**Electrokinetics of ion-exchange systems for electrodialysis and electrodeionization.**

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**Highlights**

* Electrodialysis at overlimiting currents as a way of intensification.
* Investigation of overlimiting mechanisms in a specific cell.
* Electroconvection tracked by particle image velocimetry.
* Water splitting detected mostly at anion-exchange systems.

**1. Introduction**

Intensification of processes can bring significant savings both economical and ecological. With the advent of techniques allowing the investigation of the overlimiting region at ion-exchange membrane and with better understanding of the occurrence of overlimiting current, the scientist started to work on the development of electrodialysis units working in this high intensity current regime. Until now, these processes have been operated under much smaller currents, which in turn requires much larger units.

The typical current voltage curve (CVC) of ion-exchange systems displays three parts: (i) underlimiting, (ii) limiting, and (iii) overlimiting. The underlimiting region occurs at small current densities. The increase in the current density leads to depletion of ions on one side of the membrane which is manifested as limiting region on the CVC. However, further increase in the current results in the occurrence of physical mechanisms that partially destroy the region of depleted ions. There are two major mechanisms, and these are: (i) electroconvection, and (ii) water splitting. Unlike other separation processes (e. g. pressure driven), the overlimiting region overcomes the limitation given by concentration polarization. For the engineers to be able to exploit this advantage in the industrial applications, they need in-deep understanding of the ion-exchange system behavior in this region. We have developed a special cell, that allows to (i) visualize electroconvection in the system and (ii) measure pH changes associated with the water splitting reaction. Our work should contribute to the proper understanding of aforementioned mechanisms and their dependence on the structure of ion-exchange system and the composition of the desalted electrolyte

**2. Methods**

We manufacture a fluidic cell that incorporates either a small piece of an ion-exchange membrane or a single ion-exchange resin particle. This cell allows one to characterize the systems electrochemically (current-voltage curves, chronopotentiometric and amperometric curves) and at the same time observation of the processes that occur at the interface between the ion-exchange system and the desalted electrolyte [1]. The electroconvection is tracked by solid microparticles and the results are evaluated by particle image velocimetry, the extent of water splitting reaction is directly measured by changes in pH of the respective electrolytes.

**3. Results and discussion**

Figure 1 depicts the results of a single experiment performed on a single cation-exchange particle. In a similar way these experiments can be carried out for any other ion-exchange system or for any other type of the measurement. In this particular case, we show that the underlimiting region is accompanied by formation of ion-depleted zone within which an array of vortices is formed upon reaching the limiting current. With further increase in the polarization current the vortices grow and start to affect the boundary created by the tracking particles. This growth gives rise to the appearance of the overlimiting current (first region), which is characterized by increasing slope. However, upon reaching a certain critical current, the system will transition into a second part of the overlimiting region that is characterized by constant slope of the CVC. This transition will form four large vortices on the system. We also showed that the water splitting is negligible on the cation-exchange particle. Very similar results were obtained for a small piece of a heterogenous cation-exchange particle. By contrasts, the anion exchange systems, although also showing occurrence, are easily prone to the water splitting reaction.



**Figure 1.** Current-voltage curve measured on a single cation-exchange particle and the set of images capturing the situation at the system-electrolyte interface under various polarization currents [2].

**4. Conclusions**

We monitored the processes occurring on the ion-exchange systems during polarization. Our observation confirmed the generation of the ion-depleted region followed by formation of the electroconvective vortices that are responsible for the overlimiting current exhibited by these systems. The water splitting reaction was shown to have small effect in cation-exchange membranes and reached much larger extent in anion-exchange system.

**References**

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