Short Communication

DIELECTRIC-DIFFERENTIAL THERMAL ANALYSIS.

Part V: The role of cationic conduction

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A quantitative relation is given for the temperature function of the output voltage is thermodielectric analysis. Results obtained with zeolites show the validity of the equation.

The present paper reports a quantitative relation between the output voltage [1, 2] and temperature, which is valid in thermodielectric analysis in the high-temperature range. This relation can be obtained from Eq. (1):

$$V_0 = \frac{Z_r}{Z_x} V_i = \frac{\sqrt{(\omega c_x)^2 + (\lambda \sigma x)^2}}{\sqrt{(\omega c_r)^2 + (\lambda \sigma_r)^2}} V_i \qquad (1)$$

in the case when the behaviour of the circuit is resistive, because of the fact that ωC_x and ωC_r can be neglected relative to $2\sigma_x$ and $2\sigma_r$. The transition from capacitive to resistive behaviour was followed by comparing the phases of the input and output signals in the measurement circuit [1]. The equation which results after the approximation process is

$$V_0 \simeq \frac{\sigma_x}{\sigma_r} V_i \qquad (2)$$

where σ_x and σ_r are the conductivities of the reference and sample powders. On the other hand, the temperature-dependence of the conductivity for non-conducting materials is well known [3]:

$$\sigma = \sigma_0 e^{-E/RT} \qquad (3)$$

which, combined with Eq. (2), gives

$$V_0 = \frac{\sigma_0^x}{\sigma_0^r} e^{-(E_x - E_r)/RT}$$

(4)

For corroboration of the proposed Equation (4), zeolites were used as experimental objects, in spite of the possibility of changes the cationic composition by ion-exchange. The zeolites used were NaFAU, KFAU, CaFAU and MgFAU, obtained by ion-exchange from the synthetic NaX product of REACHIM, and also NH$_4$HEU, NH$_4$MOR, NaHEU, CaHEU, NaMOR, CaMOR, NAERI and KERI, obtained by ion-exchange by the usual method [2] from natural zeolites (HEU from 80% clinoptilolite, MOR from 85% mordenite, and ERI from 85% erionite).

The obtained results are shown in Table 1, which gives the apparent differential activation energy $\Delta E - E_x - E_r$, its standard deviation and the regression coefficient for the Arrhenius plot of $\ln V_0$ vs. $1/T$.

The results show the validity of the proposed equation. The numerical results reported for the apparent differential activation energy are in accord with the ideas concerning the ionic conduction in zeolites. In this respect, the differences in activation energy for monovalent and divalent cations are evident [4].

Table 1 Apparent differential activation energy (ΔE), standard deviation of the previously defined parameter (σ_{AE}) and regression coefficient (r), measured by linear regression of $\ln V_0$ vs. $1/T$

Sample	ΔE, kJ/mol	σ_{AE}, kJ/mol	r
NaHEU	36	1	0.998
CaHEU	66	4	0.989
NaMOR	47	1	0.998
CaMOR	60	5	0.986
NH$_4$HEU	110	7	0.991
NH$_4$MOR	110	7	0.989
KERI	26	1	0.994
NaERI	25	1	0.994
NaFAU	27.2	0.2	0.999
KFAU	26.6	0.5	0.999
CaFAU	36	2	0.994
MgFAU	42	2	0.994

References

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3 B. M. Tariev, Fisica de los Materiales Dielectricos, Editorial MIR, 1978.
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