

Electrochemical Oxygen Reduction Reaction Performance of Water Hyacinth Derived Porous Non-precious Electrocatalyst in Alkaline Media

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Abstract. This research studied the possibility of converting water hyacinth biomass into the porous non-precious oxygen reduction reaction (ORR) electrocatalyst using a simple, low cost and scalable autogenic pressure method. The electrocatalyst was prepared by thermally annealing water hyacinth root contained ZnCl₂ at 700°C under autogenic pressure conditions. The phase of the catalyst was the mixture of carbon and metal oxide. In addition, rough surface morphology and high porosity were clearly observed using scanning electron microscope. The synthesized catalyst was then determined the ORR performance by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques under O₂ saturated KOH solution. The ORR performance increased as the catalyst loading was increased and the optimum catalyst loading was found to be 1.5 mg/cm² which generated the E_{onset} and E_{1/2} value of 0.93 V and 0.80 V vs. RHE, respectively. Furthermore, the E_{1/2} value of the synthesized catalyst was 230 and 130 mV greater than the catalyst synthesized without ZnCl₂ and commercial carbon (VXC-72R). ORR durability study suggested that the prepared catalyst was durable to operate ORR for 5000 cycles in alkaline media. These results suggested that the autogenic pressure conditions would be a promising technique to prepare highly active and durable biomass derived ORR electrocatalyst.

1 Introduction

Alkaline electrolyte fuel cells (AEFCs) are an highly efficient electrochemical devices that convert chemical fuel of hydrogen (H₂) and oxygen (O₂) directly into electrical energy with absolutely environmental friendliness, because only water and heat are generated as by-products [1]. The main component responsible for the performance and durability of AEFC technology is membrane electrode assembly (MEA), which comprises of an alkaline electrolyte membrane sandwiched between anode and cathode catalyst layers [1].

In AEFC, H₂ is fed into the anode electrode and undergoes electrochemical hydrogen oxidation reaction (HOR) by consuming hydroxide ions (OH⁻) of an electrolyte, generating electrons and water as by product. On the other hand, O₂ supplied to the cathode electrode electrochemically performs oxygen reduction reaction

(ORR) by gaining electrons in the presence of water producing OH⁻ ion [1].

Thermodynamically, the performance of a single AEFC cell must be constant at a potential of 1.23 V [1]. However, a practical single AEFC cell generates potential less than 1.23 V owing to three overpotential losses which are activation, ohmic and mass transport overpotentials [1]. Activation overpotential is mainly a result of the sluggish kinetic of the electrochemical HOR and ORR at the anode and cathode electrodes and it represents the main major losses of AEFC [1]. Electrochemical HOR is minimal overpotential losses (less than 20 mV) during fuel cell operation. On the other hand, electrochemical ORR exhibits large overpotential typically between 300 and 600 mV [2]. The high value of cathodic ORR overpotential strongly results in lowering the overall efficiency of the AEFCs.

In order to decrease the overpotential of the ORR, substantial amount of catalysts is need to boost up ORR

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performance in alkaline media. So far, the most highly active ORR catalyst is the precious platinum nanoparticle supported on carbon (Pt/C) [2]. However, this catalyst has a number of disadvantages, such as high cost, poor durability, susceptibility to gas poisoning and less abundance. These drawbacks are the major limitations to the successful commercialization of AEFCs technology [2]. Thus, a novel high-performance ORR cathode catalyst is essential to subsidize cost and enhance the AEFC performance and durability [3–6].

Recently, researcher succeeded in lowering the value of ORR overpotential by careful design atomic Pt. As a result, the Pt content significantly reduced from 2.0 mg/cm² to 0.134 mg/cm² in fuel cell [6]. Further diminishing Pt content, nevertheless, lead to declining the Pt electrocatalyst durability [6]. In addition, the Pt price is continuously increasing due to less abundant Pt resource and high Pt demand from other applications [6]. For this reason, development of highly active, durable non-precious Pt-free ORR electrocatalyst is highly desirable to push the commercialization of AEFCs technology.

Currently, introduction of heteroatoms (e.g., nitrogen, boron, phosphorus, sulfur) into carbon framework are highly promising candidates to replace Pt catalyst due to their low cost, tunable surface chemistry, and facile electron transfer mobility [7]. Among heteroatoms dopants, nitrogen (N) that is similar size and a bit higher electronegativity value than carbon, has been the most widely investigated as the efficient dopant to catalyze ORR [7].

Substitution of nitrogen atom into carbon framework (N-C) induces the charge of carbon atoms next to the doped nitrogen atom to be a slightly positive [8]. The positive charge of carbon atoms results in an active site for the diatomic oxygen molecule adsorption which drastically diminish ORR overpotential value [8]. In this regards, various types of independent N-C catalysts have been studied as a possible replacement for Pt including graphene, CNTs, mesoporous carbon and nanoparticle carbon [7].

An excellent example of N-C electrocatalyst has been described by Gong *et al.* [9] The nitrogen-doped vertically aligned carbon nanotubes (VA-NCNTs) electrocatalyst was prepared by thermal annealing of iron (II) phthalocyanine under NH₃ atmosphere [9]. The electrochemical ORR performance of VA-NCNT investigated by linear sweep voltammogram was superior to the noble Pt/C catalyst. In addition, the VA-NCNTs catalyst was much more durable and stable to the CO poisoning and the methanol crossover as compared to the precious Pt/C electrocatalyst [9]. Despite the outstanding ORR electrocatalytic activity and durability of N-CNT catalysts, the fabrication process is relatively complicate, high cost, low yield and difficult to scale up. Moreover, the precursor is also expensive. For this reason, numerous efforts have been devoted to develop a simple, cost effective and scalable process to synthesize N-C electrocatalyst.

Biomass, natural abundant, cost effective, renewable resources, has been a promising raw material for fabricating the highly active nitrogen doped porous

carbon nanostructure electrocatalyst. Water hyacinth is nitrogen-rich biomass because it contains several types of amino acid and it can absorb the nitrogen compound in the water reservoir [10].

Liu *et al.* [10] converted water hyacinth into N-C electrocatalyst by thermally annealing the dried water hyacinth mixed ZnCl₂ at 600 – 800°C under N₂ atmosphere. The electrochemical ORR catalytic activity of samples was then investigated in O₂-saturated 0.1M KOH electrolyte solution. The catalyst prepared at 700°C exhibited the best ORR performance. In addition, the ORR performance of the water hyacinth derived catalyst synthesized at 700°C was comparable to the precious Pt/C electrocatalyst. On the other hand, the prepared electrocatalyst was more durable and much more stable to the poison methanol than the precious Pt/C [10].

Wang *et al.* [11] succeeded in preparing highly active and durable N-C electrocatalyst derived from pomelo peel biomass. The highly porous electrocatalyst was firstly prepared by immersing the dried pomelo peel into the saturated hypersaline containing NaCl, ZnCl₂ and FeCl₃ solution. The hypersaline treated samples were accordingly pyrolyzed under ammonia atmosphere. The ORR electrocatalytic activity of the prepared catalyst was 30 mV more active than the state-of-the-art Pt/C catalyst. In addition, the hypersaline treated catalyst exhibited higher stability and more tolerate to methanol crossover as compared to the noble Pt/C catalyst [11].

Furthermore, other biomass waste including coconut shell, bagasse, soybean have also been converted into ORR non-precious electrocatalyst by calcination of the biomass precursor contained activating agent at high temperature under inert and/or ammonia atmosphere [12–14]. According to the preparation procedure of converting biomass into N-C electrocatalyst, inert gas and/or ammonia atmosphere are essentially required. Heat treatment biomass under inert atmosphere may result in incomplete decomposition carbonaceous compounds leading to high ORR overpotential.

In this report, we aimed to convert nitrogen rich water hyacinth biomass into the non-precious ORR electrocatalyst under alkaline condition. The water hyacinth derived catalyst with high porosity was thermally synthesized using autogenic pressure method at high temperature without using any inert gas and ammonia atmosphere. The parameters affected ORR activity of the prepared catalyst under alkaline media were measured using rotating disk electrode (RDE) analysis. The obtained ORR activity was compared to that of the ORR performance of the noble Pt catalyst. The novelty of this research was the synthesis and electrochemical ORR performance under alkaline media of the water hyacinth catalyst synthesized using an autogenic pressure condition which has not been reported to date. Compared to catalyst prepared by reference [10], the catalyst in this study was prepared from water hyacinth root without using any inert gas at high temperature. while, the catalyst obtained in reference [10] derived from water hyacinth trunk and thermally annealed in presence of inert atmosphere.

2 Materials and methods

2.1 Preparation of electrocatalysts

The protein rich water hyacinth root was perfectly cleaned using large quantity of DI water and dried at 80°C overnight. The dried sample was then grinded into small pieces and then the ground sample was physically mixed with ZnCl₂. The mixture powder was transferred into the high pressure cell and close tightly with the caps. The cell was then thermally heated at the temperature of 700°C under ambient atmosphere. The activating agent contained in heated sample was eliminated by dissolving the heated sample in 0.5 M H₂SO₄ solution for 8 hr at 80°C. The black solid powder sample was obtained after being washed and dried at 80°C. To compare the effect of porosity, water hyacinth was prepared the same procedure except ZnCl₂ was not included. The samples prepared with ZnCl₂ and without ZnCl₂ were named WHCR-Zn and WHCR, respectively.

2.2 Physical characterizations

Field-emission scanning electron microscope (FE-SEM, Hitachi S-4800II) with an accelerated voltage of 3 kV was employed to investigate the morphology of samples. Please note that the sample was coated with osmium before SEM analysis. The crystal structure of samples was investigated using powder X-ray diffraction (XRD, PANalytical-Empryan) using K α radiation and generation voltage of 40 kV. Thermal stability of sample was evaluated using thermal gravimetric analysis (TGA).

2.3 Electrochemical characterizations

Catalyst ink was prepared by ultrasonic mixing catalyst powder, DI-water, 5% Nafion and Isopropyl alcohol followed the literature [15]. A working electrode was prepared by dropping catalyst ink on the surface of a clean glassy carbon and left it dry under ambient conditions. The catalyst loading on the glassy carbon electrode was 0.5 mg/cm² while the amount of reference sample which is Pt/C was 60 μ g/cm². Working electrode was then assembled into an electrochemical cell where Pt wire used as a counter electrode and saturated calomel electrode (SCE) used as reference electrode were also connected. The ORR catalytic activity was evaluated under O₂-saturated 0.1 M KOH solution using rotating disk electrode (RDE) and cyclic voltametry technique (Pine instrument) with scan rate of 10 mV/s. RDE and CV experiments were repeatedly investigated at least 3 times.

3 Results and discussion

Fig. 1a represented TGA thermogram of root, leaves and trunk of water hyacinth sample under N₂ atmosphere. It was found that all samples exhibited three stages of weight loss i.e. dehydration (100°C), hemicellulose decomposition (290°C) and cellulose decomposition (370°C).

The main composition of biomass was hemicellulose, cellulose and lignin. The molecular structure of cellulose and hemicellulose was a simple sugar monomer which easily decomposed into light organic compound at a temperature lower than 450°C. Lignin was a high molecular weight hydrophobic polymer comprising of various functional group containing aromatic structure of carbon. In the heat treatment process, lignin underwent decomposing slowly in a whole range of temperature leaving condensed aromatic carbon with reduced functional groups. The residue at temperature of 700°C of root, leaves and trunk of water hyacinth was 55%, 25% and 22%, respectively. The amount of residue obtained from root was twice times larger than leaves and trunk. The high residue value suggested high carbon conversion yield. Thus, this research would like to utilize water hyacinth root to fabricate the ORR electrocatalyst. This was done by thermally heating the ground water hyacinth root mixed ZnCl₂ under autogenic pressure conditions. ZnCl₂ was used as activating agent to generate pores and it was chemically removed using 0.5 M H₂SO₄. The obtained catalyst was then investigated phase analysis using XRD technique and the result was displayed in Fig. 1b. The phase of catalyst was the mixture of carbon and metal oxides. The formation of carbon was broadly observed at 2 θ of 25 and 43 degree, corresponding to graphitic C(002) and C(100) turbostratic carbon structure [15]. In addition, various types of metal oxides, such as SiO₂, MgO, CaO, were also detected in the XRD pattern. The observed several types of metal oxides in the catalyst was due to the accumulation of inorganic compounds by water hyacinth root, leading to metal oxide after pyrolysis. Fig. 1c and 1d illustrated the morphology of catalyst visualized by SEM technique. Low magnification SEM image revealed the rod and particles morphologies (Fig 1c).

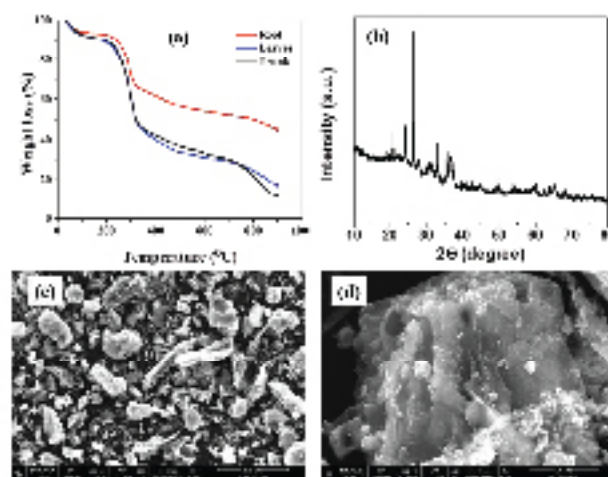


Fig. 1. (a) TGA thermogram of root, leave and trunk of water hyacinth under N₂ atmosphere, (b) XRD pattern of water hyacinth root heated at 700 °C for 1 h under autogenic pressure condition, SEM images of WHCR-Zn catalyst (c) low magnification and (d) high magnification.

In addition, uneven surface and porous structure were observed in the high magnification SEM image (Fig. 1d). Furthermore, the elemental nitrogen content was also

verified using SEM elemental mapping analysis. The nitrogen content incorporated into catalyst was 3.04 atomic%. It was reported that nitrogen was able to effectively bind to carbon with three configurations: pyridinic-like, pyrrolic-like and graphitic-like [15]. However, the precisely ORR active site has so far still debated. But pyridinic and graphitic were intensively accepted as the major ORR active sites. It should be highlighted that heat treatment of water hyacinth root contained $ZnCl_2$ at $700^\circ C$ under autogenic pressure conditions resulted in the decomposition of moisture, cellulose and hemicellulose, leading to the formation of carbon. On the other hand, $ZnCl_2$ was buried in the surface of sample and the embedded $ZnCl_2$ was completely eliminated by hot acid solution, leaving porous structure. In addition, nitrogen atom was efficiently doped into carbon framework at this pyrolysis conditions.

Next, the WHCR-Zn catalyst was electrochemically evaluated the ORR catalytic activity in an O_2 -saturated KOH solution at scan rate of 10 mV/s using cyclic voltammetry (CV) and linear sweep voltammetry (LSV) techniques. CV voltammogram of various catalyst contents were thermodynamically active for catalyzing ORR in alkaline media (Fig. 2a). To estimate the ORR kinetic, catalysts were conducted rotating disk electrode (RDE) experiments under alkaline condition at a rotation speed of 1600 rpm and the results were showed in Fig. 2b.

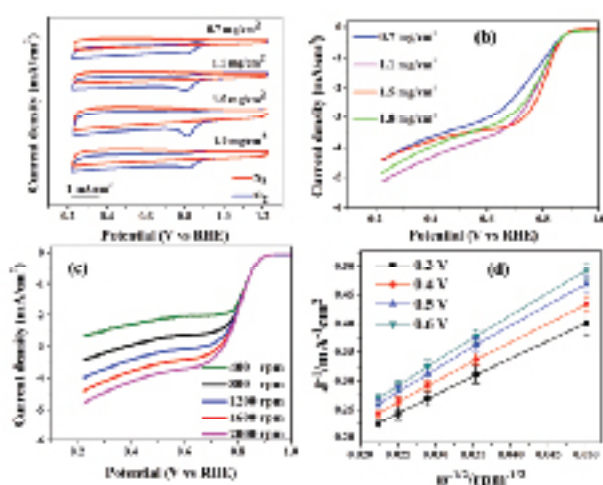


Fig. 2. ORR polarization curves of various contents of WHCR-Zn electrocatalyst by (a) cyclic voltammogram and (b) linear sweep voltammogram (LSV) at rotating speed of 1600 rpm (c) ORR polarization curve at different rotation speed of WHCR-Zn catalyst with content of 1.5 mg/cm^2 and its corresponding Koutecky-Levich plots (d) in O_2 -saturated 0.1 M KOH solution.

The LSV polarization curve (Fig. 2b) indicated onset potential (E_{onset}), half-wave potential ($E_{1/2}$) and steady state current diffusion. E_{onset} value increased as catalyst content was increased. This was mainly due to the increment of the number of active site where more oxygen molecules were able to adsorb and consequently facilitating the ORR in alkaline media. On the other hand, large amount of catalyst on RDE electrode also led

to large value of $E_{1/2}$. However, the more content of catalyst was loaded on an electrode resulted in thick catalyst layer which hindered the accessibility of an oxygen molecule to be electrochemical reduction reaction into water. Thus, the optimum loading of WHCR-Zn catalyst was 1.5 mg/cm^2 . Fig 2c illustrated the LSV plot at rotation speed of 400 – 2000 rpm of the optimum WHCR-Zn catalyst in an O_2 -saturated KOH solution. It was found that current density increased as the rotation speed was increased due to the shortening flux-diffusion. Fig. 2d shows the Koutecky-Levich (K-L) plots derived from the LSV plot (Fig. 2c) and this plot indicated good linearity and parallelism over all the potential range, suggesting the first order reaction kinetics for the ORR [16]. The electron transfer number of the synthesized water hyacinth root catalyst calculated at 0.5 V was found to be 3.6, indicating the catalyst possessed a direct four electron transfer. Fig. 3a compared CV voltammogram of WHCR-Zn catalyst with that of WHCR, commercial carbon (VXC-72R) and the noble Pt/C electrocatalysts in alkaline solution. The E_{onset} of WHCR-Zn catalyst was clearly more positive than WHCR and VXC-72R catalysts, suggesting more thermodynamically active than WHCR and VXC-72R catalysts. However, E_{onset} of WHCR-Zn catalyst was more negative as compared to the expensive Pt/C catalyst. In order to visualize ORR kinetic reaction of various catalysts, LSV experiment was performed in

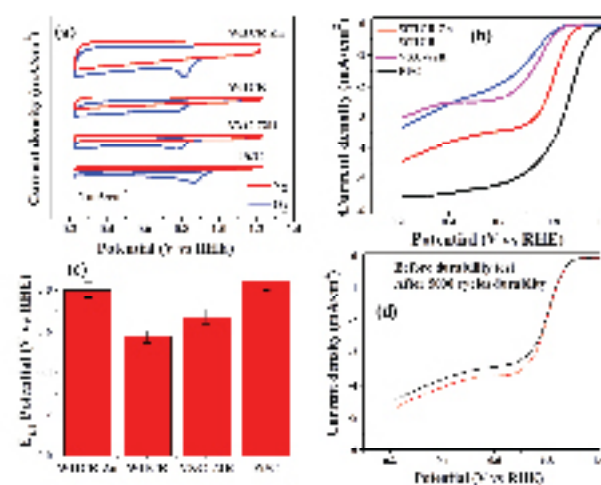


Fig. 3. ORR polarization curves of WHCR-Zn, WHCR, commercial carbon (VXC-72R) and the noble Pt/C electrocatalysts by (a) cyclic voltammogram and (b) linear sweep voltammogram (LSV) at 1600 rpm (c) its corresponding $E_{1/2}$ potential and (d) accelerated durability test for 5000 cycles of WHCR-Zn electrocatalyst in O_2 -saturated 0.1 M KOH solution.

O_2 -saturated KOH solution at rotating speed of 1600 rpm and a result was depicted in Fig. 3b and Fig. 3c. The E_{onset} value of WHCR-Zn, WHCR, VXC-72R and Pt/C catalysts was 0.93, 0.86, 0.88 and 1.0 V vs. RHE, respectively. The WHCR-Zn catalyst exhibited 170 and 150 mV more positive E_{onset} value than that of the WHCR, VXC-72R catalysts. The more positive E_{onset} value indicated less overpotential to catalyze ORR in alkaline media. On the other hand, the value of $E_{1/2}$ of

WHCR-Zn, WHCR, VXC-72R and Pt/C catalysts was 0.80, 0.57, 0.67 and 0.84 V vs. RHE. The $E_{1/2}$ value of WHCR-Zn catalyst was 230, 130 mV greater than that of WHCR and VXC-72R catalysts. The higher E_{onset} and $E_{1/2}$ value of WHCR-Zn catalyst over WHCR was mainly attributed to the higher porosity as well as high surface area of WHCR-Zn catalyst against WHCR. The higher porosity and surface area resulted in more catalyst active site, yielding excellent ORR performance. On the other hand, the greater E_{onset} and $E_{1/2}$ value of WHCR-Zn catalyst against the commercial VXC-72R was a result of the presence of N incorporated into the carbon framework as well as the formation of metal oxide which generated the ORR active site, facilitating excellent ORR catalytic activity toward VXC-72R. However, the E_{onset} and $E_{1/2}$ value of WHCR-Zn catalyst were 70 and 40 mV lower than that of the state of the art Pt/C catalyst. In order to determine the effectiveness of the electrocatalyst preparation method, we compared the $E_{1/2}$ of WHCR-Zn catalyst with that of the biomass derived electrocatalyst (coconut shell [12], soybean [13], bagasse [14]) which was prepared by thermally annealing at high temperature under inert gas and ammonia atmosphere. It was found that the $E_{1/2}$ value of electrocatalyst derived from coconut shell, soybean and bagasse was found to be 0.78, 0.74 and 0.76 V vs RHE, respectively [12-14]. The WHCR-Zn electrocatalyst exhibited outperform ORR performance relative to biomass electrocatalyst synthesized by conventional method. These results suggested that the novel autogenic pressure method was effective to prepare highly active biomass derived ORR electrocatalyst. Fig. 3d represented the accelerated durability test for 5000 cycles of WHCR-Zn catalyst in O_2 -saturated KOH solution at scan rate of 50 mV/s. The $E_{1/2}$ value of WHCR-Zn catalyst before and after 5000 cycling durability test was negative shift with a value of 10 mV. It was reported that the $E_{1/2}$ value of Pt/C catalyst after 5000 cycling durability test is 50 mV negative shift [16]. These results suggested the surface of WHCR-Zn catalyst was maintained without degradation after 5000 cycling test. However, the drastic degradation of the precious Pt/C catalyst was mainly due to the aggregation of Pt nanoparticle on the surface of carbon support leading to lower the active area. Furthermore, Pt dissolution and carbon oxidation during accelerated durability test were also contributed to the Pt/C degradation [16]. The high ORR catalytic performance as excellent as durability of biomass derive electrocatalyst could generate a promising solution to alleviate the environmental issue as well as global warming.

4 Conclusion

We demonstrated the conversion of water hyacinth biomass into ORR electrocatalyst by thermally heating

the sample contained $ZnCl_2$ under an autogenic pressure method. The prepared sample exhibited high porosity as well as high N content incorporated in to carbon and metal oxide structure. The greater porosity and N functional group resulted in high ORR catalytic activity in alkaline solution. The optimum catalyst loading was found to be 1.5 mg/cm². In comparison to the catalyst prepared without $ZnCl_2$ and commercial carbon (VXC-72R), the synthesized catalyst exhibited excellent ORR performance in alkaline media. In addition, the prepared catalyst showed highly stable cycling test for 5000 cycles with negligible ORR activity loss.

This research was funded by Faculty of Science, Energy and Environment, King Mongkut's University of Technology North Bangkok (Rayong campus). Contract no. SciEE-001/62

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