

# Space Charge Effects in the Electrolytes

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**Abstract**— Interfacial polarization in electrolytes or other ionic media is a very well known phenomenon in the connection to the relative surface potential difference. Nevertheless, the created space charge affects the distribution of charge carriers in the electrolyte itself similarly to the field effects in semiconductors. This results in the number of secondary effects from the dielectrophoresis to the varied conductivity of the media. Some of these effects, including dielectrophoresis, and electric field sensing in the electrolytes, are analyzed analytically, modeled numerically and evaluated experimentally. The physical nature of the thermoelectric effect in gels and totally ionic field effect transistor is revealed and the correspondence to experimental data is demonstrated.

**Index Terms**— Dielectric polarization; Electrochemical processes; Ions

## I. INTRODUCTION

THIS work presents the bio-derived approach to the ionic conductivity of polymer-electrolyte composites. It is inspired by the electrosensitive organs of sharks and skates (rays), *Ampullae of Lorenzini*, which contain extracellular hydrogel and are also delicate sensors of thermal end electric fluctuation. We have imitated the hydrogel by the proton-conductive polymer-ionic electrolyte structure, which implements major property of the biological analog - the thermodiffusion mechanism of ion transfer.

Thus, the temperature gradient leads to the non-uniform diffusion mobility of ions and the steady state equilibrium is established at the gradient of ion concentration. This density gradient of charge carriers (ions) is the electric space charge which electric field compensates the flow of thermodiffusion. In turn, the gradient of electric potential also establishes the ionic space charge that affects the spatial distribution of voltage and conductivity in the polymer-ionic structure.

When a voltage is applied between any two points in an electrolyte, the electric current density of type p ions  $\mathbf{j}_p$ , is given by the expression

$$\mathbf{j}_p = q_p \cdot n_p \cdot \mu_p \cdot \mathbf{E} - q_p \cdot D_p \cdot \text{grad}(n_p), \quad (1)$$

where the first term is the drift current, the second term is the diffusion current, and  $q_p$  and  $\mu_p$  are the charge and mobility of type p ions. According to Einstein's classic expression, the coefficient of diffusion is  $D_p = \mu_p kT/q_p$ . Since an electrolyte is a good conductor, the electric potential drops rapidly in the vicinity of the electrodes, and therefore the electric field  $\mathbf{E}$  can be ignored in the bulk of the fluid. Thus, the application of a voltage results only in a concentration gradient. This is in contrast both to conductors, in which the current is driven by the external electric field, and to semiconductors, in which both the field and the concentration gradient determine the currents.

If the electrolyte is placed in a structured matrix-like gel or polymer ion-conductive membrane, the mobility of ions is very sensitive to temperature because of the thermodiffusion mechanism of charge transfer (see Fig. 1).

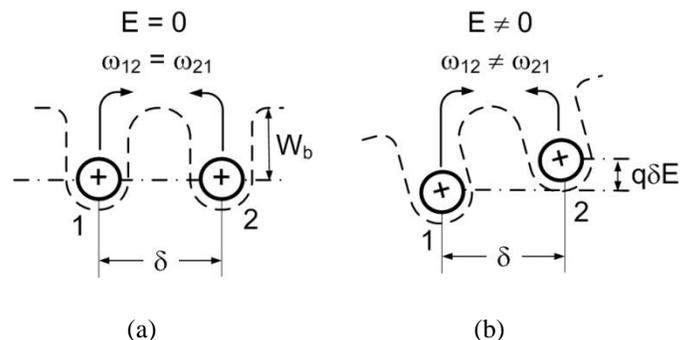


Fig. 1. Thermoactivation drives ionic conductivity in a gel structure. Potential barrier between stable positions of ions is symmetric if there is no gradient of electrochemical potential or temperature (a). If the electric field is applied (as shown in (b)) or there is the temperature gradient, probabilities for ion to jump from position 1 to position 2 and backward are not equal.

If there are two neighboring proton states, one on each side of a molecular barrier, and the height of the energy barrier is  $W_b$ , the probability of proton transition from state 1 to state 2 (designated as  $\omega_{12}$ ) exponentially depends on temperature as  $\exp(-W_b/kT)$ . The probability of the reverse transition  $\omega_{21}$  is equal to  $\omega_{12}$  if there is no gradient of electric potential or temperature (see Fig. 1(a)). If an electric field is applied, the energy barrier becomes different for state 1 ( $W_{b1} = W_b + q\delta E/2$ ) and state 2 ( $W_{b2} = W_b - q\delta E/2$ ), where  $q$  is the charge of the ion. Therefore, an electric field creates directional asymmetry in thermal ion transfer, but the driving force is the thermal activation.

The instant ionic transfer is proportional to the factor

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$$F(W_b, E, T) = \exp\left(-\frac{W_b}{kT}\right) \cdot \sinh\left(\frac{q\delta E}{2kT}\right), \quad (2)$$

which is proportional to the density of the electric current. The corresponding mobility of carriers and electric conductivity are proportional to  $F(W_b, E, T)/E$ .

If there is a difference in electrochemical potential, it produces an electric field and the concentration of carriers is changed until this difference is fully compensated for by the field of the space charge. This leads to the distribution of carriers in the familiar Boltzman's form:

$$n(T) = n_0 \cdot \exp\left(-\frac{\delta W_b}{kT}\right). \quad (3)$$

Of significant note is that there is an inequality of ion mobility for the electric gradient (electric field) and ion concentration gradient because of their opposite directions. Thus, the mobility of diffusion is smaller than the electric mobility in opposite directions by the factor  $\frac{W_b}{qT^2} \frac{dT}{dx} \delta$ . The time constant of polarization (about 1.0 ms) is relatively large, which allows any external electronic process to be considered as practically instantaneous.

Reciprocally the asymmetry of thermomigration in a temperature gradient leads to the redistribution of carriers. In the steady state, at the equilibrium of diffusion and drift flows, the thermoelectric voltage,  $\Delta V_{te}$

$$\Delta V_{te} = \frac{W_b}{2q} \ln\left(\frac{T_2}{T_1}\right) \approx \frac{W_b}{2qT} \Delta T \quad (4)$$

if  $\Delta T = \delta \cdot \text{grad}(T) = T_2 - T_1 \ll T_1$  and  $V(T_1) = 0$ .

The Seebeck coefficient  $S = W_b/2qT \approx 260 \mu\text{V/K}$ , if the activation energy  $W_b = 16.2 \text{ kJ/mol}$  is assumed to match experimental data for the white shark gel, which agrees with experimentally measured  $S \approx 290 \pm 70 \mu\text{V/K}$  [1,2]. The thermal release of ions localized at charged polymer segments produces a similar or additional thermoelectric effect that follows Eqs. (1) and (2) if the activation energy for ion transfer,  $W_b$ , is replaced by the binding energy,  $\Delta G$ . In contrast to semiconductors, the thermal conductivity of ionic conductors does not correlate with electric conductivity, and can be suppressed by preventing convection.

## II. EXPERIMENTS

### A. Thermoelectric Ionic Detector (TEID)

We have fabricated samples of TEID based on gelatin and agarose. Both gel-forming materials were placed in water to swell for 2 hour at 20°C. The swollen granules were then treated at 40°C in the water bath and sonificated for 30 min., forming a uniform solution.

Prototype substrates were fabricated of copper-laminated

epoxy composite removing the metal from the middle of the substrate, forming two isolated copper electrodes with a gap between them (see Fig. 2).

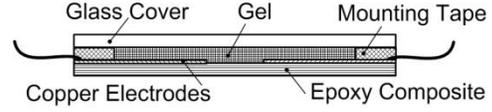


Fig. 2. Gel based sample of the Thermoelectric Ionic Detector (TEID). The thermal gradient was applied between electrodes.

Mounting tape was placed on the electrodes, and the middle of this tape was cut away so that a tape frame surrounded a window for the gel. The gel melted at 40°C was poured into this window on the substrates as shown in Fig. 2. We sealed the melted gel with a glass plate, and placed the detectors in the refrigerator to gel.

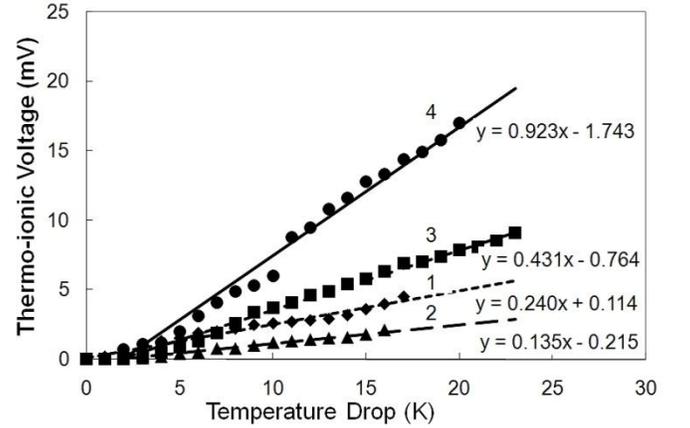


Fig. 3. Thermoelectric characteristics of gel based samples. (1, 2) gelatin gel (3,4) agarose gel.

One can see in Fig. 3 that the fresh agarose samples exhibit greater sensitivity (0.92 mV/K and 0.43 mV/K) than the gelatin samples (0.24 mV/K and 0.13 mV/K), while the threshold temperature difference (for our prototype design) is about 2 K for all the samples.

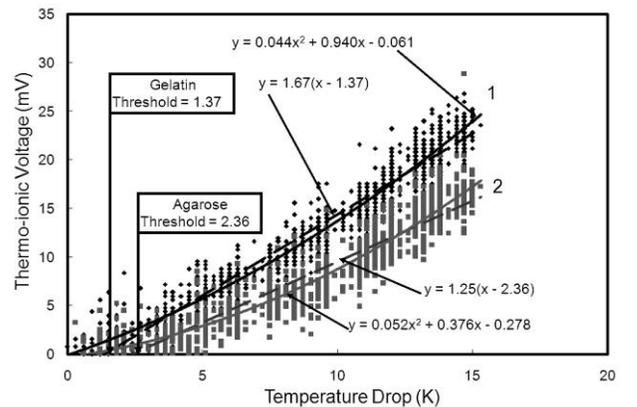


Fig. 4. Thermoelectric characteristics of gel based samples over 10 days. 1 - gelatin gel, 2 - agarose gel.

The gel needs a time for the establishment of the steady state structure. Fig. 4 presents characteristic of the same samples that in Fig. 3 but measured over 10 days after the fabrication. First one can note that sensitivity increases and gelatin exhibits superiority to agarose (1.67 mV/K for gelatin and 1.25 mV/K for agarose). Also, the threshold is 1.37 K for gelatin and 2.36 K for agarose. These threshold values were determined by linear approximation of curves, although the results better fit a quadratic approximation.

Because the lifetime of gel-based detectors is limited due to the evaporation of water, we tested the TEID detector based on the DuPont Nafion® polymer membrane. Nafion® is a perfluorinated polymer that contains small proportions of sulfonic or carboxylic ionic functional groups (ionomer). Membrane was placed on the filtering paper saturated with buffer solution. This detector demonstrated the good sensitivity and full reversibility illustrated in Fig. 5.

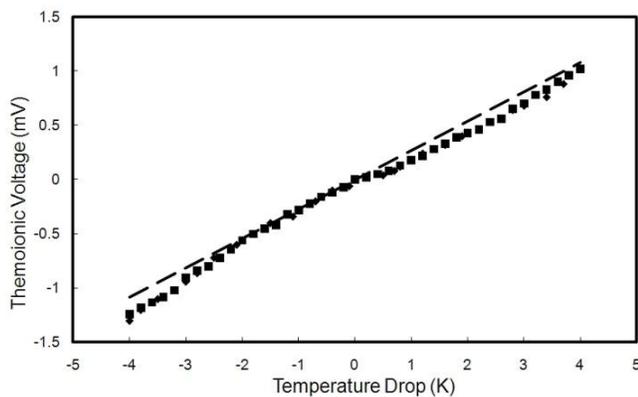


Fig. 5. Thermoelectric characteristics of Nafion® based detector.

Eq. (3) shows that the average (initial) concentration of carriers (protons) is a scaling parameter for the space charge. Therefore the increased initial concentration,  $n_0$ , leads to the decreased thermoelectric voltage,  $\Delta V_{te}$  (see Eq. (4)). We have fabricated new TEID samples based on gelatin, which were prepared with buffers of various pHs — 0.05 M carbonate-bicarbonate buffer of pH 9.6 and 0.05 M phosphate-citrate buffer of pH 5.0. Gelatin was added to buffer solutions at volume concentrations of 1:5 and treated at 45°C with ultrasound agitation over 60 min.

TABLE I  
COMPARISON OF THRESHOLD AND SENSITIVITY OF GELATIN TEID SENSORS AT VARIOUS PH VALUES

pH of solvent	Threshold of temperature drop, K*	Sensitivity, mV/K
5.0	2.55	0.17
7.0	1.43	1.54
9.6	≈ 0	2.4

\*In the linear approximation

Comparison in Table 1 of data obtained clearly shows that the threshold value decreases and sensitivity (mV/K) increases when we reduce the concentration of protons.

### B. Ionic Detector of Electric Field in the Sea Water

Because the conductivity of ionic membrane detector depends on the concentration of carriers, it can be used for the detection of electric field (actually – the electric current) in the electrolyte such as the seawater.

The scheme of detection is shown in Fig. 6.

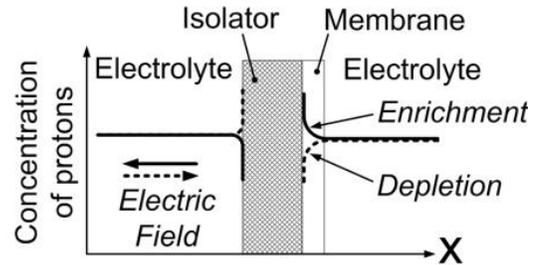


Fig. 6. Scheme of modulation for the longitudinal conductivity of the Nafion® membrane.

Fig. 6 shows the variation of the concentration profile across membrane thickness at a positive (enriched) and negative (depleted) space charge due to the capacitance of the isolator,  $C_i$ , with a large resistance  $R_i$  per unit of the surface.

For a given electric current density,  $j$ , which is proportional to the measured electric field,  $E$ , we can define the surface density of charge on the boundary of the isolator and the membrane as  $Q = jR_iC_i$  just because the voltage on the isolator  $U = jR_i$  and  $Q = UC_i$ . This charge is formed by the excess (or lack) of protons at this boundary. Suggesting that the entire space charge is located inside the membrane, the membrane thickness,  $d$ , is defined from  $\exp(-d/L_D) \approx 10^{-2}$  or  $d = 4.6 \cdot L_D$ , where  $L_D$  is the Debye length in membrane. Therefore, the excessive concentration of protons on the boundary of the membrane and the isolator can be defined as

$$\Delta n_s = \frac{Q}{e \int_0^{4.6L_D} e^{-x/L_D} dx} \quad (5)$$

or simply  $\Delta n_s(Q) = Q/(0.99 \cdot e \cdot L_D) \approx Q/e \cdot L_D$ . Therefore, if the initial conductivity of the membrane (at uniform  $n_0$ ) is  $Y_0$ , the varied conductivity  $Y(j) = Y_0 \cdot (1 + K \cdot Q/L_D)$  where  $K$  is the coefficient that accounts for the dimensions of membrane, width  $a$  and length  $b$ , and the mobility of protons in the membrane,  $\mu$ . Therefore  $K = a \cdot d \cdot \mu$  and the resistance of membrane,  $R(j) = Y(j)^{-1} = R_0$

$$R(j) = \frac{R_0}{1 + \frac{K \cdot R_i \cdot C_i \cdot j}{L_D}} = \frac{R_0}{1 + \alpha \cdot j}, \quad (6)$$

where it is notable that coefficient  $\alpha$  does not depend on the thickness of the isolator (it is proportional to the ratio of the dielectric constant and the conductivity of the dielectric).

Structure in Fig. 6 represent the kind of field effect

transistor where membrane serves as a channel and the transversal electric field is applied through the electrolyte. We built the experimental version of this “transistor” using the Nafion® membrane and tTeflon™ isolator film (see Fig. 7).

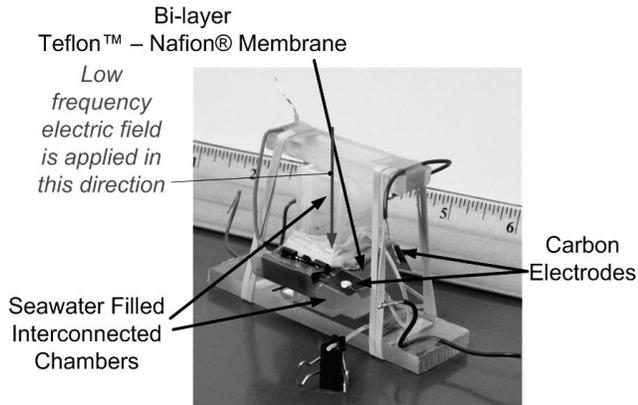


Fig. 7. Experimental sample of the ionic “transistor”. The current through the Nafion® membrane is limited by the isolator (Teflon™ isolative tape).

Rectangular pulses of voltage were applied along the membrane and low frequency (10 Hz) sinusoidal signal was applied to electrolyte at both sides of the membrane. This allows to see difference in current along the membrane with and without the transversal electric field. Example of such signal is shown in Fig. 8.

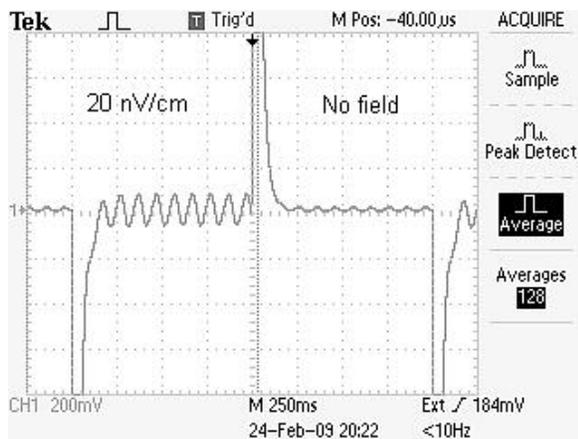


Fig. 8. Modulation of the current along the membrane when an electric field across the membrane is applied.

By the measuring the peak-to-peak amplitude of the AC signal with and without voltage applied, we determined how the signal amplitude depends on the voltage applied along the channel. This is the dynamic V-I characteristic of the device that is presented in Fig. 9 for input electric field 4 nV/cm at frequency 10 Hz.

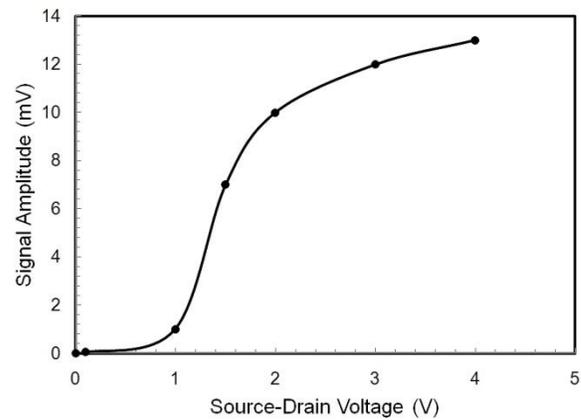


Fig. 9. Dynamic V-I characteristic of the ionic transistor at frequency 10 Hz and input field 4 nV/cm. Thickness of Nafion® membrane – 100µm..

To the best of our knowledge, this is the first demonstration of a completely ionic field effect transistor. In contrast with the known so-called iFET transistor, where an electrochemical potential of the electrolyte is applied to the gate of a traditional solid-state FET transistor, the demonstrated ionic transistor measures the true density of the electric current in the electrolyte solely by ionic processes.

### III. CONCLUSION

The advantage of electrostatic approach in some “exotic” (for electrostatics) areas such as thermoelectricity and electric field in the electrolyte is demonstrated. This allowed to reveal new properties of gel structures and polymer proton-conductive membranes that can be used for the IR sensing, thermoelectricity generation and detection of electric currents (for example, created by the corrosion) in the ocean water.

### REFERENCES

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