

Perfluoropolyethers as superhydrophobizing agents for carbon-based surfaces of fuel cell gas diffusion layers

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ABSTRACT

Perfluoropolyether (PFPE) peroxide confers superhydrophobic properties to carbon black (CB) and carbon cloth (CC) as Gas Diffusion Layer (GDL) materials by direct functionalization. The thermal decomposition of PFPE peroxide synthesizes PFPE radicals which covalently bond the unsaturated moieties on carbonaceous surfaces. PFPE-functionalized CB and CC were characterized by X-ray photoelectron spectroscopy (XPS), surface area analysis, resistivity measurements, scanning electron microscopy (SEM) and contact angle measurements. The PFPE-modified materials resulted superhydrophobic were employed for the fabrication of single and dual layer GDLs. 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.

Keywords: perfluoropolyethers, functionalization, superhydrophobicity, gas diffusion layers, fuel cells

1 INTRODUCTION

Perfluoropolyether (PFPE) peroxide has been employed in the functionalization of conductive carbon-based materials to confer them the highly hydrophobic surface properties of the perfluorinated materials. The thermal decomposition of a linear PFPE peroxide produced PFPE free-radicals that covalently bonded the unsaturated moieties on the surface of carbon-based materials such as carbon black (CB) and carbon cloth (CC). In particular, perfluorinated free-radicals can directly bond to the unsaturated structure of these carbonaceous materials without any spacer that decreases thermal or chemical stability of the resulting materials [1,2]. PFPE-functionalized materials revealed exceptional hydrophobic behavior, by showing water contact angle values over the threshold of superhydrophobicity. The relationship between the linkage of PFPE chains and the modification of surface physical-chemical properties were studied combining resistivity measurements, scanning electron microscopy (SEM) X-ray photoelectron spectroscopy (XPS), and surface area analysis with Brunauer-Emmett-Teller (BET) technique. Results on resistivity measurements were specially promising and revealed that, despite insulating

nature of PFPE, functionalized carbonaceous materials retained their conductive properties [3]. The PFPE-functionalized carbonaceous materials were tested in a fuel cell as a single- and dual-layer gas diffusion layers (GDLs) and the polarization curves were recorded. The cell testing for both single- and dual-layer GDLs was run at two temperatures, 60°C and 80°C, and two relative humidities (RH) of feeding air, 80% and 60% (hydrogen feeding gas humidity was fixed at 100%).

2 EXPERIMENTAL

2.1 Materials

The Gas Diffusion Layer (GDL) used in this study was a commercial carbon cloth (SCCG 5N purchased by SAATI a.p.a. Italy). The CB was a high conductive, commercially available graphitic CB with high surface area: the CABOT VULCAN® XC72R. The PFPE peroxide was a high molecular weight FOMBLIN® Z PFPE (Solvay Specialty Polymers) with linear structure where the monomeric units $(CF_2CF_2O)_m$, $(CF_2O)_n$ and peroxidic units $(O)_v$ were randomly distributed along the polymer chain: $T-(CF_2CF_2O)_m(CF_2O)_n(O)_v-T'$. The chemical characteristics of this peroxide are here reported: average molecular weight around 29,500 uma, 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/eq, and CF_3 , COF, CF_2COF as terminals (T , T'). The PFPE peroxide was industrially prepared by Solvay Specialty polymers by light assisted oxidation of tetrafluoroethylene (TFE) [4,5]. PFPE peroxides decompose generating radical species, with a half life of 30 min in a range of temperatures between 140 and 250°C [4]. 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.

2.2 Preparation of PFPE-functionalized Single Layer Gas Diffusion Layer

CC samples (carbon cloth, 11 cm square sheet, 0.8 mm thickness) were dipped in a solution of PFPE peroxide in Galden® HT55. Experimental details are reported in Table 1.

Sample	CC (g) ^a	PFPE (g)	C (%wt) ^b
CC-1	1.5585	0.9801	0.46
CC-2	1.5071	4.0734	1.88
CC-3	1.5437	19.8371	8.52

^a Dry weight of untreated CC after heating at 120°C for 1 h under vacuum.
^b Concentration of PFPE peroxide in the dipping solution expressed as weight percentage.

Table 1: Experimental conditions of the functionalization of CC with PFPE peroxide.

The solvent was evaporated, thereafter the PFPE peroxide was thermally decomposed with appropriate thermal treatment and work up procedure [1].

2.3 Preparation of PFPE-functionalized Dual Layer Gas Diffusion Layer

In the fuel cell assembly of dual layer GDLs the macroporous layer (*i.e.*, CC) is coated with a microporous layer (MPL) made of hydrophobized CB [6]. A PFPE-based formulation was used for the preparation of fluorinated inks suitable for the deposition of a hydrophobized MPL: CB (6 g) was dispersed by ultrasonication in a solution (120 ml) of PFPE peroxide (10%_{wt}). The application of PFPE peroxide for the production of PFPE-functionalized MPLs required the use of a perfluorinated solvent (Galden® HT55) for the PFPE solubilization and dispersion on CB. The dispersion of CB and PFPE peroxide was deposited by spray on CC. The typical low surface tension of the perfluorinated solvent (Galden® HT55) helped to disperse the carbon powder by means of spraying techniques. Functionalization was performed with a thermal treatment similar to the one described in Paragraph 2.2.

2.4 Characterization

X-ray photoelectron spectroscopy spectra were obtained using an M-probe apparatus (Surface Science Instruments). The source was monochromatic Al-K α radiation (1486.6 eV). A spot size of 200 μm x 750 μm and pass energy of 25 eV were used. Survey analyses in the whole range of X-ray spectrum were recorded.

The electrical characterization of CB samples consisted in the determination of resistivity by varying the applied pressure between 0.9 and 13.6 MPa. An experimental apparatus was purposely designed and realized on the basis of what reported in literature [7]. An AOIP OM21 Microohmmeter instrument was used to record resistance values in the range between 2 mOhm and 20 kOhm. All experimental measurements were repeated three times on each CB sample in order to obtain average values.

The scanning electron microscopy (SEM) observation of CB and CC samples was made by using a ZEISS EVO50 EP scanning electron microscope.

The contact angle instrument was a Data Physics OCA 150 and the software was SCA20 version 2.3.9. build 46. Contact angles were measured on CC with water droplets of 4 μl . Tablets were prepared with CB powder samples and 4 μl water droplets were deposited on the CB tablet surface in sessile drop technique. Each CB tablet was obtained by pressing the CB powder at 7000 kg/cm², room temperature.

The specific surface areas (SSA) of CB samples were measured by N₂ adsorption and calculated by utilizing the Brunauer-Emmett-Teller (BET) method. The instrument used for BET analyses is a Costech Instruments Sorptometer Kelvin 1042, managed by the software Kelvin 1042 v.3.05.

2.5 Single Cell Polarization Measurement

A single cell (Fuel Cell Technologies) was used for the steady state polarization measurements. The cell used in the present work has a single serpentine at the anode and a triple one at the cathode. The employed membrane electrode assembly (MEA) was a catalyst coated membrane (CCM) consisting of Nafion® 212 with a thickness of 50 μm and the catalyst layers coated directly onto such membrane. The active area was 25 cm² and two different platinum loadings were used: 0.3 mg·cm⁻² for the anode and 0.6 mg·cm⁻² for the cathode. Hydrogen and air were used as anodic and cathodic feedings, respectively. Two temperatures (60°C and 80°C) and two cathodic relative humidities (60 and 100%) were adopted; while, the hydrogen relative humidity was fixed at 80%. An electronic load (RBL488-50-150-800) measured and controlled voltage, current and electric power produced; in order to obtain the polarization curves, the cell voltage was changed from OCV to 0.15 V with steps of 0.05 V, keeping it constant for 400 seconds for each value and at each step the resulting average current was recorded.

3 RESULTS AND DISCUSSION

The hydrophobization of CCs for fuel cell GDLs is a common practice for a better water management. Typically, polytetrafluoroethylene (PTFE) is added to CC with PTFE loadings around 10%_{wt} and using several deposition techniques [6].

Sample	Linked PFPE (% _{wt})	C ^a (at.%)	F ^a (at.%)	O ^a (at.%)	Static CA
CC	-	-	-	-	n.s. ^b
CC-1	0.24	37.2	41.0	21.8	166°±3°
CC-2	0.93	38.6	44.2	17.2	171°±7°
CC-3	1.03	30.1	51.5	18.4	172°±2°

^a measured by XPS analysis;

^b droplet is not stable and is quickly adsorbed in the CC.

Table 2: PFPE linked on CCs, surface compositions and CA measurements with water on PFPE-functionalized CCs.

The carbonaceous structure of CC contains condensed aromatic moieties, suitable for the linkage of perfluorinated chains due to decomposition of PFPE peroxide. Following this approach, a polymeric PFPE layer was chemically linked to CC structure, not simply deposited like the commonly used PTFE. Thus, PFPE chains on the CC surface allowed to obtain similar superhydrophobic effects, even if the amount of PFPE linked on the CC was only 0.24%_{wt}, instead of the PTFE 10%_{wt}. In fact, it was possible to reach a very high contact angle value around 166°, that increased to 172°, linking 1%_{wt} of perfluoropolyether chains by means of PFPE peroxide (Table 2).

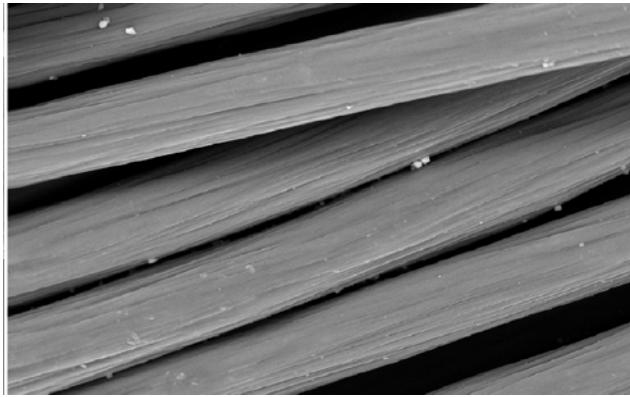


Figure 1: SEM image of PFPE-functionalized CC.

PFPE surface coating resulted uniform on CC fibers, as evidenced by SEM images (Fig 1). Furthermore, PFPE layers wrapped singularly each fiber of CC without filling the matrix porosity. Conversely, PTFE-based hydrophobizing agent forms a solid barrier that includes many fibers, covering the empty spaces between them and decreasing the porosity suitable for gases diffusion [8].

Sample	C ^a (at.%)	F ^a (at.%)	O ^a (at.%)	Static CA	SSA (m ² /g)
CB	98.4	-	1.2	n.s. ^b	262
CB-1	96.9	1.3	1.5	n.s. ^b	225
CB-2	94.2	3.5	1.9	139°±5°	194
CB-3	92.8	4.7	2.3	157°±5°	183
CB-4	82.4	12.2	5.0	174°±5°	107

^a measured by XPS analysis;

^b droplet is not stable and is quickly adsorbed in the CB.

Table 3: Surface compositions, CA measurements with water and specific surface area (SSA) of PFPE-functionalized CBs.

The CA measurement revealed that water droplets were quickly adsorbed by the carbonaceous matrix on bare CB while on PFPE-functionalized CB samples occurred a modification of the hydrophilic properties until the exceeding of the superhydrophobicity threshold (Table 3).

XPS data showed that the higher the amount of added PFPE peroxide the higher the amount of fluorine on the

surface. Moreover, BET data revealed that CB morphology CB (262 m²/g) was influenced by the chemical treatment with PFPE peroxide (Table 3). A progressive decrease in surface area, from 225 to 107 m²/g, was observed along the series of CB samples treated with PFPE peroxide. Thus the more intense the treatment with PFPE peroxide, the higher the surface area decrease. Overall the chemical treatment with PFPE peroxide leaded to the formation of a non-peroxidic PFPE layer covalently linked to the CB surface.

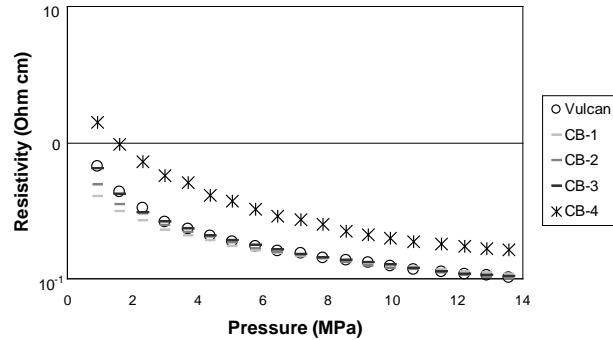


Figure 2: Electrical resistivity (in logarithmic scale) of PFPE-functionalized CBs at different pressures.

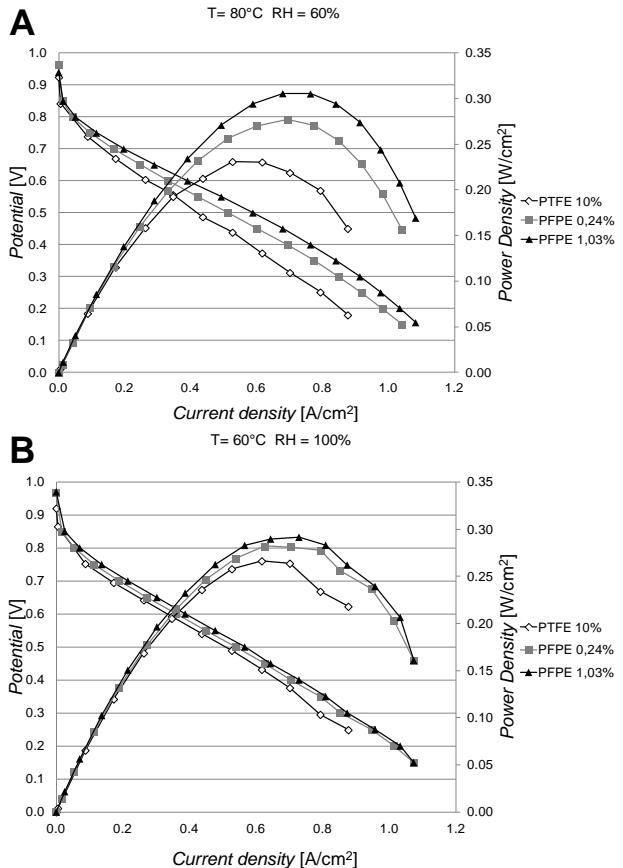


Figure 3: Polarization curves of PEM-FCs with single layer GDLs hydrophobized by functionalization with PFPE peroxide and by sintering of PTFE in wet (A) and dry (B) conditions.

The determination of CB resistivities in function of the applied pressures (from 0.9 to 13.6 MPa) allowed the characterization of the electrical properties of PFPE-functionalized CB samples (Fig. 2). The resistivity of untreated CB varied from 0.7 to 0.1 Ohm·cm, decreasing under 0.2 Ohm·cm when the compacting pressure was around 4.0 MPa. After chemical treatments, the resistivity of PFPE-functionalized CB samples remained close to the values of bare CB, even if an increment due to the typical insulating properties of fluorinated materials was expected.

The polarization curves of PEM-FCs with PFPE-functionalized single layer GDLs showed a decrease in electrical resistance in the region of ohmic overpotential compared to the cell with PTFE-sintered GDL. This increase in performances can be ascribed to the lower amount of PFPE polymer (1%_{wt}) required to obtain the same hydrophobic effect due to 10%_{wt} PTFE.

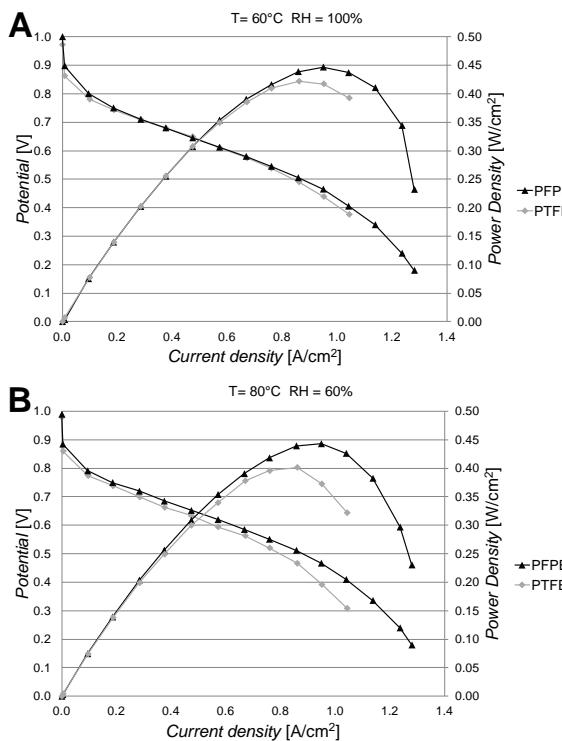


Figure 4: Polarization curves of PEM-FCs with dual layer GDLs hydrophobized by functionalization with PFPE peroxide (10%_{wt}) and by sintering of PTFE in wet (**A**) and dry (**B**) conditions.

In dry and wet conditions PFPE-functionalized GDLs performed similarly, revealing slight sensitivity to RH variations and an almost absent RH influence in highly functionalized CCs. The results showed also that CCs with 1%_{wt} of linked PFPE had better performances in the mass transport zone compared to a standard GDL hydrophobized with 10%_{wt} PTFE: the PFPE-functionalized GDLs have the voltage drop at approximately 1.07 A/cm², while the standard falls at 0.9 A/cm² [8]. Therefore, an increase of

20% in current density can be achieved by substituting 10%_{wt} standard polymer with 1%_{wt} PFPE [8]. Data from polarization curves of PEM-FCs with PFPE-functionalized dual layer GDLs confirmed that the functionalization with PFPE peroxide slightly affects the conductivity of the GDLs and ohmic resistances are similar for PFPE-functionalized and PTFE-standard GDLs (Fig. 4). In the mass transport region the voltage drops shifted from 1.0 A/cm² with PTFE to 1.3 A/cm² with PFPE, revealing an increment in current densities up to 30% due to PFPE. Thus, PFPE-functionalized GDLs largely improve the overall performances of the fuel cell because they allow a better gas diffusion due to a balanced water management and to PFPE gas permeability. Humidity variations have low influence on PFPE-functionalized GDLs that keep always their best performances, while PTFE-hydrophobized GDLs are more RH sensitive.

4 CONCLUSIONS

The replacement of standard hydrophobizing agents with PFPE functionalization improves the performances of the cell and the obtainable power density is up to 10% higher in cells using PFPE-functionalized materials. In addition, the maximum power density peak is shifted up to 10% higher current density.

PFPE-functionalized dual layer GDLs are in their early stage of development, but all preliminary fuel cell tests suggest that their overall performances are significantly better than the standard.

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