

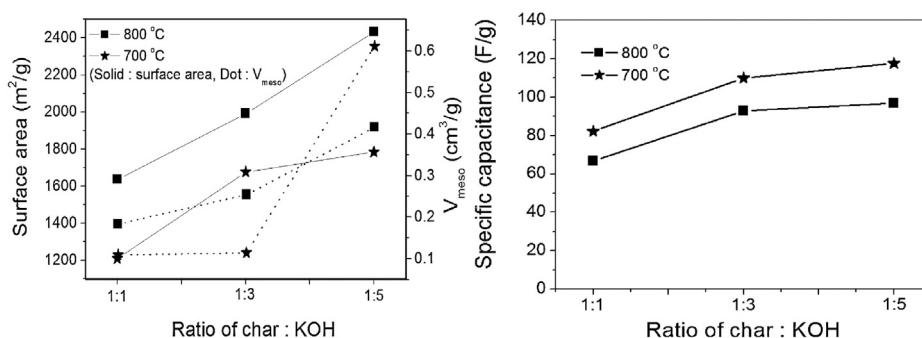
Research Paper

Sustainable fabrication of nitrogen activated carbon from *Chlorella vulgaris* for energy storage devicesKwang Se Lee^a, Miso Park^a, Chan Woo Park^b, Jong-Duk Kim^{a,*}^a Department of Chemical and Biomolecular Engineering, Korea Advanced Institute of Science and Technology (KAIST), 291 Daehak-ro, Yuseong-gu, Daejeon 305-701, Republic of Korea^b Decontamination & Decommissioning Research Division, Korea Atomic Energy Research Institute, Daedeok-daero 989-111, Yuseong-gu, Republic of Korea

HIGHLIGHTS

- Nitrogen doped activated carbon was successfully prepared from *Chlorella vulgaris* by potassium hydroxide.
- Activated carbon from *Chlorella vulgaris* contained the content of nitrogen from 21.8 to 1.4 at.% without other nitrogen doping process.
- The specific capacitance for the AC57 was 117 F/g under the current density of 0.5 A/g.

GRAPHICAL ABSTRACT



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ABSTRACT

Porous carbons were successfully prepared from nitrogen containing microalgae by the carbonization and KOH activation processes. The materials thus synthesized showed surface areas ranging from 1210 to 2433 m²/g and nitrogen contents ranging from 21.8 to 1.40 wt.% due to the use of N-rich microalgae as a carbon precursor. The samples synthesized at 700 °C with char: hydroxide = 1: 5 exhibited excellent endurance, with specific capacitances of 117 F/g at 0.5 A/g.

1. Introduction

The electrical double layer capacitor (EDLC) has received increasing attention due to its high power density, fast charge–discharge rates and long cycle life [1–3]. Among the various electrode materials, activated carbon materials with a large surface area and high electrochemical stability are preferable for the fabrication of energy storage electrodes [4–6]. These materials are appealing to address the demands of energy storage devices to allow the fabrication of electric double layer (EDL)-type supercapacitors, which is induced by the physical separation of the charge at the interface between the electrode and electrolyte. In

general, activated carbon is produced by the activation of a carbonaceous source such as corn stalk [7], coconut shell [8], or wood [9]. However, researchers have recently started to use renewable resources such as scrap waste tires [10], ash bio char [11], and slag [12] to find more sustainable ways to produce activated carbon. Unfortunately, the reported methods require additional processes such as heat treatment, sorting, and other chemical treatments to remove impurities [10].

Recently, microalgae have become a subject of special interest as a renewable bioresource because of their high photosynthetic efficiency, high growth rates, and high hydrocarbon content [13]. Moreover, the utilization of microalgae for EDLC production can also serve other

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purposes. The removal of CO₂ from industrial flue gases by algae bio-fixation [14] reduces the greenhouse gas (GHG) emissions of a company or process. The microalgae intake and accumulate contaminants in waste water such as NH₄⁺, NO₃⁻, PO₄³⁻, and hydrocarbon content also can be controlled by adjusting the ecological environment; thus, the controlled cultivation of microalgae can provide various bioresources containing a high amount of desired chemical components, such as carbon and nitrogen. After oil extraction, the resulting algae biomass can be processed into ethanol, methane, and livestock feed, used as organic fertilizer [15]. These microalgae not only have numerous advantages, but are also a nitrogen rich material. Recent reports demonstrate that the nitrogen doping into the surface of carbon gives rise to the charge delocalization and thereby facilitates electron adsorption and transfer. In addition, nitrogen doping enables faradaic reactions during charge/discharge process and dramatically increases the capacitance when used as electrode materials for supercapacitors [16–19]. In general, nitrogen doping can be achieved through post-treatment with small molecular agents such as urea [20] and ammonia gas [21]. Comparatively, the methods using post-treatment often result in the detachment of unstable functional groups, which seriously reduces the capacitive performance of the electrode after multiple charge–discharge cycles.

In this report, we investigated a sustainable approach to producing activated carbon doped with nitrogen, utilizing the inherent nitrogen and carbon in microalgae and the potential application of microalgae as the electrode materials of a supercapacitor. Simple carbonization of microalgae in the presence of potassium hydroxide efficiently promoted the incorporation of stable hetero nitrogen atoms on carbon skeletons. Moreover, pseudo-capacitive behavior resulting from reversible faradic electron-transfer chemical reactions is expected to be associated with the EDLC and exhibit synergistic enhancement of specific capacitance. *Chlorella vulgaris* was activated with various amounts of potassium hydroxide (KOH) and different times at 700 °C and 800 °C. Finally, the physical and electrochemical properties of the resulting activated carbon materials were investigated.

2. Experimental

2.1. Preparation of samples

Chlorella vulgaris (Aquanet Co. Ltd.) in aqueous medium was harvested by centrifugation, followed by freeze-drying of the dried *chlorella vulgaris*. *Chlorella vulgaris* was pyrolyzed in a furnace at 500 °C for 2 h under N₂ flow. Samples were heated at rates of 10 °C per minute. The preheated product was then mixed proportional to the concentration of the ratio of carbon to potassium hydroxide (KOH, Sigma-Aldrich) = 1:1, 1:3, and 1:5. Finally, the product was activated at 700 °C or 800 °C for 1 h under N₂ atmosphere. The obtained samples were rinsed with distilled water until the pH reached neutrality. The obtained activated carbons are denoted as AC17, AC37, AC57, AC18, AC38, and AC58. The first number represents the concentration of KOH and the second number represents the activated temperature.

2.2. Preparation of electrodes

The electrode material was prepared by mixing 85 wt.% of the activated carbon, 15 wt.% of vapor grown carbon fiber, and 5 wt.% of diluted PVDF to form a paste. This paste was then painted onto a nickel foam (1 cm × 1 cm). The mass of the active materials in the working electrode was 5 mg. The prepared working electrodes were dried overnight at room temperature.

2.3. Characterization

The morphology of the samples was observed by scanning electron microscopy (FE-SEM, S-4800, Hitachi) with an acceleration voltage of

10 kV. X-ray photoelectron spectroscopy (XPS, MultiLab 2000) analysis was carried out with a Thermo VG Scientific Sigma Probe spectrometer. The specific surface areas of the samples were determined by the Brunauer–Emmett–Teller (BET) method with Tristar II 3020 Micromeritics. Electrochemical studies were performed using cyclic voltammetry (CV) and galvanostatic charging-discharging measurements of half-cells using an Autolab PGSTAT100 (Eco Chemie). Electrochemical impedance spectroscopy (EIS) measurements were conducted for the working electrode in a frequency range of from 100 kHz to 0.01 Hz with an AC voltage of 10 mV at a potential of −1.0 V. A beaker type three-electrode cell was equipped with the activated carbon prepared from *chlorella vulgaris* on nickel foam as the working electrode, an Ag/AgCl electrode as the reference electrode, and a platinum plate (1 cm × 1 cm) as the counter electrode. For all electrochemical characterization experiments, 1 M Na₂SO₄ was used as the electrolyte solution at an ambient temperature.

3. Results and discussion

To produce activated carbon from microalgae, the *chlorella vulgaris* was pre-heated at 500 °C for 2 h under N₂ atmosphere; the mixture with KOH was then activated at 700 or 800 °C for 1 h under N₂ atmosphere. To investigate the effects of carbon to KOH ratios and activation temperature on the physicochemical properties of activated carbon, harvested *Chlorella vulgaris* was pyrolyzed in a furnace at 500 °C for 2 h under N₂ flow. The preheated product was then mixed proportional to the concentration of the ratio of carbon to potassium hydroxide. Activation was carried out at ratios of carbon to KOH of 1:1, 1:3, and 1:5 at each temperature. The obtained activated carbons are denoted as AC17, AC37, AC57, AC18, AC38, and AC58, where the first and second numbers represent the concentration of KOH and activated temperature, respectively.

The microstructures of the activated carbon were observed by scanning electron microscopy (SEM) as shown in Fig. 1 and S1. The samples had a uniform and regular pore and porous surface. Porous structures with many cavities are observed in samples with the variable size of pores with a concentration of KOH. With the increasing concentration of KOH, enlarged pores were observed from 0.25 μm to 2.5 μm. The cavities on the surface of the carbon might be due to the evaporation of the activating agent (KOH), which leaves space during activation [22]. This observation was supported by a Brunauer–Emmett–Teller (BET) analysis.

The surface properties of the synthesized carbon materials were critical for the electrochemical performance when used as an electrode material in double-layer capacitors. Fig. 2(a) and Table S1 show the surface area (m²/g), pore diameter, and pore volume calculated by the t-method at p/p₀ = 0.97 obtained by the Barrett–Joiner–Halenda (BJH) method. The low KOH concentration had a lower surface area (1210 m²/g) and a meso pore volume (0.5487 m³/g) compared with the surface area (1785 m²/g) and a total pore volume (1.084 m³/g) of the higher KOH concentration of the activated carbon at 800 °C. This was due to the higher surface area and mesopore of the activated carbon obtained from the highest KOH concentration of the activated carbon regardless of temperature. On the other hand, the pore diameter slightly decreased after further KOH activation. It is postulated that the number of large pores and small pores increase while decreasing the average pore size. It is well known that mesopores play an important role in promoting fast ion adsorption in the bulk of the material [23,24]. Another factor affecting the capacitance is the nitrogen content, as shown in Fig. 2(b) and Table S2. It has been reported that nitrogen atoms are electrochemically active because they are electron-rich [25,26]. Protons are therefore attracted to the electrode surface, inducing a reversible charging/discharging process, which was reflected by the lower coulombic efficiencies [27]. As KOH content increases, it can be seen that the nitrogen content gradually reduced. This is due to the lower bond dissociation energy of carbon and nitrogen (300 kJ/mol)

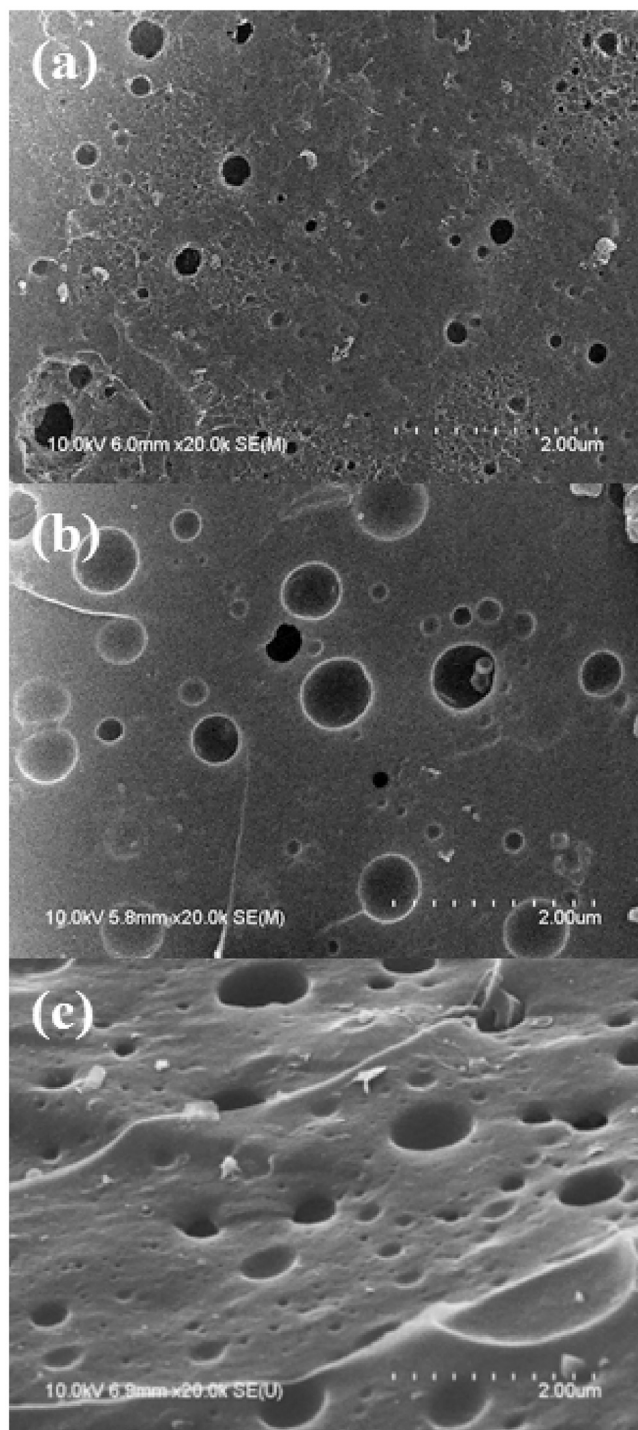


Fig. 1. FE-SEM images of activated carbon prepared from *chlorella vulgaris* with char to KOH ratios at (a) 1:1 (AC17), (b) 1:3 (AC37), and (c) 1:5 (AC57) at 700 °C.

than that of carbon–carbon (350 kJ/mol). Thus, the activated carbon at 700 °C had a higher nitrogen content than the active carbon at 800 °C. As aforementioned, the proper surface area, mesopore volume, and content can have a positive impact on increasing the capacitance of the electrode.

The electrochemical property of the activated carbon from *chlorella vulgaris* was investigated by a three-electrode cell system using Na_2SO_4 electrolyte. Fig. 3(a) and S2 show cyclic voltammogram (CV) of activated carbon electrode samples at scan rates of 5, 10, 20, 50, and 100 mV/s, and a rectangular shape of cyclic voltammogram was observed. The specific capacitance of AC57 was calculated from the cyclic

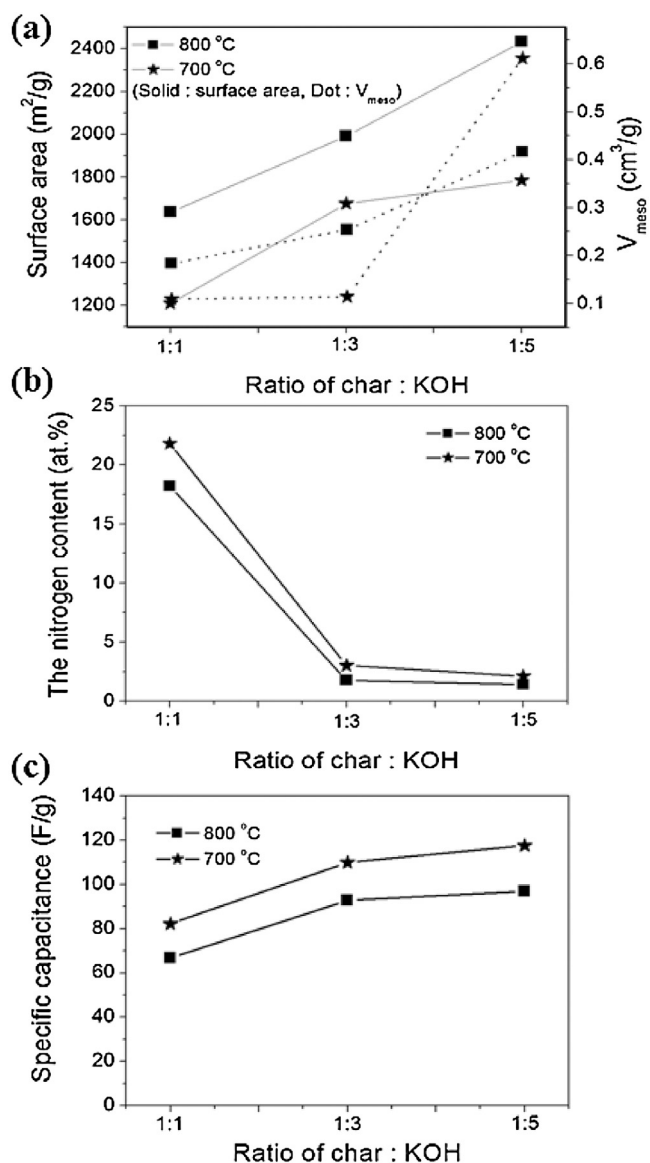


Fig. 2. (a) Surface area, (b) nitrogen content, and (c) specific capacitance of activated carbon samples prepared at different temperatures and concentrations of KOH.

voltammogram curves with values of 113, 110, 100, 88.6, and 76.9 F/g obtained at 5, 10, 20, 50, and 100 mV/s, within $-1.0-0.0$ V voltage window using the equation $C = \Delta Q / \Delta V$ [28]. When the scan rate increased to 100 mV/s, the shape of the CV curve remained symmetrically rectangular, indicating the capability of the activated carbon based capacitor to cycle at high scan rate. The contribution from nitrogen containing activated carbon derived *chlorella vulgaris* ensured only ~31% capacitance loss (113–76 F/g) when the scan rate was increased from 5 to 100 mV/s, which was much better compared to previous reports [29]. The potential of the electrode did not change linearly, and small humps were observed in each curve, which were also observed in cyclic voltammograms, indicating redox reactions of electrochemically active functional groups on the surface of the electrode. Thus, the capacitive response of the AC57 samples was due to the combination of EDLC and redox reactions, which was related to the heteroatom functionalities of the carbon materials. Furthermore, the specific capacitance of the electrode material was calculated from the galvanostatic discharge curves in Fig. S3. The specific capacitances of AC18, AC38, and AC58 prepared with different mass ratios between char and KOH are 66.7, 92.7, 96.9 F/g, respectively, under a current density of 0.5 A/g. Moreover, the capacitive properties of AC with

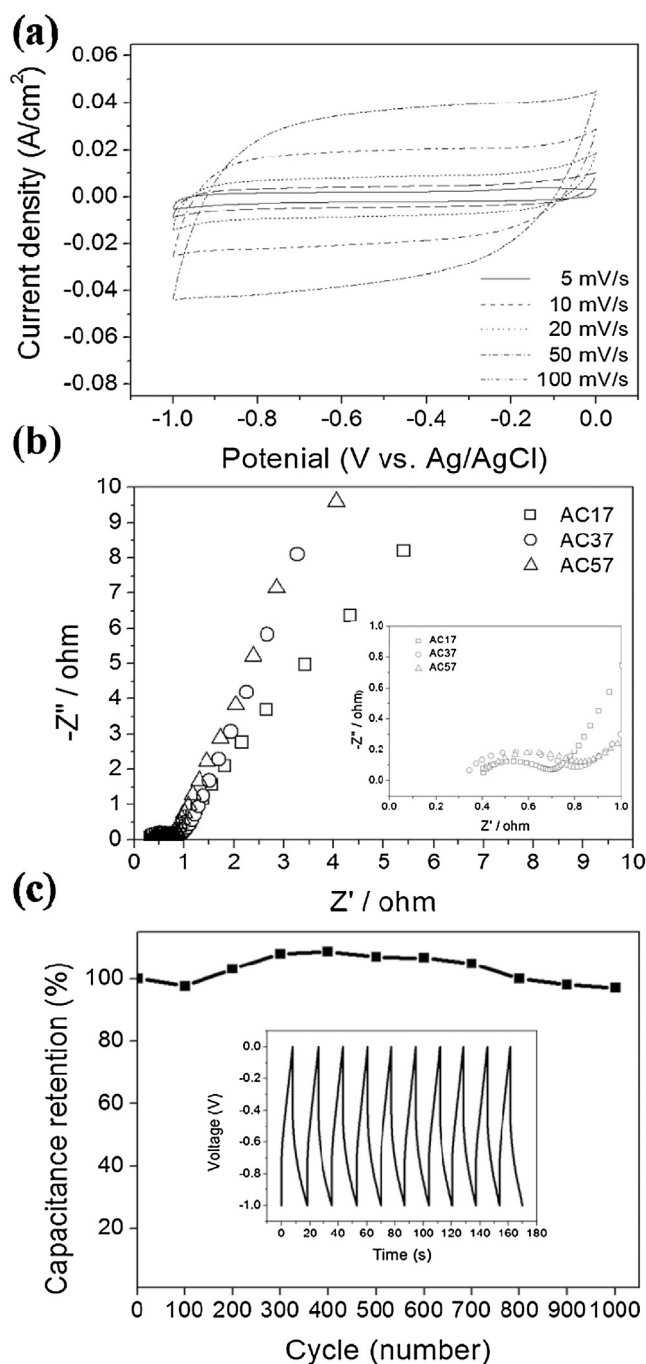


Fig. 3. Electrochemical properties of AC57 with (a) CV curves with various scan rates, (b) Nyquist plot (inset: enlarged high frequency region), and (c) cycle test (inset: galvanostatic charging-discharging curves at 5 A/g of current density).

different temperatures at 700 °C were also studied, and the specific capacitance for the AC17, AC37, and AC57 were 82.1, 109, and 117 F/g, respectively, under the same current density of 0.5 A/g due to the higher nitrogen content of activated carbon at 700 °C than that of the active carbon at 800 °C. The specific capacitance of the prepared AC57 was 117 F/g, which is much higher than that of the other reported carbon-based materials [30,31]. The test results further reveal that the specific capacitance increases with the improvement of nitrogen level, which could provide electrochemically active nitrogen atoms and specific capacitance. Even though nitrogen has a positive effect on specific capacitance, the use of the appropriate amount of nitrogen from previous data is necessary due to the collapse resulting from the lower bond dissociation energy of carbon and nitrogen (300 kJ/mol) than that

of carbon–carbon (350 kJ/mol) that is consistent with the collapse of the structure to increase the surface area. Hence, the outstanding performance of the AC57 electrode should be ascribed to the proper surface area, mesopore volume, and nitrogen doping content which provide the excellent capacitance, low-resistant pathways, and rapid transport of electrolyte ions, respectively. A more detailed investigation of the electrochemical property of the AC samples was carried out by analysis of the electrochemical impedance spectrum (EIS). The Nyquist plots of the AC electrode are shown in Fig. 3(b). In all cases, the impedance spectra are almost similar in shape, which consist of one semicircle at high frequency, and followed by a straight line at the low frequency range. The semicircle in the real axis of the Nyquist plot generated in high frequency region is solution resistance (R_s), which occurs due to ionic conductivity of the electrolyte ions. The solution resistance R_s are almost 0.38 Ω . A vertical line indicates ideal supercapacitive behavior, which is representative of the diffusion of ions at the interface between the electrolyte and the electroactive materials [32,33]. A line that is more vertical toward the imaginary y-axis indicates that the supercapacitor behaves similarly to an ideal capacitor [32]. The vertical line of AC57 leans more toward the y-axis compared to that of the other sample, which indicates that AC57 has good capacitive behavior.

In order to confirm the cycling stability of AC57, galvanostatic charge-discharge tests were conducted at a current density of 5 A/g, between -1 and 0 V for 1000 cycles (Inset of (c) in Fig. 3). During the 1000 cycles, the specific capacitance increased slightly and was then maintained, as shown in Fig. 3(c).

4. Conclusion

The sustainable approach to activated carbon preparation was demonstrated by carbonization and activation of *Chlorella vulgaris* with KOH. This simple treatment of *Chlorella vulgaris* produced activated carbon materials with high surface areas and nitrogen atom content, which are required for high performance electrode materials for super capacitors. The activated carbon electrodes for EDLCs had a high specific capacitance of approximately 117 F/g at 0.5 A/g, which is comparable with that of the commonly used AC based electrode material for EDLCs, suggesting that the nitrogen rich activated carbon has the potential for use in EDLC electrode materials. Because microalgae easily grow and exist in natural environments due to high photosynthetic efficiency and high growth rates, the presented recycling approach of microalgae will provide various carbon-based materials for electrochemical applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.colsurfa.2017.05.051>.

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