Scientific report

Structure-dynamics-properties relationships and aging effects in nanocomposite elastomers and proton exchange membranes

January –October 2016

The objectives for year 2016

O7c The characterization of proton conduction in polymeric electrolyte membranes in interaction with diverse solvents

IR spectra measurement and AFM imaging for thin films PEM membranes chemically aged

The main interaction of PEMs membranes due to their functioning regime in electric combustion cells is with water. One may question if there is another environment, probably also aqueous, which is more efficient to be used to produce electrical energy. In this sense the interaction PEM membranes – solvent should not lead to degradation of the membrane with effects on proton conduction thereof. A candidate for this type of solvents is H_2O_2, the hydrogen peroxide. Unfortunately the distilled water was proved to be a strong aging agent for PEMs membranes with destructive effects on polymeric chains of Nafion (or PFSA/SiO_2) which can be highlighted by spectroscopic methods. In the Fig. 50 are presented the FT-IR spectra measured using the ATR accessory (attenuated total reflation) at membranes' surface of initial dry Nafion (Fig. 50a) and initial hydrated (Fig. 50b) in function of hydrogen peroxide content (0-100%). The hydrogen peroxide action (Fig. 50) like an aging agent has a global effect of ATR-FT-IR spectra contrary to the effect of UV radiation (Fig. 42) meaning that with the increase of the H_2O_2 concentration, the transmittances decreases. The maximum decrease was observed for 25% of H_2O_2 concentration in H_2O after that we can observe a new increase of the spectra. We can observe different effects of Nafion membranes aged in interaction with hydrogen peroxide in function of the initial state of membrane, dry or hydrated. Major modification may be observed for Nafion membrane initial hydrated (Fig. 50b) as: i) the doublet at ~2800 and ~2900 cm^{-1} is strongly reduced under the influence of H_2O_2;ii) the absorption peak at ~1700cm^{-1} is moved at ~1600cm^{-1}; iii) the entire molecular skeleton is strongly affected for the initial hydrated Nafion under the action of H_2O_2 (Fig. 50b) compared to initial dry Nafion (Fig. 50a) as seen from modification absorption peak amplitude centered at ~1150 cm^{-1} in initial hydrated Nafion case. The quick action (first hour) and the slow action (one year) of the hydrogen peroxide aging agent it was monitored by registering the VIS-NearIR spectra as one can see in Fig. 51. A VIS-NearIR spectrum is not so

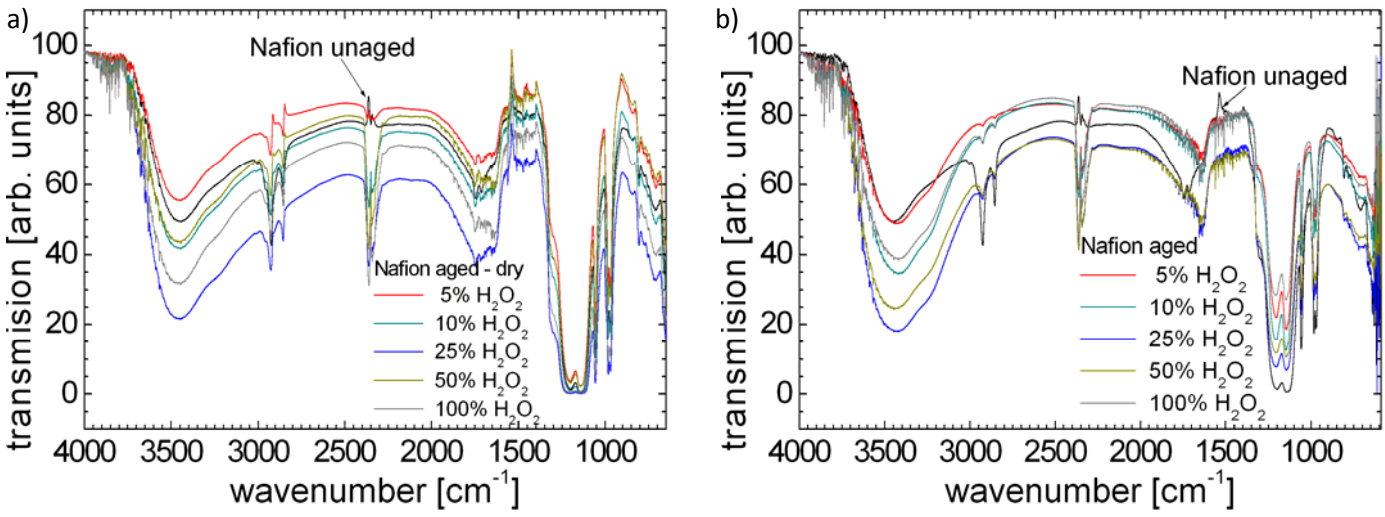

Fig. 50 The ATR-FT IR spectra measured for PEM membrane Nafion type subjected to chemical agent action (hydrogen peroxide – H_2O_2) for initial Nafion 117: a) dry and b) hydrated.

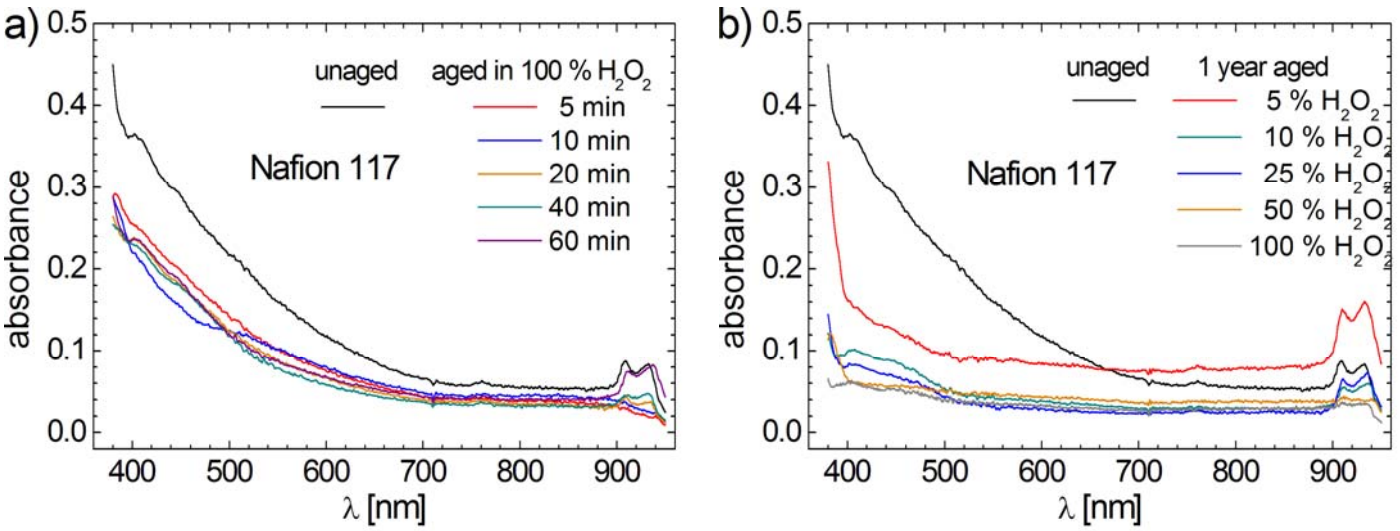

Fig. 51 The VIS-NearIR spectra registered for membrane of 117 Nafion chemical aged (in 100 H_2O_2) a) in function of aged time and b) sample aged for one year in function of the H_2O_2 concentration in H_2O.

rich in information as the IR spectra but one can observe, in all situations, a decrease of absorption for aged membrane under the action of H_2O_2. Dramatically effects can be observed in the first 10 minutes after the action of H_2O_2 (Fig. 51a) after that a slow process of the structural modification of membrane is observed. In function of the wavelength of electromagnetic radiation interacting with Nafion 117 membrane a more strong absorption it can be observed in the visible domain near to UV and a smaller one in the near-IR domain. Slowly, at small concentration (5 % in H_2O solution) the hydrogen peroxide modify the electronic bonding at the molecular level of Nafion polymeric chains, characterized by electrons with transition in visible and near IR like it can be seen from flattening at the small values of the VIS-NearIR spectra (the red curve in Fig. 51b) but don't have effect on the electrons which suffer transition in ultraviolet domain. At larger concentrations all electrons are affected under the H_2O_2 action as one can see from flattening of the VIS-NearIR spectra for the entire domain.

The structural modification at the surface of PEM membrane under the action of chemical aging agent can be observed also from the AFM image registered in the amplitude and in phase

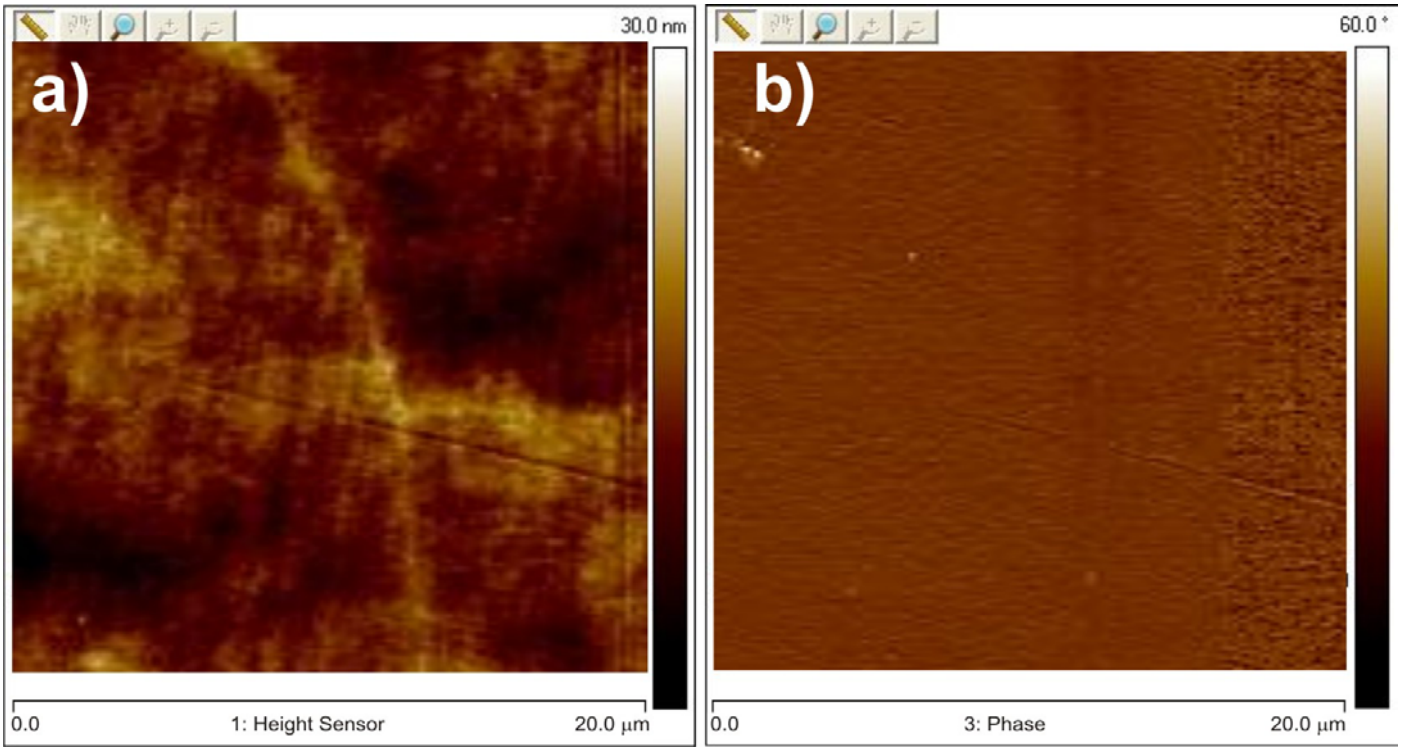

Fig. 52 The AFM images: a) amplitude and b) in phase of aged Nafion 117 membrane.

and which are presented in Fig. 52. Traces of channels, well contoured for the un-degraded Nafion (see Fig. 45), can be vague observed for the degraded Nafion 117.

O8. The temperature effect on the proton self-diffusion processes for diverse hydrated PEMs membranes.

PGSSE measurements curves of PFSA/SiO_2 hydrated membranes at different temperatures up to 70 C (90 C)

To estimating the temperature effect on the self-diffusion process, a series of NMR PGSSE type measurements were performed for PFSA/SiO_2 hydrated at temperatures between the intervals from 50ºC until 90ºC. Parts of these curves were presented in Fig. 53 for three concentrations of SiO_2 0, 3 and 5 –wt. in PESA (PFSI). In order to analyze the PGSSE curves, a dedicated fitting program was written C++ in which the theoretical model developed in 2013 at the O5 objective at the present contract, more specific the equations 10-12 were implemented. As fitting variables we had: i) the self-diffusion coefficient D whose dependence of temperature is present in Fig. 54 and of which values are observed to increase with the increases of the SiO_2 concentration; ii) exchange rates k_f from free water (f) → bound water (b) and k_b from bound water (b) →free water (f) of which dependence on temperature is presents in Fig. 55 a and 55b and iii) relaxation rates $R_{1,f}$ corresponding to free water (f) and $R_{1,b}$ corresponding to bound water (b). In general, with the increase of the temperature it can be noticed an increase of these parameters (see Fig. 54 and 55). Like an exceptions we can remark the coefficients k_f, k_b, and $R_{1,b}$ for PFSA/SiO_2 with 5 –wt. SiO_2. In addition one can observe that in temperature domain 60-70 ºC take place changes in the tendency of variation of these dynamic parameters for PFSA/SiO_2 (see Fig. 55).

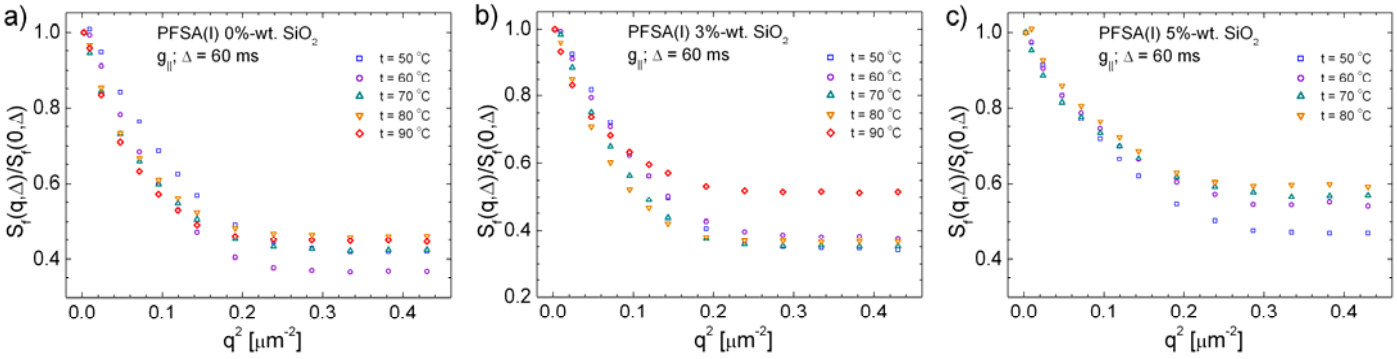

Fig. 53 The PGSSE decay curves for PFSA (I) membrane with a) 0% –wt., b) 3% –wt., c) 5% –wt. SiO_2 in function of temperature in domain 50-90°C.

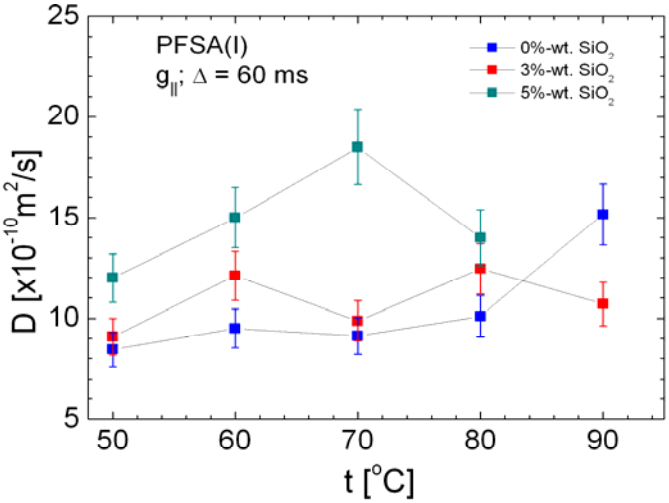

Fig. 54 The dependence of self-diffusion coefficient of free water in PEM (PFSA (I) membranes channels with different percent 0%, 3% and 5% -wt. de SiO_2) measured by PGSSE curves from Fig. 53 in function of temperature.

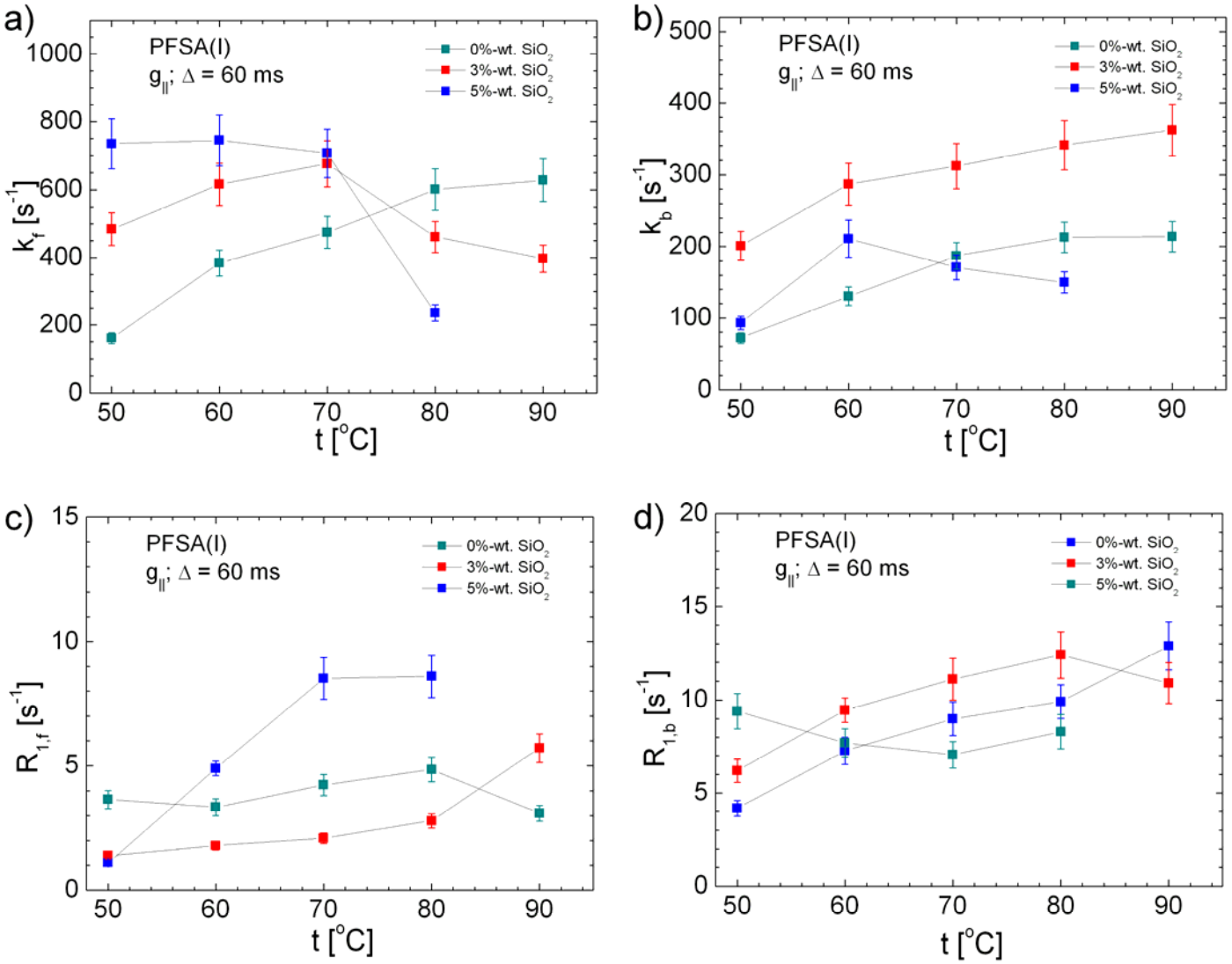

Fig. 55 The dependence of exchange rates $k_{f,(b)}$ a) free water (f) → bound water (b) and b) bound water (b) → free water (f) and relaxation rates $R_{1,f(b)}$ c) free water (f) and d) bound water (b) in PEM (PFSA(I) membranes with different percent 0%, 3% and 5% -wt. of SiO_2) calculate from PGSSE curves see Fig. 53 in function of temperature.

Determination of the conditions for obtaining anomaly diffusion

Anomaly diffusion is related to weak restrictions of water diffusion due to the structural and dynamics characteristics of the polymeric matrix of the PEM membranes leading to a non-Gaussian propagator (Fig. 56). The quantitative characterization of the propagator can be make

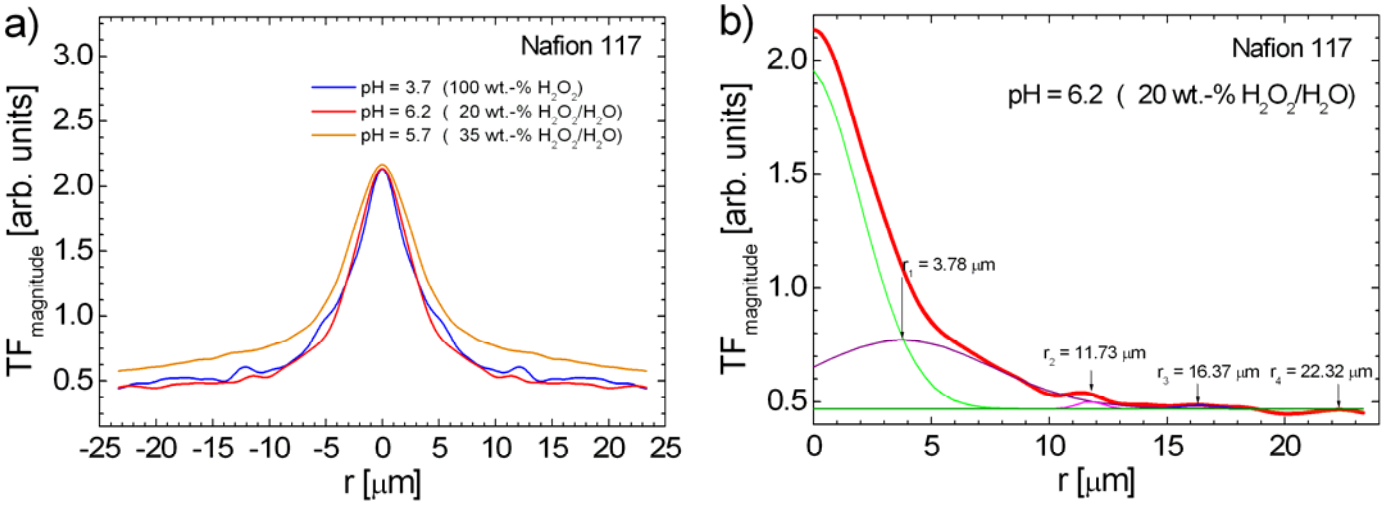

Fig. 56 a) The non-Gaussian propagator measured for PFSA(I) Nafion membranes in interaction with H_2O_2 in different concentration; b) The structure factors for Nafion 117 affected by interaction with distillated water at pH = 6.2.

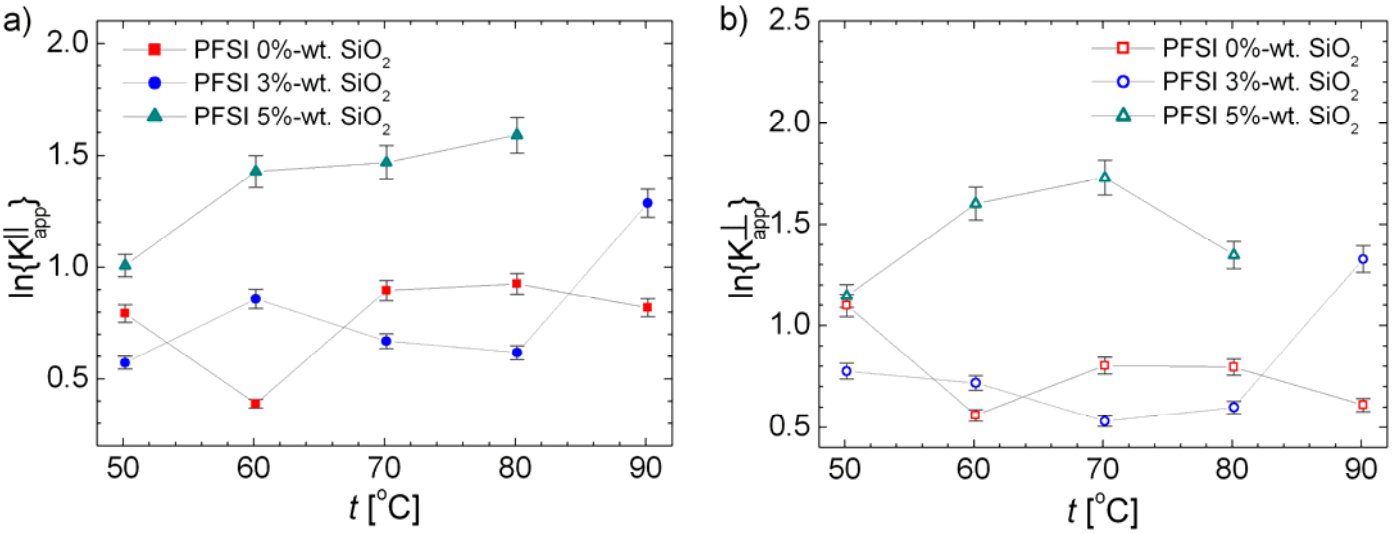

Fig. 57 The apparent kurtosis coefficient (K_{app}) dependence for a) parallel and b) perpendicular orientation measured for PFSA (I) membranes with 0% –wt., 3% –wt. and 5% –wt. SiO_2 in function of temperature in domain 50-90 °C.

used a parameter named kurtosis. The molecular self-diffusion phenomena can be described in a free model:

$$E(q,\Delta)=\int \overline{P}(X,\Delta)e^{iqX}dX\,, \tag{1}$$

where $E(q,\Delta)$ is the amplitude of the simulated echo $\overline{P}(X,\Delta)$ is the averaged propagator or the density probability function which describes the probability that a molecule from any starting position will moved to a X distance in the diffusion time Δ. In order to introduce the apparent kurtosis parameter k_{app} (vide infra) for molecules which diffuses into a specific direction given by the magnetic field gradient, we consider the developing in power series of the natural logarithm of normalized values of the stimulate echo:

$$\ln\left(\frac{E(q,\Delta)}{E(0,\Delta)}\right)\cong-\frac{1}{2}\langle X^2\rangle q^2+\frac{1}{24}\langle X^2\rangle^2\left(\frac{\langle X^4\rangle}{\left(\langle X^2\rangle\right)^2}-3\right)q^4-\ldots, \tag{2}$$

the a-dimensional diffusion parameter named kurtosis k, maybe defined as:

$$K_{app}\equiv\frac{\langle X^4\rangle}{\left(\langle X^2\rangle\right)^2}-3,$$

and which, for a Gaussian type diffusion, the scalar value is k=0, and in final we obtain function:

$$\ln\left(\frac{E(q,\Delta)}{E(0,\Delta)}\right)\cong-\Delta D_{app}q^2+\frac{1}{6}\Delta^2 {D_{app}}^2 K_{app}q^4-\ldots.$$

which is variable in the limit of short pulse gradients for which $\delta<<\Delta$, and in addition the condition: $\langle X^2\rangle^{1/2}q<<1$ must be also fulfilled.

All the objectives and activities were totally achieved.

Data
25.09.2016

Project Manager PN II Idea 307/2011,
Prof. Dr. Radu Fechete