Measuring Entropy and Enthalpy of Formation of Electrical Double Layers

Electrical double layers[1] are at the heart of batteries, fuel cells, corrosion, electroplating, and many other electrochemical devices and processes.[2] When a voltage is applied between two conducting solids in an electrolyte solution, the solid surfaces become charged and counter-charged ions from solution accumulate near the surface, thus creating two parallel layers of charge, at the solid surface and in the liquid solution: the electrical double layer (EDL).

When the EDL is formed or discharged, reversible heat is generated, as we recently demonstrated in groundbreaking experiments.[3] Even though it is only a tiny heat effect, we have developed a way to measure it very accurately (better than in ref. 3), and it is of great interest to sharpen our fundamental understanding of the EDL. Until now, experimental information about EDL formation relied mainly on electrical data: the electrical current—which gives the formation rate—and the total capacitance—which indicates how many charged ions are eventually accumulated. Physical models were developed that give a good description of the electrical data, but they do not account for the magnitude of the heat exchange. The heat production by the EDL is expected to have two main components: an entropic part, since EDL structure formation corresponds to a decrease in local entropy, and an enthalpic part, for instance as a result of changes in hydration of the ions.

The objective of this project is to determine the entropic and enthalpic contributions to the EDL heat (which has never been done before), putting further constraints on possible physical models of the electrical double layer. To do so, the student will measure the heat of EDL formation as a function of temperature. The experimental work will mainly consist in performing physical measurements and interpreting numerical data. Part of the work—with help of the supervisors—will also be theoretical, to deduce enthalpy and entropy of EDL formation from the experimental data on the basis of thermodynamic theory. An additional challenge is to find a plausible physical picture that can explain the measured values of ΔH and ΔS quantitatively.

The student will start by reading the ECHO project, as written by Ben Erné and carried out by Joren Vos and relevant literature. Practical work will start by doing simple electrochemical experiments to get familiar with the subject.

1. https://en.wikipedia.org/wiki/Double_layer_(surface_science).
2. https://en.wikipedia.org/wiki/Electrochemistry.
3. Janssen, M., Griffioen, E., Biesheuvel, P. M., Van Roij, R. & Erné, B. Coulometry and Calorimetry of Electric Double Layer Formation in Porous Electrodes. *Phys. Rev. Lett.* **119**, 1–5 (2017).