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Low-cost graphite as durable support for Pt-based cathode electrocatalysts for proton exchange membrane based fuel cells

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Abstract

Proton exchange membrane fuel cell (PEMFC) technology has reached pre-commercial viability, but their insufficient durability acts as a major roadblock in its full-fledged utilization. It has been well established that the issue of durability is majorly due to the corrosion of carbon support used for Pt. Therefore, a search for low-cost and robust alternative support is highly desirable. In this paper, different graphite (and graphene) materials as durable support for Pt-based electrocatalyst are investigated. We followed the top-down approach where a fully graphitized support is mildly wet-milled and surface-treated to give a sufficient surface modification for improved Pt deposition on these supports. All the graphite-supported Pt samples showed better durability than that of state-of-the-art commercial electrocatalysts. Considering both activity and durability the best catalyst among the investigated samples showed a comparable mass specific activity (MSA) of 0.186 A/mg and significantly higher durability (70%) after 7500 stress cycles. For HiSpec9100 and BASF commercial electrocatalysts, the normalized ESA retention value after 7500 stress cycles was 40% and 47%, respectively.

Keywords: Supported Pt, graphite support, accelerated stress test, wet-ball-milling, PEMFC.
1. Introduction

The status of proton exchange membrane fuel cells (PEMFC) technology, for example of its use in automotive vehicles, has reached close to pre-commercial viability. Furthermore, this technology has potential applications in the power demanding areas such as portable electronic devices and distributed stationary power sources with the advantages of high power density, high efficiency, and no pollution. However, there are still several challenges that hinder fuel cell commercialization, including insufficient durability/reliability and the high cost of catalysts [1, 2].

In PEMFCs, oxygen reduction reaction (ORR) at the cathode is six or more orders of magnitude slower than the anode hydrogen oxidation reaction and thus limits performance and still requires further research and development on improving the cathode catalysts and electrodes [3]. The state-of-the-art and the most practical electrocatalysts for PEM fuel cells are still carbon-supported Pt catalysts. However, the sluggish ORR causes a large overpotential during the start-up/shut-down operation of the low-temperature fuel cells which eventually leads to electrochemical oxidation of the carbon support to produce CO₂ [4]. This oxidation (corrosion) of the carbon support leads to separation of Pt particles which then become electronically isolated, leading to a low Pt utilization as well as degraded fuel cell performance. Additionally, there are other failure modes which contribute to the catalyst degradation such as Pt dissolution, sintering, as well as agglomeration [5]. With respect to the instability of carbon materials in fuel cell environments, the carbon materials (Vulcan XC-72R and Ketjen Black) currently used with fuel cell catalysts do not meet the durability requirements for automotive applications [6]. Therefore, it is necessary to explore stable alternatives to replace these carbon materials for the catalyst support to improve the durability of PEM fuel cells.

An ideal support material for ORR should have a high surface area, favouring dispersion of catalytic metals, high oxidation resistance, high electrochemical stability under fuel cell operating conditions, as well as high electrical conductivity [7]. So far, the carbon blacks (e.g. Vulcan XC-72R and Ketjen Black) satisfy most of the
mentioned criteria for electrocatalyst support in PEMFC, however, it lacks the stability and oxidation resistance under fuel cell conditions. One of the major contributing factors to the overall durability of fuel cells is the abundance of the surface (high specific surface area) and bulk structural defects in the carbon blacks (which are amorphous/disordered carbon) and therefore are most prone to degradation during the electrochemical oxidation [8]. As graphitic carbon is more resistant to electrooxidation, carbon corrosion can be reduced by increasing the graphitic content of carbon black or specific chemical modification of carbons [9].

Herein we investigate the commercially available graphite as support for Pt-based electrocatalysts as ORR catalysts in PEMFCs. To improve the surface area of low-cost graphite materials they were treated by wet-milling prior to chemical modification. These and commercially available graphite (with the different specific surface area) were used as support for deposition of Pt using a modified polyol and solvothermal technique. As the graphitic carbon has higher stability and amorphous carbon has the higher surface area, in our (top-to-bottom) approach, we start with low surface area graphite and by wet milling attempt to introduce mild amorphization to improve its specific surface area. These treated graphite supports were used as support for deposition of Pt and compared for their electrochemical activity/durability.

2. Experimental

2.1. Graphite based supports

Low-cost graphite (< 20 µm, synthetic graphite powder; Sigma-Aldrich), high-surface-area (100 and 300 m²/g; provided by IMERY Graphite, Sweden) graphite and (SA = 200 m²/g; provided by 2wiTech, USA) graphene was used as support for the investigation. The graphite and graphene supports were used as received.

To improve the surface area and modify the surface of the low-cost graphite, it was treated using wet ball-milling. Different wetting-media (i.e. acetone, acetonitrile, ethanol, ethylene glycol, isopropanol, pentane, and toluene) were used while wet-ball-milling. The various solvents used for wet milling were selected
randomly with the intention of wetting the surfaces of graphite powder and to gain the better milling efficiency for improvement in its surface area. In a typical wet-ball-milling procedure, 3 g of graphite powder was taken into a 250 ml tungsten carbide jar with tungsten carbide balls in which 10 ml of wetting-media was added. Furthermore, in some cases, Poly-vinylpyrrolidone (PVP) and 1-pyrone carboxylic acid (PCA) were added. Addition of additives was intended for increasing the nucleation sites on milled graphite support, required for efficient Pt deposition. Ball-milling was carried out using planetary ball mill (Pulverisette 5) at 300/400 RPM for 15 minutes and milling was repeated 8 times with a resting period of 15 minutes between two consecutive millings. The milled sample was initially suspended in acetone and gravimetrically filtered. The filtered sample washed using acetone several times before keeping the sample in an air-oven at 80°C for drying. The dried sample was then characterized for their BET surface area.

Table 1 shows the details of wet-milling parameters used for treating the low-cost graphite and enlist the commercially available high surface area graphite and graphene, which were used as support in this investigation. The Tolu-G2 sample showed the highest BET surface-area value (73 m²/g) among the wet-milled samples and therefore the Tolu-G2 along with pristine SG20 (for a comparison) sample was further investigated as support for Pt deposition. In our initial attempts, deposition of Pt on Tolu-G2 support resulted in lower Pt loadings than expected as the support might not have adequate nucleation centres for Pt deposition. Therefore, to improve the surface affinity for Pt deposition the Tolu-G2 sample was treated with PCA. In a typical PCA treatment, 200 mg of milled support and 10 mg of PCA in 10 ml of ethanol was ultrasonicated for 1 h [10]. After ultrasonication, the mixture was dried at 80°C. The dried powder was used as support for Pt deposition. Such treated Tolu-G2 sample is identified as an SG20-trt sample.

Table 1: Wet-milling parameters (wetting media, additive, ball to powder weight ratio and RPM) used for milling of low-cost graphite powder, resulting BET surface area and sample IDs of various samples
investigated. The commercially available high surface area graphite and graphene used in this investigation is also listed below.

<table>
<thead>
<tr>
<th>Sample-IDs of supports</th>
<th>Wetting media</th>
<th>Additive</th>
<th>Ball: Material</th>
<th>RPM</th>
</tr>
</thead>
<tbody>
<tr>
<td>SG20 (un-milled)</td>
<td>Un-milled (pristine, low-cost) graphite</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Acto-G</td>
<td>Acetone</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Actn-G</td>
<td>Acetonitrile</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Etha-G</td>
<td>Ethanol</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Etgl-pvp-G</td>
<td>Ethylene glycol</td>
<td>PVP</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isop-pca-G</td>
<td>Isopropanol</td>
<td>PCA</td>
<td>70:1</td>
<td>300</td>
</tr>
<tr>
<td>Isop-pvp-G</td>
<td>Isopropanol</td>
<td>PVP</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Isop-G</td>
<td>Isopropanol</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Pent-G</td>
<td>Pentane</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tolu-G</td>
<td>Toluene</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Tolu-G2</td>
<td>Toluene</td>
<td>-</td>
<td>80:1</td>
<td>400</td>
</tr>
<tr>
<td>SG20-trt</td>
<td>PCA treated Tolu-G2 support</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IG100</td>
<td>Commercial graphite (SA = 100m²/g, IMERY Graphite)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Graphene</td>
<td>Commercial graphene (SA = 200m²/g, 2wiTech)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>IG300</td>
<td>Commercial graphite (SA =300 m²/g, IMERY Graphite)</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

2.2. Pt deposition on supports

The Pt deposition on the support was achieved by using a modified polyol synthesis [11]. In a typical synthesis of 20 wt.% Pt deposition on a support, 10.6 mg of PVP (Mw = 55 k) and 79.8 mg of K₂PtCl₄ dissolved in 20 ml of ethylene glycol (EG) were kept under stirring in N₂ purging atmosphere. Once the homogeneous yellowish solution is formed, 150 mg of support-material dispersed in 20 ml of EG is added.
to it and the mix was refluxed at 160-180°C for 3 h. After cooling the reaction bath, the dark black suspension is centrifuged at 5000 RPM for 30 min. After removal of transparent supernatant from the centrifuged suspension, the remaining dark sample was washed with mili-Q water and re-dispersed in mili-Q water. Centrifuging and washing of the sample was repeated for several times until the pH of supernatant equals the pH value of mili-Q water. Usually, 3-5 repetitions were adequate. Finally, the precipitate is re-dispersed in mili-Q water and dried at 80°C. The dried product was then characterized using thermogravimetric analysis (TGA) to estimate the weight % of Pt and considered as Pt loading on supports.

Apart from the polyol synthesis for Pt deposition, a solvothermal technique (in collaboration with Danish Technological Institute – DTI [12]) was also used to deposit a well-controlled amount of Pt loadings (23 wt% and 43 wt%, estimated by TGA) on PCA treated graphite support (SG20-trt). In a typical solvothermal synthesis (also called as ‘Supercritical flow synthesis’), H$_2$PtCl$_6$ (dissolved) and SG20-trt support (suspended) in ethanol were mixed at supercritical conditions (250°C, 300 bar) in an automated flow reactor. Synthesized catalysts were centrifuged, washed with ethanol/water and dried in a fume hood at room temperature.

Furthermore, a combustion synthesis method was also used to deposit Pt on a high-surface-area graphite (IG300) support with different Pt loadings. In a typical deposition of Pt on the support using combustion synthesis (CS), an equimolar aqueous solution of Pt precursor (here PtCl$_4$, 96%, Sigma Aldrich) and glycine (Sigma Aldrich) was added to the desired amount of support. The aqueous solution was prepared with the minimal amount of mili-Q water needed to dissolve the precursors. The mix of precursors and support was then dehydrated on a hotplate and transferred to a preheated (450°C) muffle furnace. Although it is known that graphite decomposition starts at 350°C, for CS 450°C temperature is desired/needed for combustion of precursors. The CS synthesized samples were characterized without any further treatments. The synthesis techniques and sample IDs are listed in table 2.
Table 2: Sample IDs of Pt deposited on supports using different Pt deposition technique. The desired Pt loadings for each sample is also listed.

<table>
<thead>
<tr>
<th>Sample IDs</th>
<th>Desired Pt wt%</th>
<th>Pt deposition</th>
<th>Graphite support</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSG20</td>
<td>20</td>
<td>Modified-polyol technique</td>
<td>SG20</td>
</tr>
<tr>
<td>PtSG20-trt</td>
<td>20</td>
<td></td>
<td>SG20-trt</td>
</tr>
<tr>
<td>PtSG20-trt23</td>
<td>20</td>
<td>Solvothermal</td>
<td>SG20-trt</td>
</tr>
<tr>
<td>PtSG20-trt42</td>
<td>40</td>
<td></td>
<td>SG20-trt</td>
</tr>
<tr>
<td>PtIG100</td>
<td>20</td>
<td>Modified-polyol technique</td>
<td>IG100</td>
</tr>
<tr>
<td>PtGraphene</td>
<td>20</td>
<td></td>
<td>Graphene</td>
</tr>
<tr>
<td>PtIG300</td>
<td>20</td>
<td></td>
<td>IG300</td>
</tr>
<tr>
<td>Pt10IG300</td>
<td>10</td>
<td>Solution combustion method (SCS)</td>
<td>IG300</td>
</tr>
<tr>
<td>Pt20IG300</td>
<td>20</td>
<td></td>
<td>IG300</td>
</tr>
<tr>
<td>Pt40IG300</td>
<td>40</td>
<td></td>
<td>IG300</td>
</tr>
<tr>
<td>HiSpec9100</td>
<td>57</td>
<td></td>
<td>Commercial catalysts</td>
</tr>
<tr>
<td>BASF</td>
<td>20</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.3. Estimation of Pt loading %, microstructural and electrochemical characterizations

The Pt wt. % of Pt supported graphite sample were estimated using TGA of samples under a synthetic air atmosphere with a heating rate of 10°C/min. TGA was performed using a NETZSCH STA-449-F3 instrument with Proteus-61 data analyzing software. The crystallite size of platinum particles of Pt deposited supports was estimated by analyzing X-ray diffraction (XRD) patterns of samples. XRD patterns of the samples were collected through a Rigaku Miniflex 600 X-ray diffractometer using Cu Kα (λ = 1.5418 Å) radiation and were analyzed using X’Pert HighScope Plus software. Using the crystallite size, theoretical surface area were also
estimated. The microscopic features of Pt deposited on un-/treated graphite samples was captured (supporting information, figure S1) using Scanning electron microscopy (SEM, FEI Quanta 200).

For electrochemical characterization of Pt supported graphite samples, their inks were prepared using the standard ink-recipe reported in the literature [13]. For a typical catalyst ink preparation, 10 mg of the catalyst is mixed with 5 mL of a stock solution. The stock solution is a mix of isopropyl alcohol (HPLC grade), 5 wt% NAFION® solution (Ion Power, Dupont DS21) and mili-Q water in the proportion of 20: 0.4: 79.6, respectively. For homogenization of the catalyst ink, the mix was ultrasonicated using a high-energy ultrasonic homogenizer (Hielscher UP200St, 50 W) for a minute. An aliquot of this homogenized ink (10 μl) is then drop-casted on a 5 mm (diameter) glassy carbon (GC) rotating disk electrode (RDE) from PINE® Research Instrumentation, Inc. (attached to PINE® MSR rotator). The drop on GC-RDE was dried in the air by rotating the inverted GC-RDE at 700 RPM for 30 minutes. This GC-RDE is then used as a working electrode, in a three-electrode cell. A coiled Pt wire as a counter electrode and HydroFlex® (Gaskatel, GmbH) electrode as a hydrogen reference electrode were used. The catalyst coated GC-RDE was then characterized (in the three-electrode cell) with electrochemical workstation (ZAHNER® – Zennium Potentiostat) using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) for electrocatalytic activity/durability.

The amount of Pt on GC-RDE was estimated using a conventional method where the Pt loading is calculated using Pt wt.% of catalysts (obtained from TGA/precursor-based/from-manufacturer) and the amount of catalyst drop casted on GC-RDE. On the other hand, the Pt loading on GC-RDE was also estimated by exposing it to a portable x-ray fluorescence (XRF) spectrometer. The catalysts coated GC-RDE is then inserted in 0.1 M HClO₄ electrolyte for electrocatalytic characterizations. The catalysts were characterized using different electrochemical protocols, outlined in figure 1, for estimation of different electrocatalytic performance values (electrochemical surface area (ESA), mass specific activity (MSA), surface specific activity (SSA) and durability). The high purity (99.9999%) argon and oxygen gas were used for purging the electrolyte.
Figure 1. Different electrochemical protocols used to characterize the electrocatalytic performance values of catalysts. (a) After the activation CVs, a CV for the electrochemical surface area – ESA were carried out. (b) The ORR activity i.e. mass specific activity – MSA and surface specific activity – SSA were estimated by analyzing the LSV measured in argon (LSV for ORR activity background) and in oxygen (LSV for ORR activity) purging electrolyte with RDE rotating at 1600 RPM. (c) Finally, the durability of the catalyst (percentage of original ESA) as a function of stress cycles was estimated by carrying out CVs for ESA after every 250 stress CVs. The high purity (99.9999%) argon and oxygen gas were used for purging the electrolyte.

3. Results and discussion

The current fuel cell technology lacks the durability criterion, which is a major reason for this technology not yet being fully commercialized. The durability issues in fuel cells rise due to corrosion of the carbon support which is used to reduce the amount of Pt metal by dispersing it on high surface area carbon support for increased Pt utilization. The commercial catalyst uses carbon black (amorphous/disordered carbon) as support for Pt, as it offers a large number of defect sites, which eventually act as nucleation sites for Pt attachment/distribution, thereby enhancing the Pt utilization. However, these defects sites in carbon black are also the sites where carbon corrosion starts and leads to degradation of performance of carbon
supported Pt catalysts. It is well known that the graphitic (ordered) carbon is more resistant to 
electrooxidation and therefore by increasing the amount of ordered carbon in the carbon-based support 
the corrosion of support can be reduced [14]. In this investigation, we prepared a support by starting from 
a low-cost graphite sample and by wet-ball-milling improved its surface area. The wet-ball-milling insured 
the retention of graphitic carbon while achieving a relatively higher surface area.

3.1. Physical and electrochemical properties of supports

The low-cost graphite (SG20) sample was wet milled with a variety of wetting media (table 1). The 
differently milled samples were initially characterized using BET isotherms and analyzed to estimate the 
BET surface area. Figure 2 shows the sorption isotherms of wet-milled low-cost graphite samples. The 
estimated BET surface area indicates that the Tolu-G2 samples exhibited the relatively high surface area (73 
\( \text{m}^2/\text{g} \)) among the wet milled low-cost graphite samples. The un-milled low-cost graphite samples exhibited 
the BET surface area of 20 \( \text{m}^2/\text{g} \). Among the ball-milled samples, Tolu-G2 sample along with the SG20 
sample was further investigated.

![Figure 2. Sorption isotherms for wet-milled low-cost graphite used to estimate the BET (specific) surface area. The respective BET surface area is also listed in the inset.](image-url)
Prior to the characterization of Pt deposited supports, the inks of SG20, IG100, Graphene and IG300 support samples were investigated for their durability using accelerated stress test (AST) protocols (figure 1c) and compared their original CVs with that of after 5000 stress cycles.

In figure 3, the Graphene support showed the largest deviation from its original CV, opposed to the graphite support samples. Usually, corrosion/degradation of carbon supports increase with their specific surface area and the interlayer spacing of graphitic planes [15]. It is therefore interesting that even though the Graphene support had less surface area than that of IG300 support, it showed a relatively larger deviation from its original CV after stress cycles. The IG300 sample has the surface area of about 300 m²/g.

In general, high surface area powders consist of finer/porous particles and has more edges (defects). In graphite samples, these edges are more prone to oxidation during AST and therefore it is considered that

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Figure 3. Comparison of original (0 stress cycles) CVs with that of after stress (> 5000) CVs for SG20, IG100, Graphene and IG300 support materials.
as the surface area of graphite samples are increased their stability is decreased which leads to increased deviation in their CVs from the original CV after AST. Both of the supports with relatively low surface area, i.e. SG20 and IG100, showed a similar and relatively small deviation from its original CV after stress cycles, indicating its robustness as support in acidic media.

3.2. Microstructural properties and Pt loadings of graphite supported Pt samples

Figure 4 shows the recorded XRD patterns of Pt deposited supports. The peak width (full width at half maximum – FWHM) of Pt (111) peak used to estimate the average crystallite size (L) of the Pt-nanoparticles using the Scherer’s formula \(L = \frac{(0.9 \times \lambda)}{(\beta \times \cos(\theta))}\); where \(\lambda\), \(\theta\) and \(\beta\) are the X-ray wavelength, the diffraction angle and the FWHM, respectively. Smallest Pt crystallite size (2 nm) among Pt deposited graphite sample was obtained for the sample prepared using the solvothermal technique for 20 wt.% of Pt loading. Table 3 shows crystallite size of Pt (estimated from XRD patterns) and Pt wt.% loading (obtained from TGA) in graphite supported Pt samples. Typical SEM images of Pt deposited on treated/untreated samples polyol method are shown in supporting information (figure S1).

As can be seen in table 3, Pt deposited using modified polyol technique on graphite support (PtSG20, PtSG20-trt, PtIG100 and PtIG300) did not reach the desired loading amount (i.e. 20 wt.%), which is attributed to the lack of nucleation sites on as received graphite samples. The wet-milled and PCA treated support, i.e. SG20-trt, upon Pt deposition showed increased (almost three-fold) Pt loading compared to its untreated counterpart (SG20) support. This enhancement is attributed to improved nucleation sites in treated support.

The solvothermal technique which was optimized for well-controlled Pt loading and its distribution over support [12] was used to deposit the two different Pt loadings, namely, 20 wt.%, and 40 wt.% and resulting Pt loading was about 23.0 wt.% and 43.9 wt.%, respectively.
Figure 4. XRD patterns of Pt deposited graphite supports.

Table 3. Crystallite size of Pt (estimated from XRD patterns – figure 3) and Pt wt.% loading (obtained from TGA) in graphite supported Pt samples. \(^{a}\) Wt.% estimated by TGA. \(^{b}\) Provided by collaborator and confirmed by TGA. \(^{c}\) Wt.% based on precursors. \(^{d}\) Commercial-wt.% provided by the manufacturer.

<table>
<thead>
<tr>
<th>Sample IDs</th>
<th>Crystallite size (nm) of Pt</th>
<th>Pt wt.% loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtSG20</td>
<td>3.6</td>
<td>4.91 (^{a})</td>
</tr>
<tr>
<td>PtSG20-trt</td>
<td>4.3</td>
<td>14.77 (^{a})</td>
</tr>
<tr>
<td>PtSG20-trt23</td>
<td>2.0</td>
<td>23.0 (^{a, b})</td>
</tr>
<tr>
<td>PtSG20-trt42</td>
<td>2.5</td>
<td>43.9 (^{a, b})</td>
</tr>
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</table>
### Table:

<table>
<thead>
<tr>
<th>Sample</th>
<th>ESA</th>
<th>SSAa</th>
</tr>
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<tbody>
<tr>
<td>PtIG100</td>
<td>3.6</td>
<td>7.58</td>
</tr>
<tr>
<td>PtGraphene</td>
<td>3.7</td>
<td>18.51</td>
</tr>
<tr>
<td>PtIG300</td>
<td>3.8</td>
<td>18.50</td>
</tr>
<tr>
<td>Pt10IG300</td>
<td>20.53</td>
<td></td>
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<tr>
<td>Pt20IG300</td>
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<td>56.15</td>
<td>40</td>
</tr>
<tr>
<td>HiSpec9100</td>
<td>1.8</td>
<td>57</td>
</tr>
<tr>
<td>BASF</td>
<td>2.2</td>
<td>20</td>
</tr>
</tbody>
</table>

Though CS was a relatively easier technique to deposit the Pt on the support with no post-treatment required, the crystallite size of platinum obtained using this technique was noticeably larger (sharper XRD peaks) than that of obtained using other techniques. As CS is an exothermic reaction and known for fast synthesis at low temperature [16], the observed larger Pt crystallite can be the result of the inherent characteristic of high activity of Pt, where it tends to get agglomerated at moderately high temperature. The CS has the potential to deposit Pt on support efficiently but needs optimization of its preparative parameters so only adequate energy for nucleation of Pt will be provided and not for its growth.

### 3.3. Electrochemical characterization of Pt deposited support samples

#### 3.3.1. ESA, MSA and SSA estimations

The Pt deposited samples were initially investigated for their electrochemical surface area (ESA) using the electrochemical protocol outlined in figure 1a. Loading normalized CVs and estimated ESA values of each of samples were compared with state-of-the-art commercial electrocatalysts i.e. BASF and HiSpec9100 (figure 5). In particular to Pt nanoparticles, different features observed in CVs can be attributed to different Pt facets available in the materials under investigation. The detailed investigation on relation between CV
features and Pt facets, their reconstruction and various processes occurring during the potential cycling as well as effect of cleanliness of Pt surfaces can be found in literature [17, 18].

Figure 5. Loading normalized CVs and values are compared to that of the state-of-the-art commercial electrocatalysts i.e. BASF and HiSpec9100. (a) Loading normalized CVs and (b) estimated ESA values of each of graphite supported Pt samples. For reference, the theoretical surface area estimated using the Pt crystallite size is also shown in (b).

It was found that the estimation of the actual amount of Pt loading on the electrode is highly important while estimating the electrocatalytic performance values of electrocatalysts coated on the RDE.

Conventionally, it is considered that the TGA based catalyst loading gives an accurate estimation of catalyst loading on carbon-based support and using mere calculation with amounts of catalyst in ink preparation with weight/volume of drop casted, one can estimate the Pt loadings on the electrode. Our finding suggests that this methodology leads to erroneous results [19]. Here, for example in figure 5, the PtSG20 (PtSG20-trt) sample when investigated with conventional loading estimation approach resulted in a high ESA value
of 81.27 (66.48) m$^2$/g which is even higher than that of its theoretical surface area, which is 68.61 (53.82) m$^2$/g. To avoid such ambiguity and overestimation, we estimated Pt loading on the electrode using an XRF spectrometer, which was direct and simple. The electrocatalytic performance values reported here includes the values estimated using either, i.e. conventional and XRF based approach [19].

The data are grouped in three categories, namely, the first group consists of Pt deposited on untreated/treated low-cost graphite support, the second group consists of Pt deposited on commercial high-surface area graphite/graphene supports and the third group consists of Pt deposited on commercial high-surface area graphite IG300 using CS. In the first group for treated support i.e. SG20-trt, a trend of decrease in ESA with an increase in Pt loading is observed, suggesting decreased Pt utilization for higher loadings on SG20-trt support. In the second group of commercial graphite/graphene support relatively low surface area graphite support (IG100) exhibited relatively high ESA value and attributed to optimum catalyst utilization. The high surface area (SA) of graphite support can be a major contributor for better ESA, however, surface area higher than optimum value can block the active sites (Pt surfaces) of catalyst by layers/surfaces of support materials itself, most likely in graphite samples. Therefore, a compromise between SA and ESA is desired and based on this study one can tell the graphite support with SA about 100 m$^2$/g (IG100) can be the best choice. However, authors believe that a detailed study on this aspect is necessary to confirm this hypothesis. Among the graphite-supported Pt samples, ESA values of PtSG20-trt (50.60 m$^2$/g), PtSG-trt23 (48.30 m$^2$/g) and PtIG100 (42.06 m$^2$/g) sample are comparable to the ESA value of commercial BASF electrocatalyst (46.87 m$^2$/g). These ESA values close to the ESA value of commercial electrocatalyst is a promising factor.

The samples in third group (Pt10IG300, Pt20IG300 and Pt40IG300) showed very low ESA values. As the sample was prepared using an exothermal synthesis method (CS), the decomposition of carbon and Pt agglomeration (large crystallite sizes) might have taken place during the synthesis and affected their electrochemical performance i.e. ESA.
The ORR activity of Pt deposited graphite samples was estimated at 0.9 vs RHE using thin film rotating disc electrode (TF-RDE) experiment. The background and iR corrected ORR LSV recorded with RDE at 1600 rpm is shown in figure 6. The theoretical diffusion limited current at potentials lower than 0.6 vs RHE in O₂ saturated 0.1 M HClO₄ and electrode with a geometrical active area of 0.196 cm² should be about -5.8 mA/cm² [20]. The diffusion limited current (I_{lim}, at 0.4 V vs RHE) of PtSG20 and PtSG20-trt sample is -5.2 and -5.6 mA/cm², respectively while I_{lim} for Pt deposited using CS is > -5 mA/cm². For other Pt deposited graphite/graphene samples, I_{lim} equals the theoretical diffusion limited current. Except Pt deposited using CS, all other samples show I_{lim} within the range of theoretical diffusion limited current and are in accordance with the guidelines for a comparative investigation [20].

Comparison of LSVs in figure 6a reveals that PtIG100 and PtSG20-trt23 was showing the better ORR kinetics than that of all the other graphite supported Pt samples and it also showed an LSV profile which is at the middle of state-of-the-art commercial electrocatalysts. For the Pt deposited on commercial high-surface area graphite (IG300) and graphene support, the LSV curves are almost overlapping. Figure 6b shows the MSA and SSA values obtained by dividing the kinetic current, I_k, at ~0.9V vs RHE by Pt loading and ESA, respectively. Among the investigated samples except for PtIG300, all other samples showed better ORR activity than that of the commercial HiSpec9100 catalyst. In this investigation, the PtGraphene sample showed the highest ORR activity other than BASF commercial electrocatalyst.

For reference, SSA and MSA of unsupported Pt black is 198 µA/cm² and 0.052 A/mg, respectively [21]. In this investigation all the supported samples, except CS synthesized samples, showed better SSA/MSA values than that of unsupported Pt black [21] and attributed to relatively better utilization of active surfaces of Pt catalyst. In figure 6a (first group), it can be clearly seen that as the Pt loading in catalyst is increased current value at 0.9V is increased. However, even the PtSG20-trt42 sample has the higher Pt loading (42 wt.%) current value at 0.9V was comparable to that of BASF catalyst suggesting that in PtSG20-trt42 most of the Pt were not accessible for catalytic activities. Similar attribution can be assigned to the PtIG300 and
PtGraphene samples (with ~18.5 wt.% Pt) which showed relatively less current values at 0.9V than that of PtIG100 (7.8 wt.% Pt) sample. On the other hand, as CS samples did not showed $I_{lim}$ within the range of theoretical diffusion limited current [20], such attribution for comparison will be misleading and therefore avoided.

Figure 6. Electrode (geometric) area normalized LSVs and MSA/SSA values are compared to that of with the state-of-the-art commercial electrocatalysts i.e. BASF and HiSpec9100. (a) Electrode area normalized LSVs and (b) estimated MSA (A/mg)/SSA (mA/cm$^2$) values of each of graphite supported Pt samples. SSA values are independent of loading values.

3.3.2. The durability of Pt deposited samples

The main objective of this investigation was to screen the supports for higher durability. The supported electrocatalyst with better ORR activity along with higher durability is advantageous in point of view of the performance stability of the fuel cells.
Though the carbon corrosion occurs through the electrochemical oxidation of carbon at 0.207 V vs RHE [22], carbon's thermodynamic instability, carbon corrosion during normal fuel cell operation remains negligible at potentials lower than 1.1 V vs. RHE, due to its slow kinetic [23]. Carbon corrosion is believed to be promoted by the transition between start/stop cycle and by fuel starvation in fuel cells. According to Reiser et al. [24], the potential excursions on the cathode can exceed 1.5V due to an H2/air front in the anode compartment during shutdown/startup thus inducing the carbon corrosion. Therefore, the durability of the Pt deposited support is investigated using the protocols outlined in figure 1c, in which the catalyst coated electrode is (stressed) cycled between 1 to 1.6 V for more than 6000 cycles in an Ar saturated (fuel starved condition) electrolyte. These cycling used to simulate the fuel cell start/stop conditions and evaluate the long-term durability. The ESA was tracked after every 250 cycles to estimate the degradation in electrocatalytic performance of the catalyst. Figure 7 shows the degradation of normalized initial ESA of investigated samples as a function of number of stress cycles.

![Figure 7](image)

**Figure 7.** Durability and retained ESA % values after 7500 stress cycles are compared to that of with the state-of-the-art commercial electrocatalysts i.e. BASF and HiSpec9100. (a) The durability of normalized ESA as a function of number of stress cycles and (b) values of retained ESA % after 7500 stress cycles.
All the graphite-supported samples showed higher stability than that of both the investigated commercial electrocatalyst. Apart from samples prepared by Pt deposition using CS method (i.e. Pt10IG300, Pt20IG300, and Pt40IG300), PtSG20 and PtSG20-trt showed higher durability than that of high-surface-area graphite supported Pt. Both the Pt deposited on commercial high-surface area graphite/graphene samples (PtIG100, PtGraphene and PtIG300) using modified polyol technique and Pt deposited on SG20-trt samples (PtSG20-trt23 and PtSG20-trt42) using solvothermal technique showed almost similar durability (plots appear as a single cluster of lines – figure 7).

In figure 7b, for low cost graphite support (PtSG20, PtSG20-trt, PtSG20-trt23 and PtSG20-trt42) as Pt loading is increased from 4.95% for PtSG20 to 43.9% for PtSG20-trt42 sample, the stability of catalyst i.e. retention of ESA (%) is decreased after 7500 stress cycles from 76% for PtSG20 to 67% for PtSG20-trt42. More loading might increase more contact sites between the catalyst and support and therefore catalyze the oxidation of support leading to faster support degradation. This is in line with the observation by Kou et. al. [25], where they suggest that increased Pt loading on the support can cause faster oxidation of support. However, in case of high-surface-area commercial graphite support samples (PtIG100 and PtIG300), though the Pt loading is increased from 7.58 wt.% for PtIG100 to 18.50 wt.% for PtIG300, their degradation profile remains unaltered.

Among CS samples (i.e. Pt10IG300, Pt20IG300 and Pt40IG300), Pt40IG300 samples retained the ESA more than 100%. This can be attributed to the synthesis condition employed (>450°C), where it can be expected that most of graphite support might have decomposed and contains relatively large fraction of Pt on graphite support. As the AST was focused to accelerate the carbon corrosion, high Pt content in Pt40IG300 was initially got activated (increased ESA i.e. > 100%). As Pt40IG300 had very little or no carbon/graphite left to oxidize it sustained the ESA for 7500 stress cycles without degradation. This effect becomes milder for samples with relatively less initial Pt wt% (Pt20IG300 and Pt10IG300) and relatively high carbon/graphite content.
The disordered carbon act as starting points of its corrosion when used in PEMFC atmosphere and are the main reason for insufficient durability of PEMFCs. However, the graphitic (ordered) carbon are more resistant to oxidation and when used as supports for Pt in PEMFCs, as observed here, shows improved stability. The wet-milling with planetary ball-milling generated slip-deformation in graphite (stacked carbon layer structure) allowing generation of more surface area (by separating stacked layers) and without destroying the graphitic carbon. At the same time a slight increase in the fraction of edges as disordered carbon is possible. This is evident in figure 7, where the ESA% of Pt supported on graphite samples showed relatively less degradation and retained 67%-76% of original ESA compared to that of the commercial catalyst which retained 40-46% of its original ESA.

The best electrocatalysts among the investigated samples can be the one which shows relatively good ORR (MSA) activity and high durability. Figure 8 shows the comparison of electrocatalytic performance values sorted in ascending order of MSA values. The PtSG-trt23 and PtGraphene sample showed best performance value based on the criteria. However, in commercialization point of view, the PtSG-trt23 sample is more promising among the two, since the support used for PtSG-trt23 sample is low-cost graphite treated with low-cost and scalable wet-ball-milling.
Figure 8. Comparison of electrocatalytic performance values (ESA, MSA, and durability – ESA% after 7500 stress cycles) sorted in ascending order of MSA values.

4. Conclusions

In this investigation, we screened different graphite materials with varying surface areas as support for Pt-based fuel cell cathode electrocatalysts and evaluated for electrocatalytic performance by comparing it with state-of-the-art commercial electrocatalysts (i.e. BASF and HiSpec9100). The objective of the investigation was to find low-cost, alternative support materials with improved durability and high activity. Commercially available (high-surface area) graphite (and graphene) along with pretreated low-cost graphite supports showed better durability than that of both the commercial electrocatalyst. For an optimum balanced performance (very high durability along with good ORR activity) of fuel cell cathode electrocatalysts, the treatment outlined in this investigation can be applied to low cost (low surface area) graphite support to modify their surface for Pt deposition. Our investigation shows that the low-cost graphite can be used to create a support for Pt-based cathode electrocatalyst thereby obtaining comparable ORR activity to that of commercial electrocatalysts and significantly higher stability. Furthermore, it was observed that with increased Pt loadings the durability of graphite support decreased.

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