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Electrochemical Performance of Electrocatalyst from Discarded Textile

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As the global demand for energy continues to rise and environmental concerns escalate, fuel cells have emerged as promising clean energy conversion devices. The cathode reaction, namely Oxygen Reduction Reaction (ORR) significantly influence the overall energy conversion process, yet it is hindered by sluggish kinetics, necessitating the use of highly active catalysts. In this study, iron and nitrogen co-doped porous carbon electrocatalyst was synthesized from discarded textiles for the ORR in 0.1 M KOH electrolyte. Urea was used as the nitrogen source, with iron chloride hexahydride acting as the iron precursor and pore-forming agent. The obtained electrocatalyst showed a promising performance as the ORR catalytic activity was close to that benchmark Pt/C. The results concluded that the discarded textile is a good candidate for serving as a Platinum (Pt) alternative in the electrocatalyst development from inexpensive and more sustainable resources.

Keywords: Oxygen reduction reaction; iron and nitrogen co-doped porous carbon; textile waste

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Considering the rising demand for energy and the growing concern over environmental issues, the fuel cell is regarded as a great clean energy conversion device due to several advantages including low operating temperature, great efficiency, and no toxic emissions [1]. The cathode reaction in the fuel cell, namely the Oxygen Reduction Reaction (ORR) determines the efficiency of the energy conversion process. However, ORR is sluggish, hence it requires highly active precious metal catalysts [2]. State-of-the-art Pt has served as the benchmark electrocatalyst for the said reaction due to its high performance. However, some complications have been observed including its scarceness, expensive and unsatisfactory durability thus hampering the fuel cell large-scale commercial application [3-5]. As a result, significant efforts have been carried out to design and fabricate superior non-precious metal electrocatalysts at a low cost [6-7].

In the last 15 years, there has been a significant increase in both the production and utilization of textiles, attributed to the lower production costs, more effective operations, and rising demand driven by the rapidly evolving fashion industry [8]. As a result, discarded clothing or textile became more abundant and mostly dumped into the landfill than recycled. According to Ramamoorthy [9], difficulty of separating the components of mixed fabrics is the cause of the low recycling rate of textiles. Thus, the conversion of discarded textile or clothing into novel materials can be a sustainable approach to reducing the accumulation of discarded clothing. In recent years, there have been efforts to convert these materials into other products such as activated carbon [10-11], adsorbent [12-13] and electrocatalyst for the hydrazine oxidation reaction [14].

In the present work, we developed iron and nitrogen co-doped porous carbon for ORR from discarded clothing as a continuation of our previous work [15]. Urea was used as nitrogen source while iron chloride hexahydrate was used as a pore-forming chemical activator. The surface characteristics and electrochemical performance of the electrocatalyst were examined and compared with that of benchmark Pt/C.

EXPERIMENTAL

Chemicals and Materials

The discarded textile was obtained from a used clothing warehouse. Calcium chloride (R&M Chemicals), urea (Merck), iron chloride hexahydrate (Chemiz), hydro-chloric acid (Sigma Aldrich) and ultrapure water (18.2 MΩ.cm, Millipore).

Synthesis of Electrocatalyst

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The discarded textile was cut into small uniform pieces and soaked overnight in a solution containing $FeCl_3.6H_2O$ (0.6 M) and urea (1 M). The impregnated cuts were subsequently dried at 80 °C for 12 hours before being subjected to pyrolysis at 900 °C for 1 hour. The pyrolysis product was then pulverized using a mortar and pestle into fine powder. Following this, the powdered catalyst was subjected to acid etching in 3 M HCl for 12 hours to eliminate any inactivated and unstable species. Subsequently, it underwent multiple rinses with distilled water until the eluent reached neutral pH. Finally, the rinsed product was dried at 105 °C overnight.

Characterization Methods

The morphology of the as-synthesized electrocatalyst was characterized by Field Emission Scanning Electron (FESEM) with Energy Dispersive X-ray (EDX) microscopy (Carl Zeiss, Merlin Compact). The surface properties were evaluated by a Micromeritics 3 Flex instrument. The nitrogen adsorption-desorption characterization was performed at 77 K and the sample was degassed at 200 °C for 3 hours prior to measurement. The electrochemical measurements were carried out with a Rotating Ring Disk Electrode (RRDE) using a potentiostat, PGSTAT128N (Metrohm-Autolab). A typical three-electrode system comprising a working electrode (5 mm glassy carbon electrode), reference electrode (Ag/AgCl, 3 M KCl) and counter electrode (platinum rod) was used. The catalyst loading used on working electrode was 0.285 mg cm^{-2}. The ORR measurements were performed in N_2- and O_2-saturated 0.1 M KOH solution using Cyclic Voltammetry (CV) with a scan rate of 25 mV s^{-1}, while Linear Scan Voltammetry (LSV) was executed at 5 mV s^{-1}. Both CV and LSV tests were conducted from 0.2 to 0.9 V (vs. Ag/AgCl). The potential obtained from the measurement was adjusted to the Reversible Hydrogen Electrode (RHE) potential using the Nernst equation (1):

$$E_{RHE} = E_{Ag/AgCl} + 0.059\ pH + E^{o}_{Ag/AgCl} \tag{1}$$

All potential values reported in this study referred to V vs RHE unless stated otherwise.

RESULTS AND DISCUSSION

Characterization

The Specific Surface Area (SSA) and porous structure of the discarded textile-based electrocatalyst sample were analysed with N_2 adsorption/desorption isotherm. The results obtained for the total Brunauer-Emmett-Teller (BET) surface area of the sample is 442.8 m^2g^{-1}, while the total pore volume is 0.67 $cm^3\ g^{-1}$. The N_2 adsorption/desorption isotherm for the synthesized sample is shown in **Figure 1. (a).** The electrocatalyst exhibits a typical type-II isotherm curve with H4-type hysteresis loop at relative pressure $0.45< P/P°< 0.99$ which indicate the presence of micropores and mesopores [16]. The hysteresis loop with a H4 characteristic is observed due to capillary condensation in slit-shaped mesopores [17]. Next, the Pore Size Distribution (PSD) (**Figure 1. (b)**) was calculated via Density Functional Theory (DFT) method. The PSD displays the occurrence of pores ranging from 1 to 170 nm in size, signifying a hierarchical pore structure within electrocatalysts with mainly mesoporous structure as the PSD centred at ca. 20 nm. A mesoporous structure is favourable because mass transfer of intermediate product is more efficient in mesopores during oxygen reduction reaction [18].

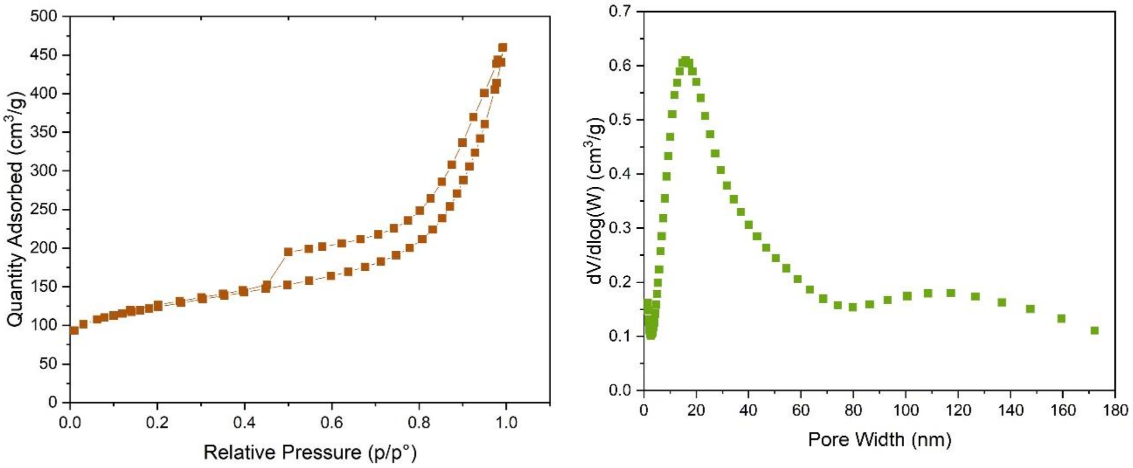

Figure 1. (a) N_2 adsorption-desorption isotherms. (b) Pore distribution of nitrogen and iron co-doped porous carbon.

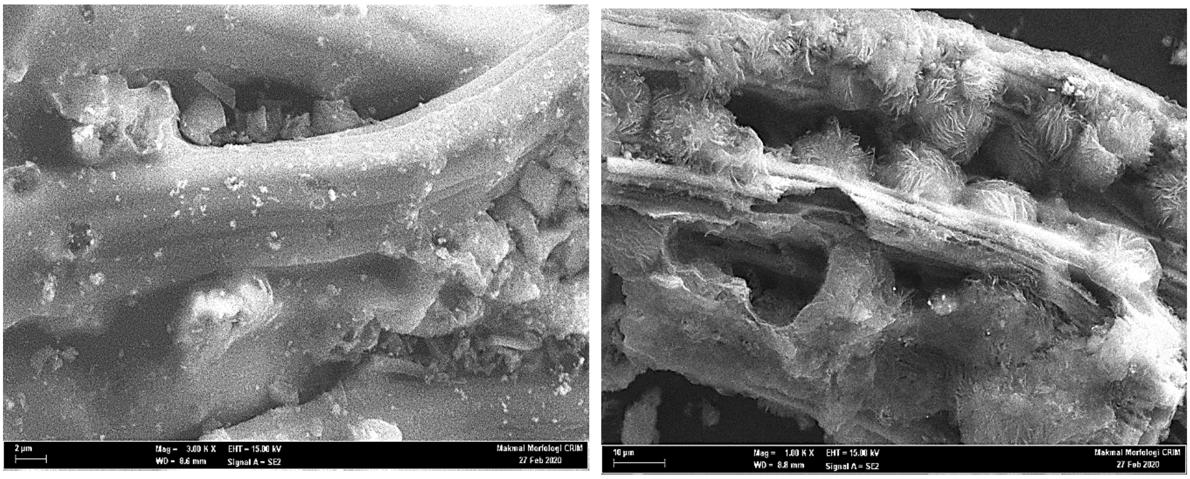

Figure 2. (a) Carbon product of discarded textile without chemical activation after pyrolysis. (b) Iron and nitrogen co-doped porous carbon.

Table 1. Chemical composition of iron and nitrogen co-doped porous carbon.

Element	Wt%
C	89.7
O	3.3
Fe	2.0
N	0.6

The surface morphology was observed using field emission scanning electron microscopy. **Figure 2. (a)** shows the carbon product of discarded textile after heat treatment without any chemical activation. The electrocatalyst particle remained in shape of fibre strand from the textile. The surface can be considered as smooth with finer particles attached to the surface. **Figure 2. (b)** shows the FESEM image of pyrolysis product of discarded textile activated with the $FeCl_3.6H_2O$ and urea. The chemical activation changed the strand surface entirely as many nodes appeared on the strand surface. The nodes also have visible layers forming a carnation flower-like appearance. Furthermore, the chemical activation also successfully created a pore structure on the surface. The change in the morphology implies that chemical activation is important to generate porosity within the bulk carbon materials.

The chemical composition of the synthesized electrocatalyst analysed using FESEM-EDX is shown in **Table 1**. The values confirmed that iron and nitrogen are successfully doped in the bulk carbon material. Previous studies have revealed that doping carbon with heteroatoms such as nitrogen alter the electronic properties of carbon materials [19]. This is due to the defective structure introduced by nitrogen, which is able to provide active sites in electrocatalytic oxygen reduction reaction [20-21]. The EDX result also shows successful incorporation of Fe element in the carbon material. Nitrogen and Fe could form Fe-Nx sites that have been demonstrated to be crucial in improving the ORR activity by altering the local electronic states of the carbon matrix [22].

Electrochemical Performance

The oxygen reduction activity of the synthesized electrocatalyst is presented in **Figure 3. (a)**. The CV profile conducted in the O_2-saturated electrolyte shows an oxygen reduction peak at about 0.74 V with peak current densities reaching -1.15 mA cm^{-1}, while the CV obtained with N_2-saturated electrolyte displays no reduction peak in the profile with only capacitive behaviour in the same potential range. This result signifies that the electrocatalyst is capable of electrocatalysing the ORR.

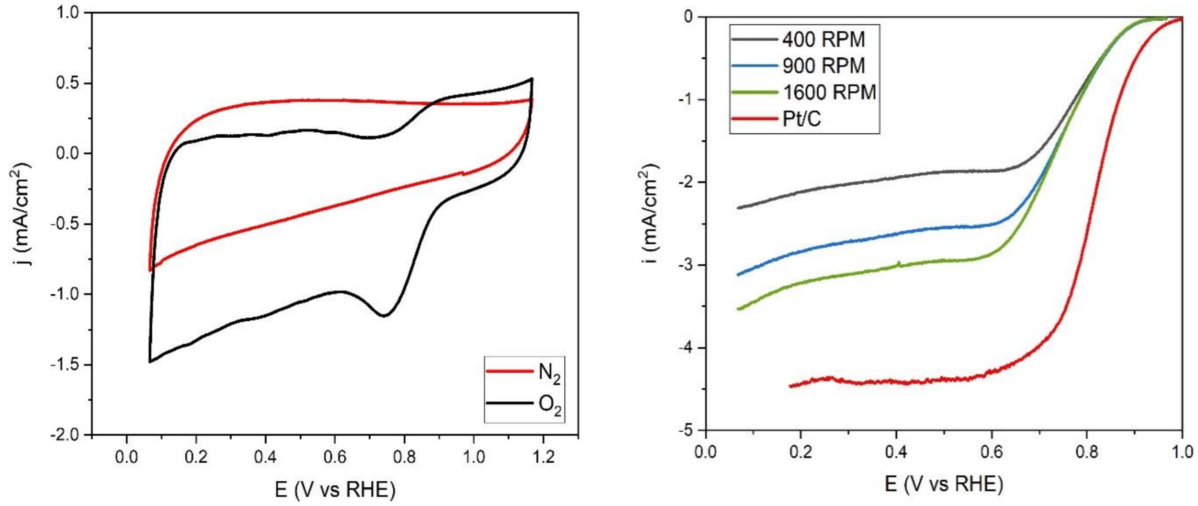

Figure 3. (a) CV curves of the iron and nitrogen co-doped porous carbon. (b) LSV curves of iron and nitrogen co-doped porous carbon and Pt/C at 1600 rpm.

LSV measurement was then further conducted in the range of 400 to 1600 rpm to assess the ORR electrocatalytic efficiency of the as-synthesized electrocatalyst. As the results shown in **Figure 3. (b),** the electrocatalyst presented a positive onset potential (Eo_{nset}) of 0.95 V, and a limiting current density ($j_{L@0.4V}$) of 3.02 mA cm^{-1}. These values are comparable to the values obtained by the benchmark Pt/C catalyst measured using the same system (Eo_{nset} =1.02 V and j_L = 4.3 mA cm^{-1}). Furthermore, the diffusion-limited current density also correspondingly increase with the increased in rotation speed. It can be deduced that the diffusion layer is thinner at a higher rotation speed, thus permitting the O_2 in the electrolyte to diffuse to the electrode surface more swiftly, and hence intensify the reaction current [23].

The kinetic parameters of the as-synthesised electrocatalyst were examined via Koutechy-Levich (K-L) equations (2) – (4) by adapting the LSV data collected at different rotation speeds, which is shown in **Figure 4.**

$$j_K = \frac{j \cdot j_L}{j_L - j} \tag{2}$$

$$\frac{1}{j} = \frac{1}{j_K} + \frac{1}{j_L} = \frac{1}{B}\omega^{-1/2} + \frac{1}{j_K} \tag{3}$$

where
j = measured current densities
j_K = kinetic current densities
j_L = diffusion-limiting current densities
ω = angular velocity (rad s^{-1})

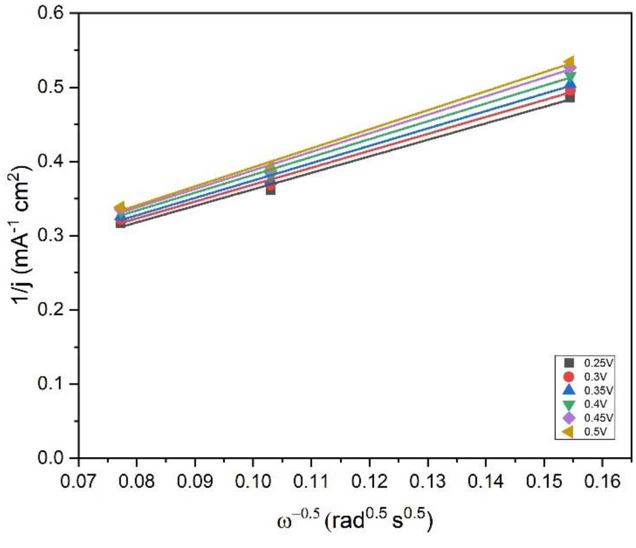

Figure 4. Kouteckye-Levich (K-L) plots.

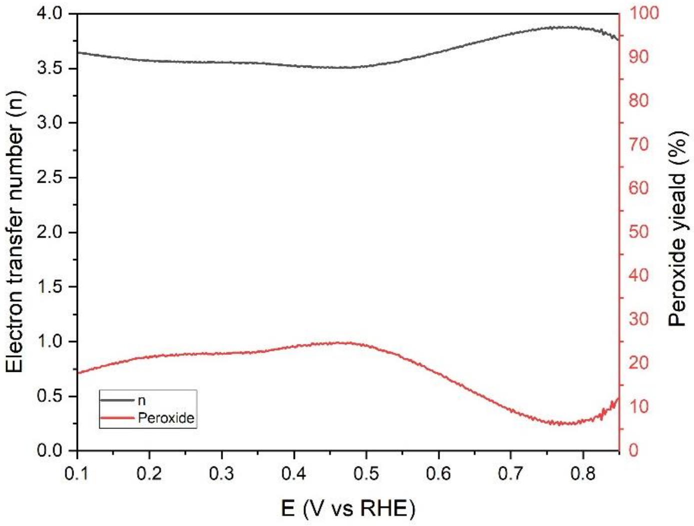

Figure 5. Electron transfer number and peroxide yield.

The proportionality coefficient, B is defined as equation (4) [24].

$$B = 0.62D^{2/3}\nu^{-1/6}nFC^{*} \quad (4)$$

where

F = 96485 C mol^{-1} (Faraday constant)
C^{*} = 1.2×10^{-6} mol cm^{-3} (Concentration of O_2 in 0.1 M KOH)
D = 1.9×10^{-5} cm^2 s^{-1} (Diffusion coefficient of O_2 in 0.1 M KOH)
N = 0.01 cm^2 s^{-1} (kinematic viscosity of 0.1 M KOH).

The K-L plots of the as-synthesized electrocatalyst displayed a good linear relationship between the kinetic current (j_K^{-1}) and the electrode rotating speed ($\omega^{-1/2}$). This indicates a first-order reaction kinetics of ORR [25]. The electron transfer number (n) per O_2 molecule calculated are 3.54 - 3.98 at 0.3-0.5 V, close to that theoretical value of 4.0 suggesting a 4 e^- transfer pathway for ORR [26]. In addition, the electron transfer number was also determined from the ring current of RRDE using equation (5) and the peroxide yield (%H_2O_2) was determined using equation (6) [27]. The number ranges from 3.5 to 3.88 in the potential range of 0.2 to 0.9 V (**Figure 5**). This is in agreement with the results obtained from K-L equations thus further verifying the 4-electron transfer pathway. The peroxide yield ranges from 5.87 to 22.0%.

$$n_{RRDE} = 4 \times \frac{i_d}{i_d + i_r/N_c} \quad (5)$$

$$\%H_2O_2 = 200 \times \frac{i_r/N_C}{i_d + i_r/N_c} \quad (6)$$

where

i_r = ring current
i_d = disk current
N_c = collection efficiency of ring electrode (N_c= 0.256)

CONCLUSION

Iron and nitrogen co-doped porous carbon was successfully synthesized from discarded textiles through chemical activation and pyrolysis methods. Iron chloride hexahydride was the pore-forming agent responsible for the mesoporous structure formation. The surface area of the as-synthesized electrocatalyst achieved was 442.8 m^2g^{-1}, with a total pore volume of 0.67 cm^3 g^{-1}. The as-synthesized electrocatalyst has good ORR electrocatalytic activity as the onset potential is just slightly inferior to the benchmark Pt/C. This result shows that discarded textiles have excellent potential for Pt substitute in electrocatalyst development of more sustainable and cheaper resources.

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