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Transient nonlinear response of dynamically decoupled ionic conductors

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The present study demonstrates that large electric fields progressively enhance the conductivity of ionic systems up to timescales corresponding to those on which their structural rearrangements take place. Yet, in many ionic materials, some regarded as candidates for electrical energy storage applications, the structural relaxation process can be tremendously slower than (or highly decoupled from) charge fluctuations. Consequently, nonlinear dielectric spectroscopy may be employed to access rheological information in dynamically decoupled ionic conductors, whereas the combination of large electric power density and good mechanical stability, both technologically highly desired, imposes specific experimental constraints to reliably determine the steady-state conductivity of such materials.

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Triggered by a continuous upsurge in the world's energy consumption, one goal of modern science is to provide up-to-date recipes for an efficient harvesting and storage of renewable electric energy.[1] Naturally, any progress in the development of novel materials suiting these needs requires the understanding of the microscopic mechanisms governing their electric conductivity.[2,3] On the other hand, for most electrochemical applications (*e.g.*, batteries), these materials should be not only electrically proficient, but also light and ductile, yet lacking liquid-related safety hazards.[4] Consequently, their mechanical behavior plays an important role as well.

Most suitable for small-size encapsulations are polymeric materials which nowadays are manufactured at relatively low costs, in a large morphological diversity, and can be cast as flexible, thin films. Hence, it is no surprise that the popular lithium-ion batteries employ polymers as structurally stable matrices hosting the mobile charge carriers.[5] Synthesized directly from ionic liquids,[6] the polymerized ionic liquids (PolyILs) are an emerging class of ionic conductors, combining a number density of charge carriers similar to that of ionic liquids with a rubbery mechanical behavior.[7] In these ionomers either the anions or the cations are covalently connected to directly build the polymeric network in which the unbonded counterions are able to perform long-range diffusion. These single-ion conductors bear significant advantages for many applications, and are excellent testing grounds for phenomenological and theoretical approaches aiming to describe fundamental aspects of both polymer dynamics and of charge transport in general.

In most PolyILs the conducting moieties are dynamically decoupled from the structural rearrangement of the matrix.[8,9] Although this decoupling phenomenon is shared by a broad array of ionic materials,[10] the underlying mechanisms controlling its magnitude are still unresolved. Nevertheless, a recent PolyILs study[11] showed how the degree of decoupling, defined as the ratio between the characteristic times of ionic and structural relaxation processes, can be tuned via the degree of polymerization: While for the monomeric (ionic) liquids charge transport is well coupled to microscopic flow,[12] the dynamical contrast between these two processes increases progressively with the increase in the chain length and may easily reach up to 7 orders of magnitude near the glass transition temperature T_g.[9,13] Such large degrees of decoupling are technologically highly beneficial, as they reflect mechanical stability combined with high charge mobility. This "super-ionic" behavior,[14] combined with the single-ion character of conductivity renders PolyILs promising candidates for the next generation of electrochemical applications.

Regarding present storage devices, as in other emerging technological areas, significant research efforts are devoted to their miniaturization. Concepts such as printable batteries[15] and nanobatteries[16] are gaining considerable attention, with the hope that they will improve the power-density shortcomings of present technologies. However, if the thickness of a conducting material is reduced to the sub-micrometer range, even small voltages (on the order of volts) may generate large electric fields which drive the material beyond linear response. In this *nonlinear* regime higher-order conduction effects start playing a significant role.[17]

Although nonlinear effects in viscous liquids have recently gained a large interest in the glass community,[18] their investigation for the case of conducting materials is scarce, with a focus on ionic liquids[19,20,21,22,23] and solid (glassy) ionic conductors[24,25] These studies reveal fascinating phenomena, not accessible via linear investigations: dynamically heterogeneous charge transport,[24] compliance with the reverse calorimetry concept,[19] accessibility of effective ionic jump lengths,[20] the emergence of "hump" features in the third-order conductivity spectra,[23] and anomalous Wien effects[22,26] for ionic liquids. To the best of our knowledge, such investigations are lacking for the scientifically and technologically highly relevant polymeric materials. Since PolyILs allow to adjust/tune the degree of decoupling, it is interesting to check how the above mentioned phenomena emerge in these materials.

Here, we report on nonlinear effects arising under high power-density conditions, specifically for highly concentrated electrolytes under the impact of high AC electric fields. The addressed questions include: To what extent does the nonlinear response of dynamically decoupled ionic materials differ from that of coupled systems such as ionic liquids? Regarding the perspective of nanostorage devices operating under nonlinear conditions: What is the timescale on which the nonlinear response of a given material reaches a steady state after a high field is applied or switched off? Our study reveals that the time scale on which the response to this nonlinear perturbation takes place matches well those of the structural rearrangements even in systems with strongly decoupled ionic conductivity. This discovery bears major theoretical and practical implications.

The investigated ion conductors belong to the poly(N-vinylethylimidazolium) bis(trifluoromethylsulfonyl)imide series of PolyILs with the chemical structure shown in the inset of Fig. 1(b). The synthesis and several characteristics of these materials have been discussed elsewhere.[11] Most interesting for the present study is that their differing degree of polymerization *n*=1, 2, 3, 10, and 109, allows for the rather unique possibility to investigate how ionic materials with tailored degrees of decoupling of ion transport from structural relaxation respond to nonlinear perturbations.

To illustrate how the polymerization of ionic liquids triggers a significant dynamical contrast between charge polarization and structural relaxation, Fig. 1(a) and (b) present the *linear* dielectric and mechanical responses of the trimer (*n*=3) sample as measured by means of an Alpha Analyzer from Novocontrol and a MCR521 rheometer from Anton-Paar (frequency range: 0.1 to 100 Hz), respectively. These results are in good agreement with previous investigations[11] The corresponding frequency-dependent results are plotted as the dielectric (M'') and the shear (G'') modulus loss, to allow for a direct comparison of the spectra provided by the two methods. The peak frequencies ν_M and ν_G yield characteristic conductivity and mechanical relaxation times, respectively. The dielectric time constant $\tau_M=1/(2\pi\nu_M)$ corresponds to charge fluctuations in the ionic relaxation process, while its mechanical counterpart $\tau_G=1/(2\pi\nu_G)$ reflects the microscopic flow events governing the local structural rearrangement. As revealed by the difference between the peak positions in Fig. 1(a) and (b), the unbonded anionic charges exhibit an about tenfold faster dynamics than the structural relaxation of the cationic trimer, despite its small degree of polymerization.

How does polymerization affect the *nonlinear* dielectric response of these materials? For the nonlinear investigations the samples were confined between two 4 mm thick well-polished disk-like electrodes made of brass and separated by a 10 µm thick Teflon ring. This small gap leads to high fields while preventing sample heating due to Joule effects.[27] The AC voltages were supplied by a HVB1000 booster from Novocontrol in the range of 3 to 450 V (corresponding to E_0 *peak* fields from 3 to 450 kV/cm).

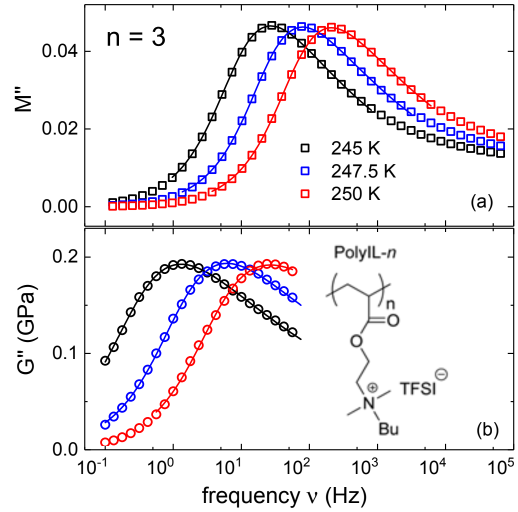

Fig. 1 (a) Dielectric and (b) shear modulus loss spectra of the trimer (*n*=3) at three selected temperatures. The chemical structure of the investigated PolyILs is depicted as inset in panel (b). Here *n* is the degree of polymerization and the acronyms "Bu" and "TFSI" stand for butyl group and bis(trifluoromethylsulfonyl)imide, respectively.

In Fig. 2 we compare the frequency dependent nonlinear conductivities obtained for (a) the dimer and (b) the 109-mer at 230 K, and 250 K, respectively. These temperatures were chosen such that the "DC" to "AC" crossover in the conductivity spectra[9] occurs in the available frequency window. The filled symbols correspond to the first-order conductivity relating the base current density j_1 with E_0 according to

$$\frac{j_1'}{E_0} = \sigma_{1,1} + \frac{3}{4}\sigma_{1,3}E_0^2 + \dots, \qquad (1)$$

and the open symbols refer to the third-order conductivity governing the higher-harmonics current density j_3 (at 3ν) via[21]

$$\frac{j_3'}{E_0} = \frac{1}{4}\sigma_{3,3}E_0^2 + \frac{5}{16}\sigma_{3,5}E_0^4 + \dots. \qquad (2)$$

The first observation is that the general characteristics exhibited in the nonlinear spectra of the dimer (practically an ionic liquid) agree with previous studies of (monomeric) liquid electrolytes.[21,22,23] Most importantly, at first glance the long-chain system seems to reveal a response which is also similar to that reported for some ionic liquids.[28] However, it is important to emphasize a critical aspect regarding the experimental procedure leading to these results: For both materials the frequency sweeps were performed in a conventional manner, with an integration time of maximum 0.5 s or one period for each data point and no time delays inserted between the probing intervals. Does this procedure enable a correct determination of the nonlinear effects? Are the latter fully established within just a few periods of the applied field?

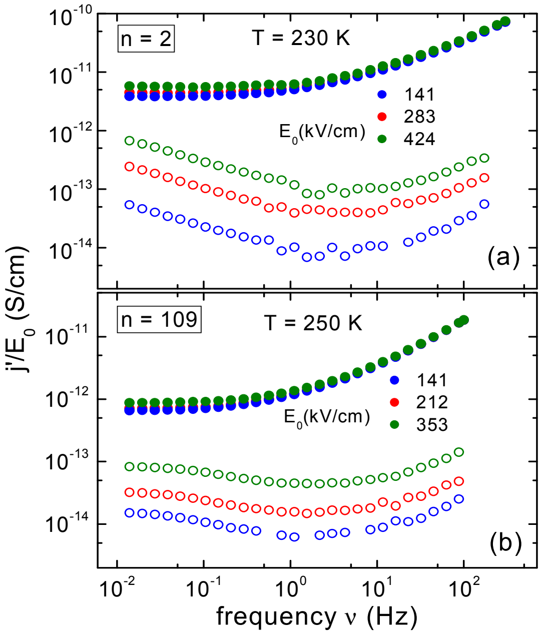

Fig. 2 First-order (j_1'/E_0, filled symbols) and third-order (j_3'/E_0, open symbols components of electrical conductivity probed at three fields for (a) the dimer at 230 K and (b) the 109-mer at 250 K. Both materials are seen to exhibit similar nonlinear behavior.

We address these questions by monitoring the time evolution of the conductivity in so-called *transient* nonlinear experiments.[17,19] The idea behind such experiments is sketched in Fig. 3(a). The procedure involves small-amplitude voltage cycles probing the linear response, followed by a step-like increase in the amplitude of the excitation for a time interval during which the material is driven out of equilibrium. Thereby, one monitors the time evolution of the nonlinear response at a given frequency. After a sufficiently long large-amplitude excitation the peak voltage is reduced so that the "dissipation" of the nonlinear effect can be monitored.

The time-dependent results obtained for n=10 are shown in Fig. 3(b) where each data point is recorded after one cycle. Here one observes that, as soon as the high AC field is applied, the response increases due to the emerging $\sigma_{1,3}(t)E_0^2$ term [see eq. (1)], but it reaches saturation only at longer times. In harmony with previous investigations,[17] the "equilibration" time τ_{eq} can be estimated from the transient data using a squared stretched exponential function, see the red solid line in Fig. 3(b). Similar results obtained for the other systems investigated in this study are presented as Supplemental Material. They reveal that τ_{eq} is a material specific constant which does neither depend on the measuring frequency nor on the amplitude of the applied field, but only on temperature, as discussed next.

In the Arrhenius diagram presented as Fig. 4 we compare the results obtained for τ_{eq} with those for τ_M and τ_G extracted from the linear electrical and rheological investigations for n=1, 3, and 10. Due to electrode polarization effects[9] which in the presence of decoupling are dominating the sub-kHz response near T_g, we were not able to monitor the temporal evolution of the *conductivity* spectral contribution for n=109. It is reasonable to consider that near T_g this experimental restriction holds also for larger n, and in general for any material with a very large degree of decoupling.

The τ_{eq} data in Fig. 4 refer to switching the high fields on and to switching them off. At a given temperature they differ by a factor of about 2, in line with previous reasoning.[17] Here the results for τ_G and τ_M are added for comparison. The finding for n=1 that τ_G is slightly smaller than τ_M is typical for well-coupled ionic liquids in which each ion hop is also a rheological event.[12] For the trimer the polymerization reduces the overall mobility of the cationic units. Enslaved by strong Coulombic interactions, the dynamics of anions slows down as well, but not so drastically. Consequently, the charge transport decouples from the structural rearrangements, as observed in Fig. 4 from the separation between τ_G and $\tau_M > \tau_G$, which increases markedly towards low temperatures.

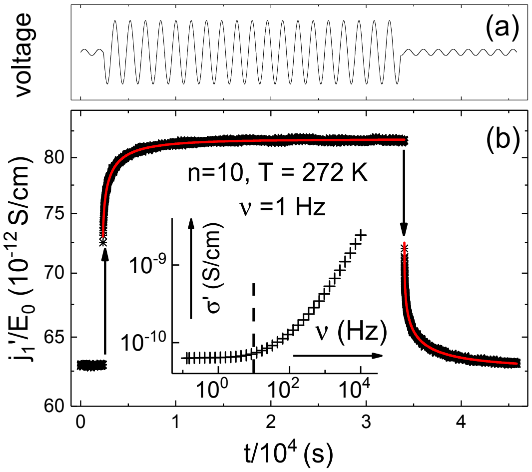

Fig. 3 (a) Schematic voltage profile used in the transient nonlinear investigations. (b) Time-resolved conductivity for n=10 at 272 K, probed at 1 Hz with an AC field with E_0 varying stepwise from 3 to 100 kV/cm and back to 3 kV/cm at the times marked by the vertical arrows. The red lines are fits with a squared Kohlrausch function, cf. Ref. 17. The inset shows a linear spectrum (probed with 3 kV/cm) taken at 272 K; the vertical line marks the frequency used in the transient experiments.

While the trimer displays only a slight decoupling, the latter is much more pronounced for the decamer (Fig. 4): Near the glass transition temperature of this material, T_g≈270 K,[11] charge dynamics is roughly five orders of magnitude faster than the structural relaxation. Reflecting the freezing-in of structural fluctuations, the corresponding τ_M displays a crossover in its temperature dependence at T_g. This behavior is shared by other systems with significantly decoupled charge dynamics,[29] and reflects a change in the transport mechanism of charges which are diffusing through a slowly relaxing viscous melt above T_g and through a frozen energy landscape at lower temperatures. The relaxation times based on linear measurements agree well with previous ones.[11]

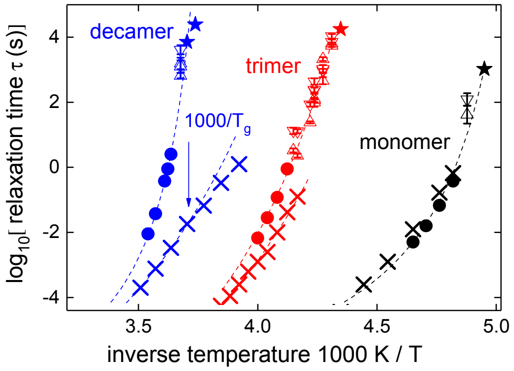

Fig. 4 Temperature-dependent time constants determined by means of linear shear rheology (τ_G, dots), linear dielectric spectroscopy (τ_M, crosses), aging experiments (τ_{ag}, stars), and time-resolved nonlinear conductivity investigations (τ_{eq}, triangles pointing downwards refer to the high fields being switched on and upwards to the switch-off situation). The time constants τ_G and τ_M have been extracted from well-defined modulus peak maxima (see Fig. 1), leading to experimental uncertainties on the order of the symbol size. The vertical blue arrow marks T_g of the decamer. The dashed lines guide the eye.

In the present work the accessibility range of the structural relaxation times was extended deep into the viscous regime by means of physical aging experiments. They are performed near T_g by monitoring the isothermal time evolution of the dielectric response subsequent to a small temperature step, thereby providing access to the structural relaxation times in glass forming materials.[30,31,32,33] The experimental details and the data analysis employed for extracting the characteristic aging times, τ_{ag}, of the presently studied systems are provided as Supplemental Material. The results for τ_{ag} are included in Fig. 4. For the monomer they agree with both τ_M *and* τ_G, whereas for the trimer and the decamer they are consistent with the rheological τ_G, only, since τ_M decouples from the structural relaxation.

Having significantly broadened the dynamic range of Fig. 4, one clearly observes that the transient high-field effects in the decoupled systems are intimately related to the local rearrangement of the ionic *environment* (the cationic matrix) and not to the mobile anions dynamics, which otherwise governs the *linear* conductivity in these materials. Based on the large contrast between τ_{eq} and τ_M for n=10 it is clear that above observation is independent of the types of analyses employed in this study (*e.g.*, using compliance instead of modulus response, using a linear rather than a squared stretched exponential function, etc.).

Based on the present results one may justify the increase of the conductivity under the influence of high fields by considering that the structural rearrangements leads to a reduction of the effective energy barriers or, alternatively, to an increase in the configurational temperature of the charge carriers.[19] Most importantly, these changes do not occur on a time scale associated with mobile ions motions, but on the time scale of the structural rearrangements, emphasizing the importance of structural cooperativity effects even for systems governed by strongly decoupled ion transport.

These results bear several important physical consequences. First of all, for decoupled ionic materials the usual experimental procedure applied for the acquisition of spectra as the ones presented in Fig. 2 does not yield equilibrium data. Highly relevant for both technical applications and theoretical description of nonlinear phenomena is that high electric fields drive ionic conductors out of equilibrium in the same way as a temperature step acts upon their structural rearrangements. Consequently, the dielectric nonlinear investigations of decoupled materials, although performed under *isothermal* conditions, deliver similar information as measurements of physical aging (*per se* also a nonlinear effect)[34] and/or rheology, as demonstrated here for the example of PolyILs. The present results rationalize recently reported time-dependent effects in nanobatteries.[35] Since they occurred in conducting films under the influence of fields as large as 1 V/Å (10^5 kV/cm) it is reasonable to assume that they are of nonlinear nature. Finally, our results call for a reexamination of previous nonlinear investigations performed in decoupled materials of ionic and perhaps also dipolar nature.[36]

In view of the wide range of applicability of these materials in currently employed storage technologies, a theoretical description of nonlinear effects in decoupled ionic conductors is highly desirable. To the best of our knowledge, suitable approaches are currently not available. Nonetheless, according to our results any theoretical description of nonlinear perturbations requires their analysis over timescales imposed by the slow structural relaxation process, a difficult task for highly decoupled systems and out of reach for glassy materials. To cut short this transient behavior in technical applications one may consider matrices formed by (flexible) polymers with low T_g and very long chains. This way one may enhance the local structural mobility while macroscopically the framework rigidity is preserved by the large degree of polymerization.[37]

In conclusion, based on results obtained via linear dielectric and rheological spectroscopies, physical aging, and transient nonlinear dielectric investigations, we analyzed the impact of large electric fields on the conduction behavior of a homologous series of oligomeric ionic liquids. The studied materials combine a large number density of charge carriers with a large contrast between mass flow and charge dynamics, all highly relevant for the next generation of electrochemical applications. Under high power-density conditions this mélange of physical characteristics leads to a conduction behavior enslaved by the slow rearrangement of the ionic matrix in these materials. This discovery bears great potential for the rationalization of the conduction mechanisms in present storage technologies and, by providing a recipe for the adjustment of the transient nature of the unavoidable nonlinear effects, it paves the way for the rational design of the next generation of conducting materials in small-size storage applications.

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