



## Short communication

## Perfluoropolyether-functionalized gas diffusion layers for proton exchange membrane fuel cells



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## H I G H L I G H T S

- CCs were treated with linear PFPE peroxide and PFPE chains were bonded on CC surface.
- CCs became superhydrophobic after hydrophobizing treatment with PFPE peroxide.
- In fuel cell PFPE-modified CCs revealed better performances than PTFE-treated CCs.

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## A B S T R A C T

Linear perfluoropolyether (PFPE) peroxide was used to confer superhydrophobic surface properties to gas diffusion layer (GDL) by means of direct functionalization of a GDL based on carbon cloth (CC) material. The thermal decomposition of a linear PFPE peroxide produces linear PFPE radicals that covalently bond the unsaturated moieties on the surface. Perfluorinated radicals are directly and covalently bound to the carbonaceous structure of the CC without any spacer that could decrease both thermal and chemical stability of the GDL. The obtained CC hydrophobicity exceeded the superhydrophobicity threshold and was enduringly stable. The relationship between the linkage of fluorinated chains and the variations of surface chemical–physical properties were studied combining X-ray photoelectron spectroscopy (XPS), resistivity measurements, scanning electron microscopy (SEM) and contact angle measurements. Despite the excellent insulating properties of the PFPE polymer, the functionalized carbonaceous materials substantially retained their conductive properties. The PFPE-modified GDLs were tested in a single fuel cell at the lab scale. The cell tests were run at two temperatures (60 °C and 80 °C) with a relative humidity (RH) of hydrogen and air feeding gases equal to 80/100% and 60/100%, respectively.

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## 1. Introduction

The history of fuel cells and fluorinated materials is strictly connected. In fact, even if the first polymeric electrolyte membrane fuel cells (PEMFC) employed hydrocarbon-based polymers for the proton exchange membrane, the major improvement of this fuel cell technology was the introduction of perfluorosulfonic membranes in 1966 [1,2]. Actually, fluorinated materials can also be found in other components of the fuel cells. In the gas diffusion

layer (GDL) fluorinated polymers (e.g. Polytetrafluoroethylene (PTFE) [3], polyvinylidene fluoride (PVDF) [4] and fluorinated ethylene propylene (FEP) [5]) are commonly used as hydrophobizing agents due to the low surface energy of this class of polymers [6,7]. The main function of the GDL is to promote the distribution of the gaseous reagents from the bipolar plates to the catalyst layer. However, it has also other important functions: it allows the electric contact for the conduction of electrons, it works as mechanical support for the catalytic layer and the membrane, it helps to remove the combustion heat, and it plays a key role in the water management [8]. In fact, the overall fuel cell performances can be dramatically limited by the accumulation of liquid water inside the cell. Therefore, a correct water management is needed to reach power densities required for commercial applications [9]. Actually,

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carbon-based materials are the reference class of materials used for GDL, because they have high gas permeability, good stability in acid environment and good electric conductivity. They can be used for the preparation of both single and dual layer GDL assembly, and they can be hydrophobized in order to obtain an efficient water management [10]. The usual treatment for the hydrophobization of a GDL is the deposition of suspension of PTFE (5–40%wt) followed by sinterization. [3,6,11]. A PTFE layer can anyway represent a physical barrier to gas diffusion and flux of electrons, being PTFE not conductive and not permeable to gases [12]. Perfluoropolyether (PFPE) derivatives have been applied as alternatives to PTFE and deposited as hydrophobic coatings for GDL [13,14]. In fact, PFPE compounds have the typical properties of perfluorinated polymers, like chemical stability, thermal stability and high hydrophobicity, and also those of perfluorinated polyethers, such as liquid physical form and high gas permeability [15]. However, several grades of commercially available PFPE derivatives contain hydrogenated moieties which are unstable when exposed to hydroxyl radicals present in the fuel cell environment [16]. To avoid this drawback a new route has been investigated: an innovative methodology to confer a stable hydrophobicity to carbonaceous materials is the chemical linkage of perfluoropolyether (PFPE) chains by chemical treatment with PFPE peroxides that do not interfere with the electronic conductivity of the carbon matrix [17]. PFPE peroxides are perfluorinated polymers whose structures are characterized by the alternation of fluorinated carbon-based units and oxygen units. In particular, carbon-based units in linear PFPEs can be perfluoromethylene ( $\text{CF}_2$ ) and perfluoroethylene ( $\text{CF}_2\text{CF}_2$ ) and oxygen-based units can be ether (O) and peroxide (O–O) [18]. A thermal treatment at 150–200 °C breaks the peroxidic moieties, generating oxygen-centered radicals. These radicals quickly decompose by  $\beta$ -scission to give more stable carbon-centered radicals that can couple or, link without any hydrogenated spacer to unsaturated structures like the ones of carbonaceous materials [19].

In this work, a GDL based on a carbon cloth (CC) was functionalized with linear PFPE chains starting from a linear PFPE peroxide. The functionalized CC was characterized to estimate its main properties, like surface chemical composition, conductivity, morphology as well as wettability, and it was finally tested in a single cell for the steady state polarization.

## 2. Experimental

### 2.1. Materials

The gas diffusion layer (GDL) used in this study was a commercial carbon cloth (S5 purchased by SAATI S.P.A. Italy). The PFPE peroxide was a high molecular weight FOMBLIN® Z PFPE (Solvay Specialty Polymers) with linear structure where the monomeric units ( $\text{CF}_2\text{CF}_2\text{O}$ )<sub>m</sub>, ( $\text{CF}_2\text{O}$ )<sub>n</sub> and peroxidic units (O)<sub>v</sub> were randomly distributed along the polymer chain: T–( $\text{CF}_2\text{CF}_2\text{O}$ )<sub>m</sub>( $\text{CF}_2\text{O}$ )<sub>n</sub>(O)<sub>v</sub>–T'. The chemical characteristics of this peroxide are here reported: average molecular weight around 29,500 u, ratio 1.15 between perfluoroethylene oxide (m) and perfluoromethylene oxide (n) groups, peroxidic content (v) of 1.32%wt, average equivalent molecular weight 12,000 g equiv<sup>-1</sup>, and  $\text{CF}_3$ , COF,  $\text{CF}_2\text{COF}$  as terminals (T, T'). On the basis of the stoichiometry of the PFPE chain structure, the F/C and F/O ratio are 2 and 2.78, respectively. The PFPE peroxide was industrially prepared by Solvay Specialty polymers by light assisted oxidation of tetrafluoroethylene (TFE) [15,18]. PFPE peroxides decompose generating radical species, with a half life of 30 min in a range of temperatures between 140 and 250 °C [15]. For the dipping procedure, the chosen fluorinated solvent was the Galden® HT55 (Solvay Specialty Polymers), that is a mixture of linear perfluoropolyether fluids with a boiling point at 55 °C.

**Table 1**

Experimental conditions of the chemical treatments of CC with PFPE peroxide.

Sample	CC (g) <sup>a</sup>	PFPE peroxide solution	
		PFPE (g)	C (%wt) <sup>b</sup>
I	1.5585	0.9801	0.46
II	1.5071	4.0734	1.88
III	1.5437	19.8371	8.52

<sup>a</sup> Dry weight of the untreated CC sample after heating at 120 °C for 1 h under vacuum.

<sup>b</sup> Concentration of peroxide in the dipping solution expressed as weight percentage.

### 2.2. Chemical treatment of carbon cloth with perfluoropolyether peroxide

Three GDL samples (carbon cloth, 11 cm square sheet, 0.8 mm thickness) were firstly washed with water, acetone and fluorinated solvent (Galden® HT55) in order to remove any possible impurity. Thereafter, the samples were dipped for 1 min in a glass vessel containing a solution of PFPE peroxide in Galden® HT55. The CC weight, the amount of PFPE peroxide used to prepare the solutions in Galden® HT55 and the corresponding concentrations are reported in Table 1.

The solvent was evaporated at 60 °C and, then, the PFPE peroxide was thermally decomposed with an appropriate thermal treatment: the temperature was ranged from 150 to 195 °C, by increasing it stepwise with a rate of 15 °C h<sup>-1</sup>, and then heated at 200 °C for 4 h. Thereafter, the samples were washed with Galden® HT55 (low boiling PFPE solvent) in order to remove the unlinked PFPE and with water to hydrolyze the acyl fluoride end-groups to carboxylic acids [19]. The samples were finally dried at 200 °C in high vacuum for 24 h. For sake of comparison a sample coated with a commercial PTFE dispersion (AlgoFlon® D 1214X, Solvay Solexis s.p.a., Italy) was used as reference. The GDL was dipped in the fluorinated dispersions for 10 min and the treated sample was roll squeezed, heated in air for 30 min up to 350 °C.

### 2.3. Chemical and physical characterization

#### 2.3.1. Contact angle measurements

The contact angle instrument was a Data Physics OCA 150 and the software was SCA20 version 2.3.9. build 46. The contact angles were measured directly on the carbon cloth surface, putting above water droplets of 4  $\mu\text{l}$ .

#### 2.3.2. XPS surface analysis

X-ray photoelectron spectroscopy spectra were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al-K $\alpha$  radiation (1486.6 eV). A spot size of 200  $\mu\text{m}$   $\times$  750  $\mu\text{m}$  and pass energy of 25 eV were used. 1s level hydrocarbon-contaminant carbon was taken as the internal

**Table 2**

Peroxide deposition and PFPE linkage on the CC samples.

Sample	CC (g)	PFPE				
		Peroxide deposited		Linked		
		(g)	(%wt) <sup>a</sup>	(g)	(%wt) <sup>a</sup>	(%) <sup>b</sup>
I	1.5585	0.0269	1.73	0.0037	0.24	13.8
II	1.5071	0.1051	6.97	0.0140	0.93	13.3
III	1.5437	0.5741	37.20	0.0159	1.03	2.8

<sup>a</sup> Referred to the weight of bare CC.

<sup>b</sup> Percent ratio between the linked PFPE and the PFPE peroxide deposited before the functionalization.

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