

CONDUCTIVE PROPERTIES AND STRUCTURE OF POLAR SOLVENTS-IMPREGNATED NAFION MEMBRANE

A. M. Affoune¹, A. Yamada² and M. Umeda²

¹Departement de Chimie Industrielle, Universite de Guelma, BP 401, Guelma 24 000, Algeria.

²Department of Chemistry, Nagaoka University of Technology, Kamitomioka 1603-1, Nagaoka, Niigata 940-2188, Japan.

Proton conductivity of Nafion membrane has been investigated in different aqueous environments by several groups [1]. However, only a few studies were reported on the conductivity of the membrane in organic solvents [2, 3]. On the other hand, the use of perfluorinated ionomer as solid electrolyte in Direct Alcohol Fuel Cells is one of the important applications of the membrane [4]. This type of fuel cells appears to be the most promising for portable applications such as cellular phones and laptop computers. Furthermore Nafion was extensively target by a large number of experimental studies using different techniques, and especially X-ray, NMR, IR and electron microscopy in order to explain the microstructure of the membrane. Many models were given and still suggestions for new ones continue to be proposed and the real structure of Nafion membranes is still considered as not well understood. Using scanning probe microscopy, especially Atomic Force Microscopy [5, 6], Nafion membrane in different forms was investigated in different conditions. Results particularly showed that tapping mode phase imaging could be used to distinguish between hydrophilic and hydrophobic domains.

In this work, we report the relationship between proton conductivity of Nafion membrane and dielectric constant of different polar solvents including water, methanol, ethanol, 2-propanol and water-alcohol mixtures. Conductivity measurements were performed using Electrochemical Impedance Spectroscopy. We also investigated the structure of the membrane by means of atomic force microscopy. All experiments were carried out in Air at room temperature.

Results showed that for Nafion acid form and even in pure alcohols (methanol, ethanol and 2-propanol), the conductivity is still higher than 1×10^{-3} S.cm⁻¹. In water-alcohol mixtures, the conductivity increased with increasing the water proportion irrespective of the nature of the alcohol. In Figure 1, we presented the dependence between the conductivity σ and the reverse of dielectric constant ($1/\epsilon$) of medium in which Nafion was previously stored. By fitting we obtained the following equation:

$$\sigma = 0.221 \exp(-82.375/\epsilon) \quad (1)$$

The exponential decay was explained on the basis of the Arrhenius and Born equations. Using conductivity and dielectric constant relationship equation, we could calculate the activation energies for proton conduction in different solvents as shown in table I. Values reported in Table I confirm that activation energy decreases from medium polar solvents to high polar ones.

Surface analysis of Nafion impregnated with polar solvents showed that topography considerably changes when samples absorb water. However, samples stored in alcohols are characterized by flat surfaces. Surface modification was linked to an expansion phenomenon during the swelling of the membrane by solvents. Tapping mode phase images showed that ionic and cluster domains are distinguishable from the surface of samples impregnated either in water or alcohols. Interaction of Nafion with solvents has been generally investigated in terms of bulk interaction. However, in this contribution we discuss the effect of solvents in terms of surface interaction.

Acknowledgment

The present work was financially supported by the research and development of polymer electrolyte fuel cell from the New Energy and Industrial Technology Development Organization (NEDO), Japan.

References

- [1] S. Slade, S. A. Campbell, T. R. Ralph and F. C. Walsh, *J. Electrochem. Soc.*, 149, A1556 (2002).
- [2] M. Doyle, M. E. Lewittes, M. G. Roelofs, S. A. Perusich and R. E. Lowrey, *J. Mem. Sci.*, 184, 257 (2001).
- [3] C. A. Edmondson, P. E. Stallworth, M. C. Wintersgill, J. J. Fontanella, Y. Dai and S. G. Greenbaum, *Electrochimica Acta*, 43, 1295 (1998).
- [4] C. Lamy, A. Lima, V. LeRhun, F. Delime, C. Coutanceau and J. M. Leger, *J. Power Sources*, 105, 283 (2002).
- [5] R. S. McLean, M. Doyle and B. B. Sauer, *Macromolecules*, 33, 6541 (2000).
- [6] P. J. James, T. J. McMaster, J. M. Newton, M. J. Miles, *Polymer*, 41, 4223 (2000).

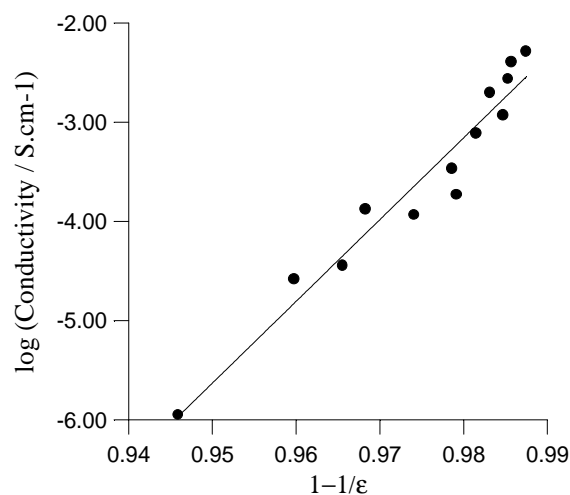


Figure 1. Proton conductivity of Nafion membrane as function of the reverse of dielectric constant of water, alcohols and mixtures.

Table I. Activation energy for proton conduction in polar solvents calculated from the equation (1).

	Water	Methanol	Ethanol	2-Propanol
Activation energy Ea, KJ.mol ⁻¹	2.56	6.14	8.16	10.08