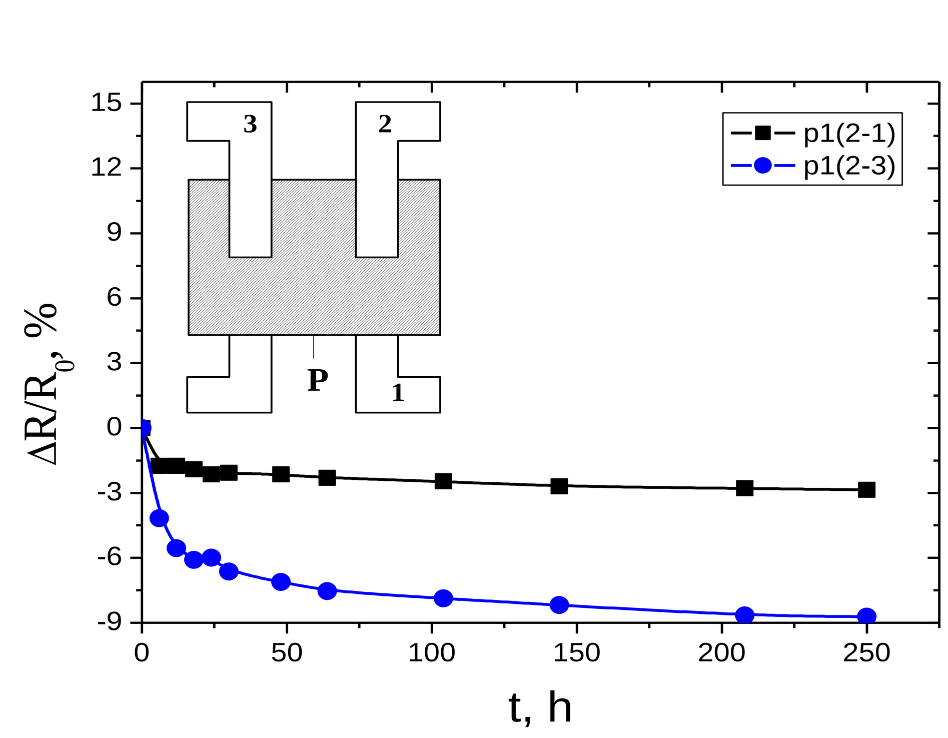
RF5

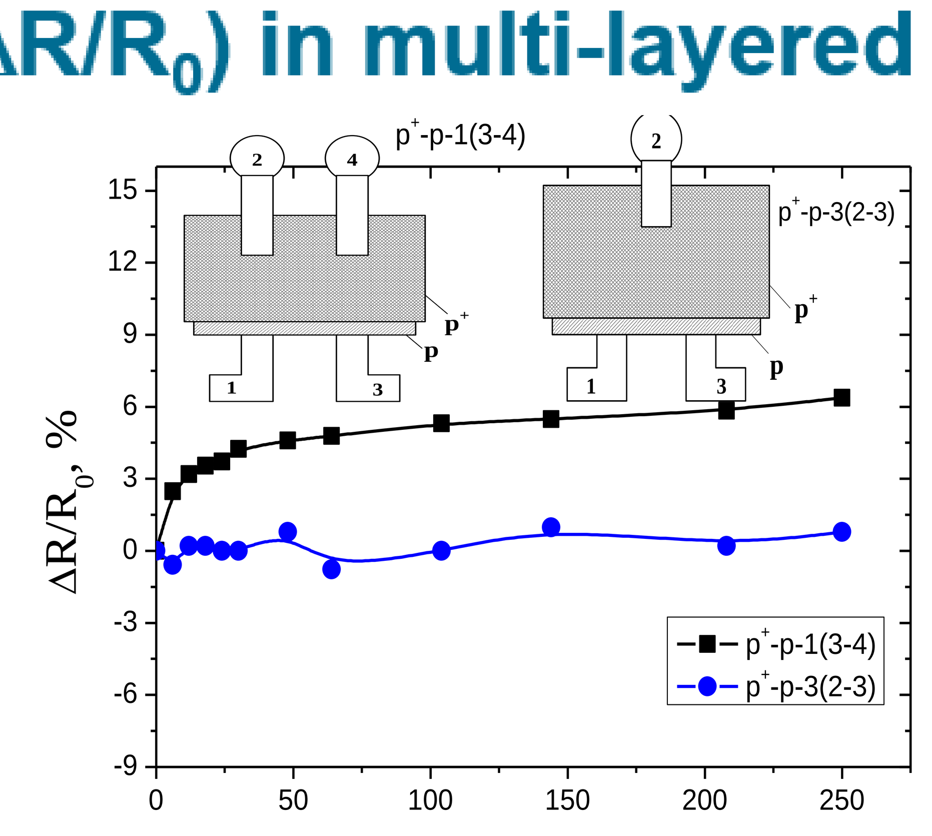


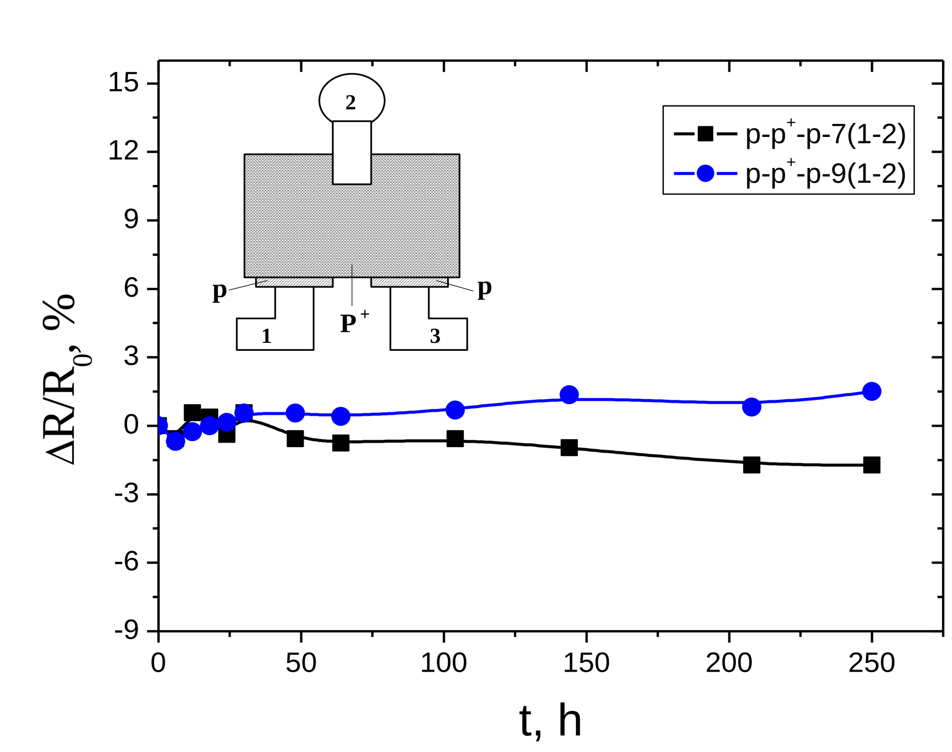
Kinetics of thermo-induced degradation of the studied thick films is adequately described by RF4. In this case, the value of *err* is rather low and is achieved for a relatively small number of fitting parameters. It should be noted that RF5 (exact solution of the main degradation equation) also gives a fairly low value of *err*, but this RF contains four adjustment parameters (*τ*, *L*, *r* and *α*), and therefore it is too cumbersome (*L* – is addition fitting parameter). Monomolecular RF1 (as well as RF2 and RF3) gives a much higher value of *err* (compared with RF4 and RF5). Consequently, RF4 is the most acceptable analytical expression for describing the threshold low-temperature degradation of investigated thick films, although the exponent (non-exponential coefficient) thus acquires characteristic values greater than 1.

Thermally-induced (170 ºC) drift ($\Delta R/R_0$) in multi-layered thick-film









Kinetic dependences for studied single-layered thick-film elements show a typical suppressed-exponential dependence on time in accordance with the known relaxation function. Such behavior is caused by burnout of organic compounds. This process is typical for structural-heterogeneous media such as thick-film ceramic structure. Typical increasing form of thermally-induced aging curve with relative saturation during prolongation of test is observed in two-layered thick-film structures in the first 50-150 hours. Maximum drift of electrical resistance is ~ 6 %. Ageing kinetics are described by extended exponential relaxation function. It should be noted that thermally-induced mechanism in these samples was complex including not only the cation redistribution, but also mass transfer processes. Unfortunately, the two- and three-layered thick film structures are characterized by relatively high stability, the drift of electrical resistivity is 1.5 %. Such highly stable components are obtained at modification of paste compositions (for achieve the required viscosity) and preparation of thick-film layers based on different compositions of ceramics.