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Platinum-Free Electrocatalyst for Oxygen Reduction Reaction Derived from the Direct Pyrolysis of Watermelon Peels

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Abstract: Carbon-based nanomaterials derived from the pyrolysis of heteroatom-containing carbonaceous precursor was shown to exhibit significant electrocatalytic activity towards oxygen reduction reaction (ORR). Biomass from agricultural waste could be seen as possible low-cost precursor for the preparation of carbon-based ORR electrocatalysts. In this study, watermelon peels (WP) were directly pyrolyzed under N_2 atmosphere to produce novel carbon-based ORR electrocatalysts. WP were oven-dried and pulverized using a mechanical grinder to produce WP powder. A weighed amount of the resulting powder was then transferred into a ceramic boat and inside a quartz tube furnace. The WP powder was pyrolyzed from room temperature to pyrolysis temperature $\boldsymbol{T}$ at a rate of 5 °C/min under N_2 atmosphere. The temperature was held at $\boldsymbol{T}$ for an hour, followed by natural cooling back to room temperature. The pyrolysis temperature was optimized, with $\boldsymbol{T}$ = 800 °C, 900 °C, and 1000 °C. The resulting pyrolysis products were characterized using cyclic voltammetry (CV), rotating disc electrode voltammetry (RDE), and scanning electron microscopy-energy dispersive x-ray spectroscopy (SEM-EDX). CV revealed that WP pyrolyzed at 1000 °C gave the most positive onset potential (E_{onset} = 0.40 V) and highest current density (j = 10.79 mA/cm^2), compared to those pyrolyzed at 800 °C (E_{onset} = 0.30 V; j = 2.047 mA/cm^2) and 900 °C (E_{onset} = 0.30 V; j = 3.494 mA/cm^2). Levich analysis from RDE data showed that the electrocatalysts prepared at 1000 °C proceeded closest to the ideal four-electron route, compared to those prepared at 800 °C and 900 °C. SEM-EDX analysis showed the changes WP underwent in terms of surface morphology and elemental composition, which are then correlated with the apparent electrocatalytic activities of pyrolyzed WP. These findings present the feasibility of using WP as low-cost precursor for ORR electrocatalysts, which could be utilized in fuel cells.

Keywords: oxygen reduction reaction; pyrolysis; Pt-free electrocatalysts; waste biomass

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1. Introduction

The rapid depletion of fossil fuels, along with its negative environmental impact, led researchers to search for new sources of clean and renewable energy [1-2]. Among the growing list of alternative energy sources, fuel cells are said to be one of the most practical renewable energy source [3]. A fuel cell is an energy device that electrocatalytically oxidizes a fuel (e.g. H_2 gas, liquid alcohol) at the anode side, where the electrons produced during the process is transmitted via an external circuit to generate electrical current before it is intercepted by oxygen at the cathode side [4]. A number of researches were focused on optimizing the electro-oxidation of the fuel at the anode side [5]. However, attention must also be directed in improving the oxygen reduction reaction (ORR) at the cathode compartment, which is controlled by slow reaction kinetics and high over potential that in turn limits the overall performance of the fuel cell [6]. Due to these limitations, researchers seek to develop novel electrocatalysts that are highly active towards the ideal four-electron route of the ORR [5, 7].

Based on various studies, platinum is considered as one of the best electrocatalysts for ORR due to its high positive open circuit potential (OCP) and the ORR proceeding via the ideal four-electron route [5, 8]. However, the search for alternative ORR electrocatalysts is still underway due to problems associated with Pt, such as high cost, low poison tolerance in operation [5], methanol/ethanol intolerance [8], susceptibility to carbon monoxide poisoning [9], and lesser stability in acidic electrolytes compared with non-precious metal electrocatalysts [10]. A number of studies considered the transition metal-based catalysts and platinum-free carbon based materials as promising substitutes for platinum-based catalysts for ORR activity [8-9, 11]. Pt-free carbon based materials are shown to have good electrocatalytic properties towards ORR, have greater resistance against catalytic poisoning, and are cheaper in terms of their precursors and production process [7, 11-12].

Biomass, particularly from agricultural wastes, was found to be an ideal precursor for Pt-free carbon-based ORR electrocatalysts. Not only that it is carbon rich, but it also contains a variety of heteroatoms such as nitrogen, sulfur, and phosphorus, which could later serve as dopants for the graphitic carbon nanostructures formed after pyrolysis at high temperatures [12]. Various waste biomass has been converted via pyrolysis into ORR electrocatalysts, such as rice straws [13], corn husks and cobs [14], tangerine peels [15], and pomelo peels [7]. Recently, Zhong and colleagues pyrolyzed watermelon rinds at the biochar temperature range (< 800 °C) to produce highly-active ORR electrocatalysts in alkaline media [16]. In this study, waste watermelon rinds (also called peels) were pyrolyzed at a higher temperature range (800 °C – 1000 °C) to produce active ORR electrocatalysts in acidic media for possible application as cathode material for proton-exchange membrane fuel cells (PEMFC).

2. Materials and Methods

2.1 Materials and Chemicals

Waste watermelon peels (WP) were taken from ripe watermelons sources from Nueva Ecija, Philippines. Sulfuric acid 98% (Suprapur) was purchased from Merck. Nafion® solution (DuPont D521) and N,N-dimethylformamide (DMF) were used as solvents for the preparation of the catalyst ink and were purchased from Dupont, USA and RCI Labscan, Thailand, respectively.

2.2 Preparation of Watermelon Peels

WP were first dried in an oven at 70 ℃ - 80 ℃ for 36 h and was pulverized using a mechanical grinder to produce powdered WP.

2.3 Synthesis of Powdered Watermelon Peels

The carbonization of the powdered WP was achieved using a tube furnace at three different temperatures (800 ℃, 900 ℃, and 1000 ℃) for 1 h inside a quartz tube furnace under N_2 atmosphere with a heating rate of $5\ ℃ \cdot min^{-1}$. The pyrolyzed WP were then allowed to cool naturally back to room temperature. The resulting powder was then used in the preparation of the catalyst ink.

2.4 Catalyst Characterization

Catalyst ink was prepared by mixing 1.0 mg of pyrolyzed WP sample with 20 μL Nafion® solution (DuPont D521) and 980 μL DMF. On the other hand, the catalyst ink for rotating disk electrode (RDE) was prepared by mixing 5.0 mg of pyrolyzed sample with 20 μL Nafion® solution (DuPont D521) and 980 μL DMF. Then, the catalyst ink was sonicated until homogeneous. Ten-microliters of the catalyst ink was drop casted on a glassy electron electrode as the working electrode and was subjected to electrochemical testing. Surface characterization of the pyrolyzed WP was done using scanning electron microscopy - electron dispersive X-ray (Phenom ProX) analysis, while the electrochemical properties and ORR activities were evaluated using cyclic voltammetry (CV) and rotating disk electrode- linear sweep voltammetry (RDE-LSV). All electrochemical experiments were performed using a potentiostat (Biologic VSP3000), 0.5 M H_2SO_4 supporting electrolyte, and a three-electrode setup, with Pt coil and Ag/AgCl as counter and reference electrodes, respectively.

CV analyses were performed both in N_2- and O_2-purged electrolyte solution between –0.3 V and 0.8 V at a scan rate of 50 mV/s. RDE-LSV was performed in O_2-saturated electrolyte solution by scanning the potential from OCP to –0.3 V at 10 mV/s while the RDE's rotation speed was varied between 500 rpm to 2000 rpm.

3. Results and Discussion

3.1 Electrochemical Characterizations

3.1.1 Cyclic Voltammetry (CV)

Figure 1 shows the comparison of the cyclic voltammograms of pyrolyzed WP at three different temperatures (800°C, 900°C and 1000°C), along with that of the commercially available Pt/C (Premetek) in N_2- and O_2- purged electrolyte. The cathodic peak seen for Figure 1A to 1C between 0 V to 0.1 V in O_2-purged electrolyte confirms the electrocatalytic activity of the pyrolyzed WP towards ORR. Their current densities and peak potentials are as follows: 800°C (2.05 mA/cm^2 & 0.0905 V), 900°C (3.49 mA/cm^2 & 0.0537 V), and 1000°C (10.8 mA/cm^2 & 0.0306 V) for pyrolyzed WP, while for commercially available Pt/C (0.845 mA/cm^2 & 0.479 V). It is worthy of note that the potential corresponding to the ORR peak is much more negative for pyrolyzed WP compared to that for Pt/C, which was similarly observed in other Pt-free carbon based ORR electrocatalysts [7, 11-12]. For the pyrolyzed WP at 1000°C, there is no evident hydrogen evolution due to metallic impurities.

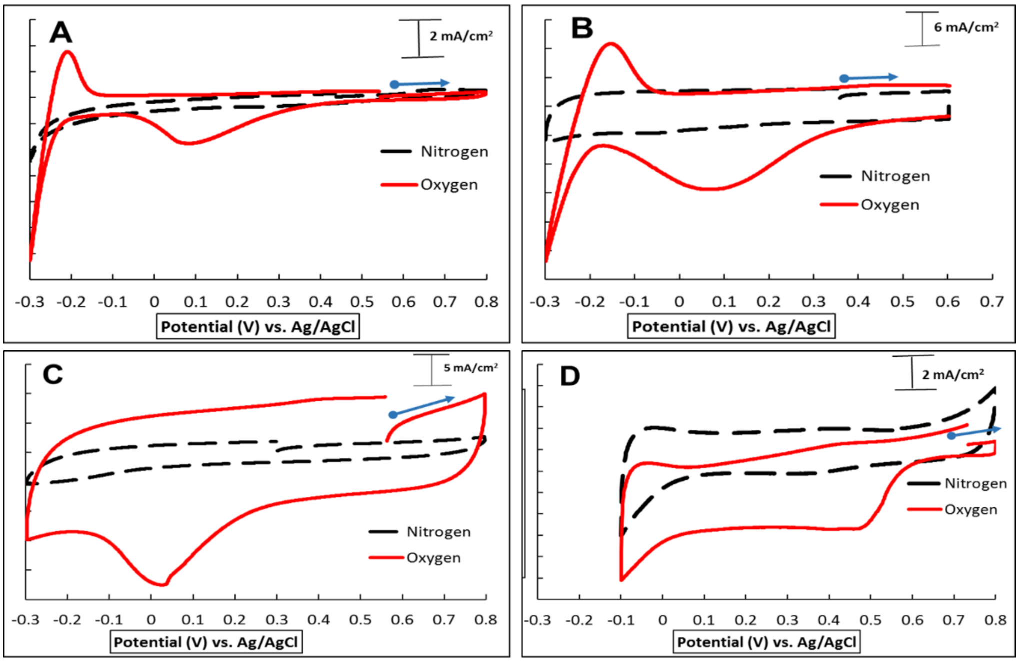


Fig. 1 - Cyclic voltammogram of pyrolyzed watermelon peels at (A) 800 °C, (B) 900 °C, (C) 1000 °C, and (D) commercially-available Pt/C (electrolyte: 0.5 M H_2SO_4, and scan rate: 50 mV/s)

3.1.2 Rotating Disk Electrode- Linear Sweep Voltammetry (RDE-LSV)

ORR polarization curves from RDE-LSV experiments were processed using Levich analysis to determine the number of electrons (n) involved in the ORR for the electrocatalysts under study. Equation (1) relates the ORR current taken at different rotation rates (ω). Other variables include the Faradays' constant (F), electrode area (A), and three non-electrochemical kinetic parameters, namely diffusion coefficient (D), kinematic viscosity (υ), and concentration of oxygen (c_a).

$$i_l = 0.620 nFAD\omega^{\frac{1}{2}} v^{-\frac{1}{6}} c_a \qquad (1)$$

The summary of the resulting n values for each electrocatalysts are presented in Table 1. WP pyrolyzed at 1000 °C has the highest value for n at 3.46. This suggests that ORR on WP pyrolyzed at 1000 °C is dominated by the 4-electron pathway, compared to those pyrolyzed at lower temperatures. Zhong and colleagues also achieved the highest *n* value for their catalyst pyrolyzed at the high end of their experimental temperature range (i.e. 700 °C), implying the importance of pyrolysis temperature in controlling the morphology, porosity, and elemental composition of the pyrolyzed product which greatly contributes to the overall electrocatalytic activity of the material towards ORR [16].

Table 1: Number of electrons transferred in ORR

Temperature (°C)	No. of electrons
Commercially available Pt/C	4.00
700 [*ref. 16]	3.26*
800	1.67
900	2.35
1000	3.46

Figure 2 shows the overlay of sample ORR polarization curves for the different electrocatalysts taken at 1500 rpm. Again, WP pyrolyzed at 1000 °C showed the highest current density corresponding to ORR, which corroborates well with the previous CV data. It should be noticed that the usual sigmoidal feature of the ORR polarization curves observed for Pt/C is not seen in pyrolyzed WP. Such a condition where the diffusional plateau is obtained slowly is also observed for other biomass-derived ORR electrocatalysts, whose nature is still not well known [14].

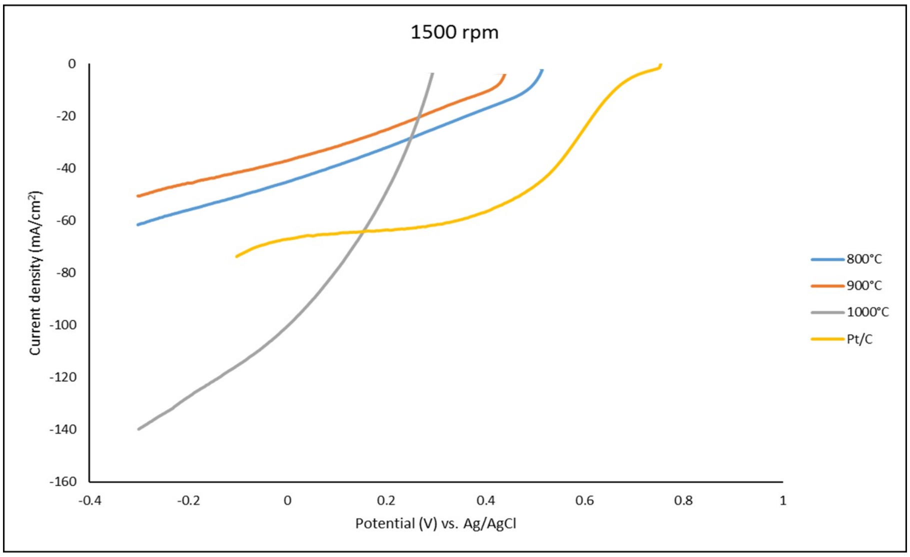


Fig. 2 - Overlaid ORR linear scan polarization curves for pyrolyzed watermelon peels at 800°C, (blue curve), 900°C (orange curve), 1000°C (gray curve), and commercially available Pt/C (yellow curve) (rotation speed: 1500 rpm; electrolyte: 0.5 M H_2SO_4, and scan rate: 50 mV/s).

3.2 Morphological and Surface Characterizations

3.2.1 Scanning Electron Microscopy (SEM)

Morphological characterization was done to correlate changes in surface features with the electrochemical performance. Figures 3 and 4 shows the SEM micrographs at 2000× and 5000× magnification, respectively. As WP is subjected to increasing pyrolysis temperatures, the surface morphology drastically transitioned from a relatively smooth surface to a surface containing multiple macroporous structures. Moreover, the characteristic honeycomb-like structures were shown to be greatly enhanced as the pyrolysis temperature was increased. The presence of various macroporous, mesoporous, and microporous structures in carbon-based electrocatalysts are recognized as important characteristics that greatly enhance electrocatalytic activity [16]. The surface features seen in this study are similar to those observed by Zhong and colleagues [16] at lower pyrolysis temperatures, which suggests how WP retains its structural framework even at high temperature treatments. WP pyrolyzed at 1000 °C appeared to have more of these pore structures (Figure 3-D and 4-D), which could explain its better ORR activity when compared with WP pyrolyzed at 800 °C and 900 °C.

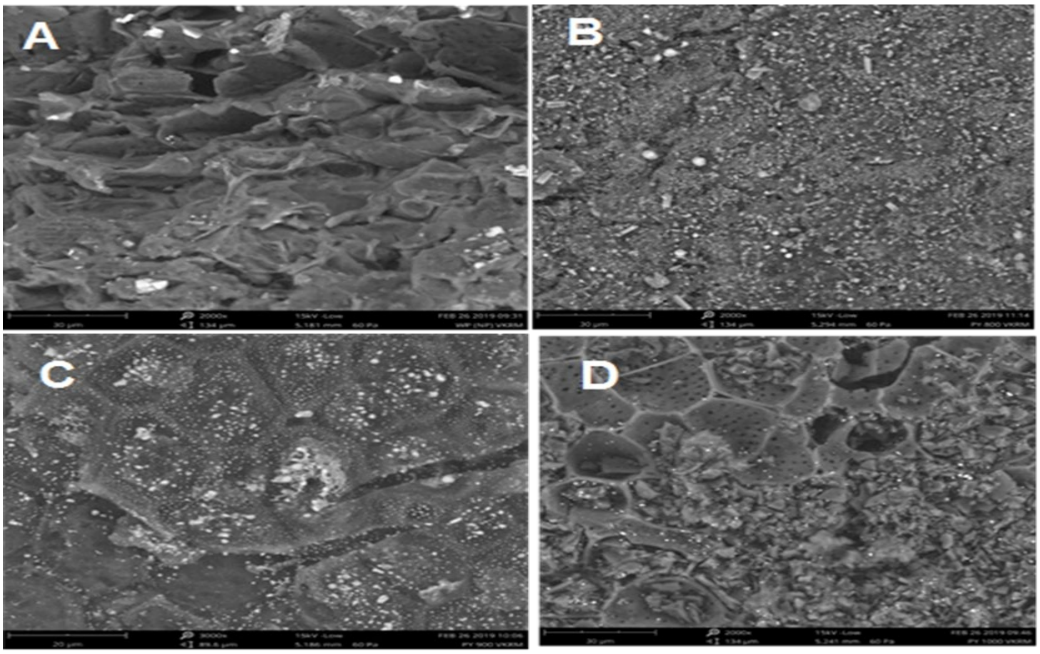


Fig. 3 - SEM images (2000x magnification) of watermelon peels: (A) non-pyrolyzed; pyrolyzed at (B) 800˚C; (C) 900 ˚C; and (D) 1000 ˚C

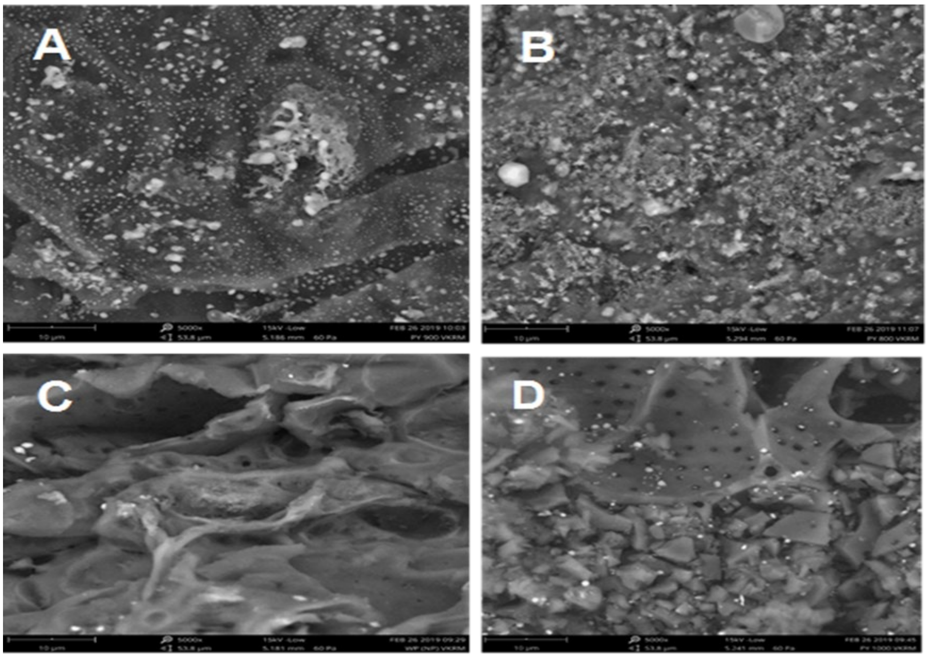
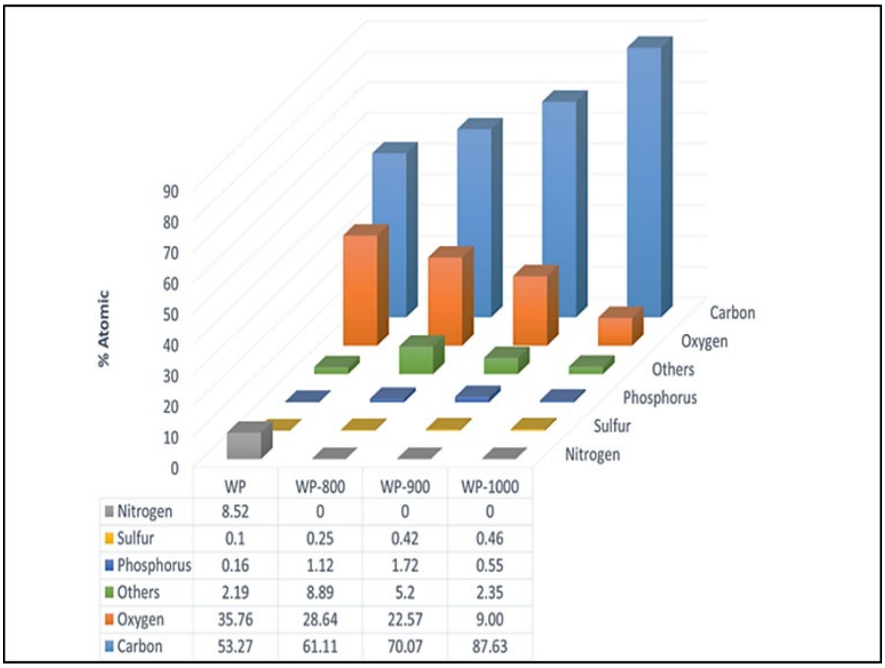


Fig. 4 - SEM images (5000x magnification) of watermelon peels: (A) non-pyrolyzed; pyrolyzed at (B) 800˚C; (C) 900 ˚C; and (D) 1000 ˚C

3.2.2 Energy Dispersive X-Ray (EDX) Analysis

EDX was used to confirm the elemental composition of the catalysts. Figure 5 shows the elemental composition of the pyrolyzed watermelon peels at 1000 °C which could explain its high catalytic activity towards ORR compared to those pyrolyzed at 800°C and 900°C and the commercially available Pt/C. Surprisingly, it was observed that the N content plummeted down to 0% after pyrolysis. This is in stark contrast to the work of Zhong and colleagues, where they noted significant N-doping from similar EDX analysis of the pyrolyzed watermelon rind [16]. It can be inferred that the higher pyrolysis temperature used in the current study resulted to the total elimination of N, converting the element into various volatile gaseous compounds [17]. Nitrogen could still be present in smaller and more integrated forms (e.g. pyridinic-N, pyrrolic-N), which could be better revealed using X-ray photoelectron spectroscopy (which is beyond the scope of this study). However, the EDX data showed that there is a significant enhancement in the amounts of P and S after pyrolysis of the WP. It is known that P and S doping could also induce enhancement in the ORR activity of carbon-based materials, [18-20]. Phosphorus has a similar valence electron configuration to that of N (i.e. both have 5 valence electrons), with the added advantage of having a larger atomic size. These features were shown to cause defect-induced active sites that could facilitate O_2 adsorption during ORR [19]. On the other hand, sulfur-doping of graphene was shown to enhance ORR activity by inducing high positive charge densities or spin densities on the adjacent carbon atoms that serve as the active sites for ORR [20]. Future studies could be done to perform X-ray Photoelectron Spectroscopy (XPS) on these materials to determine the form of S and P within the carbon matrix.



	WP	WP-800	WP-900	WP-1000
■ Nitrogen	8.52	0	0	0
■ Sulfur	0.1	0.25	0.42	0.46
■ Phosphorus	0.16	1.12	1.72	0.55
■ Others	2.19	8.89	5.2	2.35
■ Oxygen	35.76	28.64	22.57	9.00
■ Carbon	53.27	61.11	70.07	87.63

Fig. 5 - Elemental composition of the non-pyrolyzed and pyrolyzed watermelon peels

4. Conclusion

Watermelon peels pyrolyzed at 1000°C gave the highest current density of 10.8 mA/cm^2 and a positive peak potential of 0.0306 V. As observed from the Levich analysis of RDE polarization curves, it also exhibited a value (3.46) dominated by the four-electron route. SEM studies revealed more enhanced honeycomb-like macroporous structures for watermelon peels pyrolyzed at 1000°C. Moreover, EDX analysis showed an enhancement in the sulfur and phosphorus ratios in the carbon structure for the pyrolyzed watermelon peels, which could contribute to the electrocatalytic activity of pyrolyzed WP towards ORR.

5. Acknowledgements

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