

Determining the Mobility of Ions by Transient Current Measurements at High Voltages

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We present polarization and transient current experiments that allow an independent determination of the charge carrier density and the mobility of ions in polymer electrolytes at low charge carrier density. The method relies on a complete depletion of ions in the bulk electrolyte achieved by applying high voltages. Based on a qualitative model for the charge dynamics in this nonlinear regime, the method is exemplarily applied to a system of polymethylmethacrylate doped with small amounts of a lithium salt. The independently obtained values for the ionic mobility, the charge carrier density, and the conductivity are consistent for all salt concentrations studied. Criteria for the applicability of the method are discussed.

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Polymer electrolytes are composite materials consisting of dissociated ions dissolved in a polymer matrix. Understanding ionic conduction in these materials [1,2] is of basic interest due to the relation to the segmental dynamics of the matrix [3,4] and also of importance for possible applications in batteries [5]. Generally, for diffusive transport, the conductivity $\sigma = \eta q^2 \mu$ depends on salt concentration, temperature, and the interaction of the charges with the matrix polymer. Here, η is the number density of the charge carriers, μ their mobility, and q their charge. Understanding conduction mechanisms thus requires separate measurements of μ or η in addition to σ [6,7]. The mobility is often determined indirectly from diffusion coefficients measured by NMR [1,2]. This approach is normally applied at relatively high salt concentrations, at which ion induced physical crosslinks between chain segments [4], plasticizing effects [4], or formation of ion pairs [1] may complicate the situation. Another approach consists in a quantitative interpretation of the charge dynamics in polarization experiments. In this case, strict assumptions [8] about the charge distribution at the electrodes, i.e., in the double layer, are necessary. Finally, measurements of the transit time in a capacitor containing the conductor have been suggested. This technique is well established for electron conducting materials [9,10], while it is only rarely applied to ionic conductors [11–13]. In these cases, the basic theory in [9] is not directly applicable. In fact, a clear criterion under which conditions the transient current signal can be used to determine the ionic mobilities has not been formulated [7,14].

Here, we propose and demonstrate polarization and transit time measurements at high electric fields that allow to determine the charge carrier density and the mobility independently of the details of the double layer structure. The approach is valid at low salt content. Experimental criteria for the applicability are given. Additionally, we measured the conductivity σ by impedance spectroscopy. The results are consistent. We show that in the system studied, the mobility is independent of concentration for the range covered, while changes in conductivity are governed by the concentration dependence of free, mobile

ions, pointing out the precariousness of discussions of the ionic transport mechanism based on conductivity data alone.

We consider a 1:1 electrolyte between two parallel, blocking electrodes and simplify by assuming the same mobility for cations and anions, i.e., we ascribe a mean mobility to the ions. As a consequence the charge distributions will be symmetric around the center of the capacitor [15]. In polarization experiments, a steplike voltage is applied and the electric field forces positive and negative ions to migrate to the opposite electrodes and accumulate there. Thermal diffusion opposes this charge separation. The Gouy-Chapman theory describes the resulting equilibrium by solving the Poisson-Boltzmann equation for a semi-infinite electrolyte [16]. The excess charge Q near the electrodes is contained in a diffuse layer and amounts to $Q = A\sqrt{8k_B T \epsilon \epsilon_0 \eta} \sinh[eU_0/(2k_B T)]$. The capacitance of the double layer is given by [15]

$$C_D = \frac{dQ}{dU_0} = \frac{\epsilon \epsilon_0 A}{L_D} \cosh\left(\frac{eU_0}{2k_B T}\right). \quad (1)$$

The first factor is the capacity of a parallel plate capacitor of area A , with electrodes separated by the Debye length $L_D = [\epsilon \epsilon_0 k_B T / (2e^2 \eta)]^{1/2}$ filled with a medium with dielectric constant ϵ . The second factor shows that with increasing potential U_0 the thickness of the double layer decreases leading to a capacity C_D which diverges for high voltages. This part is neglected in the Debye-Hückel limit, $eU_0/(2k_B T) \ll 1$. A more realistic model avoiding this divergence is obtained by introducing a compact Stern layer of thickness L_S which takes into account the finite size of the ions and solvent molecules leading to a capacitance $C_S = \epsilon \epsilon_0 A / L_S$ in series to C_D . In this way, the total capacitance $C_{\text{tot}}^{-1} = C_D^{-1} + C_S^{-1}$ [15] remains finite for all voltages. A typical Stern layer thickness is estimated to $L_S \approx 0.5$ nm [17,18]. Application of this model seems appropriate if the charge density far away from the electrode interface is constant, i.e., the accumulation of charges at the electrodes does not consume a significant amount of the total charge present in the system. If furthermore the

double layer is much thinner than the thickness d of the capacitor, i.e., $d \gg L_D$, the cell can be described by an equivalent circuit with a resistor R_B representing the bulk electrolyte in series with two capacitors with capacity C_{tot} [15]. Within this model the charging time $\tau = RC$ does not necessarily correspond to the transit time of the ions between the electrodes, since polarization is based only on a partial shift of the charge distribution. To construct a viable interpretation of τ , the Debye-Hückel approximation, $C_{\text{tot}} = C_D(U_0 = 0 \text{ V})$, can be used [8], a strict assumption difficult to verify.

To circumvent this problem, we propose polarization and polarization reversal experiments at high fields and low ion concentrations. If the polarization is caused by a constant voltage U_0 , large enough to force all the mobile ions to migrate to the electrodes, the integrated polarization current is directly related to the total mobile ionic charge in the sample, independent of the details of charge distribution near the electrode. The integrated current that flows in the outer circuit if a charge moves a distance x is proportional to x/d , where d is the separation of the electrodes [19]. Before a potential is applied across the electrolyte film, the charge carriers are homogeneously distributed. In the final steady state, all the charges are close to the electrodes, and the charges have moved a distance $d/2$ on average. The accumulated charge $Q = \int I(t)dt$ then equals half of the total charge in the sample, i.e., $Q = \eta eV/2$, where $\eta = \eta^+ + \eta^-$ is the charge carrier density and V the volume. Of course, even at high voltages, the charge carriers will not come infinitely close to the electrodes, but the relative error for Q is smaller than $L_D/d \lesssim 10^{-3}$ for the system under consideration. In fact, the value of Q is not only largely independent of the exact charge distribution near the electrodes but also independent of whether or not the electrodes are blocking, as long as a complete charge depletion in the bulk can be achieved.

The steady state reached at the end of the polarization experiment serves as the initial state for a measurement of the transit time which is conceptually analogous to the classical electronic time of flight experiment by Many *et al.* [9,10]. In Fig. 1(a), the charge density $\rho(x)$ and the electric field $E(x)$ in this state are shown schematically. All the charge carriers are close to the electrodes. We assume though that the double layer is still able to adjust to the external field and screens the field in the bulk, i.e., the full voltage drops across the double layers. Immediately after a polarity reversal of the applied voltage, when no ions have been redistributed yet, the electric field looks as shown in Fig. 1(b). The double layers are separated from the bulk by two planes with $E = 0$. Therefore, initially only a few charges contained in the tails of the double layers will start to migrate towards the other electrode. The evolution of the charge density is sketched in Fig. 1(c). With time, the number of moving charges increases leading to an increasing current in the outer circuit. A maximum in the current is obtained, when the first ions reach the opposite elec-

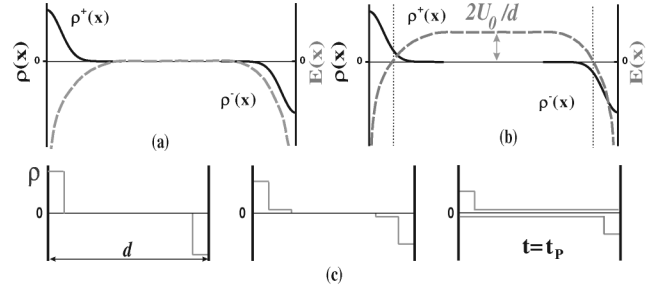


FIG. 1. A sketch of the charge density (black line) that is completely depleted in the bulk and the electric field (gray dashed line) across the capacitor before (a) and immediately after (b) the polarity of the voltage is reversed. (c) shows schematically the charge density evolution after the voltage reversal. The thickness of the double layer is strongly exaggerated.

trode, because now the accumulating charges again start to screen the field. Assuming that the small amount of moving ions does not affect the electric field substantially [20], the time t_p of the maximum current corresponds to the transit time under a constant field: $t_p = d/v = d^2/(e\mu U)$, where $U = 2U_0$ [cf. Fig. 1(b)]. For the velocity, $v = \mu eE$ is used; again, $d \gg L_D$ is assumed.

For the experiments, we used poly(methylmethacrylate) (PMMA, $M_w = 101 \text{ kg/mol}$; $M_w/M_n = 2.1$) and the salt lithiumtriflate (LiCF_3SO_3 , $M = 156 \text{ g/mol}$, ions: Li^+ and CF_3SO_3^-). Propyleneglycolmonomethyletheracetate (PGMEA), a solvent for both components was used to prepare a salt and a 10% polymer solution which were mixed to get the desired PMMA to salt ratio. All materials were used as received from Aldrich. We define the salt concentration c_m as the mass ratio: $c_m = m_{\text{Salt}}/m_{\text{PMMA}}$. The concentration c_m was varied between 10^{-5} and 10^{-3} , corresponding to a salt molecule to monomer ratio of $[\text{LiCF}_3\text{SO}_3 : \text{monomer}] = [1:156000-1:1560]$. The final solution was cast on gold plated electrodes. The films were dried for 24 h at room temperature and annealed for 72 h at 170°C in vacuum to remove remaining PGMEA and water. After cooling to room temperature in vacuum, the top gold electrode ($\varnothing = 2 \text{ cm}$) was pressed at 170°C onto the film using Kapton spacers. Film thicknesses were varied between $20 \mu\text{m}$ and $70 \mu\text{m}$. All electric experiments were performed at 165°C , well above the glass-transition temperature of PMMA ($T_g \approx 110^\circ\text{C}$). Impedance spectroscopy ($f = [10^{-1}-10^6] \text{ Hz}$) was performed using a Novocontrol Alpha Analyzer. The sample temperature was controlled via a heated, dry N_2 -stream, which additionally provided an inert atmosphere. Subsequently, the same capacitor with the sample was put into a homemade setup with temperature controlled, inert (constant N_2 -flow) sample environment for high sensitivity current measurements. A Keithley 6517A electrometer served as voltage source and Ampere meter.

A typical polarization experiment is shown in Fig. 2(a). A voltage step ($U_0 = 300 \text{ V}$) induces a polarization current which decreases with time until it reaches a steady

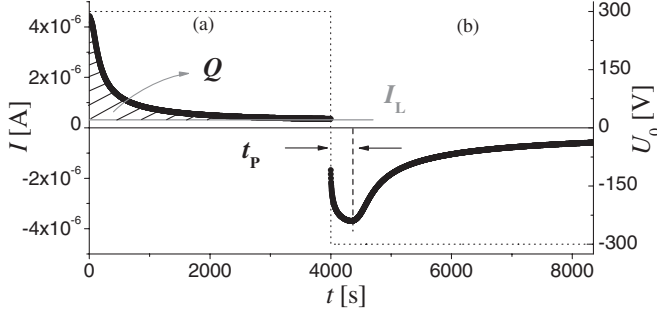


FIG. 2. Polarization (a): application of a constant voltage (dotted line) forces the mobile ions to move to the electrodes. The integrated current corresponds to accumulated charge. Voltage reversal (b): the current shows a peak at transit time t_P after the change of polarity. [$c_m = 10^{-3}$; $d = 58 \mu\text{m}$; $Q = 1.8 \text{ mC}$; $t_P = 400 \text{ s}$; $I_L = 0.32 \mu\text{A}$; $I(t=0) = 4.50 \mu\text{A}$.]

state which is determined by a leakage current I_L . The value $I_L = 3.2 \times 10^{-7} \text{ A}$ would correspond to a conductivity $\sigma_L \approx 2 \times 10^{-10} \text{ S/m}$. The leakage current is ohmic, and the corresponding resistance I_L/U_0 is constant within a factor of 2 for samples with different salt concentrations. To obtain information about the amount of ionic charge in the sample, the leakage current is subtracted before integration: $Q = \int_0^{t_{\text{steady}}} [I(t) - I_L] dt$. As discussed above, only in case of complete polarization Q corresponds to the total ionic charge in the system. Therefore, the calculated charge Q should increase with increasing U_0 until all the mobile charges are consumed and then remain constant. The result of such an experiment, for our highest salt concentration, $c_m = 10^{-3}$, is shown in Fig. 3. For voltages above about 50 V, Q/Q_{max} , where Q_{max} is the value expected if all added ions were free and mobile [cf. Eq. (2)], is approximately constant, i.e., a complete polarization was achieved. All further experiments were therefore made with voltages $U_0 \geq 70 \text{ V}$. The resulting charge carrier density $\eta = 2Q/(eV)$ is shown in Fig. 4(a) as a function of the concentration c_m . All points shown are averages over several measurements at different voltages. Assuming full dissociation and a negligible amount of intrinsic charge, the expected dependence of the charge carrier density on the salt concentration c_m for $c_m \ll 1$ amounts to:

$$\eta(c_m) = \alpha N_A \frac{\rho}{M_{\text{salt}}} \frac{c_m}{c_m + 1} \approx \alpha N_A \frac{\rho}{M_{\text{salt}}} c_m. \quad (2)$$

Here, $\alpha = 2$ is the number of ions per molecule, N_A the Avogadro number, ρ the mass density of the electrolyte. With the approximation $\rho \approx \rho_{\text{PMMA}} = 1.1 \text{ g/cm}^3$ (165°C) (extrapolation based on data from [21]), Eq. (2) yields, $\eta(c_m) = 8.5 \times 10^{27} \text{ m}^{-3} \cdot c_m$. This relation is shown as a straight line in Fig. 4(a). Good agreement is found for concentrations up to $c_m \approx 10^{-4}$. For the higher two concentrations, deviations from the linear behavior occur, i.e., dissociation was incomplete or the ions were partially immobile.

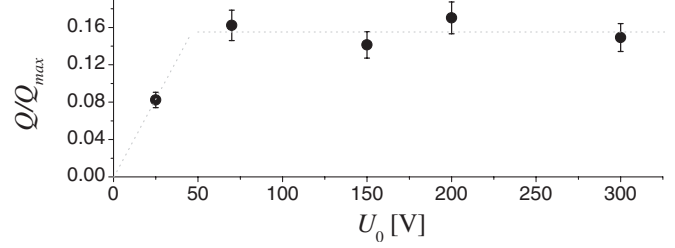


FIG. 3. Ratio of accumulated charge Q and maximum charge Q_{max} vs applied voltage U_0 for $c_m = 10^{-3}$. For complete polarization the ratio Q/Q_{max} gives the fraction of free, mobile ions.

Let us now turn to the transient current measurements obtained after voltage reversal starting from the final state after complete polarization. An exemplary data set is shown in Fig. 2(b). The current which is opposite in direction compared to the polarization experiment first increases and then decreases before reaching a steady state. The transit time t_P corresponds to the maximum at 400 s. Within the constant field assumption [see Fig. 1(b)], this value corresponds to a mobility $\mu = d^2/(et_P 2U_0) = 8.8 \times 10^4 \text{ m}^2/(\text{N s})$. The result of a series of such experiments is shown in Fig. 5(a). The velocity v is plotted as a function of the force F for different salt concentrations. The transit times t_P varied between 400 and 2500 s for voltages U_0 in between 70 and 300 V and thicknesses d in between 20 and 70 μm . Consistent with the constant field approximation, a common linear relation between v and F is observed for all concentrations. Furthermore, the result shows that the mobility $\mu = (8.4 \pm 0.5) \times 10^4 \text{ m}^2/(\text{N s})$ is independent of concentration.

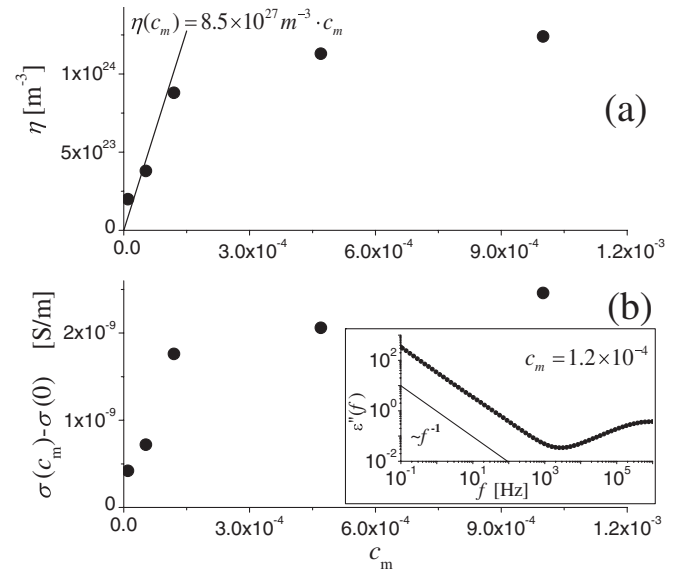


FIG. 4. (a) The charge carrier density η for small values of c_m agrees well with the expected values for full dissociation shown as a solid line. (b) Reduced conductivity $\sigma(c_m) - \sigma(0)$ vs c_m (nondoped PMMA: $\sigma(0) = 5.4 \times 10^{-10} \text{ S/m}$), as determined by impedance spectroscopy. The inset shows an exemplary measurement of the imaginary part ϵ'' of the dielectric function.

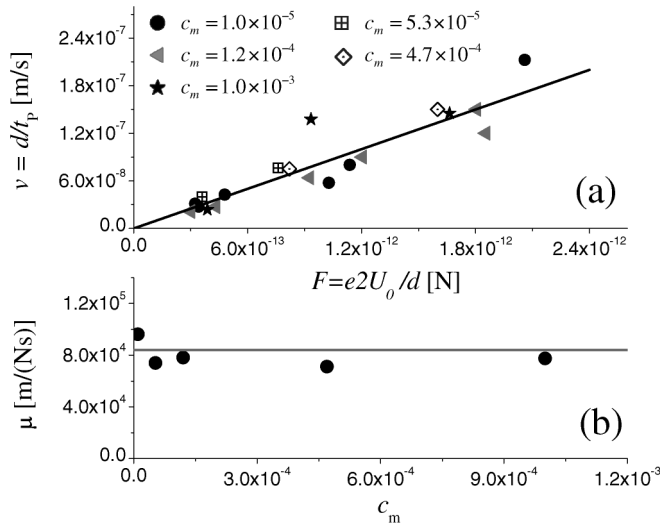


FIG. 5. (a) The velocity calculated from the sample thickness d and the transit time t_p vs the force F on the charges for different c_m . The force was varied by changing both sample thickness and applied voltage. The slope of the black line corresponds to a mobility of $\mu = 8.4 \times 10^4$ m/(N s). (b) Mobility vs salt concentration as determined from charge carrier density and conductivity (filled circles) in comparison to the value obtained by transient current measurements (solid gray line).

To check the validity of the approach described above, we performed impedance spectroscopy to obtain concentration-dependent conductivity values from the imaginary part of the dielectric function [19]: $\epsilon''(f) = \sigma / (2\pi\epsilon_0 f)$ for frequency $f \rightarrow 0$. An exemplary measurement is shown in the inset of Fig. 4(b). For the pure PMMA with no salt added, the conductivity is $\sigma(0) = 5.4 \times 10^{-10}$ S/m resulting from few but highly mobile charges in the PMMA as received. To compare the concentration dependence of the ionic conductivity and the ionic charge carrier density, a reduced conductivity $\sigma(c_m) - \sigma(0)$ is shown in Fig. 4(b). The resemblance of the two data sets in Figs. 4(a) and 4(b) is remarkable.

The combination of experimentally determined charge carrier density and conductivity allows a second, independent determination of the mobility $\mu = [\sigma(c_m) - \sigma(0)] / (e^2 \eta)$. The resulting values are shown in Fig. 5(b) together with the result from the transient current experiments. The good agreement confirms that in the range covered the concentration dependence of the conductivity is governed by the concentration-dependent number of mobile, free ions, while the mobility itself is constant. Furthermore obviously the same number of charges contributes to the polarization current where the bulk is completely depleted, as to the conductivity measured by impedance spectroscopy, where the charges are separated on a local scale only. The formation of ion-polymer com-

plexes [22] leading to an immobilization of parts of the ions or ion pairing [1] could explain such a behavior.

In conclusion, we demonstrated that transient current measurements in a polymer electrolyte starting from the well defined situation of complete polarization allow the determination of the ionic mobility on the basis of a qualitative model for the charge dynamics. The method relies on the application of large voltages and is applicable for systems with a small amount of mobile charges. For the system under consideration, the mean ionic mobility is constant in the concentration range studied. The separate determination of mobility and charge carrier density demonstrated here should be valuable for basic investigations on charge transport in ionic conductors.

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