



Improving the corrosion resistance of proton exchange membrane fuel cell carbon supports by pentafluorophenyl surface functionalization

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HIGHLIGHTS

- First-time modification of colloid imprinted carbons with pentafluorophenyl groups.
- Potential stepping and cyclic voltammetry results were rigorously analyzed.
- Surface fluorination improves the corrosion resistance of carbons by 50–80%.
- Both surface passivation and increased hydrophobicity enhance corrosion resistance.
- Pentafluorophenyl groups may block and thus protect micropores.

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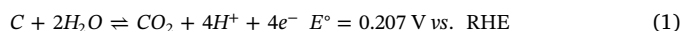
ABSTRACT

In this study, the effect of surface functionalization on the electrochemical corrosion resistance of a high surface area, mesoporous colloid imprinted carbon powder (CIC), as well as microporous Vulcan carbon (VC, serving as the benchmark), was demonstrated, primarily for PEM fuel cell applications. CIC-22, which is highly hydrophilic and was synthesized with 22 nm silica colloid templates, and as-received, mildly hydrophobic, VC powders, were functionalized with 2,3,4,5,6-pentafluorophenyl (-PhF₅) surface groups using a straightforward diazonium reduction reaction. These carbons were then subjected to corrosion testing, involving a potential cycling-step sequence in room temperature 0.5 M H₂SO₄. Using cyclic voltammetry and charge/time analysis, the double layer and pseudo-capacitive gravimetric charges of the carbons, prior to and after the application of these potential steps, were tracked in order to obtain information about surface area changes and the extent of carbon oxidation, respectively. It is shown that the corrosion resistance was improved by ca. 50–80% by surface functionalization, likely due to a combination of surface passivation (loss of carbon active sites) and increased surface hydrophobicity.

1. Introduction

Porous carbon powders are commonly used as catalyst supports and/or as electrodes in a range of electrochemical applications (e.g., in lithium batteries, redox flow batteries (RFBs), fuel cells, capacitors, etc.), primarily because of their high electrical conductivity, high surface area, ease of surface-modification, variety of microstructures, affordability, etc. For instance, in proton exchange membrane (PEM) fuel cells and electrolysis cells, high surface area carbon materials are used as the support for the Pt nanoparticles (NPs) that catalyze the fuel and

air electrode reactions [1–3]. However, carbon is susceptible to damage at high potentials [4–7], especially in acidic conditions, as the Nernst potential for carbon oxidation is relatively low, as follows:



Even so, under normal PEM fuel cell cathode operation (at a potential of 0.5 V–0.95 V vs. the reversible hydrogen reference electrode (RHE)), carbon corrosion is quite slow. However, corrosion can be quite severe under start/stop operation or fuel starvation conditions, when the potential of the cathode can reach ≥ 1.4 V vs. RHE [8–10]. Furthermore, it is known that carbon corrosion can lead to both

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agglomeration and dislodgement of the supported Pt NPs, resulting in a loss in the electrochemically active Pt surface area for the oxygen reduction reaction (ORR) [11,12]. Corrosion can also lead to deformation of the porous carbon structure, resulting in an increase in the mass transport resistance within the catalyst layer [9]. Carbon corrosion can also cause a significant increase in hydrophilicity, due to an increase in the surface concentration of oxide groups, potentially contributing to local flooding of the catalyst layer [13,14]. All of these phenomena can lead to a significant decrease in the lifetime and performance of PEM fuel cells [13].

To mitigate these forms of carbon degradation, especially for PEM fuel cells, various strategies have been offered in the literature, including (i) cell designs to prevent flooding in the catalyst layer [13,14], (ii) enhancing the corrosion resistance of the carbon materials (e.g., heat-treatment, surface modification, synthesis of new carbon materials, etc.) [13,15–18], (iii) activation of the oxygen evolution reaction (OER) through the use of OER catalysts (e.g., IrO₂) [19] to compete with and overcome carbon corrosion, and (iv) replacement of carbon supports with other materials, such as conducting metal oxides (e.g., TiO₂, WO₃, SnO₂, etc.) [20–22].

In relation to the second option, several previous studies have shown that the surface modification of carbon materials with hydrophobic functional groups (e.g., fluorine-containing moieties) can improve their corrosion resistance [17,23–25]. Using the diazonium reduction reaction, various fluorine-containing groups (e.g., 4-trifluoromethylphenyl, 4-trifluoromethoxyphenyl, 4-fluorophenyl, etc. [13,24,26–28]) have been successfully attached onto carbon surfaces. For instance, Xu, et al. [13] modified the surface of a catalyst-loaded microporous carbon (Vulcan carbon, VC) support (20 wt % Pt/VC) with -PhF₅ groups through the chemical reduction of a diazonium salt, followed by its use as a catalyst layer (CL) in a PEM fuel cell set-up. They found that the modified catalyst supports showed better performance than the non-modified ones, presumed to be due to the hydrophobicity of the -PhF₅ groups, which was suggested to prevent local flooding of the CL. However, there has been no systematic study carried out as yet in which the durability of carbons that were functionalized using diazonium chemistry has been determined, especially for PEM fuel cell applications.

In our recent work, we have focussed on the study of mesoporous carbon powders for PEM fuel cell applications, with the main goal being to deposit catalytic Pt nanoparticles (NPs) not only on the outer surfaces of the carbon particles but also inside the carbon mesopores in order to provide a high surface to volume ratio, to protect the Pt NPs from dislodgement, and to maximize Pt NP utilization [29–33]. Compared to microporous carbons, the pores in mesoporous carbons are more likely to be able to accommodate the Pt NPs, as well as Nafion, which is required for proton transfer. The larger mesopores also provide a pathway for reactants/products to reach/leave the Pt NPs.

As it is very difficult for Pt NPs and Nafion to penetrate pores smaller than 5–10 nm in diameter (such as found in ordered mesoporous carbons (OMCs), which typically have pore diameters of 1–3 nm [34]), our main focus has been on mesoporous carbon materials with larger, tunable pore sizes, such as found in colloid imprinted carbons (CICs, with pore sizes typically from 10 to 100 nm) [3,31,34–40]. Consistent with this, Pt/CIC composites (CIC pores > 10 nm) have been found to give very good oxygen reduction kinetics at rotating disc electrodes in sulfuric acid solutions [30,31,33,39]. However, the CICs are found to be very hydrophilic [41], which could exacerbate their oxidation and could also lead to flooding of the cathode in PEM fuel cells.

Therefore, in recent work [42], we surface-functionalized the CIC-22 powder (“22” indicates the particle size, in nm, of the colloidal silica used for the CIC synthesis and thus also indicates the approximate resulting mesopore diameter) with -PhF₅ groups using the straightforward diazonium reduction reaction, with microporous (< 2 nm pore size) Vulcan carbon (VC) used for comparison. This showed that these

mesoporous carbons became much more hydrophobic after -PhF₅ surface functionalization, likely due to the high electronegativity and low polarizability of fluorine [42], and thus a higher corrosion resistance for the PhF₅-functionalized carbons was expected. Our prior work, focussed on lowering the CIC powder wettability, showed the successful attachment of a single layer of -PhF₅ to the inner mesopore surfaces of the CICs, based on the measured surface area and elemental analysis [42]. In that work [42], potentiometric titration with La(NO₃)₃ was used to determine the fluorine content of the surface-functionalized VC and CIC-22, giving a F wt% of 3.7% and 7.6%, corresponding to 6.0 wt% and 12.3 wt % of the PhF₅ groups. After normalization to the external surface area of the VC and CIC-22 powders, the surface coverage of -PhF₅ on these two carbons was found to be ca. 90% [42].

In the present work, the effect of -PhF₅ surface functionalization on the corrosion resistance of mesoporous CIC-22, as well as on microporous VC, used as the benchmark, was investigated. CIC-22 powder was selected here as a representative example of the CICs, partly as its pores (roughly 25 nm) are large enough to be easily functionalized with the -PhF₅ surface groups without blocking the pores [42], and also as this is in the range of the gaps normally found in a PEM fuel cell catalyst layer between the carbon black (e.g., Vulcan carbon) particles [43]. Furthermore, the 25 nm pore size is expected to accommodate the Nafion ionomer in a membrane-electrode-assembly. As the method of preparation of the CICs with larger pore sizes (e.g., 50 or 80 nm) is identical to that of CIC-22 and also as the same carbon precursor would be used in the synthesis, very similar behaviour is expected for all of the CICs.

It is shown here that the -PhF₅ surface groups indeed do improve the corrosion resistance of both CIC-22 and VC by between 50 and 80%, depending on how this is calculated. Using X-ray diffraction (XRD), it is confirmed that surface functionalization does not change the degree of crystallinity of the carbons. Instead, the observed improved corrosion resistance of both carbons is likely due to a combination of surface passivation and enhanced hydrophobicity.

2. Materials and methods

2.1. Preparation of colloid imprinted carbon (CIC-22)

The synthesis of the colloid imprinted carbon (CIC-22) followed a procedure reported previously by our group [30,39] and others [38,40,44]. Mesophase pitch (MP, Mitsubishi Gas Chemical Company, Inc.) was used as the carbon precursor and a colloidal silica suspension (Ludox-AS-40), with a particle size of ca. 22 nm, was used as the hard template. Briefly, 1 g of MP was mixed with a 20 mL solution of ethanol (EtOH)/H₂O (60:40 v/v) by stirring for 1 h. 10 g of the colloidal silica suspension was then added dropwise to this mixture with vigorous stirring. After evaporation of the solvent at temperatures of 50–100 °C, the MP/silica composite was heated to 400 °C for 2 h under a N₂ environment, using a heating rate of 5 °C/min, and then cooled to room temperature (RT). The MP/silica composite was then carbonized at 900 °C for 2 h and cooled to room temperature (RT) under N₂, using a ramp rate of 5 °C/min. The colloidal silica was then removed by refluxing 1 g of the MP/silica composite with 100 mL of 3 M NaOH for 24 h and then washing the carbon (CIC-22) with H₂O until the solution was neutral.

2.2. Surface functionalization of carbon powders

Both as-prepared CIC-22 and as-received Vulcan carbon XC-72R (VC, carbon black, Cabot, used as received) were surface functionalized with the pentafluorophenyl (-PhF₅) groups, following a procedure reported previously in the literature [13], as shown in Scheme 1. 1 g of the carbon powder, 5.6 g of 2,3,4,5,6-pentafluoroaniline (Sigma-Aldrich), and 150 mL of acetonitrile were added to a 250 mL flask and the mixture was then sonicated for 1 h under the flow of N₂. Then, 6.2 mL

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