Cobalt and Nitrogen co-doped Carbon Composite Material Derived from Rice Husk as a cost-effective Electro catalyst for Oxygen Reduction Reaction

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High efficiency and low cost electrocatalysts are urgently developed for the commercial application of fuel cells. Herein, rice husk, an agricultural waste, was chosen as the low-cost carbon source to synthesize a novel cobalt and nitrogen codoped carbon composite (DKCoN) electrocatalyst for oxygen reduction reaction (ORR). The as-synthesized material developed via a simple impregnation and pyrolysis process has an amorphous carbon structure with ultrahigh pyridinic nitrogen-doping level (72.08% of the total doped N) in which nanoparticles are uniformly distributed. The as-synthesized samples were characterized by high resolution TEM, XPS, XRD analysis and electrochemical measurements. According to the test results, the ORR catalyzed in acidic condition by DKCoN catalyst is dominated by a nearly four-electron process (3.5-3.8). The initial oxygen reduction potential of the DKCoN-900 electrocatalyst during accelerated aging test (AAT) showed almost no significant decay, and the attenuation of the average polarization current density was about 0.22 mA cm⁻². The DKCoN catalyst displayed comparable activity and certain corrosion resistance in acidic electrolyte, demonstrating that the rice husk derived DKCoN material obtained by the efficient approach is to be a promising, cost-effective and eco-friendly electrocatalytic material for oxygen reduction in fuel cells in the future.

Keywords: rice husk; electrocatalyst; Co, N co-doped carbon; oxygen reduction reaction

1. INTRODUCTION

Fuel cell has been considered as one of the most promising future energy conversion technology for its high efficiency and environmentally friendly. However, the commercialization of fuel cells is mainly impeded by the prohibitive cost and scarcity of noble metal materials used as electrocatalysts, especially for the cathode owing to the sluggish kinetics of oxygen reduction reaction (ORR) [1]. In order to reduce the cost of electrocatalyst in fuel cells, one of the most efficient approaches is to develop...
non-noble metal electrocatalysts or metal-free electrocatalysts instead of commercial Pt or Pt alloy materials. Carbon based material has been identified as the great potential ORR electrocatalysts for the future because of their high specific surface area, appropriate pore structure, good activity and stability, accessible synthesis and preparation method [2-4].

Recently, transition metal and N atoms co-doped carbon based materials have emerged as promising electrocatalysts to take the place of noble metal-based catalyst for ORR, due to their high intrinsic electrocatalytic activity, comparable stability and excellent toxicity resistance [5-7]. As one of the most commonly used transition metal elements, cobalt salt material have attracted extensive interests, not only for their excellent performance in activity and stability for ORR, but also for the impedance on the occurrence of Fenton reaction [8,9]. Some carbon with novel structures such as graphene [10-12], carbon nanotube [13] and organic synthetic carbon [14-16] can be used as the carbon source in the catalyst synthesis process. However, their high cost and complex synthesis steps still hinder the large-scale application of metal and N co-doped carbon based catalysts. In consideration of the wide applications of fuel cells, the use of eco-friendly and renewable carbon source precursors to produce carbon based electrocatalyst is cost-effective and also worthwhile from the perspective of economical, environmental and ecological issues [17]. Due to the huge annual output of rice husk in the world and in China, the rice husk is considered as one of the promising carbon source precursors for preparing the cost-effective carbon-based catalyst to replace the limited fossil precursors.[18] Although reports on the preparation of various carbon materials (such as activated carbon) from rice husk would be available in the literatures [19,20], little attention has been paid for the novel and high-value utilization approach of rice husk. The aim of this work is to develop a facile technique to prepare low-cost carbon-based catalyst with high performance from rice husk by cobalt and nitrogen elements co-doping for ORR. The rice husk derived Co and N co-doped carbon-based (DKCoN) composite electrocatalytic material results in the microstructure with uniform metal nanoparticles and amorphous carbon structure. Particularly, DKCoN sample mainly doped by pyridinic N and Co species shows remarkably higher activity compared with N doped carbon-based (DKN) catalyst. The results showed that the activity of the DKCoN catalyst was attributed to the synergistic co-doping effect of Co and N element. The mechanism analysis of ORR demonstrates that the ORR catalyzed in acidic condition by DKCoN is almost dominated by a nearly four electron process. The rice husk derived carbon material is promising to be a potential, low-cost and renewable electrocatalyst for oxygen reduction, which would be a beneficial direction for high-value application of the waste rice husk biomass.

2. EXPERIMENTAL

2.1 Catalyst preparation

The composite electrocatalyst was prepared with a convenient pyrolysis and carbonization method. After washing and drying, a certain amount of rice husks were treated at 400 °C in muff furnace for 2 h to obtain amorphous organic carbon (AOC) materials. Then, 1.242 g rice husk AOC was mixed with cobalt acetate (C₄H₆CoO₄·4H₂O, AR, Sinopharm Chemical Reagent co. Ltd) solution containing
0.311 g cobalt metal element using the impregnation method. The rice husk derived Co and N co-doped composite carbon-based electrocatalytic material (DKCoN) was prepared under the calcination at 700-1000 °C (heating rate: 10 °C min\(^{-1}\)) for 2h with ammonia etching. The composition process is shown in Fig. 1.

![Diagram](image_url)

**Figure 1.** Preparation process of rice hull carbon Co, N co-doped carbon composite electrocatalysts.

According to different calcine temperature, the catalyst was labeled as DKCoN-T, where T was the calcine temperature of the material. For example, DKCoN-900 was prepared using the method described above with the calcine temperature of 900 °C. In order to compare the doping effect of Co element, the blank sample marked as DKN without Co doping were prepared by directly calcining AOC in ammonia atmosphere at the same temperature as DKCoN sample.

### 2.2 Electrochemical measurements

Electrochemical property measurements of the catalysts were carried out on a PGSTAT302N electrochemical station (Metrohm Corp., Switzerland) and a rotating disk electrode (RDE) system (PINE Instrument Corp., USA). A typical three-electrode electrochemical cell was employed at room temperature incorporating a Pt wire, a saturated calomel electrode (SCE) and a glassy carbon electrode (GCE, area: 0.19625 cm\(^2\)) as the counter electrode, the reference electrode and the working electrode, respectively. All electrode potentials were calibrated to the reversible hydrogen electrode (RHE) in this study. Linear sweep voltammetry (LSV) and cyclic voltammetry (CV) were conducted to measure the ORR property performances of the catalysts. The LSV experiments were carried out in 0.5 M H\(_2\)SO\(_4\) electrolyte saturated with O\(_2\)/N\(_2\) in the voltage range from 1.15 to 0.05 V at the scan rate of 5 mV s\(^{-1}\) with different rotating speeds from 400 to 2500 rpm at room temperature. The CV measurements were conducted in the same electrolyte as LSV experiment saturated with N\(_2\) at a scan rate of 10 mV s\(^{-1}\) in the potential range of 0-1.2 V.

The working electrode loaded with thin film catalyst layer was prepared as follows: a homogeneous mixture containing 5.0 mg catalyst, 1.0 mL ethanol and 50.0 μL Nafion (Du Pont Corp., 5 wt.% ) were obtained by ultrasonically blending in a weighing bottle for 20 min. After that, 10 μL of
the catalyst dispersion was coated on a clean GCE surface. The catalyst loading mass was 0.243 mg cm$^{-2}$.

The number of ORR electron transfer can be calculated by the first-order Koutecky-Levich (K-L) equation as flows:

$$
- \frac{1}{j_d} = - \frac{1}{j_k} + \frac{1}{0.2nFD^{2/3}cV^{-1/6}\omega^1/2}
$$

(1)

Where $j_d$ is the measured current density, $j_k$ is the kinetic current density, $n$ is the electron transfer number, $F$ is the Faraday constant (96485 C mol$^{-1}$), $D$ is the diffusion coefficient of O$_2$ in 0.5 M H$_2$SO$_4$ (1.4×10$^{-5}$ cm$^2$ s$^{-1}$), $c$ is the saturation concentration of oxygen in the electrolyte (1.1×10$^{-6}$ mol L$^{-1}$), $v$ is the kinematic viscosity of 0.5 M H$_2$SO$_4$ (0.010 cm$^2$ s$^{-1}$), $\omega$ is the electrode rotation speed in rpm, and 0.2 is used when the rotation speed is expressed in rpm [21].

The rotating ring disk electrode (RRDE) measurement was carried out on an AFCBP1 bipotentiotstat system (PINE Instrument Corp., USA) in the same three-electrode electrochemical cell as RDE at normal temperature with an RRDE ($S_{\text{disk}}=0.2475$ cm$^2$, $S_{\text{ring}}=0.1866$ cm$^2$) employed as the working electrode. A platinum wire and an SCE were used as the counter and reference electrodes, respectively. The thin film catalyst layer was prepared using the same method as mentioned above. 10 μL catalyst ink was spread onto the surface of the disk electrode and desiccated at room temperature with the catalysts loading mass of 0.187 mg cm$^2$. The RRDE was performed in 0.5 M H$_2$SO$_4$ solution saturated with O$_2$/N$_2$ with the potential range was from 1.15 to 0.05 V at a scan rate of 5 mV s$^{-1}$.

The selectivity of catalysts was determined by RRDE technique in the mechanism of ORR through a 4-electron or a 2-electron process. The the percentage of H$_2$O$_2$ released (%H$_2$O$_2$) and the apparent number of electrons transferred (n) during ORR can be calculated from the following equations [22]:

$$
\%H_2O_2 = 100 \frac{2I_r}{NI_d + I_r}
$$

(2)

$$
n = \frac{4I_d}{I_d + (I_r/N)}
$$

(3)

where $I_r$ and $I_d$ are the ring and disk Faradaic currents, respectively, and $N = 0.37$ is the RRDE ring collection efficiency.

An accelerated aging test (AAT) based on continuous CV potential cycling for 1000 cycles in N$_2$ purged 0.5 M H$_2$SO$_4$ electrolyte was used to evaluate the stability of the catalyst at room temperature. The scanning potential was between 0 and 1.2 V and the scan rate was 50 mV s$^{-1}$. LSV measurement was conducted to record ORR polarization curves (before and after AAT) using the same standard three-electrode electrochemical system as described above with O$_2$ saturated electrolyte at a rotating speed of 1600 rpm.

2.3 Analytical techniques

A Micromeritics Accelerated Surface Area and Porosimetry System (Micromeritics Instrument Corp, Gemini 2390) was used to analyze the specific surface area and the pore size distribution of rice
husk derived amorphous organic carbon materials by nitrogen sorption at 77 K and calculated via the Brunauer-Emmett-Teller (BET) method and Barrett-Joiner-Halenda (BJH) model.

X-ray power diffraction (XRD) was carried out on a Rigaku Rotalflex (RU-200B) PC powder diffractometer using Cu-Ka radiation (\(\lambda = 1.54056 \text{ Å}\)) with a Ni-filter to characterize the crystalline structures of the catalysts. The angle range was from 20° to 80° with the scan rate of 5° min\(^{-1}\).

Field Emission Transmission Electron Microscopy (FE-TEM) measurements were taken on a Talos F200X to study the morphology of the as-prepared catalysts.

X-ray photoelectron spectroscopy (XPS) data were obtained using an Axis Ultra DLD spectrometer and Mono (Al (Mono)) (150 W). C1s peak located at 284.6 eV was chosen as an internal standard. An XPS peak fitting program (CasaXPS Version 2.3.16 Pre-rel) was conducted to acquire the deconvolutions of XPS peak.

3. RESULTS AND DISCUSSION

3.1 Physical characterizations of catalysts

Table 1. BET surface area, total mesopore and volume and average pore size of the samples.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>BET surface area /m(^2)g(^{-1})</th>
<th>(V_{\text{meso}})/cm(^3)g(^{-1})</th>
<th>(V_{\text{micro}})/cm(^3)g(^{-1})</th>
<th>Average pore size /nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>AOC</td>
<td>351.3</td>
<td>0.5579</td>
<td>0.0420</td>
<td>6.1</td>
</tr>
<tr>
<td>DKN-900</td>
<td>104.6</td>
<td>0.0658</td>
<td>0.1371</td>
<td>4.85</td>
</tr>
<tr>
<td>DKCoN-900</td>
<td>161.5</td>
<td>0.1699</td>
<td>0.0569</td>
<td>14.9</td>
</tr>
</tbody>
</table>

Figure 2. XRD patterns of DKCoN samples obtained at different treatment temperatures
The BET special surfaces for AOC, DKN-900 and DKCoN-900 samples are 351.3, 104.6 and 161.5 m² g⁻¹, respectively. The average pore sizes of AOC, DKN-900 and DKCoN-900 samples calculated by BJH method are 6.1, 4.85 and 14.9 nm. The volume of mesoporous for AOC sample is 0.5579 cm³g⁻¹ which accounts for more than 90% of the total pore volume. The AOC sample with mesoporous as the main pore distribution would be a good support for impregnate with metal salt. Moreover, the average pore size of DKCoN-900 sample is 14.9 nm (between 2-50 nm) which believed to facilitate the formation of ORR active site channels for Nafion ion contact and mass transfer.

Figure 3. HRTEM images and the enlarged HRTEM images of DKCoN-900 (a, b) and DKN-900 (c, d).

The crystal structure of the experimental materials was analyzed by XRD. Fig. 2 shows the XRD patterns of the DKCoN samples at different treatment temperatures. As can be seen from the Fig.2, the diffraction peaks of C(002) and C(101) crystal surfaces of carbon materials at 26.3° and 42.6° are not particularly obvious. It may be related to the low degree of carbonization in heat treatment of biomass materials at the temperature from 700 to 1000°C, which demonstrates that most of the carbon materials in DKCoN samples are amorphous carbon. Two diffraction peaks occur at 44.1° and 51.5° as shown in Fig.2, which are attributed to the crystal plane diffraction peaks of Co(111) and Co(311). With the
increase of treatment temperature, the diffraction peak gradually protrudes and becomes sharper and sharper, indicating the presence of Co metal in these samples. Moreover, with the increase of treatment temperature, the grain size of Co becomes larger and larger, and the crystal surface becomes more and more obvious.

Fig. 3 shows the HRTEM photos of DKCoN-900 (a, b) and DKN-900(c, d) samples. As can be seen from Fig. 3a, The nanoparticles with particle size of about 10 nm are uniformly distributed in the DKCoN-900 sample. The research shows that the nanoparticles have obvious lattice (as shown in Fig. 3b), while there is no obvious lattice structure in the surrounding carbon material. That means the carbon material in DKCoN-900 sample is in an amorphous state. This result is consistent with the XRD data in Fig. 2. In contrast, Fig. 3c and 3d are the HRTEM photos of DKN-900 samples without Co element doped. There is no obvious nanoparticles exist in the sample. However, it is obvious that some microcosmic ordered carbon crystal structures interlaced in different directions are evenly distributed in the DKN-900 sample as shown in Fig. 3d, indicating that the material presents a certain graphitized structure. Therefore, the carbon material with Co element doped presents amorphous state in the samples. According to the report [23,24], the amorphous state of carbon material containing a lot of defective structures plays an important auxiliary role in the catalytic process of oxygen reduction reaction.

According to the XPS test spectrum, the Co, O, N contents (in atom %) relative to C in the sample were calculated and shown in Table 2. The peak area of the corresponding spectrum could be used to estimate the content of N relative to C by measuring the ratio to that of C1s. It can be seen obviously that the N1s content of DKCoN-900 sample is 2.9 % lower than that of DKN-900, suggesting that the total amount of N doped in the sample is decreased due to the addition of Co element. This is consistent with the reports on the effect of metal on N-doping in the literature [25].

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Co 2p (%)</th>
<th>O 1s (%)</th>
<th>N 1s (%)</th>
<th>pyridinic N-O B.E. (eV)</th>
<th>N (%)</th>
<th>quaternary N B.E. (eV)</th>
<th>N (%)</th>
<th>pyrrolic N B.E. (eV)</th>
<th>N (%)</th>
<th>pyridinic N B.E. (eV)</th>
<th>N (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>DKCoN-900</td>
<td>1.77</td>
<td>34.56</td>
<td>3.96</td>
<td>403.3</td>
<td>5.18</td>
<td>401.0</td>
<td>13.97</td>
<td>400.0</td>
<td>8.77</td>
<td>398.2</td>
<td>72.08</td>
</tr>
<tr>
<td>DKN-900</td>
<td>---</td>
<td>24.59</td>
<td>6.86</td>
<td>403.4</td>
<td>6.69</td>
<td>400.9</td>
<td>27.33</td>
<td>399.6</td>
<td>20.19</td>
<td>398.3</td>
<td>45.80</td>
</tr>
</tbody>
</table>

Table 2: The atom ratios comparison of Co, O, N relative to C for DKCoN-900 and DKN-900 samples from XPS Co2p, O1s and N1s regions analysis.
In order to further analyze the composition of the doped N in the samples, the deconvoluted N1s peaks from the XPS spectra of the samples are shown in Fig. 4. Generally, the N 1s high resolution can be fitted into four peaks belonging to pyridinic N-O (402.8-403.5 eV), quaternary N (400.6-401.2 eV), pyrrolic N (399.5-400.0 eV) and pyridinic N (397.6-398.4 eV), respectively [26-28]. The percentage composition of pyridinic N-O, quaternary N, pyrrolic N and pyridinic N relative to total N 1s for DKCoN-900 and DKN-900 samples are shown in Table 1. Interestingly, the addition of Co element not only affects the content of total N, but also significantly affects the configuration of N dopants. It can be seen clearly from Fig. 4 that pyridine N is the only main component of N 1s in the DKCoN-900 sample, while pyridine N, pyrrolic N and quaternary N are the three main components of N 1s in the DKN-900 sample. The high content of quaternary N is probably related to the high graphitized structure in DKN-900 sample, which is consistent with HRTEM characterization results. According to literature reports [29-31], pyridinic-N possessing six-membered heterocycle structure were considered as the mainly contribution to ORR in carbon-based catalysts. Hence, although the DKCoN-900 sample shows a lower total N doping degree, the content of pyridine N for DKCoN-900 is 72.08% of the total doped N which is significantly higher than that for DKN-900 (45.80%).

3.2 Catalyst activity and stability

As the precursor of carbon material, rice husk material have a certain catalytic effect of oxygen reduction after ammonia etching. It can be seen from the oxygen reduction polarization curve of DKN-900 sample as shown in Fig. 5 that the initial oxygen reduction potential is around 0.69V. DKCoN-900 which prepared by adding metal Co salt shows significantly better ORR activity than that of DKN-900.
Figure 5. Oxygen reduction polarization curves of DKN-900 and DKCoN-900 at 1600 rpm.

Figure 6. (a) Cyclic voltammetry curves of DKCoN samples acquired at different treatment temperatures. (b) Oxygen reduction polarization curves of DKCoN samples obtained at different treatment temperatures.

Although the initial oxygen reduction potential of the two catalysts are both around 0.69V, the polarization current density of DKCoN-900 at the potential of 0.5V is 0.524 mA cm\(^{-2}\) which significantly higher than that of DKN-900 (0.266 mV cm\(^{-2}\)). The polarization current density of DKCoN-900 at potential 0.2V was 1.595 mA cm\(^{-2}\), 0.792 mA cm\(^{-2}\) higher than that of the DKN-900 sample (0.803 mA cm\(^{-2}\)). According to the XPS result, the amount of pyridine N for DKCoN-900 is almost equal to that for DKN-900. Therefore, the enhancement of ORR activity for DKCoN-900 catalyst may be caused by the addition of Co species which plays a very critical role in the improvement the oxygen reduction performance of catalyst. The combined action of N and Co co-doping would effectively enhance the ORR activity of DKCoN-900 sample. Moreover, further optimizing the proportion of the two elements
(Co and N) and improving the synergistic effect will hopefully further improve the catalytic effect of this kind of catalyst for ORR.

In order to obtain the influence of pyrolysis temperature on the catalytic performance of materials, CV curves and oxygen reduction polarization curves (as shown in Fig. 6a and b) of the samples prepared at 700-1000°C were tested respectively. As can be seen from Fig. 6a, with the increase of heating temperature, the area surrounded by the CV curve, namely the double layer current, gradually decreases. DKCoN-800 and DKCoN-900 are close to each other, and DKCoN-1000 has the minimum current. As can be seen from Fig. 6b, with the increase of pyrolysis temperature, the oxygen reduction catalytic activity of DKCoN series samples increased first and then decreased, among which DKCoN-900 had the best catalytic activity. At the electrode voltage of 0.5 V, the current density of DKCoN-900 was 0.635 mA cm⁻², which was significantly higher than that of DKCoN-700 (0.298 mA cm⁻²), DKCon-800 (0.438 mA cm⁻²) and DKCon-1000 (0.203 mA cm⁻²). Combined with the CV data (Fig. 6a), it can be seen that in the temperature period of 700-900°C, the double electric layer decreases with the increase of temperature, but the activity of the catalyst increases with it. This may be due to the higher the heat treatment temperature, the higher the graphitization degree and the better electrical conductivity of the material. Then, with further increase of temperature (900-1000°C), the double electric layer decreases sharply, the surface of the material shrinks, and the catalytic activity of oxygen reduction decreases significantly. Therefore, the DKCoN-900 catalyst prepared at the optimum treatment temperature of 900°C shows superior oxygen reduction catalytic performance to the other samples.

The LSV measurements were performed at various rotating speeds from 400 to 2500 rpm for further insight of the ORR kinetics of the DKCoN-900 catalyst (see Fig. 7a).

![Figure 7](image_url)

*Figure 7.* (a) RDE measurements for oxygen reduction on DKCoN-900 catalyst in O₂ saturated 0.5 mol L⁻¹ H₂SO₄ electrolyte with a potential scan rate of 5 mV s⁻¹ at various rotating speeds. (b) The corresponding Koutecky–Levich (j⁻¹-ω⁻¹/2) plots for oxygen reduction of DKCoN-900 at different potentials.

The corresponding Koutecky-Levich (K-L) plots obtained from the data of RDE measurements in Fig.7a clearly show a good linear relationship in the potential range of 0.50-0.58 V (see Fig. 7b). According to the calculations from the K-L equation (Eq. (1)), the transferred number of electron (n) during the ORR is approximately 3.68 (close to 4 electrons), suggesting that the ORR catalyzed in acidic
electrolyte by DKCoN-900 occurs a direct four electron pathway. During the ORR process, most of the molecular \( \text{O}_2 \) were converted to \( \text{OH}^- \) via a 4 e\(^-\) pathway and only a small amount of \( \text{O}_2 \) transferred to \( \text{H}_2\text{O}_2 \) via a 2 e\(^-\) process.

**Figure 8.** (a) RRDE measurements on DKCoN-900 catalyst in \( \text{O}_2 \) saturated 0.5 M \( \text{H}_2\text{SO}_4 \) at 1600 rpm with the potential scan rate of 5 mV s\(^{-1}\). (b) Potential-%\( \text{H}_2\text{O}_2 \) plots and Potential-n (electron transfer number) plots for DKCoN-900 catalyst based on the RRDE results.

Furthermore, the formation of peroxide (\( \text{H}_2\text{O}_2 \)) during the ORR process was monitored by RRDE measurements as shown in Fig. 8a. According to equation (2) and equation (3), %\( \text{H}_2\text{O}_2 \) yield measured on the DKCoN-900 catalyst was calculated to be 8.0\( \sim \)20.8, and the transferred number of electron (n)
measured on the DKCoN-900 catalyst was calculated to be 3.5–3.8 in the potential from 0.05 to 0.65V as shown in Fig. 8b, which is consistent with the calculation results of the K-L plots. It is further confirmed that most O₂ molecules on the catalyst surface were reduced to water following a 4 e⁻ pathway. According to the reports, the ORR transferred number of electron (n) and %H₂O₂ yield results are comparable to the biomass derived catalysts, such as enoki mushroom derived N-C@CNT-900 catalyst (3.5 electrons at 0.3–0.5 V) [32], chitosan derived Fe-N-C catalyst (6–10% H₂O₂ yield) [33] and sucrose derived SC800 catalyst [34]. The good selectivity of DKCoN-900 makes it a potential candidate to replace noble metal electrocatalyst in fuel cells and other energy conversion applications.

To evaluate the stability of the DKCoN-900 catalyst, AAT based on continuous potential cycling was conducted by scanning back and forth between 0 and 1.2 V for 1000 cycles. The polarization curves before and after AAT were recorded and shown in Fig. 9. After 1000 cycles, the onset potential in the LSV curves for the DKCoN-900 catalyst is barely shifted in the negative direction. However, the average current density of the polarization curve after AAT is obviously lower than that before AAT, dropping by about 0.22 mA cm⁻², especially for the limiting current density (a drop of 0.433 mA cm⁻²). The half-wave potential of the catalyst was reduced by only 46 mV after AAT, demonstrating that the DKCoN-900 is a potential electrocatalyst with considerable stability and durability for commercial application.

4. CONCLUSIONS

In summary, as one kind of low-cost abandoned biomass-derived electrocatalysts, DKCoN was successfully developed via a simple impregnation and pyrolysis process for ORR in acid electrolyte. The as-obtained DKCoN-900 presents amorphous carbon structure in which nanoparticles are uniformly distributed. According to the electrochemical test results, the DKCoN-900 showed comparable activity and certain stability. The initial oxygen reduction potential of the electrocatalyst after the 1000 cycles AAT almost showed no significant decay, and the attenuation of the average polarization current density was about 0.22 mA cm⁻². Mechanism analysis demonstrated that the O₂ molecules were catalytic reduction into water by DKCoN-900 in acidic electrolyte with a dominant 4e⁻ ORR process (3.5–3.8 electrons). This study provide a facile strategy for producing biomass-derived, cost-effective and efficient electrocatalysts for energy storage and conversion reactions.

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