Bulgarian Chemical Communications, Volume 52, Special Issue C (pp. 20-25) 2020 DOI: 10.34049/bcc.52.C.0029

Chemically Activated N-doped Hydrochar flakes and Char for energy applications

A. Plavniece[1,2*], G. Dobele[1], A. Volperts[1], A. Zhurinsh[1], K. Kaare[3], I. Kruusenberg[3], J. Locs[4]

[1] *Latvian State Institute of Wood Chemistry, Riga, Latvia*
[2] *Riga Technical University, Faculty of Material Science and Applied Chemistry, Riga, Latvia*
[3] *National Institute of Chemical Physics and Biophysics, Akadeemia tee 23, Tallinn, Estonia*
[4] *Rudolfs Cimdins Riga Biomaterials Innovations and Development Centre of RTU, Institute of General Chemical Engineering, Faculty of Materials Science and Applied Chemistry, Riga Technical University, Riga, Latvia*

Hydrochar and wood char are two differently obtained forms of carbon which variate in structure. Hydrothermal carbonization for hydrochar and traditional carbonization for wood char, followed by alkali activation and nitrogen doping with DCDA was used to obtain carbon materials. Material porosity, structure and composition were studied, as well as their application as cathodes for oxygen reduction in fuel cells using rotation disc electrode. It is shown that Activated N-doped Hydrochar, as well as Chemically Activated N-doped Wood char, have demonstrated promising electrochemical behaviour.

Keywords: wood, hydrothermal treatment, activated carbon, porous structure, fuel cells

INTRODUCTION

Nowadays production of activated carbon (AC) is one of the ways to obtain commercial products with added value. Activated carbon is used in methane and hydrogen storage, air purification, decaffeination, gold purification, metal extraction, water purification, medicine, sewage treatment, air filters in gas masks and respirators, filters in compressed air, teeth whitening, and many other applications. There are a number of properties which make AC an invaluable material for electrochemical applications since it is stable in various media, has a highly developed specific surface, sufficient electric conductivity and can be produced at a relatively low cost.

It is known that it is practically impossible to obtain highly porous carbon materials with the developed nanoporous structure without alkali activation. Before activation thermal or hydrothermal treatment is used to obtain char. Hydrothermal carbonization (HTC) is a pressurized treatment in liquid media where biomass is converted into solid carbon-rich materials at relatively low temperatures under autogenous pressures [1]. Basically, HTC is a thermo-chemical conversion technique which uses subcritical water or solvent for the conversion of wet or dry biomass into carbonaceous products [2]. Carbon-rich products, which are also referred to as hydrochar, are obtained by a series of reactions such as hydrolysis, dehydration, decarboxylation, demethanation, and aromatization [3].

HTC temperature is dependent on the type of starting materials and its decomposition temperature, typically using a range of 150 - 350^{o}C [4]. The hydrochar exhibits distinct characteristics, including sphere-like morphology and core-shell chemical structure with a hydrophobic nucleus and hydrophilic shell, with high oxygenated functional group (OFG) content which makes it an effective precursor for the production of chemically activated carbon. The HTC process offers several advantages over conventional dry-thermal pre-treatments like slow-pyrolysis in terms of improvements in the process performances and economic efficiency, especially its ability to process wet feedstock without pre-drying requirement. Char produced from both processes exhibits significantly different physicochemical properties that affect their potential applications [5]. Electrochemical properties of carbon materials depend on the ratio of basal planes and edge structures, and in general, are defined by the surface concentration of structural defects. According to this, the highest catalytic activity should be exhibited by the less-ordered activated carbons [6]. AC has highly dispersed structure and their specific surface can reach more than 2000 m^2 g^{-1}. Another important feature of biomass-based AC is the presence of micropores with a characteristic size of less than 2 nm. Also, AC has various surface oxygen groups which are being formed in the process of carbons synthesis and activation [7].

One of the advantages of carbon materials lies in the vast possibilities of their modification, which leads to new areas of application. For example,

---

* To whom all correspondence should be sent:
ance.plavniece@inbox.lv

introduction of various heteroatoms into the carbon matrix makes them more active for the electrocatalytic processes like the reduction of molecular oxygen [8] and electropositive metals [9], oxidation of volatile hydrides and organic compounds [10], [11], etc. Among the various heteroatoms (N, B, P, S), nitrogen has significant advantages for the modification of graphene-like materials since nitrogen and carbon has similar atomic sizes and can form a strong covalent bond. Theoretical studies [12] demonstrated that nitrogen can be viewed as an n-type donor for transferring electrons to carbon atoms. Application of N-doped carbon materials as catalysts of oxygen reduction in fuel cells for the transformation of chemical energy into electricity is another actual and prospective approach for the use of carbon materials. Fuel cells attract attention due to their high efficiency [13], independence from the power grid and longer operation times comparing to accumulators [14]. Alkali fuel cells are among the most effective devices for the generation of electricity as their efficiency reaches 70%. It is one of the most developed technologies which has been used from the 60s by NASA for Apollo and Space Shuttle programs [15].

Despite the considerable research efforts toward the increase of performance, efficiency and durability of fuel cells, there still is no successful upscale commercialization [16], [17]. Development of new non-platinum catalysts is one of the crucial problems for the widespread application of fuel cells. Besides price considerations, platinum or other precious materials containing catalysts are prone to catalyst poisoning and have rather poor stability [18], [19]. Thus it is highly important to develop cheap, non-platinum catalysts with the same electrochemical activity and higher stability [14].

The aim of this work was to synthesize activated carbons using wood charcoal and hydrochar as precursors, dope them with nitrogen to obtain electrochemical catalysts and study them in oxygen reduction reactions for fuel cells.

MATERIALS AND METHODS

Hydrochar (HTC) was produced from birch wood chips: 300g of dry wood chips were dispersed in 4l of distilled water, followed by its transfer into a stainless steel autoclave (Parr). The HTC reactor was heated to the target temperature and time. After the target time was reached reactor was cooled to room temperature, the solid product was collected by filtration and followed by drying at 105°C. In this study, the temperature was controlled at 250°C while the reaction times were set at 4h.

Hydrochar and wood char (SIA “Fille”, Latvia) (AWC), were refined in a planetary mill, fraction ~$5x10^{-6}$ m. Activated carbons (AC) were obtained using a chemical activation method with NaOH. Activation process is described in details elsewhere [7], [20].

Nitrogen was introduced into activated samples using dicyandiamide (DCDA) solution in dimethylformamide with mass ratio of carbon material/DCDA 1:20. Doping was performed at 800°C for 1 hour in an argon atmosphere. For AWC additional heat treatment was used [21].

Porous characteristics were determined from nitrogen adsorption isotherms using Nova 4200e instrument (Quantachrome, USA).

The elementary composition was evaluated using the Vario Macro CHNSO device (Elementar, Germany).

X-ray diffraction (XRD) data were collected on a PANalytical X’Pert Pro diffractometer (Malvern Panalytical Ltd, UK). Cu Kα1 radiation was used, time per step was 50s, step size 0.050º2Θ, irradiated length 7 mm. X’Pert Highscore software and PDF-2 database were used for phase identification.

Scanning electronic microscopy (SEM) was performed using the Vega device (Tescan, Czech Republic).

The electrochemical measurements were performed with a standard three-electrode system using the rotating disk electrode (RDE) method. Saturated calomel electrode was used as a reference electrode and Pt foil was used as a counter electrode. Glassy carbon disk (GC-20SS, Tokai Carbon) with a geometric area of 0.2 cm^2 was used as a working electrode. The catalyst ink with a concentration of 4 mg mL^{-1} in isopropanol was prepared by using 0.25 % of AS-04 OH^- ionomer (Tokuyama Corp., Japan), followed by sonication for 1h. The electrodes were evenly covered with the catalyst material by drop coating with 20 μl of previously prepared catalyst ink. After coating the electrodes were dried in the oven at 60 ºC. Pine AFMSRCE (Pine, USA) rotator and speed controlling unit was used for the RDE measurements. The software used for controlling the experiments was Nova 2.1.2 (Metrohm Autolab P.V., The Netherlands) and the potential was applied with a potentiostat/galvanostat Autolab PGSTAT 128N (Metrohm Autolab P.V., The Netherlands). Measurements were performed in 0.1 M KOH solution at room temperature (23ºC) at rotation rate of 1900 rpm. Electrode preparation, electrochemical and fuel cell testing has been discussed in more detail by S. Ratso *et al.* [22], [23].

RESULTS AND DISCUSSION

Carbon materials on the base of wood and its treatment residues, synthesized using NaOH activation, have demonstrated prospective properties when applied for electrochemical purposes, specifically as electrodes in supercapacitor [24–26]. In this study, the alkali activation method was used for the synthesis of activated carbons on the base hydrochar and wood char with consequent nitrogen doping.

Yields and elemental composition of all the materials under study are presented in Tab.1.

Table 1. Yield and elemental composition of wood char (Carbonizate), hydrochar (HTC), and AC based on wood char (AWC and AWC-N) and hydrochar (AHTC and AHTC-N) pre and post nitrogen doping

Sample	Yield*	N	C	H	O
	%	%	%	%	%
Alder wood	-	0.24	49.31	5.08	45.37
Carbonizate	35	0.78	82.54	1.94	14.53
AWC	11	0.7	93.8	0.62	4.75
AWC-N	-	4.92	91.53	0.82	2.73
HTC	49	0.17	69.92	4.12	25.79
AHTC	9	1.42	91.31	1.36	6.91
AHTC-N	-	5.31	90.05	1.81	2.55

*All yields are calculated from raw materials

The yield of HTC is considerably higher than that of wood char (Carbonizate) – 49 vs 35% respectively. At the same time, HTC contains notably less carbon, only 69.92 vs 82.54% and more oxygen, 25.79 vs 14.53%. These factors are important from the standpoint of activated carbon production and can influence the feasibility of the process taking into account concepts of biorefinery. Activated carbons prepared from both precursors have remarkably similar high carbon content. In the case of AC synthesized from HTC (AHTC) a higher oxygen and nitrogen contents are observed, which can be among the number of factors influencing higher N content in the doped sample (AWC-N and AHTC-N, respectively). Nitrogen doping does not lead to mass losses.

Morphology of the samples under study was evaluated using SEM (Fig.1). It can be seen that for HTC and AHTC (Fig.1 A and B) the distinct stratified structure consisting of layers of AHTC is formed in the process of activation. For the carbonizate and AWC, the structure does not change in the process of activation, however, the size and the shape of particles alters: their size diminishes and the edges become more rigid and pronounced (Fig.1 B and C).

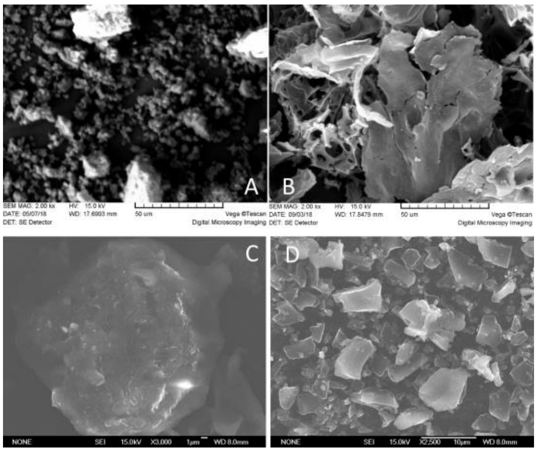

Fig.1. SEM images of hydrochar (HTC) (A), AC based on hydrochar (AHTC) (B), wood char (carbonizate) (C) and AC based on wood char (AWC) (D).

Table 2. Comparison of the porous structure of wood char (Carbonizate), hydrochar (HTC), and N-doped AC based on wood char (AWC-N) and hydrochar (AHTC-N)

Sample	Specific surface area (BET)	Total pore volume	Micropores volume (DR)	Mesopore volume
	m^2 g^{-1}	mm^3 g^{-1}	mm^3 g^{-1}	mm^3 g^{-1}
Carbonizate	6.91	72.24	35.14	37.10
AWC-N	2205	1157	767	390
HTC	4.22	11.33	1.15	10.18
AHTC-N	2853	1906	874	1032

Wood char and HTC have low porosity. AWC-N and AHTC-N demonstrate the high efficiency of alkali activation with specific surface areas 2205 and 2853 m^2 g^{-1} according to BET theory and total pore volumes 1157 and 1906 m^2 g^{-1}, respectively. As described in the previous article comparing doped and non-doped samples specific area and total pore volume insignificantly decrease [27].

Comparing AWC-N and AHTC-N, the mesopore volume increases from 390 mm^3 g-1 to 1032 mm^3 g-1 and the micropore volume is similar for both materials, 767 and 874, respectively. The input of micropores into the total pore volume in the case of AHTC-N is less than half, which points at the mesoporous nature of this material. Micropore volume was calculated using the Dubinin-Radushkevich theory (DR) [28].

X-ray diffraction (XRD), generally considered the "ideal" technique for the structural characterization of materials, not only allows the structures of different carbon allotropes and polytypes to be distinguished from each other but also enables the degree to which the structure of a given carbon form departs from the ideal graphite structure to be determined [29]. Anything that changes interatomic distances, temperature, substitutional doping and stress will be reflected by a change in peak positions (Fig.2).

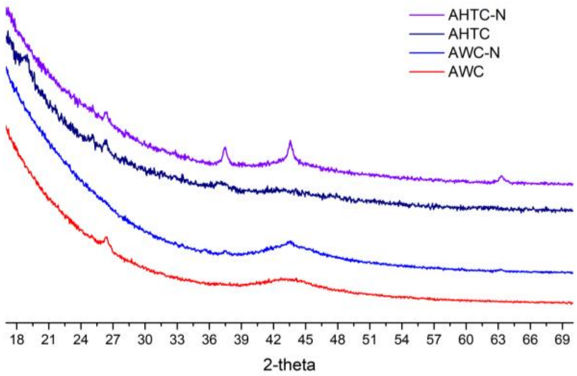

Fig.2. X-ray diffraction patterns of AC based on wood char (AWC), and hydrochar (AHTC), nitrogen-doped AC based on wood char (AWC-N) and hydrochar (AHTC-N)

All diffraction profiles exhibit two prominent broad bands centred around $2\theta = 26$ and 43°, which are currently mentioned as associated with the diffraction of the 002 and 100/101 planes, respectively, with 43° being sharper in the case of doped carbons, especially prominent for AHTC-N. The peak at around 64° belongs to (103) crystal plane, reflections assigned to graphite [30], it likely appears due to the higher temperature treatment (800^{o}C) during the doping process. These are characteristic of typical graphitic structure and are associated with the crystallite height and width, they become more prominent with the treatment of carbonaceous materials at the higher temperatures [31].

Rotating disc electrode technique is widely applied to study the oxygen reduction mechanisms at the cathode for fuel cells [32]. Fig.3. illustrates catalyst polarization curves of the electrodes made from samples under study comparing to commercial 20% Pt/C-electrode and multiwall carbon nanotubes (MWCNT). To evaluate the ORR (oxygen reduction reaction) activity of a catalyst material, the onset potential is an important criterion, which for both biomass-derived nitrogen-doped wood-based carbons is approximately at -0.09 V vs SCE. It should be noted that AWC shows good results only after additional heat treatment. Despite increasing the rotation rate, the onset potential remained the same indicating at least short-term stability of the catalyst.

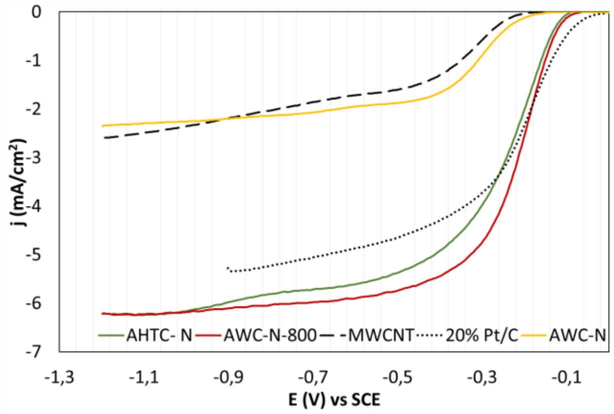

Fig.3. Comparison of RDE results for nitrogen-doped AC based on wood char (AWC-N and AWC-N-800 without and with additional thermal treatment) and hydrochar (AHTC-N), multiwall carbon nanotubes (MWCNT), and commercial 20% Pt/C catalyst in O_2 saturated 0.1 M KOH (v =10 mV/s, ω=1900 rpm)

The onset potential and half-wave potential for both N-doped wood-based catalysts are much more positive compared to multiwall carbon nanotubes (MWCNT) which are often used as electrode material in various types of fuel cells [33], [34].

CONCLUSIONS

Two methods, namely carbonization and hydrothermal treatment are compared for the synthesis of the nitrogen-doped activated carbons. Carbons porosity, structure and composition were studied and revealed differences in their structure.

Carbons porosity, structure and composition were studied and revealed differences in their structure. It is shown, that hydrothermal treatment promotes the development of mesoporosity in the materials. It is demonstrated that both pretreatment methods allow obtaining of nanporous carbons, and hytrothermal method leads to development of the higher mesoporosity. Doping with DCDA (nitrogen content 4-5%) leads decrease of oxygen in the samples and negligible alterations in the porous structure.

Both nitrogen-doped activated biomass-based catalysts were tested using rotation disc electrode for application as cathodes for oxygen reduction in fuel cells. An onset potential of -0.09 V vs SCE and a half-wave potential of -0.16-0.18 V vs SCE in an alkaline medium, along with excellent stability, are making them promising alternatives to state-of-art precious-metal-based catalysts and excellent catalyst carrier for many different applications. The superiority of the wood-derived catalysts is demonstrated with even similar oxygen reduction reaction activity comparable to the commercial 20% Pt/C catalyst in 0.1 M KOH solution. It is demonstrated that the most active catalyst was obtained in sequence of hydrothermal pretreatment, alkali activation and nitrogen doping. To reach the same catalytic properties for the materials obtained in the course of conventional carbonization, activation and nitrogen doping the additional thermal treatment was required.

Taking into account biorefinery and green chemistry concepts hydrothermal treatment offers another promising approach for the synthesis of novel highly efficient and ecologically friendly catalysts.

ACKNOWLEDGEMENTS

The study was supported by LZP-2018/1-0194 project “Nanostructured Nitrogenated Carbon Materials as Promoters in Energy Harvesting and Storage Technologies (NN-CARMA)”, Riga Technical University's Doctoral Grant programme and Latvian State Institute Of Wood Chemistry Grant “Biobased catalysts for biorefining”.

REFERENCES

[1] K. Fakkaew, T. Koottatep, and C. Polprasert, “Faecal sludge treatment and utilization by hydrothermal carbonization,” *J. Environ. Manage.*,**216**, 421–426 (2018).

[2] Z. Liu, F.-S. Zhang, J. Wu. Characterization and application of chars produced from pinewood pyrolysis and hydrothermal treatment. *Fuel*, **89**, (2), 510–514 (2010).

[3] G. K. Parshetti, S. Kent Hoekman, R. Balasubramanian. Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. *Bioresour. Technol.*, **135**, 683–689 (2013).

[4] M. Sevilla, A. B. Fuertes, and R. Mokaya. High density hydrogen storage in superactivated carbons from hydrothermally carbonized renewable organic materials. *Energy Environ. Sci.*, **4** (4), 1400 (2011).

[5] H. S. Kambo, A. Dutta. A comparative review of biochar and hydrochar in terms of production, physico-chemical properties and applications. *Renew. Sustain. Energy Rev.*, **45**, 359–378 (2015).

[6] S. L. Candelaria et al. Nanostructured carbon for energy storage and conversion. *Nano Energy*, **1**, 195–220 (2012).

[7] G. Dobele, T. Dizhbite, M. V. V. Gil, A. Volperts, T. A. Centeno. Production of nanoporous carbons from wood processing wastes and their use in supercapacitors and CO2 capture. *Biomass and Bioenergy*, **46**, 145–154 (2012).

[8] V. V. Strelko, V. S. Kuts, P. A. Thrower. On the mechanism of possible influence of heteroatoms of nitrogen, boron and phosphorus in a carbon matrix on the catalytic activity of carbons in electron transfer reactions. *Carbon*, **38** (10), 1499–1503 (2000).

[9] V. V. Strelko, Selektivnaâ sorbciâ i kataliz : na aktivnyh uglâh i neorganičeskih ionitah. Kiyv: Naukova Dumka, 2008.

[10] A. Bagreev, J. Angel Menendez, I. Dukhno, Y. Tarasenko, T. J. Bandosz. Bituminous coal-based activated carbons modified with nitrogen as adsorbents of hydrogen sulfide. *Carbon N. Y.,* **42**, (3), 469–476 (2004).

[11] S. V. Mikhalovsky, Y. P. Zaitsev. Catalytic properties of activated carbons I. Gas-phase oxidation of hydrogen sulphide. *Carbon N. Y.,* **35**, (9), 1367–1374 (1997).

[12] S. U. Lee, R. V. Belosludov, H. Mizuseki, Y. Kawazoe. Designing nanogadgetry for nanoelectronic devices with nitrogen-doped capped carbon nanotubes. *Small*, **5** (15), 1769–1775, (2009).

[13] F. Barbir, T. Gómez. Efficiency and economics of proton exchange membrane (PEM) fuel cells. *Int.*

J. Hydrogen Energy, **22** (10–11), 1027–1037 (1997).

[14] O. Gröger, H. A. Gasteiger, J.-P. Suchsland, "Review—Electromobility: Batteries or Fuel Cells?. *J. Electrochem. Soc.*, **162**, (14), 2605–2622 (2015).

[15] M. C. Williams. Fuel Cells. *Fuel Cells Technol. Fuel Process.*, 11–27 (2011).

[16] M. K. Debe, Electrocatalyst approaches and challenges for automotive fuel cells. *Nature*, **486**, (7401), 43–51 (2012).

[17] Y. M. Volfkovich, V. E. Sosenkin, and V. S. Bagotsky, "Structural and wetting properties of fuel cell components," J. Power Sources, vol. 195, no. 17, pp. 5429–5441, Sep. 2010.

[18] V. S. Bagotzky, N. V. Osetrova, A. M. Skundin. Fuel Cells: State-of-the-Art and Major Scientific and Engineering Problems. *Russ. J. Electrochem.*, **39** (9), 919–934 (2003).

[19] X. Cheng et al. A review of PEM hydrogen fuel cell contamination: Impacts, mechanisms, and mitigation. *J. Power Sources*, **165** (2), 739–756 (2007).

[20] G. Dobele, D. Vervikishko, A. Volperts, N. Bogdanovich, E. Shkolnikov. Characterization of the pore structure of nanoporous activated carbons produced from wood waste. *Holzforschung*, **67** (5), 587–594 (2013).

[21] K. Kaare et al. Highly active wood-derived nitrogen-doped carbon catalyst for the oxygen reduction reaction. *ACS Omega*, **5** (37), 23578–23587 (2020).

[22] S. Ratso et al. Highly active nitrogen-doped few-layer graphene/carbon nanotube composite electrocatalyst for oxygen reduction reaction in alkaline media. *Carbon N. Y.*, **73**, 361–370 (2014).

[23] S. Ratso, I. Kruusenberg, U. Joost, R. Saar, K. Tammeveski. Enhanced oxygen reduction reaction activity of nitrogen-doped graphene/multi-walled carbon nanotube catalysts in alkaline media. *Int. J. Hydrogen Energy*, **41** (47), 22510–22519 (2016).

[24] G. Dobele et al. Wood-based activated carbons for supercapacitors with organic electrolyte. *Holzforschung*, **69** (6), 777–784 (2015).

[25] A. Volperts, G. Dobele, D. Vervikishko, and E. Shkolnikov. Nanoporous wood based carbon materials for supercapacitors electrodes, 2014.

[26] G. Dobele, A. Volperts, A. Plavniece, A. Zhurinsh, I. Kruusenberg. Wood-based nitrogen doped activated carbons for fuel cells. 18–21.

[27] A. Volperts et al. Biomass based activated carbons for fuel cells. *Renew. Energy*, **141** (2019).

[28] R. C. Bansal and M. Goyal, Activated carbon adsorption. Taylor & Francis, 2005.

[29] E. J. Bottani and J. M. D. Tascón, Adsorption by carbons. Elsevier, 2008.

[30] J. C. Arrebola, A. Caballero, L. Hernán, J. Morales. Graphitized carbons of variable morphology and crystallinity: A comparative study of their performance in lithium cells. *J. Electrochem. Soc.*, **156** (12) (2009).

[31] H. Aso, K. Matsuoka, A. Sharma, A. Tomita. Structural analysis of PVC and PFA carbons prepared at 500-1000°C based on elemental composition, XRD, and HRTEM. *Carbon N. Y.*, **42** (14), 2963–2973 (2004).

[32] S.-J. Lee, S.-I. Pyun, S.-K. Lee, S.-J. L. Kang. Fundamentals of Rotating Disc and Ring-Disc Electrode Techniques and their Applications to Study of the Oxygen Reduction Mechanism at Pt/C Electrode for Fuel Cells. *Isr. J. Chem.*, **48**, (3–4), 215–228 (2008).

[33] N. Thepsuparungsikul, N. Phonthamachai, H. Y. Ng. Multi-walled carbon nanotubes as electrode material for microbial fuel cells. *Water Sci. Technol.* **65** (7), 1208–1214 (2012).

[34] C. Luo, H. Xie, Q. Wang, G. Luo, C. Liu. A Review of the Application and Performance of Carbon Nanotubes in Fuel Cells. *J. Nanomater.*, 1–10 (2015).