Thermal development of free volumes in Nafion membrane

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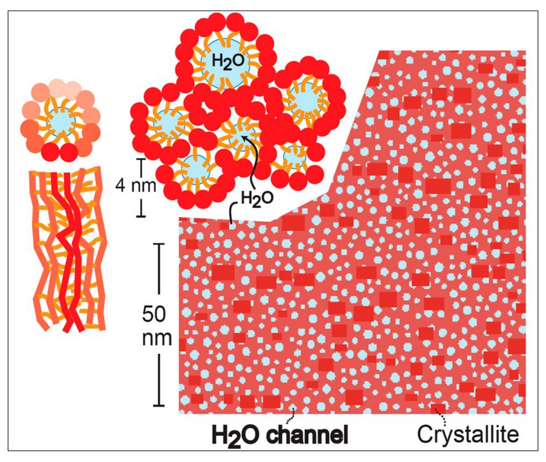
Introduction

Nafion is perfluorosulfonated cation exchange membrane developed by du Pont de Nemours & Co. Inc. Nafion exhibits ion conductivity, but no electron conductivity. This unique property enables use of Nafion as a proton exchange membrane in electrolyzers and in proton exchange membrane fuel cells. Nafion transport properties are closely related to its free volume structure. We employed positron lifetime spectroscopy and differential scanning calorimetry for investigation of the thermal development of free volumes in H^+ Nafion membrane over a broad range of temperatures from -150 to 150°C. Our investigations revealed that the mean size of free volume holes strongly increases with temperature. On the other hand, the width of the size distribution decreases with temperature. Transition temperatures corresponding to a change in the slope of the temperature dependence of ortho-positronium lifetime were identified. Results of positron lifetime spectroscopy agree well the curve obtained by differential scanning calorimetry

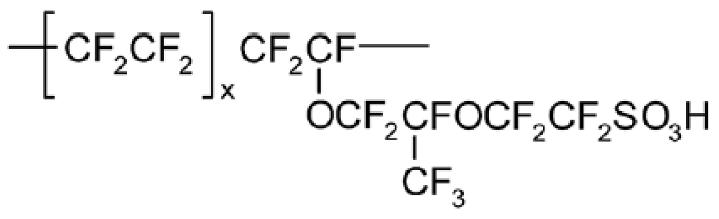
Samples

Nafion membrane N-1110

- H^+ form, equivalent weight = 1100 g/mol, thickness 0.254 mm
- dried at 80°C for 1 h prior measurement to remove absorbed water



← Parallel water-channel model of Nafion [8].



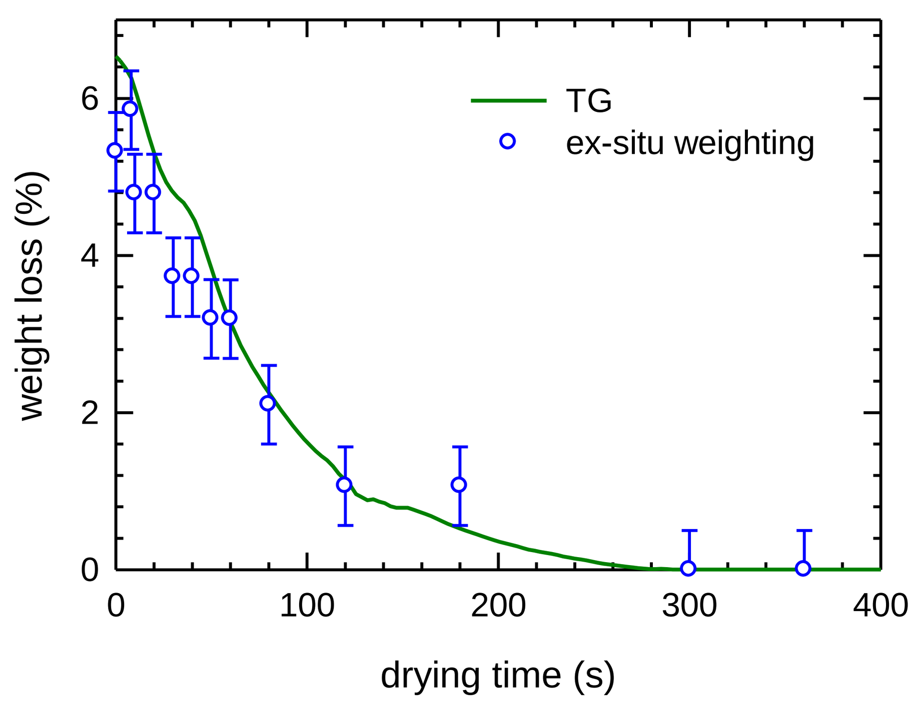
Chemical structure of Nafion

Methods of characterization

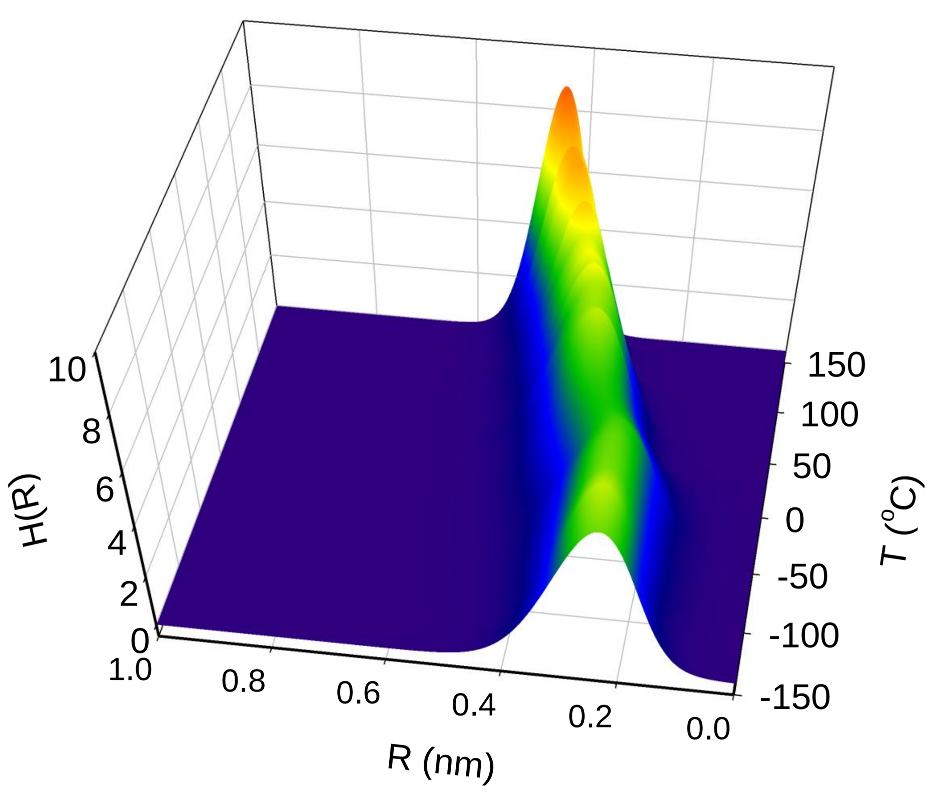
• **Positron lifetime (LT) measurements**:
- digital spectrometer with time resolution of 145 ps [1]
- ^{22}Na positron source with activity of 1 MBq deposited on 5 µm thick Ni foil. The source contribution with lifetime of 150 ps and intensity of 12% was always subtracted from LT spectra.
- Temperature-dependent LT measurements were performed in vacuum (10^{-3} mbar) in a liquid nitrogen cryostat. Positron source and sample were attached on a Cu holder plate with a heater and a Pt100 temperature sensor. Temperature of sample during the experiment was controlled with the accuracy of ± 0.1 °C.
- LT spectra were decomposed by a least square fitting program LT (version 9) [2].

• **Differential scanning calorimetry (DSC)** and **thermogravimetry (TG)**:
- simultaneous DSC/TG apparatus Setaram Labsys Evo.
- DSC measurements were performed in an Al crucible with the heating rate of 20 K/min in dynamic N_2 flow (flowing rate 20 ml/min)

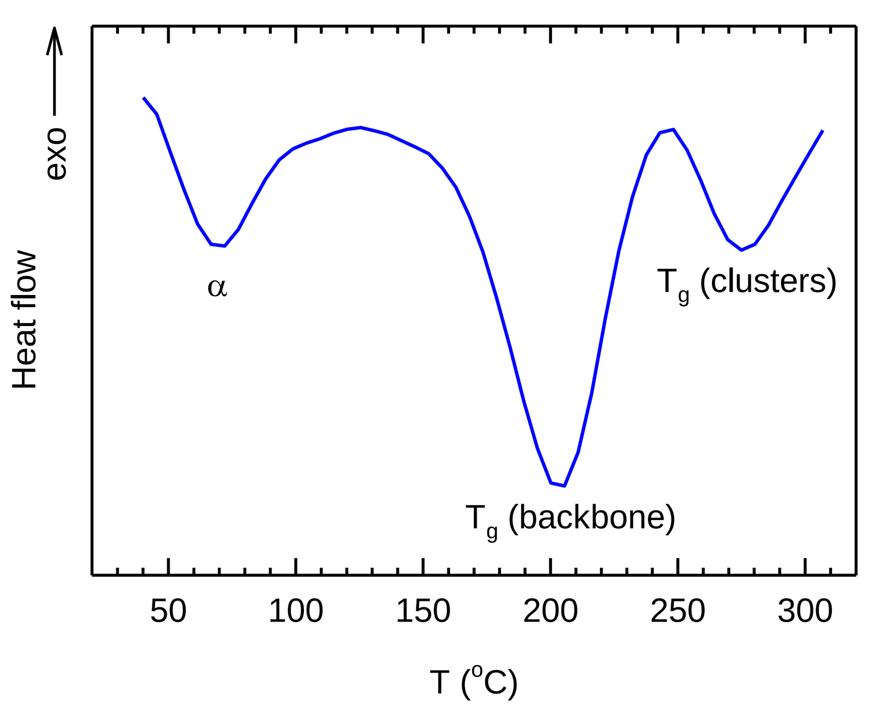
Results



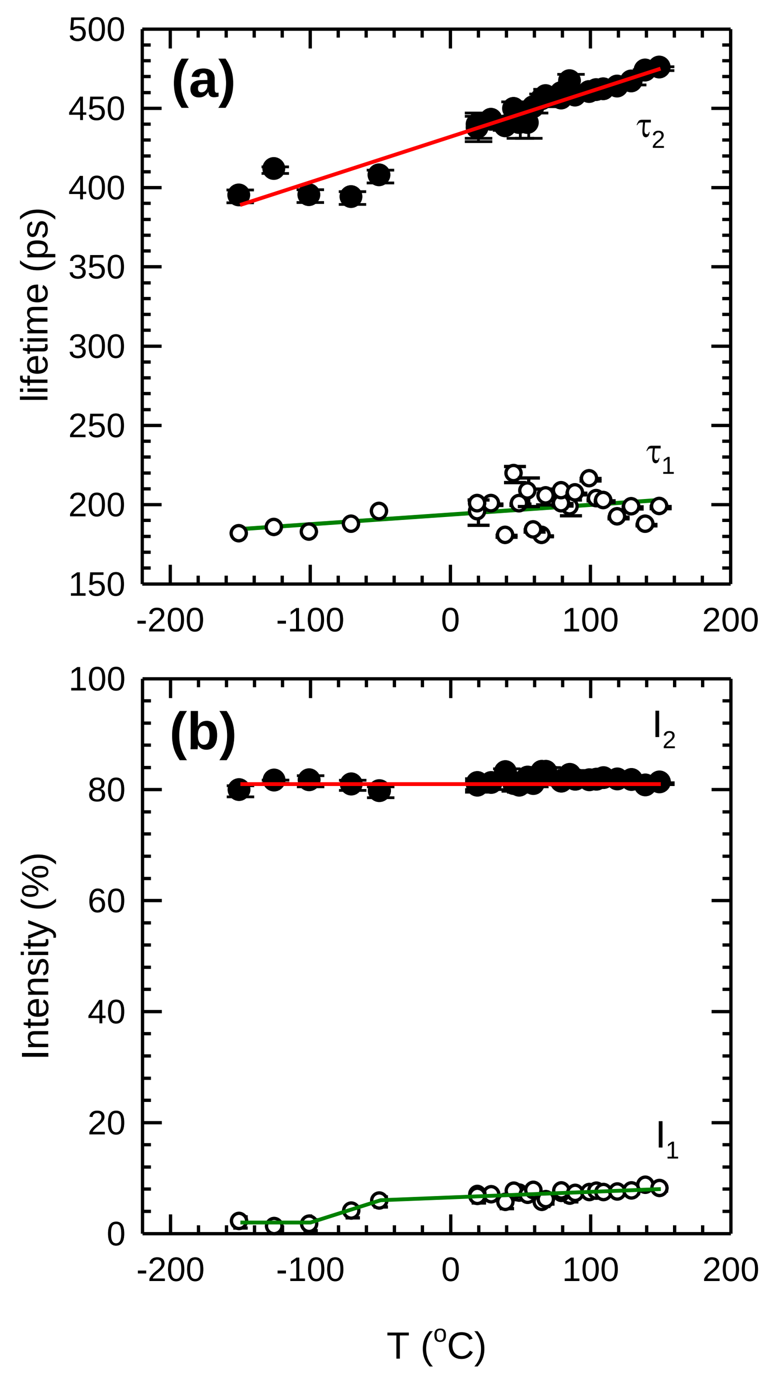
***The relative weight loss of as-received Nafion membrane during drying at 80 °C**. The weight loss was determined by ex-situ weighting (blue circles) and on other sample by TG. The water content in the as-received Nafion was ≈6 wt.% and the absorbed water was completely released from the membrane by drying at 80°C for approximately 6 min.*



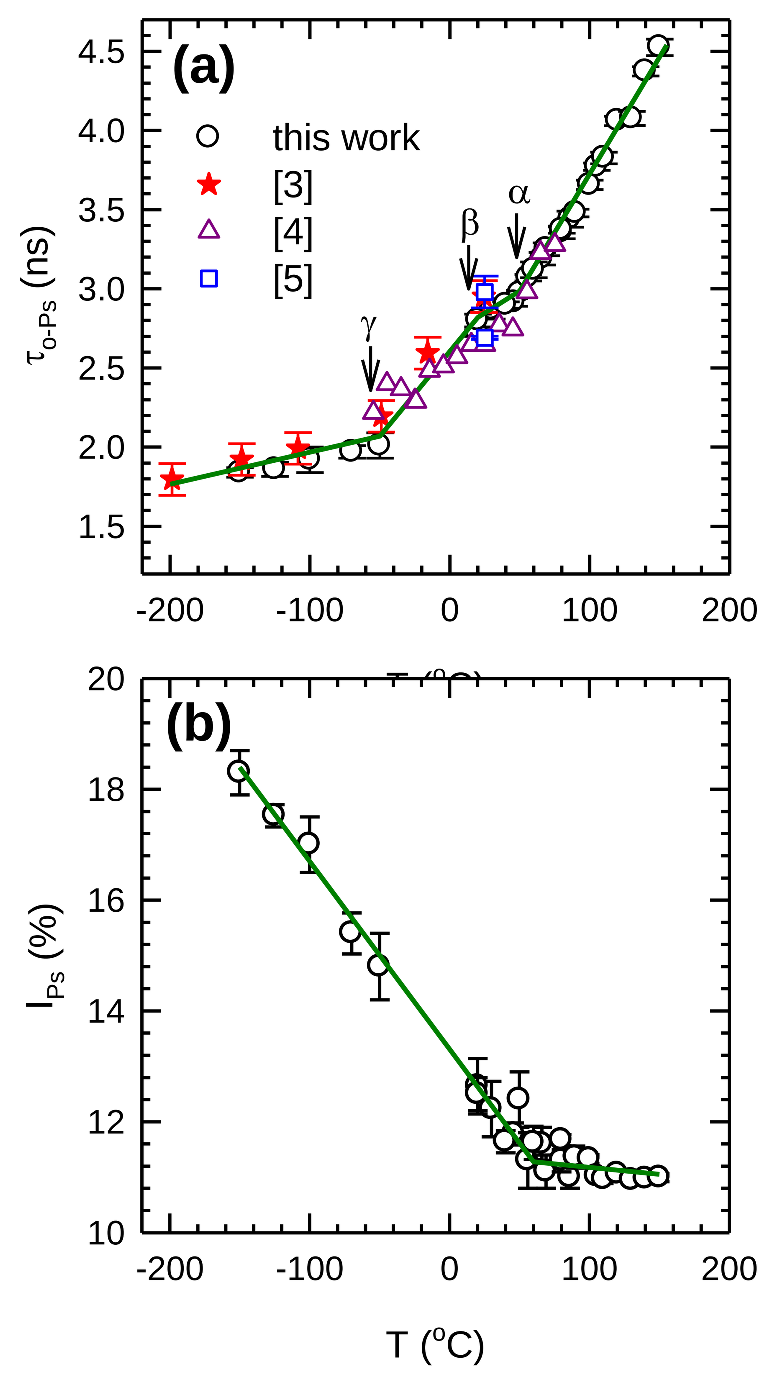
***Thermal development of the free volume size distribution H(R) in Nafion**, where R is the free volume hole radius, calculated from LT results using the Tao-Eldrup model [6,7].*



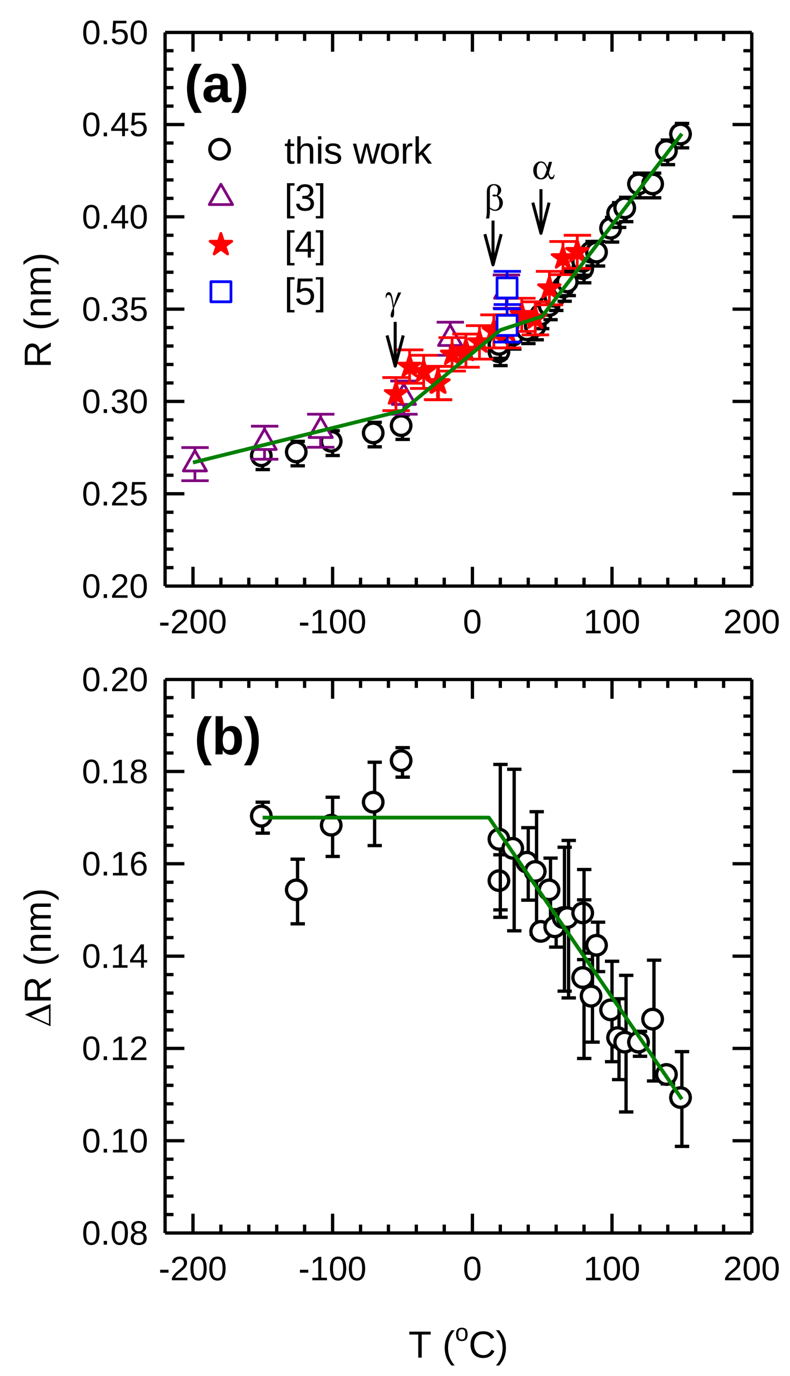
***DSC curve for dried Nafion**. The endothermic peak with maximum at 68°C which agrees well with the α-transition temperature determined by LT spectroscopy. The two endothermic processes occurring in the temperature range 150-235°C and 250-300°C can be attributed to glass transitions occurring in the polymeric PTFE backbone and inside the ionic clusters, respectively.*



***Temperature dependence of** (a) **positron lifetimes τ_1, τ_2 and** (b) **corresponding relative intensities for Nafion**. τ_1 represents a contribution of delocalized positrons and/or positrons trapped at small open volumes. τ_2 comes from trapped positrons*



***Temperature dependence of** (a) **o-Ps lifetime and** (b) **intensity of Ps contribution**. The o-Ps lifetimes for Nafion reported in literature [3,4,5] are plotted in the figure as well. The increase of o-Ps lifetimes with temperature is linear with several changes in slope occurring at temperatures where phase transitions in Nafion take place.*



*(a) **The mean radius and** (b) **width** (FWHM) **of the size distribution of free volumes plotted as a function of temperature**. The mean radius of free volume holes increases with temperature reflecting increasing flexibility of polymer chains. The width of the size distribution remains approximately constant up to the β-transition, at higher temperatures the width of the size distribution decreases.*

***The phase transition temperatures determined in H+ form Nafion by LT spectroscopy**. Results obtained in this work are compared with data available in literature.*

transition	T (°C) this work	T (°C) literature
α	60 ± 5	60-110 [3]
β	20 ± 5	20 [4]
γ	-50 ± 10	-98 [3]

References

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Summary

• The thermal development of the size distribution of free volumes in dried H^+ form of Nafion was determined by positron lifetime spectroscopy in a broad temperature range from -150 to 150 °C.

•**Positronium is formed** mainly **in** the hydrophobic **Nafion backbone**. The formation of Ps in ionic clusters is suppressed since free electrons in spur created during positron thermalization are caught by sulfonic radicals with uncompensated negative charge

•The **mean size of free volume holes increases with temperature** due to increasing motion of polymer chains.

•**Three phase transitions** were determined as changes in the slope of temperature dependence of the o-Ps lifetime:
(i) low temperature **γ-transition** at **-50°C** occurring in the **Nafion backbone**;
(ii) the **β-transition** at **20°C** taking place in the **Nafion backbone**, and
(iii) the **α-transition** at **60°C** which occurs **inside the ionic clusters**.
The α-transition was observed also by differential scanning calorimetry.

•Two additional **endothermic processes** were determined by differential scanning calorimetry:
(i) the process in the temperature range **150-235°C** can be attributed to the **glass transition in the polymeric PTFE backbone**
(ii) the process in the temperature range **250-300°C** can be attributed to the **glass transition inside the ionic clusters**

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PPC12

This work was supported by the Czech Science Agency (project P108/12/G043)