

Preparation of marine biomass derived activated carbon with high amount of mesopores by CO₂ activation and its application to EDLC electrode materials

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CO₂賦活法によるマリンバイオマス由来高メソ孔含有活性炭の
製造およびその電気二重層キャパシタの電極材としての応用

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Abstract

Fossil fuels, which are used as the main energy source in industry, account for more than 80% of energy sources. However, the use of fossil fuels is causing global warming and environmental problems due to the increase in CO₂ gas. That is why biomass, which can provide the renewable source of fixed carbon, is receiving attention. Biomass is a substance extracted from organic matter, including plants and animals and their byproducts, and is stored in large quantities on earth. When biomass is classified by cultivation, it can be divided into terrestrial biomass and marine biomass. Terrestrial biomass is biomass that is mainly extracted from wood or plants, or from residues or by-products after producing related products, or from raw materials such as animal bones, meat, and human waste. Terrestrial biomass is widely used in biomass research, but it requires land and agricultural water for cultivation. And it has the disadvantage of low solar energy efficiency of less than 1%. Marine biomass that grows in the sea among biomass is a biomass that includes marine inorganic substances such as macroalgae, microalgae, and emerging plants that grow in the sea, wetlands, or swamps, as well as plankton, fish, and marine organisms. Marine biomass is economically efficient because, unlike terrestrial biomass, it does not require separate agricultural water or separate farmland. Also, its solar energy efficiency is relatively high. It has an excellent CO₂ absorption capacity, so in places with developed coastlines such as Japan and Korea, the area available for cultivation is large, and it is emerging as a new alternative for reducing greenhouse gases through seaweed cultivation. Among marine biomass, seaweed is used as food in Asia, but in the West, it is still considered a weed of sea and is discarded. Therefore, it is necessary to find a solution that can be applied in places where seaweed is not consumed as food while reducing CO₂. However, seaweed is rich in alkali and alkaline earth metals (AAEM) such as potassium, sodium, magnesium, etc. AAEM are difficult to control during the high-temperature heat treatment required for carbon conversion and reduce product quality. In addition, AAEMs participate in reactions such as developing pores through gasification reactions

by reacting as catalysts in heat treatment processes. To utilize marine biomass, it is necessary to effectively remove AAEMs and manufacture and apply carbon materials with highly developed pores.

In this study, we intend to produce activated carbon using marine biomass, seaweed, as a raw material. In order to produce marine biomass-derived activated carbon, the following factors should be considered;

- (1) Confirm the presence of AAEMs as impurities in marine biomass and effectively remove them
- (2) Adopt an activation method to produce activated carbon with a high degree of pore development
- (3) Application suitable for the pore structure of the manufactured activated carbon

Abstracts of each chapter in this thesis are summarized as below;

In Chapter 1, the background and purpose of this study were described that the biomass utilization was necessary and classifies terrestrial biomass and marine biomass. And I explained about the manufacturing and application of activated carbon. In the application field, I introduced electric double layer capacitor in more detail. The purpose of the study was also mentioned.

In Chapter 2, the presence of alkali and alkaline earth metals (AAEMs) in marine biomass was fined by the XRF analysis method. I confirmed that AAEMs had effects such as lowering the resultant carbon content and developing pores during heat treatment and activation processes. For the removal method, I considered various acid solutions, and established a method for optimizing the removal of AAEMs by evaluating. As a result, we achieved a CHO content of 97.5%, which is higher than the removal efficiency and CHO content of 94.5% of AAEMs announced in the previous study.

In Chapter 3, I used 2-step CO₂ activation to manufacture activated carbon using marine biomass from which AAEMs were removed. I confirmed that the marine biomass developed pores through gasification reaction with the existing AAEMs as a catalyst during the heat treatment process. This resulted in the production of activated carbon having a structure in which mesopores are also developed, despite the physical activation primarily developing micropores. I performed activation

using the pressurized physical activation method for high pore development, but the catalytic reaction of AAEMs also increased in the pressurized atmosphere, which hindered the development of effective micropores for high specific surface area, making it impossible to produce activated carbon with high pore development and high yield, which is an advantage of pressurized activation. I consume the primary AAEMs through catalytic gasification by atmospheric activation, the pores were developed, and then the AAEMs appearing on the surface were removed, thereby developing the pores while minimizing the influence of AAEMs in pressurized physical activation, and finally, activated carbon with a maximum surface area of 2100 m²/g was manufactured by pressurized activation. Additional 1.5 nm micropores were developed by the diffusion of the activator through pressurized activation, and marine biomass-derived activated carbon having mesopore and micropore size distributions developed by the catalytic gasification reaction of AAEMs was produced.

In Chapter 4, I verified the applicability of uniquely developed mesoporous structure of marine biomass-derived activated carbon to electric double layer capacitors. As a comparison group, I produced phenol resin-derived activated carbon with the same heat treatment conditions and similar specific surface area but only micropores. Both activated carbons were manufactured with a surface area close to 1500 m²/g, and the marine biomass-derived activated carbon had more than 60% mesopores, while the phenol resin-derived activated carbon was manufactured with 0% mesopores. Full-cell electrochemical analysis confirmed that the EDLC of marine biomass-derived activated carbon with developed mesopores exhibited high capacitance (25.9 F/g and 29.4 F/g at 2.7 V and 3.3 V) at both low and high voltages. The content of ions in charge/discharge quantitatively evaluated by ¹⁹F solid-state NMR was more than twice as high for marine biomass-derived activated carbon at a high voltage of 3.3 V. I demonstrate the potential of marine biomass-derived activated carbon for the utilization of high-voltage double-layer capacitors as a solution to increase energy density.

In Chapter 5, the above obtained results and discussions in this thesis were summarized as conclusion.

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Chapter 1. General introduction

1.1 Marine biomass

1.1.1 Biomass

Fossil fuels, such as coal, oil, and natural gas, are the main sources of energy used in industry and account for more than 80% of the energy consumed worldwide. These resources are crucial for sustaining economic and industrial activities [1]. However, the growing reliance on fossil fuels has also led to a significant increase in greenhouse gas emissions, exacerbating environmental issues such as a decrease in the amount of radiative heat emitted from the earth and increases atmospheric temperatures, which in turn causes global warming [2,3]. The problem of global warming has a huge impact on humans as well as the natural ecosystem [4]. Also, although the reserves of fossil fuels are uncertain, they are predicted to be gradually depleting [5]. One of the alternative energy sources gaining attention is biomass, which is environmentally friendly and can provide the only renewable source of fixed carbon [6]. Biomass is a material derived from organic matter, including plants, animals, and their by-products. Unlike fossil fuels, it is a renewable and eco-friendly resource based on carbon cycle. The earth holds an immense amount of biomass, such as wood, shrubs, plant material, and animal-derived waste. Biomass stored on land is estimated about 1.8 trillion tons, while aquatic reserves amount to about 4 billion tons, providing a potential production capacity of 33,000 EJ, which is more than 80 times the world's annual energy consumption [7]. The **Figure 1-1** indicates, the potential for using biomass as an energy source is extremely high.

Biomass is diverse and there is no definitive classification method, so it can be classified based on purpose and scope. There is a method of dividing into agricultural, forestry and fishery resources, waste, and plantation biomass, a method of dividing into terrestrial and marine biomass, and a classification according to the growth environment [8]. This study, biomass is classified according to its growth environment, that is, based on the raw material.

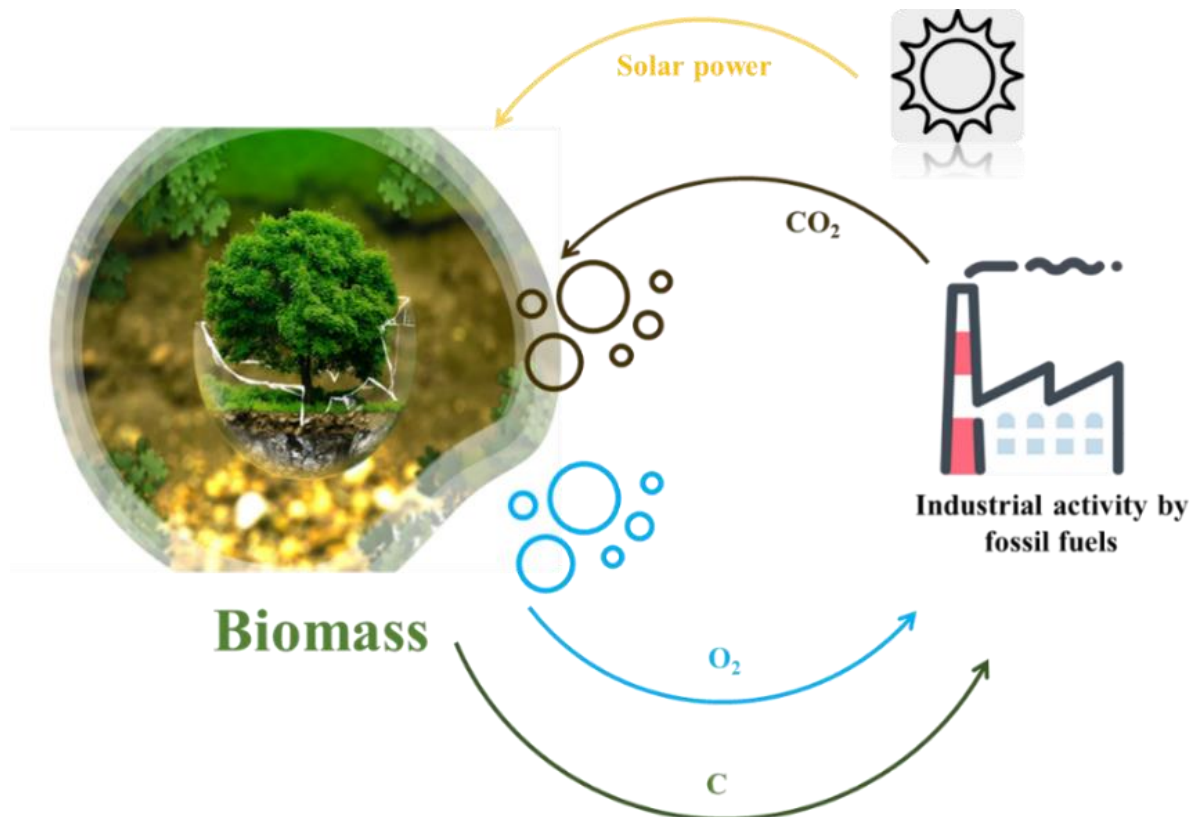


Figure1- 1. Renewable CO₂ cycle of biomass.

1.1.2 Classification by biomass raw material

When biomass is divided into raw materials, it can be classified into wood based biomass, herbaceous biomass, marine biomass, animal and human waste biomass, and finally biomass mixtures [9]. Wood based biomass is a biomass whose components are mainly cellulose and lignin, and is generally composed of materials such as wood, root bark, and leaves. It is mainly supplied from places such as residues after producing wood related products, residues of wood waste [10]. Herbaceous biomass is extracted from plants without woody stems and is a by-product of the food or fiber industries, such as grains. [11]. Animal and human waste biomass refers to biomass that is made up of animal bones, meat, excrement, and human waste. This biomass is used as fertilizer or in agricultural fields [10]. And biomass mixture refers to a case where the biomass introduced above is mixed. However, these terrestrial biomass are diffuse resources that occur over a wide area, so they require a large area of land that is costly and poses significant logistical problems for collection and transportation [6]. Terrestrial biomass that grows through photosynthesis have evolved over thousands of years to thrive under abundant sunlight, developing to protect their photosynthetic tissues from intense solar energy. And the evolved terrestrial biomass has a low efficiency in using solar energy, at less than 1 % [12]. However, marine biomass that grows in the ocean, does not undergo complex differentiation, so its solar energy efficiency is much higher than that of terrestrial biomass [13,14]. In addition, marine biomass has a higher carbon dioxide absorption capacity than terrestrial biomass, and in countries with developed coastlines such as Japan and Korea, the area available for cultivation is larger than on land, so it is emerging as a new possibility for reducing greenhouse gases through seaweed cultivation.

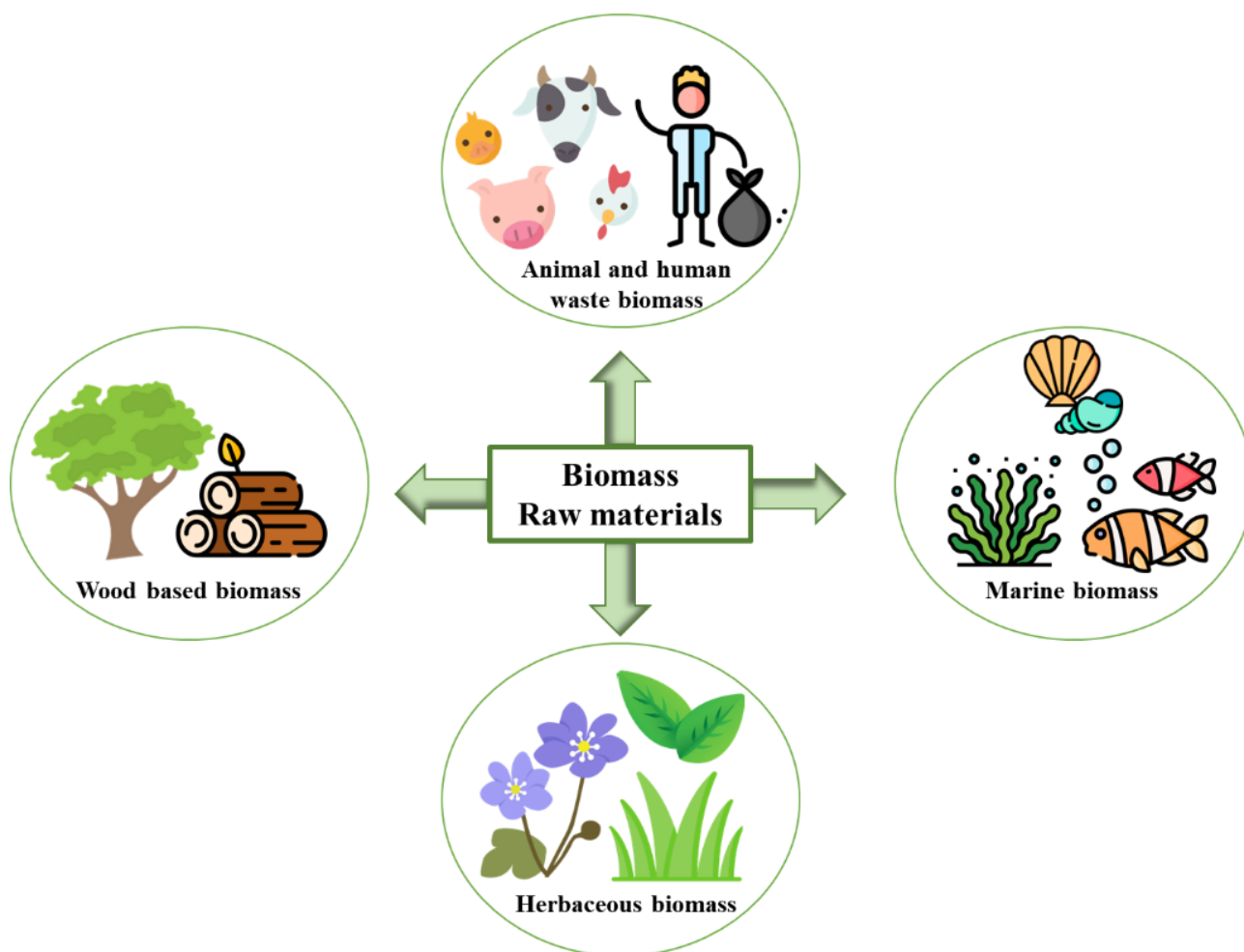


Figure1- 2. Classification by biomass raw material.

1.1.3 Marine biomass

Marine biomass refers to biomass that includes marine organic matter, including macroalgae that grow up to 60 m, microscopic organisms such as diatoms and green algae, and emerging plants that grow submerged in wetlands and swamps, as well as plankton fish [15]. Marine biomass is economically efficient because, unlike terrestrial biomass, it does not require separate agricultural water or separate farmland [16]. In addition, it has the advantage of being more efficient in solar energy, better absorbing carbon dioxide, the main culprit of global warming, and growing faster than terrestrial biomass [17]. Japan also has a large sea area and already has excellent technology to mass-produce seaweed, so it has very advantageous conditions for establishing a production system compared to terrestrial biomass [18]. Among marine biomass, macroalgae and seaweed are easy to collect and supply, can grow naturally, have high carbon content, and absorb CO₂ as they grow, making them suitable for conversion into carbon materials. Seaweed is used as an edible ingredient in Asian countries such as Japan, Korea, and China, but in the West, it is considered a seaweed and is discarded. It is important to find universal solutions that can reduce carbon dioxide by using abundant marine resources regardless of local dietary practices.

1.1.4 Alkali and alkaline earth metals in marine biomass

Seaweeds are rich in alkaline and alkaline earth metals (AAEMs) such as potassium, sodium, calcium, and magnesium, as well as chlorine [19,20]. AAEMs and Cl have a close influence on the heat treatment of marine biomass raw materials. AAEMs make it difficult to control at high temperatures and reduce product quality [21]. In particular, when AAEMs are released during high temperature reactions in carbon material conversion, they cause corrosion in the furnace, which reduces the reactivity of carbon materials [22,23]. Therefore, it is a problem in carbon conversion of marine resources. However, AAEMs confirmed that pores can be developed by participating in the

gasification reaction as a metal catalyst during the heat treatment process. This reaction enables the production of porous materials without an activation process [24–26]. However, after catalyst gasification, the removal of metal compounds present on the surface is essential. Therefore, to utilize marine biomass, it is necessary to find an effective method to remove AAEMs. Strong acids such as hydrofluoric acid (HF) are used to ensure the removal of AAEMs [27]. However, HF is highly toxic, so it has many problems such as environmental pollution and high wastewater treatment costs. In particular, it is toxic to humans, so a new method is needed [28,29]. He et al.[20] identified AAEMs present in marine biomass and removed them using CO₂ and acetic acid in an effective and simple approach in an environmentally friendly and cost-effective mechanism. This removal method was quite effective, but the remaining about 5 mass% remains a challenge to determine how it will affect subsequent processes and how to remove it further. Therefore, in-depth research and improvement are needed to utilize the potential of the remaining AAEMs and their appropriate use.

1.2 Activated Carbon

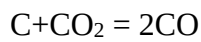
1.2.1 Activated carbon manufacturing method

Activated carbon refers to an amorphous carbon material with a large specific surface area developed into a porous structure [30]. Therefore, the structural features of the high specific surface area and developed pores of Activated carbon [31] adsorption is possible not only in the gaseous state but also in the liquid state through physical and chemical adsorption reactions [32] due to functional groups combined with carbon atoms present on the surface [33]. Adsorption is the concentration of solute molecules in a gas or liquid at the interface between solid and gas or solid and liquid [34]. In activated carbon, adsorption occurs through physical adsorption and chemical adsorption reactions. Physical adsorption occurs when gas or liquid passes between activated carbon packing layers due to the weak Van der Waals force of surface tension [35]. Physical adsorption has a weaker adsorption force as the temperature increases, a lower heat of adsorption, but a faster adsorption rate and a reversible adsorption/desorption reaction [36]. In the case of chemical adsorption, it occurs through chemical bonding by strong ionic bonds or covalent bonds [37]. As the temperature rises, the adsorption power increases, but the heat of adsorption is large and the adsorption rate is slow, so activation energy is required [38]. In addition, adsorption and desorption have reversible or irreversible reactions, and desorption is easy at temperatures above 800°C [39].

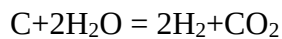
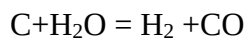
Activated carbon is produced from materials that contain carbon-rich organic matter, and can be manufactured from a variety of raw materials, such as coconut shells, coal, synthetic resins, wood, pitch, coke, and biomass [40]. Activated carbon manufacturing can be divided into two methods: physical activation and chemical activation [41]. Physical activation develops pores through a gasification reaction in carbon materials that have undergone carbonization to remove volatile substances [42]. Oxidizing gases such as oxygen, CO₂, and H₂O are used as activating agents in physical activation reactions. The advantage of physical activation is that the process is simple because the activator is inexpensive and no post-processing is required after the activation reaction [43]. In

addition, since it does not use chemical reagents, it is advantageous in terms of safety compared to the chemical activation process, and it is environmentally friendly and cost-effective as no separate environmental treatment costs are incurred [44]. However, since the oxidizing gas starts gasification from the surface of the carbon, the micropore development is limited, so it has the disadvantage of having a relatively low specific surface area and low yield [45]. That is why physical activation is used to produce low-cost activated carbon.

The carbon and gasification reactions of CO₂ are as follows [46].

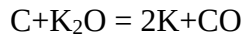
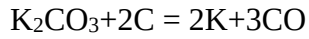
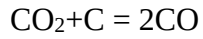
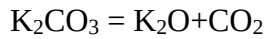
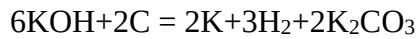


And the gasification reaction by H₂O is as follows [47].



Chemical activation occurs through a catalytic gasification reaction of metal ions and hydroxide ions of an oxidizing agent using acids and bases such as KOH, Na₂CO₃, NaOH, and H₃PO₄ [48]. It generally occurs at a lower temperature than physical activation and has the advantage of a higher activation yield compared to physical activation [48]. Compared to physical activation, activated carbon with a high specific surface area can be manufactured, but chemical activation can cause environmental pollution because the activating chemical contains a lot of inorganic substances, and additional processes such as cleaning using an acid solution are required [44]. Because these additional processes are required, the manufacturing process is complex and the activators used are also relatively expensive, which increases the cost of the process [49]. However, because it has a high specific surface area and excellent development of micropores compared to physical activation, it is used in places where high adsorption is required [50].

The typical chemical activation, KOH activation mechanism reaction is as follows [51].



Yi et al.[45] proposed a new pressurized physical activation method to solve the problems of physical activation, which has the advantage of low production cost but has low activation yield and pore development compared to chemical activation method due to poor diffusion of the activator. These results demonstrate that pressurization achieves higher levels of pore development at similar activation yields compared to atmospheric pressure. This suggests that the pressurized atmosphere can produce activated carbon with a high level of pore development by improving the diffusion of the activator at the particle level.

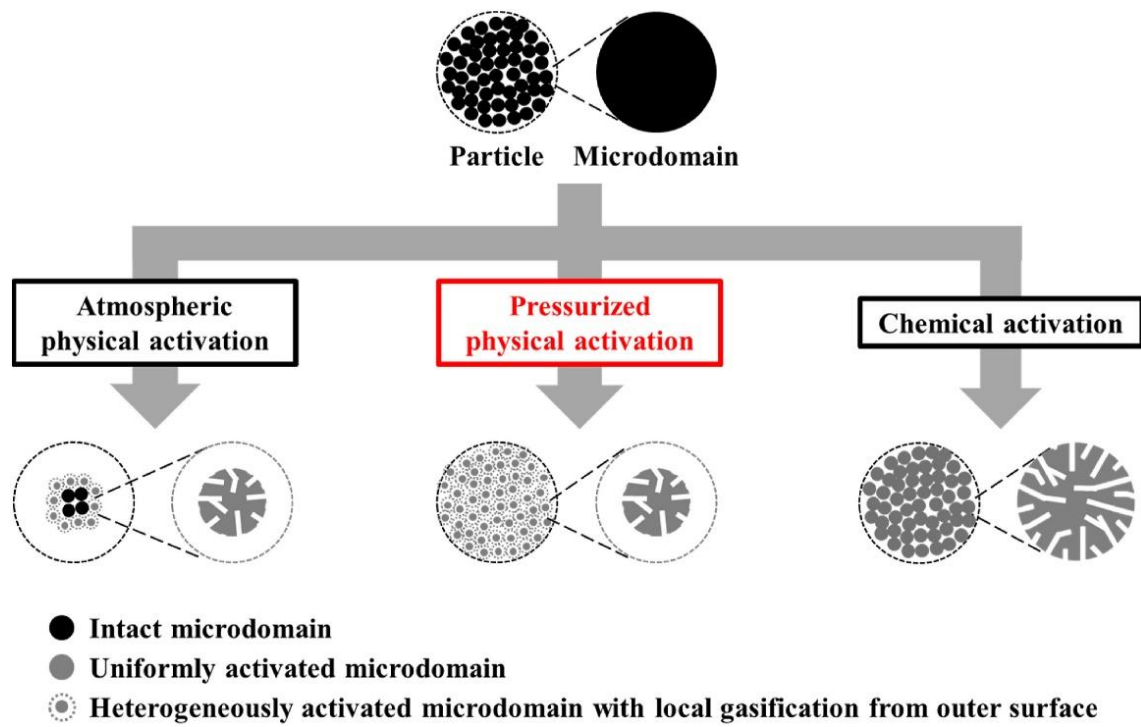


Figure1- 3. Schematic diagram of differences in atmospheric physical, pressurized physical, and chemical activation processes [45].

1.2.2 Applications of activated carbon

Activated carbon has a well-developed pore structure and surface functionality, making it widely used as an adsorbent and catalyst support in various fields. For example, it is used to purify polluted water, remove COD, BOD increasing substances, heavy metals, odorous gases, and harmful gases from the air environment caused by industrial waste gas, and as an adsorbent for removing organic substances [52]. In addition, the need for porous materials as advanced storage materials such as hydrogen energy utilization and gas transport media has recently emerged. However, hydrogen gas has a risk of explosion, so it is necessary to find a safe storage and transportation method [53]. And as a solution, research is being conducted on hydrogen adsorption of activated carbon among porous carbon materials, and research on natural gas storage is also being conducted [54]. The catalyst carrier is a material that disperses the catalyst and requires a material with a high specific surface area. This is to prevent the number of active sites from decreasing due to sintering and agglomeration of the catalyst and to prevent the deterioration of product quality due to catalyst decomposition [55]. Therefore, activated carbon with a high specific surface area is an appropriate material to be used as a catalyst support to disperse catalyst particles and maintain performance [56]. Additionally, due to the high surface area and good electrical conductivity of activated carbon, it is also used in energy storage devices such as electric double layer capacitors (EDLC).

1.3 Electric double layer capacitors

Electric double layer capacitor (EDLC) is an energy storage device that generates energy through a charging and discharging process by creating an electric double layer based on the adsorption and desorption of electrolyte ions. In general, EDLCs are characterized by superior power and long life compared to other secondary batteries, and due to their fast energy charging and discharging capabilities and high power output, they are used as replacement or complementary devices in a variety of applications, including standby power systems, portable electronic devices, and electric hybrid vehicles [57]. However, low energy density is one of the shortcomings that limits various applications as energy storage devices. The electrodes of EDLCs are usually made of porous materials with a high surface area for ion adsorption of the electrolyte. Among them, activated carbon is mainly used because it is composed mainly of micropores, has a large specific surface area, is relatively cheap, and is chemically stable [58]. The capacitance (C) of an EDLC is defined as $C = \epsilon A/d$, where A is the surface area of the electrodes, ϵ is the ionic permittivity between the electrodes, and d is the distance between the electrodes [59]. Therefore, the specific surface area of the porous material used in the electrode is important in increasing the capacitance. However, the yield of activated carbon that can be obtained by the activation method generally decreases as the specific surface area increases, so the specific surface area has a limit. The energy (E) of EDLC is expressed as $E = \frac{1}{2} CV^2$, where V is voltage [60]. The operating voltage of the charge/discharge cycle is an effective way to increase the energy density. However, high voltage operation generally reduces the capacitance.

Ideta et al. [61] confirmed that large pores in Activated carbon can have high capacitance during charging/discharging at high voltage. These results suggest that the large pores of Activated carbon can efficiently maintain ionic charges even at high voltages and lead to favorable diffusion, which can maintain enhanced capacitance. However, since the activated carbon was composed of relatively large micropores rather than mesopores and had a high specific surface area compared to the activated

carbon, it remains a challenge whether the activated carbon with a low specific surface area and mostly mesopores can maintain high electrostatic capacity at high voltage.

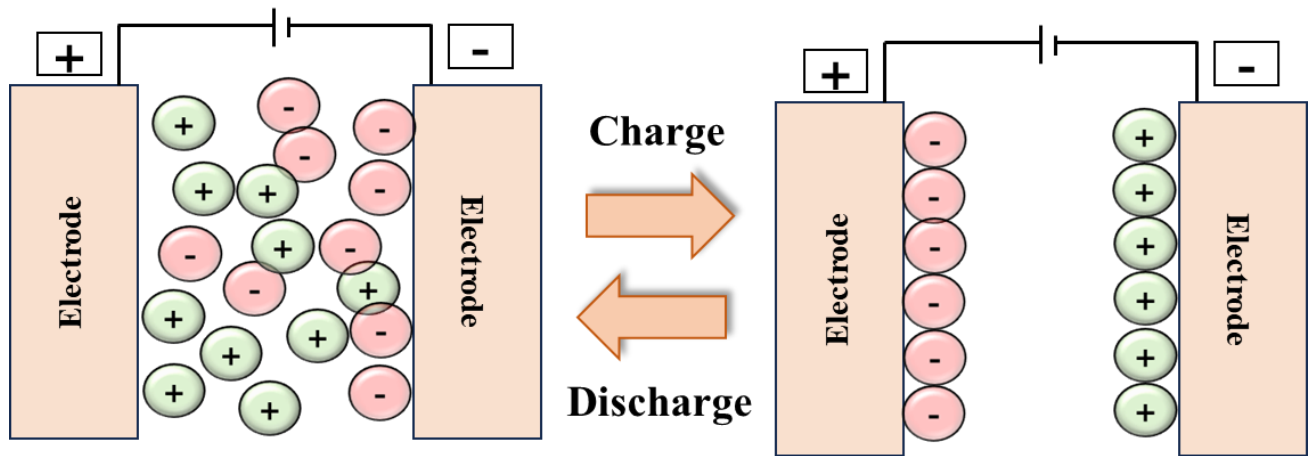


Figure1- 4. Schematic illustration of electric double layer capacitor during charging and discharging.

1.4 Objective of this study

Biomass is the basic material of the carbon cycle and has been used as a raw material for many applications and materials. Among them, marine biomass has a high potential for use as carbon neutrality and blue carbon in the future as it does not require separate farmland, has high solar energy efficiency, and grows by consuming CO₂. However, since AAEMs present in marine biomass interfere with the conversion of carbon materials, research is needed on their removal and the influence of AAEMs on the conversion of carbon materials. The purpose of this study is to propose a method for the effective removal of AAEMs from marine biomass and production of marine biomass-derived activated carbon with high pore development. In this study, I intend to perform physical activation for a low-cost process. And pressurized physical activation is introduced to develop low-cost and highly developed pore structures. Furthermore, I also reviewed the application of the developed marine biomass activated carbon to energy storage devices suitable for marine biomass derived activated carbon structure. This study is organized into five chapters as follows.

In Chapter 1, I introduce biomass, marine biomass, activated carbon production and applications, and electric double layer capacitors. I will also mention the purpose of the research.

In Chapter 2, I aimed to analyze the alkaline and alkaline metals (AAEMs) present in marine biomass, the influence of AAEMs during heat treatment, and the need for their removal. To identify the types and elements of impurities present in marine biomass, X-ray Fluorescence (XRF) elemental analysis was used to confirm the presence of AAEMs such as Na, K, and Mg. Next, we investigated the influence of these impurities during the heat treatment process and confirmed the pore structure developed when activation was performed without removing AAEMs. The low carbon content and low activity consequently suggested the necessity of AAEMs removal. And for the removal method, the existing low-concentration acetic acid and CO₂ aeration method was additionally evaluated with new concentrations and various acid solutions to establish a method for optimizing the removal of

AAEMs from marine biomass. As a result, I were able to produce a higher amount of removed marine biomass than the previously announced AAEMs.

In Chapter 3, physical activation was adopted to manufacture activated carbon from marine biomass from which AAEMs were removed. AAEMs in marine biomass develop mesopores through heat treatment via gas reaction as a catalyst. So, it was confirmed that activated carbon was produced with both mesopores and micropores developed despite the atmospheric physical activation. However, the catalytic gasification reaction of AAEMs also increased the diffusion during pressurized activation, and rather, it hindered the introduction of effective pores with a high specific surface area, which hindered the production of activated carbon with a high yield and high activation degree, which is an advantage of pressurized activation. To solve these problems, I proposed a two-step activation. The activated carbon with developed pore structure by atmospheric activation showed increased AAEMs again, and by further removing them, I confirmed that effective pores for high specific surface area were developed in pressurized physical activation. After pressurized physical activation, 1.5 nm micropores were additionally developed, and the maximum surface area was 2100 m²/g. Activated carbon with highly developed pores and developed mesopore and micropore size distributions due to AAEMs could be produced.

In Chapter 4, marine biomass-derived activated carbon was applied to a high-voltage electric double layer capacitor (EDLC). Marine biomass-derived activated carbon developed mesopores together with the influence of AAEMs despite physical activation. EDLCs have the problem of low energy density despite fast charging/discharging and high output energy. Our research group previously reported that EDLC fabricated with large-pore activated carbon electrodes produced by chemical activation exhibited high-voltage performance. The marine biomass-derived activated carbon we previously manufactured had developed mesopores despite being physically activated, and I manufactured it using phenol resin-derived activated carbon with only developed micropores manufactured under the same conditions as a comparison group. In this study, I investigated the applicability of two activated

carbons as electrode materials in high-voltage EDLC. Activated carbon derived from marine biomass with mesopores developed by more than 60% exhibited high capacitance at both low and high voltages and showed higher ion diffusivity than phenol resin-activated carbon in the impedance results. The content of ions during charge and discharge, quantitatively evaluated by F^{19} -solid NMR, was confirmed to be more than twice as high. These results demonstrate the potential of marine biomass-derived activated carbon for the utilization of high-voltage EDLC as a solution to increase energy density.

Chapter 5 summarizes the results and discussions obtained in this study and concludes them.

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Chapter 2. Removal and impact of alkaline and alkaline earth metals from marine biomass

Enhanced porosity in marine biomass-derived activated carbon via two-step CO₂ activation and acidic decontamination (J. Choi, et al., *Carbon letters*, (2024))

2.1 Introduction

The production of functional carbon materials from fossil fuels or their derivatives contributes significantly to CO₂ emissions and global warming [1, 2]. Addressing CO₂ emissions is an urgent global priority as nations strive toward carbon neutrality [3,4]. Biomass, derived from plants, animals, and their by-products, offers a renewable and environmentally sustainable alternative for carbon-based materials, aligning with the principles of the carbon cycle [5–7]. However, Japan faces challenges in securing a commercially viable biomass source. Recently, marine biomass (MB), such as seaweed, has emerged as a promising candidate due to Japan's extensive coastline, widespread seaweed farming, and advanced technological infrastructure [8–11]. Notably, MB, particularly marine algae, exhibits a rapid growth rate and efficient CO₂ fixation, surpassing that of terrestrial plants [12, 13].

Among MB, seaweed contains significant amounts of AAEMs, along with chlorine (Cl) and sulfur (S), which can exceed 6 wt% [14–16]. Our previous work on kelp and seaweed MB demonstrated that high-temperature heat treatment partially removes these impurities through evaporation [16]. Further impurity reduction was achieved through washing with pure water, CO₂-aerated water, and dilute acetic acid [16]. While these treatments enhanced the porosity of the resulting carbon materials by removing AAEMs, residual impurities remained, which could limit the performance of AC, especially for high-value applications such as energy storage [17–22]. AAEMs can catalyze gasification during activation, lowering yield and preventing the formation of high-SSA materials. Thus, effective and environmentally sustainable methods for AAEM removal are therefore essential. Although hydrofluoric acid (HF) is highly effective for impurity removal [23], its toxicity and environmental

impact, along with the high cost of waste treatment, necessitate the search for safer alternatives [24–26].

AAEMs were found to participate in gasification reactions as catalysts in heat treatment processes [17,18,27]. I focused that that AAEMs participating in the metal-catalyzed gasification reaction are advantageous to produce activated carbon among carbon materials in that they affect the mesopore development of marine biomass. In this chapter, I explore the washing method using various acid solutions to remove AAEMs with higher efficiency than previous studies, study the pore structure characteristics of marine biomass after washing and the pores developed under the influence of AAEMs during heat treatment, and examine the possibility of producing activated carbon derived from marine biomass.

2.2 Experimental

2.2.1 Pre-heat treatment process of marine biomass

The MB, specifically seaweed (WAKAME), was collected from the Japanese coast and supplied by Nippon Steel Co. Ltd. The seaweed, with an initial moisture content of 10 wt%, was further dehydrated and ground into particles smaller than 250 μm . It was then subjected to preheating at various temperatures for 2 hours under an N_2 atmosphere. The preheated WAKAME was labeled according to the treatment temperature (e.g., 800W for WAKAME preheated at 800°C).

2.2.2 Removal of AAEM from marine biomass

To remove alkali and alkaline earth metals (AAEMs), aqueous solutions of hydrochloric acid (36.5 wt%), nitric acid (69.9 wt%), acetic acid (99.9 wt%), and citric acid (99.5 wt%) were prepared at concentrations of 1 vol.% for acetic acid and 10 vol.% for the other acids. The reason is that there is a sample with only 1 vol.% concentration of acetic acid to compare it with the 1 vol.% acetic acid and CO_2 gas methods, which were the methods of our research group's previous studies. Then, 0.5 g samples of 800W were dispersed in 500 mL of each acid solution and stirred at 300 rpm for 2 hours, followed by rinsing with pure water until the pH approached neutral. For AAEM removal using CO_2 -aerated water, 0.5 g of 800W was added to 500 mL of pure water, and CO_2 gas (100 mL/min) was bubbled through the solution with stirring at 300 rpm. The acid-washed samples were labeled with the suffix "-acid type and concentration", such as 800W-Acetic acid 10 for samples treated with 10 vol% acetic acid.

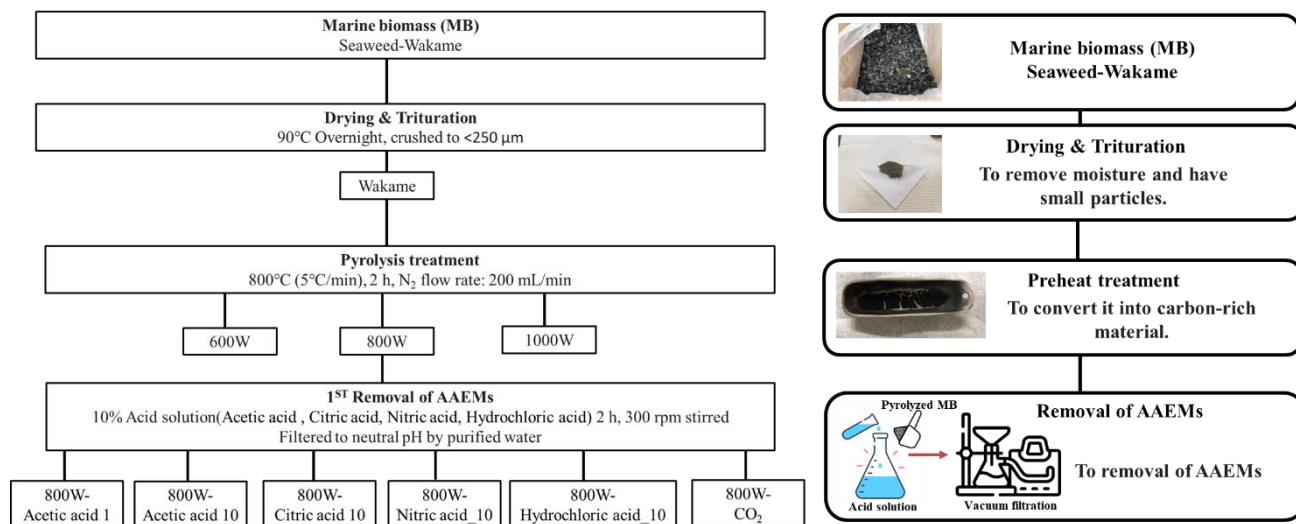


Figure 2- 1. A flowchart depicting the detailed heat treatment and removing impurities from marine biomass.

2.2.3 Characterization

Thermogravimetric analysis (TGA) was performed to investigate the thermal decomposition behavior of both raw and preheat-treated MB using a TG/DTA6200 platform (Hitachi, Japan). Elemental compositions before and after pyrolysis, AAEM removal, and activation were evaluated using X-ray fluorescence (XRF) spectrometry (ZSX Primus IV/RX9 platform, Rigaku, Japan) method and by using an elemental analyzer (CHN Coder; MT-5). Oxygen content (O_{diff.}) was derived by subtracting the sum of carbon, hydrogen, and nitrogen contents from 100%. Nitrogen adsorption and desorption isotherms at 77 K were obtained using a surface area analyzer (Nova-e series; Anton Paar Quanta Tec Inc., USA) to determine pore characteristics. Specific surface areas and pore volumes were calculated from the isotherms using α_s -plot analysis [28] and quenched solid density functional theory (QSDFT) methods [29], respectively. The mesopore volume percentage was calculated using the following formula:

$$\text{Mesopore volume (\%)} = \frac{\text{Total pore volume} - \text{Pore volume less than } 2\text{nm}}{\text{Total pore volume}} \times 100$$

2.3 Results and discussion

2.3.1 Pre-heat treatment process of marine biomass

TGA was carried out to investigate the thermal decomposition behavior and mass loss of WAKAME samples under varying temperatures and atmospheres. **Figure 2-2 (a)** shows the thermal decomposition behavior of both raw and preheat-treated WAKAME samples in an N₂ atmosphere at 600°C, 800°C, and 1000°C. The MB samples underwent progressive pyrolysis across different temperature ranges, releasing various volatile compounds alongside the thermal decomposition of carbonaceous components. The samples preheated at 600°C and 800°C (600W and 800W) exhibited significant weight loss above 800°C [16], primarily due to the evaporation of alkali metal species, with the 800°C-treated sample showing fewer volatile emissions. In addition, I measured the TGA curves of the preheated WAKAME samples in a CO₂ atmosphere (**Fig. 2-2 (b)**). All samples exhibited mass loss above approximately 700°C, indicating the onset of carbon gasification by CO₂. The sample preheated at 1000°C showed a more rapid weight decrease around 800°C compared to the others. Based on these observations, I selected 800°C as the optimal preheating temperature for further studies.

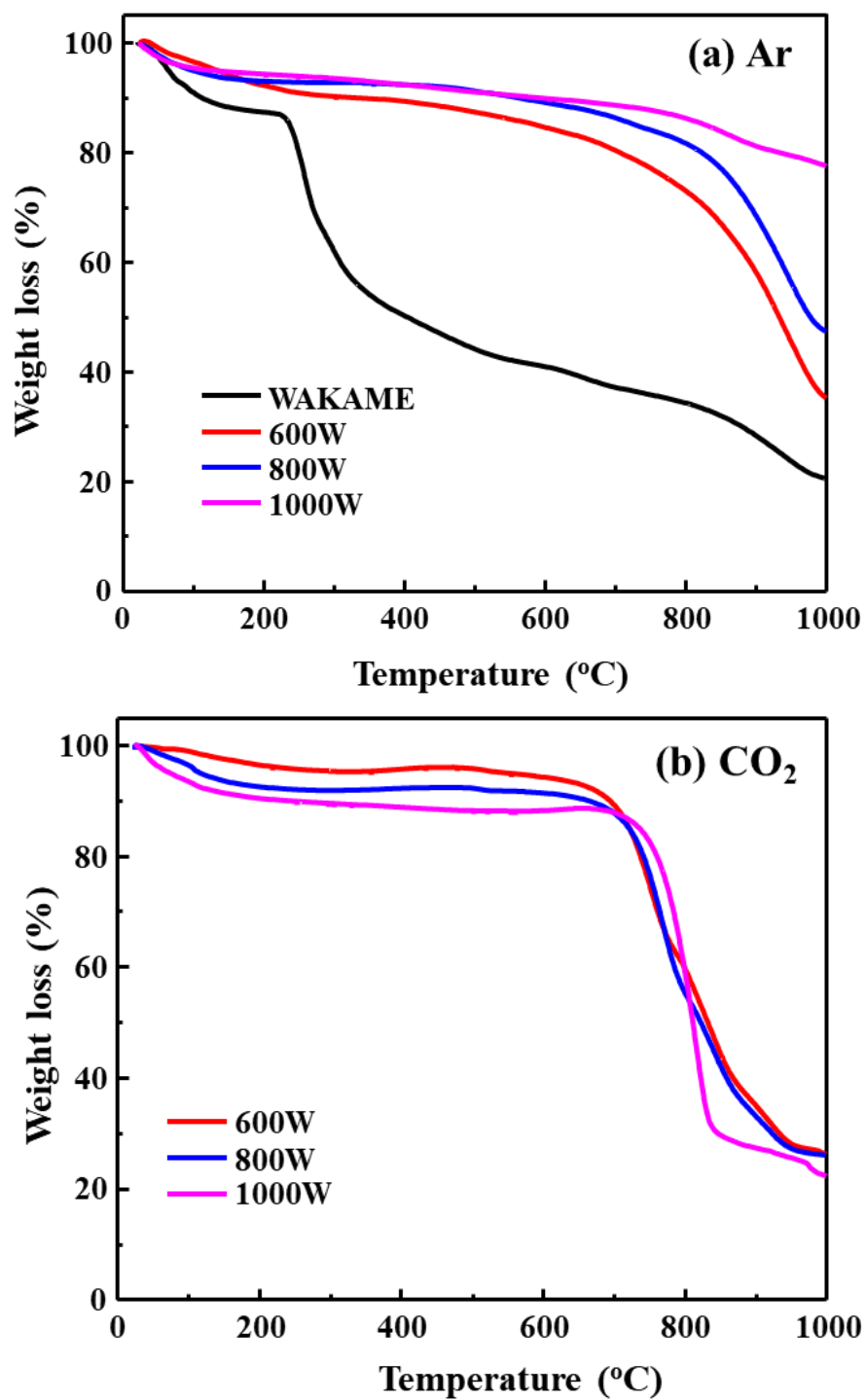


Figure 2- 2. Thermogravimetric curves: (a) Under N₂ atmosphere for raw MB and preheated MB, (b) Under CO₂ atmosphere for preheated MB.

2.3.2 Removal of AAEM from marine biomass

The yields and elemental compositions of acid washing are also summarized in **Table 1**. Treatment with 1% v/v acetic acid (800W-1Acetic acid), which was previously studied, increased the CHO content to 95.3 mass% and reduced the total content of AAEMs, Cl, and S to around 4 mass%, with Na being particularly effectively removed. However, Mg and S remained in large amounts, 1.40 mass% and 2.07 mass%. A higher concentration of acetic acid (10% v/v) further improved AAEM removal (800W-10Acetic acid), increasing the CHO content to 97.0 mass %. However, approximately 3 mass % of impurities remained, and the most abundant element was S constituting 1.17 mass %. Nitric acid is more effective than acetic acid in removing AAEMs. And it was still effective in removing Na. The nitric acid-treated sample showing the highest CHO content at 97.5 mass %. After nitric acid treatment, the impurity levels were significantly reduced: Na decreased from 8.23 to 0.15 mass %, Cl from 6.36 to 0.08 mass %, Ca from 2.51 to 0.1 mass %, and K from 1.93 to 0.05 mass %. Changes in Mg and S were less pronounced, with Mg reducing from 1.88 to 0.81 mass % and minimal changes observed for S (1.0 mass %). The CO₂-aerated aqueous solution effectively removed Na but was less efficient in removing other alkali metals (Ca and Mg) compared to nitric and acetic acid treatments. Thus, the CHO content was 95.8 mass%.

Table2- 1. Elemental compositions (mass %) of raw, preheat-treated and acid-washed MBs, determined by XRF analysis.

Sample	Ultimate analysis [mass %, daf]				Ash [mass %, db]
	C	H	N	O _{diff}	
WAKAME	35.6	4.7	2.3	47.7	9.8
WAKAME600	44.4	0.4	2.1	34.0	19.1
WAKAME1000	67.6	0.3	0.4	5.3	26.3

Table2- 2. Elemental compositions (mass %) of raw, preheat-treated and acid-washed MBs, determined by XRF analysis.

I.D.	Yield (%)	CHO	Na	Cl	Ca	K	Mg	S	etc.
Wakame		92.2	3.05	2.28	0.76	0.63	0.56	0.39	0.1
800W		77.6	8.23	6.36	2.51	1.93	1.88	1.01	0.43
800W-1Acetic acid	53	95.3	-	0.22	0.62	0.06	1.40	2.07	0.33
800W-10Acetic acid	44	97.0	-	0.11	0.32	-	1.06	1.17	0.45
800W-10Citric acid	46	94.2	0.15	1.45	0.47	0.05	1.66	1.73	0.29
800W-10Nitric acid	50	97.5	0.15	0.08	0.19	0.05	0.81	1.00	0.22
800W-10Hydrochloric acid	49	95.6	0.27	2.08	0.15	0.05	0.71	0.98	0.16
800W-CO ₂	48	95.8	-	0.22	0.72	0.10	1.89	0.81	0.43

SEM analysis was performed to verify whether the pore-blocking substances were removed before and after nitric acid washing, which was most effective in removing AAEMs after heat treatment of marine biomass. **Figures 2-3 (a) and (b)** show the surface condition of marine biomass after heat treatment. The marine biomass particles were still very large, and their shapes were not uniform even after heat treatment. In addition, it can be confirmed that metallic impurities exist on the surface. **Figures 2-3 (c) and (d)** show the surface of marine biomass after washing with nitric acid. The particles are still large, and their shapes are not uniform, but compared to after heat treatment, the particles were relatively reduced, and it was clearly revealed that the impurity particles existing on the surface were reduced.

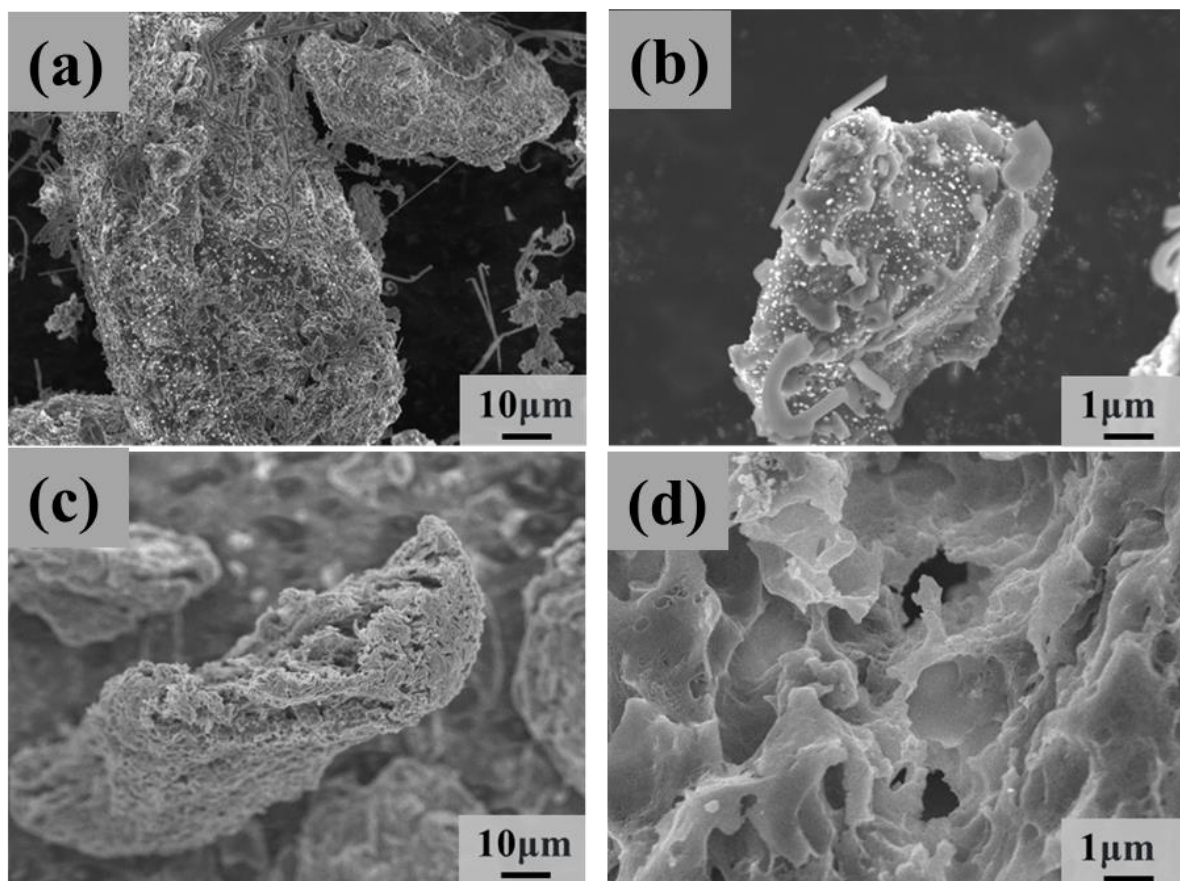


Figure 2- 3. SEM images of: (a-b) 800W, (c-d) 800W_10HNO₃.

2.3.3 Pore structure evaluations of Marine biomass with impurities removed

Then, I examined the changes in porosity and specific surface area due to the removal of AAEMs and other impurities from preheated MB samples through various acid washing treatments. **Figure 3** presents the N₂ adsorption/desorption isotherms at 77 K for 800W samples before and after acid washing, along with the corresponding pore size distributions calculated using the QSDFT method. A notable adsorption hysteresis was observed, particularly after the acid washing treatments, confirming the presence of mesopore. The pore size distribution (**Fig. 3(b)**) shows the coexistence of mesopores (3–4 nm) and micropores. Although acid washing did not alter the pore size, it significantly increased the volume of both micropores and mesopores. **Table 2-2** summarizes the pore structure parameters calculated using the α_s -plot and QSDFT methods. The specific surface area of MB after preheat treatment was relatively low at approximately 340 m²/g. However, following AAEMs removal, the surface area increased to 813 m²/g for acetic acid-washed MB, 936 m²/g for nitric acid-washed MB, and 1033 m²/g for the CO₂-aerated water-treated MB. This enhancement in surface area is attributed to the removal of AAEMs, which are known to block pore development during preheating. Washing effectively removes these impurities, resulting in a significant increase in specific surface area.

Table2- 3. Pore structural parameters of preheat-treated MBs, followed by acid washings with acetic acid, CO₂ and nitric acid.

I.D.	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
800W	340	0.14	21
800W-1Acetic acid	813	0.40	38
800W-CO ₂	1033	0.46	35
800W-10Nitric acid	936	0.45	38

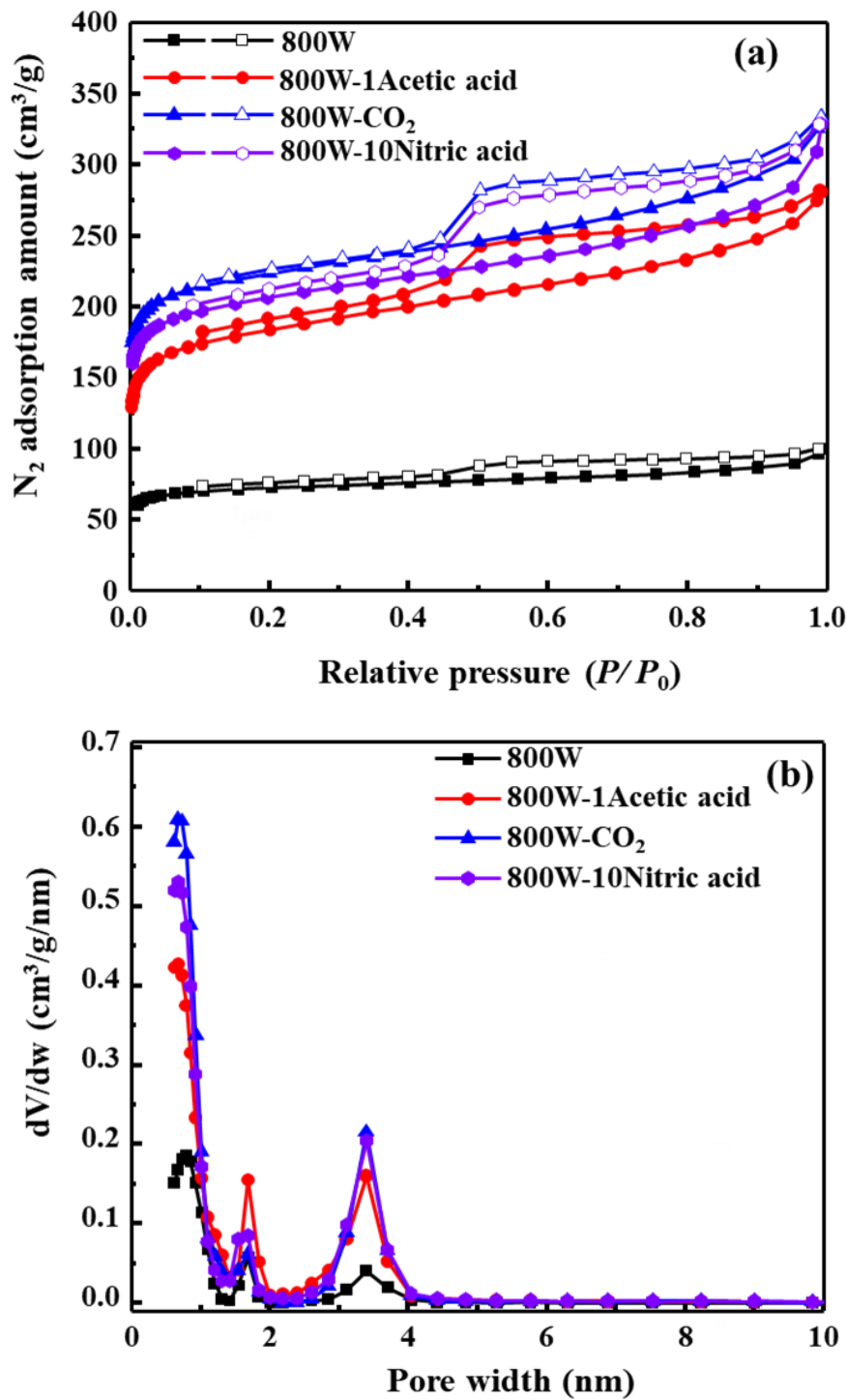


Figure 2- 4. (a) N_2 adsorption-desorption isotherms at 77 K, (b) Pore size distributions for preheated MB and MB with alkali and alkaline earth metals removed. Solid and open symbols represent adsorption and desorption, respectively.

2.3.4 Pore structure evaluations of Marine biomass with impurities removed

I first examined CO₂ and 1% acetic acid solution, which were examined in previous studies for preheat-treated and demineralized WAKAME, CO₂ activation was carried out at temperatures ranging from 800°C to 950°C under pressures of 0.1 to 1 MPa. Activation at 1000°C resulted in a low yield of approximately 7%, and the sample turned white; thus, this condition was excluded from further consideration [16] **Figure 2-5** presents the N₂ adsorption/desorption isotherms at 77 K and the corresponding pore size distributions for ACs prepared from acetic acid-treated 800W. Adsorption hysteresis became more pronounced following CO₂ activation, especially at elevated temperatures and pressures. Under atmospheric CO₂ conditions, the N₂ adsorption capacity increased with increasing activation temperature across the entire relative pressure range (P/P_0). At 950°C, a sharp rise in adsorption at higher P/P_0 values was observed, indicating the formation of larger mesopores. The pore size distribution further confirmed the development of mesopores larger than 5 nm. **Table 2-3** summarizes the pore structural parameters and activation yields. The highest specific surface area of 1581 m²/g was obtained for AC activated at 950°C and 0.1 MPa. However, when the activation pressure was increased to 1.0 MPa, both the specific surface area and activation yield decreased for the acetic acid-treated 800W. **Figure 2-5** presents the N₂ adsorption/desorption isotherms and the corresponding pore size distributions for ACs prepared from demineralized 800W, which was washed using a CO₂-aerated aqueous solution. These ACs displayed noticeable adsorption hysteresis, further confirming the presence of mesopores [30–32]. Like the atmospheric CO₂-activated samples, the porosity of these ACs varied with activation temperature, regardless of the acid washing solution used (acetic acid or CO₂-aerated aqueous solution). **Table 2-4** summarizes the activation yields and pore structural parameters. While the activation yield was higher for ACs prepared from 800W_CO₂ compared to those treated with acetic acid, the specific surface area was lower. Pressurized CO₂ activation further decreased both the specific surface area and the activation yield for the 800W_CO₂ samples. Previous studies have demonstrated that pressurization during

physical activation enhances pore development in AC by improving the diffusivity of the activation gas [33]. However, in the case of preheat-treated MB, residual AAEMs, even after acid washing, appeared to induce severe catalytic gasification of the carbon material, particularly under pressurized conditions. This led to the formation of larger mesopores (greater than 3 nm) rather than the creation of additional pores that would increase the specific surface area. To fully benefit from pressurization and achieve a higher specific surface area, it is essential to further remove residual AAEMs after the first atmospheric CO₂ activation. This is because some AAEMs species in the preheat-treated MB may remain covered by carbon layers, preventing them from being fully exposed to acid during the initial washing. However, the first activation process can gasify these carbon layers, exposing the remaining AAEMs, which can then be more effectively removed during a second acid washing step. In addition, the impurity removal method used previously was not sufficiently removed, so the specific surface area was not properly increased.

Table2- 4. Activation yield and pore structural parameters of MB-derived ACs prepared via 1% acetic acid washing, followed by atmospheric and pressurized CO₂ activations.

I.D.	Activation yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
800W_1Acetic acid_800P0.1	75	1258	0.54	31
800W_1Acetic acid_900P0.1	43	1361	0.74	49
800W_1Acetic acid_950P0.1	32	1581	1.28	65
800W_1Acetic acid_950P1	18	1326	1.37	69

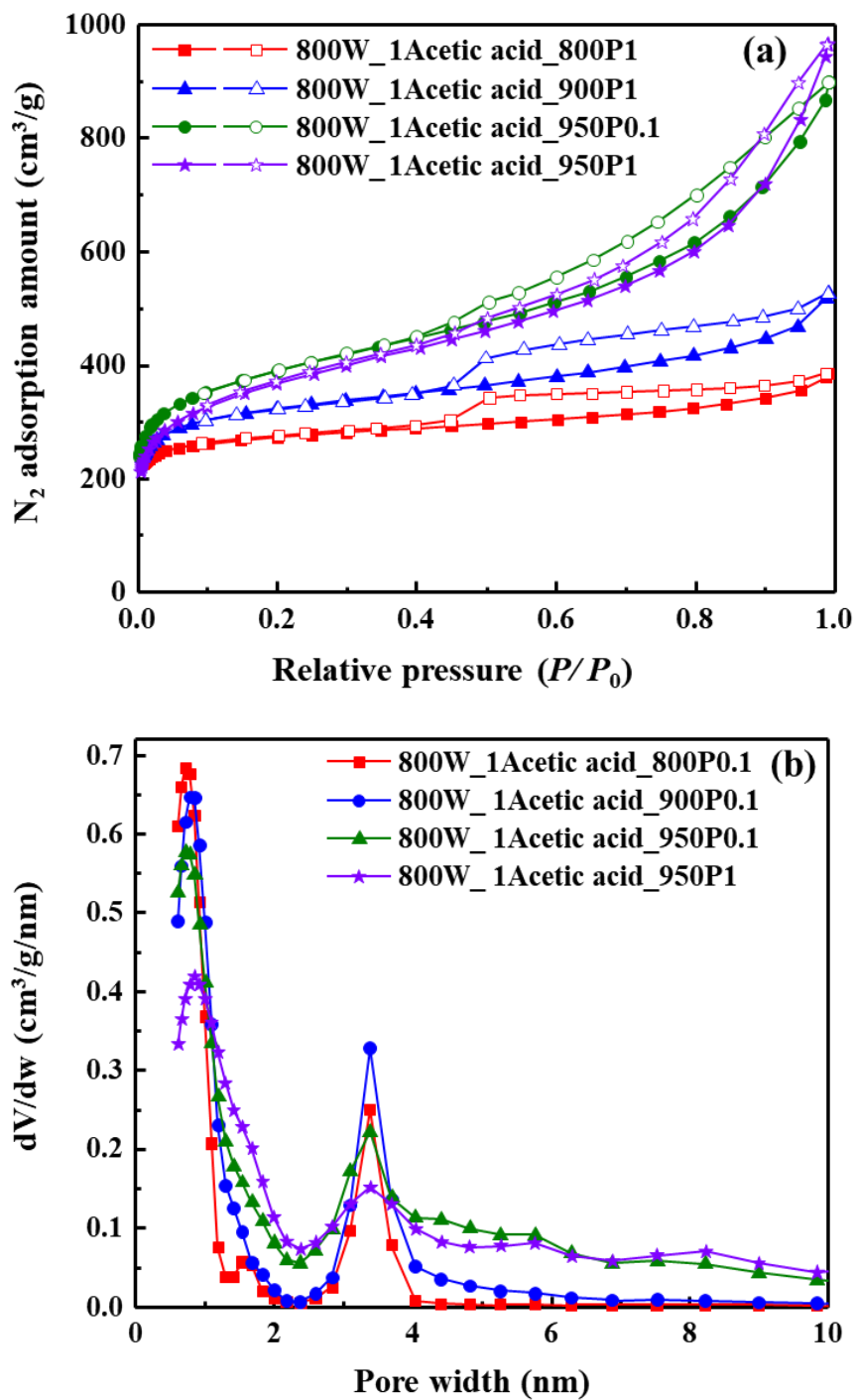


Figure 2- 5. (a) N_2 adsorption-desorption isotherms at 77 K, (b) Pore size distributions for MB with AAEMs removed using acetic acid. Solid and open symbols represent adsorption and desorption, respectively.

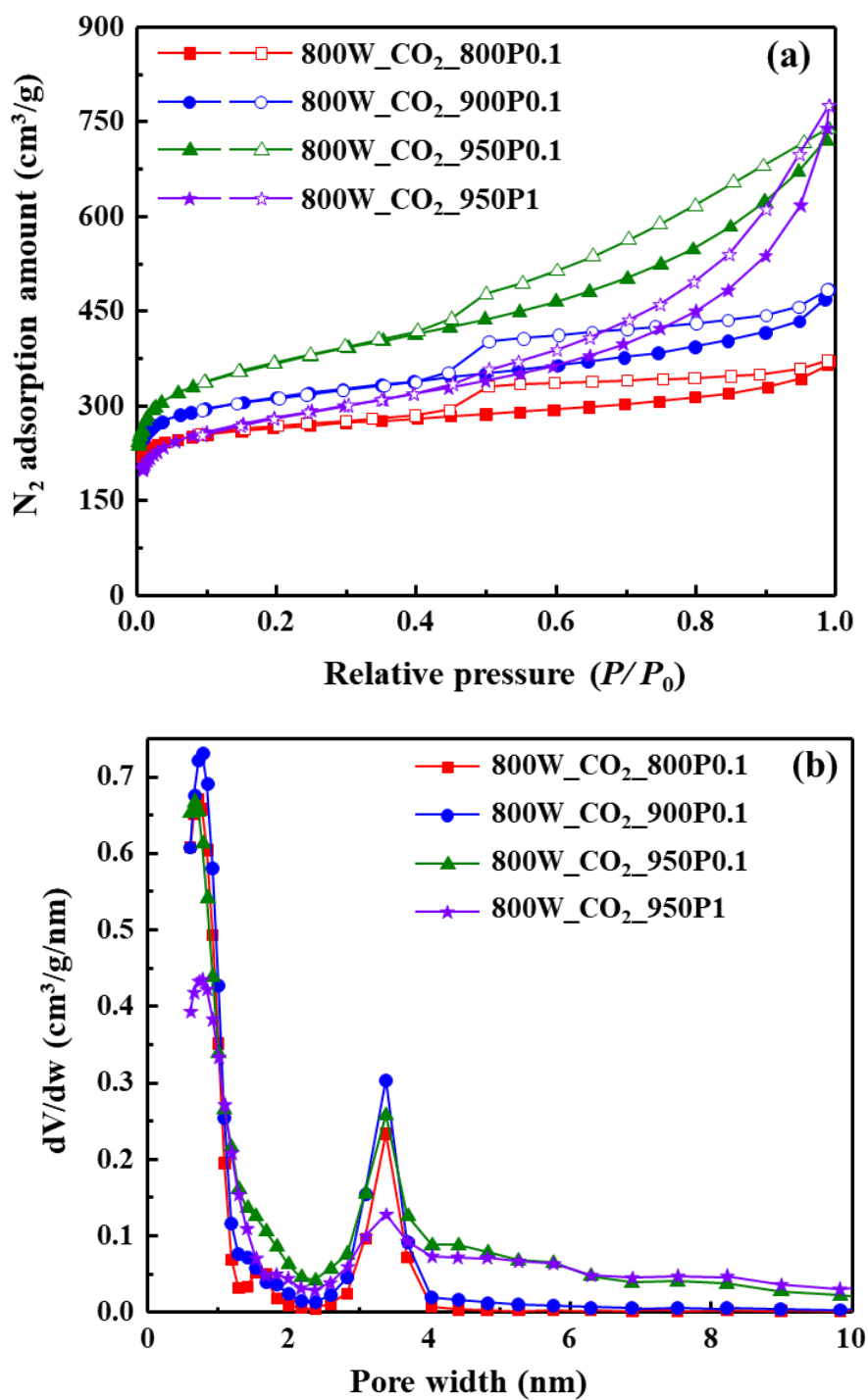


Figure 2- 6. (a) N₂ adsorption-desorption isotherms at 77 K, (b) Pore size distributions for MB with AAEMs removed using CO₂. Solid and open symbols represent adsorption and desorption, respectively.

Table2- 5. Activation yield and pore structural parameters of MB-derived ACs prepared via CO₂-aeration, followed by atmospheric and pressurized CO₂ activation.

I.D.	Activation yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
800W_CO ₂ _800P0.1	84	1226	0.52	31
800W_CO ₂ _900P0.1	65	1384	0.67	39
800W_CO ₂ _950P0.1	39	1505	1.06	58
800W_CO ₂ _9500P1	25	1126	1.07	64

2.4 Conclusion

In Chapter 2, I conducted a review of the presence of impurities and removal methods confirmed through raw material analysis of marine biomass, as well as whether it is suitable for manufacturing as activated carbon. Marine biomass is a carbon-rich renewable material, and has various advantages, including easy supply and rapid growth compared to terrestrial biomass, especially in Japan, where there is a wide coastline. However, there are impurities of rich alkali and alkaline earth metals. Through thermogravimetric analysis, marine biomass observed significant thermal weight loss, especially at 800 and 1000°C. The reduction in thermal weight was confirmed even after high-temperature heat treatment at 800 and 1000°C. This confirmed that the metal impurities in marine biomass were volatilized at high temperatures. In addition, through CHN analysis, marine biomass showed a very low carbon content of less than 80% even after high-temperature heat treatment at 1000 degrees. Therefore, it was confirmed that impurity removal is necessary for the conversion of marine biomass into carbon material. I have achieved effective removal of AAEMs by increasing the concentration of previously performed low concentration acetic acid washes and CO₂ methods, as well as by various types of acids such as nitric acid, hydrochloric acid and citric acid.

As a result, it was confirmed that when washed using nitric acid, the impurities were effectively removed, reducing the AAEMs, which were present at 22.4 mass% after heat treatment at 800°C, to 2.5 mass%. In addition, it was confirmed that the metal impurities blocking the pores on the surface were removed, and the specific surface area was also greatly increased. I reviewed the production of marine biomass-derived activated carbon through atmospheric and pressurized CO₂ activation using previously reviewed marine biomass washed with acetic acid and CO₂. It was confirmed that the manufactured activated carbon forms mesopores instead of generating effective pores that can increase the specific surface area and induce catalytic gasification especially under pressurized conditions due to the remaining AAEMs even after washing. As a result, it was difficult to manufacture highly porous activated carbon with a high specific surface area. Therefore, to convert it into activated carbon, it was

confirmed that it was necessary to additionally remove the remaining AAEMs after activation through marine biomass washed with nitric acid to remove as many impurities as possible.

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Chapter 3. Activated carbon production through 2-step regeneration of atmospheric and pressurized CO₂ activation

Enhanced porosity in marine biomass-derived activated carbon via two-step CO₂ activation and acidic decontamination (J. Choi, et al., *Carbon letters*, (2024))

3.1 Introduction

In Chapter 2, I have closely examined the presence of alkaline and alkaline earth metals (AAEMs) impurities through raw material analysis of marine biomass (MB) and the washing method using various single acids to remove them. In this chapter, after washing with nitric acid, marine biomass was removed by up to 89% after heat treatment. And I performed CO₂ activation from atmospheric to pressurized MB after low-concentration acetic acid and CO₂ washing, which was reviewed in Chapter 2. The remaining impurities developed mesopores larger than 3 nm during activation, and in particular, this catalytic gasification reaction was further promoted under pressurized activation, resulting in a decrease rather than development of the specific surface area. Through this, I confirmed that the existing AAEMs in MB developed mesopores through the reaction during activation by catalytic gasification.

In this study, I focus on the utilization of low-cost seaweed-based MB for the preparation of activated carbon (AC) with a high specific surface area (SSA) for various value-added applications. AC, with its highly porous structure, is widely used as an adsorbent for air and water purification [1,2], as a catalyst support [3], and in energy storage devices such as electrodes [4]. There is a growing demand for AC with high SSA, as it directly influences performance in these applications. However, the effective preparation of MB-derived AC with a high SSA requires the removal of intrinsic

impurities, particularly alkali and alkaline earth metals (AAEMs), which are known to inhibit pore development during preheat treatment and activation [5–8].

In this study, I aim to prepare MB-derived AC with an SSA exceeding 2000 m²/g at a relatively low cost. I employed physical activation using CO₂ as the activation gas, as this method is simpler and less expensive than chemical activation using expensive activators such as KOH and NaOH. Compared with physical activation, which does not require post-treatment, chemical activation requires anticorrosion equipment and a post-treatment step with an acid solution to remove the activator [9]. While physical activation generally results in less pore development compared to chemical activation [10], this limitation could be solved by utilizing a pressurized physical activation method, which significantly enhances pore formation [11]. Our laboratory has confirmed that high-pressure can enhance the diffusivity of CO₂, thereby enhancing the pore development, which can develop a high specific surface area comparable to that of chemical activation [11]. Using this method, I successfully prepared AC with high SSA through both atmospheric and pressurized CO₂ activation of seaweed-derived precursors, following optimal preheating and impurity removal with selected acid treatments [11].

3.2 Experimental

3.2.1 Preparation of precursor from MB

Figure 3-1 illustrates the process flow diagram for the preparation of AC from MB. The MB, specifically seaweed (WAKAME), was collected from the Japanese coast and supplied by Nippon Steel Co. Ltd. The seaweed, with an initial moisture content of 10 wt%, was further dehydrated and ground into particles smaller than 250 μm . It was then subjected to preheating at 800°C for 2 hours under an N_2 atmosphere. The preheated WAKAME was labeled according to the treatment temperature (e.g., 800W for WAKAME preheated at 800°C). To remove alkali and alkaline earth metals (AAEMs), aqueous solutions of nitric acid (69.9 wt%). The acid-washed samples were labeled with the suffix "-acid type and concentration", (e.g., 800W-nitric acid 10 for samples treated with 10 vol% nitric acid.)

3.2.2 Preparation of AC from precursor

I applied a second CO_2 activation to the nitric acid-washed samples that had undergone the first atmospheric CO_2 activation to further enhance the porosity of the derived ACs by heat treatment and nitric acid treatment. The first activation was performed on the 800W-10nitric acid sample at 900°C, 0.1 MPa, with a CO_2 flow rate of 200 mL/min for 0, 30, 60, or 90 minutes. The ACs obtained from the first atmospheric CO_2 activation were labeled as 800W_10HNO3_900P0.1M'x', where 'x' indicates the activation duration. The second AAEM removal was conducted at 50°C, with stirring at 150 rpm for 6 hours, using a mixed acid solution of 10 vol% nitric acid and 10 vol% acetic acid in a weight ratio of 7:3. After rinsing with pure water until the pH reached neutral, the samples were designated with the suffix "_Washing." Finally, the second activation was carried out under 1 MPa pressure at 900°C with a CO_2 flow rate of 200 mL/min, without any holding time. The final products after this pressurized CO_2 activation were labeled with the suffix "_900P1".

3.2.3 Characterization

I used a Laser Raman spectrophotometer (532nm, NRS-3200, Jasco), X-ray diffraction (RINT-Ultima III, Rigaku), and scanning electron microscope (JSM-6700F, JEOL) to investigate the structural properties, such as graphitic properties and surface morphologies of preheat-treated MB and MB derived AC. Elemental compositions before and after pyrolysis, AAEMs removal, and activation were evaluated using X-ray fluorescence (XRF) spectrometry (ZSX Primus IV/RX9 platform, Rigaku, Japan). Nitrogen adsorption and desorption isotherms at 77 K were obtained using a surface area analyzer (Nova-e series; Anton Paar Quanta Tec Inc., USA) to determine pore characteristics. Specific surface areas and pore volumes were calculated from the isotherms using α S-plot analysis [12] and quenched solid density functional theory (QSDFT) methods [13], respectively. The mesopore volume percentage was calculated using the following formula:

$$\text{Mesopore volume (\%)} = \frac{\text{Total pore volume} - \text{Pore volume less than } 2\text{nm}}{\text{Total pore volume}} \times 100$$

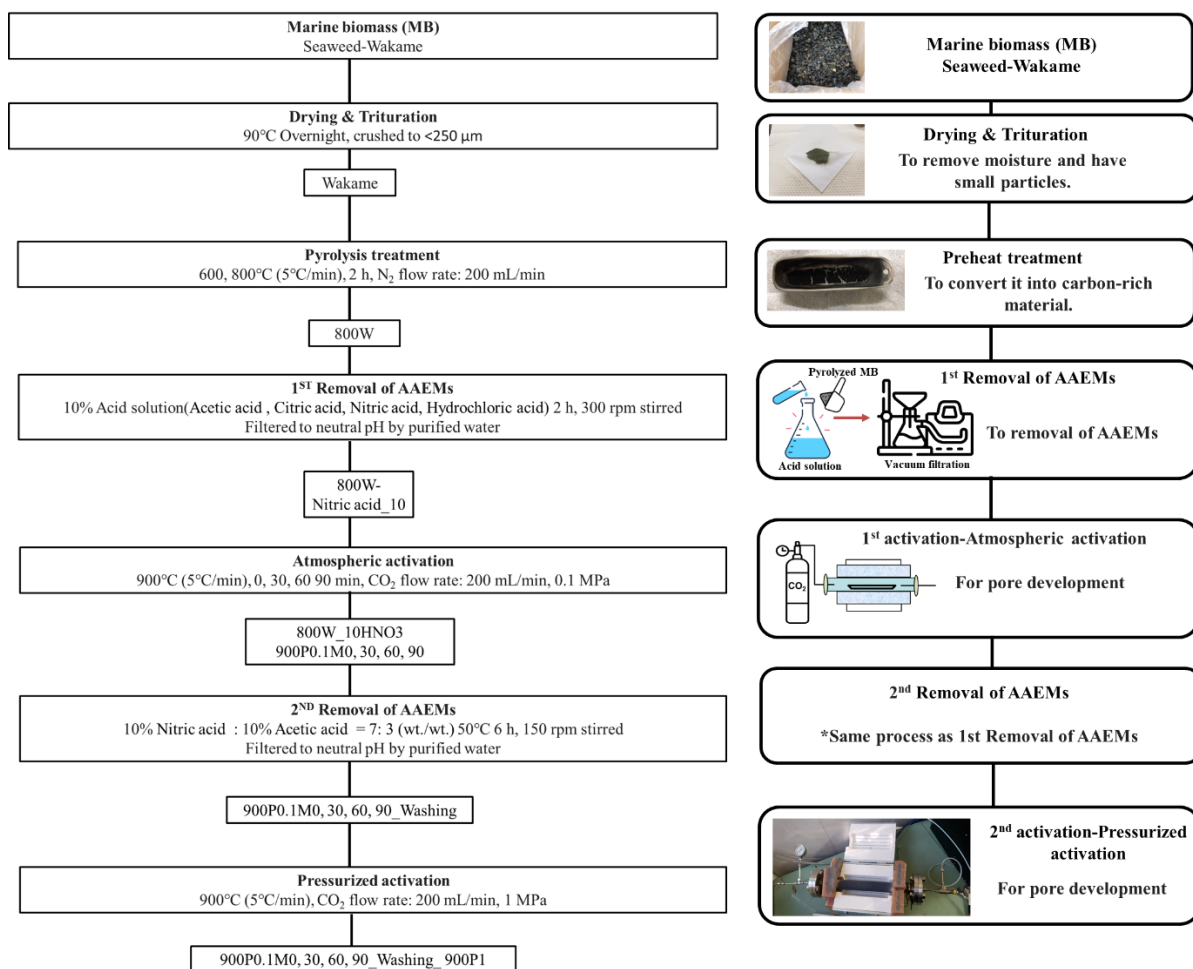


Figure 3- 1. A flowchart depicting the detailed synthetic process of MB derived ACs.

3.3 Results and discussion

3.3.1 1st CO₂ atmospheric activation

I examined the effect of atmospheric CO₂ activation at 900°C on the pore structure development of acid-washed MB, focusing on the balance between micropore and mesopore formation over varying activation durations. **Figure 3-2(a)** displays the N₂ adsorption/desorption isotherms at 77 K for ACs prepared from 800W_10HNO₃ via atmospheric CO₂ activation at 900°C for various activation durations. Chapter 3 of experiments were conducted at temperatures up to 950°C, but ACs activated at 950°C exhibited excessive mesopore development. Based on these preliminary results, 900°C was selected as the optimal temperature for the first activation, as it was expected to promote further micropore development. No significant difference in N₂ adsorption was observed at low P/P_0 for most samples, except for 800W_10HNO₃_900P0.1M0, while a marked increase in adsorption at higher P/P_0 values indicated the development of wide mesopores. **Figure 3-2(b)** shows the pore size distributions of ACs calculated using the QSDFT method. As the activation period increased, the volume of micropores smaller than 1 nm decreased, whereas both wider micropores and mesopores continued to develop. Notably, mesopores larger than 4 nm progressively increased with longer activation time. This aligns with reports that AAEMs catalyze the gasification of carbon, promoting mesopore formation [8,14–16] **Table 3-1** summarizes the activation yields and pore structural parameters for ACs prepared from 800W_10HNO₃. Without holding time at 900°C, the AC (800W_10HNO₃_900P0.1M0) exhibited an activation yield of 76%, a specific surface area of 1463 m²/g, and a total pore volume of 0.69 cm³/g. Both the specific surface area and total pore volume increased with longer activation periods. The highest specific surface area, 1712 m²/g, was obtained for the 800W_10HNO₃_900P0.1M90 sample, which had an activation yield of 20% and a total pore volume of 1.64 cm³/g. This sample also exhibited a mesopore volume ratio of 68%.

Table 3- 1. Activation yield and pore structural parameters of MB derived ACs prepared via 10% nitric acid washing, followed by atmospheric CO₂ activation.

I.D.	Activation yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
800W_10HNO ₃ _900P0.1M0	76	1463	0.69	36
800W_10HNO ₃ _900P0.1M30	57	1544	0.96	46
800W_10HNO ₃ _900P0.1M60	32	1668	1.23	57
800W_10HNO ₃ _900P0.1M90	20	1712	1.64	68

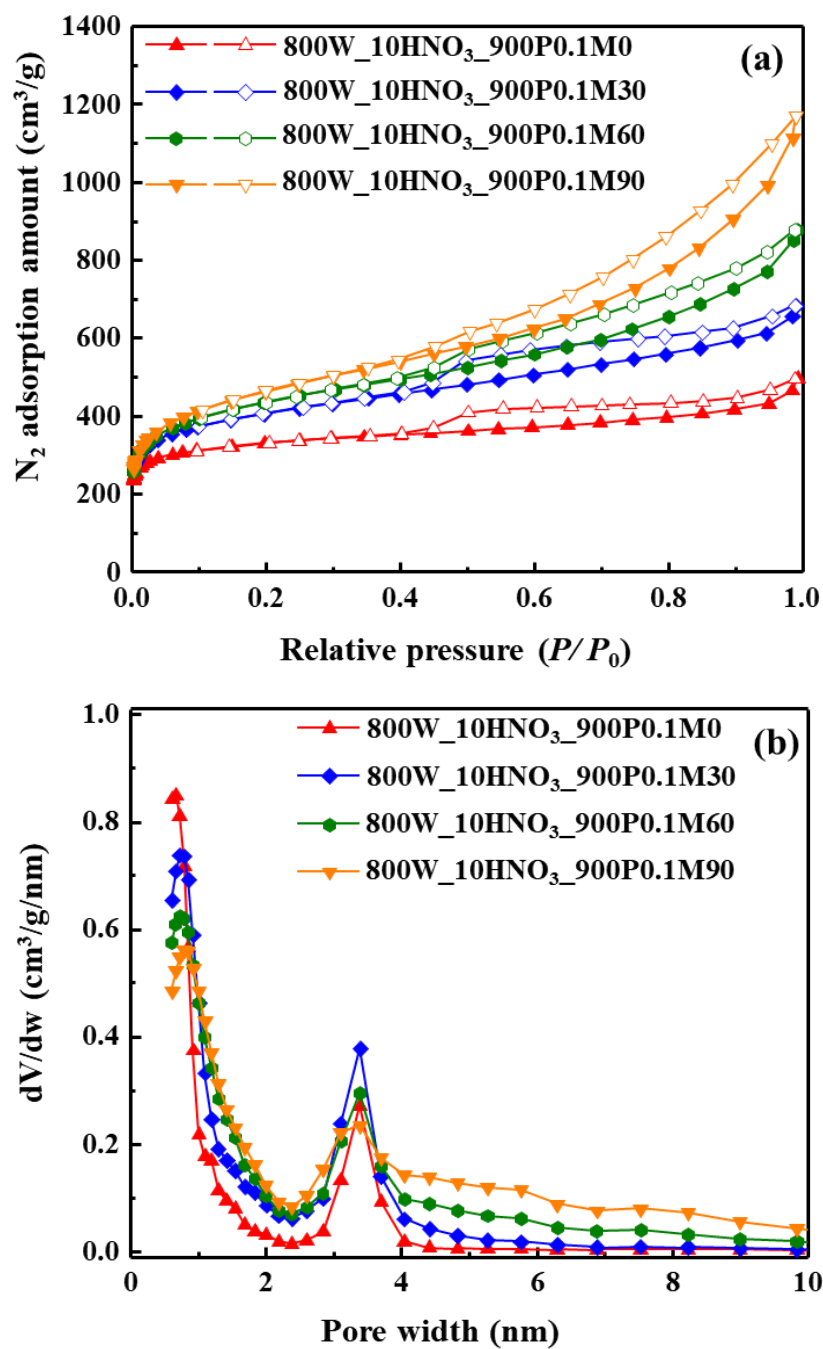


Figure 3- 2. (a) N₂ adsorption-desorption isotherms at 77 K, (b) Pore size distributions for MB derived ACs using atmospheric CO₂ activation methods. Solid and open symbols represent adsorption and desorption, respectively.

3.3.2 Additional impurities removed after atmospheric activation

Additional removal of AAEMs and other impurities from CO₂-activated MB-derived AC were carried out using a mixed acid solution to enhance carbon content and prevent residual impurities from inhibiting micropore formation. The elemental compositions after atmospheric CO₂ activation of 800W_10HNO₃ are presented in **Table 3-2**. As the activation time increased, the carbon content gradually decreased from 97.5 mass% for the parent 800W_10HNO₃ due to the activation process, which led to a relative increase in AAEMs content. To prevent residual AAEMs from inhibiting micropore formation, a further removal step was performed on the once-activated samples. Nitric acid alone was insufficient for eliminating the remaining impurities, so a mixed acid solution of nitric and acetic acids was employed for the second washing. This mixed acid treatment effectively removed most of the residual AAEMs (**Table 3-2**), with Mg being completely eliminated from all samples. The carbon content increased by 1 to 6 mass% following the second acid wash. The sample 800W_10HNO₃_900P0.1M60 achieved the highest carbon content at 99.4 mass%, with the AAEM content reduced to below 1.0 mass%.

I examined the pore structure development of MB derived AC washed with mixed acid after atmospheric CO₂ activation. **Figure 3-3(a)** displays the N₂ adsorption/desorption isotherms at 77 K for ACs prepared from washed with mixed acid after atmospheric CO₂ activation. The graph, which showed a rapid increase in adsorption at high relative pressure, like the adsorption/desorption isotherm of atmospheric CO₂ activation, indicated that mesopores were still developed. **Figure 3-3(b)** shows the pore size distributions of ACs calculated using the QSDFT method. There was almost no difference in pore development before and after washing between 8900P0.1M0_Washing and 900P0.1M90_Washing. And there was no significant increase in mesopores. **Table 3-3** summarizes the washing yields and pore structural parameters for MB derived ACs washed with mixed acid after atmospheric CO₂ activation. In most cases, the increase in surface area and total pore volume was very small or nonexistent. As with the results of the pore size distribution, 900P0.1M0_Washing and

900P0.1M90_Washing showed little increase in surface area, 900P0.1M30_Washing showed an increase of about 150 m²/g, and 900P0.1M60_Washing showed a very small increase of 80 m²/g. And the ratio of the mesopores volume was almost the same. This result suggests that the remaining AAEMs after activation were not blocking the pores but were present on the surface, and thus did not affect pore development even after removal.

Table 3- 2. Elemental compositions (mass %) of MB derived ACs, prepared through a sequential process of preheating, initial acid washing, CO₂ activation, and subsequent second acid washing, determined by XRF analysis.

I.D.	CHO	Na	Cl	Ca	K	Mg	S	etc.
800W_10HNO ₃ _900P0.1M0	97.1	0.18	0.07	0.31	0.10	1.30	0.69	0.25
900P0.1M0_Washing	99.1	0.18	0.01	0.03	0.02	-	0.06	0.06
800W_10HNO ₃ _900P0.1M30	96.4	-	0.03	0.25	0.07	1.76	1.02	0.47
900P0.1M30_Washing	98.7	0.20	0.01	0.03	0.03	-	0.95	0.08
800W_10HNO ₃ _900P0.1M60	93.5	0.34	0.05	0.70	0.17	3.28	1.41	0.55
900P0.1M60_Washing	99.4	0.22	-	0.01	-	-	0.32	0.05
800W_10HNO ₃ _900P0.1M90	92.6	0.34	0.04	0.54	0.15	3.86	1.66	0.81
900P0.1M90_Washing	98.0	0.27	0.02	0.03	0.03	-	1.59	0.06

Table 3- 3. Wash yield and pore structure parameters of after mixed acid treatment of MB derived ACs prepared using atmospheric CO₂ activation method.

I.D.	Washing yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
900P0.1M0_Washing	91	1433	0.69	38
900P0.1M30_Washing	87	1698	0.98	46
900P0.1M60_Washing	86	1744	1.28	57
900P0.1M90_Washing	85	1761	1.60	66

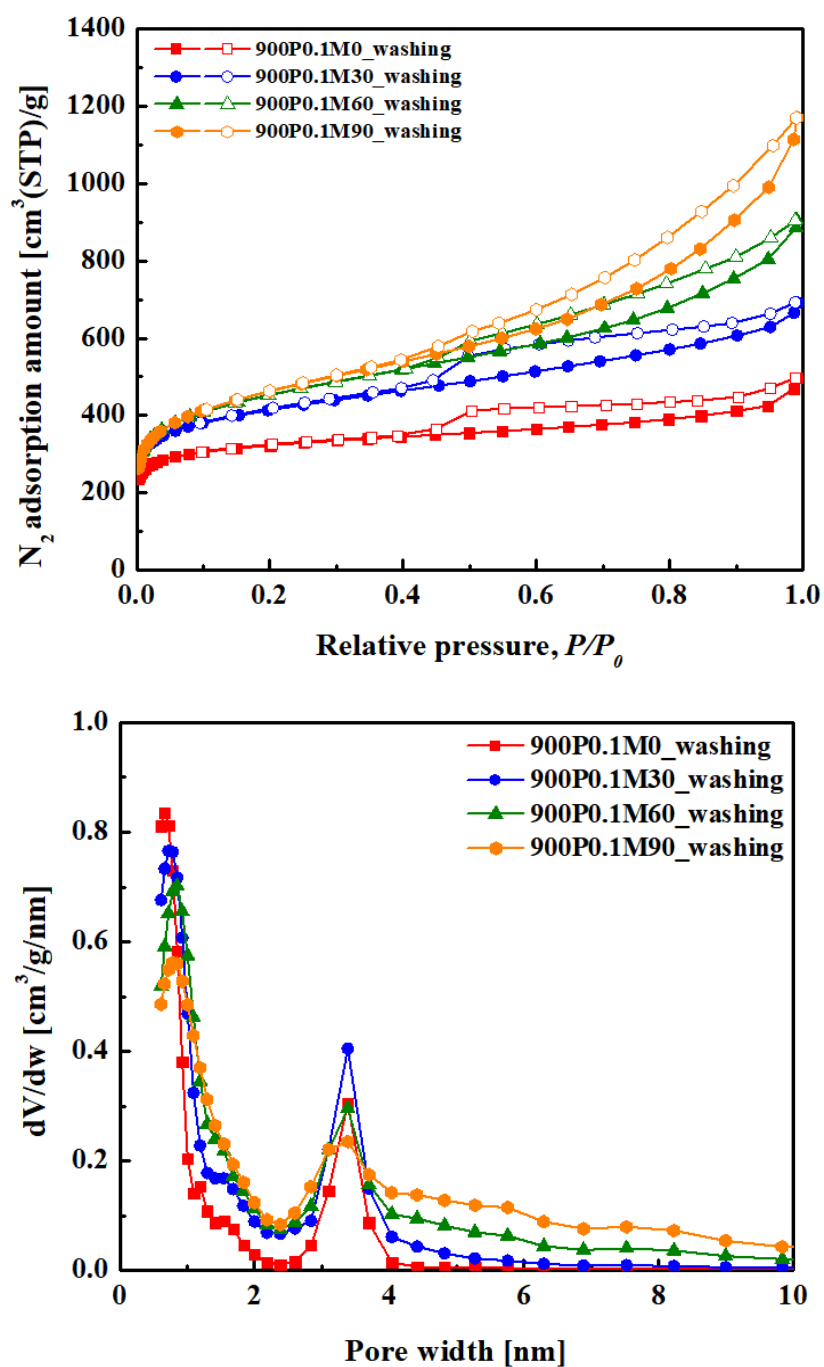


Figure 3- 3. (a) N_2 adsorption-desorption isotherms at 77 K, (b) Pore size distributions after mixed acid treatment of MB derived ACs prepared using atmospheric CO_2 activation method. Solid and open symbols represent adsorption and desorption, respectively.

3.3.3 2nd CO₂ pressurized activation

The further purified ACs, treated with a mixed acid solution, were subjected to additional CO₂ activation at 1.0 MPa to promote mesopore development and enhance the surface area. The N₂ adsorption/desorption isotherms at 77 K are shown in **Figure 3-4 (a)**. Following the second activation, the N₂ adsorption at low P/P_0 remained relatively unchanged, but significantly increased at higher P/P_0 , indicating the further development of wide mesopores [17–19]. **Figure 3-4 (b)** shows the pore size distributions of the ACs, calculated using the QSDFT method. Micropores smaller than 1 nm and mesopores ranging from 3 to 4 nm, formed during the first atmospheric activation, persisted. However, the volume of micropores larger than 1 nm and mesopores wider than 4 nm increased after the second activation. It has been reported that pressurized CO₂ activation develops wider micropores, approximately 1.6 nm in size, likely due to the formation of inter-microdomain pores [11]. **Table 3-4** summarizes the activation yields and pore structural parameters of the pressurized CO₂-activated samples. On average, the specific surface area increased by 21% following pressurized CO₂ activation (**Table 3-4** vs. **Table 3-1**). The sample 900P0.1M60_Washing_900P1 exhibited the highest specific surface area (2110 m²/g) and total pore volume (1.74 cm³/g), with an activation yield of 37%. This sample also demonstrated a large mesopore volume ratio of 57%. The ACs derived from MB exhibited unique compositions of micropores and mesopores, with significantly higher mesopore volume ratios over 46% compared to typical ACs produced from coal and terrestrial biomass [20,21]. Micropores smaller than 2 nm play a critical role in determining the specific surface area, which is the primary factor influencing adsorption capacity. However, mesopores are crucial for applications involving the adsorption of ions or molecules larger than micropores [21]. Additionally, mesopores are necessary to support fuel cell catalysts, as electrodes require mesoporous structures [22]. Furthermore, our previous studies have demonstrated that mesopores in ACs contribute significantly to the high-voltage performance of electric double-layer capacitors (EDLCs) [23]. Therefore, the high mesopore content

of MB-derived AC offers a distinct advantage for such applications, and I currently investigating its potential as an electrode material for EDLCs.

Table 3- 4. Activation yield and pore structural parameters of MB derived ACs prepared through a sequential process of preheating, initial acid washing, first CO₂ activation, second acid washing and second pressurized CO₂ activation.

I.D.	Activation yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore (>2 nm) volume ratio (%)
900P0.1M0_Washing_900P1	41	1805	1.23	46
900P0.1M30_Washing_900P1	40	1876	1.53	56
900P0.1M60_Washing_900P1	37	2110	1.74	57
900P0.1M90_Washing_900P1	35	1959	1.94	65

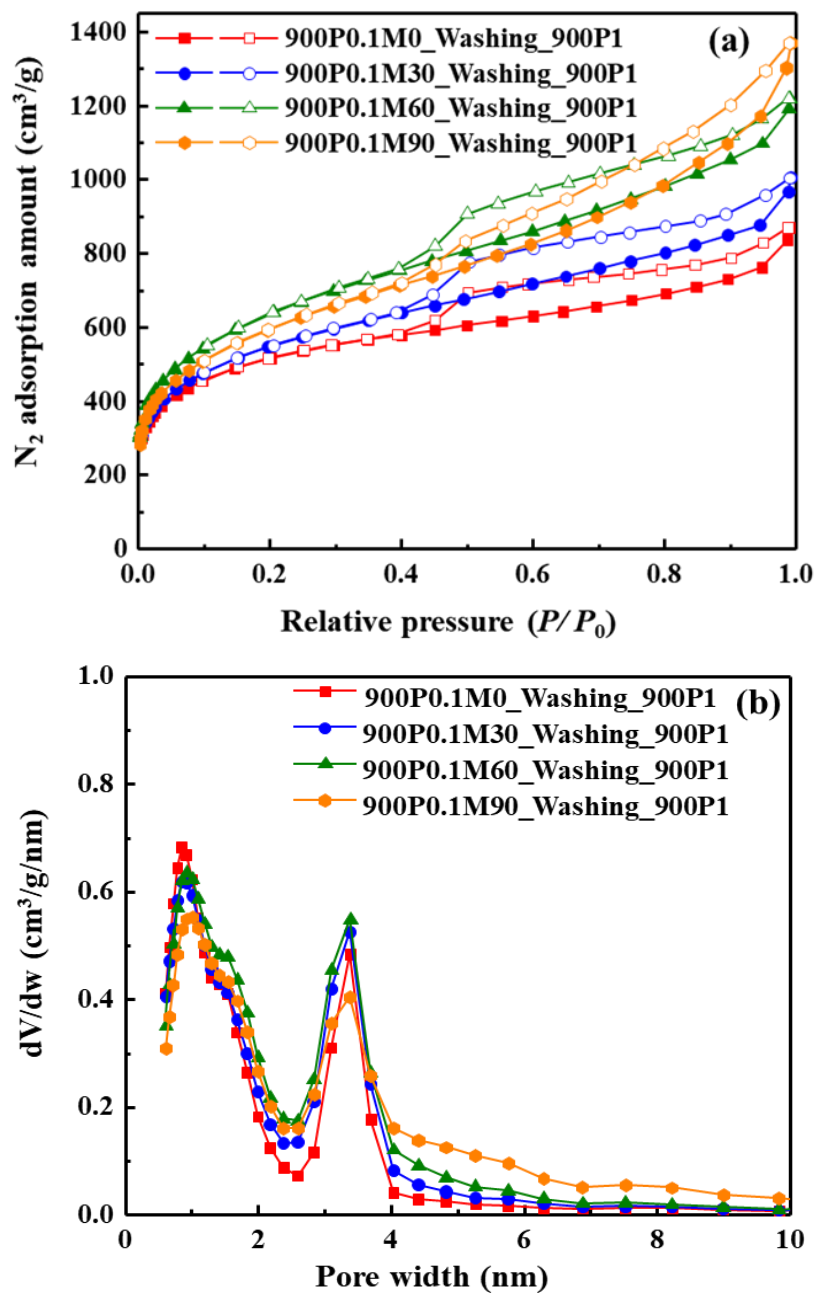


Figure 3- 4. (a) N₂ adsorption-desorption isotherms at 77 K, (b) Pore size distributions for MB derived ACs using pressurized CO₂ activation methods. Solid and open symbols represent adsorption and desorption, respectively.

3.3.4 Structural characterization of AC

I conducted structural characterizations of the selected samples using Raman spectroscopy, XRD, and SEM: preheat-treated MB (800W), preheat-treated and purified MB after the first nitric acid treatment (800W_10HNO₃), activated carbon after the first atmospheric CO₂ activation (800W_10HNO₃_900P0.1M60), the second purified sample (800W_10HNO₃_900P0.1M60_Washing) following mixed acid treatment, and the second pressurized CO₂ activated carbon (900P0.1M60_Washing_900P1). Raman spectra of all samples (**Fig. 3-5(a)**) exhibit two prominent bands: the D band (defect-induced mode) around 1350 cm⁻¹, and the G band (*E_{2g2}* mode) around 1582 cm⁻¹ [24,25]. In all cases, the intensified and broadened D bands indicate typical disordered characteristics [26]. Moreover, the *R* values (*I_D*/*I_G*, the ratio of the integrated intensity of the D band to the G band) were close to 1.00 for all samples [27–29]. After preheat treatment, the *R* value slightly decreased, likely due to the removal of additional metal impurities during atmospheric activation, but it returned to 1.00 following pressurized activation. This increase can be attributed to structural perturbations caused by pore development during pressurized activation. Furthermore, the Raman spectra showed no significant changes before and after acid washing, indicating that the acid treatment does not affect the structural order. XRD analysis proved highly effective in monitoring the removal of AAEMs in MB (**Fig. 3-5(b)**). After preheat treatment, multiple peaks appeared in the MB sample, corresponding to various metal compounds, indicating the presence of numerous AAEMs [6]. However, these peaks were almost completely removed following the first purification with nitric acid. Interestingly, peaks corresponding to MgO reappeared after atmospheric activation, which is consistent with the increased magnesium content observed in the XRF results (**Table 3-2**). After the second acid washing, the MgO peak disappeared again and did not reappear, even after the second pressurized activation. The preheat-treated MB sample also showed a broad (002) peak between 22° and 24°, which became more pronounced after the first nitric acid purification. However, the XRD peaks remained broad, confirming that the graphitic structures of MB and MB-

derived activated carbon are largely amorphous [30]. I carried out SEM observations to reveal the surface morphologies of the samples (**Fig. 3-6**). The MB particles exhibited non-uniform shapes and sizes, with relatively large particles. AAEMs were present on the surface of the preheat-treated MB, but their quantity decreased after nitric acid treatment. The particle surfaces were rough. Following atmospheric activation, the particle size slightly decreased, though the irregular shapes remained, and a small amount of AAEMs reappeared on the surface. After the second mixed acid treatment, AAEM impurities were nearly undetectable, and none were observed after the second pressurized activation. The surface of the activated carbon appeared significantly smoother after the second pressurized activation, with the rough carbon surfaces reduced along with the decreased carbon yield. SEM images confirmed that the particles remained rough and irregular in shape, with the presence of remaining AAEMs and surface conditions clearly visible.

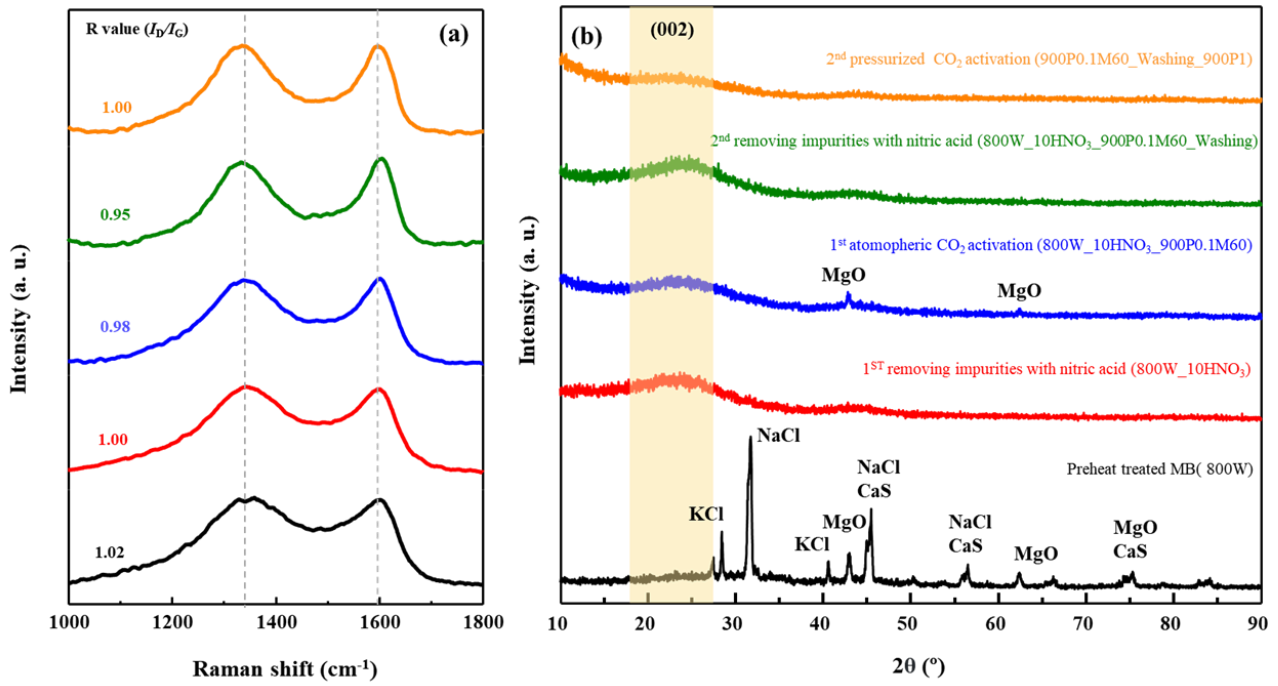


Figure 3- 5. (a) Raman spectra and (b) X-ray diffraction patterns: preheat-treated, first acid-washed, first atmospheric CO_2 -activated, second acid-washed, and second pressurized CO_2 -activated samples.

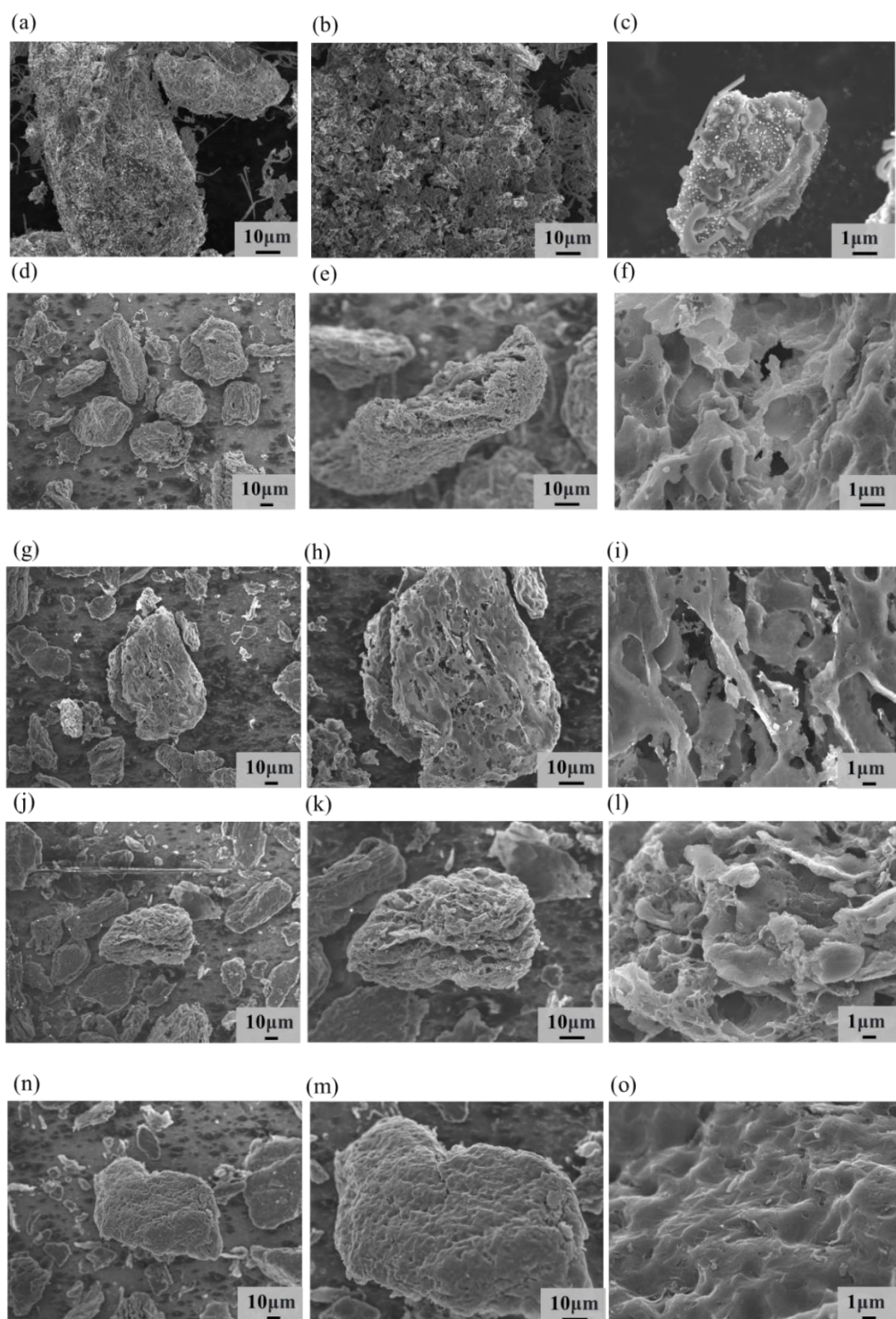


Figure 3- 6. SEM images of (a) - (c) preheat treated MB (800W), (d) - (f) 1st removing impurities with nitric acid (800W_10HNO₃), (g) - (i) 1st atmospheric CO₂ activation (800W_10HNO₃_900P0.1M60), (j) - (l) 2nd removing impurities (800W_10HNO₃_900P0.1M60 _Washing) and (n) - (o) 2nd pressurized CO₂ activated carbon (900P0.1M60 _Washing_900P1).

3.4 Conclusion

I successfully produced MB-derived AC with a specific surface area of 2110 m²/g through repeated removal of AAEMs and a two-step activation process involving atmospheric and pressurized CO₂ activations. Impurities were effectively removed using two acid treatments: 10% nitric acid and a mixed solution of 10% nitric acid and 10% acetic acid (1:1 vol./vol.). In the first purification step, nitric acid alone reduced the impurity content in the preheat-treated MB from 22.4 mass% to 2.5 mass%. After the first atmospheric CO₂ activation, a second purification with the mixed acid solution further reduced impurities in the AC to below 1.0 mass %, with a 1–6 mass % removal of residual contaminants. This progressive impurity removal significantly increased the specific surface area of both the preheated MB and the first-activated ACs. Following the first atmospheric CO₂ activation, the MB-derived AC achieved a specific surface area of 1712 m²/g, which further increased to 2110 m²/g after the second pressurized CO₂ activation. The resulting ACs exhibited a unique pore structure, with a mesopore volume ratio exceeding 36% after the first atmospheric CO₂ activation and second acid purification, and over 46% after the second pressurized CO₂ activation. This high mesopore volume ratio can be attributed to catalytic gasification by the residual AAEMs originally present in the MB.

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Chapter 4. Application of activated carbon derived marine biomass to EDLC electrode materials

Marine biomass-derived activated carbon as an electrode material for electric double-layer capacitors (J. Choi, et al., *Carbon letters*, (2024))

4.1 Introduction

The effective utilization of marine biomass (MB) as an environmentally friendly carbon source is of great interest because it grows by consuming CO₂ through photosynthesis. MB can be more easily obtained than terrestrial biomass in countries with extensive coastlines, such as Japan, and it has the advantage of growing faster than terrestrial biomass [1]. However, the large amount of impurities, such as alkali and alkaline earth metals (AAEMs), is a significant barrier to obtaining high carbon yields from MB in the preparation of functional carbon materials [2]. During the heat treatment used to obtain such materials, AAEMs within the MB cause catalytic gasification to occur, resulting in lower carbon yields and reduce micropore development [3–5]. In a previous study, I carefully controlled the degree of catalytic gasification caused by impurities within the MB by adjusting the heat treatment process and successfully prepared a unique activated carbon (AC) with a specific surface area of approximately 1000 m²/g, containing both micro- and mesopores [6].

Electric double-layer capacitors (EDLCs) generate energy by creating an electric double layer through a charge/discharge process based on the adsorption and desorption of ions, conferring superior power and long-life characteristics compared to common secondary batteries [7]. Due to their rapid energy charging and discharging capabilities and high power output, EDLCs are used as replacement or complementary devices in a variety of applications, including standby power systems, portable electronic devices, and electric hybrid vehicles [8]. However, their low energy density is a major

drawback that limits their broad application as energy storage devices [9–12]. The electrode materials of EDLCs are generally porous carbon materials with high specific surface area. Among these materials, AC has a large specific surface area composed mainly of micropores and is primarily used because it is relatively inexpensive and chemically stable [13,14].

The capacitance (C) and energy (E) stored in an EDLC are expressed according to the relationships $C = \epsilon A/d$ [15] and $E = \frac{1}{2} CV^2$ [16], where C is the capacitance, A is the surface area of the electrodes, ϵ is the ion permittivity between electrodes, d is the distance between electrodes, and V is the voltage. Accordingly, the specific surface area of AC and the electric voltage of the charge/discharge operation are important factors affecting the energy density of an EDLC [13,17]. However, there is a limit to the specific surface area of AC attainable by physical activation methods, such as steam activation, because the AC yield typically decreases with increasing specific surface area [18]. High-voltage charge/discharge of an EDLC is a more effective method for increasing its energy density. However, high-voltage operation usually lowers the capacitance of an EDLC [19–21]. I previously examined the effect of large-sized pores in ACs on charge/discharge capacitance values at 2.7 and 3.3 V and found that an AC composed of micropores and some mesopores exhibited high capacitance upon charge/discharge at the high voltage of 3.3 V. This result suggested that mesopores within the AC efficiently retained ion charges even at high voltage and could act as a buffer space for the mobility and diffusion of solvated ions, which can lead to improved capacitance retention [22].

In the present study, I sought to prepare an AC composed of micropores and mesopores using only a physical activation method, with MB as the raw material. The target volume ratio of mesopores in the AC was >50% of the total pore volume. Furthermore, I investigated the application of the newly developed MB-derived AC for EDLC electrodes suitable for charge/discharge at high voltage, e.g., 3.3 V. Finally, I elucidated the mesopore effect of the developed MB-derived AC on the development of high capacitance during charge/discharge at 2.7 and 3.3 V using fluorine-19 (^{19}F) solid-state nuclear magnetic resonance (NMR) spectroscopy. I selected seaweed-derived MB as the raw material and

pressurized CO₂ activation as the activation method to obtain the target MB-derived AC [23]. To clearly establish the pore size effect, we also prepared, as a reference, an AC with similar specific surface area and almost no mesopores from spherical phenolic resin (PR) [23].

4.2 Experimental

4.2.1 Preparation of activated carbons

The raw materials of spherical PR and dried seaweed MB (wakame; 12 wt% water content) were obtained from Asahi Organic Chemicals (Tokyo, Japan) and Nippon Steel Corp. (Tokyo, Japan), respectively. The wakame was further dried and crushed into fine particles smaller than 250 μm before use in experiments. PR and powdered MB were preheated at 800°C for 2 h under a nitrogen atmosphere. After preheating, the MB particles were treated with 10% aqueous nitric acid solution with vigorous agitation at 300 rpm for 2 h to remove AAEMs. Then, the preheated, purified MB was washed with distilled water until the pH was neutral. AC samples from pretreated PR and from preheated, purified wakame were prepared by pressurized physical activation using flowing (200 cm^3/min , 1.0 MPa) CO_2 gas as the activation agent at 700–1,000°C. The experimental conditions and apparatus are described elsewhere [23].

4.2.2 Characterization

I used a Laser Raman spectrophotometer (532nm, NRS-3200, Jasco), X-ray diffraction (RINT-Ultima III, Rigaku), and scanning electron microscope (JSM-6700F, JEOL) to investigate the structural properties of PR and MB derived AC. X-ray fluorescence spectrometry (ZSX Primus IV/RX9; Rigaku, Tokyo, Japan) was used to evaluate the elemental compositions of the PR and MB used as starting materials. The structure of AC-based electrodes was examined using scanning electron microscopy (JSM-6700F; JEOL Ltd., Tokyo, Japan). A surface area analyzer (Nova-e series; Anton Paar QuantaTec Inc., Boynton Beach, FL, USA) was used to determine the specific surface area and pore size distribution of the synthesized ACs. Nitrogen adsorption and desorption isotherms were determined at 77 K, and the specific surface area and pore structure parameters were obtained from the adsorption isotherms using an α_s plot [24]. Total pore volume and mesopore volumes were determined using the quenched solid density functional theory (QSDFT) method [25] because it is

difficult to differentiate pore volumes as micropores and mesopores using an α_s plot. The mesopore volume ratio was calculated as follows:

$$\text{Mesopore volume ratio (\%)} = [(\text{Total pore volume} - \text{Volume of pores} < 2 \text{ nm}) / (\text{Total pore volume})] \times 100$$

4.2.3 Preparation of EDLCs

The activated carbons derived from PR and MB, used as electrode materials for EDLCs, were labeled as PR800_950P1 and WAKAME800_10HNO₃_900P1, respectively. Their activation yields and pore structural parameters are summarized in Table 2. The AC samples had specific surface areas of 1,479 and 1,525 m²/g, total pore volumes of 0.50 and 1.17 cm³/g, and mesopore volumes of 0% and 64%, respectively. The prepared EDLC electrodes were composed of AC (80 wt%), conductive carbon (carbon black; 10 wt%), and polytetrafluoroethylene (PTFE) binder (10 wt%). The electrodes were cut to 12 mm in diameter. The EDLC cells were assembled as CR2032 coin-type full cells, in which the fabricated positive and negative electrodes had an average thickness of 0.25 mm and the separator (NKKTF4035; Nippon Kodoshi Corp., Kochi, Japan) was 40 μ m thick. The electrolyte was an organic electrolyte of 1 M tetraethylammonium tetrafluoroborate (TEABF₄) in propylene carbonate (PC) (Kishida Chemical Co., Ltd., Osaka, Japan).

4.2.4 Electrochemical characterizations

The capacitance of the full cell was measured using a charge/discharge apparatus (Toscat-3100; Toyo System, Fukushima, Japan) at a current density of 10 mA/g and voltages of 2.7 and 3.3 V using constant current and constant voltage methods. Cyclability was estimated up to 1,000 cycles at a current density of 100 mA/g. The capacitance of the full cell was calculated according to the relationship $C = Q/V$, where V is the potential and Q is the stored charge, calculated as the discharge

capacity of a full cell. Specific capacitance (F/g) refers to the capacitance divided by the weight of the active material of the electrode [26].

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS; HZ-3000 series; Hokuto Denko Co. Ltd., Tokyo, Japan) experiments were conducted using various full cell configurations, from 0 to 2.7 and 3.3 V and at 10, 20, 50, and 100 mV/s scan rates. EIS measurements were made over a frequency range of 10 mHz to 100 kHz at 2.7 and 3.3 V. Specific capacitance was calculated from the area of the CV curve formed by the following relationship [27]:

$$C = \frac{1}{w\Delta V} \int_0^1 i dt$$

where C is the specific capacitance (F/g), w is the mass of the active material of the electrode, i is the current, dt is the current flowing time (h), and ΔV is the range over which the current flows.

4.2.5 ^{19}F NMR spectroscopy

EDLC cells were prepared using electrodes impregnated at 0 V, charged at 2.7 and 3.3 V, and discharged at 0 V. The current density of all EDLCs during charging and discharging was 10 mA/g. The ^{19}F NMR instrument was equipped with an ECZL600G (14.1 T) HXM3.2 probe (JEOL Ltd.). A sample rotational speed of 13 kHz ensured that the PTFE peaks and spinning sidebands did not overlap with sample peaks. Accurate peak areas were obtained by setting the repetition time at 20 s, which ensured that the relaxation time of the peak with the longest relaxation time was at least five times longer than that of the sample.

4.3 Results and discussion

4.3.1 PR and MB raw material analysis

I performed elemental analysis using XRF on PR and dried MB as raw materials, as well as on preheated PR and MB, and preheated, purified MB after 10% nitric acid treatment (see **Table 4-1**). The PR consisted almost entirely of carbon, while the raw and preheated MB contained significant amounts of AAEMs and sulfur (S), with carbon contents of 92.2 wt% and 77.6 wt%, respectively. Preheating the wakame at 800°C resulted in a substantial increase in AAEMs to 22.4 wt%. Following treatment with 10% nitric acid, the AAEM content in the preheated, purified MB decreased to 2.5 wt%, while the carbon content rose to 97.5 wt%. Prior to activation, the carbon contents of the preheated PR and preheated, purified MB differed by 2.3 wt%.

Table 4- 1. Elemental compositions of raw, preheat treated PR, preheat treated MB, and preheat treated and purified MB measured by XRF.

(unit: mass %)

I.D.	CHO	Na	Cl	Ca	K	Mg	S	etc.
PR	100	-	-	-	-	-	-	-
WAKAME	92.2	3.05	2.28	0.76	0.63	0.56	0.39	0.1
PR800	99.8	0.2	-	-	-	-	-	-
WAKAME800	77.6	8.23	6.36	2.51	1.93	1.88	1.01	0.43
WAKAME800_10HNO ₃	97.5	0.15	0.08	0.19	0.05	0.81	1.00	0.22

4.3.2 Pore structure evaluations of AC derived MB, PR

The N₂ adsorption/desorption isotherms and the pore size distributions of the PR- and MB-derived ACs are compared directly in **Fig. 4-1**. The isotherm of the preheated (800°C) PR showed almost no hysteresis, whereas that of the preheated MB displayed significant hysteresis, which suggested that preheating enhanced mesopore development [28]. The isotherm profile resembled that of International Union of Pure and Applied Chemistry (IUPAC) type IV, and its shape was better cleared following nitric acid purification [29]. The PR-derived ACs displayed no significant changes in their isotherm shapes across the various pressurized activation temperatures; however, the amount of nitrogen adsorbed at low pressure was significantly higher after activation at 950°C and 1,000°C (**Fig. 4-1(b)**). All PR-derived ACs displayed IUPAC type I isotherms, indicating significant micropore content [24]. However, all MB-derived ACs displayed IUPAC type IV hysteresis isotherms at all activation temperatures from 700°C to 1,000°C (**Fig. 4-1(c)**). These isotherms had almost identical adsorption amounts at low pressure but showed large differences in their adsorption amounts at relative pressures above 0.4 P/P_0 . Nitrogen adsorption decreased at low relative pressures when the activation temperature was 1,000°C, which indicated rapid micropore reduction [30]. The pore size distributions of preheated PR, preheated, purified MB, and all PR- and MB-derived ACs were calculated using the QSDFT method [25] (**Fig. 4-1(d-f)**). Preheated PR and all PR-derived ACs contained only or almost only micropores (**Fig. 4-1(d-e)**). In contrast, preheated MB, preheated, purified MB, and all MB-derived ACs contained micropores and mesopores, and the mesopore content increased with increasing activation temperature. In the preheated MB, preheated, purified MB, and all MB-derived ACs, mesopore size ranged from 2.8 to 4.1 nm, with an average size of 3.4 nm (**Figs. 4-1(d-f)**).

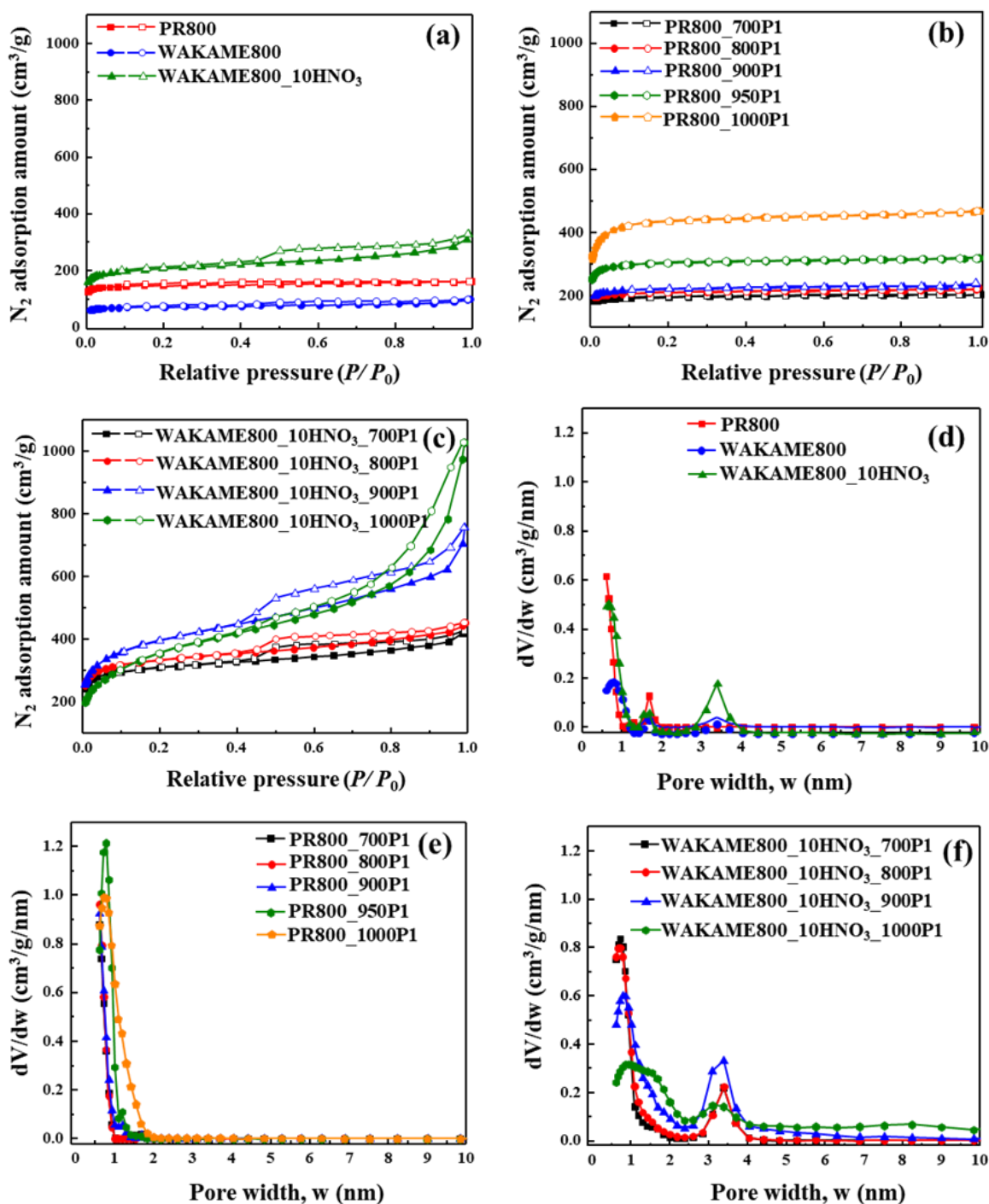


Figure4- 1. (a-c) N_2 adsorption-desorption isotherms at 77 K (solid symbols: adsorption, open symbols: desorption) and (d-f) pore size distributions of: (a,d) pre-heat treated PR, MB, and AAEM-removed MB; (b,e) PR-derived AC; and (c,f) MB-derived AC prepared by pressurized CO_2 activation.

Table 4-2 summarizes the activation yields and pore structure parameters of both ACs using the α_s plot [24] and QSDFT [25] methods. Phenolic resin preheated at 800°C displayed a higher specific surface area and total pore volume (730 m²/g and 0.25 cm³/g, respectively) than those of preheated MB (340 m²/g and 0.16 cm³/g, respectively). Notably, the preheated, purified MB had a much higher specific surface area and total pore volume (936 m²/g and 0.50 cm³/g, respectively), suggesting that ionic AAEMs impurities in the raw wakame were converted to meso-sized particles during preheating, which then behaved as catalysts for partial catalytic gasification to form mesopores; particles remaining at the entrances of developed pores partially closed the nucleated pores and were subsequently removed by 10% nitric acid treatment [6,31]. PR-derived ACs activated at 900°C, 950°C, and 1,000°C had specific surface areas and activation yields of 1,106 m²/g and 87 wt%, 1,479 m²/g and 70 wt%, and 1,918 m²/g and 55 wt%, respectively. In comparison, MB-derived ACs activated at 700°C, 800°C, and 900°C had specific surface areas and activation yields of 1,414 m²/g and 81 wt%, 1,488 m²/g and 73 wt%, and 1,525 m²/g and 40 wt%, respectively. The MB-derived AC activated at 1,000°C showed a decreased specific surface area of 1,181 m²/g despite an increased total volume of 1.59 cm³/g and low activation yield of 28 wt%.

Table 4- 2. Activation yield and pore structural parameters of PR and MB derived ACs.

I.D.	Activation yield (%)	Specific surface area (m ² /g)	Total pore volume (cm ³ /g)	Mesopore volume ratio (%) ¹⁾
PR800	-	730	0.25	0
PR800_700P1	94	1004	0.32	0
PR800_800P1	90	1077	0.35	2
PR800_900P1	87	1106	0.37	1
PR800_950P1	70	1479	0.50	0
PR800_1000P1	55	1918	0.73	3
WAKAME800	-	340	0.16	24
WAKAME800_10HNO ₃	-	936	0.50	39
WAKAME800_10HNO ₃ _700P1	81	1414	0.66	30
WAKAME800_10HNO ₃ _800P1	73	1488	0.70	30
WAKAME800_10HNO ₃ _900P1	40	1525	1.17	64
WAKAME800_10HNO ₃ _1000P1	8	1181	1.59	72

Mesopore volume ratio (%) = (Total pore volume – Pore volume less than 2 nm) / Total pore volume)
 × 100

I summarizes the specific surface areas calculated according to the α_s plot [24] and micropore ratios calculated using the QSDFT method [25] for all PR- and MB-derived ACs obtained via the pressurized CO₂ activation method (**Fig. 4-2**). The specific surface area of PR-derived ACs increased with increasing activation temperature, and micropore ratios were close to 100%. The PR-derived AC activated at 1,000°C had a mesopore volume ratio of only 3%. The specific surface area of the MB-derived ACs also increased with increasing activation temperature; a maximum specific surface area of 1,525 m²/g was attained at 900°C. Above 900°C, the specific surface area decreased, reaching 1,181 m²/g at 1,000°C. The mesopore volume ratio was 30% at activation temperatures of 700°C and 800°C, but markedly higher (64% and 72%) at 900°C and 1,000°C, respectively. This behavior suggested that any AAEMs remaining after nitric acid treatment may enhance the catalytic gasification reaction during the pressurized activation process.

The MB-derived AC obtained at an activation temperature of 900°C (WAKAME800_10HNO₃_900P1; 1,525 m²/g specific surface area; 64% mesopore volume ratio) was selected as a suitable material for high-potential charge/discharge operations using the EDLC electrode. The PR-derived AC obtained at an activation temperature of 950°C (PR800_950P1; 1,479 m²/g specific surface area; 0% mesopore volume ratio) was selected as a reference sample for comparison because it had a similar specific surface area but no mesopores. I selected these two samples because they were best suited to compare the effects of mesopores in ACs with a specific surface area of approximately 1,500 m²/g, which could be easily obtained by the physical activation method, in a high-potential charge/discharge operation.

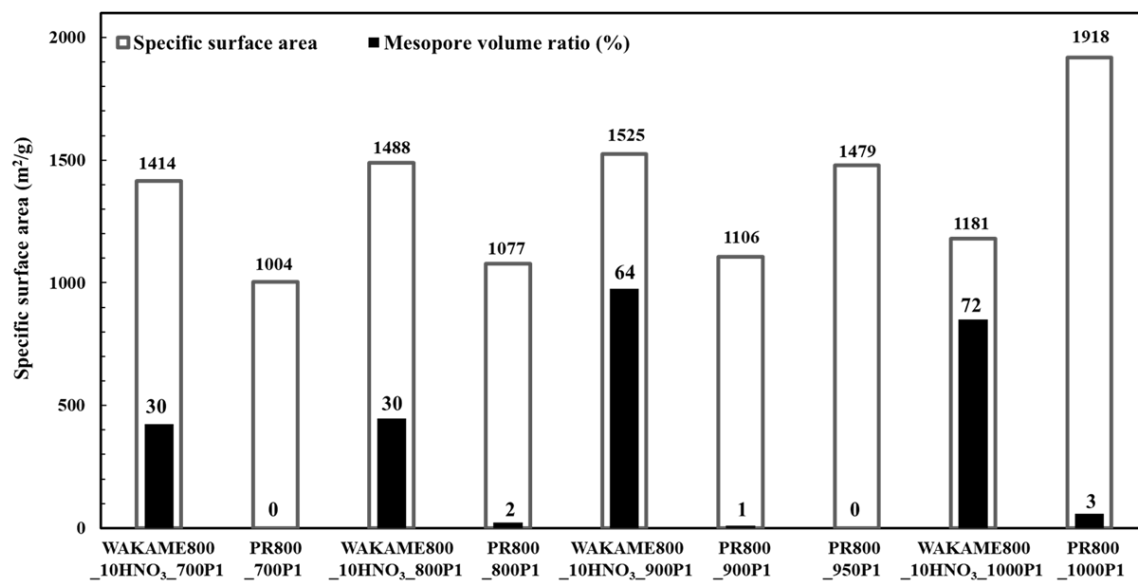


Figure4- 2. Changes in specific surface area and mesopore volume ratio of MB- and PR-derived ACs as a function of activation temperature.

4.3.3 Electrochemical performance of ELDC

The electrochemical performance of MB-derived AC were compared with those of PR-derived AC. The specific capacitance from 2.7 to 3.3 V for the EDLC assembled into a full cell is summarized in **Table 4-3**. The specific capacitance of PR-derived AC was 19.6 F/g (18.1 F/cc) at 2.7 V. When the voltage was increased to 3.3 V, the specific capacitance increased by 1.7 F/g to 21.3 F/g (18.3 F/cc). In comparison, the MB-derived AC displayed a specific capacitance of 25.9 F/g (10.7 F/cc) at 2.7 V, which was 6.1 F/g greater than that of the PR-derived AC. At the higher voltage of 3.3 V, the specific capacitance increased by 3.5 F/g to 29.4 F/g (12.6 F/cc), i.e., 8.1 F/g higher than that of the PR-derived AC. Although the PR- and MB-derived ACs had similar specific surface areas, the specific capacitances of their full cells differed significantly. This indicates that the EDLC electrode fabricated with the MB-derived AC had a more effective electric double layer than the electrode fabricated with the PR-derived AC [32]. In addition, although the specific surface area was not very high (ca. 1,500 m²/g), it had a relatively high electrostatic specific capacitance of 29.4 F/g at 3.3 V. Based on these results, the MB-derived AC, having a sufficient number of mesopores, would be effective for high-voltage capacitor applications because these require high capacitance at both low and high voltages. After 1,000 charge/discharge cycles, the MB-derived AC full cells displayed specific capacitance values of 97% and 95% at 2.7 and 3.3 V, respectively, compared with that of the first cycle, whereas the corresponding PR-derived AC capacitance values were 99% and 97%. The slightly lower capacitance retention of the MB-derived AC after 1,000 cycles is attributed to residual AAEM impurities in the MB-derived AC. During the charge/discharge process, metal impurities undergo redox reactions and accumulate on the separator, which can cause the separator to clog [33].

Table 4- 3. Capacitances obtained from full cell configurations and CV analysis.

I.D.	Full-cell capacitance (F/g)				Specific capacitance calculated from CV (F/g)							
					2.7V				3.3V			
	2.7V ₁₎	2.7V ₂₎	3.3V ₁₎	3.3V ₂₎	10 mV/s	20 mV/s	50 mV/s	100 mV/s	10 mV/s	20 mV/s	50 mV/s	100 mV/s
WAKAME800												
_10HNO ₃	25.9	25.1 (97%)	29.4	27.9 (95%)	35.1	30.2	16.9	8.1	78.5	70.3	53.1	33.8
_900P1												
PR800		19.4		20.7								
_950P1	19.6	(99%)	21.3	(97%)	15.9	13.4	9.6	6.3	42.1	34.9	26.6	15.2

¹⁾ Capacitance of the first cycle measured in the full cell

²⁾ Capacitance after the 1000th cycle measured in the full cell

Subsequently, CVs of PR- and MB-derived ACs were obtained using 1 M TEABF₄ in PC as the electrolyte at scan rates of 10–100 mV/s (**Fig. 4-3**). The parallelogram-shaped curve at a low scan rate is typical of porous carbon materials in organic electrolytes (**Fig. 4-3(a)**) [34]. Ideally, a capacitor generates a perfectly rectangular CV curve, displaying constant current during a constant voltage sweep [35–37]. However, in real capacitors, a constant current at high voltages is unattainable due to internal resistance caused by electrochemical side reactions [36–38]. In addition, the CV curve becomes more distorted with increasing resistance, i.e., less rectangular [37,38]. At all voltages, the CV curves approached a square shape at lower scan rates because at these rates, electrolyte ions sufficiently penetrated the pores to form effective double-layer capacitance. The curve was gradually distorted from this square shape as the scan rate increased to 20 mV/s. In typical CV measurements, as the scan speed increases, the curve becomes distorted due to diffusion-limited capacitance caused by the polarization effect due to internal resistance [38,39]. At 100 mV/s, the curve changed to an elliptical shape. The CV area and specific capacitance of MB-derived AC were greater than those of the PR-derived AC at all voltages and scan rates. The specific capacitance values from the CV curves are summarized in **Table 4-3** and their changes with scan speed are evident in **Fig. 4-4**. At 2.7 and 3.3 V, the specific capacitance values of the MB-derived AC were higher than those of the PR-derived AC at all scan rates. The specific capacitance values differed almost 2-fold at 2.7 V and scan rates of 10 and 20 mV/s. The specific capacitance of the MB-derived AC was nearly double that of the PR-derived AC at all scan rates at 3.3 V. At 10 mV/s, the specific capacitance of the MB-derived AC was 78.5 F/g, whereas that of the PR-derived AC was 42.1 F/g, representing a decrease of approximately 46%. At the higher scan rate of 100 mV/s, the specific capacitance of the MB-derived AC was 33.8 F/g, while that of the PR-derived AC was approximately 55% lower, at 15.2 F/g. The higher capacitance of the EDLC fabricated with MB-derived AC is attributed to its greater mesopore volume, as the PR- and MB-derived ACs differed only in mesopore volume. In a previous study, I found that electrolyte ions are more easily adsorbed and desorbed in mesopores compared to micropores due to lower

polarization resistance, which facilitates the formation of an electric double layer and thereby increases specific capacitance [22].

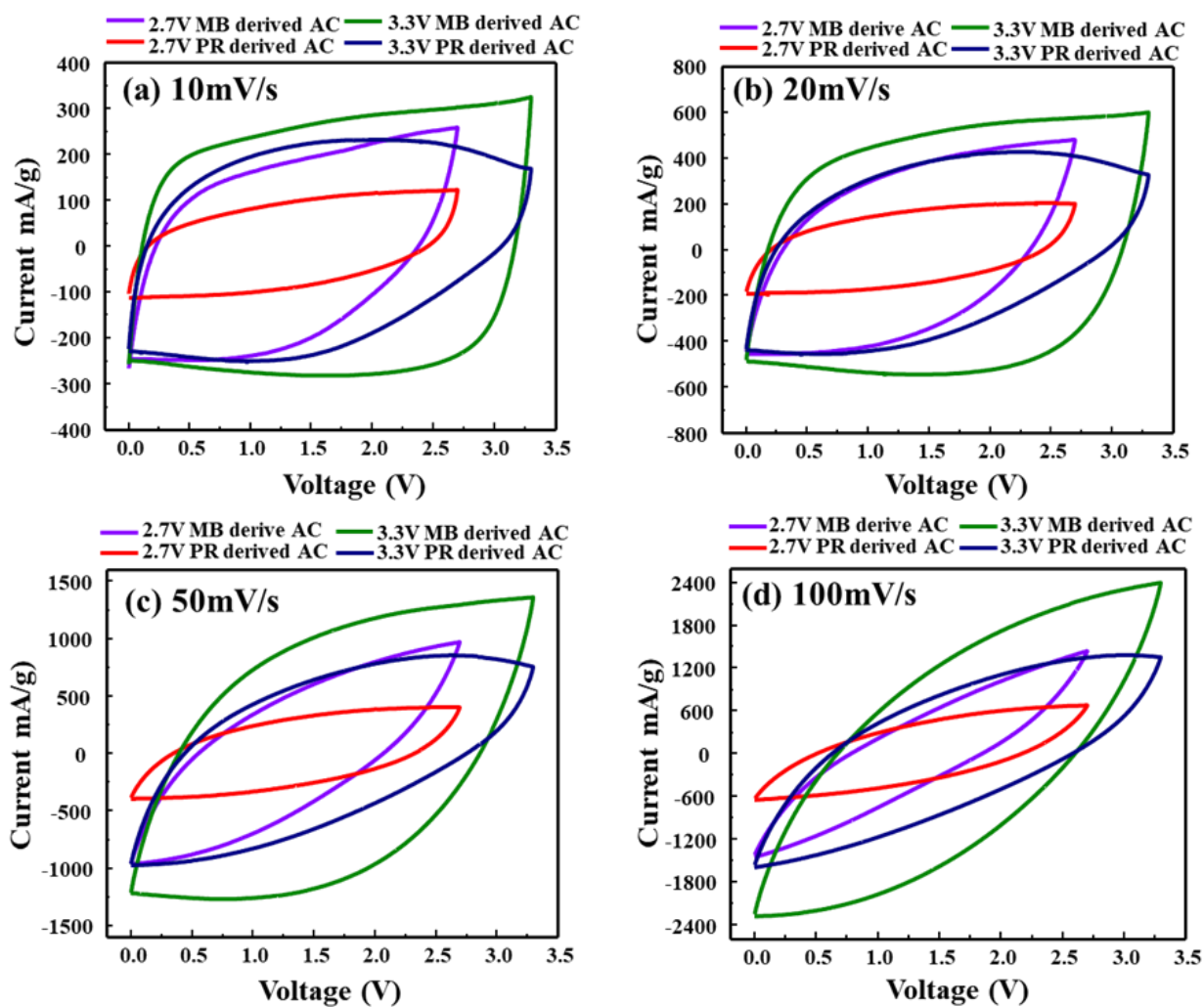


Figure4- 3. CV curves of PR- and MB-derived ACs at scan rates of (a) 10 mV/s, (b) 20 mV/s, (c) 50 mV/s, and (d) 100 mV/s at operating voltages of 2.7 and 3.3 V.

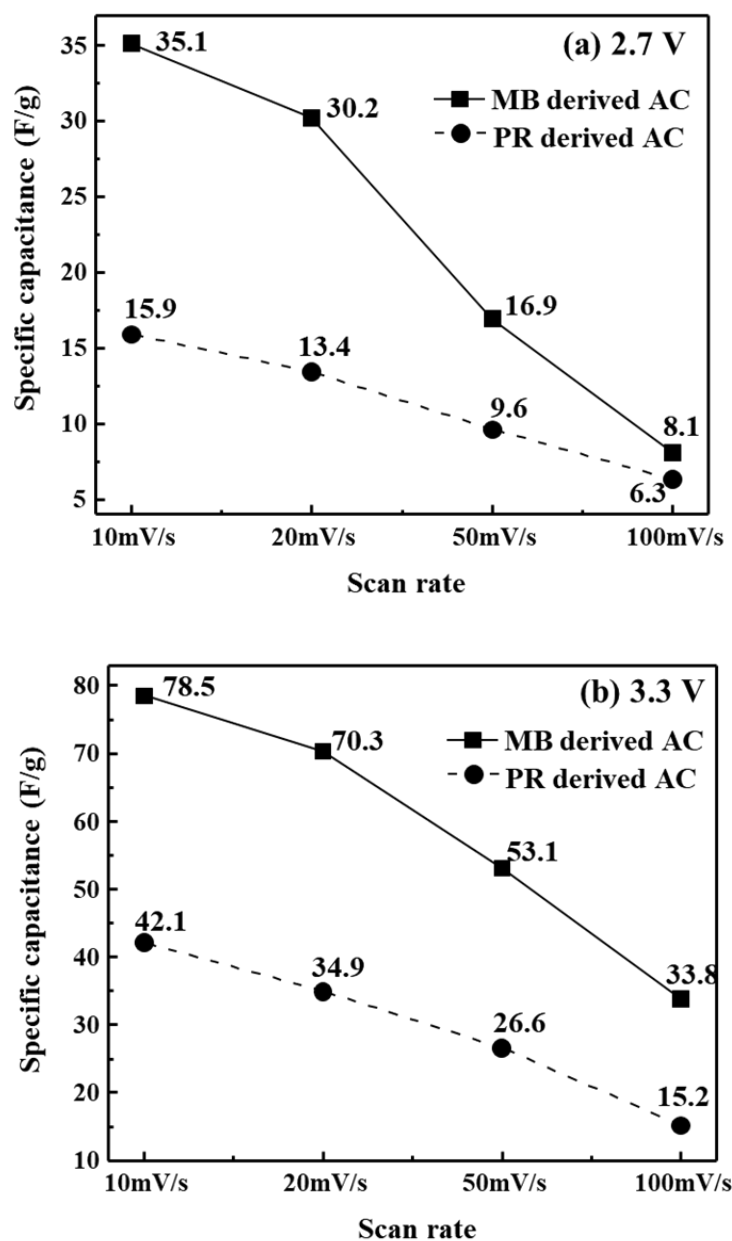


Figure4- 4. Specific capacitance of PR and MB derived AC as a depending of the scan rate (a) 2.7 V and (c) 3.3 V.

4.3.4 EIS measurements of ELDC

EIS measurements of MB-derived AC were compared with those of PR-derived AC. **Figure 4-5** shows Nyquist plots of EDLCs measured by EIS at the indicated voltages. This technique provides information about the electrochemical and electrical properties of the electrodes and electrolytes. The equivalent circuit was analyzed using a transmission line model to represent the electric double layer of the porous material [40]. The semicircle starts in the high-frequency region, allowing identification of the bulk electrolyte resistance and the system resistance between the electrodes and the current collector [41–44]. Since PR- and MB-derived ACs used the same current collector, they exhibited similar solution resistance (R_s) at all voltages. The semicircle diameter corresponds to the charge transfer resistance (R_C), representing the contact resistance of the electrode [14]. There are various factors and influences that contribute to the increase in R_C . Among them, R_C is affected by the particle size of the active material used in the electrode; therefore, electrodes with active materials of larger particle sizes exhibit higher R_C [45]. The PR-derived AC had small, uniform particles, whereas MB-derived AC had large, irregular particles (**Fig. A4.1**). In addition, it is thought that the R_C of MB-derived AC was greater due to various factors such as impurities and surface unevenness [46,47]. The straight line with a slope of 45° at intermediate frequencies represents the resistance to ion diffusion within the pores. This slope was well expressed for the MB-derived AC but was not clear for the PR-derived AC, confirming that ion diffusion within the pores was better in the MB-derived AC. [48]. The tilt of the vertical line in the low-frequency region is due to poor penetration of the electrolyte into the pores of the carbon material [49]. The vertical line of the PR-derived AC was more tilted compared to that of the MB-derived AC, indicating that the electrolyte ions were unable to sufficiently penetrate the narrow pores of the PR-derived AC compared to the MB-derived AC. Based on the results of the 45° slope at intermediate frequencies and the vertical line at low frequencies, we conclude that the MB-derived AC showed an advantage in ion diffusion compared to the PR-derived AC due to its

mesopores and sufficient pore penetration by electrolyte ions, resulting in the MB-derived AC having a higher capacity than the PR-derived AC.

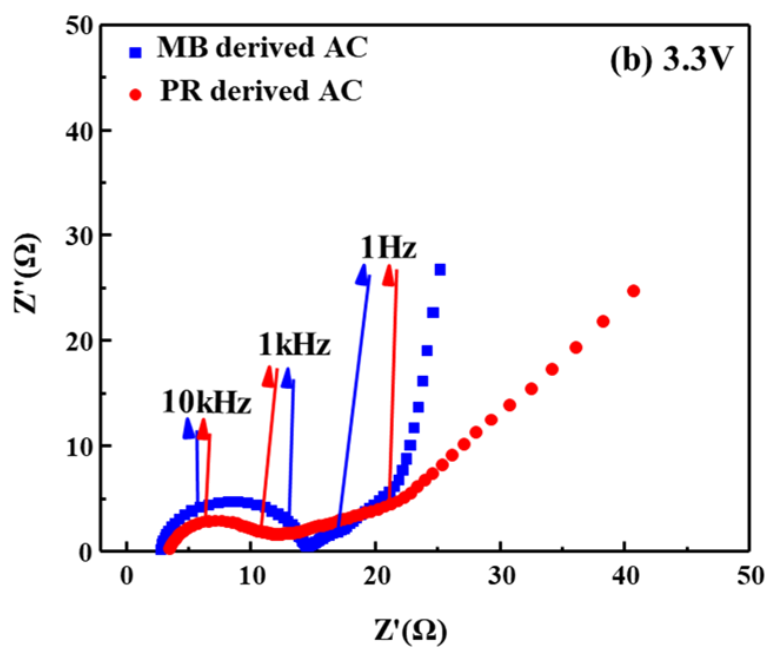
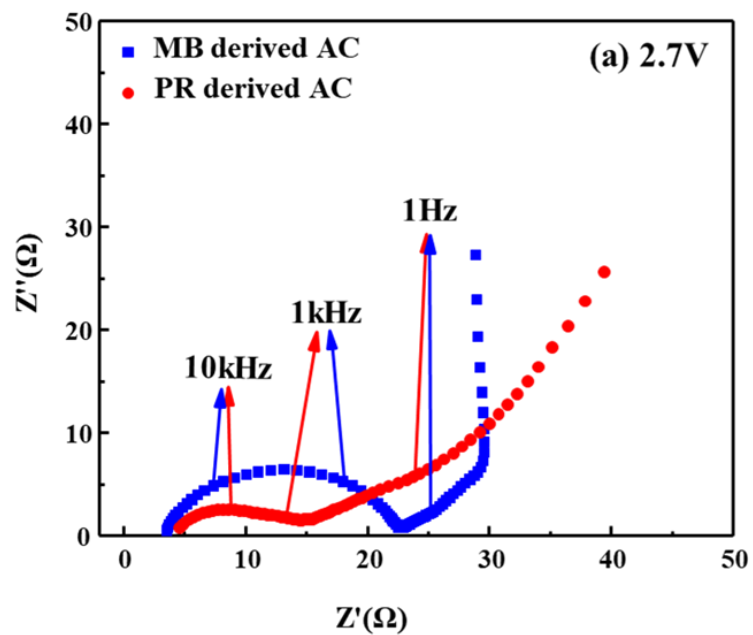


Figure4- 5. Nyquist plots of PR- and MB-derived ACs at (a) 2.7 V and (b) 3.3 V.

4.3.5 ^{19}F solid-state NMR of ELDC

I employed ^{19}F solid-state NMR to study ion mobility to establish whether the same behavior occurs with ACs with specific surface areas of approximately $1,500\text{ m}^2/\text{g}$, prepared by the physical activation method. **Figure 4-6** presents the ^{19}F NMR spectra of EDLC electrodes fabricated with PR- and MB-derived ACs. The PTFE used as binder in the electrodes enabled quantitative analysis [22]. **Table 4-4** summarizes the anion concentrations in the pores of the EDLC electrodes, as reported previously. **Figure 4-6(a)** presents the spectrum of the electrode containing MB-derived AC [22]. There was no significant change in the positions of the peaks corresponding to infiltrated BF_4^- after impregnation, charging, and discharging of the electrode. **Figure 4-6(b)** presents the spectrum of the electrode containing PR-derived AC. After impregnation and discharging of the electrode, the peak corresponding to infiltrated BF_4^- shifted to the right compared with its position after charging, due to π electrons of the AC, which react to an electrostatic field to induce a ring current and local magnetic field. The ^{19}F peak position is influenced by proximity to these π electrons of the AC [50]. After impregnation, the BF_4^- concentration of the electrode containing MB-derived AC was $12.9 \times 10^{-4}\text{ mol/g}$ and that of the electrode containing PR-derived AC was $2.3 \times 10^{-4}\text{ mol/g}$, corresponding to a 6-fold difference. After charge and discharge, the BF_4^- concentrations were also higher in the electrode containing MB-derived AC than in that containing PR-derived AC. At 2.7 and 3.3 V, the BF_4^- concentrations of the MB-derived AC-containing electrode were 17.3×10^{-4} and $19.3 \times 10^{-4}\text{ mol/g}$, respectively, and those of the PR-derived AC-containing electrode were 6.6×10^{-4} and $6.5 \times 10^{-4}\text{ mol/g}$, respectively. Moreover, after discharge, the electrode containing MB-derived AC had BF_4^- concentrations of 14.5×10^{-4} and $14.9 \times 10^{-4}\text{ mol/g}$ at 2.7 and 3.3 V, respectively; the corresponding values for the electrode fabricated with PR-derived AC were only 1.8×10^{-4} and $1.4 \times 10^{-4}\text{ mol/g}$. These results clearly indicate that the electrode fabricated with MB-derived AC contained more BF_4^- ions during charge and discharge at all voltages; these findings are consistent with the CV and full cell-derived specific capacitance data. Furthermore, it is evident that mesopores of the MB-derived

AC facilitated better ion movement than micropores, resulting in better charge/discharge performance even at the high voltage of 3.3 V [22,51]. In a previous study, I proposed a parameter (β) to estimate capacitance efficiency by quantifying the numbers of electrons and ions in the EDLC electrode [51]. β is calculated as follows:

$$\beta = [\text{Electrons}] / ([\text{BF}_4^-]_{\text{charged}} - [\text{BF}_4^-]_{\text{discharged}})$$

where [Electrons] indicates the amount of electronic charge, expressed as $\text{mol/g}_{\text{electrode}} = Q (C/\text{g}_{\text{electrode}}) / F (C/\text{mol}) = C (F/\text{g}_{\text{electrode}}) V / F$. The number of anions is given by $\Delta[\text{BF}_4^-] = [\text{BF}_4^-]_{\text{charged}} - [\text{BF}_4^-]_{\text{discharged}}$. **Table 4-4** summarizes the β values of electrodes containing MB- or PR-derived ACs at 2.7 and 3.3 V. At 2.7 V, the β values of electrodes containing MB- and PR-derived AC were 2.7 and 1.1, respectively, whereas at the high voltage of 3.3 V, these values were 2.7 and 1.4, respectively. Thus, the electrode containing MB-derived AC had a higher β value regardless of the charge/discharge potentials. In our previous study proposed that for an anion moving ideally, β approaches 2 when the electrode is charged, i.e., $[\text{Electrons}] / \Delta[\text{BF}_4^-] = 2$ [22,51], whereas for an electrode containing PR-derived AC, fewer electrons than ions are captured, such that $\beta < 2$ at both 2.7 to 3.3 V. However, for an electrode containing MB-derived AC, $\beta > 2$ at both 2.7 to 3.3 V, which is consistent with ions moving in an ideal state.

Table 4- 4. Ionic concentrations and β values of impregnated, charged and discharged electrodes of PR and MB-derived ACs [22].

EDLC sample	BF ₄ ⁻ concentration, [BF ₄ ⁻] (mmol/g)				B ¹⁾		
	Impregnated	Charged		Discharged		[electron] ^{2)/} Δ [BF ₄ ⁻] ³⁾	
		2.7V	3.3V	2.7V	3.3V	2.7V	3.3V
WAKAME800							
_10HNO ₃ _900P1	12.9	17.3	19.3	14.5	14.9	2.7	2.7
PR800_950P1	2.3	6.6	6.5	1.8	1.4	1.1	1.4

¹⁾ β , Revelation efficiency for capacitance, $[\text{electron}]/([\text{BF}_4^-]_{\text{charged}} - [\text{BF}_4^-]_{\text{discharged}})$.

²⁾ The amount of electronic charge, $[\text{electron}] \text{ (mol/g}_{\text{electrode}}) = Q$

$(C/\text{g}_{\text{electrode}})/F(C/\text{mol}) = C(F/\text{g}_{\text{electrode}}) \text{ V/F}$.

³⁾ The amount of anion, $\Delta[\text{BF}_4^-] = [\text{BF}_4^-]_{\text{charged}} - [\text{BF}_4^-]_{\text{discharged}}$.

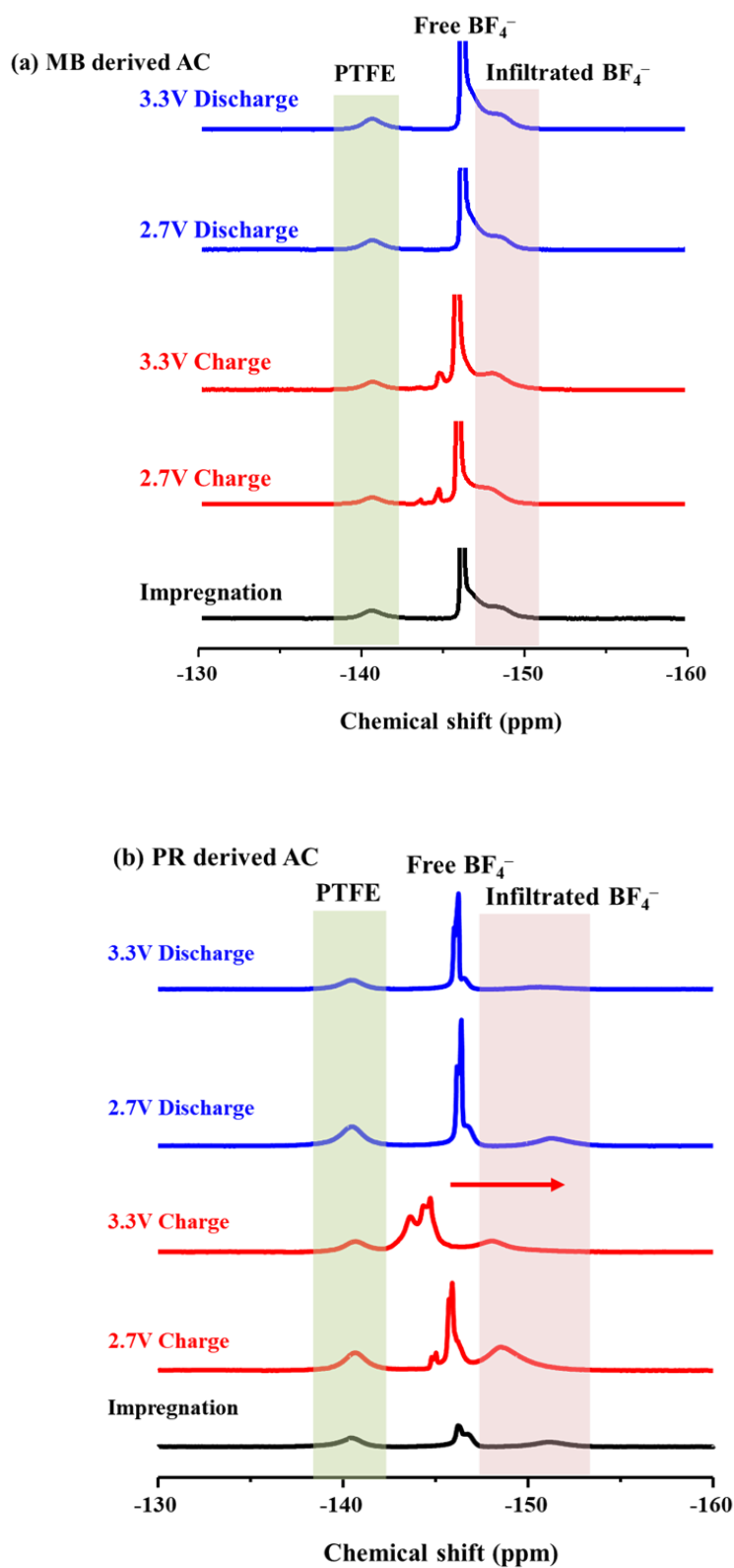


Figure4- 6. ^{19}F solid-state NMR spectra of impregnated, 2.7 and 3.3 V charged and discharged from (a) MB derived AC and (b) PR derived AC.

4.3.6 Raman spectrum of activated carbon used in electrodes

I conducted structural characterizations of the activated carbon using Raman spectroscopy: MB derived AC (800W_10HNO₃_900P1), PR derived AC (800B_950P1). Raman spectra (**Fig. 4-7**) exhibit two prominent bands: the D band (defect-induced mode) around 1350 cm⁻¹, and the G band (E_{2g2} mode) around 1582 cm⁻¹ [52,53]. PR derived AC showed a higher peak than the G peak, but it had a sharp shape. However, the D peak of MB derived AC showed a very wide peak shape compared to the G peak with almost the same height. The D peak is very broad and shows a strong peak because the two ACs are disordered and amorphous [54]. However, in the case of MB derived AC, since it showed a wider and broader D peak, the R value (I_D/I_G , the ratio of the integrated intensity of the D band to the G band) calculated through the area was close to 2 for marine biomass and 1.86 for PR derived AC [55–57]. It can be said that in the case of MB derived AC, it is due to the structural disturbance caused by the metal impurities remaining on the surface after activation and the development of pores. In addition, the MB-derived AC exhibits a broader D peak, indicating a relatively more amorphous and irregular structural feature [54].

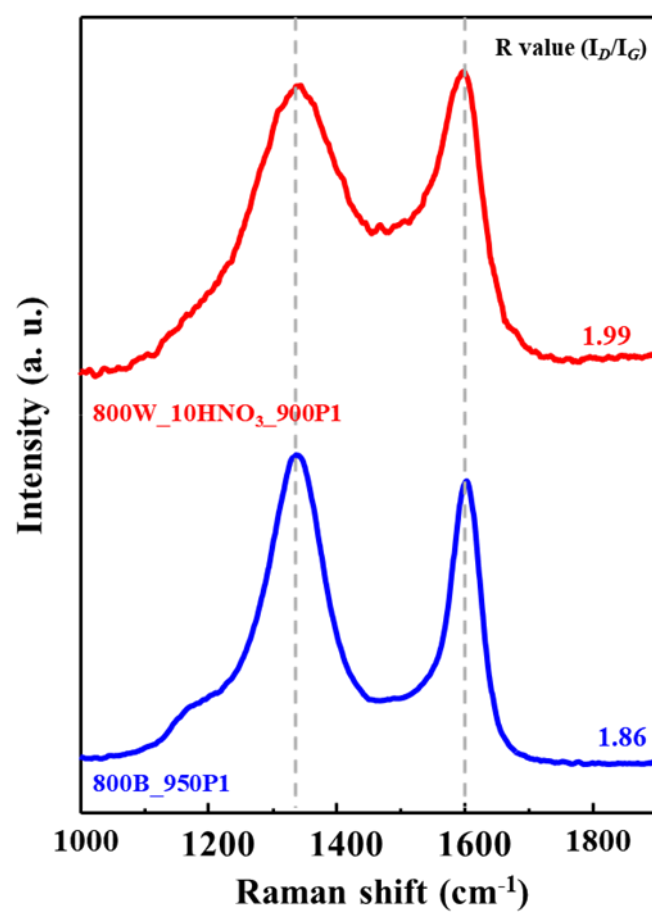


Figure4- 7. Raman spectra of PR and MB derived AC.

4.4 Conclusion

I have demonstrated that AAEMs in MB promote mesopore formation through catalytic gasification during heat treatment. In contrast, PR-derived AC, prepared under similar conditions and with a comparable specific surface area, contained only micropores smaller than 2 nm. The electrochemical behavior of EDLCs was evaluated during charge/discharge operations at 2.7 V and 3.3 V. The EDLCs were fabricated using two types of AC: MB-derived AC with 64% mesoporosity and a surface area of 1,525 m²/g, and PR-derived AC with a surface area of 1,479 m²/g. Both materials were synthesized via pressurized physical activation. The MB-derived AC demonstrated superior electrochemical performance, with higher specific capacitance (25.1 F/g compared to 19.4 F/g for PR-derived AC) at 2.7 V. This advantage was maintained at 3.3 V, where MB-derived AC achieved a specific capacitance of 29.4 F/g, compared to 21.3 F/g for PR-derived AC. Cyclic voltammetry revealed that the MB-derived AC exhibited larger CV areas across all scan rates and voltage ranges. The difference in specific capacitance was particularly pronounced at 3.3 V with a scan rate of 10 mV/s, where MB-derived AC achieved 78.5 F/g compared to 42.1 F/g for PR-derived AC. Quantitative ¹⁹F NMR spectral analysis indicated that the anion concentration in the pores directly correlated with the measured capacitance. Despite having similar specific surface areas, the mesoporous structure of MB-derived AC facilitated higher anion concentrations, which enhanced charge/discharge capabilities and electron concentration factors crucial for capacitance. These ionic charges remained stable even at elevated voltages, demonstrating the structural advantage of the MB-derived AC. The mesoporous structure of MB-derived AC provided superior ion diffusion and mobility at high voltages, contributing to sustained capacitance performance. In conclusion, MB can be effectively converted into an eco-friendly mesoporous carbon material through physical activation. The resulting mesoporous structure exhibits excellent ion diffusion properties, even at high operating voltages, making it a promising material for enhancing electrostatic capacity in EDLC applications.

4.5 Future work

The research so far has focused on the production of high surface area activated carbon and its application. Future endeavors will delve deeper into the development of mesopores, removal of impurities, and new applications. The development of 2–4 nm mesopores, which are characteristic of MB, is thought to have potential for use in catalyst carriers for fuel cells. Mesopores rather than micropores are required for catalyst carriers for fuel cells to support catalysts such as platinum. However, for application, maximum impurity removal is required in the impurity region more than before. In addition, it is most important to explore more than 80% of mesopores. In the coming stage, further pulverize the particles to control their size, and manufacture MB-derived porous carbon materials with developed mesopores through a process that can minimize impurities along with high-temperature heat treatment. I believe that additional research is needed to confirm the possibility of advancing into high value industries such as fuel cell catalyst carriers.

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Appendix for Chapter 4

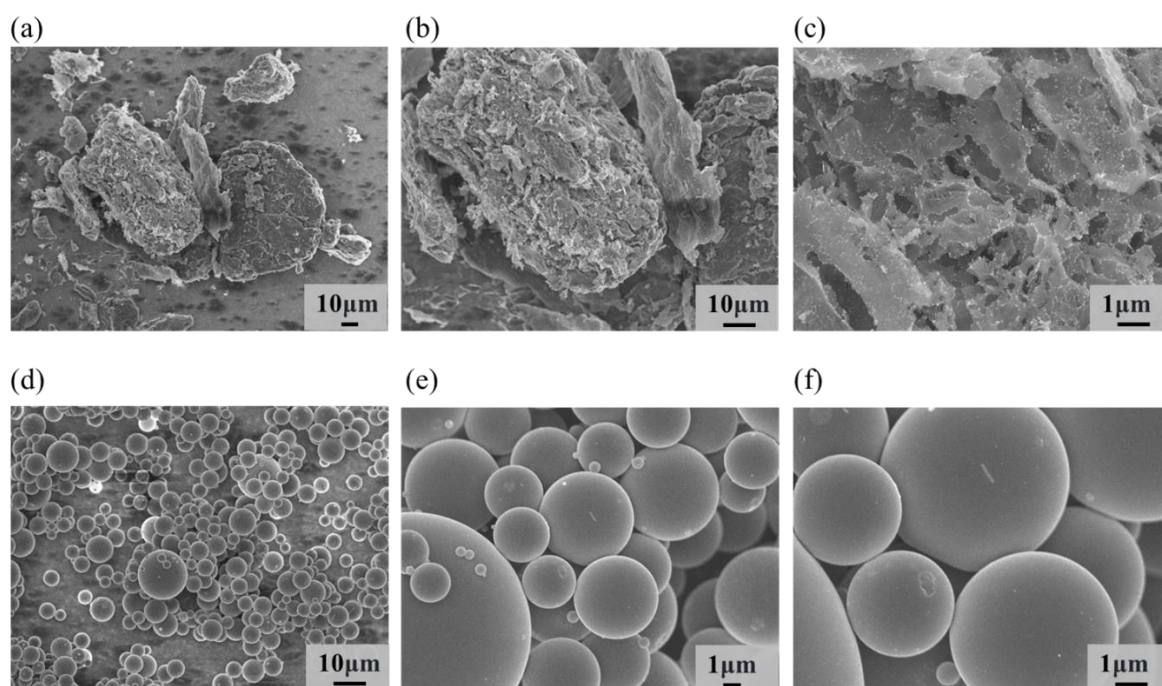


Figure A4- 1. SEM images of MB-derived AC (a-c) and PR-derived AC (d-f).

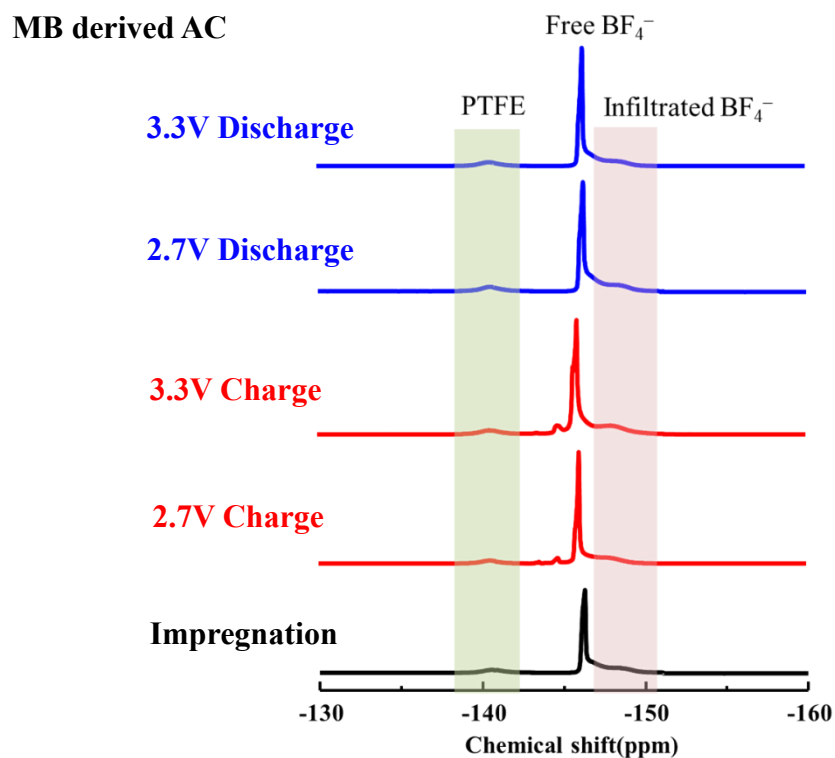


Figure A4- 2. ^{19}F solid-state NMR spectra of impregnated, 2.7 and 3.3 V charged and discharged from MB derived AC (Full spectra of **Figure 4-6 (a)** MB derived AC).

Chapter 5. Total conclusion

In this thesis, I studied the production and effective application of advanced activated carbon for high added value of marine biomass. Seaweeds have low yields and poor quality when converted to carbonaceous materials due to catalytic gasification of carbonaceous materials or pore blocking by alkali and alkaline earth metals (AAEMs). AAEMs of marine biomass were reduced from 22.4 mass% to 2.5 mass% through nitric acid. In addition, I successfully produced activated carbon containing a large amount of mesopores with a specific surface area of more than 2000 m²/g through two-stage CO₂ physical activation. The conclusions of each chapters for production activated carbon and its application results are summarized below;

Chapter 2. Removal and impact of alkaline and alkaline earth metals from marine biomass

In Chapter 2, I performed qualitative and quantitative analyses of AAEMs present in marine biomass, and discussed their removal methods. It was confirmed that the impurities present at 22.4 mass% after heat treatment of marine biomass were removed up to 2.5 mass% by nitric acid. As the impurities were removed, the pores that had been blocked by metal impurities were converted to open pores, and the specific surface area increased from 340 m²/g to 936 m²/g. Furthermore, it showed a characteristic pore size distribution in which both micropores and mesopores of 3–4 nm developed together. When marine biomass, which had been washed with acetic acid and CO₂, which had been examined in a previous study to be less effective in removing impurities than nitric acid, was activated with CO₂ from atmospheric to pressurized, the specific surface area decreased under pressurized activation due to the remaining impurities. It was found that the specific surface area was not reduced due to the development of mesopores, which are not pores effective for increasing the specific surface area,

because the catalytic gasification reaction was promoted with CO₂ gas under pressure. From these results, it was clearly confirmed that in order to manufacture activated carbon derived from marine biomass, it is necessary to remove AAEMs as much as possible before activation, and that an additional washing process is necessary after atmospheric pressure activation.

Chapter 3. Activated carbon production through 2-step regeneration of atmospheric and pressurized CO₂ activation

In Chapter 3, I described the production of activated carbon derived from marine biomass through CO₂ physical 2-step activation. marine biomass, which was first washed with nitric acid, was first activated with CO₂ at atmospheric activation to achieve a surface area of 1700 m²/g and mesopores of 66%. The manufactured activated carbon maintained the micropores and mesopores developed after nitric acid treatment, and it showed a unique pore structure in which mesopores were developed despite physical activation. However, after atmospheric activation, additional impurities of 1 to 6 mass% appeared on the surface again, and the second wash reduced the impurities to a maximum of 0.6 mass% through mixed acid treatment. However, the surface area was not affected. This suggests that the impurities were not blocking the pores but were present on the surface. The second activation achieved a surface area of 2100 m²/g through pressurized CO₂ activation. Unlike before, an additional peak appeared near 1.5 nm. However, it was manufactured as activated carbon having mesopores richer than micropores, with 57% mesopores. From these results, it was confirmed that it is possible to manufacture marine biomass derived activated carbon having a unique structure with more than 50% mesopores and a surface area exceeding 2100 m²/g by performing pressurized activation using CO₂.

Chapter 4. Application of activated carbon derived marine biomass to EDLC electrode materials

In Chapter 4, the applicability of Marine biomass-derived Activated carbon as an electrode material for high-voltage EDLC was evaluated. Marine biomass derived activated carbon manufactured through CO₂ pressurized activation had a surface area of 1500 m²/g and more than 60% mesopores, and it was applied as an electrode of an electric double layer capacitor. As a result, it showed a higher capacitance at a low voltage of 2.7 V and a high voltage of 3.3 V compared to phenol resin-based activated carbon with the same surface area and 100% micropores. Although the surface areas of the two activated carbons were similar, the marine biomass activated carbon with developed mesopores showed superior ion diffusion properties of the electrolyte through EIS analysis. In addition, the charge/discharge electrolyte ion content evaluated by the ¹⁹F solid-state nuclear magnetic resonance method was more than twice as high in the marine biomass-derived activated carbon at a high voltage of 3.3 V, and the capacitor expression efficiency β also showed a high value at a high potential of 3.3 V. Therefore, marine biomass-derived activated carbon has great potential as an electrode for electric double layer capacitors operating at high voltage.

As a consequence of this thesis, I was able to confirm the production and application of activated carbon from marine biomass. Using eco-friendly marine biomass that can consume CO₂ as a raw material, I was able to produce highly porous activated carbon with a specific surface area of more than 2000 m²/g with developed mesopores and micropores through a two-step CO₂ physical activation method. It is expected that marine biomass-derived activated carbon with developed mesopores can be effectively applied in applications that require high value-added mesopores in the future.

本論文の要約、まとめ

化石資源はエネルギー源の 8 割以上を占めず産業の主要エネルギー源であるが、CO₂ の重要な発生源としても懸念されるので、再生可能なバイオマスが化石資源の代案として浮上している。バイオマスは、生育場所によって陸上と海洋バイオマスと大別される。マリンバイオマスは、海、湖および湿地に存在する水生生物を含むバイオマスで、陸上バイオマスより太陽エネルギー効率がよく成長速度も速いため、CO₂ の除去能力が陸上バイオマスより優れる。日本では古くよりワカメ等の海藻養殖が盛んで、世界トップレベルの生育技術を保持すると共に長い海岸線に恵まれており、マリンバイオマスを化石資源を代替する炭素源として活用できれば、温暖化対策および産業育成の両面で有効と期待できる。

本研究では、石炭や石油を代替する炭素源として海藻を原料と用い、高付加価値化の一環として高級活性炭の製造やその有効な活用について研究を行った。マリンバイオマスは、アルカリおよびアルカリ土類金属類(Alkali & Alkali Earth Metals; AAEMs)系不純物の含有量率が高いため、炭素材に転換する際、AAEMs 系不純物の触媒ガス化による低収率および生成する細孔の閉塞による低比表面の原因になるため、品質低下の原因になる。本研究では、マリンバイオマスの一種であるワカメを原料と用いて、2000 m²/g 以上の比表面積の活性炭を調製およびその活性炭の電気二重層キャパシタの電極材としての有効応用を調べることを目的とした。

以下に本研究によって得られた知見を述べる。

第 1 章では、本研究の背景と目的をまとめて述べた。バイオマスの分類、マリンバイオマスを炭素源として用いた理由などを説明した。さらに、活性炭と電気二重層キャパシタについて説明を行った後、本研究の目的について述べた。

第 2 章では、原料マリンバイオマスに存在する AAEMs の定性および定量分析を行った。乾燥ワカメでは 10 mass%であった AAEMs 系不純物は 800℃熱処理によって 23 mass%まで増加した。800℃で前処理を行ったワカメを粉砕した後多様な酸水溶液による不純物の除去を行った結果、10%硝酸水溶液によって前駆体がワカメの AAEMs 系不純物量の 89%以上が除去され、最も高い除去率を示した。ワカメは、前処理と硝酸による 1 次酸洗浄だけでメソ孔が発達し 900 m²/g 程の比表面積を示した。

ワカメ等のマリンバイオマスを炭素源と用いて活性炭を製造する手法が定められてないため、ワカメを原料と選択し、多数の予備実験によって活性炭の調製手法を以下の工程で構成した：（1）800℃前処理に前駆体の調製、（2）前駆体の粉砕と AAEMs 系不純物の 1 次除去、（3）CO₂ を用いた 1 次（常圧）賦活、（4）粉砕および AAEMs 系不純物の 2 次除去、および（5）CO₂ を用いた 2 次（加圧）。

第 3 章では、10%硝酸水溶液で洗浄した前駆体ワカメを CO₂ による 1 次（常圧）賦活した結果をまとめた。CO₂ を用いた 1 次常圧賦活を行った結果、ミクロ孔だけが主に発達するフェノール樹脂由来の活性炭と異なり、ワカメ由来活性炭はミクロ孔とメソ孔が共に発達した特異な細孔構造を有し、1700

m²/g の高比表面積を示した。しかし、活性化による炭素化収率の低下に伴い AAEMs 系不純物が増加するので、混酸（硝酸/酢酸 7/3 (wt/wt)）による 2 次除去を行い AAEMs 系不純物量を 0.6 mass% まで除去した。その後、CO₂ を用いた 2 次加圧賦活を行い、2100 m²/g の高比表面積 とメソ孔が 60% 以上含まれる特異な細孔構造を有する活性炭製造に成功した。

第 4 章では、マリンバイオマス由来特異な活性炭の最も有効な応用として、高電位で作動可能な電気二重層キャパシタの電極材としての応用を検討した結果をまとめた。電気二重層キャパシタの低エネルギー密度の改善策としてキャパシタの高電圧化が提案されているが、まだ高電位に適用可能な安価な活性炭電極材は開発されていない。本研究で開発したワカメ原料と多段階の活性炭製造手法を適切に用いて、CO₂ による加圧賦活だけで、1500 m²/g の比表面積 と 60% 以上のメソ孔を有するワカメ由来活性炭および同様の手法で類似な比表面積と 99% 以上のミクロ孔だけを有する活性炭を調製し、高電位用電気二重層キャパシタの電極としての適用とそのキャパシタとしての電気化学特性を比較検討した結果、ミクロ孔だけを有するフェノール樹脂由来活性炭より 2.7 V と 3.3 V の高電位作動で 2 倍ほどのキャパシタンス容量を示し、メソ孔を有するマリンバイオマス由来活性炭が高電位用電気二重層キャパシタの電極材として有効であることが確認された。さらに、19F 固体核磁気共鳴法で評価された充放電の電解質イオン量も、マリンバイオマス由来活性炭が 3.3 V の高電圧で 3 倍以上高く、キャパシタンスの発現効率である β 値も 3.3 V の高電位で 2 倍程高い値を示すことが確認できた。

第 5 章では、マリンバイオマス由来の活性炭の製造と応用についてこれまでの内容を総括した。

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Jueun CHOI