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# Enhancing the Desalination Performance of Capacitive Deionization Using a Layered Double Hydroxide Coated Activated Carbon Electrode

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**Abstract:** Capacitive deionization (CDI) is a promising desalination technology because of its simple, high energy efficient, and eco-friendly process. Among several factors that can affect the desalination capacitance of CDI, wettability of the electrode is considered one of the important parameters. However, various carbon materials commonly have a hydrophobic behavior that disturbs the ion transfer between the bulk solution and the surface of the electrode. In this study, we fabricated a layered double hydroxide (LDH) coated activated carbon electrode using an in-situ growth method to enhance the wettability of the surface of the carbon electrode. The well-oriented and porous LDH layer resulted in a better wettability of the activated carbon electrode, attributing to an enhanced capacitance compared with that of the uncoated activated carbon electrode. Furthermore, from the desalination tests of the CDI system, the LDH coated carbon electrode showed a higher salt adsorption capacity (13.9 mg/g) than the uncoated carbon electrode (11.7 mg/g). Thus, this enhanced desalination performance suggests that the improvement in the wettability of the carbon electrode by the LDH coating provides facile ion transfer between the electrode and electrolyte.

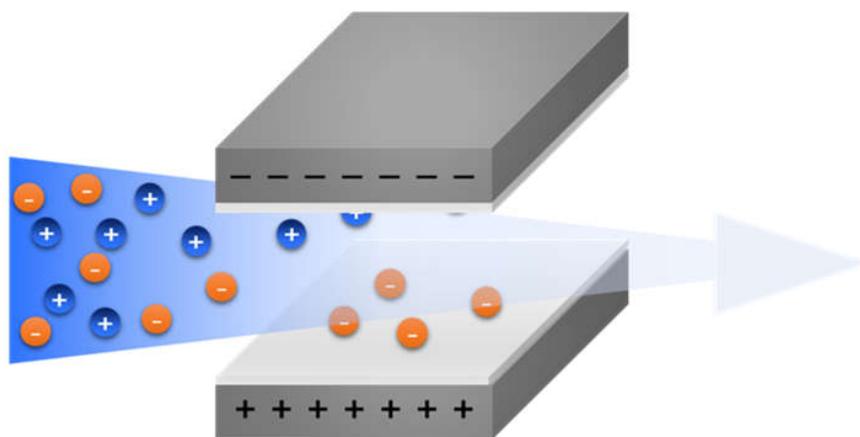
**Keywords:** capacitive deionization; layered double hydroxide; desalination; activated carbon; wettability

## 1. Introduction

Capacitive deionization (CDI) is considered as a promising desalination technology because of its environmental benign and energy-efficient characteristics. In a typical CDI system, while the feed water passes through the porous carbon electrodes, ions in the feed water are captured on the electrodes when a potential is applied between the electrodes shown in Figure 1. The water desalination process of CDI is based on the principle of the electrical double layer capacitor (EDLC), and ions in feed water are removed by the electrical adsorption onto the surface of the electrodes [1–11].

The conventional CDI system consists of a pair of porous carbon electrodes and open-meshed spacers for a flowing influent, and the desalination process in the CDI system is an interfacial process between the electrolyte and the electrode surfaces. Thus, the characteristics of a porous carbon electrode such as the surface area, pore size, electrical conductivity, chemical stability, and wettability are the major parameters to determine the desalination performance of the CDI system [5,6,12–15]. To develop

a CDI electrode with high performance, a porous carbon electrode should have a large specific surface area, optimal pore size distribution, high electrical conductivity, and good wettability to the electrolyte. Various carbon materials with different surface areas and pore size distributions have been investigated, and among them, activated carbons are one of the most suitable materials for CDI electrodes because of their large surface area and economic merits. However, CDI electrodes based on activated carbon materials exhibit a hydrophobic behavior, disturbing the accessibility of ions to the pore structure. Accordingly, various surface modifications of the activated carbon electrodes have been reported to overcome this limitation by treating with acidic and alkaline solutions, attaching functional groups, and coating the organic or inorganic materials [16–18].



**Figure 1.** Principle of a capacitive deionization system. The capacitive deionization (CDI) system consists of a pair of porous carbon electrodes, and the influent flows between the two electrodes. The ions are attracted onto the surface of the electrodes by applying a potential.

Layered double hydroxides (LDHs), known as anion exchangeable clays containing transition metal hydroxides, are a lamellar type of compound built by two-dimensional positive charged layers. The typical LDH structure is expressed with the chemical formula  $[M^{II}_{1-x}M^{III}_x(OH)_2]^{x+}(A^{n-})_{x/n} \cdot yH_2O$ , where  $M^{II}$  and  $M^{III}$  represent the divalent and trivalent metal cations, and  $A^{n-}$  means the interlayer anion [19–21]. LDH materials have many potential applications including adsorbents, catalysts, anticorrosive, metal oxide precursors, and supercapacitors in aqueous solutions not only because of their anion exchange capacity and high stability but also because of their exceptional hydrophilicity [22,23]. Recently, using the LDH precursor, various substrates were successfully coated with a well-oriented porous LDH structure, attributing to the enhanced durability as well as their wettability. [24,25].

Hence, the purpose of this paper is to improve the wettability of the porous carbon electrodes through LDH coating and to enhance the desalination performance. The LDH crystals on the surface of the activated carbon were aligned vertically using an in-situ growth method under a hydrothermal condition. The characteristics of the LDH coated activated carbon electrode were then analyzed with the scanning electron microscopy (SEM), the cyclic voltammetry, and the contact angle measurements. Furthermore, ion adsorption/desorption tests were conducted to evaluate the desalination performance.

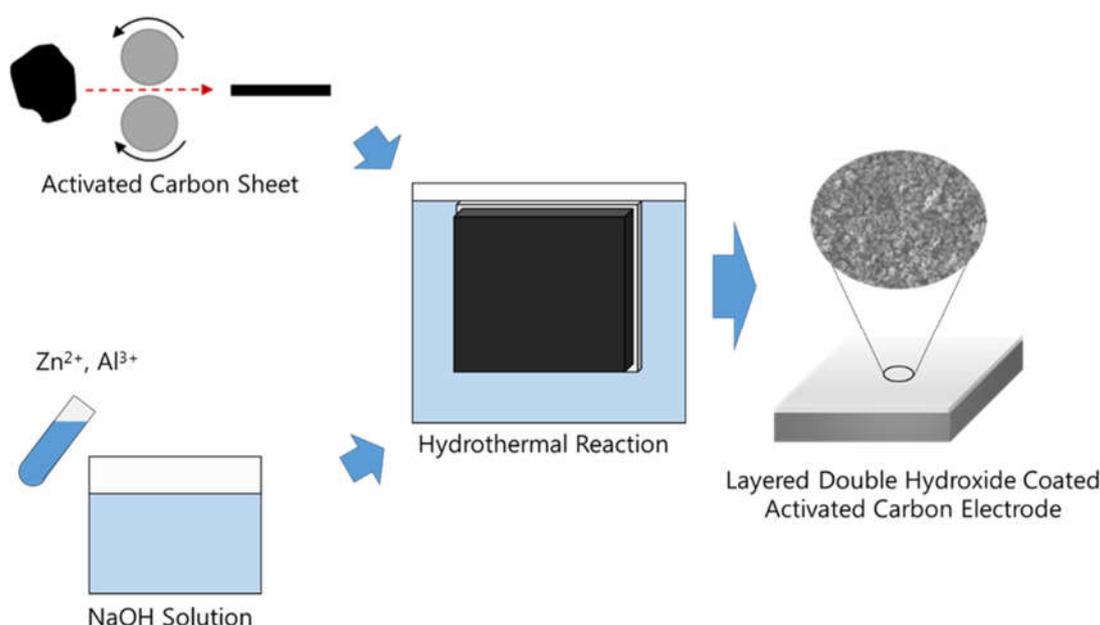
## 2. Experimental Section

### 2.1. Fabrication of the Activated Carbon Electrodes

The activated carbon electrode was prepared by mixing activated carbon with a polymer binder. The activated carbon powder (CEP-21, Power Carbon Technology Co., Gumi-Si, Korea) was mixed with carbon black (Super P, Timcal Graphite and Carbon, Bironico, Switzerland) and solution dispersed polytetrafluoroethylene (PTFE, Sigma Aldrich, USA) at a mass ratio of 86:7:7. A sheet type electrode with a 300  $\mu\text{m}$  thickness was obtained by pressing the resulting mixture using a roll-press machine.

## 2.2. LDH Coating on the Activated Carbon Electrode Surface

The LDH coating process on the activated carbon electrode is shown in Figure 2. The LDH precursors were prepared by a method similar to that showed in the previous study [24]. Briefly, 60 mL of aqueous solution containing Zn (COOH)<sub>2</sub>·2H<sub>2</sub>O (0.2 M) and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (0.1 M) were mixed with 240 mL of NaOH solution (0.15 M) under vigorous stirring at room temperature for 1 h. The resulting solution was then rinsed with deionized water using a centrifuge to remove any remaining ions from the LDH precursor and re-dispersed in 300 mL of deionized water. For the LDH coating on the surface of the activated carbon electrode, the prepared activated carbon electrode was sealed on one side by a Teflon plate and immersed vertically in the prepared LDH precursor solution. Then, it was hydrothermally treated at 70 °C for 18 h in an oven. Finally, the LDH coated electrode was washed with deionized water several times and dried in vacuum oven at 60 °C for 12 h.



**Figure 2.** Schematic representation of the fabrication process of the layered double hydroxides (LDH) coated activated carbon electrode.

## 2.3. Characterization of the Activated Carbon Electrodes

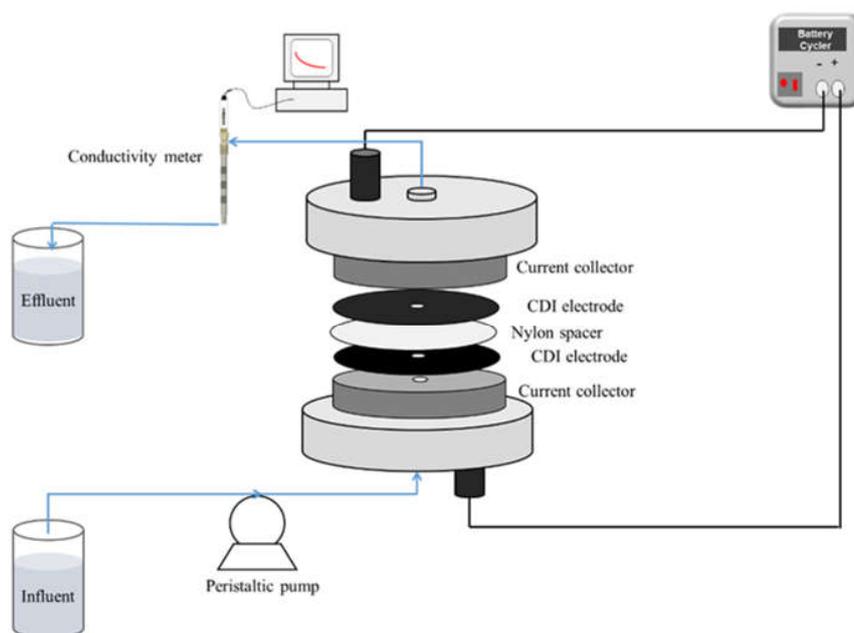
The morphology and wettability of uncoated (pristine) and LDH coated activated carbon electrodes were measured by a field emission scanning electron microscope (FESEM, JEOL JSM 6700 F, Japan) and a drop shape analyzer (DSA 100, KRÜSS GmbH, Germany). The cyclic voltammetry (CV) tests were conducted on a potentiostat/galvanostat (PARSTAT 2273, Princeton Applied Research, USA) to investigate the electrochemical performance in a typical three-electrode system. The uncoated and LDH coated activated carbon electrodes ( $d = 18$  mm) were used as the working/counter electrodes, and a KCl saturated Ag/AgCl electrode was used as a reference electrode. The specific capacitance of the uncoated and LDH coated electrodes were calculated using Equation (1) as follows:

$$C = \frac{\int |I| dV}{2v\Delta V m_e} \quad (1)$$

where  $C$  is the specific capacitance (F/g<sub>electrode</sub>);  $I$  is the current (A);  $v$  is the potential scan rate (V/s);  $\Delta V$  is the potential window (V), and  $m_e$  is the mass of the electrode (g).

### 3. Desalination Performance Tests

The CDI system experiments were evaluated using a CDI unit cell that has been described in Figure 3 and previous papers [6,18,26], and the electrodes were soaked in 10 mM NaCl for 10 min. under a vacuum condition before the desalination tests. The uncoated and LDH coated activated carbon electrodes ( $d = 5$  mm) was used as the electrodes, and a nylon spacer (thickness = 0.2 mm) was placed between the electrodes. A hole with a diameter of 4 mm was provided in the middle of the lower compartment electrode and the current collector so that the influent would flow between the two electrodes.



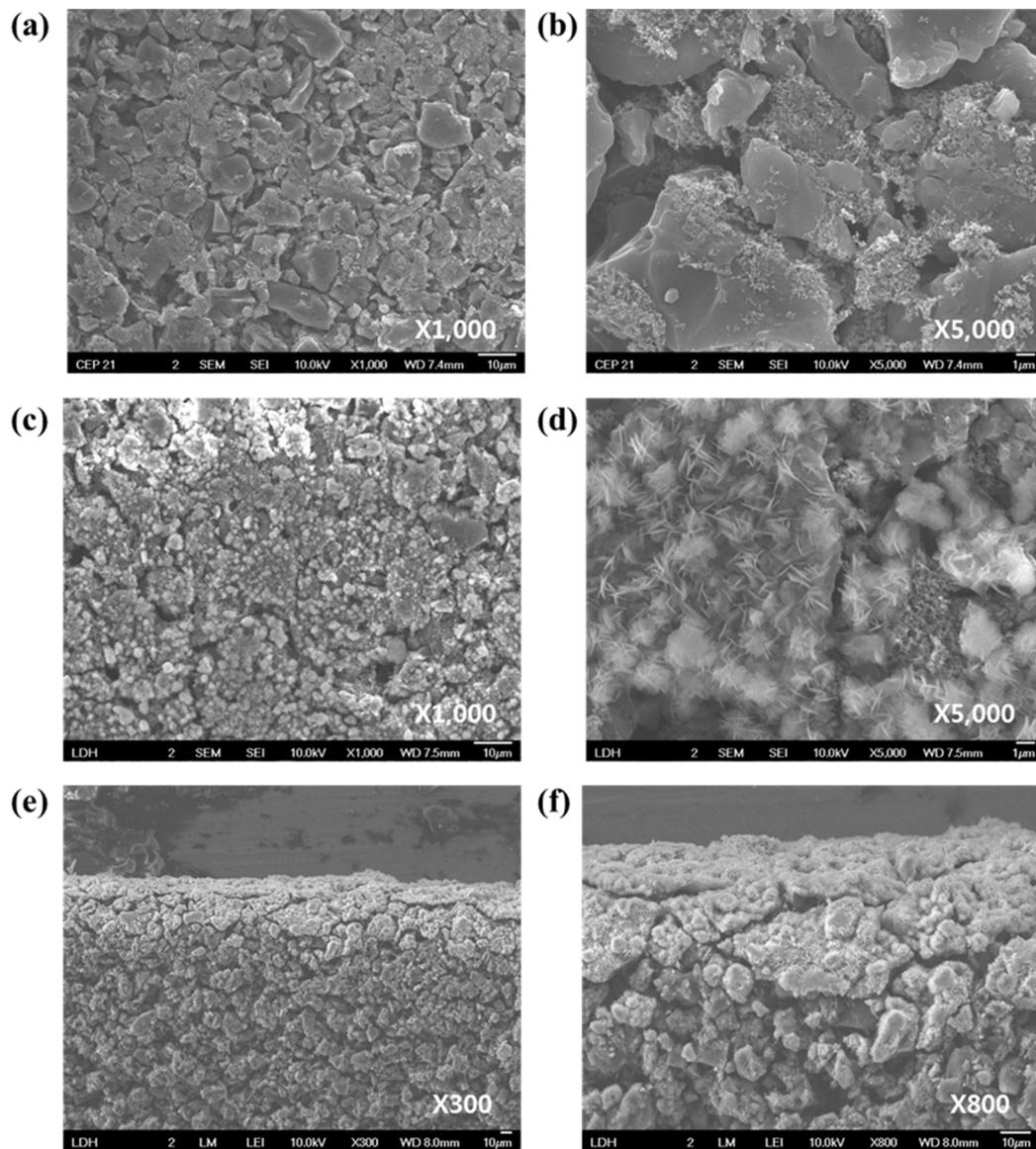
**Figure 3.** Schematic diagram of the CDI unit cell.

The 10 mM NaCl aqueous solution was pumped at a flow rate of 10 mL/min. using a peristaltic pump (MINIPLUS 3, Gilson Inc., Middleton, USA). The ion adsorption/desorption tests were carried out by applying a potential (charging: 1.2 V; discharging: 0 V) for 10 min at each step using an automatic battery cycler (WBC S3000, WonA Tech Corp., Seoul, Korea). The conductivity of the effluent was measured by a flow-type conductivity meter (F-54 BW, HORRIBA, Kyoto, Japan). The tests were held in a thermostatic chamber (KCL-2000, EYELA, Tokyo, Japan) to maintain the room temperature (298 K) during the operation. The accumulated salt adsorption capacity was calculated from the conductivity changes during the charging step. The representative desalination performance results from triplicate experiments are presented in this study.

### 4. Results and Discussion

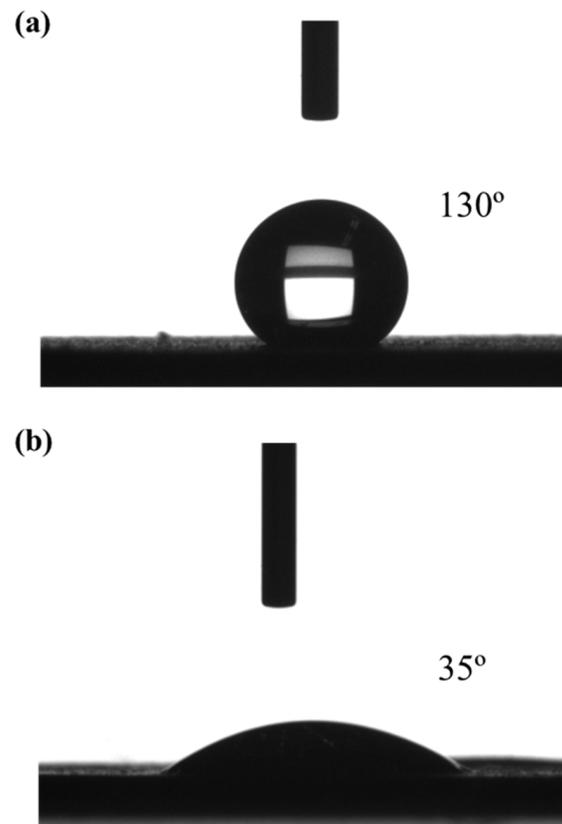
Figure 4 shows the surface images of the uncoated activated carbon ((a) and (b)) and LDH coated carbon electrode ((c) and (d)) using FESEM. As shown in Figure 4c,d, the LDH structures were aligned vertically on the surface of the activated carbon electrode, resulting in a porous LDH layer. The LDH coating layer was obtained under a hydrothermal reaction with an in situ growth method for better LDH crystal porous structure without blocking the pores on the surface of the activated carbon powder. During this coating process, the LDH nanosheets in the LDH precursor were attached onto the surface of the substrate and quickly formed a thin LDH film. After that, larger LDH particles began to grow and crystallize on top of the primary LDH film under the hydrothermal condition gradually forming a porous and well-oriented LDH layer. It was observed that the one side of the activated carbon electrode surface was well coated with the LDH layer with a depth of approximately 50  $\mu\text{m}$  (verified by the

cross-sectional SEM images in Figure 4e,f. The detailed mechanism of the porous LDH layer formation from the LDH precursor has been reported in previous [24].



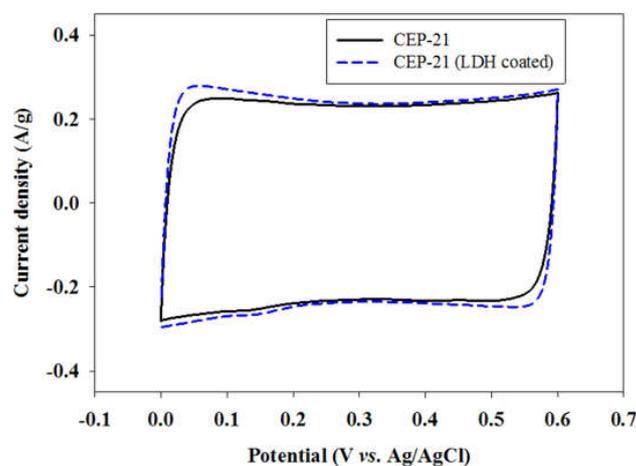
**Figure 4.** Field emission scanning electron microscope (FESEM) images of that activated carbon (CEP-21) sheet (a,b), LDH coated activated carbon sheet (c,d), and cross-sectional view of the LDH coated activated carbon sheet (e,f).

Figure 5a,b shows the contact angle images of the activated carbon and LDH coated activated carbon electrodes using distilled water. As seen in the images of the water droplets, the contact angles of the uncoated and LDH coated activated carbon electrodes were approximately  $130^\circ$  and  $35^\circ$ , respectively. These results show that the LDH coated activated carbon electrode has a better wettability than the uncoated one. Since the LDH materials have a hydrophilic characteristic because of their hydroxyl groups, the LDH coating layer results in an enhanced wettability of the activated carbon electrode [19,27].



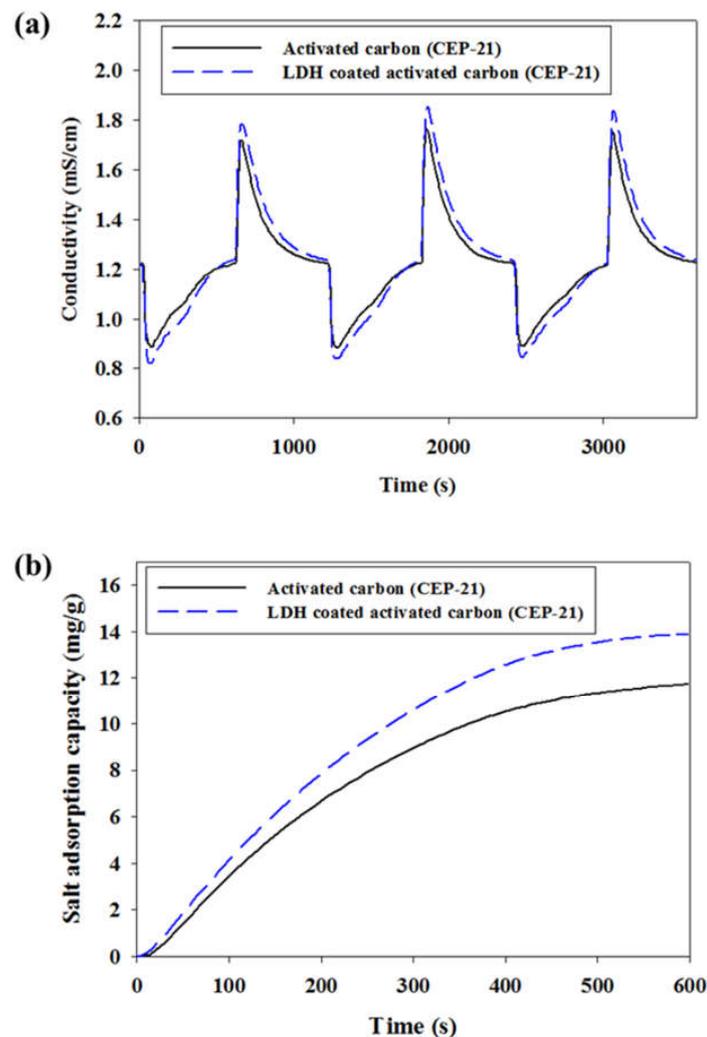
**Figure 5.** The contact angle of the activated carbon (a) and LDH coated activated carbon electrode (b).

Figure 6 shows the cyclic voltammetry (CV) curves for the uncoated and LDH coated activated carbon electrodes with a potential range of 0–0.6 V in 1 M NaCl solution. Both CV curves are nearly rectangular in shape, showing that the ions are adsorbed onto the surface of both uncoated and LDH coated electrodes by forming an electrical double layer as ideal capacitors [6,28]. The specific capacitance of the LDH coated activated carbon electrode calculated by Equation (1) was 124 F/g<sub>electrode</sub>, which shows a slightly increased (6%) value compared with that of the uncoated activated carbon electrode (116 F/g<sub>electrode</sub>). These results indicate that the LDH coating layer improves the wettability of the electrode without disturbing the pore structure in the activated carbon, and this enhancement of the wettability is attributed to the increase in the capacitance.



**Figure 6.** The cyclic voltammetry (2 mV/s) of the activated carbon electrode and LDH coated activated carbon electrode in 1M NaCl solution.

Furthermore, Figure 7a,b shows the conductivity changes during the ion adsorption/desorption tests and the salt adsorption capacity curves during the third charging step. As seen in Figure 7a, the conductivity rapidly decreased as an electrical potential (1.2 V) was applied during the charging step, while, it increased as the adsorbed ions were released during the discharging step. From the conductivity data, it was observed that the LDH coated activated carbon electrode had a better performance than that of the uncoated activated carbon electrode for overall cycles. Figure 7b shows the accumulated salt adsorption capacity during the third cycle of the charging step. Note that the salt adsorption capacity was expressed as the accumulated mass of adsorbed ions per total mass of the electrodes. The calculated salt adsorption capacity of the LDH coated activated carbon electrode was 13.9 mg/g<sub>electrode</sub>, which showed a better desalination capacity than the uncoated activated carbon electrode (11.7 mg/g<sub>electrode</sub>). Also, the value was a comparable with that of the commercially available activated carbon materials as shown in Table 1 [29]. This enhanced salt adsorption capacity indicates the improvement of the wettability of the porous carbon electrodes because of a rapid ion transfer at the interface between the electrode and electrolyte [16,18]. In conclusion, the hydrophilic LDH layer on the activated carbon electrode increases the accessibility of ions into the pores resulting in an improved desalination performance of the CDI system.



**Figure 7.** (a) The conductivity changes of the effluent in an activated carbon electrode and LDH coated activated carbon electrode system during operations (1.2 V for charging; 0 V for discharging) with 10 mL/min flow rate (source water: 10 mM NaCl). (b) Accumulated salt adsorption capacity during the third cycle of the discharging step.

**Table 1.** Electrochemical and CDI performance reported for commercially available activated carbon materials for CDI.

Activated Carbon	Electrochemical Performance		CDI Performance		Ref.
	Specific Capacitance (F/g)	Applied Cell Voltage (V)	NaCl Concentration (mg/L)	Salt Adsorption Capacity (mg/g)	
S-51HF	44	1.2	~58.4	4.1	6
SX PLUS	63	1.2	~58.4	6.2	6
YS-2	81	1.2	~58.4	7.0	6
MSP-20	124	1.2	~58.4	13.6	6
CWZ-22	—	1.2	~290	5.3	29
S-TE11	—	1.2	~290	9.1	29
YP-50F	—	1.25	~2900	9.6	29
CEP-21	116	1.2	~58.4	11.7	This work
CEP-21 (LDH coated)	124	1.2	~58.4	13.9	This work

## 5. Conclusions

In summary, the LDH coated activated carbon electrode was simply manufactured by an in-situ growth method under a hydrothermal condition, and the LDH layer was delicately formed on the surface of the activated carbon powder without blocking the porous sites of the carbon electrodes. This LDH layer significantly enhances the wettability of the surface of the electrode and increases the specific capacitance of the activated carbon electrode. Moreover, the desalination test in the CDI system showed that the LDH coated electrode has a higher salt adsorption capacity (13.9 mg/g<sub>electrode</sub>) than the uncoated activated carbon electrode (11.7 mg/g<sub>electrode</sub>). The facile ion transport between the bulk solution and the surface of the electrodes may contribute to the improvement of the desalination performance of the CDI system.

**Author Contributions:** Conceptualization, J.L. and C.K.; Investigation, J.L. and S.K.; Supervision, C.K. and J.Y.; Visualization, N.K.; Writing—original draft, J.L.; Writing—review & editing, S.K., N.K. and C.K. All authors have read and agreed to the published version of the manuscript.

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**Conflicts of Interest:** This research has no conflict of interest.

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