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ABSTRACT

Direct carbon fuel cell offers an efficient alternative to conventional combustion systems for electricity generation. The most attractive feature is its remarkably high overall system efficiency. However, the implementation of this technique is restricted by the limited solid-solid contact between the carbon fuel and electrode. This review discusses a set of chemical and physical properties of the carbon fuel that contribute to the electrochemical performance of the fuel cell. These properties include chemical composition, surface functional groups, graphitic structure and textural properties. Meanwhile, biomass can be employed as a sustainable carbon source after undergoing pyrolysis, a thermal pretreatment process. It is essential to control the pyrolysis operating conditions such as the temperature, heating rate and residence time as these conditions would affect the chemical and physical properties of the carbon fuel, ultimately contributing to the electrochemical performance of the fuel cell.

INTRODUCTION

Depletion of world’s energy reserves, particularly fossil fuel resources, has made energy sustainability a subject of worldwide debate. The energy shortage crisis acted as a stimulant in intensive development of alternatives for electricity generation process, that is, the fuel cell technologies. In the field of fuel cell, there are numerous types and forms of fuel cells which oxidize fuels such as hydrogen, methanol and methane to generate electricity. Direct carbon fuel cell (DCFC) is a type of fuel cell which produces electricity through electrochemical oxidation of solid carbon into carbon dioxide, without involving combustion reaction. The first emergence of DCFC could be traced way back to mid of 19th century, where in the year of 1839, Sir William Grooves first discovered the existence of direct carbon fuel. Eq. (1) and (2) show the half-cell reactions associated electrons while Eq. (3) depicts the overall oxidation reaction.

\[
O_2 \text{(air)} + 4e^- \rightarrow 2O^2^- \quad (1)
\]

\[
C + 2O^2^- \rightarrow CO_2 + 4e^- \quad (2)
\]

\[
C + O_2 \text{(air)} \rightarrow CO_2 \quad (3)
\]

The most promising advantage of DCFC is its remarkably high theoretical efficiency for Eq. 3 in converting chemical energy into electricity which is close to 100% (Muthuvel et al. 2009, Chien et al. 2013). Its overall system efficiency taking into account of auxiliary losses is in the range of 60-70% (Giddey et al. 2012), as compared to less than 40% for a Carnot Cycle.

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1. Critical carbon fuel properties and its effect on fuel cell performance:

One of the advantages of DCFC is its fuel flexibility; however this does not mean that all fuels perform equally in DCFC due to the difference in chemical and physical properties. The chemical properties include chemical composition and surface functional group, while the physical properties include graphitic structure and textural property.

1.1 Chemical composition:

Two major analyses are often employed for the analysis of chemical composition, namely proximate and ultimate analyses. Proximate analysis gives result in the form of percentage weight of fixed carbon, volatile, moisture and ash. As for ultimate analysis, the result generated is in the form of percentage weight of elements such as C, H, N, S, and O (Cho et al. 2012). Using four coal samples from four different places in Australia, Li et al. (2010) performed proximate analysis on coal samples and tested them in a molten carbonate DCFC. The result suggests that coal sample with highest percentage weight fixed carbon produced the highest reactivity. The importance of carbon is also reported by Ahn et al. (2013a&b), which states that the lack of percentage weight fixed carbon in biomass will leads to linear decrement of voltage at higher current density region, where voltage could not be maintained due to restricted consumption of carbon when large number of electrons are flowing through the system.

There is no report regarding the effect of moisture on the performance of DCFC. The report of the effect of volatile on DCFC performance is scarce; it is only found that high percentage weight of volatile causing solid carbonaceous fuel to exist in a liquid-like phase at elevated operating temperature. Such state of matter could aid in reducing polarization activation at the anode, which could lead to increment in DCFC performance (Kim et al. 2012). As for ash, it is reported that it produces both detrimental and beneficial effects on the performance of DCFC, depending on the inorganic matter present (Li et al. 2010). Percentage weight ash is an indication of inorganic matters that present in solid carbonaceous fuel, where they are output as ash due to combustion of solid carbonaceous fuel during proximate analysis. The inorganic matters in solid carbonaceous fuel could be determined through inductive coupled plasma optical emission spectrometry (ICPOES), where major and minor elements present in the sample will be output as percentage weight of metal oxides. Using such technique, Li et al. (2010) reported that major inorganic matters of four coal samples from Australia comprised of SiO₂ and Al₂O₃. As for minor inorganic matters, they differ with different solid carbonaceous fuels. It was also found that the inorganic matters such as Al₂O₃ and SiO₂ have detrimental effects on DCFC performance. On contrary, minor inorganic matters such as Fe₂O₃, Na₂O, K₂O, MgO and CaO were found to possess catalytic effect, where they increase current and power densities of DCFC at high anode potential region.

1.2 Surface functional group:

Carbon and oxygen functional groups at the surface of solid carbonaceous fuel play roles in promoting the electrochemical reactions in DCFC, especially at low current density region as reported by Ahn et al. (2013a&b). Several literature sources have reported the beneficial effects of carbon and oxygen functional groups on DCFC electrochemical performance (Li et al. 2010&2008, Ahn et al. 2013a). For oxygen functional group, they were reported to be able to provide reactive sites for electrochemical oxidation of solid carbonaceous fuel, therefore, improving its discharge rate (Li et al 2010). As for carbon functional groups, it is important that they are distributed widely on the solid carbonaceous fuel surface, as electrochemical reaction takes place on fuel's surface. High amount of carbon functional group will also ease the activation. However, this may leads to premature electrochemical reactions (Ahn et al. 2013a&b). It should be noted that high percentage weight fixed carbon does not indicates high surface carbon functional group. Reuse fuel was reported to possess lower percentage weight fixed carbon but higher carbon functional group (Ahn et al. 2013a&b).

Temperature-programmed desorption (TPD) could be used in extracting information regarding oxygen function groups, whereby solid carbonaceous fuel's surface releases CO and CO₂ at different temperatures. Evolution of CO₂ mainly originated from carboxylic acid and lactones at low and high temperature respectively. As for CO, it originates from phenols and carbonyls at elevated temperature. Such method is difficult to provide exact information regarding the functional group on the surface, whereby only quantitative information could be derived (Li et al. 2008).

1.3 Graphitic structure:

Carbon has the capability of forming many allotropes due to its valency, and one of the common forms is graphite. Graphite possesses an orderly layered and planar structure, and such crystalline structure made graphite an electrical conductor (Li et al. 2008). Graphitic structure is a measurement of the degree of graphitization a solid carbonaceous fuel has in its structure, and commonly, such analysis could be carried out using X-ray diffraction (XRD). Analysis of diffraction peaks caused by solid carbonaceous fuel in the XRD would give an indication of the degree of graphitization. Such diffraction peaks occur at (002) and (100) planes, where they are attributed to turbostratic crystalline structure of carbon (Li et al. 2008). The more distinct
peaks observed at these mentioned planes indicate high degree of graphitization, which means more order structure in solid carbonaceous fuel. On top of that, the quantitative crystalline parameters such as inter-planar distance, stacking height and average diameter obtained are also important. For instance, Li et al. (2008) reported that highest degree of graphitization associates with smallest inter-planar distance and largest stacking height and average diameter. The degree of graphitization closely associates with electrical conductivity, which contributes to DCFC performance. Apart from that, disordered structure of carbon also contributed to DCFC performance where such structure consists of more surface defects and edges sites which served as reactive sites (Li et al. 2008).

Solid carbonaceous fuel in DCFC does not only act as a reactant for the electrochemical reaction, but also act as a carrier for the transfer of electrons. The transfer of electrons to external circuit would first require them to be transferred through the solid carbonaceous fuel particles that were in contact with current collectors, before being transferred to external circuit (Li et al. 2008). Li et al. (2008) reported that high conductivity of solid carbonaceous fuel increases the effective surface area of anode by extending the electrode into electrolyte. However it is interesting to note that lowest reactivity was reported for solid carbonaceous fuel with the highest conductivity. Similar case was reported by Chen et al. (2010) who stated that high conductivity and low resistance graphite alone would not perform well in DCFC due to lacking of lattice defects.

1.4 Textural property:

Textural property was reported to be critical in determining the reaction of solid carbonaceous fuel in electrochemistry. Pores are classified according to range of sizes they fit in, for instance, micropore, diameter < 2nm; mesopore, 2nm < diameter < 50nm; and macropore, diameter > 50nm. Cherepy et al. (2005) reported that surface area does affect the performance of DCFC strongly. On the other hand, Li et al. (2009) reported that electrochemical process involving carbon was often highly dependent on carbon's surface characteristic, and from the experiment, it was observed that reactivity of solid carbonaceous fuel in DCFC increases with surface area and pore volume. It was found that these textural properties help in improving contact between solid carbonaceous fuel and electrolyte, as well as wetting ability of solid carbonaceous fuel, particularly in the case of molten-based DCFC (Ahn et al. 2013b). There is also a report regarding effects of different pore sizes on power density produced by DCFC, whereby Li et al. (2008) states that the pores were only able to contribute to DCFC performance if they were accessible by electrolyte. Common examination of textural property of solid carbonaceous fuel is carried out using gas adsorption, where specific surface area, total pore volume, average pore diameters could be determined.

2. Pretreatment for biomass:

2.1 Importance of pretreatment and different pretreatment processes:

As mentioned in section 2, high percentage weight fixed carbon, large numbers of surface oxygen and carbon functional groups, high surface area, extensive pores, and optimum degree of graphitization are beneficial to DCFC performance. Unlike fossil fuel such as coal, which possesses high percentage weight fixed carbon that could operate DCFC without much modification; biomass on the other hand, is difficult to be used in DCFC at its raw state. The main reason is such that biomass mainly comprised of lignin, cellulose and hemicellulose. Furthermore, it has low energy density, low grind-ability and high moisture content which are unsuitable to be used in DCFC, thus, a proper pretreatment process is required (Abdullah and Wu 2009). There are various pre-treatment processes available such as thermal pre-treatment, acid pre-treatment and alkali pre-treatment.

Thermal or heat pre-treatment includes liquefaction, gasification and pyrolysis. Liquefaction produces liquid as the main product; while gasification reaction mainly generates H2, CO, CO2 and H2O (Mohan et al. 2006). As for pyrolysis, it is defined as thermochemical decomposition of organic matter in the absence of limited or total supply of oxidizing agents and such condition converts organic matter to solid, liquid and gas (Mohan et al. 2006). In most cases, it aims to induce carbonization reaction through thermolysis process. Pyrolysis process is capable of producing biochar from biomass, which is an organic compound with high percentage weight fixed carbon, making it an important pre-treatment process in converting biomass into usable solid carbonaceous fuel in DCFC. Other than that, modification in other properties such as textural property, surface functional groups, and degree of graphitization will occur as well.

2.2 Pyrolysis:

Pyrolysis works under the absence of oxidizing agent at elevated temperature, and such requirement is achieved by purging oxidant gas using inert gas for an interval before heating the reactor, creating an inert gas atmosphere. Following that, heating commences with specified heating rate until highest temperature known as pyrolysis temperature is achieved, and subsequently, the subject will be held at such condition for an extended interval known as residence time (Basu 2010).

Pyrolysis temperature, heating rate and residence time are important in determining the biochar properties (Czernik and Bridgewater 2004). Literature sources have classified various combinations of these physical conditions into three types of pyrolysis,
namely, slow, fast and flash pyrolysis (Maggi and Delmon 1994, Apaydin-Varol et al. 2007, Onay and Kockar 2003, Bridgwater 1999). Slow pyrolysis is characterized by slow heating rate and extensive residence time; finally flash pyrolysis is reported to be working at high heating rates up to $10^4 \text{Ks}^{-1}$ followed by rapid quenching (Mohan et al. 2006, Onay and Kockar 2003). With different types of pyrolysis, different products will be yield. For example, flash pyrolysis operates at $< 650^\circ C$ favours formation of liquid products; on contrary, operation at $> 650^\circ C$ favours formation of gaseous products. Slow pyrolysis promotes production of char (Apaydin-Varol et al. 2007, Onay and Kockar 2003, Bridgwater 1999).

It is reported that pyrolysis temperature has the greatest effect on biochar produced, as fundamental physical changes such as formation and volatilization of intermediate melts are all temperature dependant [60]. As for heating rate, it is regarded as having second greatest effect on biochar physical properties (Basu 2010). Apart from that, residence time is important as well. Lengthy residence time promotes secondary cracking (Bridgwater 1999). Individual pyrolysis parameter does not contribute directly to biochar properties; but instead, it is the combination of these pyrolysis parameters that shape the biochar. For example, long residence time at pyrolysis temperature $> 500^\circ C$, primary vapour are cracked, yielding specific products along with organic liquids; when pyrolysis temperature $< 400^\circ C$, condensation occurs, forming low molecular weight liquids; slow heating rate accompanied by long residence time enable volatiles to be gradually removed and permits secondary reaction between primary char and volatiles, forming secondary char (Basu 2010, Bridgwater 1999).

2.2.1 Conversion of biomass to biochar:

Through pyrolysis pre-treatment, the biomass is converted into biochar according to Eq. 4:

$$C_{n}H_{m}O_{p} \text{(biomass)} \rightarrow \text{gas} + \text{volatile} + \text{char}$$

(4)

Under identical pyrolysis condition, not all biomasses react equally and form biochar with identical properties. In reference to the general formula of biomass in Eq. (1), it could clearly observed that different biomasses have different chemical constituents, which ultimately defines the final biochar produced. In fact, biochar was observed to be an imprint structure of the original biomass, for example, the C skeleton and mineral formation retained in the biochar structure after pyrolysis. This further suggests that pyrolysis acts in modifying the original structure but not completely changes it (Amonette and Joseph, 2009).

To simplify, major part of biomass is mainly made up of cellulose, hemicellulose, and lignin (Mohan et al. 2006, Bridgwater 1999). Each of these contents degrade at different rates, mechanisms, pathways and different temperature ranges, for instance, cellulose degrades at 240-350°C, while hemicellulose and lignin degrade at temperature range of 280-500°C and 200-260°C, respectively (Amonette and Joseph, 2009). Different types of pyrolysis aim to produce different products. Different organic components are also favourable in producing different end-products, for instance, cellulose is more likely to yield condensable vapour; hemicellulose yields non-condensable gasses; as for lignin, it degrades slower and contributes to formation of char (Basu 2010). Different organic compounds comprise of different proportion cellulose, hemicellulose and lignin. Hence, this leads to different reactivity degrees, which influence the extent of modification on physical and chemical properties of biomass.

Other than organic compounds, inorganic compounds are also crucial in shaping the final biochar structure. Unlike organic compounds, they do not react chemically during pyrolysis, but through ash fusion or sintering. The amount of inorganic compounds often remains the same after pyrolysis. Report states that high percentage weight ash causes swell and fusion effect during pyrolysis, which leads to structural loss (Amonette and Joseph, 2009). On contrary, biomass with low percentage weight ash can still exhibits minor thermoplastic property (Basu 2010).

2.2.2 Percentage weight yield and percentage weight conversion:

Percentage weight yield is defined as the ratio of mass of pyrolysis product to mass of original biomass as shown in Eq. 5:

$$\text{Percentage yield} = \frac{m_{\text{biochar}}}{m_{\text{biomass}}} \times 100\%$$

(5)

Percentage weight yield is reported to decrease as pyrolysis temperature increases (Jia and Lua 2008). Such result is associated with more volatiles being released resulting in larger mass loss (Lua et al. 2006). On top of that, it is also reported that decrease of yield is also associated with rearrangement of carbon structure, which causes release of hetero-atoms (Daud et al. 2001).

$$\text{Percentage weight conversion} = \frac{m_{\text{biomass}} - m_{\text{biochar}}}{m_{\text{biomass}}} \times 100\%$$

(6)

Percentage weight conversion indicates the thermal degradation that occurs in pyrolysis as given in Eq. 6 (Jia and Lua 2008). It is reported that percentage weight conversion increases abruptly in temperature range of 400°C – 650°C. Follow by 650°C – 850°C, the percentage weight conversion only increases slightly (Jia and Lua 2008). Jia and Lua (2008) explained that at lower temperature range, volatiles released are mainly comprise of low molecular weight volatiles; as for high temperature range, high molecular weight volatiles will be
released. Although high molecular weight volatiles are released at high temperature range, only small decrement of weight was reported.

3. Effect of pyrolysis on biochar properties:
   As discussed in previous section, pyrolysis temperature, heating rate and residence time are crucial factors in shaping biochar’s structure. This section discussed the effects of pyrolysis parameters on the various properties of biochar, such as chemical compositions, textural property, surface functional groups and graphitic structure. These properties directly affect DCFC performance, and as such, the linkage between DCFC performance and pyrolysis parameters could be established.

3.1 Chemical composition:
Biochar chemical compositions such as percentage weights moisture, volatiles, ash, and fixed carbon are greatly dependent on the pyrolysis temperature. Increase in pyrolysis temperature increases the percentage weight fixed carbon as reported by Lua et al. (2006). This increment corresponds to decrease in percentage weight volatiles, where more volatiles are released at higher pyrolysis temperature (Basu 2010). As for percentage weight moisture, there is no specific trend observed. Slight difference in percentage weight moisture after pyrolysis could be due to the differences in the original percentage weight moistures of various biomasses (Lua et al. 2006). As for percentage weight ash, it is fairly stable as it originates from biomass initially as reported by Lua et al. (2006).

Apart from pyrolysis temperature, residence time and heating rate play important roles in determining biochar chemical properties as well. Lengthy residence time enables more volatiles to be released from biomass structure, decreasing percentage weight volatiles. Moreover, lengthy residence time also provides sufficient time for secondary cracking, contributing to percentage weight fixed carbon (Mohan et al.2006). High heating rate contributes to extensive reaction rate, which also leads to more volatiles being release, causes low percentage weight volatiles. On contrary, low heating rate such as the case of slow pyrolysis enables reaction to achieve equilibrium (Onay and Kockar 2003).

3.2 Graphitic structure:
Surface functional groups on biochar are temperature dependent as reported by Xiao et al. (2010), where increase in pyrolysis temperature will lead to loss of functional groups, particularly oxygen functional groups. Such condition is associated with breakdown of functional groups, and some of them could recombine, forming volatiles and escape to the ambient environment. Similar report by Jia and Lua (2008) was found after analysing the IR transmittance of functional groups at 900°C, which found that IR transmittance peak shrank, implying possible thermal cracking of organics forming light gas species, leading to loss of functional groups.

3.3 Surface functional group:
As mentioned in previous section, increase in pyrolysis temperature causes more carbon layer rearrangement, leading to orderly arranged lattice. Such observation could be associated with increasing degree of graphitization. The increase in degree of graphitization also indicates the loss of surface defects, which act as active sites during electrochemical oxidation.

3.4 Textural property:
Textural properties such as porosity and surface area are interrelated properties. Lua et al. (2006) shows that in the range of 400 – 600°C, increase in pyrolysis temperature leads to release of low molecular weight volatiles from the biomass matrix structure, rearrangement of carbon layers occur, which leads to creation of pores. Emergence of more pores indicates increase in number of pores, which also associates with increase in pore volume (Daud et al. 2001). Further increase in pyrolysis temperature to the range of 700°C – 900°C, produces detrimental effects on textural properties, where volatiles of high molecular weight sinter and soften, causing destruction of wall between pores (Amonette et al. 2009). This leads to depolymerisation of melt and total volume shrinking (Lua et al. 2006). Destruction of wall between the pores also leads to pore-fusion, forming larger pores such as mesopores (Daud et al. 2001).

Heating rate also plays an important role in determining biochar surface area. According to Lua et al. (2006), increase in heating rate favours formation of micropores, hence surface area. However, such condition persists until heating rate is greater than 10°C/min. High heating rates causes cell structure melts down and destroyed, leading to plastic transformations. Additionally, residence time also affects surface area, where, sample is held longer at pyrolysis temperature, degree of pore formation is more extensive due to larger amount of volatiles being released from the biomass matrix structure (Lua et al. 2006). However, increasing residence time at temperature >600°C leads to decreasing surface area due to formation of intermediate melts through softening and sintering by low molecular weight volatiles. These melts are capable of sealing off the pores, decreases pores number (Lua et al. 2006).

Flow rate of purge gas affects textural property of biochar as well, whereby low flow rate produces less effective purging effect, leading to a possibility that volatiles could be entrained in nitrogen gas stream. These deposits could re-deposited on the biochar surface, such condition will lead to blockage of pore structure, leading to restriction of further formation of pores, which in turn, reducing the
surface area. On contrary, high flow rate would lead to cooling of surface of the biochar, reducing reaction rate of thermal degradation, causes less volatiles being removed, disrupting pore formation (Lua et al. 2006).

4. Conclusion:
   DCFC offers many promising advantages in terms of electricity generation and environmental aspects, as compared to the conventional combustion system. Critical properties of fuels including chemical composition, surface functional group, degree of graphitization and textural property would strongly affect the DCFC electrochemical performance. While employing biomass as the carbon fuel for DCFC, these chemical and physical properties should be carefully-controlled by fine-tuning the pyrolysis conditions including the heating rate, residence time and pyrolysis temperature.

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