

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

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Received 13 October 2013

Received in revised form

31 January 2014

Accepted 6 February 2014

Available online 25 February 2014

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 (CF₂) and perfluoroethylene (CF₂CF₂) 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 β-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 (CF₂CF₂O)_m, (CF₂O)_n and peroxidic units (O)_v were randomly distributed along the polymer chain: T–(CF₂CF₂O)_m(CF₂O)_n(O)_v–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⁻¹, and CF₃, COF, CF₂COF 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) ^a	PFPE peroxide solution	
		PFPE (g)	C (%wt) ^b
I	1.5585	0.9801	0.46
II	1.5071	4.0734	1.88
III	1.5437	19.8371	8.52

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

^b 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⁻¹, 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 (Alcoglon® 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 μl.

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-Kα radiation (1486.6 eV). A spot size of 200 μm × 750 μm 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) ^a	(g)	(%wt) ^a	(%) ^b
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

^a Referred to the weight of bare CC.

^b Percent ratio between the linked PFPE and the PFPE peroxide deposited before the functionalization.

Table 3
Surface composition and static C.A. measured on the functionalized samples.

Sample	Linked PFPE (%wt)	Amount (at.%) ^a			F/C ^b	Static C.A. ^c
		F	C	O		
Untreated CC	0	—	80.1	19.9		n.s. ^b
I	0.24	41.0	37.2	21.8	1.10	166°±3°
II	0.93	44.2	38.6	17.2	1.15	171°±5°
III	1.03	51.5	30.1	18.4	1.71	172°±2°
PTFE 10%wt ^d	—	59.5	38.6	1.9	1.54	148°±3°

^a Measured by XPS analysis.

^b In pure PFPE, the F/C ratio is 2 (see details in [Materials](#) paragraph).

^c The water droplet is not stable and is adsorbed on the CC porous matrix in few seconds.

^d GDL treated with 10%wt PTFE used as reference.

reference at 284.6 eV. For each sample, survey analyses in the whole range of X-ray spectrum were performed and for bare carbon cloth high-resolution XPS spectrum in the region of C 1s was also recorded.

2.3.3. Scanning electron microscopy

The scanning electron microscopy (SEM) observation of CC samples was made by using a ZEISS EVO50 EP scanning electron microscope. The samples were analyzed without applying surface etching or conductive layer coating techniques. The SEM parameters were as follows: working distance of 7.0 mm, beam current of 20 pA, acceleration voltage of 17.0–17.5 kV and different magnifications with respect to a 1024 × 768 pixel image.

2.3.4. 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. The flow rates were 0.2 N l min⁻¹ of hydrogen and 1.0 N l min⁻¹ of air, corresponding to a stoichiometric ratio $\lambda = 1.2$ –2.0 A C⁻¹@1 A cm⁻², and were controlled and detected by a calibrated flow meter. Two temperatures (60 °C and 80 °C) and two air (cathodic gas) relative humidities (60 and 100%) were adopted; while, the hydrogen (anodic gas) relative humidity was fixed at 80%. The degree of humidity and the gas temperature were controlled by humidifiers and temperature controllers. 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 s for each value and at each step the resulting average current was recorded (potentiostatic mode).

3. Results and discussion

The organic fluorinated peroxides are a well known source of perfluorinated radicals for the introduction of fluorinated chains in several substrates, such as aromatic compounds and carbonaceous substrates [20–25]. Previous experiments verified that perfluoroalkyl radicals are able to link covalently the unsaturated moieties [17]. The linkage of this kind of radicals confers to the substrates some characteristics of perfluorinated materials, like hydrophobicity [17,26]. This effect has been studied especially in the case of perfluoropolyethers peroxides, which can be used to link PFPE chains to carbonaceous materials to reach high levels of hydrophobicity, until and over the threshold of

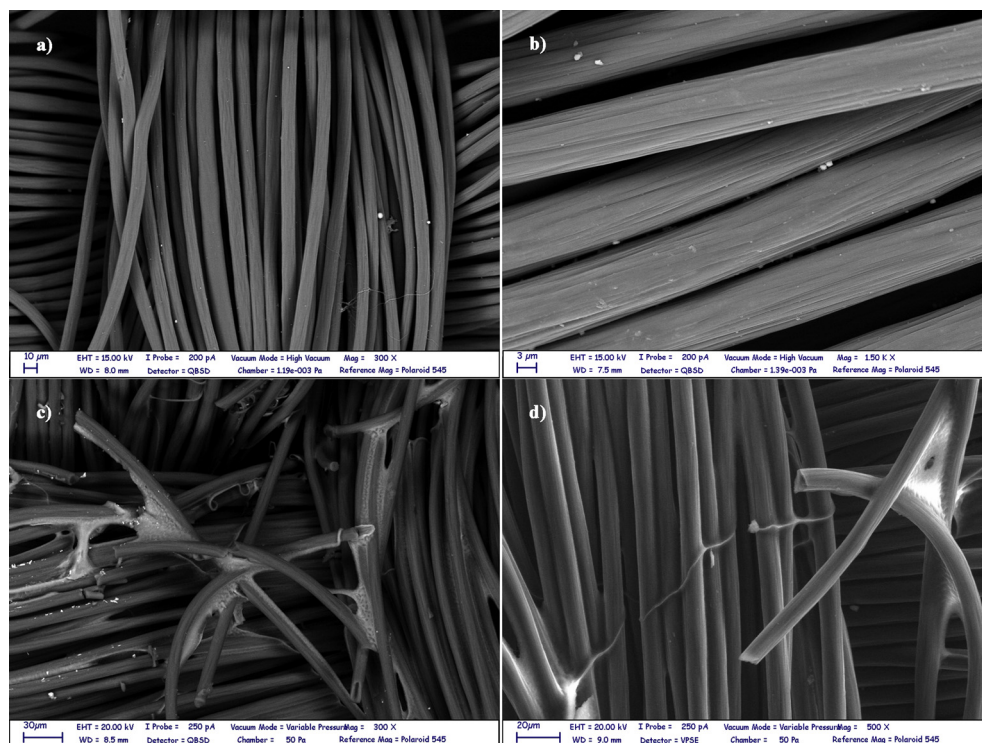


Fig. 1. SEM images of PFPE-functionalized sample III (a, b), and GDL treated with 10%wt PTFE (c, d). Panel c was reproduced with permission from ECS Transactions 12(1) (2008) 51–57. Copyright 2008, The Electrochemical Society.

superhydrophobicity. This characteristic can be usefully applied in the design of materials for fuel cell water management.

The carbonaceous structure of CC contains condensed aromatic cycles, suitable for the linkage of perfluorinated radicals formed in the decomposition of PFPE peroxide. Due to this characteristic, the treatment of CC with PFPE peroxide allowed to covalently bond a polymeric layer of PFPE to the CC structure, in order to obtain an hydrophobic effect. Actually, the most appropriate treatment for the hydrophobization of CC is a deposition of perfluorinated polymer (PTFE), reinforced by a sintering process.

Three CC samples were dipped in peroxidic solutions with increasing content of PFPE peroxide, as reported in Table 2: 0.46%_{wt} (I), 1.88%_{wt} (II) and 8.52%_{wt} (III), as reported in Table 1. The sample (II) dipped in the 1.88%_{wt} solution shows a value of deposited peroxide 3.9 times higher than the one dipped in 0.46%_{wt} solution (I) and the linked PFPE in sample (II) is almost 3.8 times higher than the same in sample (I). Considering the sample dipped in 8.52%_{wt} solution (III), it can be noticed that the amount of deposited peroxide is 5.5 times higher than in sample (II) but the amount of linked PFPE is only 1.1 times higher. Thus, the proportion between deposited peroxide and linked PFPE is not linear in the experimental range of concentrations. This trend is probably due to the fact that the radicals link mostly on the surface of CC fibers and not into the bulk.

XPS analysis determined the composition of bare carbon fibers (Table 3) and revealed that they are mainly made of graphitic carbon (75%) with hydroxyl and carbonyl groups (Table S.I.1-1). Carbon-centered perfluorinated radicals produced during the thermal decomposition of the PFPE peroxide can attack these graphitic moieties acting as radical scavengers on the surface of the carbon fibers [19]. XPS analysis confirmed that the functionalization with PFPE peroxide occurred mostly on the CC surface because high fluorine content was measured on the surface of all the samples (Table 3). It can be noticed that in samples I and II F/C ratios were slightly greater than 1, because of a stoichiometric excess of C which can be ascribed either to a PFPE layer with an incomplete GDL coverage or with a thickness lower than the XPS depth detection. In sample III F/C ratio was increased to 1.71, due to a thicker PFPE layer or with a better GDL coverage. Sample III has only 1.03%_{wt} of linked PFPE and 51.5%_{at} of fluorine content on the surface. Assuming that linked PFPE chains maintained mostly the C₁/C₂ ratio in the molecular structure (see details in Materials paragraph), it can be estimated that, due to the fluorine content in sample III, more than 95% of the surface atoms belongs to PFPE chains. The same evaluation on samples I and II revealed that both samples are highly covered by PFPE chains too, being PFPE atoms approximately 75% and 80% of the total surface atoms, respectively.

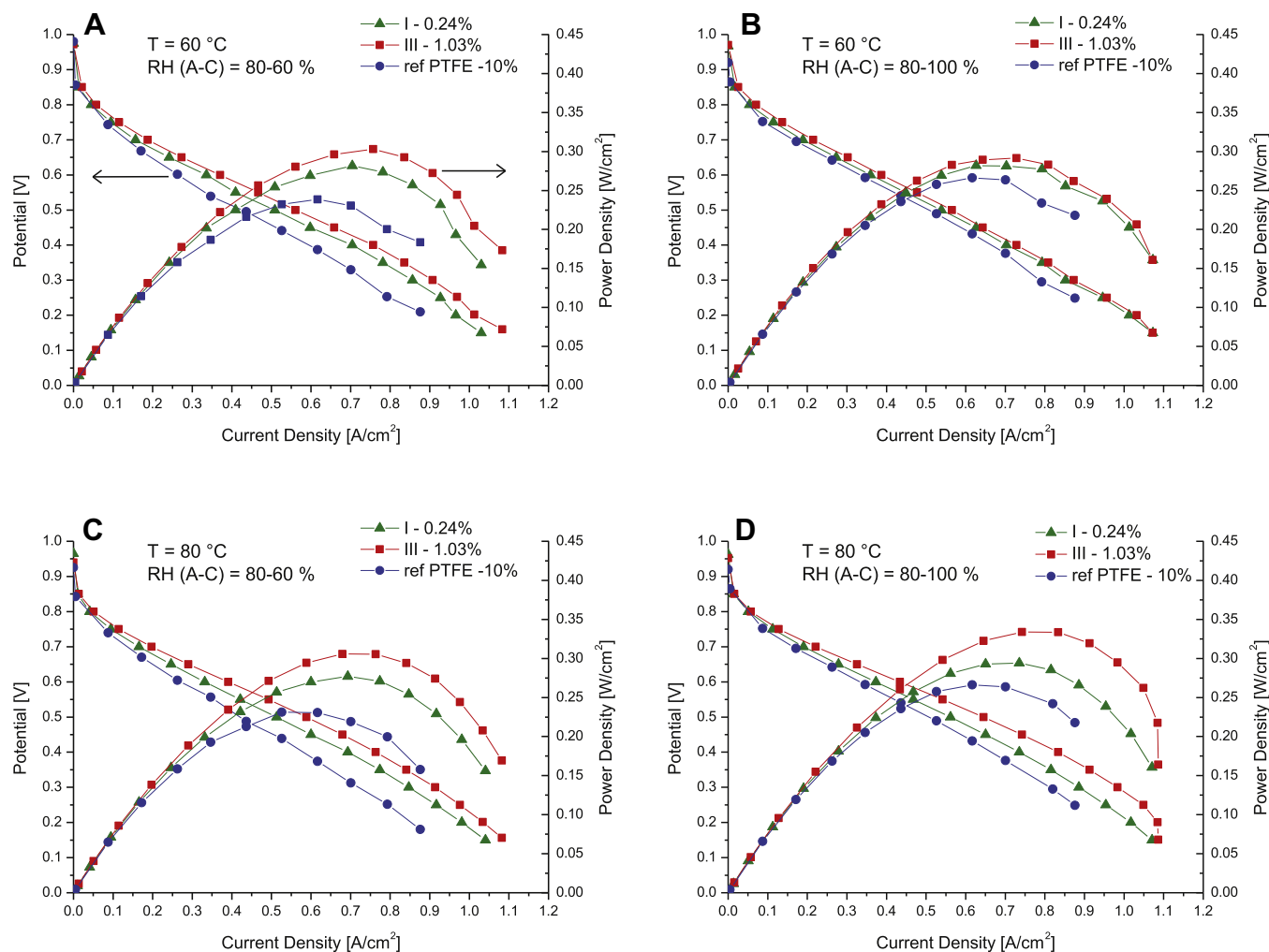


Fig. 2. Polarization curves of samples I – 0.24% (green), III – 1.03% (red) and (ref)PTFE – 10% (blue) at two operating temperatures (60 °C and 80 °C) and two different relative humidity of the inlet feedings (80–60% and 80–100%) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article).

The chemical treatment of CC ended in a hydrophobization effect that can be evaluated by contact angle measurements, as reported in Table 3. The water droplets deposited directly on the surface of unmodified CC are not stable and they are quickly absorbed by its porous structure. Conversely, on the sample of CC with the lowest amount of linked PFPE (0.24%_{wt}) water droplets were durably stable and it was possible to measure a water contact angle of 166°. Thus, hydrophobic properties have been conferred to the surface of CC, exceeding the threshold of superhydrophobicity (*i.e.* 150°). The other two CC samples with a PFPE content of 0.93%_{wt} and 1.03%_{wt} revealed even higher hydrophobicity with contact angle values of 171° and 172°, respectively. Thus, PFPE-treated CC samples are definitely more hydrophobic than commonly used PTFE-treated ones that usually showed contact angle values comprised between 120 and 140° [3,27,28]. This comparison is even more relevant taking in consideration that the usual PTFE coating uses 5%_{wt} to 45%_{wt} of polymer, while the amount of PFPE on the three samples here presented ranges from 0.24%_{wt} to 1.03%_{wt}.

As evidenced by SEM images, PFPE surface coating is uniform along the surface of CC fibers (Fig. 1a). Furthermore, PFPE layers wrap singularly each fiber of CC and doesn't fill the matrix porosity (Fig. 1b). On the opposite, the commonly used PTFE-based hydrophobizing agent forms a solid barrier that includes many fibers (Fig. 1c), covering the empty space between them and decreasing the porosity suitable for gases diffusion (Fig. 1d) [29].

The steady state current density–potential and current density–power curves of the cell assembled with the PFPE-based GDLs are reported and compared to those obtained with a traditional GDL treated with 10%_{wt} PTFE (Fig. 2). Firstly, it can be noticed that the presence of PFPE allowed to improve the electrical performance of the cell at each operating condition. In particular, the higher the content of PFPE, the better the performance in terms of maximum power density and slope of polarization curve. Thus, the novel GDLs seem to be able to reduce the ohmic resistance of the whole system. Moreover, the GDL containing 1.03% PFPE also showed small improvements when, at constant RH (for both cathodic RH values), temperature was increased from 60 °C to 80 °C; at fixed temperature, only at 80 °C there was a slight increase in generated power density shifting from low to high RH, likely due to a higher proton conductivity, which in fact is influenced both by temperature and by the degree of humidity.

4. Conclusions

A commercial CC has been treated with linear peroxidic PFPE in order to obtain the covalent linkage of PFPE chains to its surface. The resulting material showed superhydrophobic properties typical of fluorinated materials, despite the low amount of linked PFPE (0.24–1.03%_{wt}). In fact, PFPE chains were linked on the surface and wrapped singularly each material fiber, covering them almost completely. Two samples of functionalized CC were used as GDL in a fuel cell to test their performances, also in comparison with a standard GDL hydrophobized by 10%_{wt} PTFE. Polarization and power curves showed in all conditions of temperature and

humidity that PFPE-functionalized GDLs allowed better performances, especially in terms of ohmic resistance, than PTFE-hydrophobized GDLs used as reference. This result can be ascribed to the use of a lower amount of perfluorinated polymer combined with a higher hydrophobizing effect of PFPEs and their typical high gas permeability. Thus, PFPE-modified superhydrophobic CCs demonstrated to be promising materials for the application as gas diffusion layer in PEM fuel cells.

Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version.

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