Chemical Activation of Nitrogen-doped Carbon Derived from Chitosan with ZnCl_2 to Produce a High-performance Gas Diffusion-type Oxygen Electrode

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ABSTRACT

In this study, we fabricated nitrogen-doped carbons (NDCs) derived from chitosan using a new synthesis method that combines the thermal decomposition of chitosan and chemical activation with ZnCl_2 . Then, the effect of the activation temperature on the microstructure of NDCs was investigated. The performance of a gas diffusion-type oxygen electrode (GDE) using the obtained NDCs was evaluated using an oxygen reduction reaction in an alkaline solution. Finally, the relationship between the microstructure of NDCs and electrode performance was discussed. The surface area and total pore volume of the fabricated NDCs tended to increase with activation temperature, despite decreasing nitrogen content. Additionally, we found that the overpotential of GDE decreases with an increase in specific surface area and total pore volume. The microstructure of the NDCs was found to play a key role in improving the performance of GDEs. Furthermore, the GDE composed of fabricated NDCs with a high surface area and high pore volume exhibited a reduced activation overpotential than that of conventional Pt-loaded carbon black.

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Keywords : Oxygen Reduction Reaction, Gas Diffusion-type Electrode, Porous Carbon, Nitrogen-doped Carbon

1. Introduction

Gas diffusion-type oxygen electrodes (GDEs) have potential applications in various energy-related fields, such as brine electrolysis, fuel cells, and metal–air batteries. To achieve high cathode performance, there has been investigations into the development of new catalyst materials able to promote the oxygen reduction reaction, such as noble metals,^{1–3} alloys,^{4–6} metal oxides^{7–10} and oxynitride,¹¹ and the control of the size and dispersion of the catalyst on carbon black (CB, with a hierarchical porous structure).^{12,13}

Recently, due to extensive reporting on the high oxygen reduction activity of nitrogen-doped carbons (NDCs),^{14,15} NDCs are expected to be catalyst-free GDEs for oxygen reduction electrodes. The improvement in catalytic activity and an understanding of the origin of its high oxygen reduction activity have been well-researched using the rotating disk electrode.^{16–18} In the structures of NDCs, nitrogen is incorporated into the hexagonal net face of carbon as quaternary N, pyridinic-N, pyrrolic-N, and oxidized N. Recent results have demonstrated that quaternary N and pyridinic-N are effective in enhancing the oxygen reduction reaction.^{19–22} Thus, many types of NDC synthesis methods have been reported in order to improve the oxygen reduction activity

of the NDC itself, enabling the introduction of effective nitrogen species into carbon structures. These methods include the thermal decomposition of N-contained biopolymers and ionic liquids and surface modification of CB. The thermal decomposition of natural biopolymers is a noteworthy synthesis method for NDCs as these biopolymers are renewable raw materials, facilitating the production of ecofriendly and cost-effective NDCs.

In terms of the practical use of NDCs, a GDE shows promise as an electrode structure²³ because it has been reported as an excellent cathode exhibiting low overpotential, even for high current densities exceeding 100 mA cm^{-2} .² The GDE has a laminated structure comprising a gas diffusion and a reaction layer. The gas diffusion layer consists of a highly hydrophobic carbon and polytetrafluoroethylene (PTFE), both of which act to prevent electrolyte leakage and enhance oxygen diffusion into the reaction layer. The reaction layer consists of catalyst-loaded hydrophilic carbon and PTFE, where the triple-phase boundary is secured by partial penetration of the electrolyte into the catalyst layer. Here, the penetration of the electrolyte into the reaction layer and gas diffusion to the triple-phase boundary through the pore of carbon are strongly dependent on the microstructure of carbon; this includes the surface area, pore volume, and pore size. In fact, Hyodo et al.²⁴ reported that the GDE

performance is highly dependent on the specific surface area of the carbon and pore volume of the electrode. This dependency is due to the increase in the number of reaction sites and the enhancement of mass transport (electrolyte and oxygen). As such, to produce highly efficient GDEs consideration must be given to the oxygen reduction activity and the well-designed microstructure of NDCs.

Kucinska et al.²⁵ first reported on the excellent performance of a GDE that had a reaction layer made of NDCs prepared by the thermal decomposition of natural biopolymers. They demonstrated that NDCs derived from chitosan, which may be produced from the shells of crustaceans, exhibited lower overpotential than that of Pt-loaded CB. However, the overpotential was still higher than that of a Pt-free catalysis-loaded CB that has been reported as the state-of-art electrode material.²⁶ As such, further improvement of electrode performance based on the chitosan-derived NDC is necessary to realize a catalyst-free electrode. GDE electrode performance is governed by catalytic activity and the microstructure of carbon. For instance, Tachibana et al. reported on NDC preparation by means of a cyanamide coating for CB and evaluated GDE performance.²⁷ Their proposed synthesis method for NDCs was advantageous in that the hierarchical microstructure of CB could be used as a template for the microstructure of NDCs. They were able to successfully fabricate a highly porous NDC and demonstrated better GDE performance than that of the chitosan-derived NDCs,²⁷ despite a much lower nitrogen content. These results strongly suggest that further microstructure control of chitosan-derived NDCs is required to improve GDE performance.

This study aims to further improve GDE performance using NDC derived from chitosan as the reaction layer, and focuses on microstructure control via chemical activation with ZnCl_2 . In a previous study,²⁸ ZnCl_2 and chitosan were mixed in the solid state; however, the contact between ZnCl_2 and chitosan was inadequate. As such, this study opted to dissolve chitosan and ZnCl_2 in HCl solution, and use this solution as a precursor for thermal decomposition to disperse ZnCl_2 on chitosan as uniformly as possible. We also focused on high-temperature activation to control the microstructure of NDC. It is general practice to activate the NDCs at temperatures less than 800 °C to prevent nitrogen delamination at elevated temperatures.^{28,29} However, as this study focuses on microstructure control as opposed to the nitrogen content, chemical activation was conducted at temperatures from 800 to 1050 °C. We investigated the effect of the chemical activation temperature on the microstructure of chitosan-derived NDCs, and examined the relationship between the microstructure and GDE performance in alkaline solution.

2. Experimental

2.1 Material synthesis

Chitosan-derived NDCs were prepared by thermal decomposition and carbonization of chitosan and ZnCl_2 mixed solution. To prepare the precursor solution, 1.5 g of chitosan 10 ($\text{C}_6\text{H}_{11}\text{NO}_4$)_n, (161.16n, Wako Pure Chemical Industries), 1.05 mL of concentrated hydrochloric acid (36 %, Wako Pure Chemical Industries), and 0.168 g of zinc chloride (98.0 %, Kishida Chemical) were dissolved in 20 mL of distilled water and then mixed in a mortar. This solution was heated to dryness and calcined for 5 h at 800–1050 °C under N_2 flow. The NDCs obtained after calcination were referred to as NDC800, NDC900, NDC950, NDC1000, and NDC1050. The obtained powder was ground in a mortar. To remove ZnCl_2 from the sample, the obtained powder was washed with 35 wt% hydrochloric acid, and then washed with 1 M sodium carbonate (99.5 %, Wako Pure Chemical Industries) to remove residual chloride-ions. Then, the powder was washed with distilled water several times and dried at 120 °C for 5 h. As there have been previous reports that the residual metal acts as the active site for the oxygen reduction

reaction,³⁰ we checked the amount of residual Zn by X-ray photoelectron spectroscopy (XPS). There was no zinc peak in the XPS spectra of the synthesized NDCs, indicating that zinc had either been completely removed by washing with concentrated hydrochloric acid or had evaporated during heat treatment.

2.2 Characterization

The crystal structure of the NDCs was characterized using powder X-ray diffraction (XRD; RINT2000, $\text{CuK}\alpha$, 40 kV, 30 mA, RIGAKU, Japan). The specific surface area and pore size distribution were evaluated via the nitrogen adsorption/desorption method using BELSORP-miniII (BEL, Japan). Pore size distribution was quantified using the Barrett–Joyner–Halenda method based on a nitrogen adsorption/desorption isotherm.³¹ XPS (ESCA-3400, SHIMADZU Co., Japan) with $\text{Mg-K}\alpha$ was used to investigate the nitrogen content and nitrogen species in the NDCs.

2.3 GDE performance using the half-cell

The synthesized NDCs and commercial Pt/C (TEC 10A30E, Pt, 27.7 wt%, Tanaka Kikinzoku Kogyo) CB (Ketjen black EC600JD, Lion), as reference samples, were used as the reaction layer in the GDE. One hundred milligrams of these powders, dispersion with 17.6 mg of PTFE (Polyflon Series D-210C, Daikin Industries) and 2 mL of 1-butanol (Kishida Chemical) were added to 100 mL of distilled water whilst stirring for 15 min. The amount of PTFE was set to 15 wt% in the NDCs for the reaction layer. A powder for the reaction layer was acquired following filtration and drying at 120 °C. Hydrophobic carbon (FX-35, specific surface area: $133 \text{ m}^2 \text{ g}^{-1}$, Denka) was used for the gas diffusion layer. First, 1 g of Triton-X (Kishida Chemical) was added to 30 mL of distilled water and stirred. Then, 1 g FX-35 and dispersion (0.429 mg PTFE) were added to the solution in sequence. The amount of PTFE was set to 30 wt% in the FX-35 for the diffusion layer. A powder for the gas diffusion layer was acquired following filtration and drying at 250 °C. A 25 mg powder disk with a diameter of 15 mm for the reaction layer, and a 40 mg powder disk with a diameter of 20 mm for the gas diffusion layer were stacked on a Ni mesh (100 mesh, Nilaco), and cut into a circle with a diameter of 22 mm. Then, they were press-formed into sheet at 11.6 MPa and hot-pressed under 23.2 MPa at 330 °C. These fabricated GDEs were set to a window with a diameter of 14 mm on the PTFE cell, based on the methodology of a previous study.³² The cathodic polarization in 8 M KOH aq. at 60 °C was measured under O_2 flow using 50 cm^2 of Pt foil as the counter electrode, a potentiostat/galvanostat (HJ1001SD8, Hokuto Denko Co. Ltd., Japan) and an Hg/HgO reference electrode ($E_{(\text{Hg}/\text{HgO})} = 0.098 \text{ V}$ versus NHE). The insulation resistance (IR) resistance of the half-cell was measured using the same settings as cathodic polarization using an IR compensation instrument (HI-203, Hokuto Denko Co. Ltd., Japan).

3. Results and Discussion

The crystal structure of the synthesized NDCs activated at different temperatures was confirmed by XRD; Fig. 1 shows the XRD patterns of the NDC activated at 800–1050 °C. For all samples, the low-crystalline graphite structure was confirmed with two broad peaks at 26.8° and 44.9°. Notably, the peak intensity and width of the two peaks became lower and broader with an increase in activation temperature, although the crystallinity of the material generally increased with the heat treatment temperature. Deng et al.²⁸ also reported the same tendency for chitosan-derived carbon with ZnCl_2 molten salt methods. Activation in carbon, including the formation of pores and defects, occurs during activation at the elevated temperature. As such, activation at the elevated temperature appeared to be underlying cause for the degradation of graphite crystallinity with increasing activation temperature. This was also

Figure 1. XRD patterns of NDCs activated at 800–1050 °C.

well-supported by the temperature dependence of the microstructure, demonstrated in next section.

Nitrogen adsorption/desorption measurements were used to confirm the effect of chemical activation with ZnCl_2 on the microstructure of NDCs. Figure 2a shows the nitrogen adsorption/desorption isotherms of NDCs activated at 800–1050 °C. This figure shows that with increasing activation temperature, the nitrogen adsorption volume increases at all relative pressures. Additionally, based on the International Union of Pure and Applied Chemistry (IUPAC)³³ classification, the adsorption types of NDC800 and NDC900 were assigned to type I, suggesting that only micropores were formed. For NDC950–NDC1050, the type of adsorption had altered to a mixture of types I and IV. The hysteresis pattern classified as a H4 type was also observed, indicating that slit-like mesopores may be formed by activation at temperatures exceeding 950 °C. Figure 2b shows the pore size distribution of the NDCs activated at different temperatures. For all samples, it was confirmed that the highest peak was approximately 2 nm in diameter, while the pore volume of micropores increased with activation temperature. It was also found that there was an increase in the pore volume for the 2–10 nm pore diameter for NDC1000 and 1050. In contrast, there was no observed change in the pores over 30 nm in diameter. This suggests that activation with ZnCl_2 mainly affected the formation of micropores, and a small amount of mesopores may be formed by

Table 1. BET surface area and pore volume of NDCs activated at 800–1050 °C.

Samples	Activation temperature (°C)	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	Total pore volume ($\text{cm}^3 \text{g}^{-1}$)
NDC800	800	1030	0.432
NDC900	900	1580	0.713
NDC950	950	1740	0.856
NDC1000	1000	2160	1.37
NDC1050	1050	2350	1.27
CB	—	1390	3.57
Ref. 29	800	738	0.477

activation at high temperature. Unfortunately, it is difficult to explain why the effect of chemical activation with ZnCl_2 was dependent on the activation temperature. We recommend that future research attempt to understand this dependency between the ZnCl_2 chemical activation effect and activation temperature.

The specific surface area and total pore volume are summarized in Table 1, in order to compare the microstructure of the synthesized NDCs. With an increase in activation temperature, the surface area and total pore volume tended to increase. When comparing to the results reported by Ilnicka et al.,²⁹ the synthesized NDCs exhibited a higher specific surface area and pore volume. In fact, although the type of chemical activator, the mixing method of the chemical activator with chitosan, and the chemical activation temperature in this study were completely different from methods reported in the literature, the result confirmed that the surface area and porosity of the chitosan-derived NDC had been successfully improved using our method. Notably, the specific surface of NDC900–1050 was much higher than that of CB while the total pore volume was much lower; CB is the conventional carbon support for GDEs. As previously stated, chemical activation with ZnCl_2 is likely to affect the formation of micropores. As the increase in mesopores is likely to be effective in increasing total pore volume, a new approach to promote the formation of macro-pores in chitosan-derived NDCs should be considered.

XPS was used to estimate the amount of nitrogen and type of nitrogen species in the synthesized NDCs. Figure 3 shows the nitrogen concentration in the NDCs activated at different temperatures; an increase in activation temperature led to a decrease in the

Figure 2. (a) Nitrogen adsorption/desorption isotherms; and (b) pore size distribution of NDCs activated at 800–1050 °C.

Figure 3. The activation temperature dependence of nitrogen concentration in the NDCs.

nitrogen content. The nitrogen content (0.8–2 at%) in the NDCs synthesized in this study was much lower than that of NDCs reported by Deng et al.²⁸ and Ilnicka et al.²⁹ (5–10 at%). Both the total pore volume and the surface area of the NDCs increased while the crystallinity decreased with increasing activation temperature due to the activation of carbon. Thus, this reduction in the nitrogen content with increasing activation temperature may be attributable to the preferential elimination of nitrogen during the formation of pores and defects in the carbon structure by the utilized activation process. However, the obtained nitrogen content in this study is comparable to that of NDCs prepared by surface modification of CB, that exhibit high GDE performance.²⁷ As such, it is considered that the lower nitrogen content obtained (less than 2 at%) would be also effective in enhancing its oxygen reduction activity.

Peak separation of the N 1s spectra and the assignment of these peaks was conducted to determine the nitrogen species in the carbon structure. Figure 4 shows the N 1s spectra of the NDCs activated at different temperatures. For all samples, the N 1s peak was separated into four peaks; these occurred at 398.5, 400.1, 401.2, and 402.9 eV. The two main peaks at 400.1 and 401.2 eV were attributed to pyrrolic-N (pyridonic N) and quaternary N,³⁴ respectively. The other peaks, corresponding to 398.5 and 402.9 eV, were assigned to pyridinic-N and oxidized N, respectively. Figure 5 shows the nitrogen group contents of the NDCs activated at different temperatures. The concentrations of quaternary N and pyrrolic-N were higher than that of the other types of nitrogen groups in all samples; these concentrations also tended to increase with the activation temperature. Deng et al. reported that chitosan-derived carbon with ZnCl₂ molten salt contained the largest amount of pyridinic-N (or pyrrolic-N).²⁸ In contrast, the carbon obtained in this study contained almost the same amount of pyridinic-N (or pyrrolic-N) and quaternary N, despite using the same starting material as the carbon source. In their method, a mixture of chitosan solid and ZnCl₂ was activated below 700 °C. In contrast, we used chitosan dissolved in HCl solution with ZnCl₂ as the starting material and activated above 800 °C. Thus, the dispersion of ZnCl₂ in the intermediate carbon and the activation temperature were completely different to Deng et al. These results indicate that the type of nitrogen group in NDC is heavily dependent on the activation process. Tachibana et al.²⁷ argued that the most active nitrogen species in nitrogen-doped porous carbon was quaternary N. Notably, the ratio of quaternary N in the synthesized NDCs was much higher than the other types of nitrogen groups,^{28,29} indicating that the method proposed in this study has the advantage of introducing quaternary N; this group is effective in enhancing oxygen reduction activity into the carbon structure selectively.

Figure 4. The N 1s spectra of NDCs activated at 800–1050 °C.

Figure 5. The nitrogen group content of the synthesized NDCs as a function of activation temperature.

To evaluate electrode performance, a GDE was fabricated using the synthesized NDCs as the reaction layer. The electrode potential of the GDE was measured in 8 M KOH solution at 60 °C as a function of current density. Figure 6a shows the polarization curves of the GDEs with the synthesized NDCs. As a comparison, the results of CB and the NDC reported by Ilnicka et al.²⁹ are also shown in Fig. 6a. In the current density range of 100 mA cm⁻², all NDCs demonstrated a higher electrode potential than CB. We infer that these high potentials are caused by the nitrogen-doping effect; Tachibana et al.²⁷ reported that nitrogen-doped carbon exhibits a higher electron transfer number than CB, resulting in higher

Figure 6. (a) Polarization curves of GDEs with the synthesized NDCs and Ref. 29; (b) IR-free Tafel plots of the GDEs with the synthesized NDCs and CB; (c) diffusion overpotentials (η_{diff}) and activation overpotentials (η_{ac}) of synthesized NDCs calculated from the Tafel plots. The relationship between overpotentials at 100 mA cm^{-2} from polarization curves; (d) specific surface area; and (e) total pore volume; (f) short-term stability test of the GDE using NDC1000 under a galvanostatic condition of 300 mA cm^{-2} .

electrode potential. They also suggested that selective doping of quaternary N is effective in terms of electrode performance, despite the presence of a lower amount of nitrogen.²⁷ The obtained NDC contains a high ratio of quaternary N, despite the total nitrogen content being low. Thus, according to their findings,²⁷ it seems that the higher electrode potential of NDCs derived from chitosan than CB may also be attributed to an increase in the electron transfer number due to nitrogen doping and selective doping of quaternary N.

All synthesized NDCs, with the exception of NDC800, exhibited higher electrode potentials than NDCs reported in the literature,²⁹ although the nitrogen content of the NDC reported by Ilnicka et al.²⁹ was eight times as high as the NDCs synthesized in this study. It is also noteworthy that only NDC800 exhibited a lower electrode potential than that of CB in the current density range exceeding 150 mA cm^{-2} , although NDC800 had the highest nitrogen content of all the synthesized NDCs. These results strongly indicate that

Figure 7. (a) Polarization curves of the GDEs with the synthesized NDCs and Pt/C; (b) diffusion overpotentials (η_{diff}) and activation overpotentials (η_{ac}) of NDC1000 and Pt/CB calculated from Tafel plots; and (c) pore size distribution of NDC1000 (activated at 1000 °C) and CB.

electrode potential is governed by nitrogen content and other factors. At such a high current density range, the oxygen reduction reaction was limited by charge transfer as well as mass transfer and resistance overpotential. Thus, to understand the relationship between the electrode performance and chemical activation temperature, the overpotential of each electrode was investigated using Tafel plots excluding the influence of the resistance overpotential (Fig. 6b). Here, the overpotential was defined as the difference between the electrode potential at each current density and the electromotive force (rest potential). The resistance overpotentials of the cell were very low and did not have a significant effect. The activation overpotential (η_{ac}) and the diffusion overpotential (η_{diff}) were estimated from the Tafel plots. Figure 6c shows the overpotentials of the synthesized NDCs separated into activation overpotentials and diffusion overpotentials at 100 mA cm⁻²; for all NDCs, the activation overpotential was much higher than the diffusion overpotential. These results indicated that electrode performance was mainly limited by the activation overpotential at 100 mA cm⁻². Additionally, NDC800 exhibited the highest activation and diffusion overpotentials of 126 and 40 mV, respectively. With an increase in activation temperature, the activation and diffusion overpotential tended to decrease. This is consistent with the fact that an increase in activation temperature results in a decrease in the number of doped nitrogen and the development of the microstructure. Thus, the microstructure of the NDC may be attributed to the change in activation and diffusion overpotentials. Figures 6d and 6e show the activation and diffusion overpotentials at 100 mA cm⁻² as a function of the specific surface area and the total pore volume, respectively.

This figure clearly shows that the activation and diffusion overpotentials tend to decrease, as the specific surface area and total volume may reduce the diffusion and activation overpotential. These results suggest that the developing microstructure of NDC plays a dual role in terms of increasing the number of reaction sites and diffusion pathways. Thus, the proposed synthesis method in this study presents itself as a significant synthesis method for chitosan-derived NDC with a microstructure suitable for a GDE. To demonstrate its potential as a catalyst-free GDE, the short-term stability of electrode performance was investigated using NDC1000; this NDC exhibits the lowest overpotential in the high current density range. Figure 6f shows the short-term stability of the electrode potentials under a galvanostatic condition of 300 mA cm⁻² for a GDE using NDC1000. There were no critical potential drops under galvanostatic measurement at 300 mA cm⁻², indicating that the NDCs demonstrated high potential as catalyst-free GDEs.

Finally, to understand the electrode performance of NDC1000, electrode performance was compared to that of state-of-the-art electrode materials such as 27.7 wt% Pt/C. Figure 7a shows the polarization curves of the GDEs. In the low current density range below 100 mA cm⁻², NDC1000 exhibited an electrode potential comparable to that of Pt/CB. NDC1000 has a high surface area and pore volume, indicating the formation of numerous triple-phase boundaries in the reaction layer. Additionally, quaternary N, which is able to enhance the oxygen reduction reaction, was selectively introduced into the carbon structure. Thus, we infer that such a high electrode performance in the lower current density range may be attributed to the well-developed microstructure and quaternary N.

However, with an increase in the current density in excess of 100 mA cm^{-2} , the electrode potential of NDC became slightly inferior to that of the other NDCs. In this region, the contribution of the diffusion overpotential to the electrode potential increases. Figure 7b shows the activation and diffusion over the voltage of NDC1000 and Pt/CB at 500 mA cm^{-2} . The total overpotential of NDC1000 was lower than that of Pt/CB, and NDC1000 exhibited a lower activation potential than Pt/CB while the diffusion overpotential was much higher. Pt loaded on CB has a well-designed pore structure for the reaction layer of GDE.²⁴ The pore size distributions of CB and NDC1000 were completely different, as shown in Fig. 7c, and CB had a higher pore volume of micro and mesopores than NDC1000. Thus, the number of micro and mesopores need to be increased in order to further improve the electrode performance of NDC1000 in the high current density range.

4. Conclusions

This study reports on a new synthesis method for chitosan-derived NDC using chemical activation with ZnCl_2 at $800\text{--}1050\text{ }^\circ\text{C}$ to control the microstructure of this type of NDC such that it is suitable for a GDE. With increasing activation temperature, there was an increase in the specific surface area and total pore volume because of the selective formation of micropores by ZnCl_2 activation at high temperatures. It was found that quaternary N could be maintained selectively in the carbon structure, despite the reduction in the nitrogen content in the synthesized NDC with an increase in activation temperature. The performance of the GDE of the synthesized NDC was evaluated through the oxygen reduction reaction in 8 M KOH solution at $60\text{ }^\circ\text{C}$. It was demonstrated that the overpotential tends to decrease with an increase in the surface area and pore volume because of an increase in the number of triple-phase boundaries and the enhancement of mass transfer. The highest electrode potential of -69 mV versus Hg/HgO at 300 mA cm^{-2} was achieved when the activation temperature was set to $1000\text{ }^\circ\text{C}$. At current densities below 100 mA cm^{-2} , the synthesized NDCs exhibited electrode performance comparable to that of Pt/CB. In the high current density range, the electrode performance of the synthesized NDCs were slightly inferior to that of Pt-supported CB because of the lack of mesopores in the former to promote mass transfer. Based on these findings, we can conclude that the developed thermal decomposition of chitosan with a solution-based precursor and ZnCl_2 activation at elevated temperatures are effective in controlling the NDC microstructure such that it is applicable in the reaction layer of GDEs. We also suggest that greater precision in the control of micro and mesopores in chitosan-derived NDCs will facilitate the realization of high-performance catalyst-free GDEs.

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