Enhanced Salt-removal Percentage in Capacitive Deionization of NaCl Solutions with Modified Activated Carbon Electrodes by HNO₃

Diani Ainun Nisa and Endarko
Department of Physics, Institut Teknologi Sepuluh Nopember
Jl. Arif Rachman Hakim, Sukolilo Surabaya (60111), Indonesia
endarko@physics.its.ac.id

Abstract. Carbon electrodes for desalination system have successfully been synthesized with and/or without modified activated carbon by chemically activated using HNO₃. The freezing-thawing method was used to synthesize the carbon electrodes. In this study, 5 cycles of freezing-thawing were applied in the synthesized carbon electrodes (1 cycle is 12 hours for freezing and 6 hours for thawing). Electrochemical properties of the synthesized carbon electrodes with and/or without modified activated carbon were characterized and observed by cyclic voltammetry (CV) and Electrical impedance spectroscopy (EIS). The salt-removal percentage experiments were conducted to evaluate the performance of capacitive deionization (CDI) cell using the two pairs of carbon electrodes with each pair consisting of two parallel electrodes that separated by a spacer. The result showed that the salt removal percentage of the carbon electrodes with modified activated carbon has greater than the carbon electrodes without modified activated carbon, with reduction level at 55.7 and 24.8%, respectively.

1. Introduction
Global warming is tied to our huge demand for energy and the consequent burning of fossil fuels. Furthermore, energy and water are also related. Energy is needed to deliver water and water is needed to generate energy. Indeed, one does not site a nuclear power plant in the middle of the desert but rather near a major water body such as a river, lake or the sea. By the same token, we are likely, not able to produce energy such as bio-fuels without a sufficient supply of water [7]. On the other hand, we need large quantities of energy to desalinate seawater for potable use. The scarcity of clean water is often hit several parts of the world due to the dry season and pollution of water resources. The challenge to solve this problem is to convert seawater and brackish water into clean water. Researchers have been conducted to meet the needs of fresh water using brackish water and sea water as a source of fresh water. Desalination process for getting fresh water from seawater has been growing rapidly in several developed countries [3].

Many methods that have been developed for desalinating of seawater such as Multi-Stage Flash (MSF) and Reverse Osmosis (RO). According to energy consume RO system is suitable for processing with low energy while MSF system needs high energy. Despite energy consume in the RO is low, but the cost production for RO desalination system is still expensive. For the reason, capacitive deionization (CDI) is one of the technologies that can be applied to the desalination process of brackish water and seawater [8].
Capacitive deionization (CDI) is a method for removing salt from aqueous solutions through an electrochemically controlled by an external power supply. The significant factor of an electrode in the CDI cell is when the electrode has a high specific surface area regarding the electrosorption process quantitative and attractive for water treatment [1]. The performance of CDI largely depends on the physical and structural properties of the electrode materials. An ideal electrode should have excellent electrical conductivity for effective charge holding, a high specific surface area for ionic accumulation, suitable pore size, and networks for easy ionic motions as well as good electrolyte wettability. Currently, most of the electrodes for CDI are made of different carbon materials including activated carbons, carbon aerogel, ordered mesoporous carbon and carbon nanotubes [4].

In the present work, the carbon electrodes will be synthesized using freezing-thawing method for CDI cell with or without modified activated carbon. The electrochemical properties and surface morphology are measured and observed to show the performance of the carbon electrode. Furthermore, the molecular bonds contained in active carbon with and without modified are also analyzed. Desalination experiments to determine the desalting performance of CDI cell will also be studied using NaCl solution.

2. Material and Methods

2.1 Materials

The materials used in this study namely nitric acid (60% HNO₃), polyvinyl alcohol (PVA) (Merck Co.), aquades, graphite sheet as a current collector, and activated carbon.

2.2 Fabrication of carbon electrode

Carbon electrodes were prepared with unmodified carbon and modified carbon (adding nitric acid 60% to the mixture) using the freezing-thawing method. 1 g of polyvinyl alcohol (PVA) and 100 mL distilled water at 100 °C were placed on a magnetic stirrer and was then stirred for 1 hour. Subsequently, the mixture was added with 20 g of activated carbon powder and was then stirred for 20 mins. Afterward, the paste was coated onto graphite sheet with a size of 6×8 cm² and was then dried at room temperature. Furthermore, the dried carbon electrodes were placed in the freezer at -14°C for freezing process (12 h). Two variations of the time for thawing process (at 30°C) namely 6 and 12 h were used in this study. The carbon electrodes were synthesized by a freezing-thawing method with 3, 4 and 5 cycles.

2.3 Characterization of carbon electrode

Scanning Electron Microscopy (SEM) FEI-Inspect S25-EDAX was used to characterize the morphology of the carbon electrodes. Hereafter, Cyclic Voltammetry (CV) and Electrical Impedance Spectroscopy (EIS) (Autolab PG-Stat 302 Methrom) were used to investigate the electrochemical properties of the carbon electrodes. EIS was performed using three electrodes method in 0.5 M KCl solution. CV measurement was conducted with the voltage spans from -0.5 – 0.5 V (vs. Ag/AgCl) at 10 mV/s for 10 cycles whereas EIS is performed with frequency in the range of 0.01-10 Hz at 10 mV peak to peak.

2.4 Desalination System of Capacitive Deionization

Desalting performance has been optimized by passing a solution of 0.0025 M NaCl. The conductivity and salinity measurements were then conducted using a salinity meter and conductivity meter in the initial condition of the salt solution and after it passed from the CDI system. Desalination efficiency can be calculated according to the following equation [7]:

\[
\text{Desalination efficiency} = \frac{C_0 - C_t}{C_0} \times 100\%
\]

where \(C_0\) and \(C_t\) are initials for initial conductivity and conductivity at each duration \(t\).
3. Result and Discussion

3.1 Carbon Analysis by FTIR Test

The Activated carbon adsorption capacity is not only determined by the pore structure but also influenced by the chemical nature of the surface. Properties of activated carbon surface chemistry can be selectively modified with the aim to further enhance the adsorption capacity. Results of activated carbon modified by HNO$_3$ can be seen through the test FTIR.

Fourier transform infrared spectroscopy (FTIR) is a technique which is used to obtain an infrared spectrum of absorption or emission of a solid, liquid or gas. An FTIR spectrometer simultaneously collects high spectral resolution data over a wide spectral range. This confers a significant advantage over a dispersive spectrometer which measures intensity over a narrow range of wavelengths at a time.

![Figure 1. The frequency spectrum of modified and unmodified carbon by FTIR test.](image)

FTIR testing aims to determine the molecular bonds (force element) which is in active carbon. On activated carbon modified by an additional functional group that is the wave number 1058.58 cm$^{-1}$. The wave numbers indicate a functional group ether (C-O). So that the activated carbon modification has two functional groups which aromatic groups (C=C) and the functional group ether (C-O). The addition of oxygen-containing groups can increase uptake is possible to increase the value of the capacitive electrochemical. Based on research conducted by Gokce and Over in 2014 increased the carboxylic group can increase the adsorption methylene liquid blue and phenol for carboxylic group adding electrostatic interactions on the surface of the carbon decisive role in the adsorption process [6].
3.2 Carbon Electrode Morphology

Scanning Electron Microscopy (SEM), also known as SEM analysis or SEM microscopy, is used very effectively in microanalysis and failure analysis of solid inorganic materials. Scanning electron microscopy is performed at high magnifications, generates high-resolution images and precisely measures very small features and objects. The composition of the carbon electrodes was measured and characterized by Scanning Electron Microscopy coupled with Energy Dispersive X-ray (SEM/EDX). SEM cannot determine the composition of the observed carbon electrode.

Figure 2 shows the composition of the carbon electrode structure which measured by SEM/EDX. It can be analyzed that the cycle variation does not influence the composition of the carbon electrodes.

**Figure 2.** SEM image of modified electrode was fabricated for 5 Cycles.

![Figure 2. SEM image of modified electrode was fabricated for 5 Cycles.](image)

**Figure 3.** SEM image of unmodified electrode was fabricated for 5 Cycles.

Freezing-thawing process on the fabrication of carbon electrodes resulted in gelation process, so that made a strong electrode and insoluble in water. In the freezing process, the solvent will freeze and form crystals along microphase of solute carbon [6] PVA which is not frozen because of the concentration of the liquid becomes very small so that the concentration of gel increases triggered gel formation. When it freezes, solvents crystal is grown to touch the outer portion of the crystal to another, so that after melting the interconnection system of porous appears in gels. Gelation can be occurred at any phase of the process of freezing – thawing [7]. When melted, the surface tension between the liquid solvent and the gel phase causing carbon coarse pores arranged. Conversion
between spongy cryogels and non-spongy relies on freezing, the concentration and composition of solute [6].

Figure 3 shows the elements of the carbon electrode in the unit (%). The result showed that around 70% the electrode is formed by carbon and 20% from oxygen and less than 1% from K, Si, Ca, Na and Fe.

3.3 Electrochemical Properties of Carbon Electrode

Besides the physical characterization, the carbon electrodes are also characterized by the electrochemical property. The electrochemical properties were characterized by CV and EIS. Cyclic voltammetry or CV is a type of potentiodynamic electrochemical measurement. In a cyclic voltammetry experiment, the working electrode potential is ramped linearly versus time. Unlike in linear sweep voltammetry, after the set potential is reached in a CV experiment, the working electrode's potential is ramped in the opposite direction to return to the initial potential. These cycles of ramps in potential may be repeated as many times as desired. The current at the working electrode is plotted versus the applied voltage (i.e., the working electrode's potential) to give the cyclic voltammogram trace. Cyclic voltammetry is generally used to study the electrochemical properties of an analyte in solution. CV measurement was performed with the voltage ranging from 0.5 – 0.5 V (vs. Ag/AgCl) at a scan rate of 10 mV/s for 10 cycles whereas EIS is carried out in the frequency range of 0.01-100,000 Hz at a signal amplitude of 10 mV peak to peak. CV test results for carbon electrode modification and without modification is shown in Figure 4.
Based on data from CV curves in Fig. 4, value of capacitance of carbon electrodes can be calculated using equation as follows [7]:

\[ C = \int \frac{dq}{dV} = \int \frac{dt}{dv} = \frac{I}{v} \]  

where \( q \) is a charge (C), \( V \) is the potential difference (V), \( I \) is intensity (A), \( t \) is time (s) and \( v \) is scan rate (V/s). Meanwhile, the value of specific capacitance can be calculated with equation (2) divided by mass of the carbon powder. From Figure 4 shows that the modified carbon electrodes have the largest area compared to the unmodified carbon electrode. The specific capacitance for both the carbon electrodes with and/or without modification which are synthesized by the freezing-thawing at 5 cycles can be calculated at 26.78 and 22.77 F/g, respectively. Voltammogram curve of the carbon electrode is ideally a rectangular-shaped [5] which shows the flow reduction and oxidation are clear and stable. The CV curve in this study showed the approaching the rectangular-shaped as shown in Fig. 4. It indicates that the carbon electrodes have a potential for CDI cell application. The greater the value of the electrode capacitance possessed the greater the ability of the electrode to reduce salt because salt ions more easily attracted and retained on the electrode surface. The greater the value of the electrode capacitance possessed the greater the ability of the electrode to reduce salt because salt ions more easily attracted and retained on the electrode surface [5]

The EIS test was used to determine the kinetics of electrochemical parameters related to electrical quantities such as capacitance, resistance, and inductance. Electrical impedance is the measure of the opposition that a circuit presents to a current when a voltage is applied. Based on the CV measurement, the carbon electrodes which is synthesized with 5 cycles using freezing-thawing method could potentially be used as an electrode for CDI cell, so that the EIS measurement only is done for it. EIS measurement was carried out for its ability to distinguish resistance from capacitance. Hereinafter, the specific capacitance can be calculated using equation as follows [8]

\[ C = \left| \frac{1}{\omega Z'} \right| \]  

---

**Figure 5.** CV curve of carbon electrodes for unmodified carbon and modified carbon for 5 cycles.
Where $\omega$ is the angular frequency of alternating current (AC) signal and $Z''$ is the imaginary impedance data. EIS curve for the carbon electrode is shown in Fig 5. It can be analyzed that the largest specific capacitance using equation 2.

![Graph showing specific capacitance vs frequency for modified and unmodified activated carbon](image.png)

**Figure 6.** Specific capacitance to frequency chart on modified and unmodified carbon.

In addition to determining the nature of capacitive and resistive electrodes, EIS test can determine the value of the electrode capacitance. From Figure 5, it can be seen that the greatest value of specific capacitance measured at 9.25 F/g at 0.01 Hz frequency for modified electrode. Meanwhile, the electrodes without modification only at 2.78 F/g. The capacitance value is obtained using the equation 2. Specific capacitance value decreases with increasing frequency and constant at high frequencies; this is because the low-frequency current is applied, the electron transfer is not disturbed by the frequency [7]

3.4 Desalination performance of capacitive deionization

To evaluate the salt removal performance of the carbon electrodes, 596 $\mu$S/cm NaCl solution was pumped to the CDI cell with flow rate at 25 mL/min. The two pairs of carbon electrodes were constructed to CDI unit cell with each pairs consisted of two parallel electrodes separated by a spacer. The salt removal experiments consisted of two steps namely is desalination (adsorption) and regeneration (desorption). Desalination process was applied a cell potential of 2 V for 1 hour and 4000 sample data.
Figure 7. Graphic adsorption and desorption of processes in the CDI system for modified and unmodified carbon 5 cycle.

Fig. 7 shows the desalination process and regeneration process for CDI cell with modified carbon electrode using freezing thawing 5 cycles. After that, the salt-removal percentage can be calculated using equation as follows [9]:

\[ \% \Delta \text{Salt} = \frac{\sigma_f - \sigma_p}{\sigma_f} \times 100\% \]  

(4)

where \( \sigma_f \) is the initial conductivity (\( \mu S/cm \)) and \( \sigma_p \) is the final conductivity (\( \mu S/cm \)). Finally, It can be deduced from figure that the greatest value of salt-removal percentage was achieved at 55.70 % when the solution flowed to the CDI cell with the modified carbon prepared with freezing-thawing for 5 cycles. The salt removal value of unmodified carbon 5 cycle was achieved at 24.80 %. It shows that modified carbon more efficience than unmodified carbon 5 cycle.

4. Conclusion
A desalination system with stack-type CDI method has been successfully fabricated. Desalination process is performed at 0.0025 M NaCl solution. The result showed that the salt removal percentage of the carbon electrodes with modified activated carbon has greater than the carbon electrodes without modified activated carbon, with reduction level at 55.7 and 24.8 %. It showed that the most of NaCl ions adsorbed by carbon electrodes. Characterization and optimization of the results of the CDI system acquired good results so that the system is highly prospective to be developed into a desalination system to produce fresh water.

5. References
[1] Y. Oren 2008 Capacitive deionization (CDI) for desalination and water treatment — past, present and future (a review) Desalination, 228 (1–3) 10–29
[2] C.-H. Hou, J.-F. Huang, H.-R. Lin, and B.-Y. Wang 2012 Preparation of activated carbon sheet electrode assisted electrosorption process J. Taiwan Inst. Chem. Eng 43(3) 473–479
[3] M. A. Anderson, A. L. Cudero, and J. Palma 2012 Capacitive deionization as an electrochemical means of saving energy and delivering clean water. Comparison to present desalination practices: Will it compete? Electrochimica Acta 55 (12) 3845–3856
[4] B. Jia and L. Zou, Graphene nanosheets reduced by a multi-step process as high-performance electrode material for capacitive deionisation 2012 Carbon 50 (6) 2315–2321
[5] Nadakatti S, Tendulkar M, Kadam M. 2011 Desalination 268 182–188
[6] N. E. Vrana 2009 *Use of Poly Vinyl Alcohol (PVA) Cryogelation for Tissue Engineering: Composites, Scaffold Formation and Cell Encapsulation*. (School of Mechanical and Manufacturing Engineering - Dublin City University, Ireland).

[7] Li Haibo 2010 *Separ. Purif. Technol.* **75** 8–14

[8] Park B-H, Kim Y-J, Park J-S, Choi J 2011 *J Ind Eng Chem.* **17** 717–722

[8] Endarko, I. Fatimah and I.P. Sari 2016 *Measurements of the salt-removal of NaCl, KCl and MgCl using a carbon electrode prepared with freezing thawing method in capacitive deionization* by AIP Conference Proceedings **1725**, 020015

[9] Endarko and I.P. Sari 2016 *Enhanced salt-removal percentage in capacitive deionization with addition of ionexchange membrane using carbon electrode synthesized with freezing thawing method*. by AIP Conference Proceedings **1725** 6