

SHANNON ENTROPY ASSOCIATED WITH THE DISTRIBUTION OF IONS OBTAINED BY THE ELECTROCHEMICAL METHOD IN SOLUTION

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In this work, we discuss Shannon entropy associated with ions redistribution using model electrochemically triggered local ion fluxes. For this purpose, we utilized bare gold electrodes as well as covered by polyelectrolyte layers and lipids. Modification of the electrode surface leads to a change of ion flux triggered by hydroquinone oxidation. Consequently, various distribution of ions in solution can be obtained. Discussion of ion solutions informational entropy is essential for consideration of ions as information carriers in iontronic devices.

Entropy is a function that quantifies the number of microstates available to a system. Thus, thermodynamic entropy growth is a driving force of many physicochemical processes. In solutions, the number of microstates at high concentrations is less than for low concentrations. For charged species, the electrostatic driving force opposes the entropic one. Since ions are good candidates to perform chemical calculations, we consider electrochemically generated ion fluxes in terms of Shannon entropy. Shannon's entropy is a fundamental concept of information theory. This value is a measure of unpredictability of the state, which is equal to its average information content.

In this work, we studied entropy associated with ions redistribution using model electrochemically triggered local ion fluxes. Local ion signals can easily be generated using the electrochemical approach. Proton flux was triggered at the solid-liquid interface by the oxidation of hydroquinone solutions in KNO_3 at a constant electric current. When hydroquinone is oxidized electrochemically, acidification of the near-electrode region occurs. A two-step hydroquinone oxidation was performed at a gold microelectrode surface.

Electron transfer in the quinone-hydroquinone system is associated with proton transfer. Protons produced during hydroquinone oxidation is a three-dimensional pH wave described by Fick's laws. The driving force for ion movement is the dispersal of energy into a more probable distribution. Usually, as a substance becomes more dissipated, the thermal energy carried by this substance also spreads over volume, followed by entropy.

The diffusion of oxidation products is highly affected by the structure of the electrode surface. Polyelectrolyte modified electrodes are of high interest. Layer-by-layer (LbL) polyelectrolyte assemblies containing many charged moieties do not allow ions freely pass through. Polyelectrolyte protonation/deprotonation phenomenon is involved in ion pathways.

Since molecules of hydroquinone and quinone are rather small and uncharged, they can pass freely through polyelectrolyte/lipid layer, and multilayer assembly on top of electrodes leads to no change in redox processes at the electrode/hydroquinone solution interface.

The concentration of protons close to the surface of gold microelectrode was investigated using Scanning Ion-Selective Electrode Technique (SIET). This instrumentation based on potentiometric principles allows characterizing local ionic currents in solution and ion concentration gradient measurement. SIET measured ion concentration and obtained pH maps were recalculated to entropy maps as for pristine gold working electrode (WE), WE covered with polyelectrolyte multilayers gold/(PEI/PSS)₃/PEI, and WE covered with polyelectrolyte multilayers and lipid layer on top gold/(PEI/PSS)₃/PEI/lipid.

Spatial redistribution of protons takes place self-consistently and occurs together with a redistribution of local electric potential during the minimization of the system free-energy.

Therefore, the self-organization and the redistribution of pH-fields are directly associated with each other and, thus, the change of entropy can be illustrated using the fields of pH.

Considering the system described above, we can easily vary ion distribution. For instance, taking the spatial distribution of cations determined experimentally in cases of a bare electrode, as well as for electrode covered by polyelectrolyte multilayer (PEI/PSS)₃ and lipid bilayer, we obtained the spatial distributions of entropy.

A model electrochemical system creating local ion-fluxes was demonstrated. The LbL assembly of polyelectrolyte multilayers is suggested as an instrument to control horizontal and vertical ion propagation with the ability to correlate it with the spatial distributions of entropy. In contradistinction to thermodynamic entropy, informational Shannon entropy associated with ions redistribution decrease with solution dilution. The spatial distribution of Shannon entropy was studied for ion fluxes generated electrochemically.