ESF – Exchange Grant – Applicant: Dr. Anton Knyazev
Scientific Report

Project:
Carbon nanotube functionalization and production toward toxicity investigation of well-established and characterized systems (Ref. N° 2834).

Background and Motivation

The word 'nano' became a synonymous to progress our days. A large part of scientific community is dedicating its effort to investigation of the nano-world. Multiple applications based on architectures ordered at the scale down to nanometer exist today and many others are up-coming.[1]
One of the important concerns of the contemporary society is the renewable energy sources. The fuel cell technology, available for about a half of century, is one of the most promising in terms of its environment friendly and high reliability aspects[2]. The proton-exchange membrane (PEM) is a critical part of a fuel cell. The basic function of membrane is to enable proton transport, while being simultaneously impermeable for electron and gas. Recently, a new, biomimetic approach has been postulated[3]. The inspiration comes from water and ion-conductive nano-channels, e.g. aquaporin. The core concept of the project is to use different types of fillers (e.g. carbon nanotubes, CNT and titanate nanotubes, TNT) to improve the mechanical and better control the electrical properties of commercially available membranes.

Project Outline

The discovery of carbon nanotubes[4] in the early nineties gave rise to a great deal of ideas how it can be used for technological purposes. The poly(composites) based on polymeric matrix filled with nanowires are promising for a large spectrum of applications.[5] The fuel cell's characteristics such as proton conductivity, electrical conductivity, thermal and mechanical strength and the current and power densities may be improved by these means. The design of new proton exchange membrane (PEM) and gas diffusive electrodes (GDE) for the hydrogen/oxygen fuel cell applications is in the scope of the present study.

Exchange Benefits

The hosting laboratory (Laboratory of Physics of Complex Matter (LPMC) at Ecole Polytechnique Fédérale de Lausanne) is a pole of excellence for the new electronic materials study. The main activities of the group are going from the synthesis of high purity nanotubes and nanowires to nanoparticles toxicity investigation. The use of state of the art facilities as well as benefiting of expertise in above mentioned fields are the purpose of present collaboration.

The knowledge and skills in chemistry of materials of visitor (my-self) combining with the solid-state physics competencies of the hosting laboratory (LPMC) are the strike force we need to succeed in the present work. The nanofibers used in this study were produced exclusively at home-made facilities of LPMC so that there was no

need for extra expenses and/or time. All measurements reported hereafter were performed using facilities of the following EPFL's departments:

- Institute of Condensed Matter Physics (ICMP) for Raman and FT-IR;
- Interdisciplinary Centre for Electron Microscopy (CIME) for SEM and TEM;
- Institute of Materials (IMX) for electrochemical impedance spectroscopy EIS.

Results and Discussion

The commercial perfluorosulfonic acid/PTFE copolymer poly(electrolyte) known by the commercial name of Nafion® was used as a scaffold in present work. In order to improve the mechanical and transport characteristic of the latter the carbon nanotubes (CNT) and titanate nanotubes (TNT) were employed. First, a simple model has been used. Poly(methyl methacrylate) was chosen as a cheap and readily available alternative to Nafion®. The infiltration and casting techniques were first worked out on this simple example and the resulted methodology was then transferred to the Nafion/CNT and Nafion/TNT cases.

In order to compare the characteristics of prepared membranes with literature the following parameters need to be evaluated:

- water content (X_V, vol.-%)
- water uptake (S, wt.-%)
- hydration number (λ)
- ionic exchange capacity (IEC, mmol SO_3H g^{-1})

All above mentioned values are relevant for the proton conductivity (σ, Scm^{-1}), i.e. one of the key parameter of ionic exchange membranes for fuel cell application (IEMFC).[6] In case of a polymer with high water content, although the proton mobility remains high upon dilution, the acid concentration lowers and as a result the proton conductivity is eventually reduced. In order to estimate the interest for fuel cell application of newly designed membranes one has to reduce the potential swelling of a membrane on one hand and keep the hydration number as high as possible on another.

The overall strategy was composed of the following steps: CNT growth, "hydrophylisation", degasation, infiltration and casting. First, the multiwall carbon nanotubes (MWCNT) were grown by water assisted chemical vapor deposition (WACVD) technique[7]. The resulted samples were carpets of 1cm x 1 cm x 60-300 μm made of CNT aligned perpendicularly to the substrate plane (Figure 1 and 2 for fine tube structure).

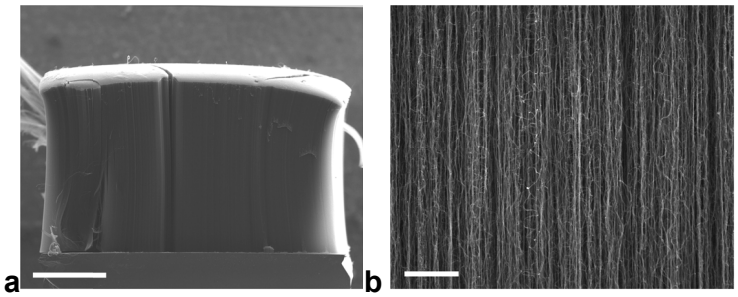

Figure 1 SEM images of CNT as-grown carpet; the scale bares are 1 mm and 2 µm for (a) and (b) respectively

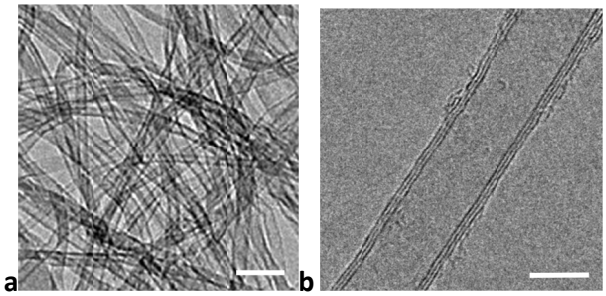

Figure 2 TEM images of as-grown carbon nanotubes; bare scales are 20 and 4 nm for (a) and (b) respectively

The as-grown CNT carpets (bare CNT) are hydrophobic (contact angle more than 100°, data not shown) and could not be properly infiltrated by the polymer aqueous solution. The hydrophilization step was simply a heat treatment in air for several minutes (to give ox-CNT). Although some thermal oxidation was expected on the nanotubes wall, no significant difference by Raman (λ_{ex} = 488 nm, D/G ratio, data not shown) could be seen. The degasation step was performed by simple immersion of ox-CNT into an appropriate solvent overnight. Finally the degased ox-CNTs were soaked in home-made Nafion® dispersion[8] for 24 h and then casted on polished Teflon® sheet. The infiltration exhaustiveness was investigated by the means of scanning and transmission electron microscopies (SEM & TEM respectively). The results can be seen bellow (Figure 2 and 3).

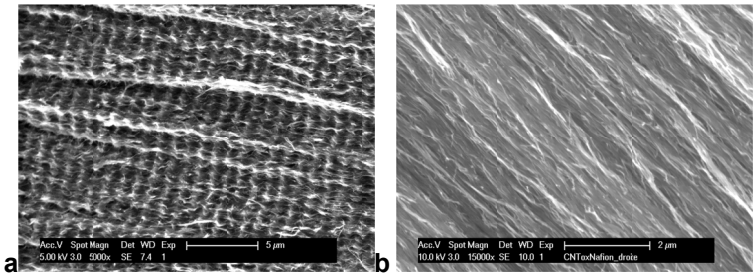

Figure 3 SEM caption of the side-view of Nafion/CNT membrane

The “wavy” structure which can be distinguished in Figure 2a is typical of CNT forest when infiltrated with polymer solution. The Figure 2b shows a satisfactory

infiltration's level, the polymer fills homogeneously inter-tubular space. TEM micrographs of cross-sectional view are presented in Figure 3 (a) and (b). Dark "pinheads" correspond to the tubes going through membrane plane and forming right angle with it. Not all of them are oriented at that direction though. We assume that because of the difference in toughness between polymer matrix and carbon nanotubes (soft vs. hard) the latter follow the diamond blade of microtom during the TEM sample preparation. Adhesion of Nafion® to the blade could be another reason. Nevertheless, the alignment of CNT before and after infiltration can clearly be established with SEM, so that no additional proves are necessary.

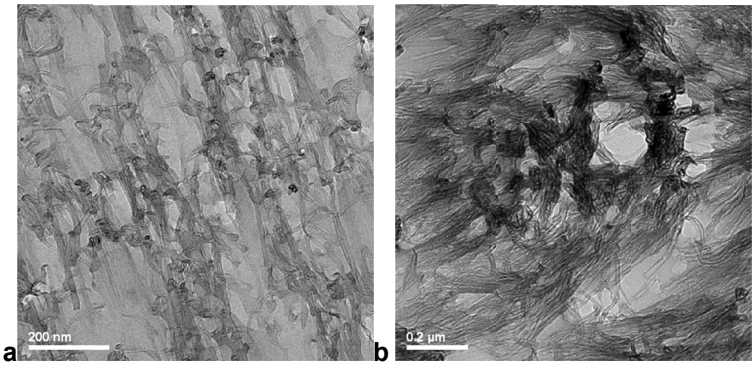

Figure 4 TEM image of cross-sectional view (normal angle to the CNT axis)

Electrochemical impedance spectroscopy (EIS) has been used for the proton conductivity measurements. The technique is a powerful tool for solid electrolyte investigation.[9] Generally the imaginary part of impedance (ImZ) is plotted against real part (ReZ), both as function of frequency log. Such a complex-plane plot is referred to as Nyquist diagram. Analysis of experimental data can provide estimates of the parameter R (bulk resistance of membrane) and hence lead to quantitative estimates of conductivity and relaxation time. The first result can be seen in figure 4 and 5. Since the NR211 membrane (sample of reference purchased from DuPont) is manufactured by casting, the isotropic behavior is assumed so that there is no difference between through plane and in plane conductivity. In our study all IS data are in-plane measured at room temperature.

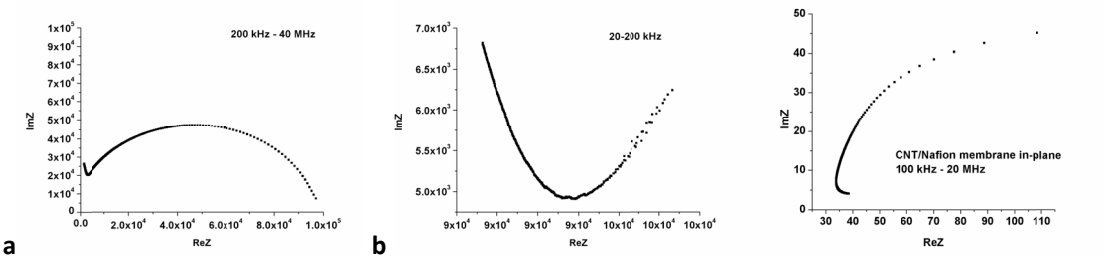

Figure 5 Nyquist plot of commercial Nafion NR211 boiled in 0.5 M sulfuric acid (dots are the measured points) (a,b) and Nafion/CNT membrane (c)

Semicircular arc typical of solid membrane with one type of charge carriers can be seen in figure 5a. The frequency increases from the right to the left. Figure 5b shows the minimum of ImZ from which the bulk resistance of membrane is extracted. In figure 5c the data for Nafion/CNT membrane are presented. The results are summarized in table 1. All samples were dried at room temperature first and then annealed at 80°C in vacuum (5 mbar) for 3 h in order to get N-form[10] Nafion® before it were further treated by different means (see caption of Table 1). The membranes were taken out of water and quickly blotted with a weeping tissue. The time between the removal of the sample from water and measurement was kept as short as possible (within 10 min).

Table 1 In-plane conductivity for Nafion® based composites

	EW, g/mol	h, µm	S, wt.-%	σ, S cm^{-1}
NR-211 lit.	1100	25	43[11]	0.061[12]
Nafion/CNT-4wt.%	~960	232	40[a]	0.81
Nafion/TNT-33wt.%	~670	218	49[b]	under investigation

(a) sample was boiled 1 h in 0.5 M sulfuric acid and 1 h in distilled water prior to measure; (b) sample was stored in distilled water for 24 h prior to measure; Nafion® used for composite preparation was NR40 (supplied by DuPont) dispersed in aqueous-alcoholic solution (EW=1000 g/mol)

It can be seen from the table 1 that the Nafion/CNT conductivity values are higher than the references' ones. These first encouraging results are preliminary and need the additional proofs.

Nafion/TNT membrane

The home-made TNT dispersion (14 wt-%) was used for the composite preparation[13]. TNT were subjected to sonication with a power tip together with Nafion® dispersion (10 wt-%) and then casted on a flat Teflon® surface. The TNT loadings between 1 and 50 wt-% have been prepared. The agglomeration of TNT during the casting process seems to be the limitation step in preparation of Nafion/TNT membranes. We can see an example of Nafion/TNT-33 (wt-%) in figure 6.

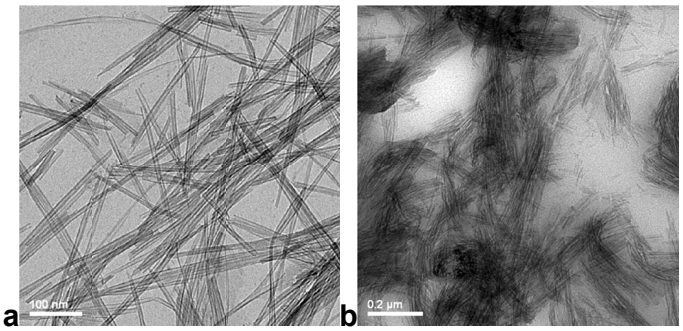

Figure 6 TEM micrographs of (a) TNT as synthesized and (b) Nafion/TNT-33 (wt-%) membrane

The dispersion quality is assumed to be casting conditions and pH sensitive. Further work is under way for elucidation of the preparation conditions most suitable for this type of membrane.

Conclusions and Outline

To the best of our knowledge it was the first time that Nafion® membrane with built-in aligned CNT was prepared. The resulted material is highly anisotropic and additional investigations are in-progress in order to get the better knowledge of newly designed materials. This kind of membrane is assumed to be of particular interest for the diffusive gas electrode (DGE) design, thanks to its electrical and proton conductivities.

The second type of composites we were investigating during this stay was Nafion/TNT membrane. As could be seen already, the actual water uptake of this kind of membrane is sensibly higher than for bare Nafion®. As was mentioned here above, the water uptake is directly related to the proton conductivity and so that we are assuming some positive results regarding this behavior. Moreover, the TNT are insulating, therefore this part of the work is aiming to contribute to the proton exchange membrane evolution.

To conclude I would like to point out, that six months of exchange which I have benefited, thanks to the ESF exchange grant, were of great importance for my further scientific career. It gave me a better understanding for new electronic materials design logic and extra knowledge in the field I was not familiar with before. For instance use of electron conductive vs. insulating fillers (CNT vs. TNT) or microscopic techniques I have been trained. We are actually performing the last measurements in order to submit a paper as soon as possible.

(1) Goesmann, H.; Feldmann, C. *Angew. Chem.-Int. Edit.* **2010**, *49*, 1362.
(2) Zegers, P. *J. Power Sources* **2006**, *154*, 497.
(3) Fang, H. P.; Wan, R. Z.; Gong, X. J.; Lu, H. J.; Li, S. Y. *Journal of Physics D-Applied Physics* **2008**, *41*.
(4) Iijima, S. *Nature* **1991**, *354*, 56.
(5) Coleman, J. N.; Khan, U.; Blau, W. J.; Gun'ko, Y. K. *Carbon* **2006**, *44*, 1624.
(6) Peckham, T. J.; Schmeisser, J.; Rodgers, M.; Holdcroft, S. *J. Mater. Chem.* **2007**, *17*, 3255.
(7) Magrez, A.; Seo, J. W.; Smajda, R.; Mionić, M.; Forró, L. *Materials* **2010**, *3*, 4871.
(8) Grot, W. G.; Du Pont De Nemours & Co E I (Dupo).
(9) Macdonald, J. R. *Impedance spectroscopy : emphasizing solid materials and systems*; New York, N.Y. : Wiley, 1987.
(10) Hinatsu, J. T.; Mizuhata, M.; Takenaka, H. *J. Electrochem. Soc.* **1994**, *141*, 1493.
(11) Peron, J.; Mani, A.; Zhao, X. S.; Edwards, D.; Adachi, M.; Soboleva, T.; Shi, Z. Q.; Xie, Z.; Navessin, T.; Holdcroft, S. *J. Membr. Sci.* **2010**, *356*, 44.
(12) Soboleva, T. Y.; Xie, Z.; Shi, Z. Q.; Tsang, E.; Navessin, T. C.; Holdcroft, S. *Journal of Electroanalytical Chemistry* **2008**, *622*, 145.
(13) Tétreault, N.; Horváth, E.; Moehl, T.; Brillet, J. r. m.; Smajda, R.; Bungener, S. p.; Cai, N.; Wang, P.; Zakeeruddin, S. M.; Forró, L. s.; Magrez, A.; Grätzel, M. *ACS Nano* **2010**, null.