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Thermal development of free volumes in Nafion membrane

O. Melikhova[1,*], J. Čížek[1], L. Košinová[1], P. Hruška[1]

[1]*Faculty of Mathematics and Physics, Charles University, V Holešovičkách 2, 18000, Praha 8, Czech Republic*

[*]email: Oksana.Melikhova@mff.cuni.cz

Nafion is perfluorosulfonated cation exchange membrane developed by du Pont de Nemours & Co. Inc. Nafion exhibits a high proton conductivity and excellent thermal and chemical stability. These properties make Nafion very attractive for applications in fuel cells and gas separation processes. Nafion exhibits mesoscopic structure consisting of hydrophobic polytetrafluoroethlylene (PTFE) skeleton and hydrophilic ionic clusters.

Gas transport through Nafion membrane is controlled by the morphology and size distribution of nanoscopic free volume holes providing suitable pathways. This makes characterization of free volume holes in Nafion extremely important. Ortho-positronium (o-Ps) is a unique probe of nanoscopic free volume holes due to pick-off annihilation process which makes the o-Ps lifetime sensitive on the size of free volume hole where o-Ps is confined.

In this work we employed positron lifetime spectroscopy for investigation of the thermal development of free volumes in Nafion over a broad range of temperatures from -150 to 150°C. Positron lifetime studies were combined with differential scanning calorimetry.

Our investigations revealed that the mean size of free volumes strongly increases with temperature. Two transition temperatures corresponding to a change in the slope of the temperature dependence of o-Ps lifetimes $\tau_{o\text{-}Ps}$ were identified, see Fig. 1a. The width of the size distribution of free volumes increases with temperature as well, see Fig. 1b. On the other hand, the Ps yield decreases with temperature as shown in Fig. 1c. Results of positron lifetime spectroscopy agree well with the curves obtained by differential scanning calorimetry.

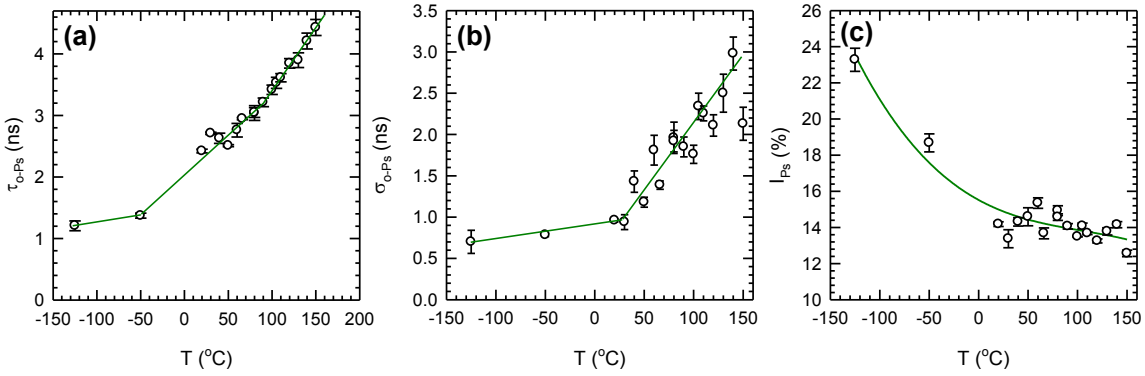

Fig.1. Temperature dependence of (a) the mean o-Ps lifetime $\tau_{o\text{-}Ps}$; the width (one standard deviation) $\sigma_{o\text{-}Ps}$ of the size distribution of free volumes; (c) the intensity of the Ps contribution in positron lifetime spectra.