Water mobility in fluoropolymer membranes investigated by means of time domain terahertz spectroscopy

M. Sztyber[1], M. Kaczkan[2], K. Majewska[1] and M.Siekierski[1]
[1]Warsaw University of Technology, Faculty of Chemistry, ul. Noakowskiego 3, 00-664 Warszawa,
[2]Warsaw University of Technology, Institute of Microelectronics and Optoelectronics, Koszykowa 75, 00-662 Warsaw, Poland

e-mail: michalsztyber007@gmail.com

The rapid development of green hydrogen related technologies such as water electrolysis leads to the situation that the massive introduction of fuel cells is more and more viable. Fluoropolymer based proton-exchange membrane are widely recognized as an industrial standard for both water electrolyzers (PEMEL's) and transport applications targeted fuel cells (PEMFCs). Despite of their advantages they suffer from significant and practically important deterioration of their protonic conductivity upon drying e.g. such resulting from operation in temperatures above 100 ºC or related to the transient current density fluctuations and subsequent hot-spotting. Thus, investigation of humification related conductivity changes, as well as, mobility of water molecules incorporated into the polymer pore-space are investigated by means of various methods such as NMR [1] and molecular [2] spectroscopies.

Thus, the terahertz radiation spectroscopy and imaging which relies on the part of the electromagnetic spectrum, which is placed between infrared and microwaves regions, will be here applied to study the weak interactions between the said water molecules, as well as, to trace their mobility. The method proposed was previously applied to the investigation of water molecules clustering in biological systems [3], as well as for the determination of the molecular network stretching in water based solutions [4]. The later report attributes the latter to the frequency range between 5 and 10 THz. On the other hand previously presented studies of the THz properties of fluoropolymer based membranes such as Nafion® [5] are focused on their dielectric properties not water mobility. Herein we claim, therefore, the possibility of determination of the water mobility changes upon the Nafion® specimen drying on the basis of the shift of the position of the respective THz absorption band (see Figure 1a), as well as, on the basis of the changes in the respective optical density of the materials resulting in changes of the Thz signal delay occurring in it (Figure 1b). Moreover, the similar dependencies can be observed upon ion exchange processes (Li^+, Na^+, K^+) undergoing in the same material.

Acknowledgement: *Research was funded by POB Energy project* ***1820/40/Z01/POB7/2021*** *of Warsaw University of Technology within the Excellence Initiative: Research University (IDUB) programme.*

References

[1] R. Basnayake, W. Weverand C. Korzeniewski. Electrochimica Acta. 2007. 1259–1264. 10.1016/j.electacta.2007.03.060.
[2] F. Xu, S. Leclercand D. Canet. The Journal of Physical Chemistry B. 2013. 6534–6540. 10.1021/jp311062h.
[3] [K. Johnson. Journal of Biological Physics. 2012. 85–95. 10.1007/s10867-011-9238-4.
[4] Novelli, B. Guchhaitand M. Havenith. Materials. 2020. 1311. 10.3390/ma13061311.
[5] Novelli, B. Guchhaitand M. Havenith. Materials. 2020. 1311. 10.3390/ma13061311.