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Synthesis of a Spherical Carbon-TiO_2 Composite as Electrode Material for Capacitive Deionization

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Activated carbon is widely used as an electrode material for capacitive deionization. However, it has low wettability with electrolytes and a low ion-adsorption capacitance. To enhance the wettability of activated carbon, in this study, a carbon-metallic oxide composite was synthesized using poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-block copolymer and titanium dioxide (TiO_2). The TiO_2 supporting material was synthesized by a sol-gel method, and activated carbon was prepared by high-temperature calcination at 550 °C in a nitrogen atmosphere. The active material containing 50 % TiO_2 exhibited the highest positive and negative capacitances of 109.5 and 121.3 F g^{-1}, respectively. Finally, when this material was used as a capacitive deionization electrode, the maximum ion removal rate was approximately 92 %. These results indicate that the carbon-TiO_2 composite electrode was more effective than the raw carbon electrode. In the end, we demonstrated the potential of a metallic oxide with activated carbon for desalination water treatment.

Keywords: TiO_2, Carbon-TiO_2 composite, Triblock copolymer, Capacitive deionization, Total dissolved solids

1. INTRODUCTION

Water shortages and pollution have been pressing issues since the start of the 20th century. Currently, usable water constitutes less than 1 % of the total amount of water on earth, excluding sea water and glaciers. As of 2011, one billion people do not have access to clean water, and 2.6 billion people live in establishments without basic indoor plumbing and sewers. Therefore, recycling water by retreatment is focus of the research and industrial communities [1-4]. For that reason, conventional desalination technologies, such as thermal distillation, reverse osmosis, ion exchange, electric dialysis, and capacitive deionization (CDI), have been widely studied [5, 6]. Among them, CDI is an electrochemically controlled method for removing salt from aqueous solutions by taking advantage of the excess ions adsorbed in the electrical-double-layer region on the electrode that are electrochemically charged by an external power supply [7, 8].

Activated carbon has been widely used as an electrode material not only for CDI [9, 10] but also for energy storage devices, such as lithium-ion batteries [11], lithium-ion capacitors [12], and supercapacitors [13], because of its advantages such as low cost, eco-friendless, and natural abundance [14, 15]. However, despite these advantages, activated carbon has low wettability with electrolytes. For this reason, pretreatment of activated carbon is an essential condition for using it for electrode materials. To solve this issue, many researchers studied methods to enhance the wettability of activated carbon. Qu reported that the wettability of activated carbon is influenced by the nature of functional groups on the surface [16]. The author revealed that several factors, such as the crystal orientation of the surface, the difference between the edge and basal orientation, and the state of surface functional groups affect the wettability of activated carbon. Seredych et al. synthesized surface-modified activated carbon by an oxidation process and generated nitrogen and oxygen-containing functional groups on the surface of activated carbon [17]. They revealed the relationship between the number of basic groups determined by functionalization and the improved capacitance at high current loads.

The purpose of this study is to apply the environmentally friendly process of capacitive deionization for water treatment using activated carbon-metallic oxide composites. In this process, electrical differences between the cathode and anode produce an electrical double layer of anions and cations on the cathode and anode, respectively, for deionization. This process is advantageous because it can be applied modularly, and it has high energy efficiency compared to other chemical treatments. Furthermore, secondary liquid wastes are not produced [18, 19]. Therefore, we aimed to develop electrode materials for the deionization of water solutions on the basis of the formation of the electrical double layer [20-22].

Activated carbon, which has been used as an electrode for capacitive deionization, has a low ion adsorption capacitance because of its low electrolyte wettability [23, 24]. As a result, metallic oxides are typically added to the electrode to increase the wettability [25]. However, metallic oxides interfere with pores in activated carbon that are responsible for the actual capacitance, thereby leading to a capacitance decrease. In this work, we attempted to synthesize TiO_2 by a sol-gel method to increase the wettability of the electrode and formed a composite of the TiO_2 and carbon material to improve conductivity and capacitance. In addition, we applied the carbon-TiO_2 electrode to CDI and determined the optimal content ratio by testing the deionization rate for different carbon materials with varying levels of TiO_2 content.

2. EXPERIMENTAL

2.1. Preparation of spherical carbon-TiO_2 composite

For the synthesis of the carbon-TiO_2 composite, TiO_2 was synthesized by the sol-gel method. Titanium tetra-isopropoxide (Junsei Chemical Co., Ltd.) was agitated in 2-propanol (J. T. Baker Co., Ltd.) for 3 h. Ultrapure water was added to the mixture to form TiO_2; afterward, the mixture was allowed to mature for 48 h at ambient temperature and dried for 24 h at 120 °C. The dried material was calcined in air for 5 h. Next, 1 g of the triblock copolymer composed of poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol) (Pluronic P123, O-BASF Corp.) was dissolved in 10 mL of ultrapure water, and appropriate amounts of TiO_2 were added according to the content ratio [26, 27]. The resulting mixture was agitated for 6 h [28-30]. To initiate condensation with water, 1 mL of H_2SO_4 (purity of ≥97.0 %, Sigma-Aldrich) was added and agitated for 3 h, after which the mixture was heated to 160 °C and further agitated for 3 h. Finally, the material was dried for 6 h at 120 °C, washed with ultrapure water, and calcined for 2 h at 550 °C in a nitrogen atmosphere for carbonization of triblock copolymer. The crystal structure of the material was determined by X-ray diffraction (XRD; D8 Discover with GADDS area detector, Bruker), and the carbon and TiO_2 content levels were determined by thermogravimetric analysis (TGA; TMA 2940, TA Instruments) from 50 to 900 °C with a heating rate of 5 °C min^{-1}. The particle size and surface characteristics were determined by scanning electron microscopy (SEM; Ultra 55, Zeiss).

2.2. Preparation of the electrode

Using the kneading method [31], the electrode was prepared using 80 wt% of kneading-type activated carbon (P-60, Kuraray Chemical Co., Ltd.), 20 wt% of carbon-TiO_2 composite as the active material, and polytetrafluoroethylene (PTFE; 60 wt%, Sigma-Aldrich) as the binder mixed with a weight ratio of 96:4. The mixture was then kneaded and rolled into a thin sheet. The electrode fabricated by the kneading method was attached to the collector at 150 °C using graphite foil (supplied by Beijing Great Wall Co., Ltd.) and an applied pressure. The composited carbon-TiO_2 electrode was used as the working electrode, Ag/AgCl (sat. KCl) was used as the reference electrode, and Pt was used as the counter electrode. The electrochemical behavior of the carbon-TiO_2 composite was tested by cyclic voltammetry (CV, Ivium stat). The efficiency of deionization during CDI was determined by charging/discharging tests. CV measurements were carried out over the open-circuit voltage (OCV) range 0 V to -0.8 V and +0.8 V vs Ag/AgCl at a scan rate of 5 mV s^{-1} in 1 M NaCl, and the deionization efficiency was determined by calculating the total dissolved solids (TDS; EC-470L, Istek Inc.) with a flow rate of 30 mL min^{-1} and a cell voltage of 1.5 V.

3. RESULTS AND DISCUSSION

The crystalline structure of the carbon-TiO_2 composite was investigated using XRD. Figure 1 shows the XRD patterns of the carbon-TiO_2 composite as a function of the amount of TiO_2 from 30 to 90 %. The broad peak at 25°, corresponding to the (002) planes, is mainly caused by the amorphous structured carbon. In addition, the small broad peak at approximately 45°, corresponding to (100) and (101) planes, is due to the *a* axis of the graphite structure [32, 33]. This finding indicates that the carbon synthesis method that used calcination of the triblock copolymer at 550 °C was successful. However, the TiO_2 diffraction peaks are not well defined. Due to this result, we suspect that the excessive amount of carbon interrupted the XRD measurement. In Figure 1 (b), the TiO_2 peaks are slightly visible. Figure 1 (c) and (d) exhibit the XRD pattern of 70 and 90 % of TiO_2 in the carbon-TiO_2 composite. The peaks centering at 2θ = 26°, 37°, 48°, 54, 56°, and 63° are assigned to typical peaks of anatase-TiO_2 because there is agreement with the reference peaks (JCPDS card No. 21-1272). From these results, we confirmed that the carbon-TiO_2 composite synthesized by the sol-gel and calcination method at 550 °C has an anatase TiO_2 structure.

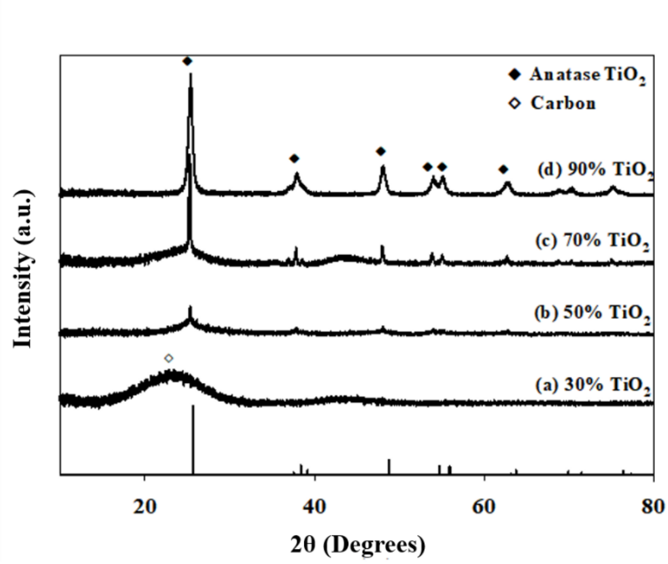

Figure 1. XRD patterns of carbon-TiO_2 composite containing: (a) 30 % TiO_2, (b) 50 % TiO_2, (c) 70 % TiO_2, and (d) 90 % TiO_2 that formed anatase TiO_2. Powder diffraction data for the anatase phase of TiO_2 (JCPDS card No. 21-1272) are included for reference.

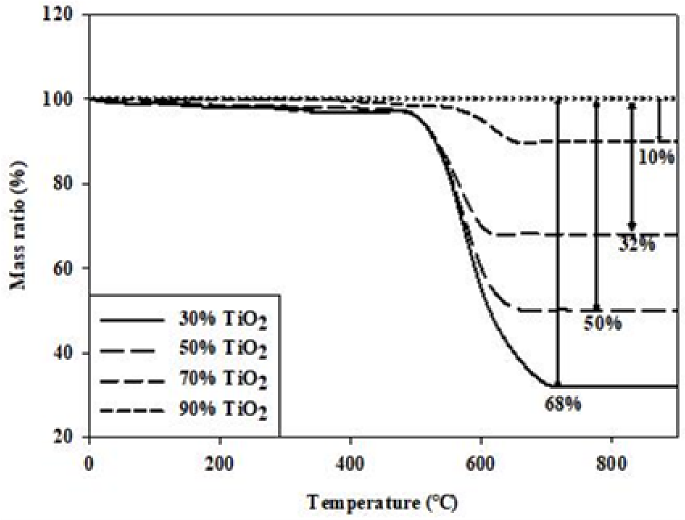

Figure 2. TGA thermogram of carbon-TiO_2 composite materials.

To measure the amounts of carbon and TiO_2 in the carbon-TiO_2 composite, TGA analysis was conducted in air from 50 to 900 °C with a heating rate of 5 °C mi^{-1}. Figure 2 shows the TGA thermogram of the carbon-TiO_2 composite as a function of the different amounts of TiO_2 from 30 to 90 %. It is obvious that the TiO_2 content increases proportionally with the addition of titanium tetra-isopropoxide during synthesis. The slight weight decrease from 50 to 200 °C can be detected and ascribed to the evaporation of the residual moisture from carbon. A rapid decrease in the mass ratio of carbon-TiO_2 was detected between 500 and 700 °C, implying the combustion of carbon in the air. The remaining inorganic material is believed to be TiO_2, which confirms the TiO_2 content of the carbon-TiO_2 material. The TiO_2 contents were determined to be approximately 32 wt % for carbon-30 % of TiO_2, 50 wt % for carbon-50 % of TiO_2, 68 wt % for carbon-70 % of TiO_2, and 90 wt % for carbon-90 % of TiO_2. The synthesis method of carbon-TiO_2 using sol-gel and calcination at 550 °C had a margin of error of approximately 3~7 % from the intended value.

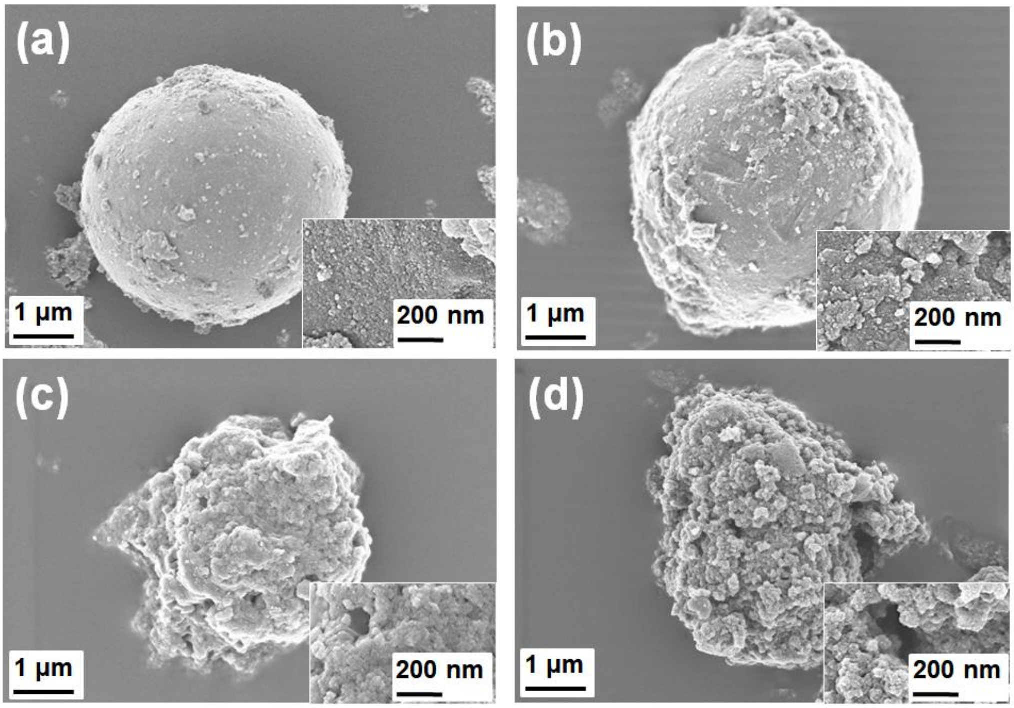

Figure 3. SEM images of the carbon-TiO_2 composite: (a) 30 % TiO_2, (b) 50 % TiO_2, (c) 70 % TiO_2, and (d) 90 % TiO_2.

Figure 3 shows SEM images of the carbon-TiO_2 composite for various amounts of TiO_2. Figure 3 (a) and (b) demonstrates the carbon-TiO_2 that has 30 and 50 % TiO_2. Both samples show aggregated particles assembled into spheres with a mean particle size of approximately 5 μm. It is well known that triblock copolymers Pluronic P123 could form aggregated particles where the hydrophobic group from PPO and the hydrophilic group from PEO are formed as core/corona structures, as shown in Figure 4 [34]. From that result, we confirmed that the addition of 30-50 % of TiO_2 has no effect on the formation of the spherical shape of the carbon-TiO_2 composite. On the other hand, the particles synthesized using 70 and 90 % TiO_2 show the ununiformed aggregated particles in Figure 3 (c) and (d). In addition, it was revealed that the TiO_2 particles were present on the carbon-TiO_2 surface. This is because the pure TiO_2 particles were formed on the carbon surface due to the addition of the high content of TiO_2 during the synthesis process. From this result, we suspected that the addition of TiO_2 influences the formation of particle shapes and depends on the amount of TiO_2.

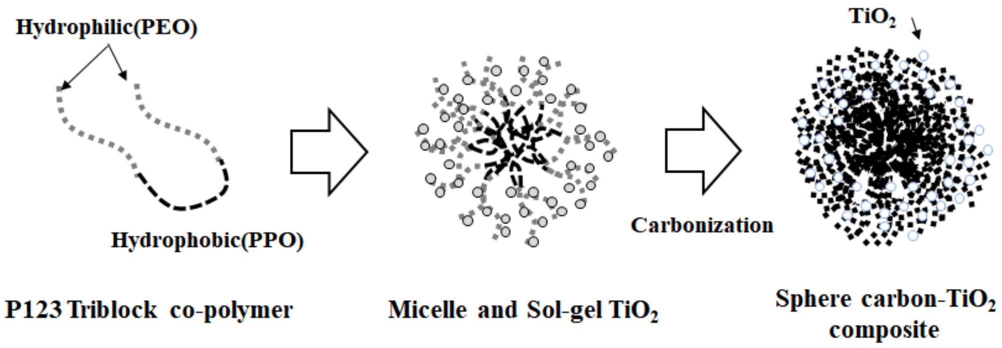

Figure 4. Schematic for synthesizing the carbon-TiO_2 composite using a triblock copolymer.

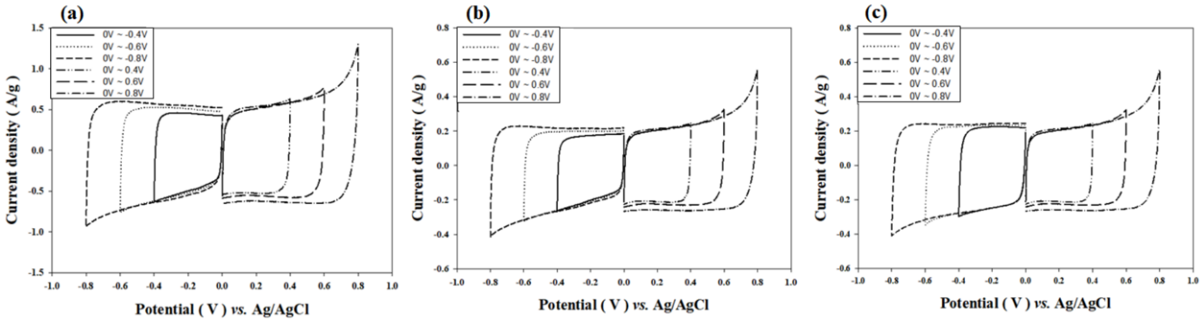

Figure 5. Cyclic voltammogram of the carbon-TiO_2 composite electrode with various potential ranges: (a) 50 % TiO_2, (b) 70 % TiO_2, and (c) 90 % TiO_2 with a scan rate of 5 mV s^{-1} in 1 M NaCl.

For the water treatment experiment using CDI technology, the water was used as an electrolyte between the two electrodes. Additionally, it is well known that the water is electrolyzed at 1.23 V and generates hydrogen. Moreover, the electrolysis voltage of water is changes depending on various conditions, such as type of activated material, kind of salt, and content of the electrodes [35-37]. For that reason, it is important to determine the voltage range for electrochemical analysis in the CDI system. In this study, before the electrochemical analysis, the carbon-TiO_2 electrode was tested using CV with various voltages ranging from 0 to 0.8 and 0 to -0.8 V vs. Ag/AgCl to determine the voltage ranges for electrochemical analysis. The cyclic voltammograms of the carbon-TiO_2 as a function of different amounts of TiO_2, from 50 to 90 %, are illustrated in Figure 5 (a)-(c). All samples exhibited a rectangular shape, which is typical electrical double-layer behavior. The rectangular region of the three samples decreased as the amount of TiO_2 increased, indicating the low capacitance of the electrodes. As described above, TiO_2 particles were formed in the carbon composite. Additionally, it could be suggested that the generated TiO_2 particles block the pores of the carbon composite, resulting in a low surface area. These results imply that the amount of TiO_2 influences the electrochemical performance of the carbon-TiO_2 composite as an electrode for the CDI cell. By collecting cyclic voltammograms with various voltages, we confirmed that electrolyte degradation did not occur with the potential range from 0 to 0.8 or -0.8 V vs. Ag/AgCl.

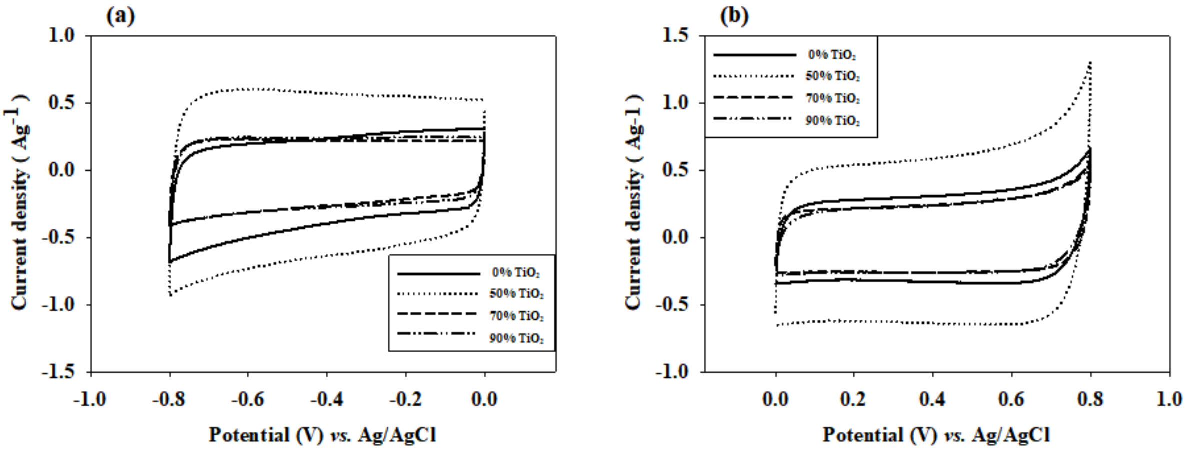

Figure 6. Cyclic voltammogram of the carbon-TiO_2 composite electrode with different TiO2 contents: (a) negative and (b) positive potential ranges with a scan rate of 5 mV s^{-1} in 1 M NaCl.

Figure 6 shows CV curves of the carbon-TiO_2 composite depending on different amounts of TiO_2 from 0 to 90 %. CV measurements were performed in 1 M NaCl solution with a scan rate of 5 mV s^{-1} separately for the positive and negative potential regions. The ion adsorption capacitance of the electrodes was determined using CV results. The capacitance increased as the TiO_2 content increased up to 50 % of TiO_2 because of the hydrophilic functionalization of TiO_2 particles. Chen et al. reported highly hydrophobic silk fabrics by introducing TiO_2 particles. The deposition of TiO_2 particles on the silk fabric enhanced the surface roughness, resulting in a high surface area. This finding implies that the improved hydrophilic functionalization by the addition of TiO_2 could be applied not only to carbon materials but also to other materials, such as silk [38]. In addition, the adsorption of the electrolyte on the carbon-TiO_2 composite electrode was substantially improved by the introduction of TiO_2 owing to the increase in the charge density of ions in the electric field [39]. However, in the case of using 70 % of TiO_2, the capacitance decreased. From these results, we suspected that the use of proper amounts of TiO_2 into the carbon composite enhances the capacitance by the polarity of TiO_2, but use of an excessive amount of TiO_2 particles leads to poor performance because the TiO_2 particles form on the carbon surface and block the pores, resulting in a decrease in the porosity. These results are in good agreement with Figure 5. Table 1 shows the capacitance calculated with the CV results. For this, Eq. (1) was used to calculate the capacitance from the CV curve:

$$C = \frac{1}{wv}\int idt \qquad \textbf{(1)}$$

where v is the scan rate and w is the mass of the active material in the electrode.

The sample with 50 % TiO_2 showed the highest capacitance of 109.5 F g^{-1} and 121.3 Fg^{-1} in the positive and negative voltage regions, respectively, of the samples considered in this study. As we described above, the sample that was synthesized with appropriate amounts of TiO_2 had the highest capacitance compared to that of the other samples.

Table 1. Comparison of capacitance with contents of TiO_2.

	0 % of TiO_2	**30 % of TiO_2**	**50 % of TiO_2**	**70 % of TiO_2**	**90 % of TiO_2**
Positive region capacitance (F/g)	82.5	83.4	109.5	72.9	66.5
Negative region capacitance (F/g)	97.6	103.8	121.3	77.4	76.8

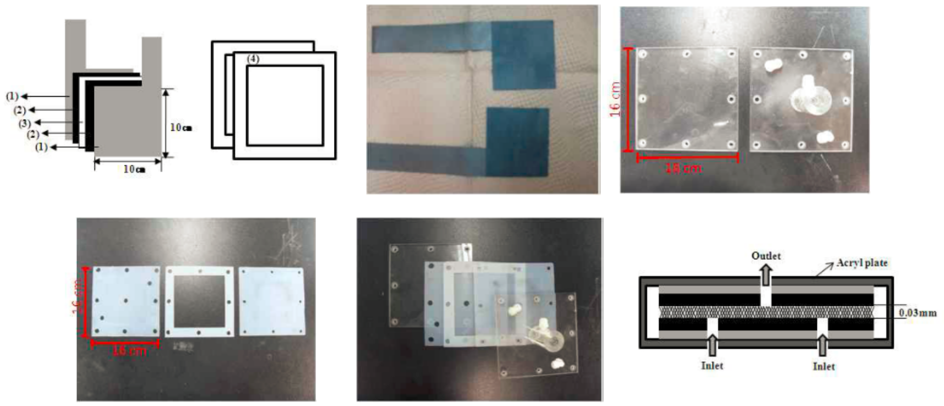

Figure 7. Schematic diagram of the electrode and CDI unit cell.

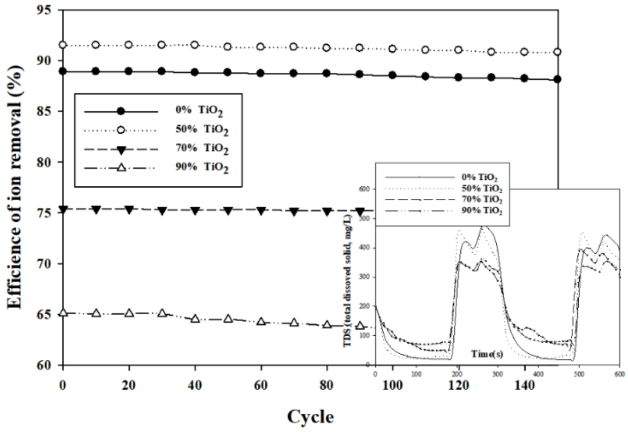

Figure 8. Cycling ability of CDI unit cells with different amounts of carbon-TiO_2 composite material, different TiO_2 content, and different amounts of ions. The cell with 50 % TiO_2 and 0 % TiO_2 composite was the most stable. Flow rate: 30 mL min^{-1} and cell voltage: 1.5 V.

We revealed that the carbon-TiO_2 composite that has 50 % TiO_2 has the highest capacitance because of enhanced wettability with the electrolyte through the CV test. This finding implies that the use of 50 % TiO_2 is the best way to obtain the highest ion removal performance. For further study, we investigated the cyclability of carbon-TiO_2 composites as electrodes for CDI cells. The CDI cell was assembled using a 10 cm × 10 cm electrode prepared by kneading, as shown in Figure 7. The electrolyte consisted of 200 ppm of NaCl solution. The charge-discharge condition was set at 1.5 V, and the flow speed was 30 mL min^{-1}. The charging and discharging times were 5 min and 50 s, respectively. The deionization rate was calculated from the total dissolved solid (TDS) in the electrolyte passing through the single cell using the following equation [40]:

$$\text{Salt removal rate (\%)} = (C_f - C_p) / C_f \times 100 \qquad (2)$$

where C_f represents the concentration of the solution before entering the cell and C_p represents the minimum concentration after passing through the cell. The problem with conventional carbon materials is the small amount of ions that are released. The amount of ion emission increased with increasing TiO_2 content, providing an estimate of the wettability owing to TiO_2. Figure 8 shows the results of the CDI cyclability test. The raw activated carbon electrode exhibited a good ion removal efficiency of over 88 % for 150 cycles. On the other hand, the other samples, including 70 and 90 % TiO_2, showed lower ion removal performances of 75 and 65 %, respectively, for 150 cycles. As mentioned above, using a large amount of TiO_2 leads to the formation of TiO_2 particles on the carbon surface and blocks the pore on the surface of carbon, resulting in a decrease in the reaction area during an electrochemical test. For that reason, although activated carbon has low wettability with electrolytes, it shows better performance than other samples, including 70 and 90 % TiO_2. However, when using 50 % TiO_2, the carbon-TiO_2 electrodes delivered an ion removal efficiency over 92 % for 150 cycles. This result implies that 50 % of TiO_2 is the proper amount for a carbon-TiO_2 composite to be used as an electrode for a CDI cell. Additionally, these results suggest that the hydrophilicity of TiO_2 led to a higher deionization rate and that the stable structure of TiO_2 served to increase the lifespan of the electrode.

4. CONCLUSION

We prepared TiO_2 materials using the sol-gel method and carbonized the PEO-PPO-PEO tri-block copolymer to synthesize the carbon-TiO_2 composite. The obtained material had a particle size of 5 µm. In the electrochemical property analysis, the active material with 50 % TiO_2 showed the highest electrical-double-layer capacitance, as measured by CV. In the analysis of the capacitive-deionization efficiency, the active material with 50 % TiO_2 showed the highest deionization rate of 92 % when a 200-ppm NaCl solution was used, and the material was stable through more than 100 charge/discharge cycles. We believe that the carbon-TiO_2 composite synthesized by the sol-gel method and calcination at 550 °C offers a straightforward approach for high-performance electrode materials, including TiO_2 used in the CDI system, owing to its improved hydrophilic functionalization compared with commercial carbon materials.

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