## Accepted Manuscript

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Jakub Mališ, Martin Paidar, Tomas Bystron, Libuše Brožová, Alexander Zhigunov, Karel Bouzek

PII: S0013-4686(18)30025-2

DOI: 10.1016/j.electacta.2018.01.011

Reference: EA 30993

To appear in: Electrochimica Acta

Received Date: 3 October 2017

Revised Date: 31 December 2017

Accepted Date: 2 January 2018

Please cite this article as: J. Mališ, M. Paidar, T. Bystron, Libuš. Brožová, A. Zhigunov, K. Bouzek,

Changes in Nafion<sup>®</sup> 117 internal structure and related properties during exposure to elevated temperature and pressure in an aqueous environment, *Electrochimica Acta* (2018), doi: 10.1016/ j.electacta.2018.01.011.

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## Changes in Nafion<sup>®</sup> 117 internal structure and related properties during exposure to elevated temperature and pressure in an aqueous environment

Jakub Mališ,<sup>a</sup> Martin Paidar,<sup>a</sup> Tomas Bystron,<sup>a</sup> Libuše Brožová,<sup>b</sup> Alexander Zhigunov,<sup>b</sup> Karel Bouzek<sup>a</sup>,\*

<sup>a</sup> University of Chemistry and Technology Prague, Technicka 5, Prague 6, 16628, Czech Republic.

<sup>b</sup> Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Heyrovsky Sq. 2, 162 06 Prague, Czech Republic

\* Corresponding author, e-mail: bouzekk@vscht.cz tel.: +420 220 444 019

Keywords: Nafion, elevated temperature, excessive swelling, morphology, internal structure.

## Abstract

In this study the behaviour and structure of a Nafion<sup>®</sup> 117 membrane exposed to liquid water at temperatures and pressures of up to 150 °C and 700 kPa, respectively, were investigated. The results clearly showed that, as the temperature of the environment approaches or exceeds the glass transition temperature of the membrane, it undergoes extensive swelling. This is connected with several changes in the membrane structure which have a predominantly detrimental influence on the functional properties of the membrane, such as ionic conductivity and ionic exchange capacity. The extent and rate of the changes increase with both rising temperature and pressure. While the changes at 150 °C and 700 kPa take place in the order of tens of minutes, at 110 °C and 500 kPa several hundreds of hours are required. The changes are enabled by amorphisation of pseudo-crystalline domains which are responsible for keeping the membrane structure intact. The changes in the internal structure were followed using small-angle X-ray scattering and visualised by current-sensing atomic force microscopy.

## 1. Introduction

Significant progress in electrochemical technology over the last 50 years was to a large extent made possible by ion-selective membranes based on perfluorinated sulfonated acids (PFSA), introduced by DuPont. Today PFSA membranes are produced by several other companies besides DuPont, such as Dow Chemicals, Asahi Glass and Fumatech under various commercial names like Dow<sup>®</sup>, Nafion<sup>®</sup>, Flemion<sup>®</sup> and Fumapem<sup>®</sup>. Their products differ by the equivalent weight and length of the side chains. The largest-scale application of these ionomers is in chlor-alkali electrolysis. Both products of this technology, *i.e.* chlorine and sodium hydroxide, rank among the top ten chemical compounds produced worldwide. Currently, PFSA membrane-based cells have already almost completely replaced traditional mercury and diaphragm technologies. The application of PFSA membranes allows utilisation of the zero-gap cell arrangement characterised by the direct contact of the electrodes with an ionomer membrane, minimising the inter-electrode distance. This configuration enables a substantial reduction of ohmic losses and consequently improves the energy efficiency of the process [1].

PFSA membranes are also practically exclusively used as proton-exchange membranes (PEMs) in PEM water electrolysers as well as in low-temperature PEM fuel cells (LT PEM FCs). Thus, they represent an inseparable part of the conversion of electrical energy into chemical energy and the reverse conversion technologies of the hydrogen economy scheme [2-4]. The concept of the hydrogen economy was introduced in order to effectively utilise the electrical energy produced by renewable energy sources which is characterised by high variability of electrical energy production [5]. The key

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