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Electrochemical softening using capacitive deionization (CDI) with zeolite modified carbon electrode (ZMCE)

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ABSTRACT

Divalent ions such as calcium and magnesium ions are thought to cause hardness in water inducing scale problems in the pipelines of boilers and heat exchangers. Thus, water softening has gained wide interest in water treatment technology. Although zeolite particles have been widely used as a material for the removal of divalent ions, its low ion-exchange efficiency based on diffusion-dependent process has limited their applications in water softening. Herein, we report effective electrochemical softening using zeolite with capacitive deionization (CDI), which is a desalination technology with electrochemical ad/desorption in an electric double layer. The carbon electrode with zeolite (denoted as a zeolite modified carbon electrode (ZMCE)) was prepared by the slurry and pasting method with zeolite particles and carbon black. ZMCE exhibited a significantly enhanced efficiency in the removal of divalent ions in softening using the CDI process compared to the normal softening process based on diffusion. This enhanced ion removal efficiency was attributed to the migration force as a result of the electrical energy during CDI operations.

Keywords: Zeolite modified carbon electrode; Calcium and sodium ions; Electrochemical softening; Capacitive deionization (CDI)

1. Introduction

Divalent ions such as calcium and magnesium ions, which cause hardness in water, cause scale problems in the pipelines of boilers and heat exchangers [1,2]. Various methods have been widely used to control scaling. For example, there is the acidification of water, chemical precipitation, ion-exchange resin, and membrane system [3–5]. Although, they are highly efficient in softening, a number of limitations exist such as using harmful chemicals in drinking water and the high operating and maintenance costs for membranes; additionally, ion-exchange resins used in softening need to be highly efficient and cost-effective [2].

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On the other hand, the process using zeolite has been widely used as a useful softening technology due to its low cost and efficient energy consumption [6–9]. Zeolite is known as a material that has a nanoporous structure composed of aluminosilicate [10]. According to the ratio of aluminum to silicon, various types and shapes of zeolite particles including, ZSM-5 and zeolite X and Y have been reported [11–14]. Additionally, they accommodate various cations such as H^+, Na^+, K^+, Ca^{2+}, and Mg^{2+} in the zeolite structure [8,9,15], and they have an excellent ion-exchange property due to the high mobility of the cations in the zeolite structure. Nevertheless, it has low divalent ion removal efficiency due to diffusion-dependant process which has limited its applications in water softening. Thus, it is necessary to enhance the divalent ion removal efficiency using zeolite particles.

Capacitive deionization (CDI), which has emerged as an alternative to conventional ion removal technology [16–21], could be one of the solutions to enhance the divalent ion removal efficiency of zeolites. CDI as a promising ion removal technology uses electrochemical ad/desorption in an electric double layer (EDL), which takes place between oppositely positioned electrodes without a charge transfer reaction. During the operating cycles, charged ions can be captured and expelled during the charging and discharging step on the polarized electrode surface. CDI operations could be repeatedly carried out because of the reversible ad/desorption process. Many researchers have investigated how to enhance the desalination efficiency of CDI in terms of theoretical approaches, reactor design, operation conditions, and electrode material [22,23]. In general, porous carbon materials have been considered as a good candidate for electrode materials because of their high specific surface areas and good electrical conductivities [24–26]. Furthermore, novel kinds of carbon materials (e.g. graphene and carbon nanotube) [27–29], acid/alkali treatments [30] and the addition of organic/inorganic materials [31–33] have been investigated to increase the ion removal efficiency.

In this study, we developed an efficient water softening technology based on a CDI system with a zeolite modified carbon electrode (ZMCE) which was fabricated to overcome the nonconductive property of zeolite. During the softening process, cations are adsorbed on the surface of the ZMCE by forming an EDL, and the divalent ions are captured by the ion-exchange performance of the zeolite. The removal of Ca^{2+} ions in water softening was shown with the ZMCE equipped in a CDI unit cell.

2. Experimental section

2.1. Preparation of the ZMCE and its characterization

The ZMCE was prepared by mixing zeolite (78 wt %, Aldrich Co., USA), carbon black as a conductive material (15 wt%; Super P., TIMCAL Graphite & Carbon, Swiss), and binder (7 wt%; polytetrafluoroethylene (PTFE, Aldrich Co., USA)). Ethanol was selected as the solvent. After forming a homogeneous mixture upon stirring for 1 h, the mixture was rolled to a thickness of 300 μm. The electrode was dried in a vacuum oven at 60˚C for 12 h to evaporate the solvent. A carbon electrode (CE) was prepared without zeolite with the same procedure. Surface analysis of the ZMCE and CE was characterized by scanning electron microscopy (SEM, JSM-6700F, JEOL). To investigate the electrocatalytic activities of the ZMCE and CE, cyclic voltammetry was measured in a three-electrode cell using a potentiostat/galvanostat (PARSTAT 2273A, Princeton Applied Research, USA) in 9 mM $CaCl_2$ (1,000 mg/L) as the base electrolyte. The ZMCE and CE were used as the working/counter electrode (d = 1.8 cm) and Ag/AgCl (saturated KCl) as the reference electrode. Representative results from duplicate or triplicate experiments are shown in this study. The deviation of the results was below 5%.

2.2. Experimental procedure

The spontaneous ion-exchange property of the ZMCE was examined in a batch system (V = 50 mL) without electrical energy. Two ZMCEs (d = 1.8 cm) were soaked in deionization (DI) water and 0.45 mM $CaCl_2$ (50 mg/L); the ion concentration and pH were measured with ion chromatograph (DX-120, DIONEX, USA) and a pH meter (pH and conductivity meter, F-54, Horiba., Japan). The Ca^{2+} ion removal was examined in a CDI unit cell shown in Fig. 1. The CDI unit cell was used to investigate the softening efficiency of the ZMCE (d = 5 cm; 300 μm thickness) as a cathode. Carbon cloth was selected as the counter electrode. A nonconductive nylon cloth (thickness of 200 μm) was selected as a separator between the two parallel electrode sheets in the unit cell. Graphite sheets were installed on the back side of the electrodes as current collectors. Holes (d = 4 mm) were provided on the lower compartment electrode and current collector to create a flow channel. The solution used for the softening test was 0.9 mM $CaCl_2$ (100 mg/L) and supplied to the CDI unit cell from the reservoir (V = 100 mL) by a peristaltic pump with a volumetric flow rate of 10 mL/min. The voltage of the CDI unit cell was controlled with an automatic battery cycler (WBC S3000,

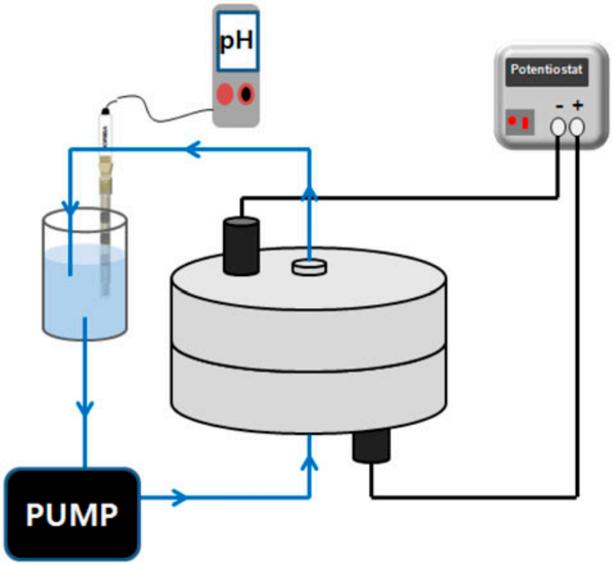

Fig. 1. Scheme for electrochemical softening using a semi-batch type CDI process.

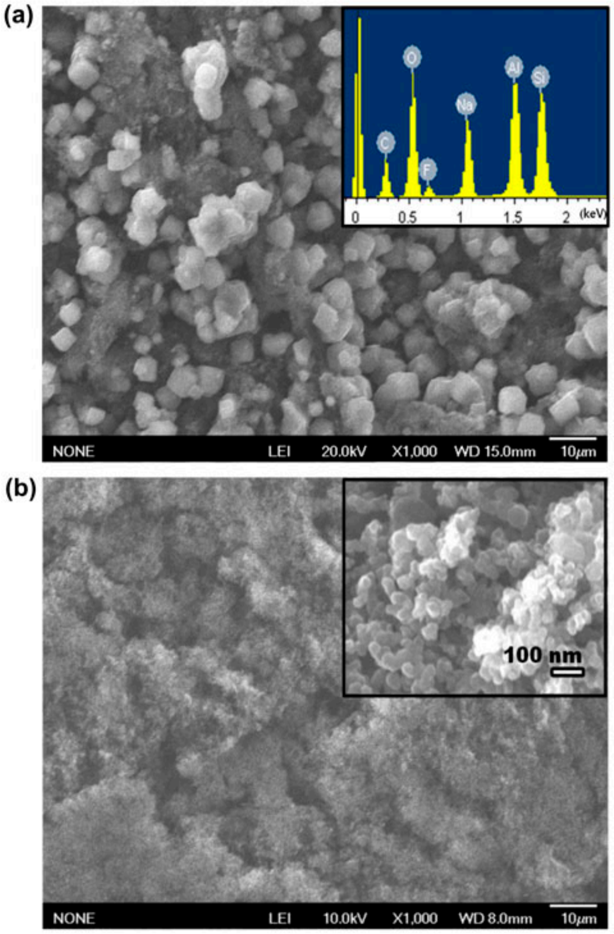

Fig. 2. Surface morphologies of the ZMCE and CE examined by SEM: The insets of (a) and (b) show the result from the energy dispersed spectroscopy (EDS) of zeolite particles on the ZMCE and carbon black particles on the CE, respectively.

WonA Tech Corp., Korea). The softening was initiated from the charging step which achieves adsorption by applying voltage (1.2 V) for 30 min. (softening using the CDI process), and the ion concentration was measured. Its softening efficiency was compared to the normal softening process which achieves adsorption in the absence of applying a voltage.

3. Results and discussion

3.1. Characterization of electrodes

Fig. 2(a) and (b) shows SEM images of the ZMCE and CE, respectively. As shown in Fig. 2(a), zeolite particles with a cube shape were well dispersed on the CE, and the energy dispersed spectroscopy result in the inset of Fig. 2(a) shows that the components of the particles were aluminum, silicon, and oxygen which are well known to be part of the general zeolite chemical composition [11]. On the other hand, a plain surface morphology was observed for the CE (Fig. 2(b)) and its surface which was composed of carbon black nanoparticles 50 nm in size. In addition, the zeolite particles were not removed after scrubbing by hand, meaning that the zeolite particles were strongly bonded by the binder onto the CE.

Fig. 3(a) and (b) shows the ion-exchange property of the ZMCE in DI water and $CaCl_2$ solution and the stoichiometric relation of the ion exchange between Ca^{2+} and Na^+ ions during spontaneous ion exchange which is the so-called softening in the batch system. As seen in Fig. 3(a), Na^+ ions (Δ) were spontaneously released from the ZMCE into DI water. As the Na^+ ions desorbed from the ZMCE, the pH increased from neutral to 9.85. Additionally, the amount of released Na^+ ions (O) in the $CaCl_2$ solution was 1.5 times higher than that in DI water. The concentration of the Ca^{2+} ions (●) was simultaneously reduced as the amount of Na^+ ions increased, while the CE did not exhibit any ion-exchange property. With respect to the ion exchange of the ZMCE in DI water, release of Na^+ ions (Δ) from the ZMCE can be interpreted as the adsorption of protons which results from spontaneous ion exchange of accommodated Na^+ in the zeolite framework on the ZMCE [9]. This was well supported by the increase in pH. The existence of Ca^{2+} accelerated the desorption of Na^+ ions indicating that softening proceeded. Especially, the ion-exchange property of the ZMCE exhibited stoichiometrically

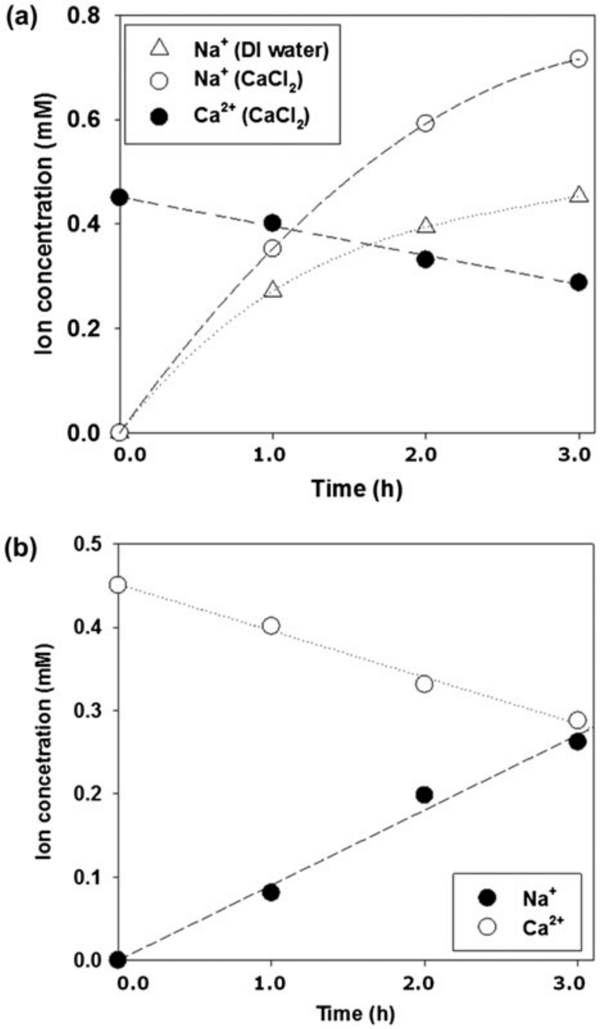

Fig. 3. (a) Spontaneous ion exchange on the ZMCE with the batch system in DI water and $CaCl_2$ solution (diameter of ZMCE = 1.8 cm, $[CaCl_2]_0 = 0.45$ mM) and (b) stoichiometric ion-exchange property between the Na^+ and Ca^{2+} ions from the ZMCE: The Na^+ concentration in Fig. 3(b) was evaluated by the difference in the Na^+ concentration released from the ZMCE between the DI water and $CaCl_2$ solution.

good linearity between Ca^{2+} and Na^+ ions (Fig. 3(b)). Note that the amount of Na^+ ions in Fig. 3(b) was calculated with the difference in the Na^+ concentration released from the ZMCE between the $CaCl_2$ solution and DI water to exclude the amount of released Na^+ ions caused by the proton adsorption. This suggests that the zeolite particles on the ZMCE have a critical role in the removal of Ca^{2+} ions.

Fig. 4(a) and (b) shows the electrochemical properties between the ZMCE and CE in $CaCl_2$ solution examined by cyclic voltammetry and electrochemical

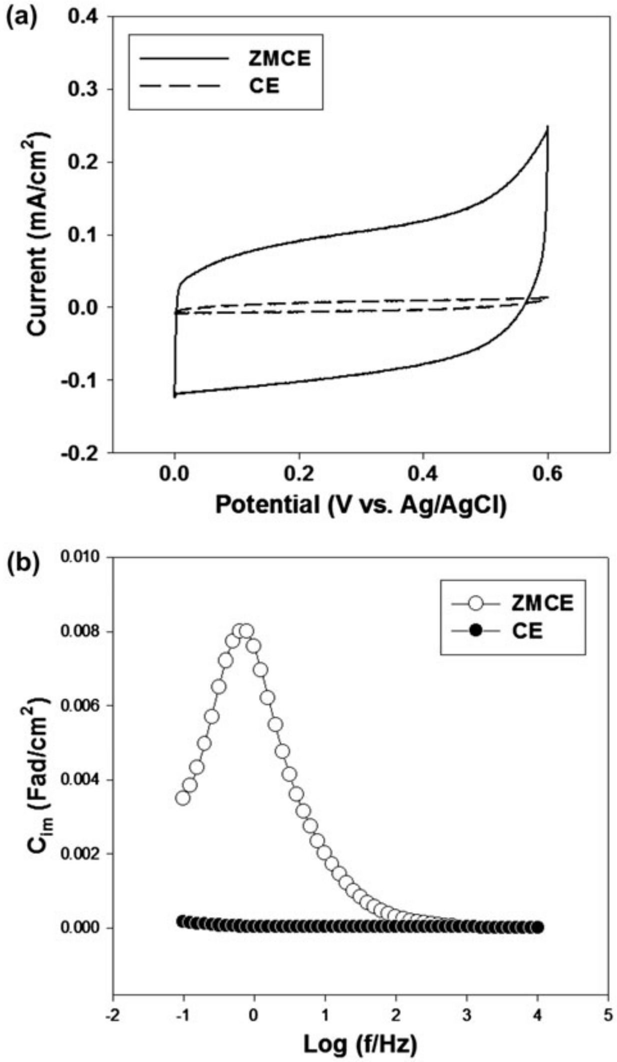

Fig. 4. Cyclic voltammograms (scan rate = 5 mV/s) (a) and complex capacitance measured at an AC potential = 10 mV and DC potential = open circuit potential (b) of the ZMCE and CE ($[CaCl_2]_0 = 9$ mM).

impedance spectroscopy measurements. In the results shown in Fig. 4(a), a distinct cyclic voltammogram (CV) of the ZMCE was observed from that of the CE. The ZMCE provided nearly a rectangular shape, and had a significantly high magnitude for the plateau current compared to the CE. This result means that the ZMCE exhibited an electrical double layer capacitor (EDLC)-like property [33–35]. Concerning the nature of the zeolite particle as an insulator, it is plausible that the EDLC-like property of the ZMCE is attributed to the concentration change in the electrolyte resulting from the ion exchange between the Ca^{2+} and Na^+ of the zeolite particles. The EDLC-like property of the ZMCE can also be well examined from

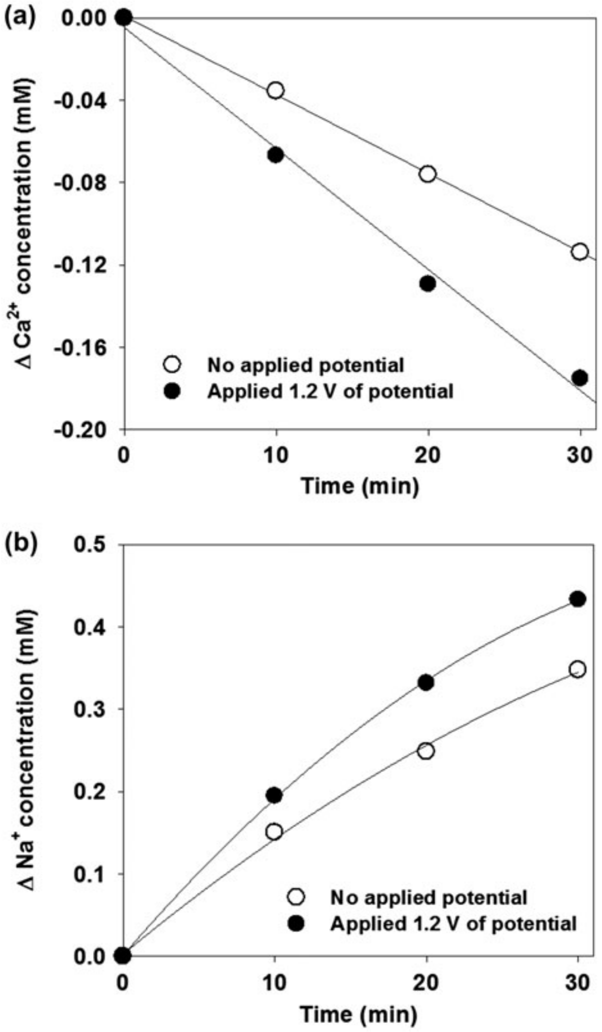

Fig. 5. Effect of the electrical energy on the ion exchange of (a) Ca^{2+} and (b) Na^+ ions in the CDI process with the ZMCE (electrode diameter = 5 cm, $[CaCl_2]_0$ = 0.9 mM, applied cell potential = 1.2 V).

the results of the complex capacitance (Fig. 4(b)). As shown in Fig. 4(b), the complex capacitance of the ZMCE showed a large integrated area and position for the capacitive peak compared to that of the CE indicating excellent double layer capacitance and rate capability of the ZMCE, respectively [36,37]. These results mean that the ZMCE exhibited a notable difference from the CE in terms of electrochemical properties. It is worth noting that the capacitive ZMCE was well fabricated with nonconductive zeolite particles.

Fig. 5(a) and (b) shows the effect of the electrical energy on the ion-exchange property between the Ca^{2+} and Na^+ in the ZMCE using the CDI process. The concentration of ΔCa^{2+} and ΔNa^+ ions indicates the differences in concentration between the ion-exchanged solution and initial solutions. As shown in Fig. 5(a), the Ca^{2+} ions were removed by the CDI process as the operating time increased in the absence (normal softening) or presence (softening using the CDI process) of applying a voltage. The removal efficiency of Ca^{2+} ions by the ZMCE was remarkably enhanced when a voltage was applied to the CDI system compared to normal softening, whereas the amount of released Na^+ ions was increased in softening using the CDI process (Fig. 5(b)). This enhanced removal efficiency of Ca^{2+} ions can be explained as follows: the enhanced capacitive property of the ZMCE provides an accumulation of Ca^{2+} ions on the surface of the ZMCE possibly leading to the enhancement of ion exchange between Na^+ and Ca^{2+}. As a result, we can conclude that softening with the ZMCE using the CDI process was successfully demonstrated.

4. Conclusion

In this study, we developed an electrochemical softening system using zeolite with the CDI process. The ZMCE, which was fabricated with zeolite and carbon, exhibited good ion exchange and excellent capacitive properties. The softening efficiency of the ZMCE was remarkably enhanced with the CDI process compared to normal softening. This result can be attributed to the accumulated Ca^{2+} ions from the electrical field during the CDI process leading to the enhanced ion-exchange efficiency.

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