CAPACITIVE DEIONIZATION (CDI): AN ENVIRONMENTALLY FRIENDLY WATER PURIFICATION TECHNIQUE

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Abstract: A porous carbon electrode for capacitive deionization was prepared by a simple screen printing technique. Polymeric binder suspension was utilized to form a solid activated carbon-based electrode. The prepared carbon electrode electrochemical property and specific capacitance were analyzed using a three-electrode cyclic voltammetry system. The specific capacitance of the developed electrode was almost identical even at various set scan rate and NaCl solution concentration, an indication of the electrode having constant ion adsorption capacity. Thus validated the experimental results, which **c**learly showed that the ion adsorption capacity of the fabricated electrode presents slight difference at different NaCl solution concentrations, wherein the highest ion adsorption capacity of 6.2 mg/g was achieved in 818 mg/L NaCl solution initial concentration.

Keywords: *capactive deionization, water purification, carbon electrode, cyclic voltammetry*

1. INTRODUCTION

The effects of global warming have been instigating devastation to the environment and to society. Drought or El Niño season is taking longer time than its usual period especially in the tropical region, thus causing lesser food production and economic fluctuations. The increasing shortage of clean water has become more challenging as it threatens food supply and industrialization (Bian *et al.*, 2015). Other serious issues include rapid population growth and water pollution. All these stimulated scientists and engineers to develop desalination technologies using seawater and brackish water for industrial and human consumption (Chang *et al.*, 2015). Of late, several water purification technologies such as reverse osmosis, multi-stage flash distillation, electrodialysis and membrane processes are being improved for higher production of clean fresh water; however, aside from their drawbacks these techniques are incommensurate in terms of alleviating such global water scarcity (Dong *et al.*, 2015). Therefore, it is timely to introduce an alternative eco-friendly water purification technique to decrease the global water shortage.

Although it is still in its infancy, capacitive deionization (CDI) with accompanying energy regeneration by charge sequestering has the potential to resolve both water and energy shortages (Park *et al.*, 2007; Andreson *et al.*, 2010). Figure 1 demonstrates the principle of capacitive deionization. CDI is a potential induced system in which a positively and negatively charged electrode adsorbs negative and positive ions, respectively. The adsorption of ions at the electrode surface utilizes the principle of electric double layer theory (Farmer *et al.*, 1995), wherein the ions from the ionic liquid are adsorbed due to coulombic interaction rather than electrochemical reaction (Oh *et al.*, 2006). Once the electrode reaches its maximum adsorption capacity and the electrode pores are saturated with ions, the adsorbed ions can be regenerated by simply reversing the applied current or short-circuiting the parallel electrodes. One of the key advantages in CDI is that the stored energy at the electrodes that are electrically charged can be reused for another process in an optimized energy recovery system. CDI is environmentally friendly because there is no need to use chemicals during regeneration. This technique is a simple and nearly maintenance-free system. Furthermore, by utilizing the energy recovery system, the running cost in CDI is more cost-effective than reverse osmosis (RO). In fact, the energy needed to desalinate seawater in RO is 3.5 to 2.5 kWh/m^3 with < 30 to 40% water recovery, whereas in CDI, it is only 2 to 1 kWh/m^3 with > 80 to 90% water and energy recovery. Thus, CDI is three times more economical than RO for the treatment of 1 million gallons per day of brackish water (Welgemoed and Schutte, 2005).

In this paper, activated charcoal-based electrode was made, and its electrochemical properties were evaluated using cyclic voltammetry (CV) analysis. The ion adsorption/desorption performance of the fabricated CDI cell equipped with a pair of developed electrode was carried out in a NaCl solution with various concentrations.

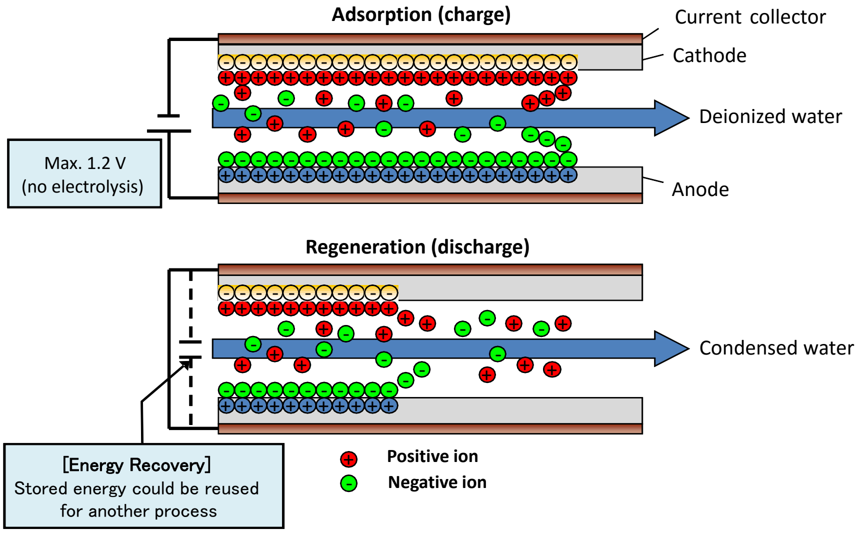


Figure 1. Capacitive deionization and electrode regeneration process.

2. METHODOLOGY

2.1 Fabrication of activated charcoal electrodes

The carbon electrodes were fabricated by mixing activated charcoal powder (ACP, Dainen Corp., Japan, specific surface area = 1,964 m^2/g), conductive carbon black (CCB, Nippon Graphite Industries Ltd., Japan, SP-270, average particle size = 4 μm, BET surface area = 250 m^2/g), polyvinyl-alcohol (PVA), and N-methyl-2-pyrrolidone (NMP, Nacalai Tesque, Inc., Japan, 99.5%). PVA and NMP were used as the polymeric binder and organic solvent, respectively. The screen printing technique was performed by directly pouring the slurry on a screen to form a solid activated charcoal electrode. These electrodes were dried at room temperature for 24 h, followed by subsequent drying for several hours at 50 °C in a constant temperature oven to evaporate all organic solvents in the electrode pores. The amount and thickness of the dried electrode were then measured. The optimum composition of the electrode was 75% ACP: 10% CCB: 15% PVA mainly due to its high mechanical stability (Andres *et al.*, 2014).

2.2 Cyclic voltammetry analysis

Figure 2 illustrates the experimental set-up and schematic set-up of a three-electrode system when conducting a cyclic voltammetry (CV) analysis. The electrochemical properties of the fabricated electrodes were characterized by three-electrode CV measurement using a potentiostat (HAL 3001, Hokuto Denco, Japan) at 10 mV/s, 5 mV/s and 1 mV/s potential scan speed in 0.5 mol/L and 0.05 mol/L NaCl solution concentrations at 25 ºC by keeping the potential scan speed to 1/(dV/dt) constant, the capacitance (C) can be directly calculated as follows:

$$C=\frac{1}{m\upsilon(V_F-V_{R.P})}\int_{R.P}^{F} IdV \qquad (1)$$

where C (F/g) is the specific capacitance of the carbon electrode, I (A) is the current, $V_{R.P}$ (V) is the rest potential of the electrode and V_F (V) the maximum potential set for CV tests, υ (V/s) is the potential scan rate, and m (g) is weight of the electrode including the binder and CCB after drying (Tian *et al.*, 2015).

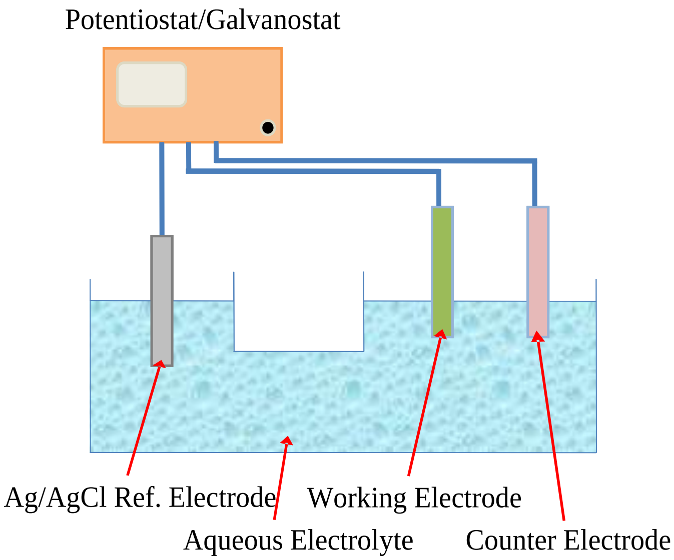


Figure 2. Cyclic voltammetry schematic set-up of a three-electrode system.

The charge efficiency (Λ) was calculated during the ion adsorption process to measure the ions adsorbed on the electrodes through electric double layer interaction (Liu *et al.*, 2015), as described based on the following equation:

$$\Lambda = \frac{\Gamma \times F}{\Sigma} \qquad (2)$$

where F is the Faraday constant (96,485 C/mol), Γ is the ion adsorbed capacity (mol/g) and Σ (charge, C/g) was obtained by integrating the corresponding current.

2.3 Ion adsorption/desorption performance

The system structure of the capacitive deionizer was assembled having asymmetrical capacities with a δanode: δcathode thickness ratio of 2:1 as illustrated in Figure 3.

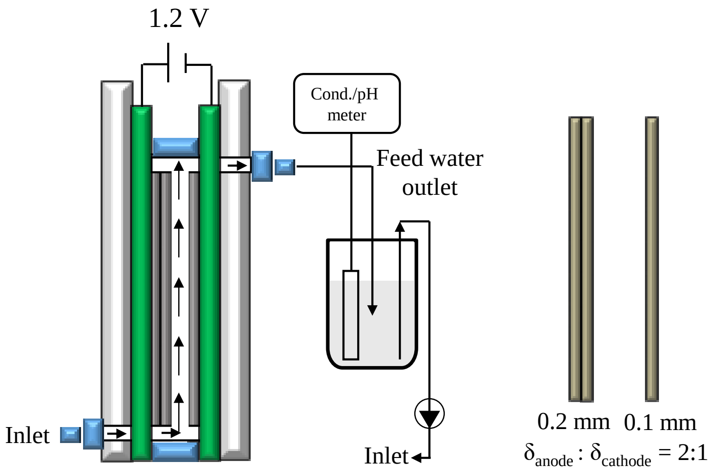


Figure 3. Capacitive deionization flow-process experimental set-up. Electrode pair with asymmetrical capacity.

The apparent amount of the φanode: φcathode were 0.47 g: 0.23 g. The ion adsorption/desorption performance of the CDI was carried out in a continuous flow-through process using the prepared NaCl solution with initial ion conductivity range 0.7 to 5 mS/cm. The 150 mL of feed water was constantly flowing using a tube pump with a constant flow rate of 20 mL/min, whilst the changes of ion conductivity was measured using an online ion conductivity probe (pH/conductivity meter, Laqua F-74, HORIBA, Japan) with an interval time of 2 s. For the analysis of electrode ion adsorption capacity, (Q_e) is defined as follows:

$$Q_e = \frac{(C_i - C_f) \times V}{m} \qquad (3)$$

where C_i and C_f represent the initial and final NaCl concentration (mg/L), respectively, and V is the total amount of the feed solution flowing within the CDI cell in liters (L), and m is the total weight of the activated charcoal electrode in grams (g).

3. RESULTS AND DISCUSSION

3.1 Cyclic voltammetry analysis

Analysis with cyclic voltammetry is an accurate tool to characterize the electrosorption capacity and electrochemical property of carbon electrode, since it follows the same working principle of the electric double-layer by charge separation (Hou *et al.*, 2013). Figure 4 presents the cyclic voltammographs obtained in scan rates of 1, 5 and 10 mV/s for 0.5 and 0.05 mol/L NaCl solutions. The summary of the specific capacitance measurements are shown in Table 1. It can be clearly observed that the cyclic voltammographs in Figure 4(a) using high NaCl concentration electrolyte solution showed good electric double layer characteristics, which close to a rectangular shape. On the other hand, the cyclic voltammographs in low NaCl concentration in Figure 4(b) exhibited slight distortion in particular at 1 mV/s scan rate. These changes of CV characteristics are largely because of the resistance of the liquid electrolyte rather than electrode resistance, wherein low NaCl solution may not be suitable when evaluating the electrochemical characteristics of the electrode. Moreover, Table 1 shows the summary of the specific capacitance and electrical charge during deionization process calculated using equation 1 and 2. The specific capacitance of the electrode varies with scan rate and NaCl solution concentration; however, the average specific capacitances were almost equal, indication of the electrode having constant ion adsorption capacity. The absence of any significant oxidation/reduction peaks in the cyclic voltammographs for both high and low concentration NaCl solutions elucidate ideal behavior of electrochemical double-layer capacitance and highly reversible electrosorption process (El-Deen *et al.,* 2015).

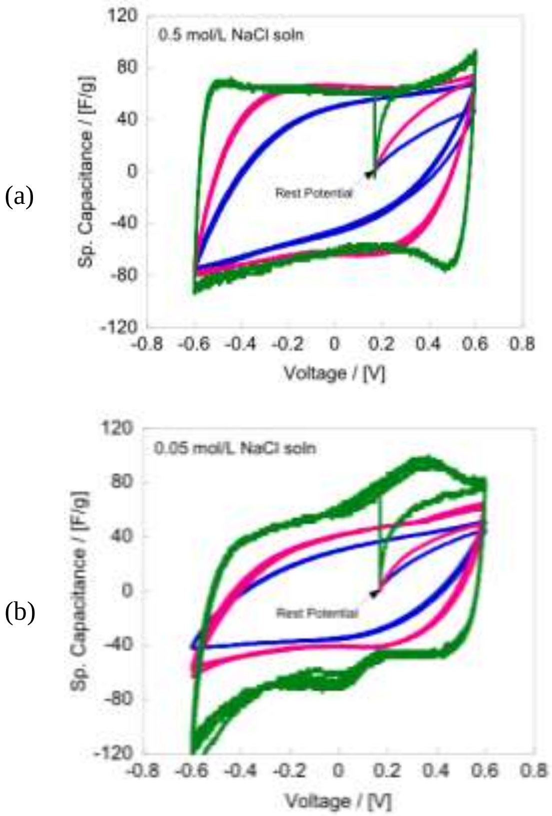


Figure 4. Cyclic voltammographs of the prepared electrode at scan rates of 1, 5 and 10 mV/sec (from outside to inside) in (a) 0.5 mol/L and (b) 0.05 mol/L NaCl.

3.2 Ion adsorption/desorption performance

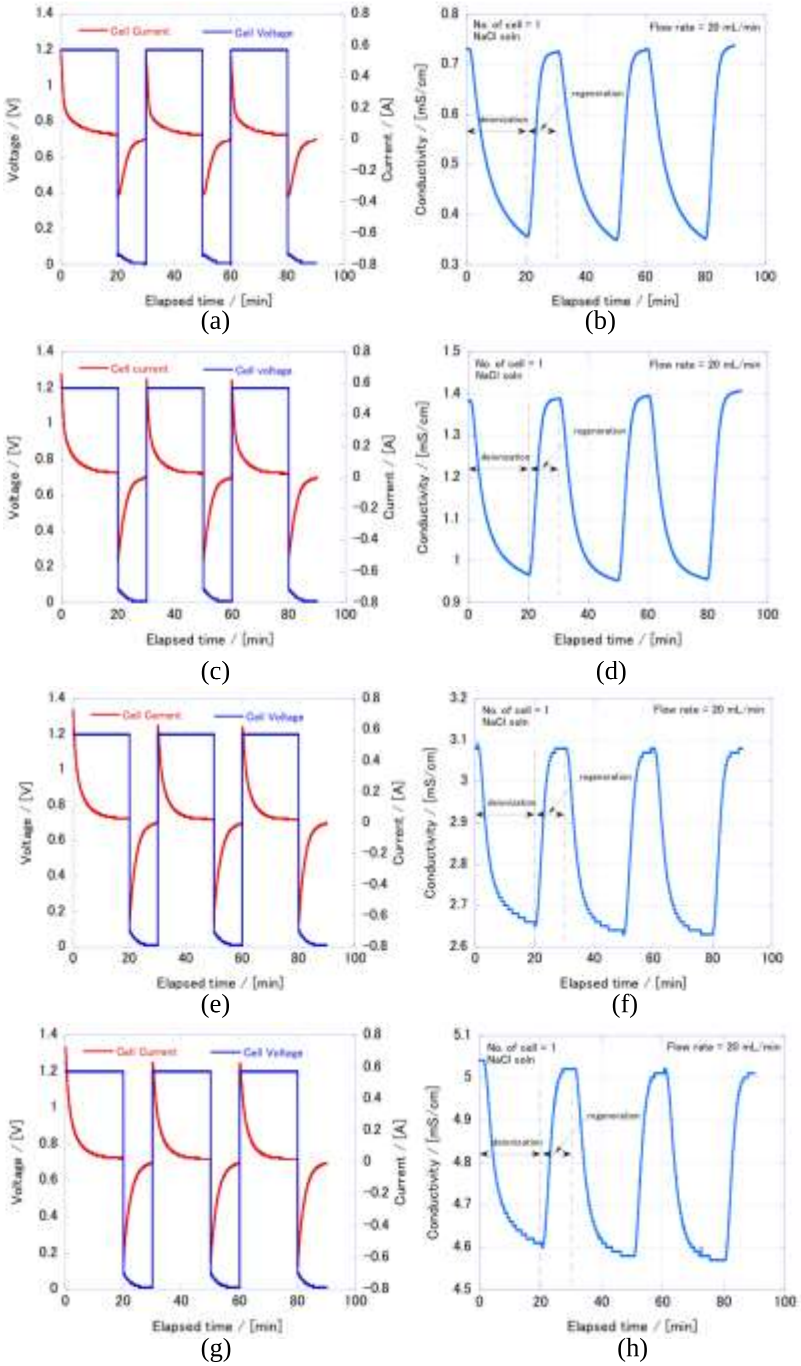
In order to further evaluate the ion adsorption/desorption performance of the developed electrode, comparative ion adsorption/desorption experiments were executed using different NaCl solution concentrations such as: 426 mg/L (0.730 mS/cm), 818 mg/L (1.40 mS/cm), 1,750 mg/L (3.08 mS/cm), and 2,922 mg/L (5.04 mS/cm) at 1.2 V. Figure 5 presents the voltage-current profiles and ion adsorption/desorption performances of the electrode at various NaCl solution concentrations. And the results of these experiments were summarized in Table 2. Clearly, the ion adsorption performance of the fabricated electrode shows slight difference in ion adsorption capacity at different NaCl solution concentrations, wherein the highest ion adsorption capacity of 6.2 mg/g was achieved in 818 mg/L NaCl solution initial concentration. The charge efficiency normally indicates a lower value than the ideal, mainly caused by the electrode contact resistance with the current collector in addition to the blocking effect of the polymeric binder (Liu *et al.*, 2015). Although the 68% charge efficiency was obtained in 818 mg/L NaCl solution initial concentration, the difference was minimal compared to other NaCl solution concentrations, indicative of a constant ion adsorption capacity of the electrode.

Table 1. Capacitance evaluation of the ACP electrode by CV analysis.

	Sp. Capacitance [F/g]		Charge [Coulomb]	
Scan rate [mV/sec]	0.5 mol/L	0.05 mol/L	0.5 mol/L	0.05 mol/L
10	15	27	62	60
5	45	30	91	70
1	64	62	130	126
AVERAGE	41	40	94	85

Table 2. Ion adsorption characteristics of the ACP electrode.

Initial NaCl conc. [mg/L]	Ion adsorption capacity [mg/g]	Coulomb efficiency [%]
426	5.28	64
818	6.20	68
1,750	6.00	64
2,922	6.10	62



(a) (b)

(c) (d)

(e) (f)

(g) (h)

Figure 5. Ion adsorption performance of the electrodes at various NaCl solution concentrations, such as 0.730 mS/cm (426 mg/L), 1.40 mS/cm (818 mg/L), 3.08 mS/cm (1,750 mg/L), and 5.04 mS/cm (2,922 mg/L) at 1.2 V.

To be able to know the competitiveness of this study, the comparative results with regards to the amount of ion adsorption capacity using various electrode materials were summarized in Table 3. In this study, the obtained ion adsorption capacities using various NaCl solution concentrations was very interesting because of its consistency. And compared to many reported electrode materials which uses complicated method of electrode fabrication, the ion adsorption capacity in this study is strongly considerable. Thus, this ideal result could be used as a guide when fabricating CDI module with respect to specific use; for instance, for low and high concentration aqueous electrolytes.

4. CONCLUSIONS

It is known that the electrosorption efficiency of the electrode in capacitive deionization process is directly related to the electro-chemical characteristics of the electrode material and the electrolyte solution concentration. In this paper, the electrochemical property of the developed electrode was characterized by a three-electrode cyclic voltammetry at different NaCl concentrations. The results indicate that utilizing higher concentration liquid electrolyte can provide clearer characteristics of the electrode. Moreover, various NaCl solution concentrations were used as liquid electrolyte to realize the ion adsorption and desorption efficiency of the carbon electrode. Thus, experimental results demonstrated that the ion adsorption capacity and charge efficiency of the CDI system equipped with the developed carbon electrode were almost identical, an indication of performance consistency. This result also means that all effective areas of the carbon electrode can be utilized without electrochemical reaction.

Table 3. Comparison of the capacitive deionization performance on various electrodes.

Original material	Initial NaCl conc. [mg/L]	Operation voltage [V]	Ion adsorption capacity [mg/g]	Reference
GO-PCNF	100	1.2	7.8	Bai *et al.*, 2014
PCNF	100	1.2	5.9	Bai *et al.*, 2014
GO-PCNF	450	1.2	13.2	Bai *et al.*, 2014
PCNF	450	1.2	9.4	Bai *et al.*, 2014
ACP	600	1.2	4.2	Y.Zhao *et al.*, 2014
ACP	1000	1.2	8.6	Y.Zhao *et al.*, 2014
ACP	600	1.6	7.5	Y.Zhao *et al.*, 2014
PCS1000	500	1.6	5.8	Y.Liu *et al.*, 2015
ACNF	500	1.6	10.5	J.Liu *et al.*, 2014
CNT/ACNF	400	1.2	6.4	Q.Dong *et al.*, 2015
ACP	426	1.2	5.3	This study
ACP	818	1.2	6.2	This study
ACP	1,750	1.2	6.0	This study
ACP	2,922	1.2	6.1	This study

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