Relaxation phenomena in cryogenic electrolytes

V. Shikin[1], I. Chikina[2], and S. Nazin[1]

[1]*Institute of Solid State Physics of RAS, Moscow distr., Chernogolovka 142432, Russia*

[2]*IRAMIS, LIONS, UMR SIS2M 3299 CEA-CNRS, CEA-Saclay, F-91191 Gif-sur-Yvette Cedex, France*
E-mail: shikin@issp.ac.ru

Proposed is a scenario for development of observed relaxation phenomena in the cryogenic electrolyte with the structure of "liquid hydrogen + injected ions". Ions of one sign are generated in the bulk of liquid hydrogen in the presence of external field $E_\perp$ by a stationary radioactive source of $\pm$ ions at the bottom of the vessel. After accumulation near the free surface of the liquid with a finite density n_s the ions can break its stability producing a pulse of ion current to the collector located above the liquid surface. The outlined process is periodically repeated. Its period contains information on the ion mobility and, which is most interesting, on dissociation (association) processes occurring in a system of charged particles placed in an external field. The cryogenic problem is a good model for dissociation in the presence of external field occurring in normal electrolytes without any external ion sources.

Relaxation oscillations of the current accompanying its stationary flow are rather frequently observed in various conductors. Among others, one should mention ion density modulation stimulated by the current flowing through the gaseous plasma column (formation of fixed or moving strata [1]), high-frequency Gunn effect [2], so-called recombination waves in semiconductors with deep impurity and dislocation levels [3–5], etc. Usually, major efforts in the study of oscillations arising at the background of dc current-voltage curve (IVC) are focused on establishing the nature of the instability resulting in the development of oscillations. Proposed in the present report is a relatively simple and very transparent scenario for the development of relaxation oscillations in the ionic current through the vapor–liquid interface of weak liquid electrolytes (including cryogenic ones) driven by electric field $E_\perp$ normal to the liquid surface. In that case details of the IV curve allow to extract information on real behavior of the important parameter of the electrolyte, its degree of dissociation α, under the conditions of transport current.

Actually, the problem with α for electrolytes is as follows. The dissociation degree is defined [6,7] as the ratio

$$\alpha = n_i/n_0, \quad 0 < \alpha < 1, \tag{1}$$

where n_0 is the density of neutral donors and n_i is the density of ions arising due to the dissociation of neutral donors. According to Refs. 6,7, the main source of data on α is the electrolyte Ohmic conductivity σ_i calculated as

$$\sigma_i = en_i\mu_i, \quad n_i = \alpha n_0, \tag{2}$$

where μ_i is the mobility of the relevant type of ions. If independent data on n_0 and μ_i are available, one can extract from the measured conductivity σ_i the values of α for different temperatures, solvents, etc.

The simple and natural reasoning concerning properties of α outlined by Eqs. (1) and (2) is actually complicated by the real processes involved in formation of σ_i. The point is that among the details affecting behavior of IVC one should take into account the structure of the ions (for simplicity, we neglect various factors complicating the IVC at the metal–electrolyte interface). All ions are surrounded by a zone with higher density solvent (solvation (hydration) effect [6,7] , snowball effect in superfluid helium [8]) and thus form charged clusters of radius $R_i > R_B$, where R_B is the effective Bohr radius of the bare charge. Therefore, the charged cluster core should first leave the surrounding shell before exchange its charge with the electrode, which is an additional (along with the α temperature dependence) poorly defined thermo-activated process affecting the structure of IVC. Thus, available data on $\alpha(T)$ derived from the Ohmic part of the IVC by employing Eq. (2) may contain some inherent uncertainty. Proposed in the present paper is an alternative technique allowing to reduce this uncertainty. The indicated technique can be applied to helium where direct dc transport measurements cannot be performed.

We consider the current passing through vapor–liquid interface of a weak electrolyte driven by electric field $E_\perp$ normal to the liquid surface. Weak current flowing from the bulk to the liquid surface gradually charges the liquid–vapor interface up to the critical density Θ_c at which the surface becomes unstable (the definition of Θ_c is given by Eq. (6) below). Then a breakdown occurs, the surface charge flows to the electrode, and accumulation of the charge under the liquid surface governed by the field $E_\perp$ is repeated again. It is important that the quantity Θ_c does not depend on the internal structure of ions arriving to the free liquid surface unlike the liquid-metal interface.

Charges leaving the liquid electrolyte can be generated by natural dissociation in bulk liquid (which, in the presence of nonzero $E_\perp$, is an interesting process in itself). In cryogenic electrolytes finite ion density is maintained by some external source.

1. For the implementation of the outlined program, consider a flat capacitor almost completely filled with liquid electrolyte (see Fig. 1). The exact filling degree of the capacitor with the solvent is not critically important. The only vital feature is the presence of a free surface near the top electrode. In Fig. 1 the free surface almost touches the electrode to avoid additional boundary conditions in the electrostatic part of the problem.

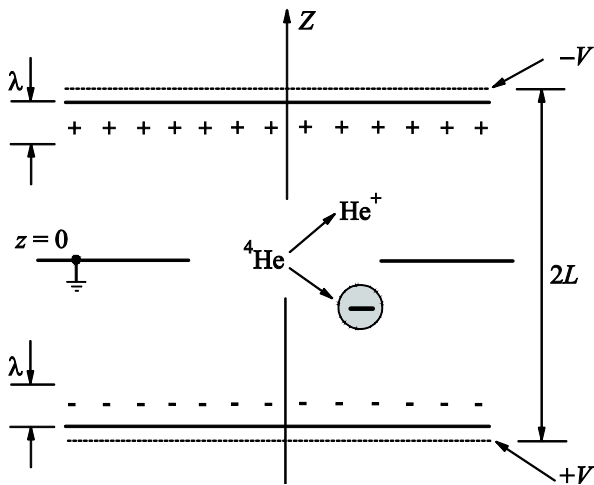The lower part of the liquid in the cell is in ohmic contact with the bottom electrode. The electric field $E_\perp$

Fig. 1. Cell proposed to produce $2D$ ion layers near the boundaries of bulk liquid with thickness L in the presence of external field $E_\perp$. The top metal electrode is shown with the dashed line. The lower electrode resides in the plane $z = 0$ and is grounded, as indicated in the figure. Solid line near the top electrode represents the vapor–liquid interface which has no electric contact with the electrode while the lower part of the liquid has an ohmic contact with the bottom electrode residing in the plane $z = 0$. The lower part ($-L < z \le 0$) of the figure is a mirror image of the upper part of the cell. Dissociation of a He atom produces a positive ion (cluster) and an electron bubble (shown by a circle with the "minus" sign inside). The layer thickness λ is diefined by Eq. (5).

within the cell is created by applying the potential difference V to the liquid boundaries at $z = 0, L$. While the charge of one sign is being accumulated in the vicinity of the liquid–vapor interface almost coinciding with the plane $z = +L$, the opposite sign charges escape to the bottom grounded electrode maintained at zero potential $V = 0$ (or move to the boundary $z = -L$ which which is artificially introduced to simplify calculations and is the image of the top boundary $z = L$ in the mirror plane $z = 0$). During the discharge phase, the excessive charge at the liquid–vapor interface escapes to the top electrode (sharp surges of this current are registered with the electrometer connected to the top electrode), the liquid as a whole becomes neutral and the system becomes ready for the next cycle.

The main task is to estimate the rate at which the external perturbation is screened by the electric field arising within the electrolyte and compensating the driving field $E_\perp$ as the two-dimensional charged layers with the density $n_s(t)$ and thickness λ are formed at the boundaries $z = \pm L$.

Under nonuniform conditions we are interested in, the properties of cryogenic electrolyte are described by employing the methods of semiconductor theory [9]. Such a medium can be assumed to be an intrinsic semiconductor whose major energy characteristic is the energy gap E^g. In the cryogenic problem, the gap E^g_{He} has the sense of dissociation energy of a single ion dipole. No calculations for E^g_{He} have yet been performed; in any case $E^g_{\text{He}} < 0.1$ eV [8]. Experimental data on E^g_{He} are also currently unavailable.

For other weak electrolytes, the parameter $E^g_{\text{H}_2\text{O}}$ is relatively accurately measured for pure water. Actually, known here is the behavior of the dissociation constant $K(T)$ appearing in the Ostwald law,

$$K(T) = \frac{\alpha^2 C}{1 - \alpha} \equiv \frac{\alpha^2}{(1 - \alpha)V}, \qquad (3)$$

where α is the dissociation degree defined as the ratio of the number of ionized molecules to the total number of neutral molecules; C is the electrolyte molar concentration, V is the dilution or volume per, and K is the dissociation constant exponentially depending on temperature T. Its structure is similar to the expression yielding the product of electron and hole densities for intrinsic semiconductor [9]. Making use of this correspondence, one finds for water

$$E^g_{\text{H}_2\text{O}} \simeq 4.8 \cdot 10^3 \text{ K}. \qquad (4)$$

This result defines the energy scale for the problem of finding energy characteristics of water. The value of $\alpha(T)$ at room temperature proves to be $\alpha \sim 10^{-7}$.

In the presence of the field $E_\perp$ the intrinsic semiconductor (in our case, the cryogenic electrolyte or pure

water) completely screens it within the cell after accumulation ion layers with the density n_s are formed at the liquid boundaries. Estimating the maximum densities as $n_s^c \leq 10^{10}$ cm^{-2} and assuming the bulk density of charges in liquid to be consistent with $\alpha \sim 10^{-7}$, one can verify that the ion accumulation layers can be calculated within the Debye approximation. The corresponding length λ

$$\lambda^2 = \frac{\varepsilon T}{4\pi e^2 n_+} \qquad (5)$$

for water at room temperature ($\varepsilon \simeq 80$, $T \simeq 300$ K, $n_+ = \alpha n_{aq} \sim 10^{15}$ cm^{-3}, $n_{aq} \sim 10^{22}$ cm^{-3} is the bulk concentration of water molecules) has the order of

$$\lambda \sim (10^{-4} – 10^{-5}) \text{ cm} << L. \qquad (5a)$$

In spite of low dissociation degree, the value of n_+ entering the expression for λ (5) is sufficient for the inequality $\lambda \ll L$ to be satisfied.

Now some comments on the critical charge concentration $n_s^c \leq 10^{10}$ cm^{-2}. According to Ref. 10, the critical value of the surface charge density Θ_c resulting into the development of surface instability can be calculated as

$$\Theta_c^4 = \rho_{aq} g \alpha_{aq} / (4\pi^2), \qquad (6)$$

where ρ_{aq} is the liquid density, g is the acceleration due to gravity, and α_{aq} is the surface tension at liquid–vapor interface. For water ($\rho_{aq} \simeq 1$ g/cm^3, $\alpha_{aq} \simeq 72.75$ erg/cm^2) $\Theta_c \simeq 3.667$ CGSE. The corresponding ion surface concentration is $n_s^c \leq 10^{10}$ cm^{-2}. It is important (as already mentioned earlier), that the left side of Eq. (6) is valid for arbitrary origin and structure of the charges. Therefore, ions in the electrolyte can break the surface stability remaining in their hydration shells.

For helium the ion localization length near free surfaces is mainly governed by image forces arising in the vicinity of the vapor–liquid interface [10] rather than their electrostatic interaction. The interplay between these forces pushing ions from the surface into the bulk liquid and the field $E_\perp$ pressing them towards the surface determines the equilibrium position z_0 of the ion layer with respect to liquid surface

$$z_0^2 = \frac{|e|(\varepsilon-1)}{4\varepsilon(\varepsilon+1)E_\perp}. \qquad (7)$$

The typical scale of z_0 for ions in helium is $z_0 \sim 10^{-5}$– 10^{-6} cm.

2. The outlined equilibrium picture is also useful for kinetic estimates. First of all, just as in equilibrium, the two-component ion kinetics splits into two parts which are only related by electrostatics. Second, within the entire range $-L < z < +L$ (Fig. 1) except for Debye layers the diffusion part of the ion fluxes can be totally neglected. Thus, each component satisfies the standard continuity equation

$$e\frac{\partial n_\pm}{\partial t} + div\,\mathbf{j} = 0, \quad \mathbf{j} = -\sigma_\pm \nabla \varphi,$$

$$\sigma_\pm = n_\pm(0)e^2\tau_\pm/m \equiv n_i e^2/(6\pi R_i \eta), \qquad (8)$$

$$\varphi(\pm L) = \pm V, \quad n_-(t=0) = n_+(0).$$

where $n_+(x,t)$ is the bulk density distribution of positive ions within the sample, $\varphi(x)$ is the local electrochemical potential, σ is the electrolyte conductivity (here the relaxation time τ_+ should be expressed through the solvent viscosity η and the ion radii R_i by employing the Stokes formula), $n_+(0)$ is approximately uniform ion density in the central part of the cell. Just as in equilibrium, the problems for positive and negative ions can be treated independently and $n_+(0) = n_-(0)$, $\tau_+ \simeq \tau_-$.

Focusing on the qualitative analysis only, we can integrate Eq. (8) over the coordinate into the cell interior and take the difference of the density distributions of positive and negative ions $n_\pm(x,t)$:

$$e \int_{-L}^{+L} \frac{\partial(n_+ - n_-)}{\partial t} dz = e \frac{\partial n_s}{\partial t} = \sigma_\pm [E_\perp \varepsilon^{-1} - 4\pi e n_s(t)], \qquad (9)$$

$$E_\perp = V/2L, \quad n_s(t=0) = 0.$$

To simplify further estimates, the conductivities of both components are chosen to be equal.

When working with Eq. (9), it is convenient to employ the surface charge density $\Theta = en_s$ and introduce dimensionless time t normalized to the conductivity $\sigma_\pm$. Then

$$\int_0^\Theta \frac{d\theta}{\varepsilon_\perp - 4\pi\theta} = s, \quad s = t\sigma_\pm, \quad \varepsilon_\perp = E_\perp \varepsilon^{-1}. \qquad (10)$$

The integral in Eq. (10) can be calculated analytically. However, it is actually useful to keep it in the presented form. In particular, it is clearly seen from Eq. (10) that the full time required to reach equilibrium (which corresponds to the denominator $\varepsilon_\perp - 4\pi\theta$ becoming zero) depends, of course, on the amplitude $\varepsilon_\perp$. However, the typical relaxation time $\tau_{relax} = \sigma_\pm^{-1}$ has the Maxwell origin and, according to Eqs. (1) and (8), contains the dissociation degree of the intrinsic electrolyte. It is also obvious that for doped electrolyte (when impurities are added to the solvent) with limited number of doping donors there exists a threshold value of $\varepsilon_\perp$ above which the relaxation is stopped (to be more precise, it is governed by the processes occurring in the solvent).

An example of the relaxation oscillations of the current through free liquid surface for the system of positive ions in liquid hydrogen taken from Ref. 11 is shown in Fig. 2. The series of surges labelled (*1*) is recorded for $V = 550$ V and the series (*2*) for $V = 700$ V. A finite slope of the IVC within the intervals separating two consecutive jumps is
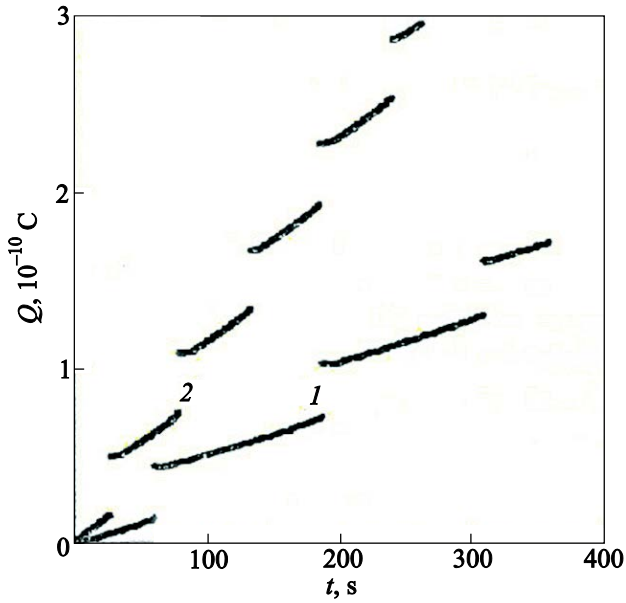
Fig. 2. Relaxation oscillations of the charge $Q(t)$ passing through the free liquid surface for the system of positive ions in liquid hydrogen.

explained by variations in the capacity of the gap between the charged liquid surface and the metal electrode during its charging by the bulk ion flux between the breakdowns. This circumstance allows one to study relaxation phenomena under the conditions where reaching critical values of charge density Θ_c (6) is not required. Qualitatively similar picture holds also for negative ions crossing the electrolyte surface. This similarity confirms independence of the threshold (6) from the sign of the ion charge.

Here are a few numerical estimates. For hydrogen, where typical mobilities $\mu_{\pm} = e/(6\pi R_{\pm}\eta)$ are of the order of $\mu_{\pm} \sim 10^{-2}$–10^{-3} m^2/(V·s) [11], and the typical times following from Fig. 2 are $\tau_{\mathrm{relax}} \sim 100$ s, the bulk ion density following from Eqs. (8) and (10) are $n_i \sim 10^{11}$–10^{12} cm^{-3}. For water where all the parameters necessary for the estimation of τ_{relax} are known ($R_i \sim 2\cdot10^{-8}$ cm, $\eta_{aq} \sim 0.1$ CGSE (g/(cm·s), $n_+(0) = n_-(0) \simeq 10^{15}$ cm^{-3} (this estimate assumes $\mathrm{pH}_{aq} \simeq 7$, so that $\alpha \sim 10^{-7}$), the mass of a single water molecule is $m_{\mathrm{aq}} = 18/N_A$, $N_A = 6.025\cdot10^{23}$ is the Avogadro number and density of water $\rho_{aq} = 1$ g/cm^3, $n_{aq} \simeq 0.3\cdot10^{23}$ cm^3, $n_+(0) = \alpha n_{\mathrm{aq}}$) one finally obtains for the time τ_{relax} required for establishing electrically inhomogeneous electrolyte state

$$\tau_{\mathrm{relax}} \simeq \frac{6\pi R_i \eta}{e^2 n_i} \sim 2\cdot10^{-4} \text{ s.} \tag{11}$$

The time scale τ_{relax} (11) seems to be surprisingly short. All parameters determining this time are known with considerable uncertainty, and the most vulnerable quantity is, of course, the degree of dissociation. This point makes possible observations of the current oscillations of the type shown in Fig. 2 in water with the period of order τ_{relax} arising under the conditions of $\varepsilon_{\perp} > \varepsilon_{\perp}^c$ and exhibiting the instability critical field uniquely determined by θ_c (6) even more interesting.

Summary. Discussed in the paper are the relaxation phenomena of critical origin arising when electric field $E_{\perp}$ induces the ion flux through the electrolyte liquid–vapor interface in the cell shown in Fig. 1. Details of the relevant current-voltage curve contain data on the electrolyte equilibrium degree of dissociation α and possible effects of the external field on this parameter. It should also be noted that kinetics of filling of the subsurface electrolyte layer with ions can be studied not only under the critical conditions $\varepsilon_{\perp} > \varepsilon_{\perp}^c$ where a periodic breakdown of the liquid–vapor interface is possible but also in the opposite case $\varepsilon_{\perp} < \varepsilon_{\perp}^c$. In this nonthreshold scenario variations in the ion density $n_s(t)$ can be detected by changes in the capacity between the top electrode and the charged electrolyte surface due to the deformation phenomena occurring at the charged liquid surface (*e.g.*, see Ref. 8).

1. A. Nedospasov, *Usp. Fiz. Nauk* **94,** 439 (1968).
2. Yu. Piter and M. Cardona, *Foundations of Semiconductor Physics*, Fizmatlit (2002); K. Shalimova, *Semiconductor Physics*, Energoizdat, Moscow (1985) (in Russian).
3. O. Konstantinov and V. Perel, *Fiz. Tverd. Tela* **6**, 3364 (1964).
4. O. Konstantinov, V. Perel, and G. Tsarenkov, *Fiz. Tverd. Tela* **9**, 1761 (1967).
5. V. Grazhulis, V. Kveder, V. Mukhina, and Yu. Ossipyan, *Fiz. Tverd. Tela* **22**, 512 (1980).
6. R. Robinson and R. Stokes, *Electrolyte Solutions*, Butterworths Scientific Publications, London (1959).
7. Yu. Lukomskii and Yu. Gamburg, *Physico-Chemical Foundations of Electrochemistry*, Intellect, Dolgoprudnyi (2008) (in Russian).
8. V. Shikin, *Usp. Fiz. Nauk* **181**, 1241 (2011).
9. V. Bonch-Bruevich and S. Kalashnikov, *Semiconductor Physics,* Nauka, Moscow (1977) (in Russian).
10. L.D. Landau and E.M. Lifshitz, *Course of Theoretical Physics*, *Vol. 8*: *Electrodynamics of Continous Media*, Nauka, Moscow (1982) (in Russian).
11. A. Levchenko, *Doct. Thesis*, Chernogolovka (2003) (in Russian).