CHEMICAL ENGINEERING TRANSACTIONS
VOL. 84, 2021
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.cetjournal.it
Guest Editors: Paolo Ciambelli, Luca Di Palma

ISBN 978-88-95608-82-2; **ISSN** 2283-9216
DOI: 10.3303/CET2184022

Influence of Carbon Based Nanofillers Addition on the Properties of Microporous Layers Prepared via Phase Inversion

Antonio Comite, Camilla Costa, Marcello Pagliero*, Jacopo Perrone, Ilaria Rizzardi

Membrane&membrane Research Group, Department of Chemistry and Industrial Chemistry (DCCI), University of Genoa, Via Dodecaneso 31, 16143, Genova, Italy.
marcello.pagliero@unige.it

Gas Diffusion Layers (GDLs) must have good electrical conductivity and a great hydrophobicity to prevent the pore flooding. These properties can be enhanced by adding a Micro Porous Layer (MPL) based on carbon composites. In this work several MPLs were prepared using carbon-based fillers, such as exfoliated graphite, carbon black and nanotubes, incorporated at very low loadings (<1% wt) in a porous PVDF based matrix obtained by the phase separation technique. The samples were characterized by measurements of electrical resistance, gas permeability and contact angle as well as observations with both optical and field emission electron microscopy.
Carbon black has given overall interesting results as it can be well dispersed in the polymeric matrix and can improve all the fundamental properties required for an MPL.
Exfoliated graphite showed an interesting decrease of the electrical conductivity only after compression of the MPL, probably due to its two-dimensional structure. Nanotubes showed a strong tendency to agglomeration, so the final properties mainly depend on the homogeneity of the dispersion of these aggregates.

1. Introduction

Fuel cells are devices which convert the chemical energy of a reaction between a fuel and an oxidant directly to electrical energy without the normal heat-work-energy conversion (Bagotsky V.S., 2012). The Proton Exchange Membrane Fuel Cells (PEMFC) have a complex structure and are constituted by different components each of which must be optimized to achieve the best performance and maximum efficiency (Metha V. et al., 2003). Among these, the proton exchange membrane and the Gas Diffusion Layers (GDLs) play key roles. GDLs are microporous layers that act as reagent distributors, as a path for electron transport and as mechanical support (Cinderella et al. 2009). Therefore, GDLs must have good electrical conductivity as well as a great hydrophobicity to prevent the pore flooding that could hinder the diffusion of the reactants. These properties can be enhanced by incorporating an additional Micro Porous Layer (MPL) based on carbon composites (Qi Z. et al., 2002) between the GDL and the electrode. MPLs can be prepared using polyvinyldene fluoride (PVDF) as binder, creating a porous structure exploiting the non-solvent induced phase separation (NIPS) technique (Bottino et al., 2015). Carbon-based fillers (e.g. graphite, carbon black and carbon nanotubes) can be added to the starting polymeric dope solution in order to obtain an electro conductive film. Ong et al. (2008) studied the effects of various parameters involved in MPLs preparation, such as the polymer and filler concentrations, the type of filler and of solvent used, on the characteristics of the final composite layer. The homogeneity and the stability of the filler dispersion resulted to be key parameters governing the performance of the MPLs.
The aim of this work was the preparation of stable dispersions of carbon-based fillers in dimethyl sulfoxide (DMSO) in order to obtain some homogeneous PVDF solution with low concentrations of fillers (<1% in respect with the polymer solution mass). Electroconductive MPLs were then created via nonsolvent induced phase separation. The effect of addition of different carbon fillers on various MPL relevant properties, as well as electrical resistance, gas permeance and hydrophobicity was studied. Four different fillers were

Paper Received: 28 May 2020; Revised: 26 November 2020; Accepted: 11 February 2021
Please cite this article as: Comite A., Costa C., Pagliero M., Perrone J., Rizzardi I., 2021, Influence of Carbon Based Nanofillers Addition on the Properties of Microporous Layers Prepared via Phase Inversion, Chemical Engineering Transactions, 84, 127-132 DOI:10.3303/CET2184022

investigated: a carbon black commonly used for the preparation of MPLs by conventional techniques, commercial multi walled carbon nanotubes and two synthetic graphites with different surface area. The conditions required to achieve a good filler dispersion in the solvent for the MPL preparation were investigated.

2. Materials and Methods

2.1 Filler dispersions preparation

Different kinds of carbon-based fillers were dispersed in dimethyl sulfoxide; the dispersions were then used to prepare PVDF solutions and create various MPLs.
The fillers, with their main characteristics are listed in Table 1.

Table 1: Properties of the used fillers.

Filler code	Type	Producer	Size [nm]	Surface area [m^2/g]
Ketjen black EC600JD	Carbon-black	Lion Specialty Chemicals - Japan	35-40	1270
Timrex HSAG 300	Graphite	Imerys Graphite & Carbon - Switzerland	1.2x32	300
Timrex HSAG 100	Graphite	Imerys Graphite & Carbon - Switzerland	2.8x43	100
Taunit M	Carbon nanotubes	Nanotech - Russia	20x4000	250

The dispersions were prepared exploiting different ways of mixing, in order to evaluate the most effective technique: in particular, hand mixing, mechanical stirring using a vortex mixer and sonication were investigated.

2.2 MPL preparation and characterization

In order to prepare the dope solutions, the filler dispersions were first sonicated for 30 minutes at 70°C and after the PVDF powder (M_w: 140 kDa) was added. The polymer concentration was fixed at 9% (w/w) and the dissolution was obtained by stirring the solution for 4 hours at 50°C.
The homogeneous polymer solutions were then casted on a flat glass at 40°C using a doctor blade with a gap of 160 µm and then immersed in water kept at 20°C to induce the polymer phase precipitation. The films were left in deionized water for 2 hours to remove all the solvent from the structure and then they were detached from the glass and dried between two filter paper sheets at room temperature for at least 24 hours.
The MPLs were characterized through gas permeability tests, contact angle measurements to assess the hydrophobicity, electrical resistance measurements using procedures described elsewhere (Ong et al., 2008.) (Pagliero et al., 2020). Moreover, morphological information was obtained using both optical digital and electron microscopy. Optical microscopy was carried out without sample preparation using Dinolite instrument (magnification x400-600). Instead, scanning electron microscopy analysis were performed using a Zeiss Supra 40 VP instrument. In this case, a drop of the dispersion was deposited on a Lacey carbon TEM grid and dried in a vacuum oven overnight before being analysed.

3. Results

3.1 Characterization of DMSO-filler dispersions

Figure 1 reports the state of the various dispersions prepared in DMSO, after 48 hours.

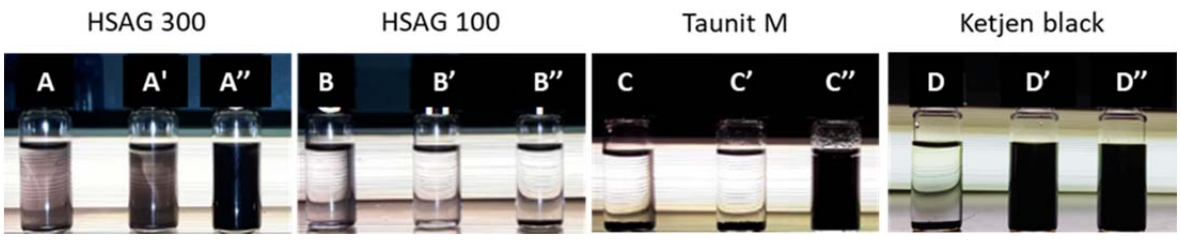

Figure 1: Images of the dispersion of the fillers in DMSO after 48 hours. Fore each filler from left to right: hand mixed, vortex mixed and sonicated.

Among all the tested fillers, from the HSAG 300 graphite it was obtained the best dispersion. The main difference between the two graphites is the specific surface area. The HSAG 300 is an expanded graphite which has a larger surface area than the HSAG 100 (Table 1) and DMSO can enter between the various layers interacting with them resulting in an easier exfoliation of the graphite structure and towards both graphene and thin graphite multilayers in agreement with the literature findings (Xu et al., 2018). Instead, the low surface area graphite (HASG 100) has a more compact structure and it was not possible to achieve an effective exfoliation, with the applied techniques. The different dispersion systems exploited gave different results. Generally, the use of an ultrasound bath resulted in the most uniform and stable dispersions while the hand mixing was inadequate for every sample. In particular, sonication was the only effective technique to disperse the carbon nanotubes. The vortex mixer was enough effective for the HSAG 300 and the Ketjen Black samples. All the dispersions obtained remained stable for over 2 months after being prepared.
The FE-SEM analysis allowed to evaluate the structure of the particles dispersed by means of sonication and are reported in Figure 2.

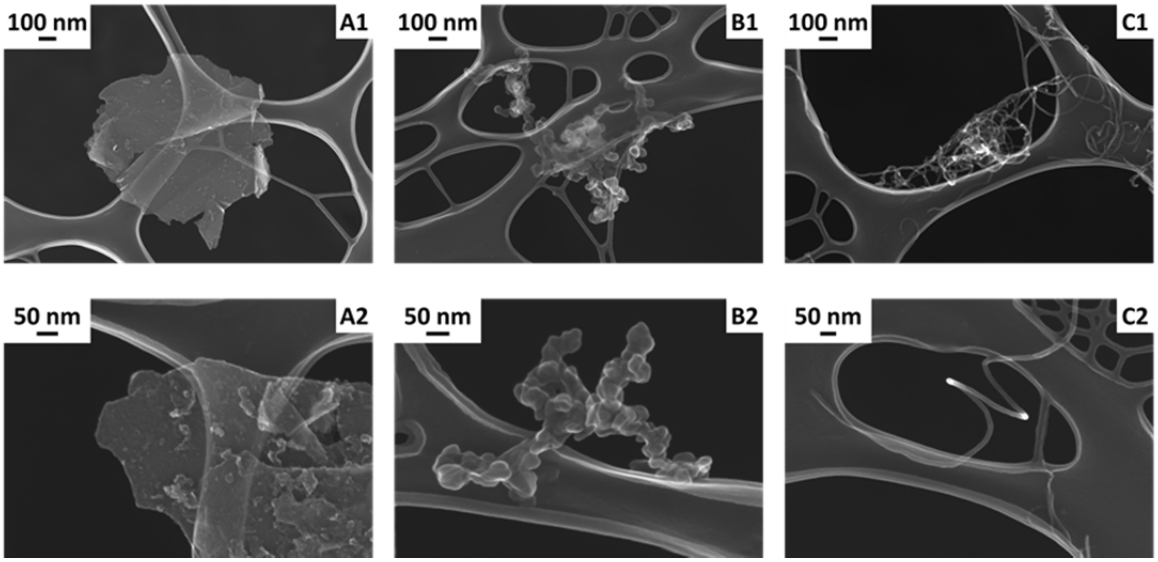

Figure 2: FE-SEM images of the dispersions of the fillers at two different magnifications; A1) and A2) HSAG 300, B1) and B2) Ketjen Black, C1) and C2) carbon nanotubes.

Figure 2A2 shows the thin graphite layer obtained after sonication of the HSAG 300 graphite. The particles appeared to be composed by few graphene layers and were well dispersed in the analysed sample. Figure 2B represents the Ketjen black and highlights the formation of small aggregates generated by several smaller particles. The nanotubes dispersion is reported in Figure 2C1: despite the sonication performed many entangled nanotubes were still found in the sample and only a small part of isolated particles was seen (Figure 2C2).

3.2 MPL characterization

In Figure 3 the images obtained with the optical digital microscope of the surface of four MPLs prepared with 0.9% of various fillers are reported.

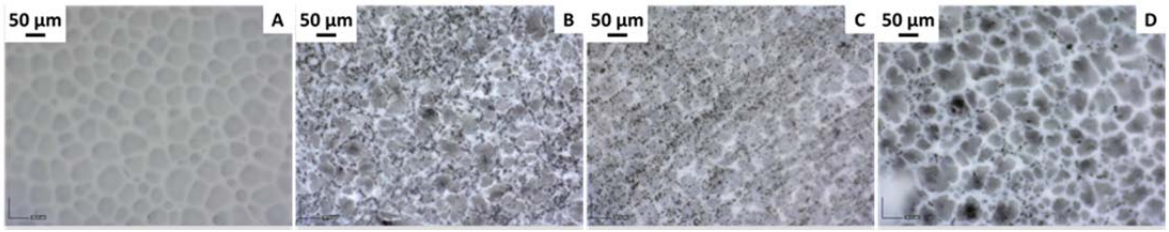

Figure 3: Digital microscope images of the MPLs surface: A) no filler, B) 0.9% Ketjen Black; C) 0.9% HSAG 300 and D) 0.9% carbon nanotubes.

The film prepared using the HSAG 300 graphite showed the best dispersion of the particles in the polymer matrix while the Ketjen black created some small aggregates. Moreover, the mean dimensions of the particles of carbon black is higher than that of the graphite. Instead, the carbon nanotubes were hardly dispersed into the polymer matrix. The entanglements between the long tubes seen during the FE-SEM analysis inhibited the mixing with the PVDF and big aggregates were formed.
The addition of fillers did not modify the structure of the PVDF films but allowed to create electroconductive MPLs. The electrical resistance for the different samples is showed in the graph in Figure 4.

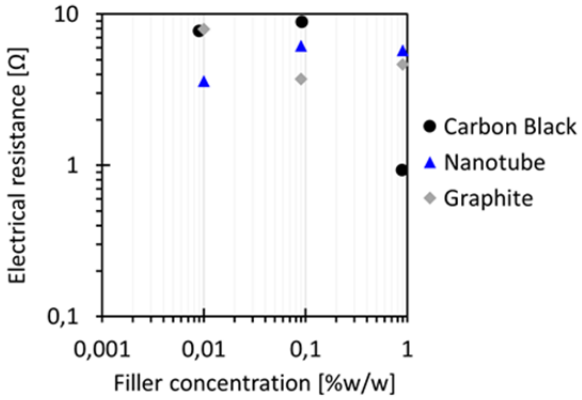

Figure 4: Electrical resistance values of the MPLs prepared with different concentrations of Ketjen black (●), HSAG 300 (◆) and nanotubes (▲).

The films showed different electrical resistance profiles by increasing the filler concentration. All the MPLs showed an electrical resistance in the order of few Ohms at the investigated filler concentrations. The carbon black was able to create a better conductive path across the cross-section of the MPL at filler concentration of about 1%. The exfoliated graphite, instead showed a slighter decrease of the electrical resistance when its concentration in the polymer matrix was increased up to 1. While the dispersion of the exfoliated graphite was appreciable, the bi-dimensional configuration graphene favours the intercalation of the polymer chains, hindering the electrical conduction between the layers.
The carbon nanotube addition had only minimal effects on the electrical resistance. The formation of agglomerates inhibited the formation of effective electroconductive paths and also the increase of the filler concentration did not improve the conductivity of the MPLs.
The effect of the fillers concentration on the porous structure was evaluated by means of gas permeation measurements, showed in Figure 5.

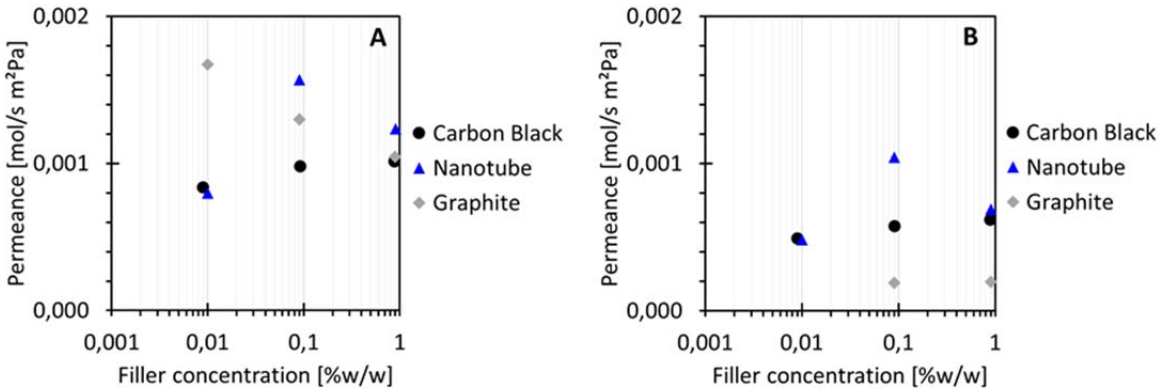

Figure 5: Gas permeance of the prepared MPLs using A) helium and B) nitrogen.

The gas permeance measurements highlighted different behaviours for the three kind of fillers used. The increase of the concentration of carbon-black improved the gas permeance of the films both for helium and nitrogen creating a pore porous structure. The HSAG 300 graphite had more complex results: the helium

permeance remained high for every tested particle concentration while the values registered using nitrogen were greatly lower. The graphite layers seem to increase the pressure drop across the MPL more for nitrogen than for helium. As seen during others tests – such as the electrical resistance – the carbon nanotube effect was less clear since the aggregation of the nanotubes in bigger structures appeared to have a greater influence than that of the single nanotubes. The hydrophobic character was evaluated measuring the water contact angle and the results are showed in Figure 6.

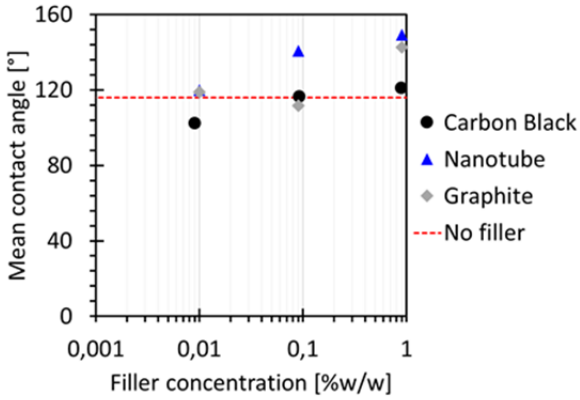

Figure 6: Water contact angle of the MPLs prepared with different concentrations of Ketjen black (●), HSAG 300 (◆) and nanotubes (▲).

The addition of carbon nanotubes was the most effective in improving the contact angle of the MPLs. Moreover, the increase of the filler concentration was beneficial to a higher hydrophobic character, since a contact angle of almost 147° was achieved by addition of 0.9% of nanotubes to the polymer solution. The observed effect probably is due to the terminals of carbon nanotubes emerging from the MPL surface. In the case of carbon black, the contact angle was close to the porous polymer layer without fillers. At concentration close to 1% both the exfoliated graphite and the nanotubes showed a remarkable effect on the contact angle. In the case of the exfoliated graphite the effect might be related to the edges of the payer? emerging from the MPL surface.

4. Conclusions

In this work, various electroconductive MPLs were prepared using PVDF and low amounts of carbon-based fillers, exploiting the nonsolvent induced phase separation. The effect of different additives on the structure and some features of the porous layer (e.g. electrical resistance, gas permeance and hydrophobicity) was evaluated. Particular attention has been paid in obtaining homogeneous filler dispersions both in the polymer solvent and in the final MPL. To this scope, different mixing techniques have been tested, such as manual mixing, vortex agitation and sonication; for all the tested fillers the latter has been found to be the most effective.

The two tested graphites showed deeply different behaviours. In fact, only the sample with the higher surface area generated a stable and uniform dispersion in DMSO. Carbon black was easily dispersed also by using the vortex mixer while the carbon nanotubes created aggregates in all the tested conditions.

From optical microscopy results the best dispersion of the filler in the different MPL's has achieved with the addition of graphite because of the exfoliation.

Among all the prepared MPLs, the one prepared with 0.9% of carbon black was characterized by the lower electrical resistance while graphite and carbon nanotubes had minor impact.

The effect of carbon black addition on the hydrophobic character was less pronounced. In terms of gas permeability, the addition of carbon black seems to improve the performance if compared with graphite or nanotubes. Carbon nanotubes had the greater effect in the improvement of the contact angle of the MPL reaching values above 145° as well as the exfoliated graphite only at the highest concentration.

The next step of this research will be focused on the application of the prepared MPLs in fuel cell in order to evaluate their effects on the performance of the cells.

Acknowledgments

The authors acknowledge Mrs. Laura Negretti from the Laboratory of Electron Microscopy (LEM) of DCCI at University of Genoa for her valuable help for FE-SEM sample preparation and observations.

References

Bagotsky V. S., 2012, Fuel cells — problems and solutions, John Wiley& Sons, 2nd ed, Hoboken, New Jersey.

Bottino A., Capannelli G., Comite A., Costa C., Ong A.L., 2015, Microporous layers based on poly(vinylidene fluoride) and sulfonated poly(vinylidene fluoride), International Journal of Hydrogen Energy, 40, 14690-14698.

Cindrella L., Kannan A.M., Lin J.F., Saminathan K., Ho Y., Lin C.W., Wertz J., 2009, Gas diffusion layer for proton exchange membrane fuel cells — A review, Journal of Power Sources, 194, 146-160.

Metha V., Cooper J. S., 2003, Review and analysis of PEM fuel cell design and manufacturing, Journal of Power Sources, 114, 32-53.

Ong A.L., Bottino A., Capannelli G., Comite A., 2008, Effect of preparative parameters on the characteristic of poly(vinylidene fluoride)-based microporous layer for proton exchange membrane fuel cells, Journal of Power Sources, 183, 62-68.

Pagliero M., Bottino A., Comite A., Costa C., 2020, Novel hydrophobic PVDF membranes prepared by nonsolvent induced phase separation for membrane distillation, Journal of membrane science, 596, 117575

Qi Z., Kaufman A., 2002, Improvement of water management by a microporous sublayer for PEM fuel cells, Journal of Power Sources, 109, 38-46.

Xu, Y., Cao, H., Xue, Y., Li, B., Cai, W., 2018, Liquid-Phase Exfoliation of Graphene: An Overview on Exfoliation Media, Techniques, and Challenges, Nanomaterials, 8, 942.