

Lignin-derived Porous and Microcrystalline Carbon for Flow-Electrode Capacitive Deionization

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Capacitive deionization (CDI) is an emerging desalination technique with full potential to produce freshwater from brackish and sea water. To fulfill such potential, it is of great importance to prepare carbonaceous electrode with high desalination performance and low cost, and using environmental-friendly raw materials. Herein, we prepared a porous carbon by KOH activation of alkali lignin which is a by-product and organic pollutant of the pulp industry. It was shown lignin is a good carbon source due to a high carbon yield over 30%, yet a relatively high degree of graphitization can be obtained at 800 °C. The KOH-activated carbon exhibited a specific capacitance of 123.9 F g⁻¹ in a 1 M NaCl at 1 A g⁻¹, and a salt adsorption capacity of 11.4 mg g⁻¹ at a voltage of 1.4 V. Furthermore, the as-prepared carbon was dispersed into water and assembled into a flow-electrode CDI system, which displayed a salt removal rate of 0.00025 mmol cm⁻² min⁻¹ at a low voltage of 1.4 V and low concentration of feed solution. These results suggest porous carbons with high capacitive performance can be produced from lignin, which would extend the utilization of this organic pollutant.

Keywords: Lignin; Porous carbon; Capacitive deionization; Flow electrode

1. INTRODUCTION

Environmental (water) pollution and shortage of freshwater are the major crisis people are facing all over the world [1, 2]. Removing the salts from brackish and sea water is an effective means to mitigate these issues, and various techniques have been developed to fulfill such purposes, such as reverse osmosis and multi-effect distillation [3]. Capacitive deionization (CDI), or electrosorption, which works on the basis of adsorbing ions electrostatically on the porous electrodes, is emerging as a

promising desalination technology and attracting enormous interests recently [4, 5]. These interests are associated with the theoretically low energy consumption, the low requirement on equipment, and high desalination efficiency applicable for both purification of brackish water and producing fresh water from sea water.

One of the key issues that hinder the practical application of CDI technique is the lack of ideal electrode materials. Porous carbons are considered as the most suitable electrode due to the large surface area, good chemical stability and electrical conductivity, and the high adsorption capacity [6, 7]. These materials are particularly promising when biomass were used as the raw material due to the environmental benignity, the porous structure of biomass that can be inherited by their pyrolytic carbons, as well as the low cost [8, 9]. As such, a variety of carbons produced from biomass with good CDI performance, have been reported in the past decades, such as those prepared from lotus stems [10], citrus peels [11] and chitosan [12], to name only a few. However, less attention has been paid to fabricating carbon from lignin, which is the second most abundant biopolymer on earth [13]. Lignin is mostly disposed as organic waste into environment at 60 M tons per year worldwide during industrial production, e.g. in pulping waste liquor [14]. This process not only leads to severe environmental pollution but is also a waste of resource. In fact, lignin is an ideal precursor for producing functional carbonaceous materials for a range of applications due to the high content of carbon element and its three-dimensional cross-linked structure that endows it with good chemical stability, as well as its polar groups that can be tailored for numerous functionalities [15]. Furthermore, lignin can be readily converted to graphitic structure at a relatively low carbonization temperature [16]. Such a graphitization tendency is related to the Scholl reaction, originating from its aromatic rings, and is beneficial for achieving high electrical conductivity.

Another crucial aspect and effective approach to improving the CDI performance is to optimize the configuration of the electrodes and the processing conditions, such as through membrane CDI [17], flow-through CDI [18], hybrid CDI [19] and flow-electrode CDI (FCDI) [20]. Particularly, by dispersing the electrode materials in flowing electrolytes, the anode and cathode after adsorbing salts could neutralize such that the electrode could be regenerated and pumped back to the desalination unit instantly, and thus the system could operate continuously. Furthermore, the theoretical adsorption capacity is unlimited as long as the side reactions (e.g. Faradaic reaction) are suppressed [21]. However, FCDI is more complex and several critical issues still need to be solved. For instance, the conductivity of the flow electrodes are generally much lower than the static counterpart such that a high loading of carbon in the electrode is needed, the concentration between the flowing electrolyte and feed solution needs to be balanced, and the voltage window needs to be maximized yet good energy (charge) efficiency has to be retained.

In this work, we prepared porous and microcrystalline carbon from lignin. This was achieved by a simple and scalable process, i.e. by stabilizing lignin in air at 200 °C and followed by KOH activation at 800 °C. The lignin-derived carbon displayed good capacitive performance as supercapacitor, and a salt adsorption capacity of 11.4 mg g⁻¹ when assembled into capacitive deionization system. Moreover, the as-prepared carbon was dispersed in salt solution to yield stable flow electrodes, which also exhibited excellent electrosorption performance in flowing mode.

2. EXPERIMENTAL

2.1 Preparation of porous carbon

Alkali lignin (Sigma-Aldrich) was first heat-treated in a tube furnace with flowing air (20 mL min^{-1}) at 200°C for 2 h to stabilize the precursor. Two methods were then employed to prepare carbon: (1) The pretreated precursor was heat treated at 800°C with a ramp rate of 5°C min^{-1} for 2 h in nitrogen, followed by thorough wash with hydrochloride acid and deionized water. The product was termed as LDC-800. (2) The pretreated precursor mixed with KOH powder with a mass ratio of 1:1, which was then treated in nitrogen at 800°C for 2 h. The residues were rigorously stirred in 1.0 M hydrochloride and stirred for 3 h and then thoroughly washed with deionized water to remove the remaining KOH and inorganic salts. The product was termed as KLDC-800. The synthesis process is shown in Fig 1.



Figure 1. Schematic illustration of the formation process for LDC-800 and KLDC-800.

2.2 Characterization

The morphology and microstructure were inspected using Field emission scanning electron microscopy (FESEM, JEOL JSM-7800F) and transmission electron microscopic TEM (JEM-2100). The surface area and pore structure were examined through N_2 adsorption-desorption isotherm (Micromeritics ASAP 2020). The crystallite structure was characterized using XRD (Bruker/D8 Advance) with $\text{Cu K}\alpha$ radiation. Raman spectroscopic analysis was performed on a Renishaw INVIA REFLEX spectrometer coupled with a laser with $\lambda=633 \text{ nm}$. X-ray photoelectron spectroscopy (XPS) was conducted on an Ultra DLD using a monochromic Al X-ray source. Thermogravimetric analysis (TGA) was carried out using a Jupiter Netzsch STA 449C instrument.

2.3 Electrochemical tests

The working electrode was fabricated as follows: 2 mg of active materials, 0.25 mg of Super P and 0.25 mg of PVDF were firstly mixed. The mixture was then casted onto the graphite paper and dried at 70 °C for 12 h. The electrochemical properties of the working electrode were determined by cyclic voltammetry (CV) and galvanostatic charge discharge (GCD) conducted on a CHI 760E electrochemical workstation using NaCl solutions (1 mol L⁻¹), platinum wire and Ag/AgCl electrode as the electrolyte, counter electrode, and reference electrode, respectively. Specific capacitance (C, F g⁻¹) derived from GCD curves was calculated through Equation (1):

$$C = \frac{I \times \Delta t}{m \times \Delta V} \quad (1)$$

where I (A) is the current, Δt (s) is the discharge time, m (g) is the mass of the active materials, ΔV (V) is the voltage window.

2.4 Static mode CDI tests

Static mode CDI test was described in detail in our previous work [22]. Specifically, The CDI electrodes were fabricated by mixing active materials, Super P and poly(vinylidene fluoride) at 8:1:1 ratio in weight. Then the mixture was loaded on Ti current collectors and dried at 70 °C for 12 h. Each electrode contains 0.04 g of the active materials. The NaCl solution with the original concentration of 500 mg L⁻¹ was continuously pumped with a peristaltic pump into the cell at a flow rate of 10 mL min⁻¹, and the volume of the NaCl solution was 30 mL. The salt adsorption capacity (SAC, mg g⁻¹) and the salt adsorption rate (SAR, mg g⁻¹ min⁻¹) were calculated using the following equations:

$$SAC = \frac{(C_0 - C_t) \times V}{m} \quad (2)$$

$$SAR = \frac{SAC}{t} \quad (3)$$

where C_0 (mg L⁻¹) is the initial concentration of NaCl, C_t (mg L⁻¹) is the concentration of NaCl at t min, V (L) is the volume of NaCl solution, m (g) is the total mass of the active materials, t (min) is the charge time.

2.5 Flow-electrode CDI tests

The FCDI cell is consisted of end plate/graphite plate/cation-exchange membrane/separator/anion-exchange membrane/graphite plate/end plate. A graphite plate (121 mm×115 mm×10 mm) was used as the current collector with a carved column-shaped flow path (5.9 cm in length, 2 mm in both width and depth). There were 17 channels on each graphite electrode. A cation exchange membrane (CEM, Neosepta CMX, Japan) and an anion exchange membrane (AEM, Neosepta AMX, Japan) were inserted in the cell, and the effective contact area between flow channel and ion exchange membrane was 22 cm². The separator was made of a silicone gasket and a 3 mm-thick PEEK plate between the two membranes.

The operational mode was short-circuited closed-cycle/bath-mode in our experiments. 60 mL of 500 mg L⁻¹ NaCl solution was continuously pumped into the separator by a peristaltic pump at a

flow rate of 10 mL min⁻¹. The flow-electrodes composed of active materials (2wt%), Super P (0.2wt%), and deionized water were recycled at a flow rate of 1 mL min⁻¹ by a peristaltic pump. To evaluate the performance, the salt remove efficiency (η , %), the average salt removal rate (ASRR, mmol cm⁻² min⁻¹) and charge efficiency (%) were calculated using the following equations:

$$\eta = \frac{C_0 - C_t}{C_0} \times 100\% \quad (4)$$

$$ASRR = \frac{(C_0 - C_t) \times V}{M \times A \times t} \quad (5)$$

$$\text{Charge efficiency} = \frac{F \times (C_0 - C_t) \times V}{1000 \times M \times \int_0^t I dt} \times 100\% \quad (6)$$

where M (58.5 g mol⁻¹) is the molar mass of NaCl, A (cm²) is the effective area between flow electrodes and ion exchange membranes and F (96485 C mol⁻¹) is Faraday constant.

3. RESULTS AND DISCUSSION

3.1 Structural characterization

Carbonization and KOH activation of lignin resulted in porous carbon with three-dimensionally interconnected pores, as can be seen from the SEM image in Fig. 2a and 2c. The resultant carbon is amorphous in general, but curved graphitic structure with small microcrystalline domains, with a separation of 0.35 nm between the graphene layers, can be also seen from TEM images (Fig. 2b and 2d). The identifiable graphitic lattice suggests a relatively high graphitization degree for this material. It should be noted such a graphitization degree is obtained at a relatively low carbonization temperature, while unexpected, could be attributed to the high aromaticity of lignin. The numerous aromatic rings could merge into larger sp²-hybridized network in alkaline condition through Scholl reaction, giving rise to graphitic domains. The high graphitization degree obtained at a low temperature is beneficial to retain a porous structure, which is favored for both charge and mass transportation and thus desired for CDI performance [23].

The high aromaticity of lignin also leads to a high yield of carbon, ~35% at 800 °C, as can be seen from TGA curve in Fig. 3a. A high carbon yield is of practical significance as the energy consumption and pollution could be lowered, making scalable production possible. Alkali lignin contains a small amount of sodium carbonate which was determined by XRD (Fig. 3b). The XRD pattern reveals an overall amorphous nature for LDC-800 and KLDC-800, but the relatively strong and broad diffraction at 26° corresponding to (002) plane of graphitic crystallite still suggests a relatively high graphitization degree. Such a feature was further confirmed by Raman spectroscopy. As can be seen from Fig. 3c, there are two prominent peaks at 1340 cm⁻¹ and 1585 cm⁻¹, characteristic to the vibration for disordered carbon (D-band) and tangential vibration in sp²-hybridized graphitic carbon (G-band) [24]. The I_D/I_G ratios of LDC-800 and KLDC-800 are 0.97, 1.01 respectively. These results suggest lignin is an ideal precursor for porous carbons.

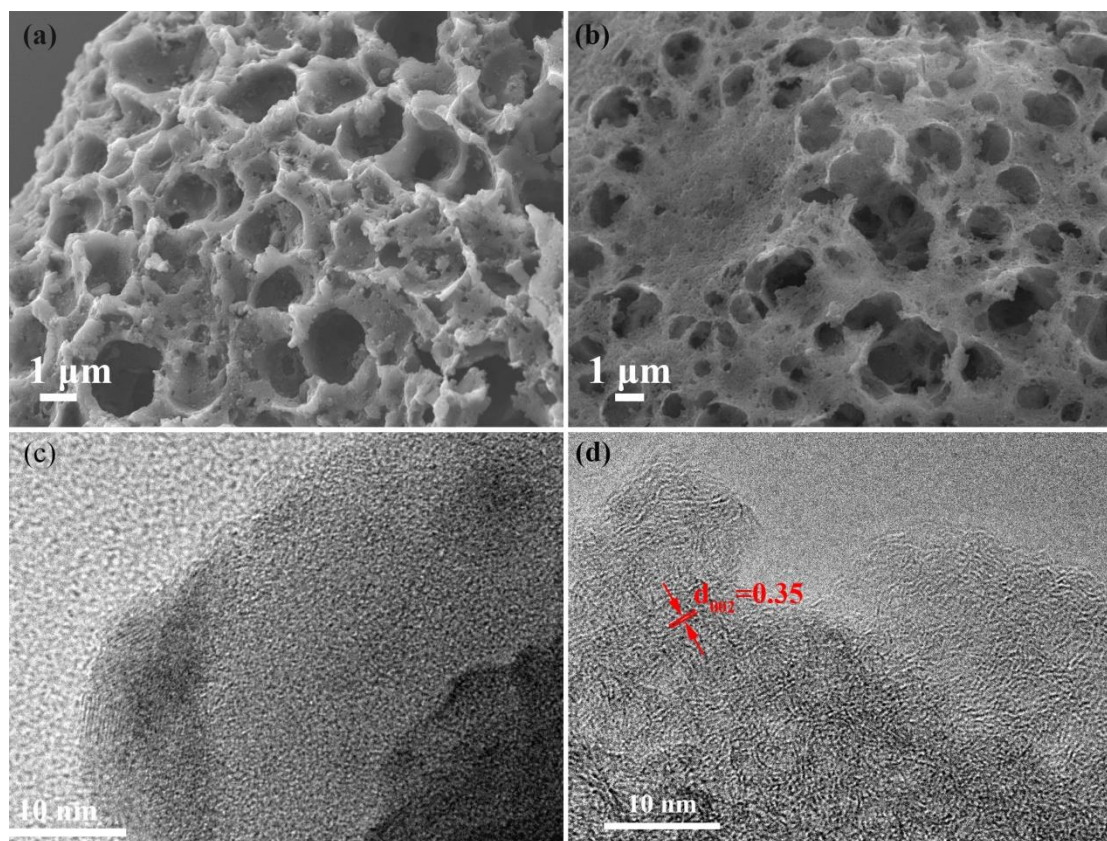


Figure 2. SEM images of: (a) LDC-800, (b) KLDC-800; and TEM images of: (c) LDC-800, (d) KLDC-800.

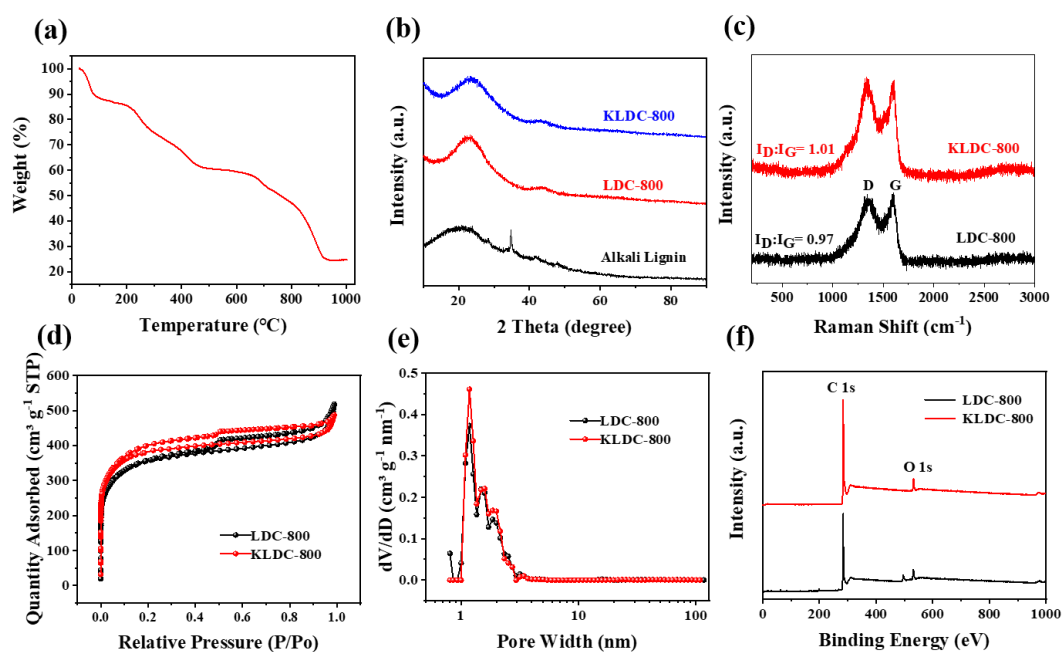


Figure 3. (a) TGA curve of Alkali lignin; (b) XRD patterns of Alkali lignin, LDC-800 and LLDC-800; (c) Raman spectra, (d) N₂ adsorption-desorption isotherms, (e) DFT pore size distributions and (f) XPS spectra of LDC-800 and KLDC-800.

The porous nature was disclosed by N₂ adsorption-desorption isotherm (Fig. 3d). A typical type IV adsorption-desorption behavior was seen, indicating the presence of both micropores and mesopores. Previous studies have well-documented that a hierarchical porous structure is most favored for efficient charge storage and transportation. The BET surface area was increased from 1327 m² g⁻¹ (LDC-800) to 1435 m² g⁻¹ (KLDC-800), and the average pore diameter for LDC-800 and KLDC-800 were 4.5 and 4.1 nm respectively (Fig. 3e). It is thought the sodium carbonate in alkali lignin can serve as the activation agent, which leads to a high surface area for LDC-800. As KOH is an even stronger activation agent, the surface area can be further increased by KOH activation through the following reaction [25]:



The chemical composition was also analyzed by XPS (Fig. 3f), the C and O contents in LDC-800 were 90.92 and 9.08 wt%, and those in KLDC-800 were 92.48 and 7.52 wt%.

3.2 Electrochemical properties

The electrochemical properties were first evaluated using a three-electrode system. As can be seen from Fig. 4a and Fig. 4d, the CV curves for both LDC-800 and KLDC-800 display rectangular shape with no obvious distortion in the potential range -0.5 V ~ 0.5 V (vs Ag/AgCl) even at a scan rate up to 100 mV s⁻¹, which suggests an ideal electrical double layer feature with excellent rate performance (i.e. fast charge storage) [26].

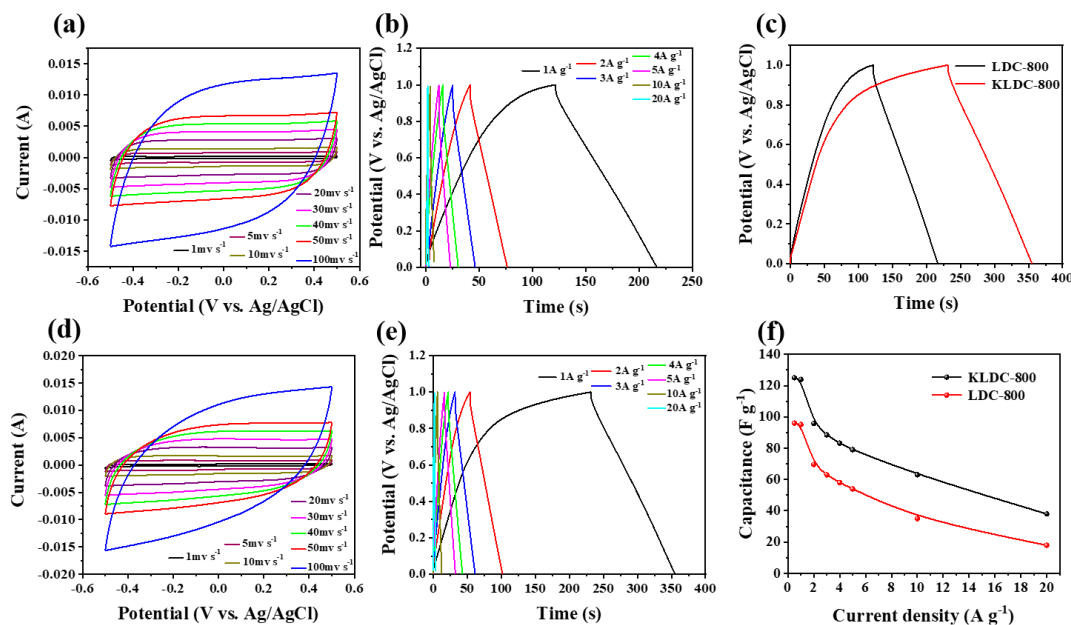


Figure 4. Electrochemical performances of LDC-800 and KLDC-800: CV curves of (a) LDC-800 and (d) KLDC-800; GCD profiles of (b) LDC-800 and (e) KLDC-800; (c) GCD profiles of LDC-800 and KLDC-800 at 1 A g⁻¹; (f) capacitances versus current densities.

The EDLC behavior was also corroborated with the linear and symmetric GCD curves shown in Fig. 4b and Fig. 4e (i.e. high Coulombic efficiency, characteristic EDLC). At 1 A g^{-1} (Fig. 4c), the specific capacitance of LDC-800 was 95.1 F g^{-1} , which increased significantly to 123.9 F g^{-1} upon activation for KLDC-800. The capacitance was plotted as a function of the current density and shown in Fig. 4f. As the current increased to 20 A g^{-1} , the two materials still exhibited capacitances of 20 F g^{-1} and 38 F g^{-1} , respectively, again showing their excellent rate performance. It should be noted that such values were attained with a 1 M NaCl solution as the electrolyte. When tested in a 6 M KOH solution which is more popular for study of the capacitive performance, the capacitances for these two materials are even better due to a higher conductivity and larger number of ions in this electrolyte.

3.3 CDI performance

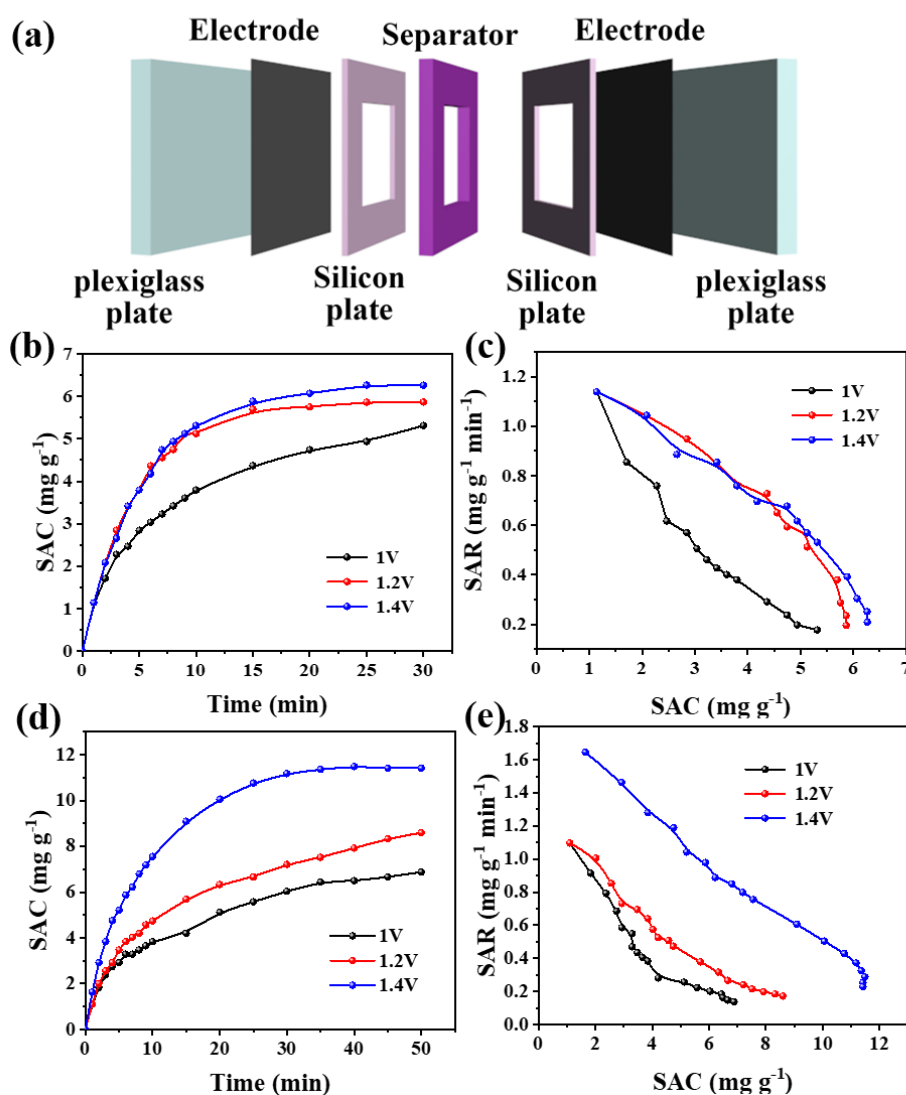


Figure 5. (a) Experimental setup for static CDI tests; The SAC over time for: (b) LDC-800 and (d) KLDC-800; SAR as a function of SAC for: (c) LDC-800 and (e) KLDC-800.

Encouraged by the excellent capacitive storage performance, the materials were pressed into larger electrodes and assembled first into static CDI setup to evaluate the desalination performance (Fig. 5a). For each test, the electrode was stabilized in the electrolyte (brine water) until the electrical conductivity remains constant before applying voltage, to allow the full chem-physical adsorption. Upon applying 1 V, the conductivity decreased rapidly with the initial 25 mins, after which only slight change was observed. The variation of conductivity was converted to the concentration of the solution to calculate SAC and the SAC for LDC-800 and KLDC-800 were demonstrated in Fig. 5b and Fig. 5d. The SAC was 5.3 mg g^{-1} for LDC-800 and increased to 6.9 mg g^{-1} for KLDC-800. As expected, the adsorption capacity increased with the operation voltage, to 6.3 mg g^{-1} for LDC-800 and 11.4 mg g^{-1} for KLDC-800 at 1.4 V. The higher voltage also drives a faster adsorption process, with the major adsorption occurs within the initial 20 mins. However, increasing the voltage beyond 1.4 V led to significant water electrolysis and/or electrode degradation. The Ragone plots (SAR as a function of SAC) for LDC-800 and KLDC-800 at different voltages were demonstrated in Fig. 4c and Fig. 4e [27]. These metrics are comparable with the leading results for biomass-derived carbon reported recently, such as 9.73 mg g^{-1} for Cocoon-derived carbon [28] and 10.79 mg g^{-1} for citruses-derived carbons [29].

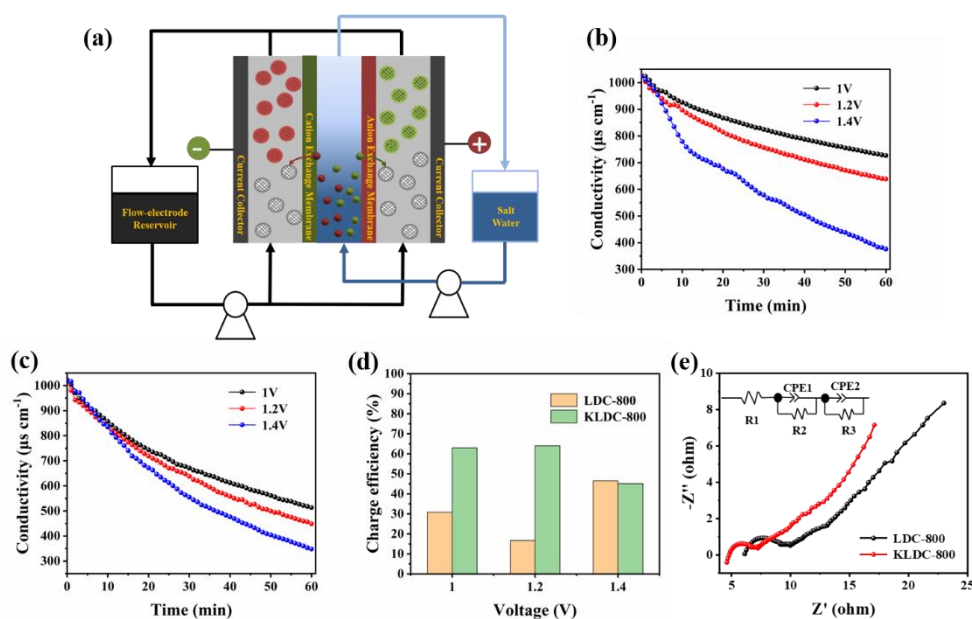


Figure 6. (a) Schematic of the FCDI cell; The variation of conductivity for (b) LDC-800 and (c) KLDC-800; (d) Charge efficiency; (e) the Nyquist plots.

Furthermore, we also dispersed the two materials in water to generate flowable and conductive suspension and assembled them into a FCDI setup, operating in a short-circuited close-cycle batch mode (Fig. 6a). The variation of conductivity for LDC-800 and KLDC-800 were demonstrated in Fig. 6b and Fig. 6c. Upon applying a constant voltage of 1 V, the conductivity of the effluent decreased steadily within 60 mins, suggesting the removal of salt ions from the feed chamber. The fraction of salt adsorbed increased with the increase of voltage, from 29% at 1 V to 63% at 1.4 V for LDC-800 and from 50% at 1V to 66% at 1.4 V for KLDC-800, corresponding to the salt adsorption from 8.83 mg g^{-1} at 1V to 19.01 mg g^{-1} at 1.4V for LDC-800 and from 14.96 mg g^{-1} at 1V to 19.69 mg g^{-1} at 1.4 V for

KLDC-800, i.e. the adsorption capacity is much higher operated in FCDI than in static mode. These changes are accompanied by the average SAR, from $0.00012 \text{ mmol cm}^{-2} \text{ min}^{-1}$ at 1 V to $0.00025 \text{ mmol cm}^{-2} \text{ min}^{-1}$ at 1.4 V for LDC-800 and from $0.00019 \text{ mmol cm}^{-2} \text{ min}^{-1}$ at 1 V to $0.00026 \text{ mmol cm}^{-2} \text{ min}^{-1}$ at 1.4 V for KLDC-800. The charge efficiency, defined as the fraction of energy for salt removal among the total charge input into the system, generally decreased with the increase of voltage (Fig. 6d), which can be understood that Faradaic reactions are triggered at higher voltage.

EIS was employed to further understand the underlying electrochemical processes. Fig. 6e shows the Nyquist plots of the impedance spectra of the FCDI cells, in which the inset shows the equivalent circuit for data analysis [30]. In FCDI, R1 represents both electrolyte resistance, including ion and electron transfer reaction, and electrical resistance at the interface between the flow electrode and current collector [31]. R2 and Q1 (CPE1 in Fig. 6e) represent the resistance and constant phase element of the interfacial charge transfer of the flow electrodes, respectively, and R3 and Q2 (CPE2 in Fig. 6e) are the resistance and constant phase element of the interfacial adsorption of ions on the surface of the flow electrodes, respectively [32]. The fitting parameters from the equivalent circuit are summarized in Table 1. The fitting results suggest that the electrolyte resistance decreases from 5.3Ω (LDC-800) to 4.8Ω (KLDC-800) and the overall interfacial resistance of the flow electrode decreases from 12.8Ω (LDC-800) to 9.8Ω (KLDC-800). These results also indicate that the conductivity both in the electrode and between the electrode and the electrolyte is enhanced upon KOH activation. It has been documented in literature that the FCDI process is influenced by a number of factors such as the electrolyte concentrations in the flow electrode and the feed solution, the content of carbonaceous active material, the type and content of conductive additives, the voltage and the operation mode (such as single pass or batch mode) [33-35]. The values for salt removal rate and charge efficiency herein were achieved at a much lower content of carbon in the electrode, lower concentrations in both the electrode and feed solution, and low voltages. As the preliminary tests showed promising electrochemical capacitance for our lignin-derived carbon, it is envisioned the desalination performance in FCDI will be further enhanced by optimizing the operation conditions, which remain our future work.

Table 1. EIS fitting parameters for FCDI electrodes

	R1(Ω)	R2(Ω)	R3(Ω)
LDC-800	5.3	4.4	8.3
KLDC-800	4.8	2.0	7.7

4. CONCLUSIONS

In summary, it was demonstrated that lignin is a suitable precursor to prepare porous and microcrystalline carbon, which was attributed to the high atomicity and rigidity of this biopolymer. The material produced through a facile KOH activation process displayed good capacitive performance, showing a specific capacitance of 123.9 F g^{-1} as supercapacitor electrode and a NaCl

adsorption capacity of 11.4 mg g⁻¹. It has also demonstrated that FCDI is superior to the static flow-by CDI in terms of the adsorption capacity. However, further efforts are needed to optimize the operation mode and conditions of FCDI to foster the practical application of this technique.

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