Numerical Simulation of Frequency-dependent Nonlinear Interfacial Polarization in Electrolytes with Blocking Electrodes

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ABSTRACT

Time dependent distributions of mobile ions in a sample material with blocking electrodes resulting from sinusoidal external electric fields have been simulated. Harmonic components appearing in the resulting time dependent electric displacement have been used to compute linear and nonlinear permittivity spectra.

Index Terms - **Nonlinear systems, Simulation, Permittivity**

1 INTRODUCTION

POLYMER ELECTROLYTES have potential for use in sensors, membranes of fuel cells, and energy storage. Solid polymer electrolytes as basis of lightweight batteries are of particular importance [1, 2, 3]. Understanding the ionic transport mechanism may aid optimization of such electrolytes [4]. Ionic conduction especially influences the low frequency behavior of such materials because of interfacial effects (Maxwell-Wagner-Sillars effect) preventing charge carriers from leaving the sample, which leads to an accumulation of charges near the electrodes, i.e. an interfacial polarization. Thus, studying charge transport in the low frequency range is of great interest. Linear conduction spectroscopy is a standard technique to study the dynamics of ion transport in ionic conductors allowing e.g. to determine mobile ion concentration and mobility of single ion conductors [5]. Nonlinear conductive spectra have found interest recently [6] and the influence of hopping dynamics on nonlinear conduction spectra has been investigated [7,8]. In this work the time-dependent distribution of ions reacting to an external electric field has been simulated numerically.

2 SIMULATION

2.1 PARAMETERS

The simulation algorithm used to compute time-dependent distribution of ions in response to an external electric field has been described in detail earlier [9].

Analytical results for ion distributions under static electric fields for the condition that significant charge accumulation occurs only in regions very close to the blocking electrodes is available in the literature [10]. Simulated ion distributions are in excellent agreement with these analytical results [9].

A number of parameters defining the physical properties of the sample have to be input into the simulation: diffusion coefficients δ_p and δ_n of positive and negative ions, which need not be equal, the densities of positive and negative ions p and n, sample length L, and temperature T. Applicability of the Einstein relation is assumed, thus ion mobilities μ_p and μ_n are determined by diffusion coefficients.

The sample is divided into N_{cell} cells as shown in Figure 1. The cells have width $\Delta x = l/N_{\text{cell}}$. Each cell is assigned a positive and negative ion density and electric field.

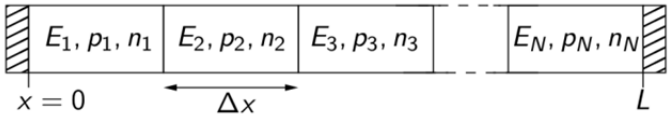

Figure 1. Sample with discrete cells; E_i, p_i, n_i are electric fields, positive and negative ion densities of i-th cell.

2.2 HARMONIC EXCITATION

Time-dependent ion distributions resulting from harmonic excitation are calculated by discretizing space and time as shown in Figures 1 and 2. The oscillation period T is divided into N_{osc} time steps of length T/N_{osc} during which the voltage is considered constant. Ion distributions are calculated at times t_k. The number of discrete voltages during one period of the excitation is typically $N_{\text{osc}} \approx 250$.

During the duration of constant voltage, the ion distributions are iterated using time steps Δt. The number of time steps is typically a few hundred up to few thousand. The exact number of iteration depends on the electric field strength, as is it necessary to assure that during one Δt the ion concentration changes not too much as described in [9], in order to obtain convergent and physically meaningful results. In short, this is done by dynamically reducing Δt until the

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