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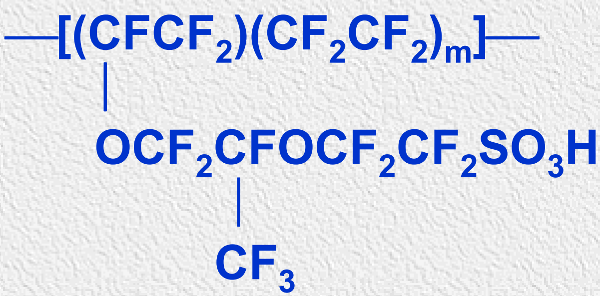
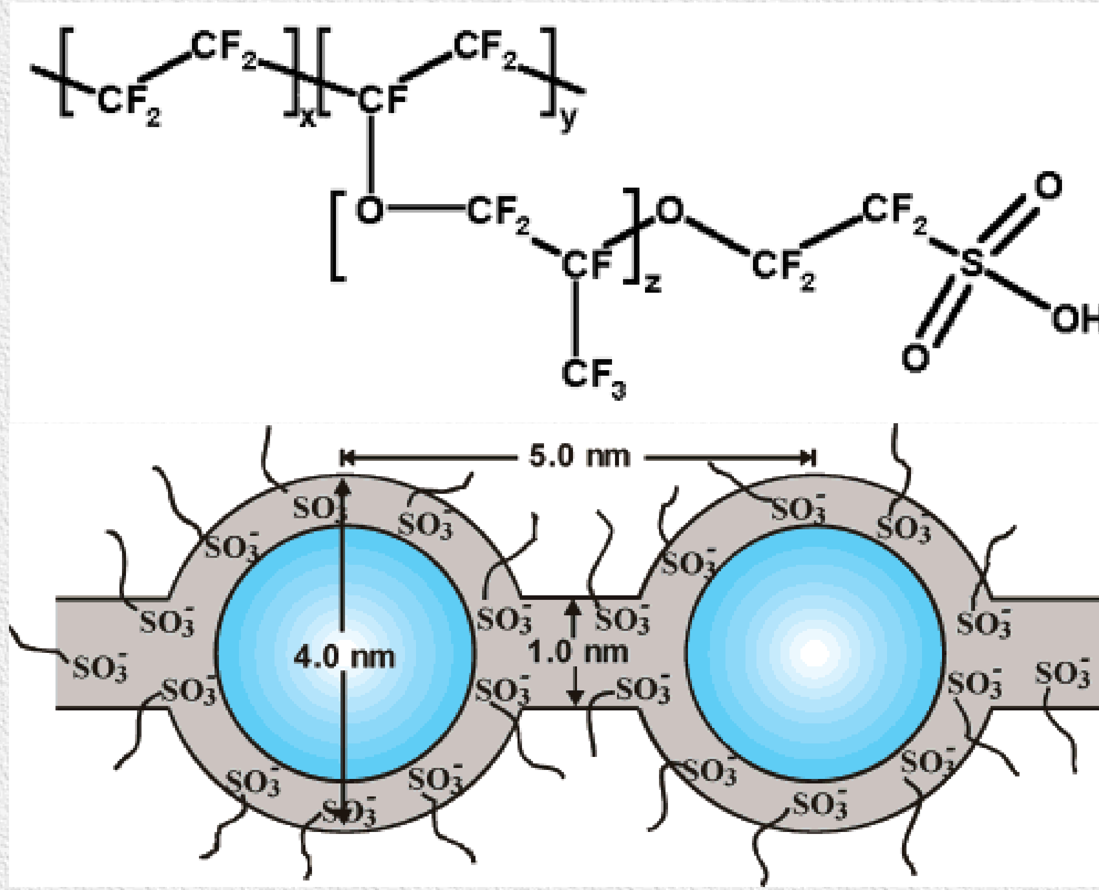
Phase Transitions in system Nafion-water

N.F. Bunkin, S.D. Zakharov, A.A.Zinchenko,

V.A. Kozlov, A.V. Shkirin

Motivation of the study (1)





Nafion Structure

K.A.Mauritz, R.B.Moore, State of understanding of Nafion, Chem. Rev., 104, 4535-4585 (2004).

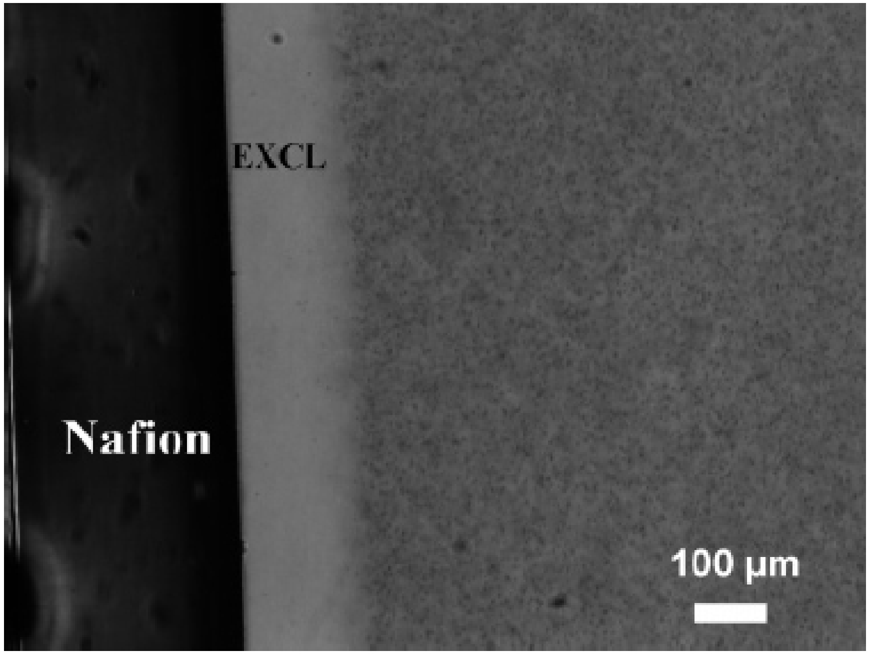
Motivation of the study (3)

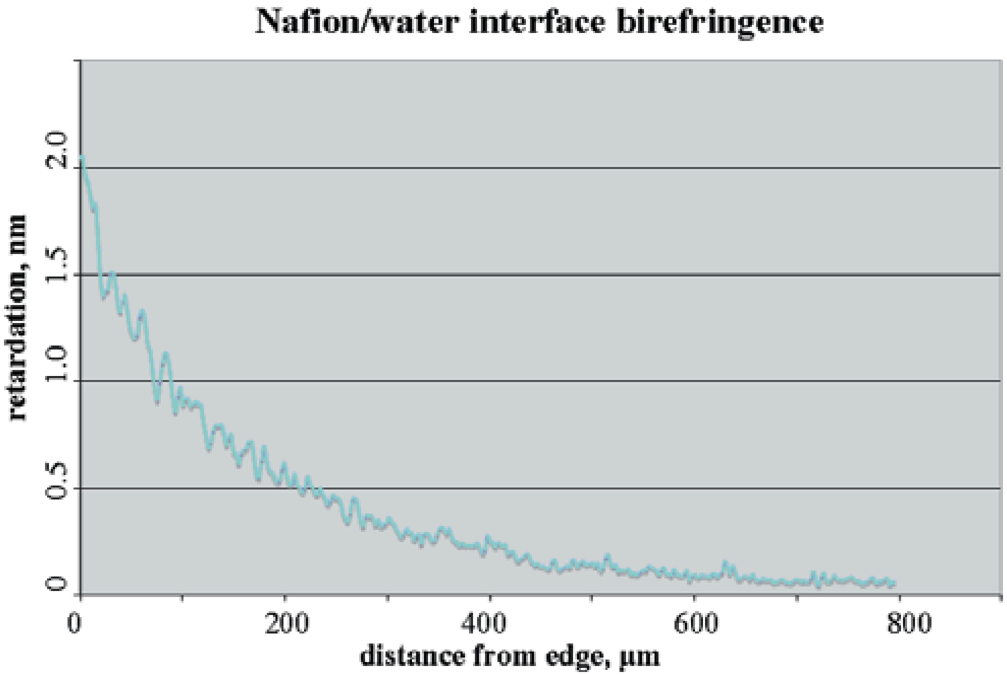
B.Chai, J.Zheng, Q.Zhao, G.H.Pollack, Spectroscopic Studies of Solutes in Aqueous Solution, J. Phys. Chem. A 2008, 112, 2242-2247

Water: The Forgotten Biological Molecule, Ed.: D. Le Bihan, H. Fukuyama, 2011, Pan Stanford Publishing Pte. Ltd.

Chapter 7,

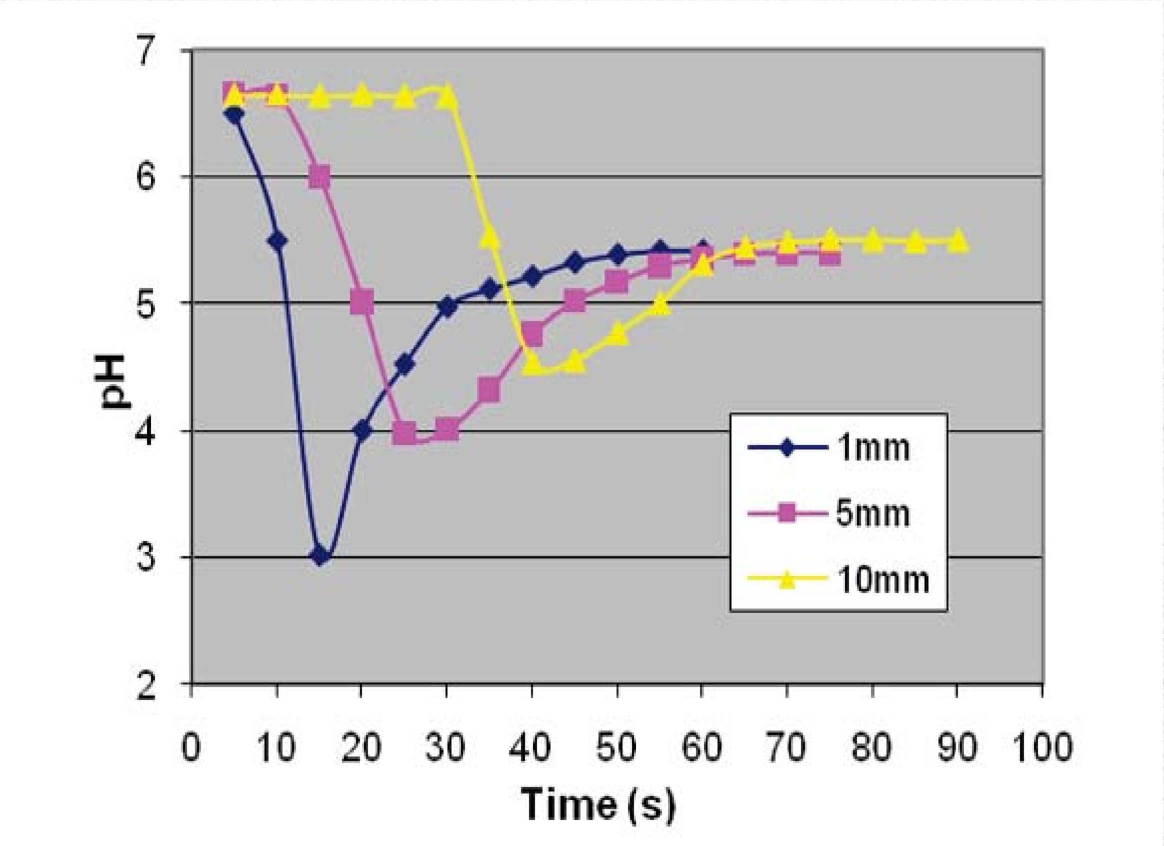
H. Yoo, D.R. Baker, C.M. Pirie,B. Hovakeemian, G.H. Pollack, CHARACTERISTICS OF WATER ADJACENT TO HYDROPHILIC INTERFACES





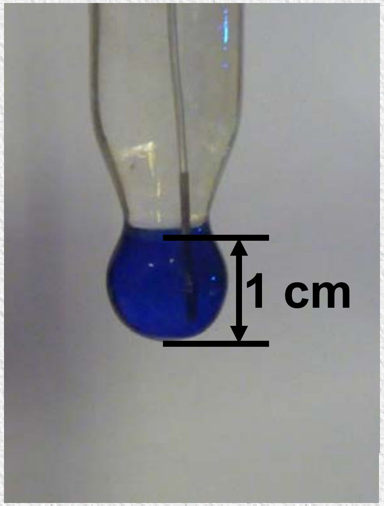
Motivation of the study (5)

B.Chai, H.Yoo, G.H. Pollack, Effect of Radiant Energy on Near-Surface Water, J.Phys.Chem. B 113, 13953–13958 (2009);

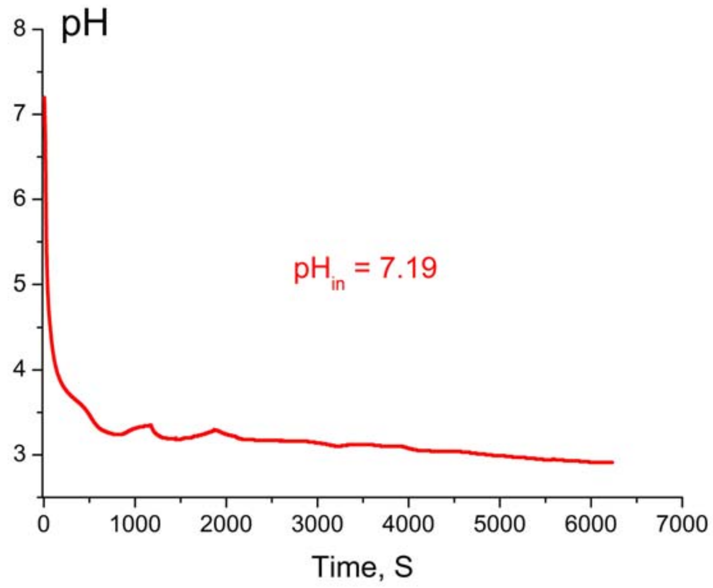


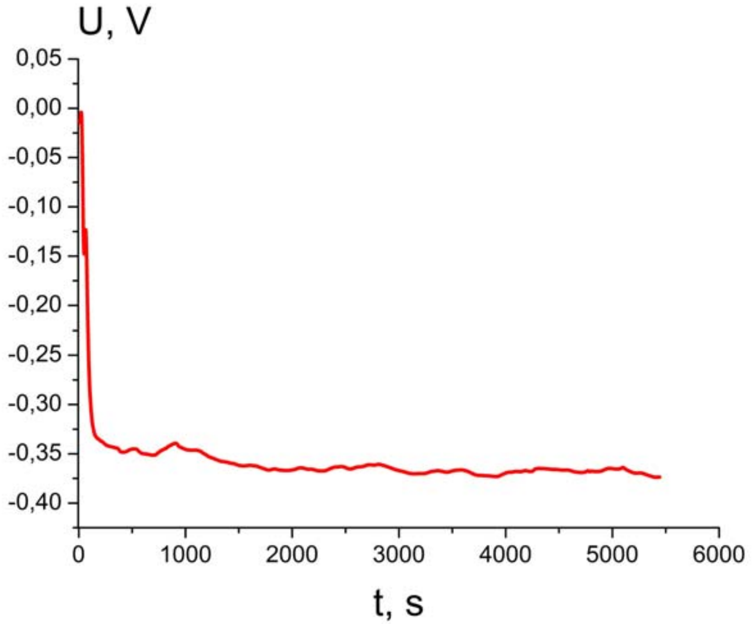
EXPERIMENTAL RESULTS (1)

Size of Nafion plate:
3×2 cm^2



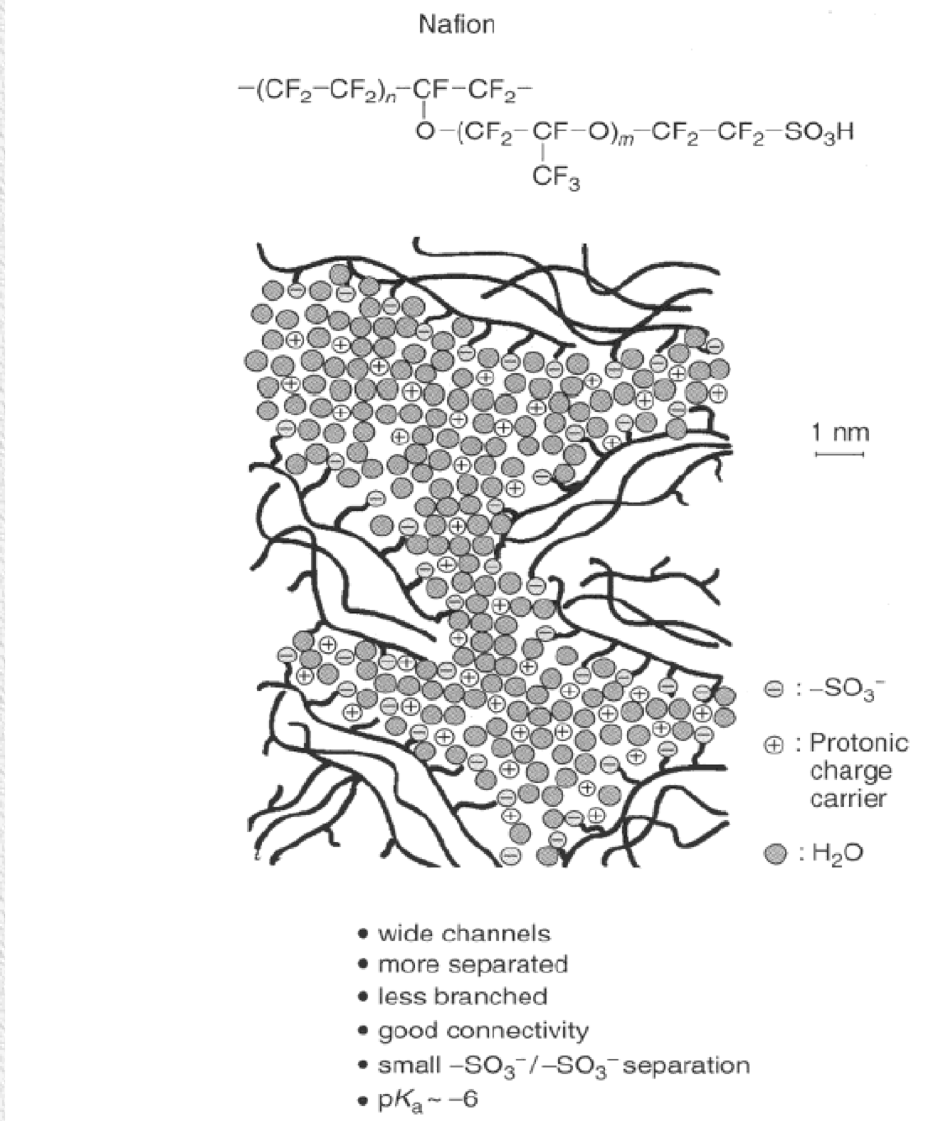
T = 20 C





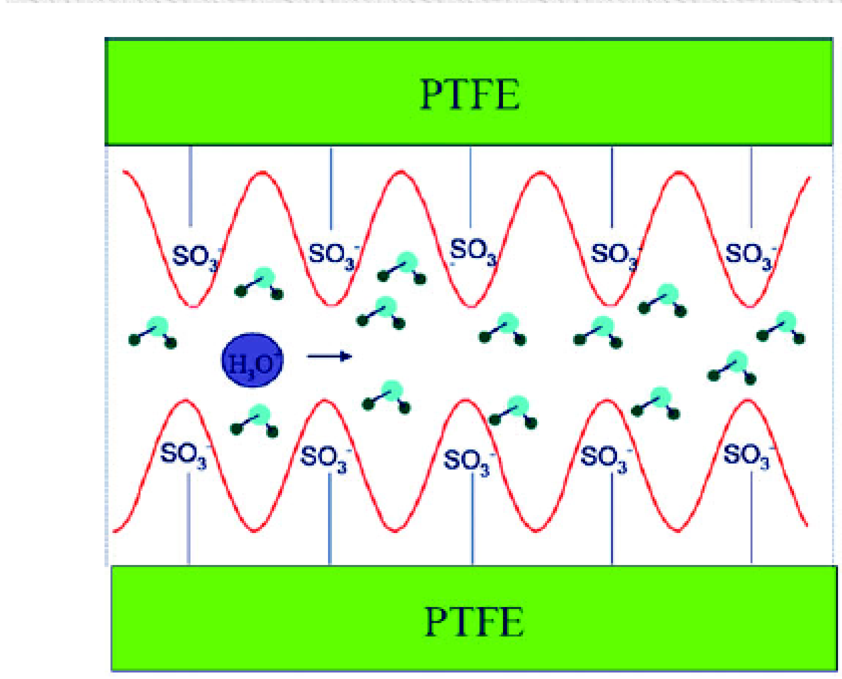
CHARGING OF NAFION SURFACE

$$[OCF_2CFOCF_2CF_2]\text{—}SO_3H + H_2O \Leftrightarrow [OCF_2CFOCF_2CF_2]\text{—}SO_3^- + H^+ + H_2O$$



Kreuer, K. D. J. Membr. Sci. 2001, 185, 29.

J.A. Elliott, S.J. Paddison, Phys. Chem. Chem. Phys., 2007, 9, 2602–2618



BREAKDOWN OF COVALENT BOND AT SWELLING IN WATER???

$$[OCF_2CFOCF_2CF_2]—SO_3H + H_2O \Leftrightarrow [OCF_2CFOCF_2CF_2]^+ — SO_3H^- + H_2O$$

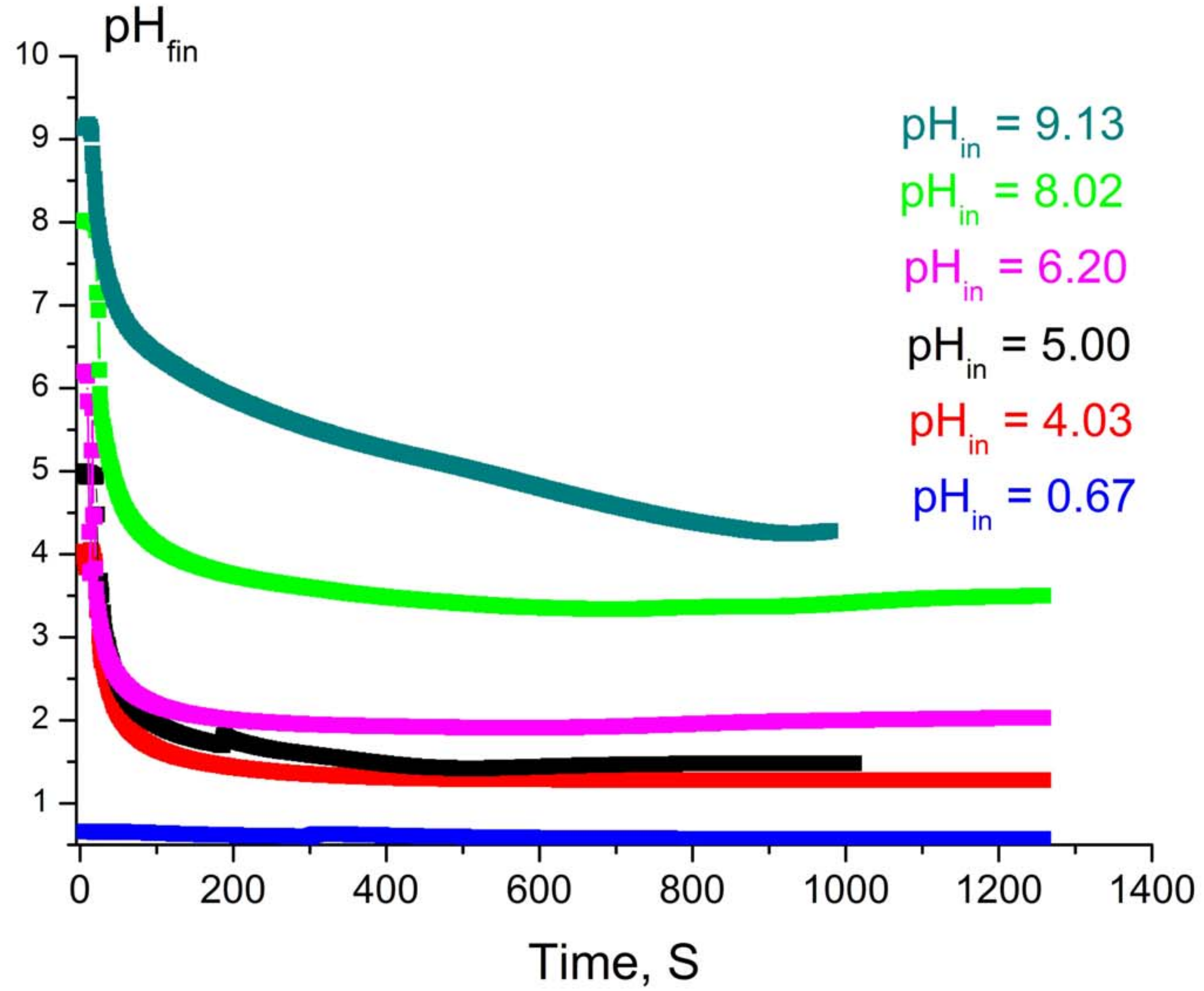
$$[OCF_2CFOCF_2CF_2]—SO_3H + H_2O \Leftrightarrow [OCF_2CFOCF_2CF_2]—SO_3^- + H^+ + H_2O$$

$$H^+ + SO_3H^- + H_2O \Leftrightarrow H_2SO_3 + H_2O$$

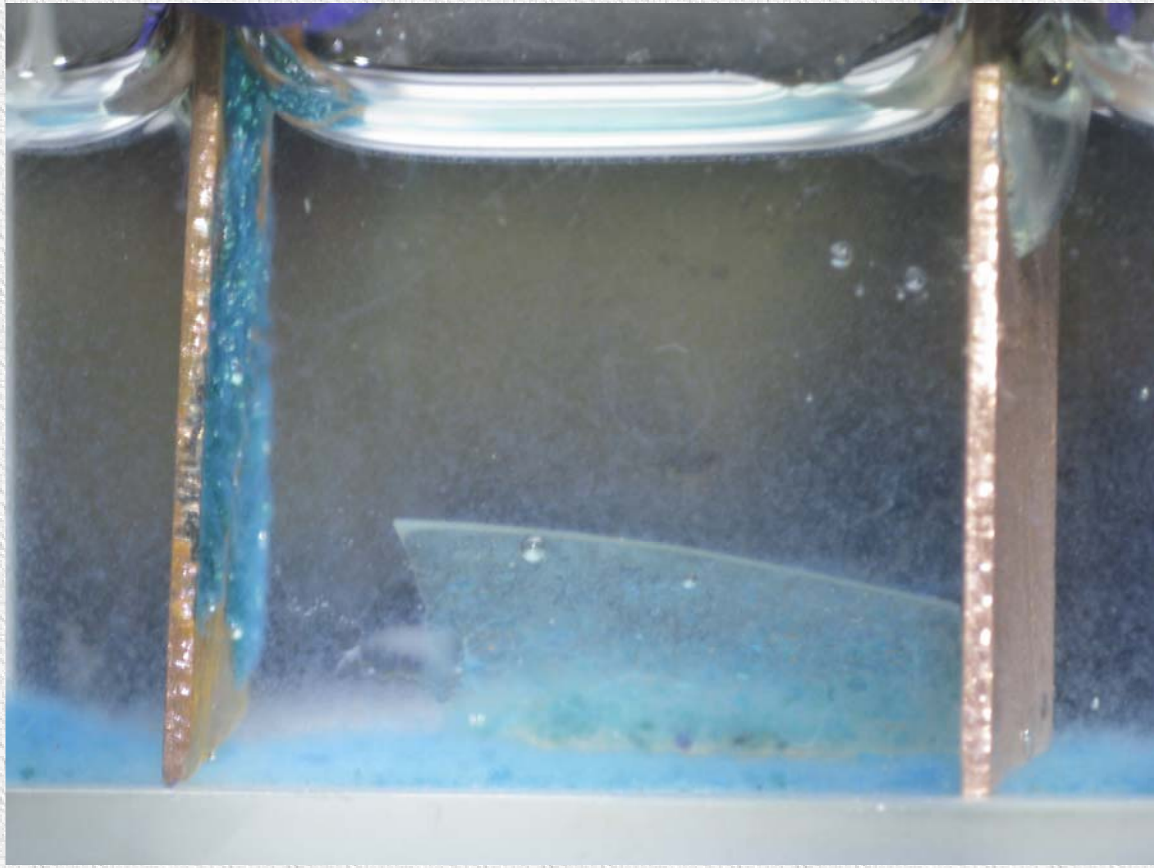
H_2SO_3????

Study of pH

To stabilize Nafion an acidic medium is required



EXPERIMENTAL RESULTS (2)



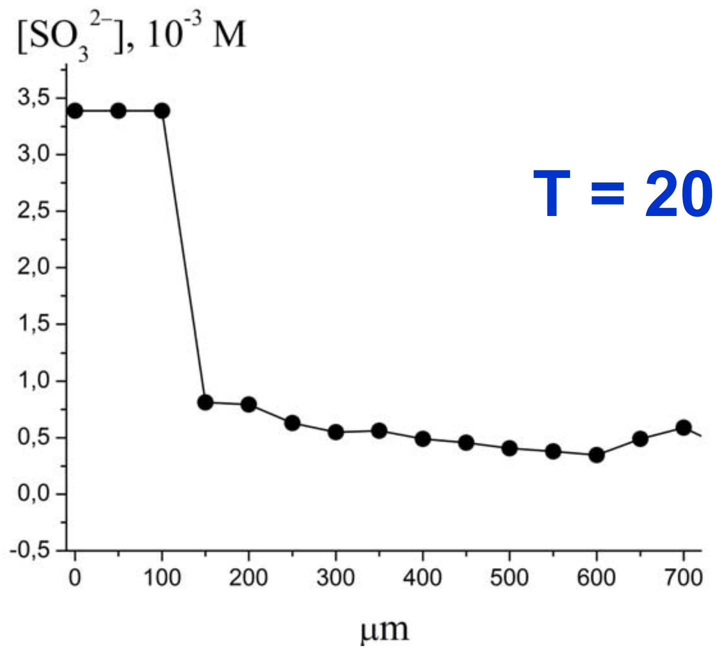
SO_3^{2-}, SO_4^{2-} - sensitive electrode, $5 < T < 45$ C;

~~SO_4^{2-}~~

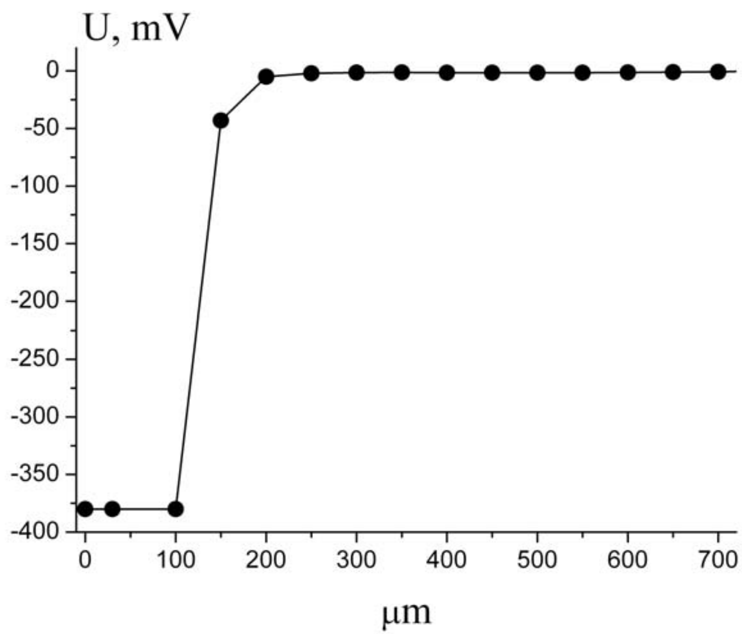
$$5\ SO_3^{2-} + 6\ H^+ + 2\ MnO_4^- \Leftrightarrow 5\ SO_4^{2-} + 2\ Mn^{2+} + 3\ H_2O;$$

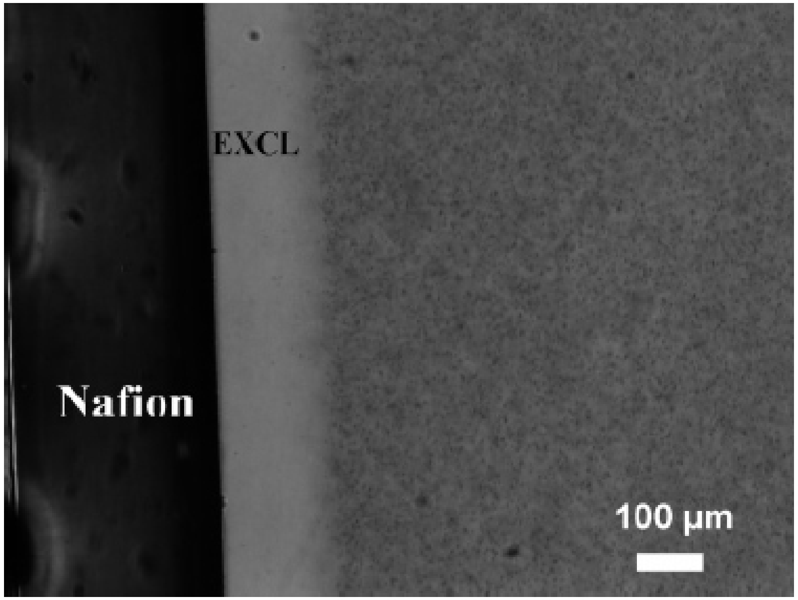
EXPERIMENTAL SETUP

EXPERIMENTAL RESULTS (3)



T = 20 C

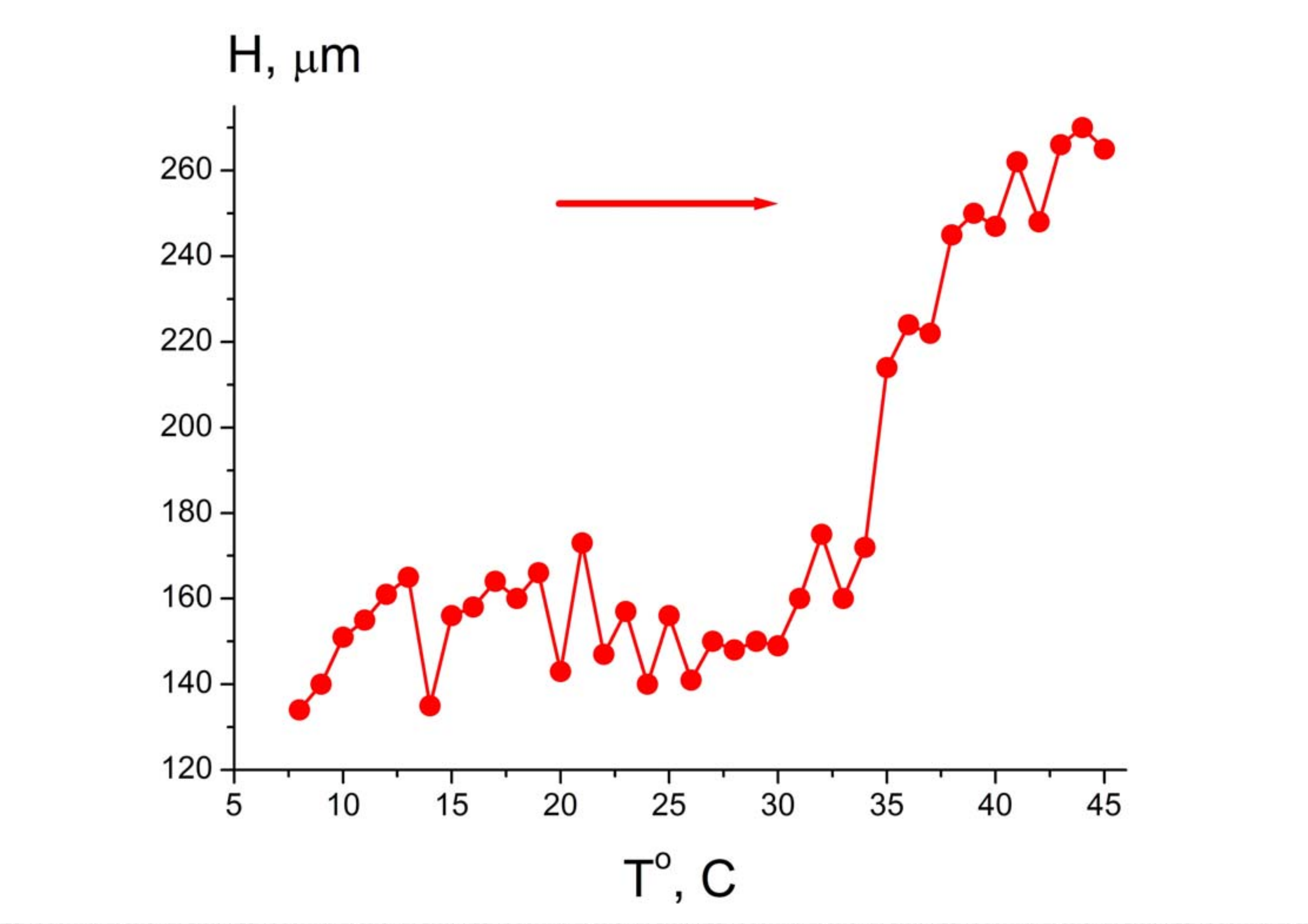




B.Chai, J.Zheng, Q.Zhao, G.H.Pollack, Spectroscopic Studies of Solutes in Aqueous Solution, J. Phys. Chem. A 2008, 112, 2242-2247

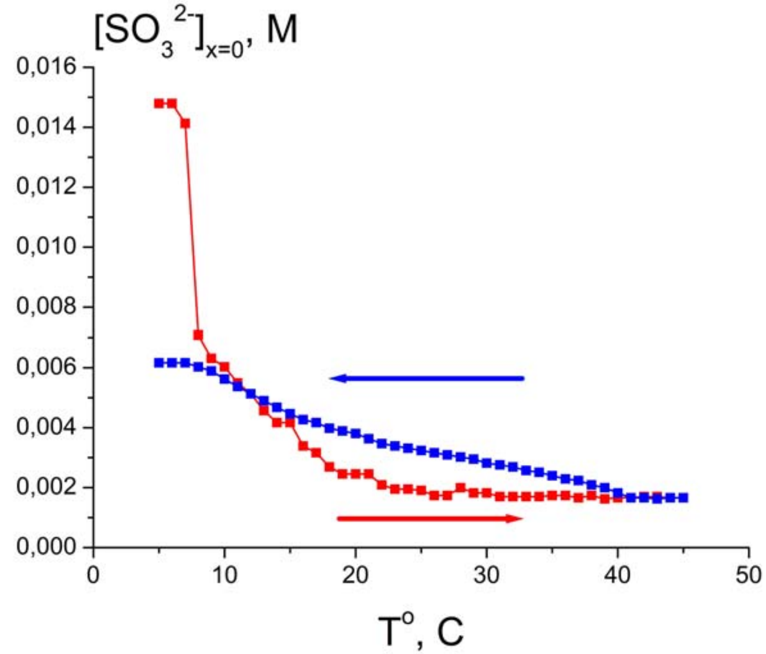
Na_2SO_3

TEMPERATURE DEPENDENCE OF THE EXCLUSION ZONE SIZE

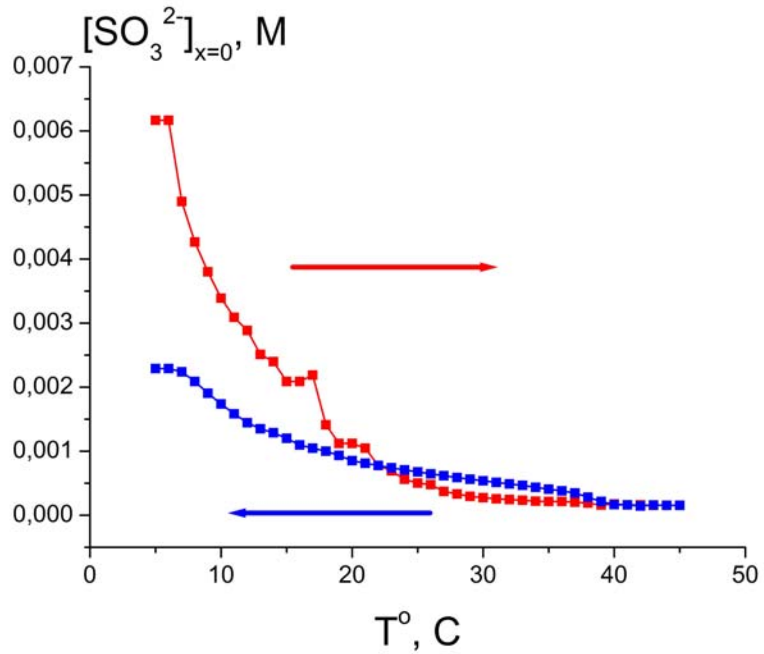


EXPERIMENTAL RESULTS (4)

22 C – the temperature of Nafion storage

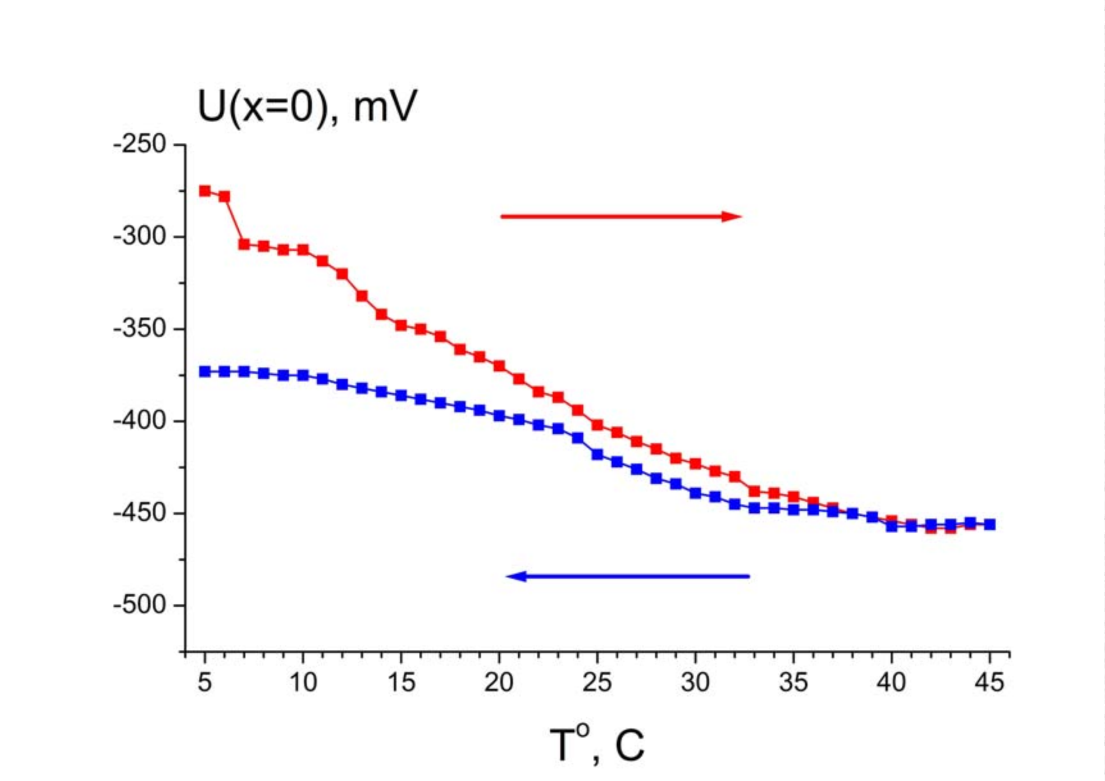


15 minutes of swelling



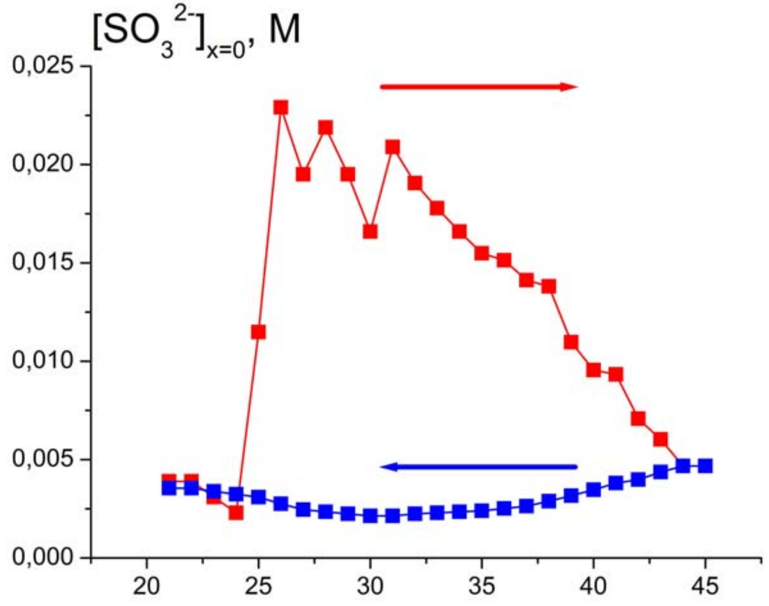
2 hrs of swelling

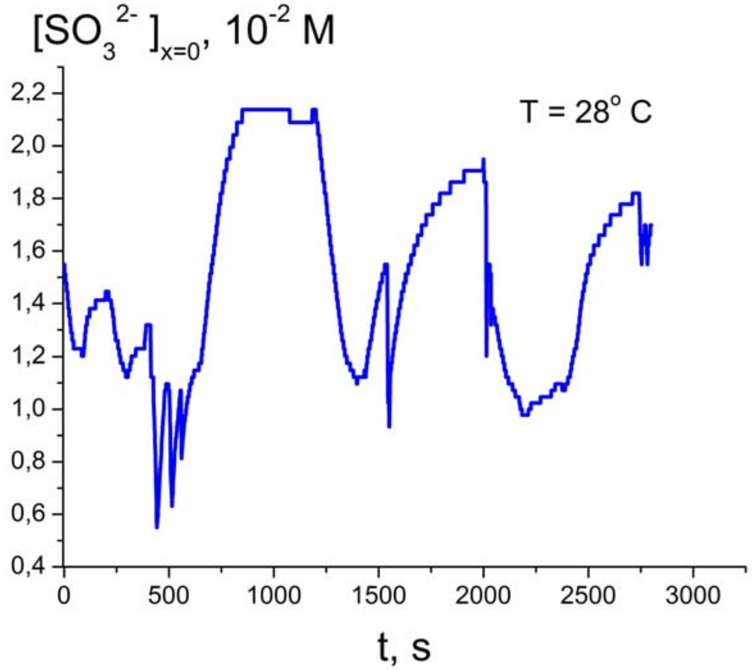
Experimental results (5)

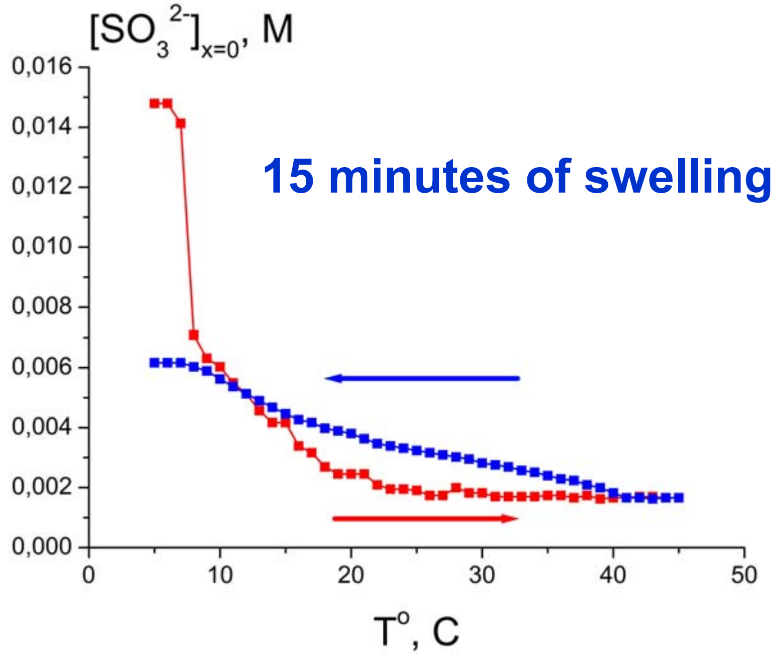


15 minutes of swelling

EXPERIMENTAL RESULTS (6)







DISCUSSION OF RESULTS

Vol 464 | 11 March 2010 | doi:10.1038/nature08863 nature

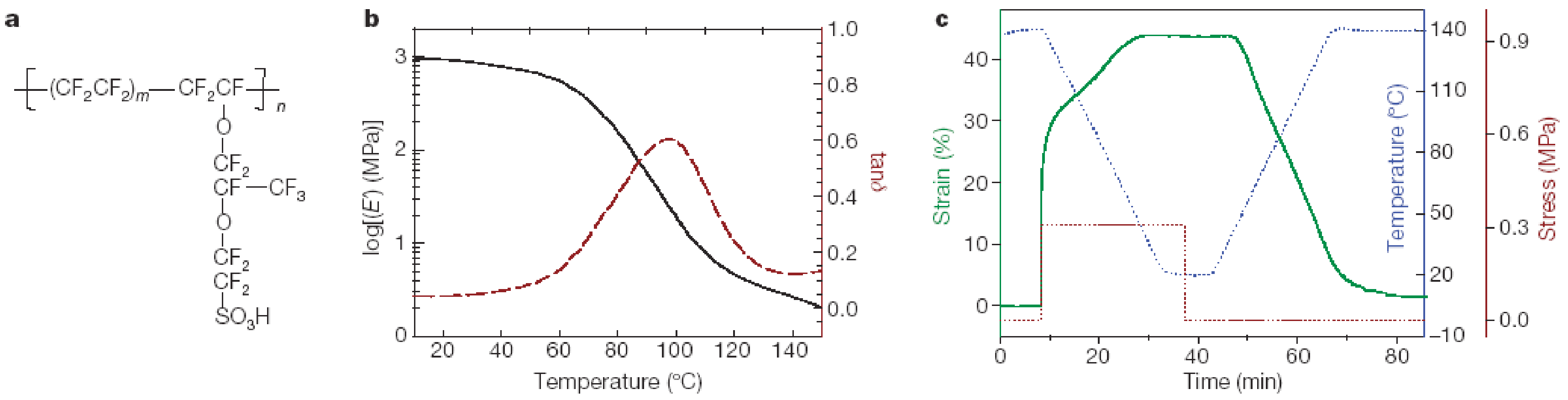
170 μm; 25 μm

LETTERS

Tunable polymer multi-shape memory effect

Tao Xie[1]

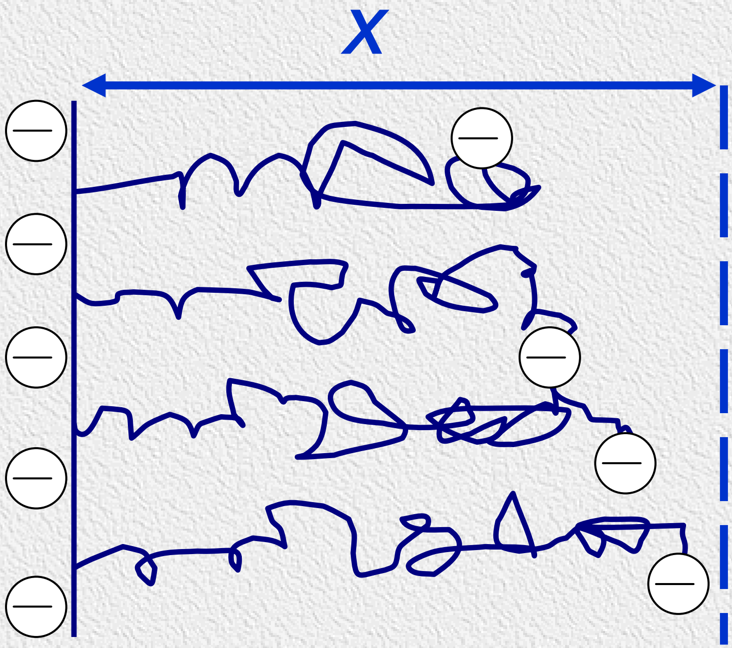
$$E' = \frac{\sigma_0}{\varepsilon_0}\cos\delta; \quad E'' = \frac{\sigma_0}{\varepsilon_0}\sin\delta;$$



Exclusion zone formation????

$$[OCF_2CFOCF_2CF_2]—SO_3H + H_2O \Leftrightarrow [OCF_2CFOCF_2CF_2]—SO_3^- + H^+ + H_2O$$

$$—[(CFCF_2)(CF_2CF_2)]_m—$$

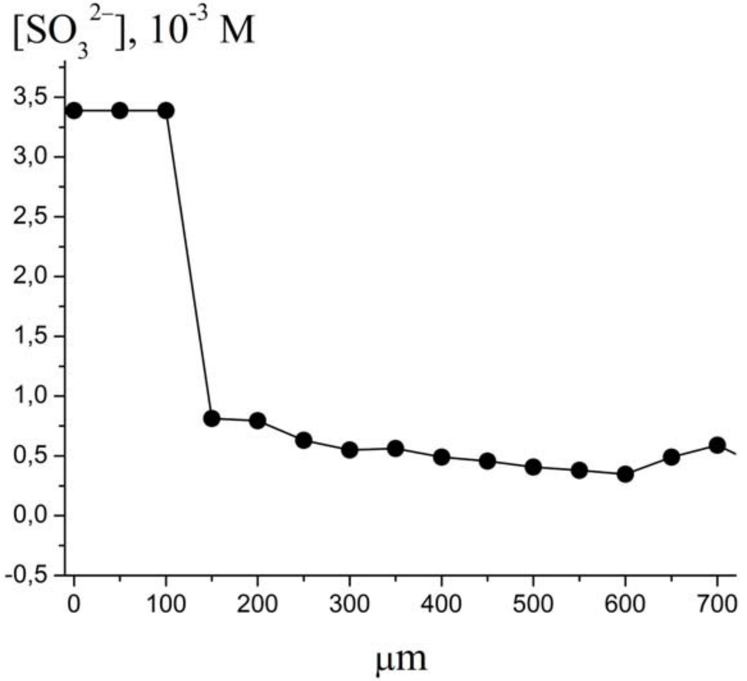


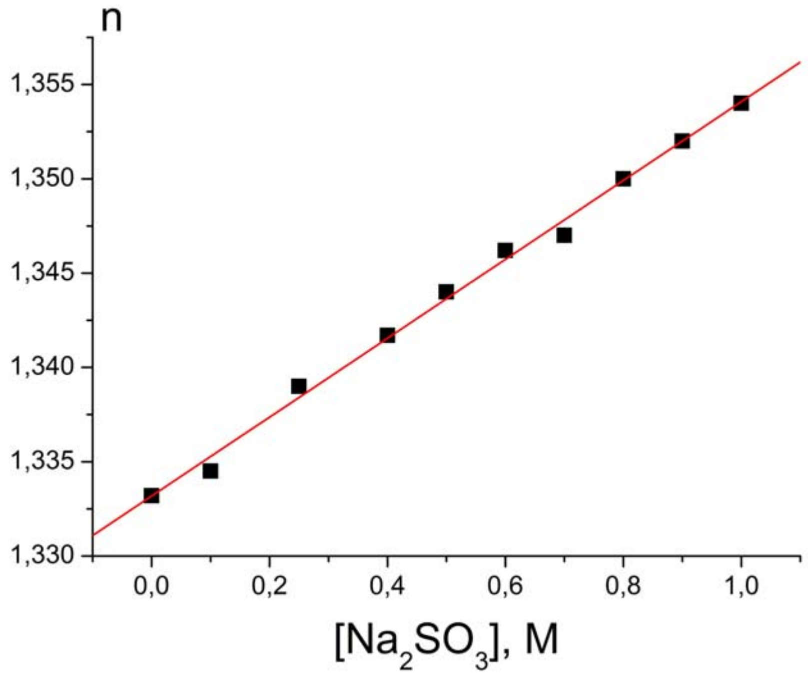
$X \sim 150\ \mu m \Leftrightarrow m \sim 10^6$

$\ominus \rightarrow SO_3^-$

EXCLUSION ZONE IS HYDROGEL???

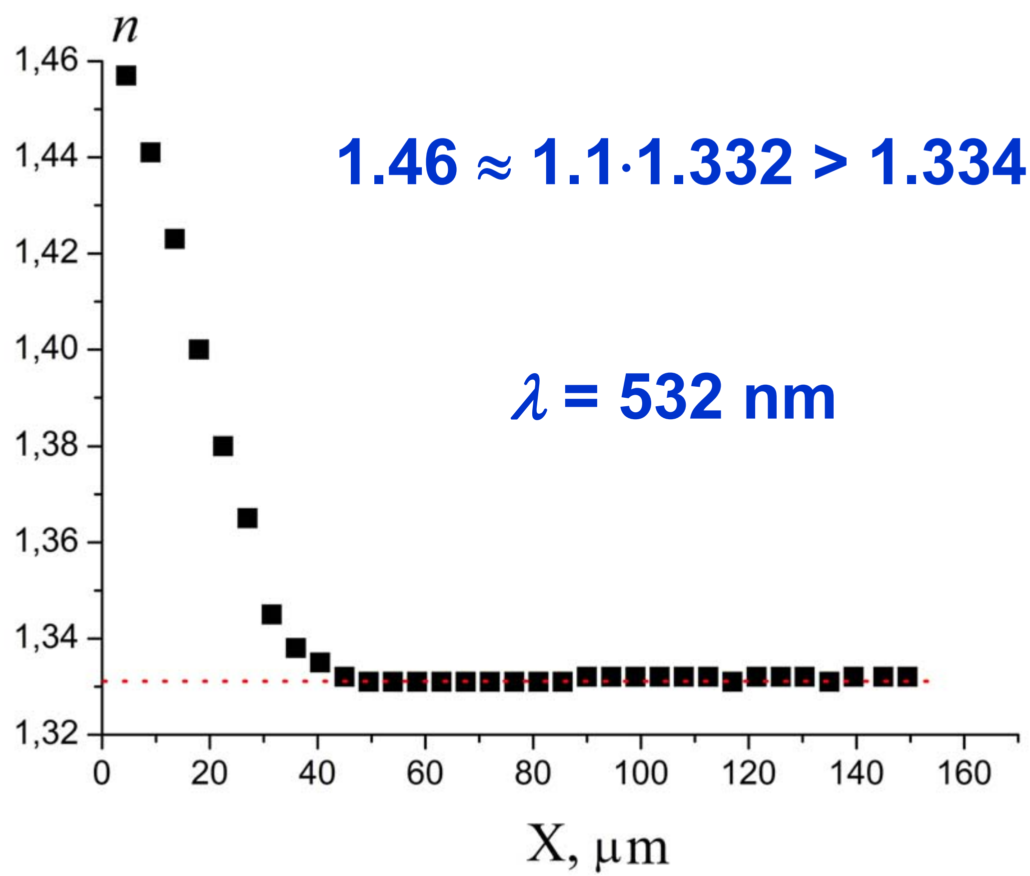
STUDY OF REFRACTIVE INDEX OF WATER CLOSE TO NAFION INTERFACE





$[Na_2SO_3] = 0.03$ M ⇔ $n = 1.334$

REFRACTIVE INDEX OF WATER AT THE NAFION INTERFACE; pH = 6.7, T = 22 C



$1.46 \approx 1.1 \cdot 1.332 > 1.334$

$\lambda = 532$ nm

EXPERIMENTAL SETUP:

N.F. Bunkin, N.V. Suyazov, A.V.Shkirin, P.S. Ignatiev, K.V. Indukaev,

J. Chem. Phys., 130, 134308 (2009)

DISCUSSION OF THE RESULTS

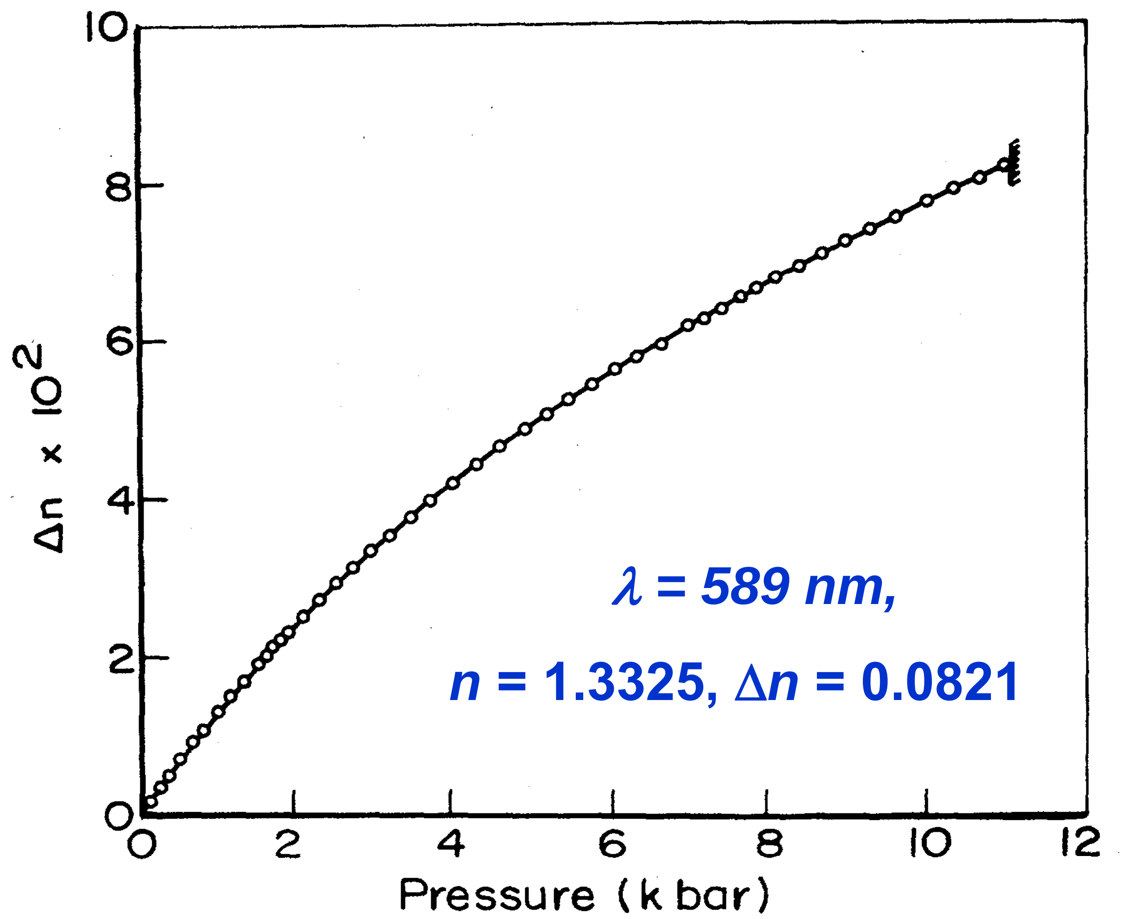


FIG. 1. Variation of refractive index of water with pressure at $T = 25°C$.

K.Vedam, P.Limsuwan, Piezo-optic behavior of water and carbon tetracloride under high pressure, Phys. Rev. Lett., 35, 1014 – 1016 (1975)

DATA ON THE REFRACTIVE INDEX OF DRY NAFION

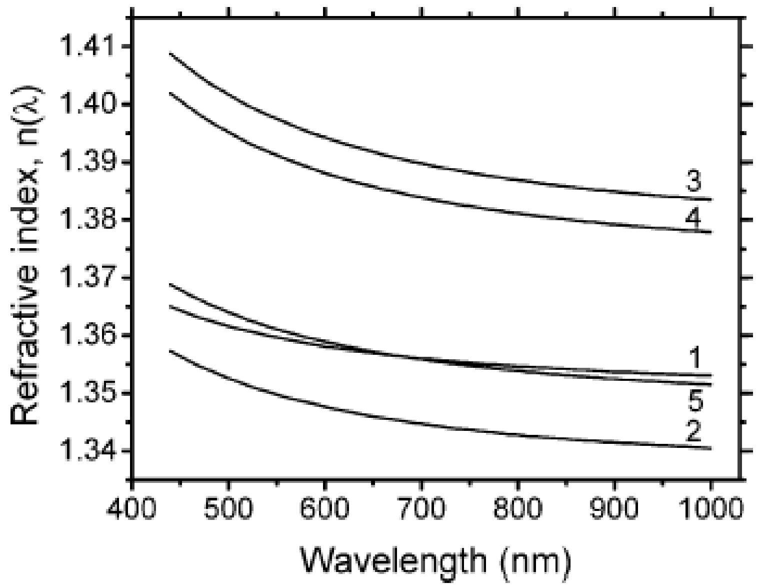
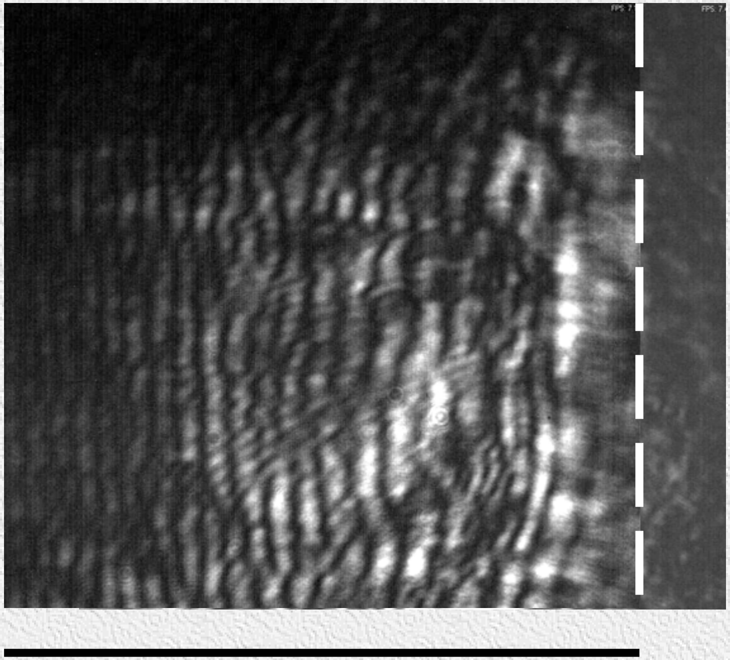


Figure 4. Refractive index $n(\lambda)$ vs wavelength for the dry Nafion film (1) and films equilibrated in 0.1 M NaCl (2), 3×10^{-3} M 2,2′-bipyridine in 0.1 M NaCl (3), bpy-loaded film in 0.1 M NaCl (4), and in 1×10^{-5} M Fe^{2+} (5) solutions. The soaking solutions were again injected into the flow cell one after another.

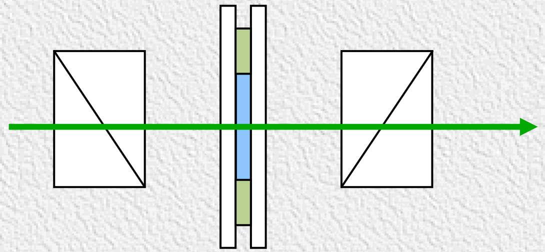
N. Pantelic, C.M. Wansapura, W.R. Heineman, C.J. Seliskar, Dynamic In Situ Spectroscopic Ellipsometry of the Reaction of Aqueous Iron(II) with 2,2'-Bipyridine in a Thin Nafion Film, J. Phys. Chem. B 2005, 109, 13971-13979

REFRACTIVE INDEX ANISOTROPY; QUASI-CRYSTALLINE STRUCTURE?

Nafion



40 μm



170 μm

BASIC RESULTS (1)

Experiments on measuring the bulk density of SO_3^- anions and electrostatic potential close to the Nafion interface confirmed the Exclusion Zone existence. The density of SO_3^- anions is the parameter, which can be easily measured in a direct experiment. This provides a qualitatively new level in measuring the Exclusion Zone size. However the question of the Exclusion Zone origin is still open.

BASIC RESULTS (2)

As was obtained in experiments on measuring the temperature dependences of the EZ characteristics, the bulk density of SO_3^- anions depends on the way of changing temperature: heating or cooling. The temperature hysteresis loops have been observed, which points to the existence of multi-stability in the system. These results can be associated with the known shape memory effect, specific for thermoplastic polymers. Thus we can assume that the polymer properties are transmitted to the adjacent water layer.

BASIC RESULTS (3)

The refractive index *n* of water drastically rises at the interface Nafion – water. This cannot be connected with the increase of ionic density. Water itself is practically incompressible, and its refractive index can be changed only at very high pressure. It is important that the value of *n* is higher than that for dry Nafion, thus the effect cannot be explained by dissolving Nafion in water. Furthermore, the liquid area of increased refractive index demonstrates birefringence. This can be explained by the influence of polymer upon the properties of adjacent water layers.

EXCLUSION ZONE IS HYDROGEL????