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# **ORIGINAL ARTICLE**

# Preparation of activated carbon from alkali lignin using novel one-step process for high electrochemical performance application



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# **KEYWORDS**

Na-lignin; Carbon; One-step process; Electrocapacity; Electrocatalyst

Abstract As the second most abundant bio-resource and as a byproduct of lignocellulose material processing, alkali lignin has to become a quantitative issue due to its difficulties to handle. On the other hand, lignin has high natural carbon contents, so it has the potential to act as a precursor for carbon materials. However, many previous researchers do three steps to transform it into high porous carbon: precipitation by reducing the alkaline compound, calcination to transform it into carbon, and carbon activation by adding alkaline compound again. In this study, the porous carbon material from alkali lignin in a one-step process for use as an electrode in supercapacitor and electrocatalyst is examined. The evaporation and especially carbonation temperature are studied to obtain the high porous carbon. After varying calcination temperatures, the carbon material's characterization was investigated to examine porosity, morphology, crystallinity, specific electrocapacity, and Oxygen Reduction Reaction (ORR) electrocatalyst activity. The carbon derived from Na-lignin via calcination at 700 °C had the highest electrocapacity of 168.29F/g. The electron transformed number is 2.23, indicating that the carbon derived from Na-lignin via calcination is promising for an electrode agent of supercapacitor and electrocatalyst for ORR.

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# 1. Introduction

The abundance of lignin as a byproduct of lignocellulose material processing has become a global problem, primarily an environmental issue. By increasing industries that use woodbased material such as paper, cellulose-based fabric, and



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1878-5352 © 2021 The Author(s). Published by Elsevier B.V. on behalf of King Saud University. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/). biofilter, pure cellulose becomes the primary material. The raw material was previously treated to separate the cellulose from hemicellulose and lignin, commonly known as delignification (Rocha et al., 2014; Banek et al., 2018; Prinsen et al., 2013). Original lignin is synthesized by plants to act as a resin providing strength to the cellulose fibers, making lignin a relatively non-oriented material (Sagues et al., 2019). As the chemical properties itself, lignin contains millions of p-hydroxyphenyl, guaiacyl, and syringyl as monomer building blocks (Fang et al., 2017). Due to the chemical bonding, lignin becomes very difficult to degrade by nature because it is insoluble in water unless using a particular compound or treatment naturally. On a large scale, lignin has usually been concentrated and burnt to manage the amount and prevent it from coming to the river or sea (Rocha et al., 2014; Sagues et al., 2019). Kraft cooking is becoming the most extensive process that is used to disrupt the cellulose-hemicellulose-lignin complex. The basic concept uses some alkali material to break the O-H bounding in lignin resulting in dissolved lignin in the alkaline solution.

On the other hand, lignin contains a high amount of carbon, becoming one of the most valuable materials, primarily used for energy storage. The high porosity of lignin-based carbon properties led to the carbon from lignin that is potentially used as an electrode in supercapacitors (Widiyastuti et al., 2020). There are many previous studies to modify lignin into a highly porous carbon. Most of them (Xiao et al., 2012; Hu and Hsieh, 2017; Rodríguez Correa et al., 2017) used commercial lignin to obtain powdered lignin, which has an unaffordable price. Lignin used in the industrial process is usually found in a liquid condition and has high pH coming from alkaline compounds to dissolve it. Acid is usually added to precipitate lignin, then the pH decreased, and lignin content could be precipitated and easily modified into carbon. However, after lignin is carbonized, it is often treated with alkaline compounds (NaOH or KOH) to make the carbon more active and have high porosity (Widiyastuti et al., 2020). It makes the alkaline content from the raw material becomes waste even though it is potentially used for the activation treatment. The process becomes longer in three steps: acid precipitation, carbonation, and activation.

Therefore, in this work, we use a novel process to carbonize lignin without removing the alkaline content after the delignification process (one-way process carbonization). In the present work, besides being used as a delignification agent, the same NaOH is also used as an activating agent for producing the activated carbon at the varied temperature range of 300–900 °C. We also study the electrochemical performance obtained by this method.

### 2. Materials and method

## 2.1. Materials

The Na-lignin was collected from the delignification of coconut husk prepared by 6 wt% of sodium hydroxides at approximately 100 °C for 4 h (C: 47.87%; O: 46.29%; Na: 2.44%; S: 0.73%; atomic ratio). The coconut husk itself was obtained from the traditional market in Keputih Surabaya, Indonesia. The sodium hydroxide (NaOH) in analytical grade was purchased from Merck.

#### 2.2. Experimental

### 2.2.1. Preparation of carbon

The aqueous liquor was first evaporated on a stirring hot plate at 85 °C to eliminate 80% water content and produce a thick Na-lignin. The thick liquor was then dried in the oven at 100 °C for 12 h. The dried Na-lignin size was reduced randomly using a crusher to make it fit in a ceramic boat. The following process was calcination in a flowing N2 tubular furnace through a ceramic cylinder with a dimension of 25 mm inside diameter and 400 mm length. The first step of the temperature set was 100 °C, with the N2 flowing rate was 150 mL/min for about 30 min to purge the oxygen content in the sample and cylinder itself. After that, the N<sub>2</sub> flowing rate was reduced to 50 mL/min, and the temperature was increased to 300, 500, 700, and 900 °C gradually. The ramp-up temperature-time was 30 min, then continued to the calcination for 1 h for each temperature observed, as shown in Fig. 1. After calcination, the samples were washed using the demineralized water until the conductivity obtained was the same as the solvent.

#### 2.2.2. Characterization

The powders' crystallographic structures were investigated using a Philips: Expert Pro X-ray diffractometer equipped with Cu K $\alpha$  (0.1541841 nm) radiation over the 2 $\theta$  range of 10–70°. The microstructure of the sample was observed with a Hitachi FLEXEM 1000 scanning electron microscope (SEM). A field emission scanning electron microscope (FE-SEM S-5200, Hitachi Technologies Co.) was utilized for further microstructure observation. The specific surface area was measured by multi-point nitrogen adsorption at its boiling point (Nova 1200, Quantachrome, US). The samples were then degassed at 300 °C under flowing nitrogen gas for 3 h before the measurement of nitrogen adsoption-desorption isotherms. The measurement was carried out at the nitrogen boiling point temperature, at -195.79 °C. The Brunauer-Emmet-Teller (BET) method was used to calculate the samples' specific surface area.

Raman spectra were acquired with a Raman imaging microscope using a micro confocal Raman Spectrometer provided by HORIBA with a laser at a wavelength of 532 nm. Deconvolution of the baselined spectra was observed with the peak type set to Gaussian-Lorrentzian area mode to obtain D and G bands. Ratios of peak intensities were determined based on the amplitude height of deconvoluted peaks.

The cyclic voltammetry (CV) was performed to investigate carbon electrochemistry performance using a potentiostat/galvanostat instrument (Autolab PGSTAT 302 N, Metrohm). The electrochemistry performance was divided into electrocapacity and electrocatalyst.

The electrocapacity performance of carbon was carried out using a three-electrode system with electrode sample as the working electrode, platinum as the counter electrode, and Ag/AgCl 3 M KCl (0.21 V vs. SHE) as the reference electrode. The CV was measured for 10 cycles at a scan rate of 10 mV/s. The potential applied was measured between -1.0 and 0 V in a 0.1 M of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> electrolyte. The sample was mixed with Polyvinylidene difluoride (PVdF) as a binder and several drops of 1-methyl 2-pyrrolidone (NMP) to obtain a carbon paste coated onto one side of 1.5 cm<sup>2</sup> Ni-foam, which is assigned as a working electrode.



Fig. 1 The calcination temperature scheme of Na-lignin using  $N_2$  flow tubular furnace.

The carbon obtained was then mixed with PVdF and NMP to produce a paste to measure the Oxygen Reduction Reaction (ORR). A droplet of the sample paste was put onto a 2 mm diameter of glassy carbon electrode to obtain a thin film of carbon, which next been dried at approximately 50 °C. The CV measurement was carried out by scanning the potential between -1.0 and 1.0 V (vs. Ag/AgCl) at a scan rate of 10 mV/s in 0.1 M KOH solution. The solution is already saturated previously with the flowing of oxygen and nitrogen for 30 min. Finally, linear sweep voltammetry (LSV) on a rotating disk electrode (RDE) was obtained to investigate the carbon sample's ORR activity. The measurements were performed at different rotating speeds from 400 to 2000 rpm at an interval of 400 rpm with the scan rate of 10 mV/s using the same electrolyte as the previous one.

### 3. Result and discussion

# 3.1. Thermogravimetric analysis of Na-Lignin

The thermogravimetric analysis was performed to study the calcination temperature of Na-lignin further. The thermogravimetric analysis (TGA) curves obtained from 25 to  $1000 \text{ }^{\circ}\text{C}$  at  $10 \text{ }^{\circ}\text{C}/\text{min}$  heating rate are shown in Fig. 2.

The thermal degradation profile of Na-lignin started from 85 °C and was completed at 1000 °C. The typical weight loss accompanying the structural change was 5 wt% at 85–110 °C, 11 wt% at 290–515 °C, 4 wt% slightly at 515–790 °C, and 15 wt% after the heating process. They correspond to the thermal stability of the compounds presents loss of moisture content (A), loss of other organic volatiles (B), loss due to the decomposition of lignin into carbon (C), and loss due to combustible matter after switching to an oxidizing atmosphere (D) (Bredin et al., 2011). Several references studied that there is no standardized definition of these components; however, it is generally agreed that they are defined as indi-



Fig. 2 TGA curves of Na-lignin sample under N<sub>2</sub>.

cated in Fig. 2 and referred to as follows. The moisture content (section A) are classified as water, the other organic component (section B) are those responsible for the polymer degradation products that will be lost in the range of 300-500 °C (Rahmatika et al., 2018). The decomposition phase of lignin to be transformed as carbon (section C) and combustible matter (section D) refers to non-volatile but oxidizable material in its yet unoxidized form. Based on Fig. 2, the next calcination temperature applied, especially to the carbon properties, would be studied at 500, 700, and 900 °C.

# 3.2. The physical appearance of Na-lignin-based carbon at various temperature

The visual appearance of dried Na-lignin and carbon derived from Na-lignin via calcination at 300, 500, 700, and 900 °C are shown in Fig. 3. As seen, the dried Na-lignin color was



Fig. 3 Visual appearance of (a) dried Na-lignin; and carbon derived from Na-lignin via calcination at (b) 300, (c) 500, (d) 700, and (e) 900 °C.

brownish-red and bulky form and going darker with the increase of temperature. The presence of NaOH that hygroscopic makes the lignin was agglomerated. Carbon derived from Na-lignin via calcination at 500 to 900 °C shows black and shiner caused by the decomposition of some lignin's organic material into volatile gases and solid carbon, which carbon is physically not soluble in NaOH. It will make the separation process during washing with demineralized water become easier (Widiyastuti et al., 2020).

# 3.3. Crystallography patterns of carbon derived from Na-lignin via calcination at various temperatures

Samples were analyzed by X-ray diffraction (XRD) to investigate further the carbon character at each temperature except the dried Na-lignin itself. All lignin and carbon fractions showed broad diffraction of amorphous carbon phase with a maximum at about  $2\theta = 26^{\circ}$ . However, as displayed in Fig. 4, the diffraction of prominent peaks for Na-lignin calcined at 300 °C are at 28.53°, 26.46°, and 34.17°, which is identic to the prominent peak of sodium ICDD pattern (ICDD card No. 00–001-0850). It seems that sodium content remains in the carbon structure even though it has been washed with demineralized water. The physical properties of lignin are soluble in NaOH solution and carbon is not (Ponomarev and Sillanpää, 2019). Therefore, we can conclude that at the calcination temperature of 300 °C, lignin had not been entirely transformed into carbon structures yet.

On the other hand, the X-ray patterns of Na-lignin calcined at 500, 700, and 900 °C did not exhibit a well-defined peak besides at range  $\sim 26^{\circ}$  as the prominent peak. The second peak is slightly shown at  $\sim 43^{\circ}$ , identical to the amorphous carbon phase (ICDD Card No.00–056-0159). Furthermore, the most



**Fig. 4** X-ray diffraction (XRD) diffractogram of the carbon derived from Na-lignin via calcination at 300, 500, 700, and 900 °C.

important is the absence of sodium peak indicates that at calcination temperature of 500, 700, and 900 °C, the Na-lignin has already been entirely transformed into carbon.

### 3.4. Nitrogen adsorption-desorption analysis

The specific surface area of dried Na-lignin and carbon derived from Na-lignin were determined by measuring the Nitrogen adsorption–desorption isotherms and BET modeling. Their pore volume distributions were analyzed by the Barret-Joyner-Halenda (BJH) method using desorption isotherm data. The Nitrogen adsorption–desorption isotherms curves of dried lignin to the carbon at the various temperatures are shown in Fig. 5 and Table 1.

The lower portion of the loop was traced out on the adsorption, and the upper portion was traced out on the desorption. All samples revealed the mixed character of type IV of Brunauer's classification. That is a behavior that reflects the coexistence of mesopores (Widiyastuti et al., 2020). However, the particles of dried Na-lignin and calcined Na-lignin 300 °C represented a low N<sub>2</sub> adsorption volume. The lignin particle performed a flat adsorption curve, which indicates the low porosity content. Because the lignin content is soluble in NaOH, so the NaOH itself filled the pore of lignin. Like the dried Na-lignin, at a temperature of 300 °C, the lignin structure has not transformed into carbon completely. Therefore, the particle was still agglomerated, caused by the hygroscopic of NaOH and the less porous particle (Chatterjee and Saito, 2015).

The BET specific surface area (SSA) and pore properties of the rest treatment of carbon derived from Na-lignin via calcination at various temperatures are shown in Table 1. Calcined Na-lignin 700 °C has the highest BET SSA value (1573.99 m<sup>2</sup>/ g). The increasing rate of N<sub>2</sub> volume adsorbed was slower at the lower relative pressure, indicating monolayer adsorption and a growing N<sub>2</sub> adsorption rate faster at the higher relative pressure due to the capillarity condensation (Tian et al., 2017). Calcined Na-lignin 900 °C shows a lower specific surface area compared to those which calcined at 700 °C. According to the pore volume and pore size diameter in Table 1, and after seeing the TGA pattern in Fig. 2, the phenomenon was possibly caused by the carbon structure's sintering effect from the sample of calcined Na-lignin 900 °C. The temperature also indicates the beginning of the carbon decomposition phase. Compared to the previous study (Widivastuti et al., 2020), the performance of carbon derived from Na-lignin through conventional three-step synthesis shows that the specific surface area of lignin carbonization at 500, 700, and 900 °C were



Fig. 5 The adsorption–desorption curves of  $N_2$  at – 195.79 °C for dried Na-lignin and carbon derived from Na-lignin via calcination at 300, 500, 700, and 900 °C.

Table 1Pore structure parameters of dried Na-lignin and the<br/>carbon derived from Na-lignin via calcination at 300, 500, 700,<br/>and 900 °C.

Sample	Specific surface area (m <sup>2</sup> /g)	Pore diameter (nm)	Pore volume (cm <sup>3</sup> /g)
Dried Na-lignin	196.69	2.86	0.14
Calcined Na-	576.27	3.10	0.45
lignin 300 °C			
Calcined Na-	806.27	4.50	0.91
lignin 500 °C			
Calcined Na-	1573.99	5.38	2.12
lignin 700 °C			
Calcined Na-	1174.37	4.81	1.41
lignin 900 °C			

157.621, 642.501, and 541.177  $m^2/g$ . It described a similar pattern that lignin at a calcination temperature of 900 °C showed a lower specific surface area compared to those which calcined at 700 °C. However, precipitation using HCl will generate NaCl salt as a byproduct trapped inside the pore, leading to decreased active pore. Even though the particles have already been washed using demineralized water, the salt content could not be entirely eliminated when they pass through the micropore.

### 3.5. Graphitic carbon type identified by Raman spectroscopic

Raman spectra (Fig. 6) of carbon derived from Na-lignin via calcination at various temperatures were deconvoluted into two pseudo-Voigt-shaped peaks centered at ~ 1356 (D band) and ~ 1594 (G band), respectively. Often the intensity ratio of D-band and G-band, which is respected as  $(I_D/I_G)$ , is used as a calcination parameter, reflecting the amounts of the surface/edge defects of carbon sheets (Zhang et al., 2017). As the increasing calcination temperature from 300 to 700 °C, the D-band and G-band start to develop as the indication of the pyrolyzed material's aromatization process is begun (Paris et al., 2005). As reported before (Zhang et al., 2017), either the D-band or G-band indicated  $sp^2$  bonded turbostratic carbon nanocrystallites and graphitic carbon crystallites, which exhibit a reduction of the amorphous phase for  $sp^2$ bonded carbon with the increasing of calcination temperature (Ishimaru et al., 2007).

The increase of  $I_D/I_G$  of carbon derived from Na-lignin via calcination from 300 °C (0.42), 500 °C (0.63) to 700 °C (1.03) confirms the grafting of oxygen-containing functional groups to the graphitic planes. After reaching 900 °C calcination temperature, the sintering effects make the surface reduced. Moreover, the high  $I_D/I_G$  has another advantage, such as a high electrocatalytic performance (Zhang et al., 2017; Zhang et al., 2017; Tian et al., 2017; Perumbilavil et al., 2015; Zhang et al., 2017). It would be discussed further in the following paragraph.

# 3.6. The morphology of carbon derived from Na-lignin via calcination

The SEM images of carbon derived from Na-lignin via calcination at 500–900  $^{\circ}$ C are demonstrated in Fig. 7. Carbon parti-



Fig. 6 Raman spectra for carbon derived from Na-lignin via calcination at various temperatures.

cles show an irregular shape and tend to agglomeration with a size of a few micrometers. The increase of calcination temperature led to the decomposition of more volatile components left behind the mesoporous carbon particles. The formation of pores for carbon derived from Na-lignin via calcination increases the specific surface area explained in Table 1.

At higher magnification, superstructures at the single object level using Field Emission Scanning Electron Microscopy (FE-SEM, Fig. 8), the particles' structure can be observed as a rough porous. The pore number increase with the increase of calcination temperature from 500 to 700 °C. The increasing calcination temperature led to the decomposition of more volatile components left behind the microporous and mesoporous carbon particles. The formation of pores for carbon derived from Na-lignin via calcination increases the specific surface area, as explained in Table 1. However, the carbon derived from Na-lignin via calcination at 900 °C exhibits some denser carbon structures compared to the other lower temperature treatment. At a calcination temperature of 900 °C, a sintering effect and shrinkage of the carbon derived from Na-lignin reduced the pore areas. The carbon derived from Na-lignin via calcination at 900 °C also reduced the specific surface area because the sintering effect results in some pores' sealing. Overall, high calcination temperature had detrimental effects on micropore areas' development due to a shrinkage effect on the carbon microstructures (Guo and Chong Lua, 1998; Youseffi et al., 2000).

# 3.7. The electrocapacity performance of carbon derived from Na-lignin

As a highly porous and conductive material, carbon can commonly be used as a supercapacitor source and experimentally evaluate carbon's capacitive performance derived from Nalignin. The electrochemical tests were conducted in 0.1 M Na<sub>2</sub>- $S_2O_3$  at a potential range of -1 to 0 V.

As shown in Fig. 9, all CV curves do not exhibit a precise rectangular curve as the double layer capacitive material commonly performs. However, the curves have no noticeable reaction peaks and have a countable area indicating that the carbon has a supercapacitor's behavior. Compared to the other two carbon samples, the carbon derived from Na-lignin via calcination at 700 °C presents a higher specific capacitance with 168.29F/g, determined by measuring the CV areas. This electrocapacity data is relevant to the highest specific surface area, the morphologic structure, and the Raman spectra data of carbon derived from Na-lignin via calcination at 700 °C, as explained previously. Moreover, as a comparison, the carbon derived from Na-lignin synthesized through traditional three-steps (Widiyastuti et al., 2020) exhibits lower specific capacitances of 1.96, 4.13, 28.84, and 17.90F/g for calcination temperature of 500, 700, and 900 °C, respectively. Therefore, it is clearly described that the effect of NaCl salt trapped inside the pore matrix can reduce the active side of carbon pore, impacting the reduction of specific capacitance as well.

3.8. Electrocatalytic performance for ORR provided by cyclic and linear sweep voltammetry using rotating disk electrode

Referring to the previous study, alkali lignin is included in lowsulfur lignin that can be a sulfur co-doped carbon with good



Fig. 7 SEM images of carbon derived from Na-lignin via calcination at (a) 500 °C (b) 700 °C, (c) 900 °C at a magnification of 3,000×.



**Fig. 8** FE-SEM images of carbon derived from Na-lignin via calcination at (a) 500 °C, (b) 700 °C, and (c) 900 °C at a magnification of 40,000×.



Fig. 9 Cyclic voltammograms of carbon derived from Na-lignin via calcination at 500–900 °C at 10 mV s<sup>-1</sup> on Ni-Foam surface in 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution.

Oxygen Reduction Reaction (ORR) performance (Zhang et al., 2016; Shen et al., 2019; Demir et al., 2018). Therefore, to observe the electrocatalyst device's application, we need to identify the Oxygen Reduction Reaction (ORR) of the electrocatalyst agent. In this study, carbon derived from Na-lignin via calcination at 700 °C, as the best graphitic crystallites, was used for ORR performance. The cyclic voltammetry (CV) measurement was first evaluated using a comparison of a three-electrode system in 0.1 M KOH solution saturated with  $O_2$ - or  $N_2$ - using Ag/AgCl as a reference electrode with a scan rate of 10 mV s<sup>-1</sup> (Fig. 10).

The electrocatalyst's CV curves exhibited no cathodic peak in the N<sub>2</sub>-saturated solution, as shown in Fig. 10(a). In contrast, a pronounced cathodic peak at -0.375 V was observed in O<sub>2</sub>-saturated solutions at the current density of -0.67 mA/cm<sup>2</sup>, attributed to the electrocatalytic oxygen reduction reaction on the electrode. Furthermore, to examine the best electrocatalytic performance among those three kinds of temperature treatment carbon, all CV measurements were performed using O<sub>2</sub>-saturated 0.1 M KOH, as shown in Fig. 10 (b). The carbon samples present distinct single oxygen reduction peaks, suggesting the conspicuous catalytic activity for the ORR. The shape of all samples' CV curves was similar and showed a reduction peak at -0.37 V for carbon derived from Na-lignin via calcination at 500 and 700 °C, and -0.41 V for carbon derived from Na-lignin via calcination at 900 °C with the approximate current density of -0.8 mA cm<sup>-2</sup>. The phenomenon is indicating that the carbon structure from Na-lignin was sulfur-doped since the atomic ratio of sulfur to carbon content was 1.52% which prove the content of S co-doped porous carbon could further boost the catalytic performance due to a synergetic effect, so it has a potential usage to support the electrocatalyst (Ito et al., 2015; Wang et al., 2016; Wu et al., 2017; Su et al., 2016).

The carbon sample was further quantitatively evaluated to measure the electron transfer number using the rotating disk electrode (RDE) measurements. The carbon derived from Na-lignin via calcination at 700 °C has the best specific surface area and graphitic crystallites. The rotating rates from 400 to 2000 rpm were conducted, allowing further insight into the ORR kinetics and electrocatalytic processes on the catalysts.

As shown in Fig. 11(a), the  $J_{\rm L}$  increased gradually with the increasing rotating speed due to the shorter diffusion distance of oxygen at higher speeds. Furthermore, the ORR kinetics of the electrocatalyst composite was further analyzed using the Koutecky-Levich plots of  $J^{-1}$  versus  $\omega^{-1}$  calculated based on the potential linear range from the LSV curves. As shown in Fig. 11(b), the plots exhibit excellent linearity and parallelism at the potential range of -0.45 to -0.55 V, revealing first-order reaction kinetics (Shao et al., 2019). Moreover, the electron transfer number of carbon derived from Na-lignin towards ORR n = 2.23 is calculated based on the Koutecky-Levich equation (Xing et al., 2014). Those shows that the carbon derived from Na-lignin demonstrated the electrocatalytic activities for ORR via a two-step two-electron pathway in an alkaline solution as follows (Ma et al., 2019):

$$O_2 + H_2O + 2e^- \rightarrow HO_2^- + OH^-(-0.364Vvs.Ag/AgCl)$$

 $H_2O + HO_2^- + 2e^- \rightarrow 3OH^-(0.59Vvs.Ag/AgCl)$ 

The defect-rich graphitic structure of carbon derived from Na-lignin produced by direct activation may increase the electrocapacity so it can potentially be developed in supercapacitor application and increase carbon conductivity. Therefore, it can support the Oxygen Reduction Reaction in a metal-air battery application. For further research, this inexpensive carbon product can be potentially composited with Pt material (Balgis et al., 2017) or some other non-noble metal to increase their function as support of metal-air battery electrocatalyst (Mahmudi et al., 2018; Nurlilasari et al., 2020).



**Fig. 10** ORR performance of (a) CV curves of carbon derived from Na-lignin via calcination at 700 °C in N<sub>2</sub>-saturated and O<sub>2</sub>-saturated solutions, and (b) CV curves of carbon derived from Na-lignin via calcination at 500, 700, and 900 °C in O<sub>2</sub>-saturated solutions.



Fig. 11 (a) LSV curves of the electrocatalyst at different rotating rates and (b) The Koutecky-Levich plots of electrocatalyst based on the RDE data.

# 4. Conclusion

In summary, we have successfully developed a high electrocatalytic and electrocapacity performance carbon through a simple calcination method and without further chemical activation from coconut husk-based lignin. The obtained carbon has high possibilities to be utilized as an electrocatalyst for metal-air battery application or supercapacitor. The onestep process without eliminating NaOH in lignin solution significantly enhances the conductivity and catalytic activity of carbon and makes the process more efficient. The carbon derived from Na-lignin via calcination at 700 °C reached the highest specific surface area and has the highest electrocapacity. Furthermore, as the electrocatalyst supports, it showed an excellent electron transform number. The direct carbon activation treatment from lignin can make the defect intensity of carbon drastically increase, which leads to the increase of the specific capacitance and the electrocatalytic activity for Oxygen Reduction Reaction.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### References

- Rocha, G.J.M., Nascimento, V.M., da Silva, V.F.N., Corso, D.L.S., Gonçalves, A.R., 2014. Contributing to the environmental sustainability of the second generation ethanol production: Delignification of sugarcane bagasse with sodium hydroxide recycling. Ind. Crops Prod. 59, 63–68. https://doi.org/10.1016/j.indcrop.2014.05.002.
- Banek, N.A., Abele, D.T., McKenzie, K.R., Wagner, M.J., 2018. Sustainable Conversion of Lignocellulose to High-Purity, Highly Crystalline Flake Potato Graphite. ACS Sustain. Chem. Eng. 6 (10), 13199–13207. https://doi.org/10.1021/ acssuschemeng.8b02799.
- Prinsen, P., Rencoret, J., Gutiérrez, A., Liitiä, T., Tamminen, T., Colodette, J.L., Berbis, M.Á., Jiménez-Barbero, J., Martínez, Á.T., del Río, J.C., 2013. Modification of the Lignin Structure during Alkaline Delignification of Eucalyptus Wood by Kraft, Soda-AQ, and Soda-O 2 Cooking. Ind. Eng. Chem. Res. 52 (45), 15702– 15712. https://doi.org/10.1021/ie401364d.
- Sagues, W.J., Jain, A., Brown, D., Aggarwal, S., Suarez, A., Kollman, M., Park, S., Argyropoulos, D.S., 2019. Are lignin-derived carbon fibers graphitic enough?. Green Chem. 21 (16), 4253–4265. https:// doi.org/10.1039/C9GC01806A.
- Fang, W., Yang, S., Yuan, T.-Q., Charlton, A., Sun, R.-C., 2017. Effects of Various Surfactants on Alkali Lignin Electrospinning Ability and Spun Fibers. Ind. Eng. Chem. Res. 56 (34), 9551–9559. https://doi.org/10.1021/acs.iecr.7b02494.
- Widiyastuti, W., Rois, M.F., Setyawan, H., Machmudah, S., Anggoro, D., 2020. Carbonization of Lignin Extracted from Liquid Waste of Coconut Coir Delignification. Indones. J. Chem. 20, 842. https:// doi.org/10.22146/ijc.46484.
- Xiao, G., Ni, M., Xiao, R., Gao, X., Cen, K., 2012. Catalytic carbonization of lignin for production of electrically conductive charcoal. J. Biobased Mater. Bioenergy. 6 (1), 69–74. https://doi. org/10.1166/jbmb.2012.1190.
- Hu, S., Hsieh, Y.-L., 2017. Lignin derived activated carbon particulates as an electric supercapacitor: Carbonization and activation on porous structures and microstructures. RSC Adv. 7 (48), 30459– 30468. https://doi.org/10.1039/C7RA00103G.
- Rodríguez Correa, C., Stollovsky, M., Hehr, T., Rauscher, Y., Rolli, B., Kruse, A., 2017. Influence of the Carbonization Process on Activated Carbon Properties from Lignin and Lignin-Rich Biomasses. ACS Sustain Chem. Eng. 5 (9), 8222–8233. https:// doi.org/10.1021/acssuschemeng.7b01895.
- Bredin, A., Larcher, A.V., Mullins, B.J., 2011. Thermogravimetric analysis of carbon black and engine soot - Towards a more robust oil analysis method. Tribol. Int. 44 (12), 1642–1650. https://doi.org/ 10.1016/j.triboint.2011.06.002.
- A.M. Rahmatika, Y. Weilin, A.F. Arif, R. Balgis, K. Miyajima, G.M. Anilkumar, K. Okuyama, T. Ogi, Energy-efficient templating method for the industrial production of porous carbon particles by a spray pyrolysis process using poly (methyl methacrylate), (2018). https://doi.org/10.1021/acs.iecr.8b02564.
- Ponomarev, N., Sillanpää, M., 2019. Combined chemical-templated activation of hydrolytic lignin for producing porous carbon. Ind. Crops Prod. 135, 30–38. https://doi.org/10.1016/j. indcrop.2019.03.050.
- Chatterjee, S., Saito, T., 2015. Lignin-Derived Advanced Carbon Materials. ChemSusChem. 8 (23), 3941–3958. https://doi.org/ 10.1002/cssc.201500692.
- Tian, W., Li, W., Yu, W., Liu, X., 2017. A Review on Lattice Defects in Graphene: Types. Generation, Effects and Regulation, Micromachines. 8, 163. https://doi.org/10.3390/mi8050163.
- Zhang, J., Zhang, F., Yang, Y., Guo, S., Zhang, J., 2017. Composites of Graphene Quantum Dots and Reduced Graphene Oxide as Catalysts for Nitroarene Reduction. ACS Omega. 2 (10), 7293– 7298. https://doi.org/10.1021/acsomega.7b0090810.1021/acsomega.7b00908.s001.

- Paris, O., Zollfrank, C., Zickler, G.A., 2005. Decomposition and carbonisation of wood biopolymers—a microstructural study of softwood pyrolysis. Carbon Nanotub. Graphene. 43 (1), 53–66. https://doi.org/10.1016/j.carbon.2004.08.034.
- Zhang, X., Yan, Q., Leng, W., Li, J., Zhang, J., Cai, Z., Hassan, E., 2017. Carbon Nanostructure of Kraft Lignin Thermally Treated at 500 to 1000 °C. Materials (Basel). 10, 975. https://doi.org/ 10.3390/ma10080975.
- Ishimaru, K., Hata, T., Bronsveld, P., Nishizawa, T., Imamura, Y., 2007. Characterization of sp2- and sp3-bonded carbon in wood charcoal. J. Wood Sci. 53 (5), 442–448. https://doi.org/10.1007/ s10086-007-0879-7.
- Tian, W., Li, H., Zhou, J., Guo, Y., 2017. Preparation, characterization and the adsorption characteristics of lignin/silica nanocomposites from cellulosic ethanol residue. RSC Adv. 7 (65), 41176– 41181. https://doi.org/10.1039/C7RA06322A.
- Perumbilavil, S., Sankar, P., Priya Rose, T., Philip, R., 2015. White light Z-scan measurements of ultrafast optical nonlinearity in reduced graphene oxide nanosheets in the 400–700 nm region. Appl. Phys. Lett. 107, https://doi.org/10.1063/1.4928124 051104.
- Zhang, Y., Wang, F., Zhang, D., Chen, J., Zhu, H., Zhou, L., Chen, Z., 2017. New type multifunction porous aerogels for supercapacitors and absorbents based on cellulose nanofibers and graphene. Mater. Lett. 208, 73–76. https://doi.org/10.1016/ j.matlet.2017.04.141.
- Guo, J., Chong Lua, A., 1998. Characterization of chars pyrolyzed from oil palm stones for the preparation of activated carbons. J. Anal. Appl. Pyrolysis. 46 (2), 113–125. https://doi.org/10.1016/ S0165-2370(98)00074-6.
- Youseffi, M., Wright, C.S., Jeyacheya, F.M., 2000. Effect of carbon content, sintering temperature, density, and cooling rate upon properties of prealloyed Fe–1.5Mo powder. Powder Metall. 43 (3), 270–274. https://doi.org/10.1179/003258900666041.
- Zhang, X., Yu, D., Zhang, Y., Guo, W., Ma, X., He, X., 2016. Nitrogen- and sulfur-doped carbon nanoplatelets via thermal annealing of alkaline lignin with urea as efficient electrocatalysts for oxygen reduction reaction. RSC Adv. 6 (106), 104183–104192. https://doi.org/10.1039/C6RA21958F.
- Shen, Y., Peng, F., Cao, Y., Zuo, J., Wang, H., Yu, H., 2019. Preparation of nitrogen and sulfur co-doped ultrathin graphitic carbon via annealing bagasse lignin as potential electrocatalyst towards oxygen reduction reaction in alkaline and acid media. J. Energy Chem. 34, 33–42. https://doi.org/10.1016/ j.jechem.2018.09.021.
- Demir, M., Farghaly, A.A., Decuir, M.J., Collinson, M.M., Gupta, R. B., 2018. Supercapacitance and oxygen reduction characteristics of sulfur self-doped micro/mesoporous bio-carbon derived from lignin. Mater. Chem. Phys. 216, 508–516. https://doi.org/10.1016/ j.matchemphys.2018.06.008.
- Ito, Y., Cong, W., Fujita, T., Tang, Z., Chen, M., 2015. High catalytic activity of nitrogen and sulfur co-doped nanoporous graphene in the hydrogen evolution reaction. Angew. Chemie - Int. Ed. 54 (7), 2131–2136. https://doi.org/10.1002/anie.201410050.
- Wang, F., Song, S., Li, K., Li, J., Pan, J., Yao, S., Ge, X., Feng, J., Wang, X., Zhang, H., 2016. A "Solid Dual-Ions-Transformation" Route to S, N Co-Doped Carbon Nanotubes as Highly Efficient "Metal-Free" Catalysts for Organic Reactions. Adv. Mater. 28 (48), 10679–10683. https://doi.org/10.1002/adma.201603608.
- Wu, M., Liu, Y., Zhu, Y., Lin, J., Liu, J., Hu, H., Wang, Y., Zhao, Q., Lv, R., Qiu, J., 2017. Supramolecular polymerization-assisted synthesis of nitrogen and sulfur dual-doped porous graphene networks from petroleum coke as efficient metal-free electrocatalysts for the oxygen reduction reaction. J. Mater. Chem. A. 5 (22), 11331–11339. https://doi.org/10.1039/C7TA03264A.
- Su, Y., Yao, Z., Zhang, F., Wang, H., Mics, Z., Cánovas, E., Bonn, M., Zhuang, X., Feng, X., 2016. Sulfur-Enriched Conjugated Polymer Nanosheet Derived Sulfur and Nitrogen co-Doped Porous Carbon Nanosheets as Electrocatalysts for Oxygen Reduction

Reaction and Zinc-Air Battery. Adv. Funct. Mater. 26 (32), 5893– 5902. https://doi.org/10.1002/adfm.v26.3210.1002/ adfm.201602158.

- Shao, Q.i., Liu, J., Wu, Q., Li, Q., Wang, H.-G., Li, Y., Duan, Q., 2019. In Situ Coupling Strategy for Anchoring Monodisperse Co 9 S 8 Nanoparticles on S and N Dual-Doped Graphene as a Bifunctional Electrocatalyst for Rechargeable Zn–Air Battery. Nano-Micro Lett. 11 (1). https://doi.org/10.1007/s40820-018-0231-3.
- Xing, W., Yin, G., Zhang, J., 2014. Rotating Electrode Methods and Oxygen Reduction Electrocatalysts, Elsevier. Amsterdam. https:// doi.org/10.1016/C2012-0-06455-1.
- Ma, R., Lin, G., Zhou, Y., Liu, Q., Zhang, T., Shan, G., Yang, M., Wang, J., 2019. A review of oxygen reduction mechanisms for metal-free carbon-based electrocatalysts. Npj Comput. Mater. 5, 78. https://doi.org/10.1038/s41524-019-0210-3.
- Balgis, R., Widiyastuti, W., Ogi, T., Okuyama, K., 2017. Enhanced Electrocatalytic Activity of Pt/3D Hierarchical Bimodal Macroporous Carbon Nanospheres. ACS Appl. Mater. Interfaces. 9 (28), 23792–23799. https://doi.org/10.1021/acsami.7b0587310.1021/acsami.7b05873.s001.
- Mahmudi, Widiyastuti, W., Nurlilasari, P., Affandi, S., Setiawan, H., 2018. Setiawan, Electrolysis Synthesis of MnO2 in Acidic Environment and Its Electrochemical Performance for Supercapacitor Electrolysis Synthesis of MnO2 in Acidic Environment and Its Electrochemical Performance for Supercapacitor. J. Phys. 1093, 012021. https://doi.org/10.1088/1742-6596/1093/1/012021.
- Nurlilasari, P., Widiyastuti, W., Setyawan, H., 2020. Novel monopolar arrangement of multiple iron electrodes for the large-scale production of magnetite nanoparticles for electrochemical reactors. Adv. Powder Technol. 31 (3), 1160–1168. https://doi.org/10.1016/j. apt.2019.12.043.