

**Figure 1.** A schematic showing the inner components and operations of a direct methanol fuel cell.

performance of catalyst technology but has also added to the cost of production.<sup>7</sup>

The next step in achieving the commercialization of the direct methanol fuel cell would be to continue decreasing the price of the electrocatalyst through decreased platinum mass loading and finding an alternative to current carbon nanotechnology as they are expensive.<sup>8</sup>

One method of decreasing the cost of the electrocatalyst and its production is the utilization of materials derived from common waste. Value added materials such as biochar and activated carbons have been investigated as support materials.<sup>9</sup> Biochar is a high carbon content solid material produced when organic waste undergoes pyrolysis.<sup>10</sup> Although biochar and activated carbons have not seen much application in direct methanol fuel cells there are other areas of application where they have successfully been used as an immobilization supports for metallic nanoparticles.<sup>11</sup> Due to their success as a support material in adjacent fields, it is clear that biochar should be investigated for its catalytic properties and its potential application in direct methanol fuel cells as a support material.

## 2. INTRODUCTION TO FUEL CELLS

Fuel cells are electrochemical devices that convert the stored chemical energy in the fuel to usable electrical energy. Fuel cells come in many variations; the differences between the fuel cell types are the electrolyte and electrocatalysts. Some examples of the different variants are the proton exchange membrane fuel cell (PEMFC), direct alcohol fuel cell (DAFC), solid oxide fuel cell (SOFC), alkaline fuel cell (AFC) and molten carbonate fuel cell (MCFC).<sup>12</sup>

Fuel cells are split into two groups; the first are low temperature fuel cells. Two examples of low temperature fuel cells are the proton exchange membrane fuel cell and the direct alcohol fuel cell. The proton exchange membrane fuel cell (PEMFC) uses hydrogen gas as its fuel and works in a temperature range of 40 to 90 °C. PEMFCs have a theoretical voltage of 1.18 V. The PEMFC uses a platinum catalyst at both the anode and cathode, while DAFC uses a platinum-ruthenium alloy catalyst at the anode to prevent carbonyl formation and a platinum catalyst at the cathode. Direct alcohol fuel cells use alcohols such as methanol and ethanol as fuel. They operate at the same temperature as the proton

exchange membrane fuel cell and have similar theoretical voltages. The direct alcohol fuel cells however are a more viable option for small scale application than the PEMFC as it does not need an extensive infrastructure to store its fuel which is needed for the hydrogen gas.<sup>13</sup>

The second group of fuel cells is called high temperature fuel cells. Two examples of high temperature fuel cells are molten carbonate and solid oxide fuel cells. Both fuel cells have an operating temperature more than 600 °C with the solid oxide fuel cell operating up to 1000 °C. Both SOFC and MCFC use nickel-based catalysts and use purified coal gas or natural gas as fuel. They offer a lower theoretical voltage of 1.11–1.16 V and are more suited for stationary energy generation.<sup>13,14</sup>

Of the above-mentioned fuel cell types, direct alcohol fuel cells (DAFC) show the greatest promise for small device applications as their power output is not high enough for large power applications. Alcohols are easier to transport, operate at lower temperatures, and require less intense storage requirements in comparison to the hydrogen used in proton exchange membrane fuel cells. Alcohols also offer a higher energy density and are currently produced using renewable methods. Of the alcohols used in direct alcohol fuel cells (methanol, ethanol, and ethylene glycol), methanol is seen as the most ideal fuel. This is due to its low molecular mass compared to other alcohols and its high energy density.<sup>15</sup>

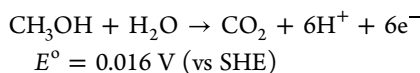
It is the aforementioned characteristics of methanol and the simplistic design of the direct methanol fuel cell and its ease of operation that make DMFCs very appealing to the commercial market.<sup>16</sup>

**2.1. Direct Methanol Fuel Cell (DMFC).** Direct methanol fuel cells directly convert the stored chemical energy of methanol into usable electrical energy.<sup>17</sup> DMFCs are seen as the most promising alternative power sources for portable small-scale electrical devices. Direct methanol fuel cells have potential application in small scale portable electronic devices such as phone chargers, LEDs, and sensors.<sup>18</sup> They gained popularity due to the high-energy density of methanol (4800 Wh L<sup>-1</sup>), a theoretically high energy conversion efficiency of 96%, and a thermodynamic potential of 1.21 V when operating at room temperature. Methanol is preferred as the fuel of choice as it is currently produced using sustainable renewable resources and is easier to store compared to hydrogen, which is

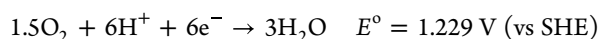
used in polymer electrolyte membrane fuel cells that require extensive fuel delivery and storage systems.<sup>3,19,20</sup>

Direct methanol fuel cells consist of a proton exchange membrane (PEM), external circuit, gas diffusion layers (GDL), bipolar plates (BPP), and anode and cathode electrodes which are made of a catalyst material coated on a carbon support (Figure 1). DMFCs operate as follows; the fuel feed system feeds methanol and water through field flow plates to the anode on one side of the fuel cell and oxygen, in the form of air from the environment, to the cathode on the other side of the fuel cell. The methanol undergoes oxidation at the anode, which consists of a carbon support coated by a platinum-ruthenium catalyst. The platinum-ruthenium electrocatalyst causes the methanol and water mixture to dissociate into carbon dioxide (CO<sub>2</sub>), protons (H<sup>+</sup>), and electrons (e<sup>-</sup>). The gas diffusion layer then transports the electrons and protons to the bipolar plate. The gas diffusion layer also transports the carbon dioxide produced out of the fuel cell through the exhaust on the anode side. The proton exchange membrane made from a fluorocarbon membrane called Nafion which only allows cations to flow through the membrane therefore, only the protons can flow across the electrolyte membrane to the cathode and the electrons have to flow through the external circuit producing a usable electrical current.<sup>15</sup> The protons and electrons recombine at the cathode to form hydrogen atoms. The cathodic electrocatalyst causes the reduction of oxygen in which it reacts with the hydrogen atoms to form water. The water and the remainder of the gas taken in from the environment flow out at the exhaust on the cathode side of the fuel cell.<sup>21</sup>

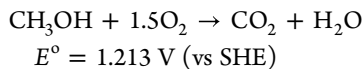
The reaction at the anode is



The reaction at the cathode is



The overall cell reaction is



<sup>8,19,22</sup>

Despite the attention direct methanol fuel cells have gained as an alternative method of environmentally friendly energy generation. Its delayed commercialization is due to the fact that current DMFCs are not achieving theoretical performance figures such as theoretical energy conversion efficiency of up to 96%. The underperformance of these fuel cells are linked to slow methanol oxidation reaction (MOR) kinetics at the anode, and this is due to current electrocatalyst being the limiting factor.<sup>19,20</sup>

**2.2. Fuel Cell Electrocatalysts.** The electrocatalyst plays a very pivotal role in DMFCs as they are responsible for the methanol oxidation reaction (MOR) at the anode and the oxygen reduction reaction (ORR) at the cathode which are the basis on which the direct methanol fuel cell generates energy.<sup>23</sup> The current electrocatalysts used in industry consist of two parts: the catalytic material and the support. The current catalysts used in industry are a platinum-ruthenium (Pt-Ru) catalyst supported by carbon black for the anode and a platinum catalyst supported by carbon black (CB) at the

cathode. Platinum is used as the catalytic material of choice as it offers high activity to both the methanol oxidation and oxygen reduction reactions.<sup>24</sup>

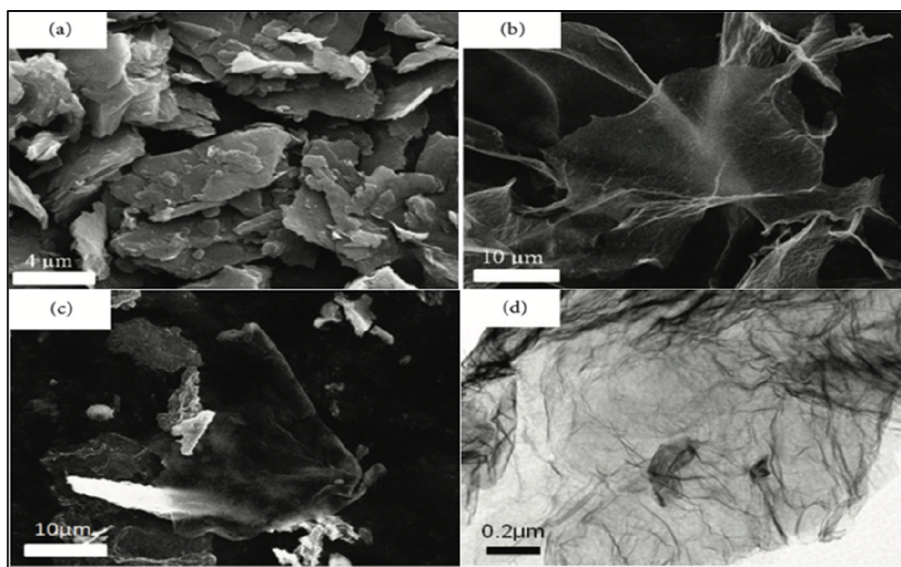
The reason a bimetallic catalyst such as the platinum-ruthenium alloy is used at the anode is to prevent catalyst poisoning which platinum is very prone to when in the presence of carbonyl groups (CO). Catalyst poisoning occurs when a molecule or atom occupies one of the active sites on the catalytic material rendering it unable to partake in the reaction. The presence of ruthenium prevents this as the ruthenium forms an alloy with platinum in such a way that ruthenium prevents the carbon monoxide which is formed during the oxidation reaction from reaching the active sites of the platinum particles.<sup>14,25,8</sup>

Although platinum offers high activity toward the methanol oxidation reaction and the oxygen reduction reaction, it limits the fuel cell from reaching its theoretical potential as it has poor stability under the acidic environment found in the fuel cell stack. The poor stability leads to chemical corrosion and agglomeration of the catalytic material to which metals from the platinum metal group are prone. Agglomeration is defined as the formation of clumps of catalytic material, which causes the deactivation of active sites lowering the total electroactive surface area. Scientist have attempted to combat agglomeration by incorporating a carbon skeletal structure called a support to which the platinum metal binds.<sup>26</sup> The current support used in industry is a material called carbon black, which is produced from the combustion of heavy petroleum fuel oils.

**2.3. Supports.** Supports play a very crucial role in how well a catalyst performs as they alter characteristics such as stability, electrochemical activity, and durability. For a support to be considered a good candidate it has to have the following characteristics: high electron conductivity, be stable in both acidic and basic environments to prevent chemical corrosion, and have a high specific surface area and good porosity.<sup>23,27</sup> The main issue with carbon black is that it is prone to chemical corrosion, which leads to the loss of catalytic activity and stability. This has forced scientists to look at other carbon-based materials as carbon offers good characteristics in all the aforementioned criteria that make a good support. Therefore, scientist have started to look at carbon nanomaterials as they offer high stability in acidic and basic environments due to their structure, high surface area per gram of material for good dispersion of the catalytic material and high electron conductivity.<sup>27</sup>

**2.3.1. Carbon Nanomaterials.** Carbon nanomaterials come in many variations due to the many hybridization states that are possible. Of all the three sp<sup>3</sup>-hybridization states, it was found that carbon nanomaterials of the sp<sup>2</sup> hybridization state fared best as their hybridization offers strong structural rigidity, high resistance to chemical corrosion, and good surface areas. An example of sp<sup>2</sup> hybridized carbon nanomaterials is graphene sheets.<sup>28,29</sup>

Although carbon nanomaterials offer great upsides as an electrocatalyst support, they too have downsides. Graphene sheets are prone to stacking which decreases the overall surface area available for the deposition of catalytic material and the need for functionalization with strong acids to integrate carbonyl functional groups into the carbon skeleton to form graphene oxide which could change the morphology of the sheet.<sup>30</sup> However, there are methods to prevent the stacking of graphene sheets such as the low temperature exfoliation method done by Loryuenyong et al., 2013.<sup>31</sup> This method

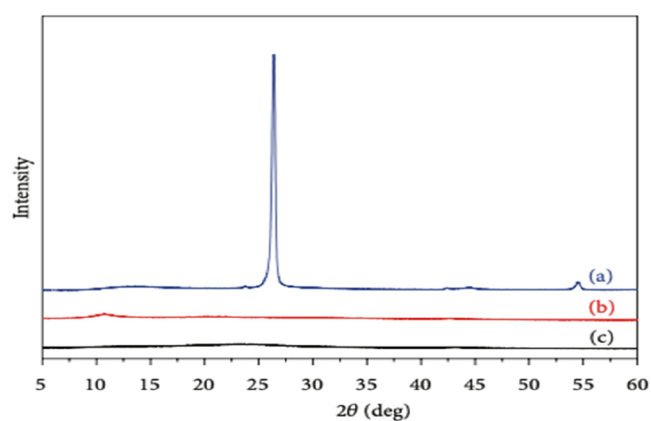


**Figure 2.** (a-c) HR-SEM images: (a) pristine graphite, (b) exfoliated GO, (c) reduced graphene oxide. (d) HR-TEM image: reduced graphene oxide. Reproduced with permission from ref 31. Copyright 2013 Vorrada Loryuenyong et al., Hindawi.

involves heating and ultrasonating graphite oxide, which was prepared using a modified Hummers method. The ultrasonication causes the elimination of oxygen functional groups and an increase in interlayer spacing between the layers which was confirmed by using XRD, FTIR, and HR-TEM.<sup>31</sup>

The difference in morphology between pristine graphite, exfoliated graphene oxide, and reduced exfoliated graphene oxide can be seen in Figure 2a-c. In image a the flake like nature of pristine graphite can be seen compared to the thin transparent individual sheet like nature of the exfoliated graphene oxide. This layer sheet like nature of exfoliated graphene oxide shows an increase in total surface area. The SEM and TEM images (c,d) of reduced graphene oxide show that the sample possesses a large amount of wrinkling in the sheets as seen by the high contrast areas in the TEM images.<sup>31</sup>

The sharp peak,  $2\theta = 26.38^\circ$ , seen in the XRD spectrum of pristine graphite (Figure 3 trace a), is due to the high level of layer organization. This peak relates to an interlayer spacing of 0.34 nm. The intensity and angle of the peak,  $2\theta = 10.8^\circ$ , decrease once the graphite undergoes the modified hummers



**Figure 3.** XRD results of (a) pristine graphite, (b) exfoliated GO, (c) reduced exfoliated graphene oxide. Reproduced with permission from ref 31. Copyright 2013 Vorrada Loryuenyong et al., Hindawi.

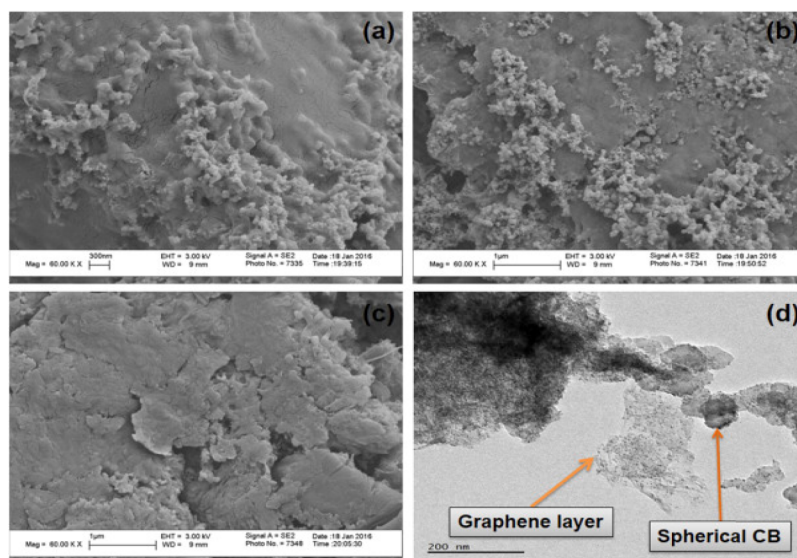
method and exfoliation to show a decrease in layer organization and an increase in layer spacing to 0.82 nm.<sup>31</sup>

**2.3.2. Carbon Nanocomposites.** Although methods such as exfoliation exist to prevent stacking, scientists have looked at other methods to prevent stacking. One such method is the use of hybrid supports, also known as nanocomposites. A nanocomposite is a support consisting of two or more monosupports. The use of hybrid supports allows the nanomaterials present to work in a synergistic manner. The use of hybrid supports results in an increase in reaction rates, higher stability to chemical corrosion, increased electron conductivity, and improved total surface area.<sup>32</sup>

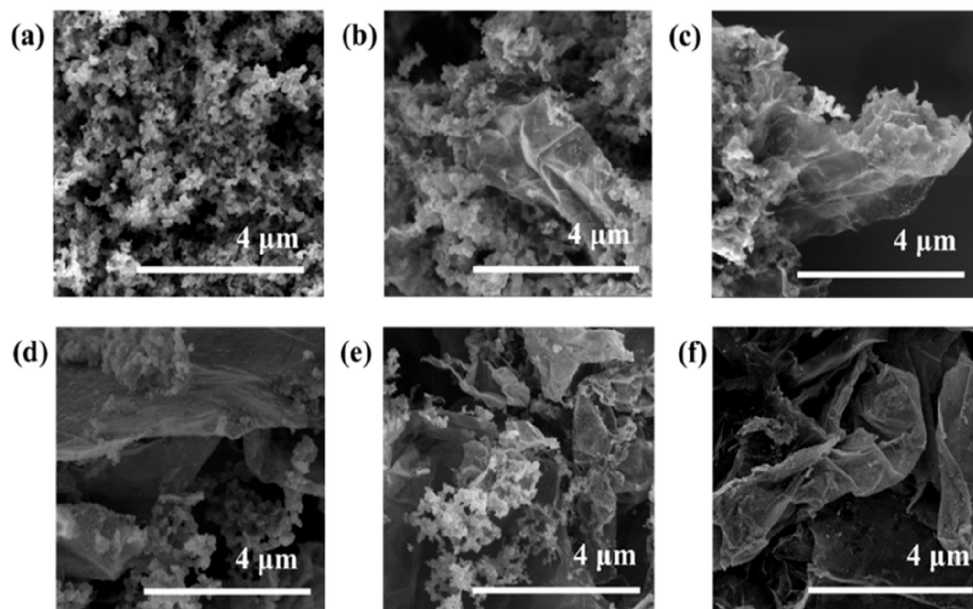
There are many examples of recent studies in which scientists have used nanocomposite supports to achieve increased catalyst characteristics. One example of how nanocomposites are used to overcome the stacking issue of graphene layers is the incorporation of carbon black done by İşikel Şanlı et al., 2017.<sup>33</sup> They used a hybrid support of reduced graphene nanoplatelets and carbon black in different ratios. The carbon black behaves as a separator between the platinum impregnated graphene layers such that they cannot form a graphite-like structure minimizing the platinum active sites available for catalyst which was confirmed using both high resolution transmission electron microscopy and scanning electron microscopy (Figure 4).<sup>33</sup>

A second example of how a nanocomposite was used to overcome the shortcomings of one of its constituents is presented in Ji et al., 2021.<sup>34</sup> In their research they combined the characteristics of reduced chemically exfoliated graphene and carbon black to improve the stability, electrochemical activity, and durability of the platinum hybrid supported electrocatalyst (Pt/rEGO-CB) in comparison to a platinum electrocatalyst supported by just carbon black (Pt/CB) when used in a low temperature hydrogen fuel cell (Figure 5).<sup>34</sup>

The SEM imaging seen above demonstrates how the introduction of the reduced exfoliated graphene oxide to the supports reduces the amount of agglomeration that occurs with carbon black supports due to the van der Waals forces between carbon black particles. This will help to create a larger surface area for catalytic material deposition. It can also be seen that



**Figure 4.** HR-SEM (A-C) and HR-TEM (D) images of the Pt/rGO/CB electrocatalyst with different rGO:CB ratios. (A) 25:75. (B) 50:50. (C) 75:25. HR-TEM of 50:50. Reproduced with permission from ref 33. Copyright 2016 Elsevier.



**Figure 5.** SEM imaging of (a) Pt/CB, (b) Pt/rEGO1-CB4, (c) Pt/rEGO2-CB3, (d) Pt/rEGO3-CB2, (e) Pt/rEGO4-CB1, and (f) Pt/rEGO. Reproduced with permission from ref 34. Copyright 2021 Elsevier Ltd.

the presence of carbon black decrease the amount of stacking which takes place in the reduced exfoliated graphene oxide layers.<sup>34</sup>

**2.4. Alternative Catalyst Support Materials.** A large factor that prevents widespread commercialization is the price of production. To produce an electrocatalyst that will be able to perform well requires high quality materials which can become quite expensive due to the high price of the catalytic metals used or the fairly novel nanocarbon supports which are currently produced using very costly methods.<sup>35</sup> One solution to decreasing the price of the electrocatalyst is finding cheaper alternatives for the carbon supports such as seen in the work done by Kalyani, Anitha and Darchen, 2013.<sup>35</sup> These authors looked at using activated carbon (G-AC) produced from grass biomass as a support for a platinum electrocatalyst for use in

water electrolysis. The results of their study showed that the platinum electrocatalyst (Pt/G-AC) was comparable to commercially available platinum electrocatalysts.<sup>35</sup>

Gan et al. 2019,<sup>36</sup> conducted a study which used carbon nanofibers derived from cellulose to immobilize cobalt ferrite for its use in water treatment. The cobalt ferrite supported by carbon nanofibers was then tested for its catalytic activity toward peroxymonosulfate. Their work found that the incorporation of the carbon nanofibers increase the activity of cobalt ferrite by reducing agglomeration and increasing the electron transfer rate.<sup>36</sup>

The research work mentioned above shows that activated carbon derived from biomass has a large potential for widespread application in fuel cell technology as it possesses highly favorable characteristics such as good electrochemical

activity, great stability, high porosity, and large specific surface areas and can be produced at a much cheaper price when compared to many other carbon nanomaterials.<sup>35–37</sup>

### 3. AGROWASTE BIOMASS AND ITS PRODUCTS

The world produces over one billion tons of organic waste in the form of agrowaste biomass each year. With the lack of proper waste management techniques and appropriate facilities, a large portion of the waste goes unutilized and ends up being burnt which produces a large amount of carbon dioxide further contributing to global warming. Scientist have therefore started looking into ways in which to utilize the waste such as the production of biochar, biofilms, and other carbon products.<sup>38</sup>

One product of biomass waste that gained large interest is the conversion of biomass waste into activated carbon due to its high tunability, which allows it to be used in a variety of applications. Activated carbons consist of fused aromatic rings, to which functional groups are bound. They are known for being good absorbents for both organic and inorganic materials in most environments. They possess large surface areas with well organized macro-, meso-, and micro-pore structures, great stability in a wide variety of environment conditions, and great conduction properties.<sup>39,40</sup>

There are many examples of methods in which different biomasses have been converted into activated carbon that possess different qualities. Danish and Ahmad, 2018, produced activated carbon using wood biomass as its precursor via a pyrolysis method which was then tested for its wastewater cleaning capabilities.<sup>40</sup> Adinata, Wandaud, and Aroura, 2007,<sup>41</sup> used palm shell biomass as the precursor to the activated carbon which they then tested to observe how well it adsorbed carbon dioxide. The results showed that activated carbon has a large specific surface area of  $1170 \text{ m}^2 \cdot \text{g}^{-1}$  and great pore structure.<sup>41</sup>

A second product of biomass waste that has gained a large amount of interest is biochar. Biochar is defined as the product formed after biomass undergoes thermal conversion. Biochar mainly consists of carbon, oxygen, and hydrogen but include a variety of trace elements such as nitrogen group elements, metals, metalloids, and nonmetals. The elemental composition of the biochar is dependent on the biomass from which it is derived. Biochar has been tested as an absorbent for both air and water pollution. It was found that it performed well in both applications due to biochar having large specific surface areas, tune able pore structure, and functional groups present on its surface.<sup>42,43</sup>

Based on the catalyst support selection criteria outlined by Wang et al., 2016,<sup>27</sup> both biochar and activated carbon have the necessary characteristics to perform well as catalyst supports for catalysts in proton exchange membrane fuel cells (PEMFCs).<sup>27,39</sup>

#### 3.1. The Effect of Production Conditions on Biochar.

There are many synthesis methods for biochar production, and each produces biochar with different characteristics even though they are derived from the same feedstock. These methods of production affect characteristics such as total surface area, porosity, pore distribution, functionalization, and elemental composition.<sup>44</sup> Biochar is produced through the thermal conversion of biomass. The most commonly used methods are slow pyrolysis, intermediate pyrolysis, fast pyrolysis, and gasification (Table 1).<sup>45</sup>

**Table 1. Different Production Methods of Biochar. Temperatures, Residence Times, and Product Composition**<sup>45</sup>

process	temp (°C)	residence time	liquid (bio-oil) (%)	solid (biochar) (%)	gas (syngas) (%)
fast pyrolysis	300–1000	short (<2 s)	75	12	13
intermediate pyrolysis	~500	moderate (10–20 s)	50	25	25
slow pyrolysis	100–1000	long (5–30 min)	30	35	35
gasification	>800	moderate (10–20 s)	5	10	85

Tan et al., 2021,<sup>46</sup> conducted research to observe the difference slow pyrolysis and fast pyrolysis would have on the production of biochar from lignocellulosic and lignin biomass. They found that using fast pyrolysis conditions produced a biochar with low surface areas, poor porosity, and biochar yield due to the depolymerization of the biochar's surface. Hence using the slow pyrolysis conditions are more favorable for producing better quality biochar.<sup>46</sup>

#### 3.2. The Effect of Production Conditions on Activated Carbon.

Activated carbon can be produced using either a one-step or two-step process. These processes consist of either physical activation, chemical activation, or a combination of the two being physiochemical activation. Physical activation uses thermal conversion to convert biomass into activated carbon. Chemical activation uses alkali metals, alkaline earth metals, and acids along with low temperature heating to produce activated carbon from biomass. Physiochemical activation combines both physical and chemical activation methods to produce activated carbon.<sup>39,47</sup>

Kim et al., 2017,<sup>48</sup> conducted a study that showed chemical activation produced better results than physical activation when comparing the characteristics of an activated carbon made from phenol resin-based spherical carbon. The authors compared thermal activation in the form of steam to chemical activation using KOH. They found that chemical activation produced a uniform pore development and greater yield, which was attributed to the potassium behaving like a catalyst.<sup>48</sup>

#### 3.3. Biochar and Activated Carbon Application in Fuel Cells and Adjacent Fields.

Activated carbon has good characteristics to be a catalyst support as it possesses high surface areas, it is inert in acidic and basic conditions, and the pore structure can be altered to suit the necessary requirements of the application.<sup>49</sup>

Gao et al., 2018,<sup>50</sup> conducted experimentation on nickel-cobalt electrocatalysts for a direct glucose alkaline fuel cell in which they used traditionally produced activated carbon as the support material.<sup>45</sup> Dong et al., 2019,<sup>51</sup> conducted experimentation on  $\text{FeCo}_2\text{O}_4$  macaroon-like structures which were supported on activated carbon for use in a direct glucose alkaline fuel cell. In both Gao et al., 2018,<sup>50</sup> and Dong et al., 2019,<sup>51</sup> the catalysts showed an improvement in fuel cell performance which was dually attributed to the improvement in the catalyst and the support material.<sup>50,51</sup> Although there is proof of application for traditionally produced activated carbon being used as a catalyst support, there are very limited examples of activated carbon produced from biomass being used. This is most likely attributed to the novelty of the research.

Biochar has a wide range of applications such as an absorbent, soil amendment, catalysts, and others. Biochar has seen application in fuel cells, not as an electrode but rather as the fuel in direct carbon fuel cells and in phosphoric acid fuel cells.<sup>42</sup>

Although biochar has not been directly used as an electrode in fuel cell technology, it has been used in adjacent fields such as supercapacitors. Like for fuel cells the performance of the supercapacitor is based on the electrodes used.<sup>23,52</sup> The characteristics that make a good superconductor electrode are similar to those of what is needed for a good support material in fuel cells. They need high surface areas, high conductivity, high stability to increase the lifespan, and high energy density. The materials used for supercapacitor electrodes are carbon material, conductive polymers, and transition metal oxides which are similar to the materials tried as support materials for fuel cell electrocatalysts.<sup>53,54</sup>

Zhang et al., 2022,<sup>52</sup> conducted experimentation on apple-pomace-based biochar for use in a supercapacitor. The apple-pomace-based biochar had a high specific surface area of 2010.16 m<sup>2</sup>·g<sup>-1</sup> and showed high material stability by retaining 95.7% of its capacity after 5000 cycles in 6 M KOH.<sup>47</sup> The lack of research into biochar as a catalyst support material is most likely due to its novelty but the research done by Zhang et al., 2022,<sup>52</sup> and others proves that biochar possesses all the necessary requirements to be a strong catalyst support material.

#### 4. SUGGESTED PHYSICAL CHARACTERIZATION

Potential support materials need to possess the following characteristics which were outlined by Wang et al., 2016:<sup>27</sup> sufficient electron conductivity, high specific surface area, suitable pore structure, high stability in acidic and basic environments, and strong adhesion between support and catalyst material.<sup>27</sup>

Specific surface area and suitable pore structure are important characteristics when assessing potential catalyst supports. The most widely used method for determining these two quantities is the use of the Brunauer–Emmett–Teller (BET) isotherm which uses the physical adsorption of nitrogen gas onto a solid surface to determine the specific surface area and average pore size and volume.<sup>55</sup> Kumar et al., 2020,<sup>56</sup> synthesized high surface area biochar from dry seaweed (*Sargassum tenerrimum*) as a support material for a nickel-cobalt bimetallic catalyst for the selective hydrogenation of phenols. The authors used BET to observe the effect that KOH pre-impregnation ratio, temperature, heating rate, and residence time will have on the surface area.<sup>56</sup>

Fourier transport infrared (FTIR) spectroscopy is an important characterization technique for catalyst support materials. FTIR is used to detect the presence and intensity of surface functional groups present on the support material. The surface functional groups are important as they assist in mass transporting and are the binding sites for the catalytic material.<sup>57,58</sup>

X-ray diffraction (XRD) analysis is a powerful characterization technique which can offer a large quantity of information about crystallinity, crystal defects, structures, and average grain size.<sup>59</sup>

This information is important as it gives information on necessary characteristics, such as conductivity, particle size and texture, and interlayer spacing.

Liu et al., 2021,<sup>60</sup> synthesized a biochar from corn straw which was used as a support material for a silicon-manganese

binary catalyst for the adsorption and removal of Cu(II) from water. The authors used FTIR to confirm the surface functional groups present on the biochar support and used XRD in conjunction with the FTIR results to confirm how the catalytic metals were bound to the functional groups in the form of SiO<sub>2</sub>, MnO<sub>x</sub>, and MnSiO<sub>3</sub>.<sup>60</sup>

Electron conductivity is important for support materials as these materials need to provide a good electron transfer pathway, as it is the basic premise on which fuel cells operate. Conductivity meters are used to determine the conductivity of materials.<sup>27</sup>

Scanning electron microscopy (SEM), energy-dispersive X-ray (EDX) spectroscopy, and Raman spectroscopy are a group of techniques usually coupled together. SEM gives an overview of the morphology of the sample, while EDX provides chemical composition of the sample. Raman spectroscopy is used to detect defects in the material.<sup>61</sup>

Chia et al., 2012,<sup>62</sup> conducted experimentation on a wood derived biochar in its unmodified and modified state with Fe(II) and bentonite. The authors used a combination of FTIR and Raman spectroscopy to determine the effect that the modification had on the bond distribution in the biochar and conducted SEM-EDX to determine if there was an effect on the elemental composition of the biochars.<sup>62</sup>

Transmission electron microscopy (TEM) is a technique used to observe the structure of the studied material. TEM offers the ability to observe the actual structure of the material instead of the predicted structure provided by techniques such as XRD and NMR.<sup>63</sup>

#### 5. CONCLUSION

Direct methanol fuel cells offer great potential for application in small scale portable devices. However, DMFCs still face many challenges which prevent its commercialization such as the cost of materials and current catalysts technologies which limit their performance. Although carbon nanomaterials have been used to improve performance, cost is still a challenge. Therefore, the use of carbon based materials derived from biowaste could alleviate a portion of the cost, as they are relatively much cheaper to produce than most novel carbon nanomaterials. The great characteristics of carbon-based materials derived from biomass waste match that of what is required for a support material for electrocatalysis in direct methanol fuel cells. It is due to this and the positive impact they have already had as support materials for catalysts in other applications that it can therefore be concluded that the utilization of these activated carbons and biochars as monosupports or alongside other carbon nanomaterials in a nanocomposite support should result in the enhancement of the performance of the platinum based electrocatalyst in a direct methanol fuel cell.

#### 6. LIMITATIONS AND FUTURE OUTLOOK

Great progress has been made regarding the development of electrocatalysts for direct methanol fuel cells. Much of this progress can be attributed to further research and development into carbon nanomaterials as supports for the electrocatalysts. This technology has shown high potential as a viable solution and could be the basis of many breakthroughs which allow the direct methanol fuel cell to reach its true theoretical potential.<sup>4</sup>

However, this technology like DMFC faces its own set of challenges such as cost, synthesis methods, platinum loading

issues, and electrode preparation methods. Much of the cost related to fuel cells is due to the price of producing the electrocatalyst. The price of the electrode is due to two components, the platinum and the support material.<sup>5,6</sup>

The price of the platinum electrocatalyst could decrease with the development of single atom catalysis (SAC) technology which has seen a decrease in the amount of platinum mass loading needed in order to achieve current catalyst performance figures and therefore, will decrease the overall price.<sup>64,65</sup>

The high cost of the support materials is attributed to the novelty of carbon nanomaterials and their expensive synthesis methods. This cost could decrease with time as more affordable and sustainable methods of synthesis are discovered. The price of the support materials could also decrease due to the use of biomass derived carbon nanomaterials, such as some of the work mentioned above. The utilization of biomass derived carbon materials as support materials for electrocatalysts is a fairly new area of research and can prove fruitful due to the great characteristics that biochars and activated carbons possess.

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### Notes

The authors declare no competing financial interest.

### Biographies



**Lindiwe Khotseng** is a Professor at the Chemistry Department, University of the Western Cape, South Africa since 2023. Prior to working at the Chemistry Department, she worked as the Managing Director of ESKOM Centre for Electrocatalytic Research at the South African Institute for Materials Research, University of the Western Cape, South Africa since 2008. Lindiwe obtained her Ph.D. in Chemistry from the University of Stellenbosch, South Africa, in 2004 and PG Diploma in T&L (HE) at the University of the Western Cape in 2022. Her research focus is on sustainable energy nanomaterials.

She has published in qualified international journals or specialized books and presented in international chemical meetings. She has graduated 16 MSc and 8 Ph.D. students. She has served in various leadership committees at her Faculty and National Research Foundation (SA) panels. She obtained the Department of Trade and Industry (SA) Technology award as the Outstanding Black Researcher in her research field in 2013. She is a professional member of South African Chemical Institute (SACI), Organization for Women in Science for the Developing World (OWSD), and International Society of Electrochemistry (ISE).



**Dr Ntalane Sello Seroka** received his BSc in Physical Science degree in 2016 and BSc Honors degree in 2017 from Sefako Makgatho University, a Master of Nanoscience in 2019 from University of Johannesburg, and last Ph.D. degree in Chemistry from University of the Western Cape in 2023. Currently he is a postdoctoral researcher at the University of the Western Cape under the lead of Prof. Lindiwe Khotseng. His research focuses on the development of nanomaterials for biomass conversion, energy conversion, and energy storage.



**Evan Visser** received his BSc. Chemical Sciences degree in 2020 and BSc. Honours degree in 2021 from the University of the Western Cape. Currently he is completing his Masters degree in Chemical Sciences at the University of the Western Cape under the supervision of Prof. Lindiwe Khotseng and Dr. Ntalane Sello Seroka. His research focuses on the development of support materials for platinum electrocatalysts used in direct methanol fuel cells.

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## REFERENCES

- (1) Dai, L.; Chang, D. W.; Baek, J. B.; Lu, W. Carbon nanomaterials for advanced energy conversion and storage. *Small*. **2012**, *8* (8), 1130–1166.
- (2) Ng, J. C.; Tan, C. Y.; Ong, B. H.; Matsuda, A. Effect of Synthesis Methods on Methanol Oxidation Reaction on Reduced Graphene Oxide Supported Palladium Electrocatalysts. *Procedia Engineering* **2017**, *184*, 587–594.
- (3) Yang, H.; Geng, L.; Zhang, Y.; et al. Graphene-templated synthesis of palladium nanoplates as novel electrocatalyst for direct methanol fuel cell. *Appl. Surf. Sci.* **2019**, *466*, 385–392.
- (4) Li, H.; Zhang, Y.; Wan, Q.; Li, Y.; Yang, N. Expanded graphite and carbon nanotube supported palladium nanoparticles for electrocatalytic oxidation of liquid fuels. *Carbon N Y.* **2018**, *131*, 111–119.
- (5) Li, L.; Chen, M.; Huang, G.; et al. A green method to prepare Pd-Ag nanoparticles supported on reduced graphene oxide and their electrochemical catalysis of methanol and ethanol oxidation. *J Power Sources*. **2014**, *263*, 13–21.
- (6) Ponnada, S.; Kiai, M. S.; Gorle, D. B.; Nowduri, A.; Sharma, R. K. Insight into the Role and Strategies of Metal-Organic Frameworks in Direct Methanol Fuel Cells: A Review. *Energy and Fuels*. **2021**, *35* (19), 15265–15284.
- (7) Kaur, A.; Kaur, G.; Singh, P. P.; Kaushal, S. Supported bimetallic nanoparticles as anode catalysts for direct methanol fuel cells: A review. *Int J Hydrogen Energy*. **2021**, *46* (29), 15820–15849.
- (8) Gong, L.; Yang, Z.; Li, K.; Xing, W.; Liu, C.; Ge, J. Recent development of methanol electrooxidation catalysts for direct methanol fuel cell. *J Energy Chem.* **2018**, *27* (6), 1618–1628.
- (9) Zago, S.; Bartoli, M.; Muhyuddin, M.; Vanacore, G. M.; Jagdale, P.; Tagliaferro, A.; Santoro, C.; Specchia, S. Engineered biochar derived from pyrolyzed waste tea as a carbon support for Fe-N-C electrocatalysts for the oxygen reduction reaction. *Electrochim. Acta* **2022**, *412*, 140128.
- (10) Liang, L.; Xi, F.; Tan, W.; Meng, X.; Hu, B.; Wang, X. Review of organic and inorganic pollutants removal by biochar and biochar-based composites. *Biochar*. **2021**, *3* (3), 255–281.
- (11) Pereira Lopes, R.; Astruc, D. Biochar as a Support for Nanocatalysts and Other Reagents: Recent Advances and Applications. *Coord. Chem. Rev.* **2021**, *426*, 213585.
- (12) Daud, W. R. W.; Rosli, R. E.; Majlan, E. H.; Hamid, S. A. A.; Mohamed, R.; Husaini, T. PEM fuel cell system control: A review. *Renew Energy*. **2017**, *113*, 620–638.
- (13) Fan, L.; Tu, Z.; Chan, S. H. Recent development of hydrogen and fuel cell technologies: A review. *Energy Reports*. **2021**, *7*, 8421–8446.
- (14) Ramli, Z. A. C.; Kamarudin, S. K. Platinum-Based Catalysts on Various Carbon Supports and Conducting Polymers for Direct Methanol Fuel Cell Applications: a Review. *Nanoscale Res Lett.* **2018**, *13*, 13.
- (15) Awasthi, R.; Singh, R. N. Graphene-supported Pd-Ru nanoparticles with superior methanol electrooxidation activity. *Carbon N Y.* **2013**, *51* (1), 282–289.
- (16) Rivera Gavidia, L. M.; Sebastián, D.; Pastor, E.; Aricò, A. S.; Baglio, V. Carbon-supported Pd and PdFe alloy catalysts for direct methanol fuel cell cathodes. *Materials (Basel)*. **2017**, *10* (12), 580.
- (17) Kamarudin, S. K.; Achmad, F.; Daud, W. R. W. Overview on the application of direct methanol fuel cell (DMFC) for portable electronic devices. *Int J Hydrogen Energy*. **2009**, *34* (16), 6902–6916.
- (18) Alias, M. S.; Kamarudin, S. K.; Zainoodin, A. M.; Masdar, M. S. Active direct methanol fuel cell: An overview. *Int J Hydrogen Energy*. **2020**, *45* (38), 19620–19641.
- (19) Jung, S. High-performance direct methanol fuel cell with optimized membrane electrode assembly: A theoretical approach. *Int J Hydrogen Energy*. **2016**, *41* (21), 9022–9034.
- (20) Xia, Z.; Zhang, X.; Sun, H.; Wang, S.; Sun, G. Recent advances in multi-scale design and construction of materials for direct methanol fuel cells. *Nano Energy*. **2019**, *65* (June), 104048.
- (21) Qiu, D.; Janßen, H.; Peng, L.; Irmischer, P.; Lai, X.; Lehnert, W. Electrical resistance and microstructure of typical gas diffusion layers for proton exchange membrane fuel cell under compression. *Appl Energy*. **2018**, *231*, 127–137.
- (22) Sundmacher, K.; Schultz, T.; Zhou, S.; Scott, K.; Ginkel, M.; Gilles, E. D. Dynamics of the Direct Methanol Fuel Cell (DMFC), Experiments and Model-Based Analysis. *Chem. eng. Sci.* **2001**, *56*, 333.
- (23) Basri, S.; Kamarudin, S. K.; Daud, W. R. W.; Yaakub, Z. Nanocatalyst for direct methanol fuel cell (DMFC). *Int J Hydrogen Energy*. **2010**, *35* (15), 7957–7970.
- (24) Dai, Y.; Liu, B.; Zhang, Z.; Guo, P.; Liu, C.; Zhang, Y.; Zhao, L.; Wang, Z. Tailoring the d-Orbital Splitting Manner of Single Atomic Sites for Enhanced Oxygen Reduction. *Adv. Mater.* **2023**, *2210757*, 1–10.
- (25) Altarawneh, R. M. Overview on the vital step toward addressing platinum catalyst poisoning mechanisms in acid media of direct ethanol fuel cells (DEFs). *Energy and Fuels*. **2021**, *35* (15), 11594–11612.
- (26) Li, L.; Hu, L.; Li, J.; Wei, Z. Enhanced stability of Pt nanoparticle electrocatalysts for fuel cells. *Nano Res.* **2015**, *8* (2), 418–440.
- (27) Wang, Y. J.; Fang, B.; Li, H.; Bi, X. T.; Wang, H. Progress in modified carbon support materials for Pt and Pt-alloy cathode catalysts in polymer electrolyte membrane fuel cells. *Prog Mater Sci.* **2016**, *82*, 445–498.
- (28) Suda, Y.; Shimizu, Y.; Ozaki, M.; et al. Electrochemical properties of fuel cell catalysts loaded on carbon nanomaterials with different geometries. *Mater Today Commun.* **2015**, *3*, 96–103.
- (29) Martínez-Huerta, M. V.; Lázaro, M. J. Electrocatalysts for low temperature fuel cells. *Catal Today*. **2017**, *285*, 3–12.
- (30) Punetha, V. D.; Rana, S.; Yoo, H. J.; et al. Functionalization of carbon nanomaterials for advanced polymer nanocomposites: A comparison study between CNT and graphene. *Prog. Polym. Sci.* **2017**, *67*, 1–47.
- (31) Loryuenyong, V.; Totepvimarn, K.; Eimburanaprat, P.; Boonchompo, W.; Buasri, A. Preparation and characterization of reduced graphene oxide sheets via water-based exfoliation and reduction methods. *Adv Mater Sci Eng.* **2013**, *2013*, 1.
- (32) Sharma, S.; Pollet, B. G. Support materials for PEMFC and DMFC electrocatalysts - A review. *J Power Sources*. **2012**, *208*, 96–119.
- (33) İşikel Şanlı, L.; Bayram, V.; Ghobadi, S.; Düzen, N.; Alkan Gürsel, S. Engineered catalyst layer design with graphene-carbon black hybrid supports for enhanced platinum utilization in PEM fuel cell. *Int J Hydrogen Energy*. **2017**, *42* (2), 1085–1092.
- (34) Ji, Z.; Perez-Page, M.; Chen, J.; Rodriguez, R. G.; Cai, R.; Haigh, S. J.; Holmes, S. M. A structured catalyst support combining electrochemically exfoliated graphene oxide and carbon black for enhanced performance and durability in low-temperature hydrogen fuel cells. *Energy* **2021**, *226*, 120318.
- (35) Kalyani, P.; Anitha, A.; Darchen, A. Activated carbon from grass - A green alternative catalyst support for water electrolysis. *Int J Hydrogen Energy*. **2013**, *38* (25), 10364–10372.
- (36) Gan, L.; Zhong, Q.; Geng, A.; Wang, L.; Song, C.; Han, S.; Cui, J.; Xu, L. Cellulose derived carbon nanofiber: A promising biochar support to enhance the catalytic performance of CoFe<sub>2</sub>O<sub>4</sub> in activating peroxymonosulfate for recycled dimethyl phthalate degradation. *Sci. Total Environ.* **2019**, *694*, 133705.
- (37) Okiemute Akpasi, S.; Michael Smarte Anekwe, I.; Adedeji, J.; Lewis Kiambi, S. Biochar Development as a Catalyst and Its Application. *Biochar - Productive Technologies, Properties and Application [Working Title]* **2022**, 105439 DOI: 10.5772/intechopen.105439.
- (38) BS, G. Review on Application of Agro-Waste Biomass Biochar for Adsorption and Bioremediation Dye. *Biomed J Sci Tech Res.* **2017**, *1* (7), 1928–1930.
- (39) Ao, W.; Fu, J.; Mao, X.; et al. Microwave assisted preparation of activated carbon from biomass: A review. *Renew Sustain Energy Rev.* **2018**, *92* (May), 958–979.
- (40) Danish, M.; Ahmad, T. A review on utilization of wood biomass as a sustainable precursor for activated carbon production and application. *Renew Sustain Energy Rev.* **2018**, *87*, 1–21.

- (41) Adinata, D.; Wan Daud, W. M. A.; Aroua, M. K. Preparation and characterization of activated carbon from palm shell by chemical activation with  $K_2CO_3$ . *Bioresour. Technol.* **2007**, *98* (1), 145–149.
- (42) Cha, J. S.; Park, S. H.; Jung, S. C.; et al. Production and utilization of biochar: A review. *J Ind Eng Chem.* **2016**, *40*, 1–15.
- (43) Li, J.; Dai, J.; Liu, G.; et al. Biochar from microwave pyrolysis of biomass: A review. *Biomass and Bioenergy.* **2016**, *94*, 228–244.
- (44) Kamarudin, N. S.; Dahalan, F. A.; Hasan, M.; et al. Biochar: A review of its history, characteristics, factors that influence its yield, methods of production, application in wastewater treatment and recent development. *Biointerface Res Appl Chem.* **2021**, *12* (6), 7914–7926.
- (45) Ahmad, M.; Rajapaksha, A. U.; Lim, J. E.; et al. Biochar as a sorbent for contaminant management in soil and water: A review. *Chemosphere.* **2014**, *99*, 19–33.
- (46) Tan, H.; Lee, C. T.; Ong, P. Y.; et al. A Review On The Comparison Between Slow Pyrolysis And Fast Pyrolysis On The Quality Of Lignocellulosic And Lignin-Based Biochar. *IOP Conf Ser Mater Sci Eng.* **2021**, *1051* (1), 012075.
- (47) Bedia, J.; Peñas-Garzón, M.; Gómez-Avilés, A.; Rodríguez, J. J.; Belver, C. Review on Activated Carbons by Chemical Activation with  $FeCl_3$ . *C — J Carbon Res.* **2020**, *6* (2), 21.
- (48) Kim, D. W.; Kil, H. S.; Nakabayashi, K.; Yoon, S. H.; Miyawaki, J. Structural elucidation of physical and chemical activation mechanisms based on the microdomain structure model. *Carbon N Y.* **2017**, *114*, 98–105.
- (49) Iwanow, M.; Gärtner, T.; Sieber, V.; König, B. Activated carbon as catalyst support: Precursors, preparation, modification and characterization. *Beilstein J Org Chem.* **2020**, *16*, 1188–1202.
- (50) Gao, M.; Liu, X.; Irfan, M.; Shi, J.; Wang, X.; Zhang, P. Nickel-cobalt composite catalyst-modified activated carbon anode for direct glucose alkaline fuel cell. *Int J Hydrogen Energy.* **2018**, *43* (3), 1805–1815.
- (51) Dong, F.; Liu, X.; Irfan, M.; et al. Macaroon-like  $FeCo_2O_4$  modified activated carbon anode for enhancing power generation in direct glucose fuel cell. *Int J Hydrogen Energy.* **2019**, *44* (16), 8178–8187.
- (52) Zhang, S.; Li, Y.; Du, Y.; Ma, X.; Lin, J.; Chen, S. Apple-pomace-based porous biochar as electrode materials for supercapacitors. *Diam Relat Mater.* **2022**, *130* (July), 109507.
- (53) Samad, S.; Loh, K. S.; Wong, W. Y.; et al. Carbon and non-carbon support materials for platinum-based catalysts in fuel cells. *Int J Hydrogen Energy.* **2018**, *43* (16), 7823–7854.
- (54) Zhang, Q. Z.; Zhang, D.; Miao, Z. C.; Zhang, X. L.; Chou, S. L. Research Progress in  $MnO_2$ -Carbon Based Supercapacitor Electrode Materials. *Small.* **2018**, *14* (24), 1–15.
- (55) Al-Ghouti, M. A.; Da'ana, D. A. Guidelines for the use and interpretation of adsorption isotherm models: A review. *J Hazard Mater.* **2020**, *393*, 122383.
- (56) Kumar, A.; Kumar, J.; Bhaskar, T. High surface area biochar from *Sargassum tenerrimum* as potential catalyst support for selective phenol hydrogenation. *Environ Res.* **2020**, *186*, 109533.
- (57) Luo, C.; Xie, H.; Wang, Q.; Luo, G.; Liu, C. A review of the application and performance of carbon nanotubes in fuel cells. *J Nanomater.* **2015**, *2015*, 1.
- (58) Zhang, X.; Zhang, J.; Huang, H.; Jiang, Q.; Wu, Y. Platinum nanoparticles anchored on graphene oxide-dispersed pristine carbon nanotube supports: High-performance electrocatalysts toward methanol electrooxidation. *Electrochim. Acta* **2017**, *258*, 919–926.
- (59) Bunaciu, A. A.; Udristoiu, E. g.; Aboul-Enein, H. Y. X-Ray Diffraction: Instrumentation and Applications. *Crit Rev Anal Chem.* **2015**, *45* (4), 289–299.
- (60) Liu, J.; Liu, H.; Yang, X.; Jia, X.; Cai, M.; Bao, Y. Preparation of Si-Mn/biochar composite and discussions about characterizations, advances in application and adsorption mechanisms. *Chemosphere.* **2021**, *281* (March), 130946.
- (61) Cardell, C.; Guerra, I. An overview of emerging hyphenated SEM-EDX and Raman spectroscopy systems: Applications in life, environmental and materials sciences. *TrAC - Trends Anal Chem.* **2016**, *77*, 156–166.
- (62) Chia, C. H.; Gong, B.; Joseph, S. D.; Marjo, C. E.; Munroe, P.; Rich, A. M. Imaging of mineral-enriched biochar by FTIR, Raman and SEM-EDX. *Vib Spectrosc.* **2012**, *62*, 248–257.
- (63) Kwiecińska, B.; Pusz, S.; Valentine, B. J. Application of electron microscopy TEM and SEM for analysis of coals, organic-rich shales and carbonaceous matter. *Int J Coal Geol.* **2019**, *211* (May), 103203.
- (64) Peng, B.; Liu, H.; Liu, Z.; Duan, X.; Huang, Y. Toward Rational Design of Single-Atom Catalysts. *J Phys Chem Lett.* **2021**, *12* (11), 2837–2847.
- (65) Wang, Y.; Chu, F.; Zeng, J.; et al. Single Atom Catalysts for Fuel Cells and Rechargeable Batteries: Principles, Advances, and Opportunities. *ACS Nano.* **2021**, *15* (1), 210–239.