

# The Electrochemical Characteristics of Lithium-Ion Capacitors According To Pre-Doping Conditions of Lithium Ions

Minji Kang, Gabjin Hwang, Cheolhwi Ryu

Graduate School, Department of Green Energy Engineering, Hoseo University, Asan, Republic of Korea

**ABSTRACT:** Lithium ion capacitors (LICs) were assembled using electrochemical pre-lithiated graphite anode and activated carbon(AC) cathode. Although various pre-doping methods have been proposed, electrochemical pre-doping has the advantage of forming stable SEI and enabling uniform doping. As a result of the experiment, electrochemical lithium doping was found to increase the amount of lithium inserted into the electrode when doped for a long time at low current through ICP analysis. It can be seen that the amount increases by 30.9% when doped to  $0.5 \text{ mA/cm}^2$  compared to  $1 \text{ mA/cm}^2$ . As a result of pre-doping by temperature, a capacity of 2.1 F was secured at  $10^\circ\text{C}$ , a capacity of 2.4F at  $20^\circ\text{C}$  and a capacity of 2.9F at  $30^\circ\text{C}$ . As a result of cyclic voltammetry and charge/discharge experiments, it was confirmed that the same capacity as the result was realized.

**KEYWORDS** Li ion capacitor, pre-lithiation, graphite anode, capacity.

Date of Submission: 14-10-2023

Date of acceptance: 30-10-2023

## I. INTRODUCTION

Because fossil fuels are highly concentrated in resources, they are always subject to instability in terms of price and supply, and as a finite resource, the limits of their reserves are clear. As the rapid development of society leads to an increasing consumption of fossil fuels, the limitations of these resources are emerging, leading to concerns about their depletion. To address this issue, the development of new energy sources, such as green energy technology, which has infinite resources, is receiving significant attention. However, renewable energy sources face fluctuations in output due to weather conditions, which can lead to issues with securing and stabilizing power supply. As a result, there is a growing demand for energy storage devices that offer stability, reliability, and high-capacity storage to address these challenges.

Lithium-ion batteries(LIBs) are a type of rechargeable battery in which lithium ions serve as the medium for storing electric energy within the electrode. Lithium-ion batteries have high energy density, are stable, and have a long lifespan when discharged at low power. However, because they use the insertion reaction of lithium ions into the electrode, they are unable to charge large amounts of energy in a short time and lack the ability to provide high-power energy[1-2].

To meet these demands, research is being concentrated on a new energy storage device, the supercapacitor, which provides instantaneous charging and discharging as well as high power density. Supercapacitor types include electric double-layer capacitors(EDLC) that utilize the electric double layer, which reflects the high-power characteristics of the capacitor, and have high power density and fast response speeds. They can be divided into hybrid capacitors that combine the high power density of conventional electric double-layer capacitors with the high energy density of lithium-ion batteries, and pseudocapacitors that utilize the principle of redox reactions.

A type of hybrid capacitor, the lithium-ion capacitor, can store more than five to ten times the amount of energy compared to an electric double-layer capacitor[3-5]. Compared to traditional capacitors, it has the advantages of high energy density, high power density, and long lifespan, which leads to its use in electronic communication devices such as smartphones and digital cameras, as well as in the electric vehicle industry and various other industrial sectors [6-7].Lithium-ion capacitors consist of an asymmetric structure. They are a hybrid of the structures of an electric double-layer capacitor for the positive electrode and a lithium-ion battery

for the negative electrode. The positive electrode uses activated carbon electrode material, and the negative electrode is composed of pre-doped lithium-ion graphite material connected in series [8-9].

The lithium-ion battery has excellent energy density (Wh/kg), but low power density (W/kg), while the electric double-layer capacitor has superior power density (W/kg), but low energy density (W/kg). The lithium-ion capacitor compensates for these shortcomings by maintaining the high power density (W/kg) of the electric double-layer capacitor and increasing the energy density. It has high energy density and is compatible with lithium-ion batteries [10-11]. It also has excellent cycle characteristics, high voltage, and high temperature stability. Additionally, it is easy to control the charging and discharging speed, and has a low self-discharge rate [12-14].

In this paper, we aimed to increase the cell capacitance of lithium-ion capacitors, which have these characteristics, by pre-doping lithium ions into graphite, anode material for lithium-ion batteries. The electrochemical properties were investigated according to the doping conditions.

## II. MANUFACTURING METHOD OF THE ELECTRODE

The manufacturing of the anode sheet electrode used artificial graphite MAGE-E3 (Timcal), conductive agent Super-P (Timcal), and binder CMC/SBR (Hansol Chemical). Graphite, conductive agent, and binder were mixed in a ratio of 90:5:5 to produce the sheet electrode. A planetary mixer/Deaerator (Kurabo Mazerustar, KK-250S) was used to mix the materials, and the resulting powder was slurried using ethyl alcohol (Daejung Chemical) as the solvent. The slurry was dried in a drying oven at 80°C for 10 minutes, and then a roll press (Puree chem) was used to press and produce the sheet electrode. The cathode materials for lithium-ion capacitors include artificial graphite, which is a secondary battery-type carbon material, low-crystalline materials such as soft carbon and hard carbon. Artificial graphite, a typical graphite-like carbon material, has a well-developed crystal structure, which allows lithium ions to easily insert into the layers of graphite. In this study, we selected artificial graphite MAGE-E3, which has a well-developed crystal structure due to being sintered at a high temperature of 2,000°C or higher and carried out the experiment.

For the manufacture of the cathode sheet electrode, the materials used were carbon black, conductive agent, and binder, specifically MSP-20 (Kansai Coke and Chemicals), Super-P (Timcal), and PTFE (Daiichi Kogyo Seiyaku). The method for manufacturing the sheet electrode is the same as for the anode electrode. The carbon black, conductive agent, and binder were mixed in a ratio of 85:10:5 to produce the sheet electrode.

## III. ELCTROCHEMICAL PRE-LITHIATION METHOD

The electrodes manufactured in the above process were used with a reference electrode of Lithium metal to form a tri-electrode cell system (Puree chem). The tri-electrode cell is a cell structure designed to confirm the potential driving form of both the cathode and anode potentials, and the measurement method involves performing charging and discharging of the cathode and anode while simultaneously connecting the reference electrode to the cathode electrode, and the reference electrode to the anode electrode to check the driving.

For lithium doping, a relative electrode of Lithium metal ( $\varnothing$  16 mm) was used in a glove box filled with nitrogen gas with a moisture content of less than 1.0 ppm. The working electrode was Artificial Graphite MAGE-E3 ( $\varnothing$  16 mm), and doping was performed by applying a current density of 0.5 mA/cm<sup>2</sup>, 1 mA/cm<sup>2</sup> using the Li metal to the graphite. The voltage range was set between 3.1 V and 0.005 V. The doping was carried out in a constant temperature and humidity chamber, TH-40BS (Irea Tech) at 20°C, using the WMPG 1000 (WonA Tech) charge/dischargecycler. The structure of the tri-electrode cell used is shown in Fig. 1.

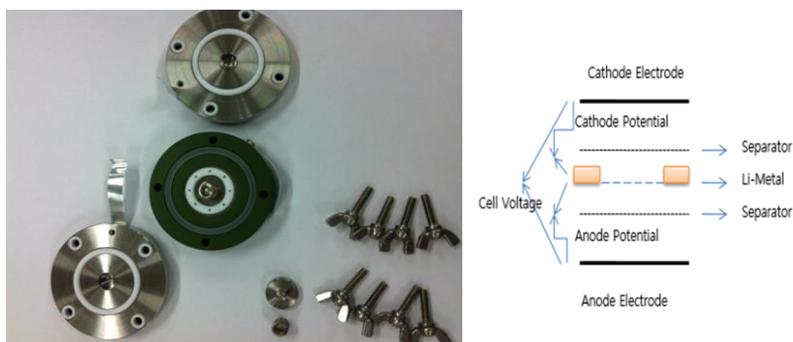


Fig.1. Three electrode cell schematic diagrams

#### IV. ASSEMBLY OF CELLS AND ELCTROCHEMICAL TEST

The electrode doped electrochemically was collected inside a glove box, and an asymmetric 2032 coin-type supercapacitor was manufactured using a non-lithium-inserted conventional carbon electrode. The electrolyte was adjusted to 0.5~1 mL. When manufacturing the full cell, a separator was placed between the cathode material, Lithium doping MAGE-E3 ( $\phi 16$  mm), and the anode material, MSP-20 ( $\phi 15$  mm), to form a cell ( $\phi 16$  mm coin type). An electrolyte containing  $\text{LiPF}_6$  in EC/DMC 1:1 (v/v) was added in 1 mL to analyze the electrochemical properties.

Impedance spectroscopy was measured using the Modulab (Solartron) electrochemical analysis equipment with an amplitude of 10 mV and a frequency range of 10 mHz to 100 kHz. For cyclic voltammetry electrochemical experiments, a driving voltage with a scan rate of 5 mV/s and a voltage range of 2.2 to 3.8 V was set, and the measurements were carried out using WMPG 1000 (WonATech). Periodic voltage was applied to the interface between the electrode and the electrolyte, and the resulting current changes were observed. Charge-discharge experiments were conducted using the constant current and constant voltage methods, and the unit cell of the fabricated lithium-ion capacitor was tested using WMPG 1000 (WonATech). The current was applied at 1 mA/cm<sup>2</sup> during charging and discharging, and the voltage range was set from 2.2 to 3.8 V for the charge and discharge process.

#### V. RESULTS AND DISCUSSIOIN

According to the current density, the cathode was doped with lithium ions using MAGE-E3 ( $\phi 16$  mm) and a separator Tapyrus ( $\phi 19$  mm). The doping time was found to be 89,000 seconds for a current density of 0.5 mA/cm<sup>2</sup> and 56,000 seconds for a current density of 1 mA/cm<sup>2</sup>. ICP analysis was conducted to determine the amount of lithium doping according to the current density. The results of ICP analysis showed that the electrodes doped at 0.5 and 1 mA/cm<sup>2</sup> contained 5.207% and 3.978% lithium, respectively, based on the total mass of the electrode. In the case of the half-cell using lithium metal as the reference electrode, during the discharge process, lithium ions are extracted from the lithium metal and inserted into the carbon electrode, while during the charge process, lithium ions are extracted from the carbon electrode and move to the lithium metal in the opposite direction [15]. The pre-doping profiles according to the current density were shown in Figures 2 and 3, respectively. It was observed that as the doping time increased up to 0.005 V at low current densities, the lithium content increased.

During the process where lithium ions and anions are segregated and move towards the electrode in the electrolyte of a lithium-ion capacitor, if the replenishment of lithium ions from the original cathode is not sufficient, the lithium ions may not be inserted into the interlayer and instead undergo a simple adsorption reaction on the electrode surface, resulting in a lower capacitance. Therefore, if it is possible to supplement the movement of lithium ions in the electrolyte, the existing lithium ions will diffuse into the interlayer of the carbon electrode, leading to a relatively higher capacitance compared to the original pure carbon electrode.

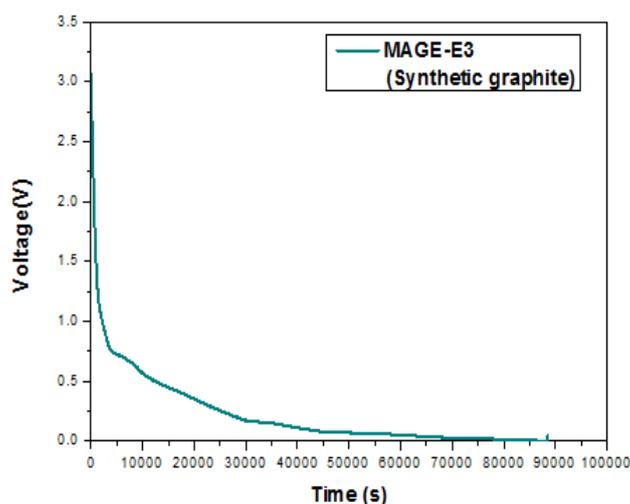
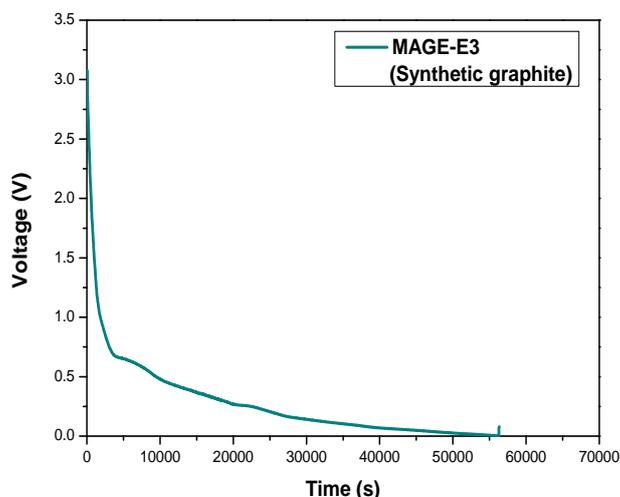


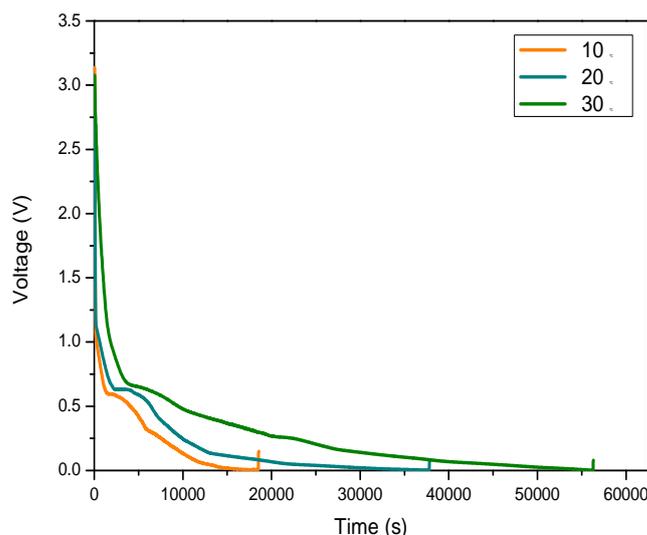
Fig.2. Li pre-doping profile of the artificial graphite with current density 0.5 mA/cm<sup>2</sup>



**Fig.3. Li pre-doping profile of the artificial graphite with current density 1 mA/cm<sup>2</sup>**

Pre-lithiation techniques can be categorized into methods that utilize lithium-containing powder additives, metallurgical alloying reactions, electrochemical lithiation reactions, and chemical lithiation reactions. Among them, techniques that can uniformly lithiate all active materials within the electrode and avoid localized over-lithiation can be referred to as electrochemical pre-lithiation and chemical pre-lithiation techniques that utilize liquid-solid reactions.

Doping behavior according to temperature was investigated at temperatures of 10, 20, and 30 °C using a current density of 1 mA/cm<sup>2</sup> and TF4035 as the separator. The results are shown in Figure 4, and it was observed that the longest doping time occurred at 30 °C, lasting for 56,345 seconds. Figure 5 represents the images of the doped electrode using MAGE-E3, which is an anode material that changes with time during lithium doping. The experiments conducted in this study had the characteristic of low current density, but it took excessive time for pre-lithiation. It is deemed necessary to conduct further research on various methods within the electrochemical pre-lithiation approach that allow for uniform pre-lithiation, such as potential control or pulse application.



**Fig.4. Li pre-doping profile according to temperature**

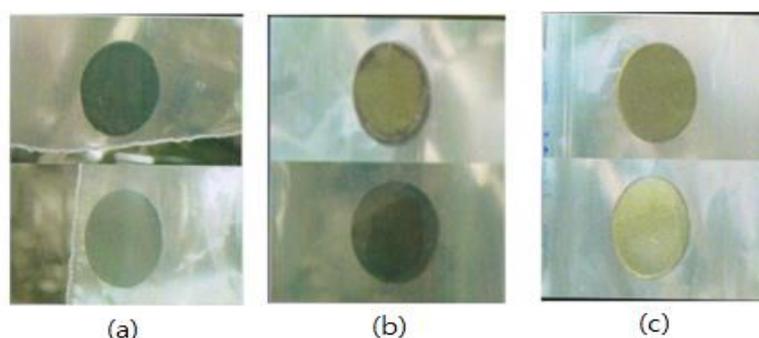


Fig.5. Images of electrodes Lithium pre-doped at (a) 10°C, (b) 20°C and 30°C

Electrochemical pre-doping is a commonly used method on a laboratory scale, where a makeshift battery or half-cell is assembled to reduce and lithiate the electrode or undergo multiple charge-discharge cycles to complete irreversible lithium loss and SEI formation before dismantling the battery to recover the electrode [16]. In general, the electrochemical cell components are consumables, and the assembly and charge-discharge equipment for cells must be available, making it a costly approach. When going through the formation cycle, the pre-lithiation reaction occurs at very low current densities, resulting in a time-consuming process ranging from a few hours to several days, which is considered a limitation. On the other hand, advantages of electrochemical pre-doping include the ability to form a stable SEI, precise control of the extent of pre-lithiation through capacity calculations, and the occurrence of reactions within the liquid electrolyte, allowing for a more homogeneous reaction throughout the electrode compared to the two methods mentioned earlier.

The electrodes, manufactured by conducting pre-doping according to temperature at a current density of  $1 \text{ mA/cm}^2$ , were separated and used to assemble full cells in a glove box. Electrochemical analysis was performed, including electrochemical impedance spectroscopy and cyclic voltammetry, and the results were presented in Figure 6 and Figure 7, respectively. The capacity measurements showed that at  $10^\circ\text{C}$ , a capacity of 2.1 F was obtained, while at  $20^\circ\text{C}$  it was 2.4 F, and at  $30^\circ\text{C}$  it was 2.9 F.

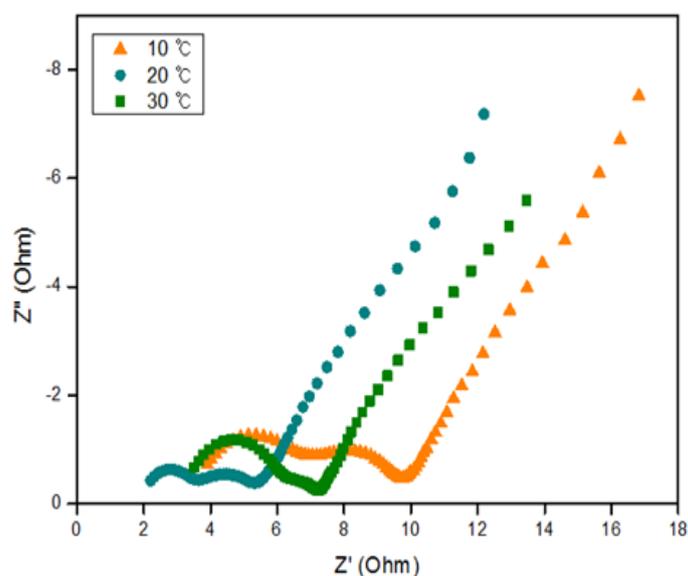


Fig. 6. Nyquist plots of the LIC with various temperature

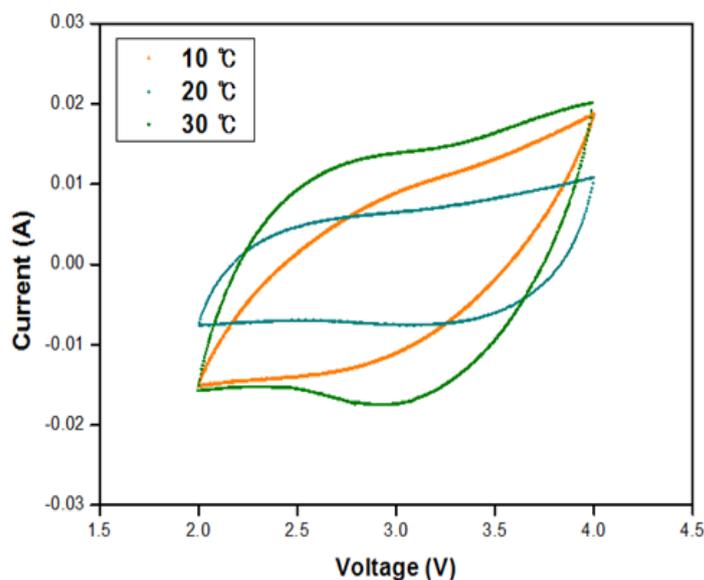


Fig. 7. Cyclic voltammetry of the LIC with various temperature

The results of the capacity comparison experiment conducted through charge-discharge experiments are shown in Figure 8. It was observed that the measured values obtained through cyclic voltammetry at 10°C, 2.1 F; 20°C, 2.4 F; and 30°C, 2.9 F were consistent. When doping was conducted at 30°C, a capacity of 2.9 F was obtained, but the resistance was higher compared to doping at 20°C, and the doping time increased by 18,465 seconds. It can be observed that the resistance increases proportionally to the area when using a micro-capacitor. Therefore, when comparing doping time, resistance, and capacity, doping at 20°C was determined to be the most optimal condition.

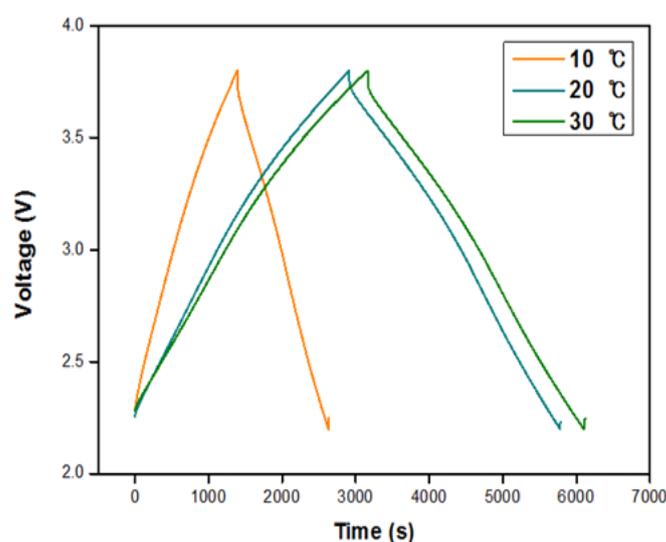


Fig. 8. Charge discharge profile of the LIC with various temperature

## VI. CONCLUSION

Pre-doping is essential for the fabrication of lithium-ion capacitors. Various pre-doping methods have been proposed, but electrochemical pre-doping has the advantages of forming a stable solid electrolyte interface and enabling uniform doping. In this study, activated carbon MSP-20 and artificial graphite MAGE-E3 were

used as electrode materials for electrochemical pre-doping. The experimental results showed that electrochemical lithium doping increased the amount of lithium inserted into the electrode at a low current for a long duration, as confirmed by ICP analysis. The amount increased by 30.9% when doping at 0.5 mA/cm<sup>2</sup> compared to 1 mA/cm<sup>2</sup>. Pre-doping at different temperatures resulted in a capacity of 2.1 F at 10°C, 2.4 F at 20°C, and 2.9 F at 30°C. The capacity showed a similar trend to the results of cyclic voltammetry and charge-discharge experiments.

#### ACKNOWLEDGEMENTS

This work was supported by the Technology Innovation Program (20014576 & RS-2022-00155791) funded by the Ministry of Trade, Industry & Energy.

#### REFERENCES

- [1]. L. Lu, X. Han, J. Li, J. Hua, and M. Ouyang, A review on the key issues for lithium-ion battery management in electric vehicles, *J. Power Sources*, 226-272, 2013.
- [2]. Q. Wang, P. Ping, X. Zhao, G. Chu, J. Sun, and C. Chen, Thermal runaway caused fire and explosion of lithium ion battery, *J. Power Sources*, 208-210, 2012.
- [3]. A. Payman, S. Pierfederici, F. Meibody Tabar, "Energy control of super capacitor/fuel cell hybrid power source", *energy conversion and management*, 49, 1637-1644, 2008.
- [4]. J. Wang, Y. L. Xu, X. Chen, X. F. Du, "Electrochemical supercapacitor electrode material based on poly (3,4-ethylenedioxythiophen)/poly pyrrole composite", *J. Power Source*, 163, 1120-1125, 2007.
- [5]. Do-Hyun Kim, "Preparation and characterization of Non-aqueous Super- capacitor by using Lithium Metal Oxide /Carbon Composite Electrode" Chung-ang University, 2008.
- [6]. M. Endo, T. Takeda, Y. H. Kim, K. Koshiba, K. Ishii, "High power electric double layer capacitor from operating principle to pore size control in advanced activated carbons", *J. Carbon Science*, 1, 117 2001.
- [7]. S.R. Sivakkumar, A.G. Pandolfo, "Evaluation of lithium-ion capacitors assembled with pre-lithiated graphite anode and activated carbon cathode", *Vol 65, 30, 280-287*, 2012.
- [8]. Soo-Jin Park, Byung-Joo Kim "Carbon materials for Electrochemical capacitors" *Carbon science*, Vol 6, No 4, 2005.
- [9]. J. Jurewicz, R. Pietrzak, P. Nowicki, H. Wachowska, "Capacitance behaviour of brown coal based active carbon modified through chemical reaction with urea", *Electrochem. Acta*, 53, 5469-5475, 2008.
- [10]. Young-In Choi, "High energy density hybrid capacitor using chemical activation method" Chung-buk University, 2013.
- [11]. V. Ruiz, C. Blanco, E. Raymundo-Pinero, V. Khomeiko, " Effects of thermal treatment of activated carbon on the electrochemical behavior in supercapacitor", *Electrochimica Acta*, 52, 4969, 2007.
- [12]. Jeong Eun Choi, Ga Yeong Bae, Jeong Min Yang and Jong Dae Le "The Electrochemical Characteristics of Hybrid Capacitor Prepared by Chemical Activation of NaOH", *Korean Chem. Eng. Res.* Vol 51, 308-312, 2013.
- [13]. Hidetaka Konno, Takashi Kasashima, Kazuhisa Azumi, "Application of Si-C-O glass-like compounds as negative electrode materials for lithium hybrid capacitors", *Vol 191, Issue 2, 623-627*, 2009.
- [14]. W. Xinga, S.Z. Qiao, R.G. Ding, F. Li, G.Q. Lu, Z.F. Yan, H.M. Cheng "Superior electric double layer capacitors using ordered mesoporous carbons", *Vol 44, Issue 2, 216-224*, 2006.
- [15]. Ryegyeong Oh, Jungeui Hong, Wongeun Yang, and Kwangsun Ryu, "Study of Lithium Ion Capacitors Using Carbonaceous Electrode Utilized for Anode in Lithium Ion Batteries", *Appl. Chem. Eng.*, Vol 24, No 5, 489-493, 2013.
- [16]. Wang F, Wang B Li J, Wang B, Zhou Y, Wang D, Liu H, Dou S, "Preolithiation: A Crucial Strategy for Boosting the Practical Application of Next-Generation Lithium Ion Battery", *ACS Nano*, Vol 15 (2), 2197-2218, 2021.