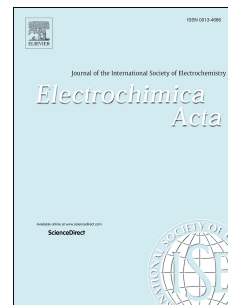


# Accepted Manuscript

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# PHENOMENON OF TWO TRANSITION TIMES IN CHRONOPOTENTIOMETRY OF ELECTRICALLY INHOMOGENEOUS ION EXCHANGE MEMBRANES

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## Abstract

Transition time in chronopotentiometry is an important parameter, which is widely used for electrochemical characterization of various systems. Occurrence of multiple transition times is typical for multicomponent or multilayer electrode and membrane systems. In this paper we show that there may be another cause of multiple transition times. It is electrical heterogeneity of ion exchange membrane surface. It is found that there are two transition times on the chronopotentiograms of a commercial anion-exchange MA-41 (Shchekinoazot) and two specially prepared cation-exchange heterogeneous membranes in dilute electrolyte solutions (0.02 M NaCl in the experiment). It is found that both transition times are determined by diffusion limitations of ion delivery to the membrane surface in the depleted diffusion layer. The value of the first transition time depends on the dimensions of the conductive regions and their surface fraction; this transition time is determined as the time necessary for the depletion of electrolyte concentration near the conductive regions of the surface. The rate of concentration depletion depends on the electromigration through the conductive regions, on the one hand, and on the normal the tangential ion diffusion to the conductive surface regions, which mitigate the concentration decrease, on the other hand. The experimental value of the first transition time for the laboratory-made membranes is in a good agreement with simulation using a 3D electrodiffusion model. The value of the second transition time is in a good agreement with the Sand theory, hence it is conditioned by the normal diffusion delivery of electrolyte from the solution bulk to the entire membrane surface. The tangential diffusion plays a secondary role in this stage of concentration polarization since current-induced convection levels off the concentrations along the heterogeneous membrane surface.

**Keywords:** Transient ion transport; Surface heterogeneity; Ion-exchange membrane; Track-etched membrane; Chronopotentiometry.

## Introduction

The effect of surface heterogeneity of the materials used in electrochemical systems on mass transfer is an important issue in a large number of cases: microelectrodes [1,2], partially blocked electrodes[3,4], fuel cells and batteries [5,6]; flow electrochemical devices, such as electrolyzers, electrolysers and membrane bioreactors [7,8], electrochemically heterogeneous

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