

Nonlinear Conductivity of Ion-Complexed Polyethylene Oxide

Steffen Hahne
Bernd Ploss*

Department of SciTec

University of Applied Sciences (FH) Jena,
Carl-Zeiss-Promenade 2, 07743 Jena, Germany

* Corresponding author, Email: Bernd.Ploss@fh-jena.de

Kensuke Yoshida
Takeo Furukawa

Faculty of Science

Tokyo University of Science
Shinjuku, Tokyo 162-8601, Japan

Abstract—The electric polarization in polyethylene oxide complexed with LiClO₄ has been investigated over the frequency range from 10 mHz to 10 kHz. The exciting electric fields have been chosen so high that nonlinear components in the dielectric response are evident. Nonlinear dielectric and conductive spectra are determined and their temperature dependence is studied.

It is found that the nonlinear relaxation shows a temperature dependence similar to the linear relaxation. With rising temperature the phenomena shift to higher frequencies and the relaxation strength increases. To evaluate relaxation frequencies and strengths theoretical functions are fitted to the experimental data. While the linear spectra are reproduced well over the whole frequency range, a reasonable agreement between experimental data and theoretical curves is found in a limited frequency range only for the nonlinear spectra.

Index Terms—Conductivity, Polarization, Spectroscopy, Non-linearities, Relaxation processes

I. INTRODUCTION

Ion-conducting polymers are utilized as solid state electrolytes in electrochemical devices and have been extensively investigated. Typical examples of such systems are polyethylene oxide (PEO) or polypropylene oxide (PPO) complexed with alkali metal salts like LiClO₄ or NaCF₃SO₄.

Analysis of the nonlinear components of the relaxation phenomena can give further insight into the nature of the microscopic mechanisms involved and additional information about dipolar and ionic motion can be attained [1]. One example where nonlinear spectroscopy was successfully applied is in testing the ion hopping model [2], [3], as done by several authors [4], [5], [1]. Here, from n -th order direct current conductivities σ_n^{dc} , ion hopping lengths a can be estimated. Using the relation between first and third order dc conductivity one finds: $\sigma_3^{\text{dc}}/\sigma_1^{\text{dc}} = (q_e^2 a^2)/(24kT^2)$ (q_e -elementary charge, k -Boltzmann's const., T -temperature). Ion hopping lengths in the range of a few nanometers to some ten nanometer were obtained in that manner.

Furthermore, with data obtained from nonlinear spectroscopic measurements the polarization as given in the Langevin function can be estimated over the whole range of electric field strength [1] and subsequently it is possible to find approximate values of the saturation polarization.

While a number of papers report on nonlinear investigation of ion conducting polymers, the physical significance of the

third order permittivity or conductivity ($\varepsilon_3^* = \varepsilon_3' - i\varepsilon_3''$, $\sigma_3^* = \sigma_3' + i\sigma_3''$) is still not fully understood. Such understanding could, in turn, provide new approaches for the development of high-performance batteries—lithium polymer electrolytes find application in today's most widely used batteries—and for the design of optimized sensor films, by tailoring the conductivity of the polymer matrix material.

II. THEORY

The dielectric induction of a nonlinear nonrelaxational system can be expanded in odd powers of the electric field [6]:

$$D(\omega) = \varepsilon_1(\omega)E + \varepsilon_3(\omega)E^3 + \varepsilon_5(\omega)E^5 + \dots \quad (1)$$

In dielectrics with inversion symmetry (no zero-field polarization: $D_0 = 0$ and $D(E) = -D(-E)$) only odd powers contribute to the series-development [7, p.3]. In (1) the term ε_1 defines the linear permittivity, the ε_n with $n = 3, 5, \dots$ are n -th order nonlinear permittivities [1].

Nakada suggested to write the nonlinear response of a relaxational system as sum of multiple convolutions [8]. $D(t)$ denotes the dielectric induction caused by the time-dependent electric field $E(t)$:

$$\begin{aligned} D(t) = & \int_0^\infty E(t-t_1) \varepsilon_{1p}(t_1) dt_1 \\ & + \int_0^\infty \int_0^\infty \int_0^\infty E(t-t_1)E(t-t_2)E(t-t_3) \times \\ & \quad \times \varepsilon_{3p}(t_1, t_2, t_3) dt_1 dt_2 dt_3 \quad (2) \\ & \vdots \\ & + \int_0^\infty \dots \int_0^\infty E(t-t_1) \dots E(t-t_n) \times \\ & \quad \times \varepsilon_{np}(t_1, \dots, t_n) dt_1 \dots dt_n. \end{aligned}$$

In (2) the nonlinearity of the system is described by extended pulse response functions $\varepsilon_{np}(t_1, t_2, \dots, t_n)$, that characterise the system's response to a series of n pulse excitations. This equation can be understood as a generalisation of