Full Length Article

Improvement in the surface properties of activated carbon via steam pretreatment for high performance supercapacitors

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ABSTRACT

Highly controlled steam pretreatment was employed to improve the surface properties of activated carbon (AC) which was extensively applied as electrode materials for electrical double layer capacitor (EDLC). The steam pretreatment at 700 °C followed by hydrogen (H_2) gasification was found to be the optimal condition for enhancing the surface area, pore size and pore volume of AC. Structural and surface analysis revealed the significant reduction in hydroxyl groups after H_2 gasification during the steam pretreatment on AC. The electrochemical characterizations aroused the considerable improvement in the electrocatalytic and capacitive properties of AC electrode after the steam pretreatment at 700 °C. Fabricated EDLC with bare AC electrode exhibited relatively low capacitance of 155.2 F/g, whereas EDLC with steam-treated AC electrode showed the appreciable increment in the capacitance of 187.2 F/g which might be due to improve surface area, and pore volume. The steam-treated AC electrode presented the excellent stability by recording 92% of initial capacity after 1000 cycles.

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1. Introduction

Electrochemical capacitors (ECs) such as electrical double-layer capacitors (EDLCs), ultracapacitors, pseudo-capacitances etc. have owned a great deal of attentions because of their unique energy storage via the formation of electrolyte ions on the surface of electro-active materials [1–4]. In recent years, the electrochemical supercapacitors are recognized as novel power devices due to their high power density, impressive recyclability, and excellent recharging capability with good long stability [5]. Importantly, the electrochemical supercapacitors have shown the bridging function of traditional dielectric capacitors and batteries/fuel cells in terms of energy and power densities with applications in computer power back-up, electric vehicles and power electronics [6,7]. Electrical or electrochemical double layer capacitors (EDLCs) are recently very popular energy storage devices because of their fast charge–discharge rate, high energy density, large cycle life, and environment friendly technology [8]. Electrode materials in EDLCs are crucial component to define the ability of energy storage [9]. In EDLC, the carbon materials are the basic electrode materials owing to their highly porous structure, large surface area, good adsorption property, and high electrical conductivity [10–13]. In order to improve the supercapacitor properties, carbons must depict the well-developed porosity and pore size distribution, which can well match to the ion size and pore size for common electrolyte system.

In most of EDLC, the activated carbons are utilized as common electro-active materials due to high surface to volume ratio, inexpensive as compared to other carbon materials [14–17]. AC materials have generally depicted many disordered micropores which limit the gravimetric capacitance via weak charging/discharging because they make barriers for the accessibility of electrolyte and constrict the space for charge accommodation within the pore wall [18]. AC materials also possess the low electrical conductivity that can confine their applications in high power density supercapacitors, energy storage devices etc. [19]. To improve the pore disorders in AC, many pretreatments such as N_2, NH_3 and mechanical pretreatments have already been used [20]. An understanding of the influence of pretreatments on the physicochemical properties of ACs is very important in manufacturing carbons with a desired structure. In our previous report, the water vapor or steam pretreatment on ordered mesoporous carbon was carried out for the improvement in the catalytic activity of silicon tetrachloride (STC) conversion to trichlorosilane (TCS) [21]. In this work, the steam pretreatment on AC materials has been performed

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to enhance the porous behavior and surface to volume ratio of the materials. The steam pretreated AC materials are extensively applied as electro-active materials for the fabrication of EDLCs. As compared to bare AC, the considerable improvements are observed in the surface properties such as pore size, pore volume and surface area of AC after steam pretreatment. It is also noticed that the electrochemical properties of AC electrode are lifted after the steam pretreatment at 700 °C.

2. Experiment details

2.1. Preparation of steam pretreatment on activated carbon

The steam pretreatment was carried out for improving the surface properties of AC (20–40 mesh, granular, Sigma-Aldrich). U-tube reactor was used for the steam pretreatment performing under highly controlled high temperature system. Desired amount of AC powder was first packed into the U-tube reactor and then connected with the steam line which generated from deionized (DI) water in a heating mantle. A DI water filled round bottle flash was used for the supply of steam via steel pipes. The flash was connected with two lines; one supplied the water and second supplied N_2 gas. The outlet of flash was connected to U-tube reactor for continuous supply of steam. The supply of N_2 gas was made the inert atmosphere inside the flash during the steam formation. Finally, the heating was executed at 700 °C for 2 h. After finishing the pretreatment, the pretreated AC powder in U-tube was cooled under nitrogen (N_2) gas (100–200 sccm) flow to room temperature and collected. Afterward, pretreated AC powder was degassed at 500 °C with 100 sccm H_2 gas under N_2 (150 sccm) flow.

2.2. Measurements of physical properties

N_2 adsorption-desorption isotherms were measured by porosity analyzer (Micromeritics ASAP 2020, USA) after the carbon was degassed at 150 °C–20 mTorr for 12 h. The specific surface areas (S_{BET}) were determined from nitrogen adsorption isotherms using the Brunauer-Emmett-Teller (BET) equation. The total pore volume (V_{Total}) was determined from the amount of gas adsorbed at the relative pressure of 0.99. The pore size distribution (PSD) was derived from analysis of the adsorption branch using the Barrett-Joyner-Halenda (BJH) method. The Fourier transform infrared (FTIR) experiments on the carbon samples were carried out in the wavenumber range of 4000–400 cm^{-1} by a FTIR spectrometer (Nicolet 8700, Thermo Scientific, USA).

2.3. Electrode preparation

The electrodes of bare AC and steam-treated AC powder were prepared according to the following steps. In the beginning, the mixture of 80 wt.% AC materials, 10 wt.% Super-P, and 10 wt.% polytetrafluoroethylene (PTFE, Sigma-Aldrich), and styrene-butadiene rubber (SBR) were well mixed and then was pressed onto an aluminum foil serves as a current collector. Finally, the electrodes were dried in a vacuum oven at 80 °C for 30 min to remove the solvent totally.

2.4. Electrochemical performance

The electrocatalytic behavior of bare AC and steam treated-AC electrodes was studied by measuring the cyclic voltammetry (CV) using the Potentiostat/Galvanostat (VersaSTAT4, AMETEK, Inc.) at different scan rates from 0.1 to 0.5 Vs^{-1} in the voltage range of −1.0 to 1.0 V. For electrochemical measurement of EDLCs, the electrodes were separated by a cellulose nanofibers membrane wetted with the 2 M tetraethyl ammonium tetrafluoroborate
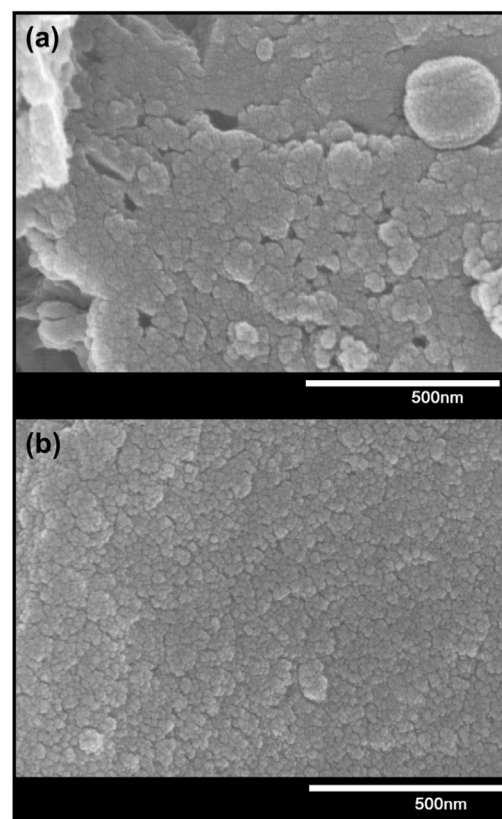

Fig. 1. FESEM images (a) bare-AC and (b) steam-treated AC at high magnification.

(TEABF$_4$, $C_8H_{20}BF_4N$) electrolyte solution. The three layers were then pressed in a coin-type test cell. The capacitive performance of fabricated coin-type electrochemical cell was examined by performing the charge-discharge measurements using a potentiostat (WMPG–1000S, Wonatech. Co.). The electrochemical impedance spectroscopy (EIS) measurements were performed using a Potentiostat/Galvanostat (VersaSTAT4, AMETEK, Inc.) over the frequency ranging from 0.1 Hz to 1 MHz. The charge and discharge current densities were ranged from 0.5 to 10 A g^{-1} with cutoff voltage of 0–2.0 V for supercapacitors based on AC electrodes. The specific capacitance of the supercapacitor can be evaluated from the charge/discharge test together with the following equation:

$$C_s = 2I \cdot \Delta t / (\Delta V \cdot m)$$

Where C_s is the specific capacitance of the capacitor (F/g), I is the current of the charge-discharge, and Δt is the discharging time period in seconds for the potential change ΔV, in volts. The m is the mass load of active materials (include positive and negative electrode). All electrochemical measurements were carried out at room temperature.

3. Results and discussion

The surface morphology of AC materials is determined by field emission scanning electron microscopic (FESEM) images, as shown in Fig. 1. Before pretreatment, the large aggregates, non-uniformity in the particles have been observed, however, the steam pretreatment considerably improves the uniformity of particle sizes. From Fig. 1(b), it is seen that steam treated AC displays highly uniform, porous and less aggregated surface. The highly uniform and porous structure of steam treated AC materials could offers the high surface area to volume ratio [22].
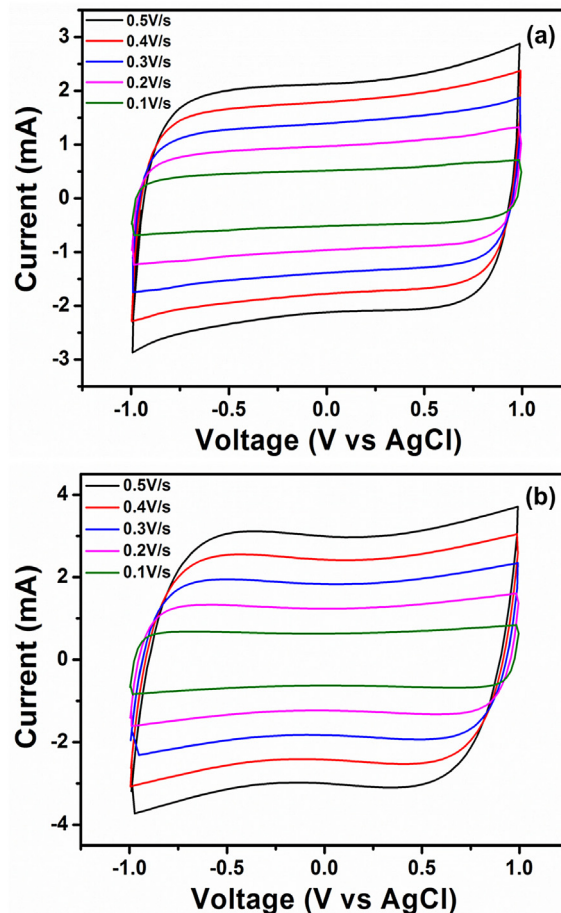
Table 1
Surface analysis of bare-AC, steam-treated AC materials and capacitance parameters of EDLCs with AC electrodes.

Physical properties			Capacitance parameters					
	bare-AC	steam-AC						
Pore size(nm)	2.04	1.87	Current density	$(A\,g^{-1})$	10	5	1	0.5
V_T $(cm^3\,g^{-1})$	0.483	1.005	Specific Capacitance	bare-AC	92.1	96.05	117.58	155.16
S_{BET} $(m^2\,g^{-1})$	948.9	2155.95	$(F\,g^{-1})$	steam-AC	136	143.42	168.1	187.21
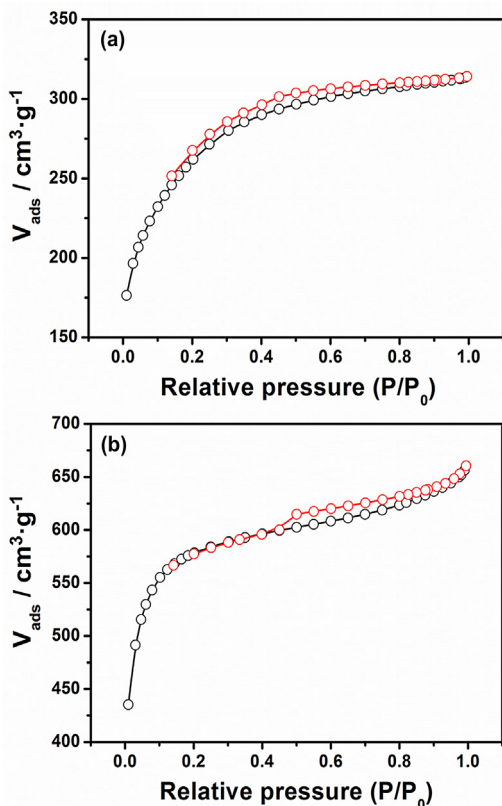
Fig. 2. Nitrogen adsorption-desorption isotherms of (a) bare-AC and (b) steam-treated AC.
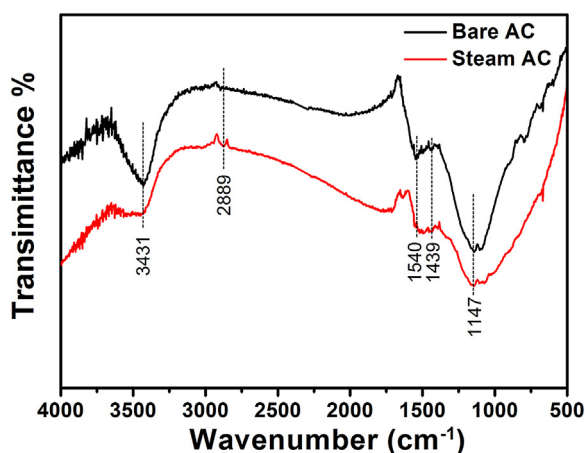
Fig. 3. FTIR spectra of bare-AC and steam-treated AC in the range of 4000–500 cm^{-1}.

Fig. 4. Cyclic voltammograms of (a) bare-AC, (b) steam-treated AC electrodes measured at various scan rates in 2.0 M TEABF$_4$.

The surface properties of AC materials in terms of pore structure and the surface area have been obtained by the nitrogen (N$_2$) adsorption method. Fig. 2 shows the N$_2$ adsorption-desorption isotherms of bare AC and steam-treated AC materials. Surface properties such as BET surface area, pore size and pore volume are summarized in Table 1. It is seen that steam treated AC exhibits a hysteresis loop showing a typical type IV isotherm, suggesting the highly mesoporous surface of AC. On the other hand, bare AC shows a weak hysteresis loop in N$_2$ absorption-desorption isotherm, as shown in Fig. 2(a). After steam pretreatment, the significant increases in BET surface area of 2155.95 m^2/g and pore volume of 1.005 cm^3/g are recorded, which results from the existence of hysteresis loop in N$_2$ absoprtion-desorption isotherm (Fig. 2(b)). It is known that the pore size distribution and proportion of mircopores within AC are very important properties for the high charge transportation in supercapacitors [23]. In addition, the average pore size is decreased from 2.014 nm to 1.78 nm after the steam pretreatment on AC at 700 °C, which might be due to the release of volatile matter and collapse of partial thin pore walls under high temperature. In case of capacitors, the pore size of ~2 nm is wide enough for the proper ions absorption of electrolytes such as TEABF$_4$, LiPF$_6$, (C$_2$H$_5$)$_4$NBF$_4$ in propylene carbonate (PC) [24]. Therefore, the carbon surface pores are improved by generating new functional groups through oxidation reactions and large active sites after the steam pretreatment on AC at 700 °C.
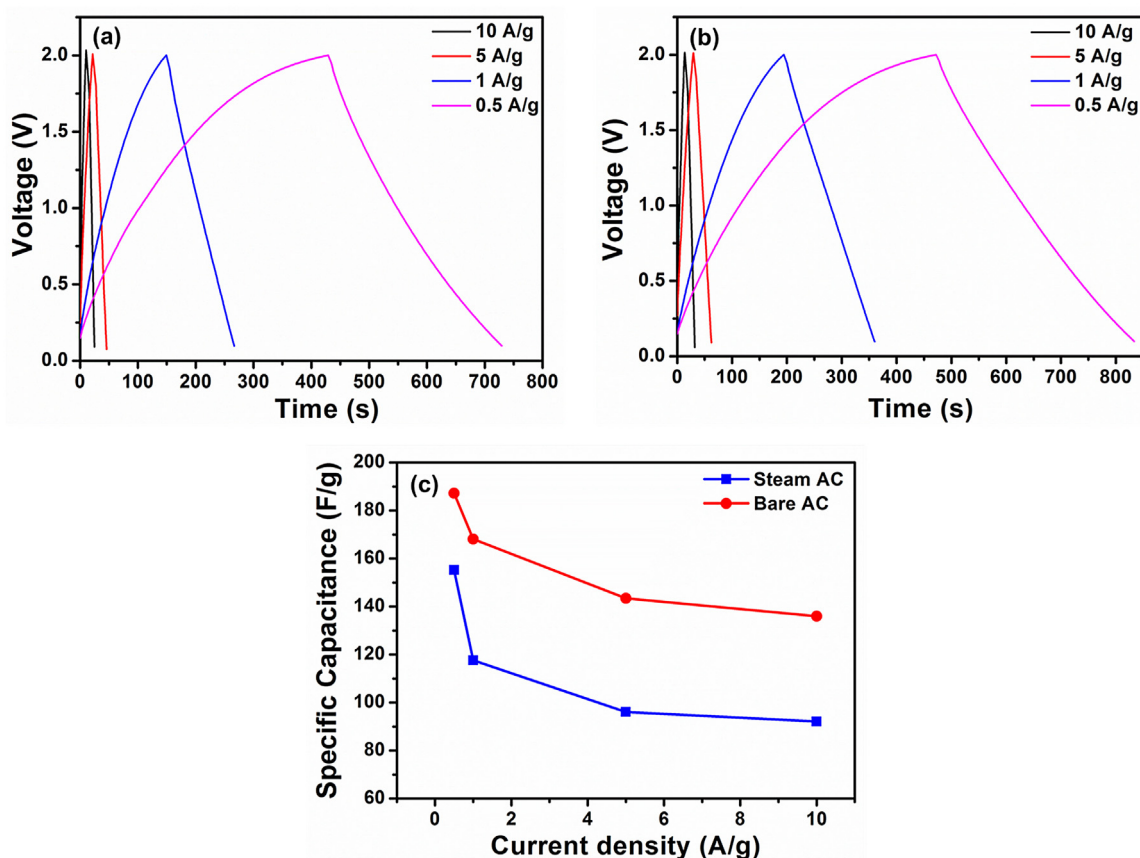
Fig. 5. Representative galvanostatic charge-discharge curves of EDLCs with (a) bare-AC and (b) steam-treated AC electrode at various current densities from 5 to 10 Ag^{-1}, and (c) representative plot of specific capacitances versus current densities for EDLCs with bare-AC and steam-treated AC electrodes.

The FT-IR spectra of the carbon materials was shown in Fig. 3 and the IR bonds at 3431, 2889, 1540, 1439, 1147 cm^{-1} are observed for bare AC and steam-treated AC materials. The IR bands at 3430 cm^{-1} and 2889 cm^{-1} are assigned to —OH stretching vibration [25] and C—H vibration, respectively [26]. However, IR bands at 1540, 1439 cm^{-1} and 1147 cm^{-1} could be ascribed to OH bending, C=C and C—O vibration [27,28]. From Fig. 3, the appearance of a small IR band at 1640 cm^{-1} in steam-treated AC suggests the generation of new functional groups i.e. COO$^-$ after steam pretreatment.

The electrochemical behaviors of bare and steam-treated AC electrodes are studied by cyclicvoltammetry (CV) in 2 M TEABF$_4$ electrolytes with a potential window of −1.0 to 1.0 V vs. SCE using a three-electrode system at room temperature. Fig. 4 shows the CVs of the bare-AC and steam-AC electrodes at different scan rates from 0.1 to 0.5 V/s. Both AC electrodes present rectangular-like CV plots without obvious redox currents on both positive and negative sweeps in the whole potential range of investigation, which are resembled to the reported CV characteristics of EDLCs [29,30]. It is notable that the shape of CV plot is retained at high scan rate of 100 mV/s for bare AC and steam treated AC electrodes based on EDLCs, reflecting good capacitive properties and excellent contact. From Fig. 4, the steam-treated AC electrode expresses the larger redox current and larger area of rectangle CV than that of bare-AC, indicating the high faradic redox reactions which is usually due to generation of active oxygen-containing groups on the carbon based electrode after steam pretreatment.

Galvanostatic charge-discharge measurements were conducted in a two-electrode system under the cutoff voltage of 0–2.0 V in TEABF$_4$/PC organic electrolyte at room temperature with different current density ranging from 0.5 Ag^{-1} to 10 Ag^{-1}, as shown in Fig. 5.

From Fig. 5, the discharging time in galvanostatic charge/discharge curves of the steam-treated AC electrode is longer as compared to bare-AC electrode at high and low current densities. It suggests that the steam-treated AC might possess a large specific capacitance, which is in good agreement with CV results. The galvanostatic charge/discharge curves have been used to evaluate the specific capacitance of fabricated EDLCs, as summarized in Table 1. Fig. 5(c) displays the specific capacitances with respect to the current densities of the fabricated EDLCs. With the increase of current densities, the specific capacitance values gradually decrease, which might be due to the limited diffusion of the active ions on the electrode's surface during the fast charging at current density. The steam-treated AC electrode accomplishes the high specific capacitance of 187.21 Fg^{-1} at current density 0.5 Ag^{-1} whereas, a relatively low specific capacitance of 155.16 Fg^{-1} is achieved by the fabricated EDLC based on bare AC electrode, as seen in Table 1. As seen in surface properties, the steam pretreatment process on AC is considerably increase the porosity and improves the active sites over the surface. In general, the large porosity facilitates the mass transfer among the AC granules, tending to enhance the high-rate ion capability [31]. However, the excessive increment in porosity of AC might deteriorate the electrical conductivities of AC electrode, resulting in the high-rate capability [32]. Moreover, the steam-treated surface leading the surface functionalization of AC might increase the wettability of electrolyte, which is beneficial for fast ions transportation to achieve high specific capacitance. In addition, the presence of mesopores can enhance utilization of the exposed surface for charge separation and provide resistance pathways for the ions through the porous particles [33]. Thus, the high specific capacitance of fabricated EDLC based on steam-AC electrode is
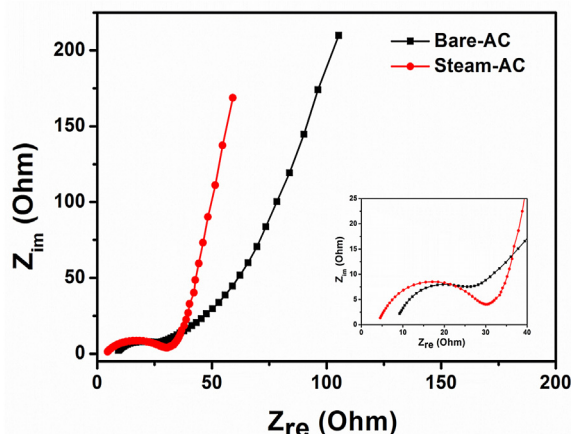
Fig. 6. Nyquist plot for bare-AC and steam-treated AC electrodes based EDLCs using the frequency range from 0.1 Hz to 10 MHz.

attributed to the high specific surface area and large pore volume of steam-treated AC materials.

To further investigate the electrochemical properties of AC electrodes, an electrochemical impedance spectroscopy (EIS) has been performed. EIS measurements have been carried out to elucidate the characteristic frequency response of supercapacitor and the capacitive phenomena occurring in both of the electrodes. Fig. 6 shows the Nyquist plots of fabricated EDLCs with bare-AC and steam-treated AC in the frequency range of 0.1 Hz–1 MHz. At low frequency region, both EDLCs present the vertical curves, representing the ions diffusion within electrode structure, which is the indicative of ideal capacitive behavior of AC materials. On the other hand, the intercept of plot in Z_{re} axis at high frequency is explained the low series or electrolyte resistance, which define the ionic resistance of electrolyte, intrinsic resistance of carbon (AC) active materials, and contact resistance with the current collector [34]. It is visible that steam-treated AC electrode exhibits the low series resistance of 4.56 Ω as compared with bare AC electrode, resulting from the improved pore size, pore volume and high surface area of AC after steam pretreatment which facilitate the diffusion and good penetration of electrolyte ions and decrease the ions diffusion distance [35,36]. Moreover, the Warburg resistance at low frequency region originated from the ion diffusion/transport from electrolyte to electrode surface. Less inclined or straight line observes in the steam-treated AC electrode, suggesting the good ion diffusion into the pore structures. Therefore, it is clear that the steam pretreatment on AC substantially advances the surface properties like surface area, pore volume and pore distribution which significantly increase the electrochemical and capacitive properties of AC electrode.

The EDLC performances of the bare-AC and steam-AC electrodes at higher current density were recorded by continuous increase in current density (initially 0.5, 0.7 and then 1 A g^{-1}) after every five charge-discharge cycles, and the representative data are presented in Fig. 7(a). Steam-treated AC electrode expresses the stable specific capacitance values as the cycle progresses; however, the slight decrease in capacitance values are recorded with 173 F g^{-1} and 168 F g^{-1} at 0.7 A g^{-1} and 1.0 A g^{-1} with the increase of current densities, respectively. The loss in capacitances with the increase of cycles might be associated to the disordered nature of AC, which can restrict faster movement of electrolyte ions to reach adsorption sites to some extent. From Fig. 7(a), bare-AC based electrode illustrates the higher decrease in specific capacitance like 132 F g^{-1} at 0.7 A g^{-1} and 117 F g^{-1} at 1.0 A g^{-1}. Fig. 7(b) shows the variation in specific capacitance with respect to cycles. EDLC with steam-treated AC electrode displays the superior stability by maintaining
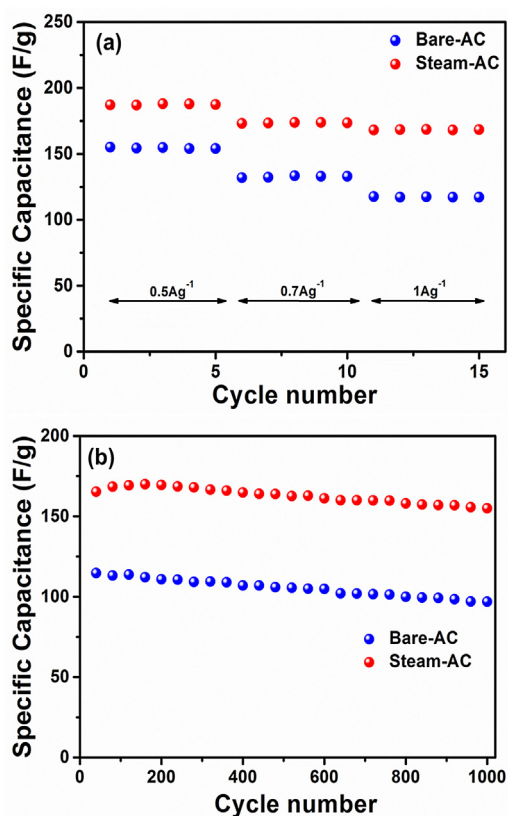

Fig. 7. (a) Capacitive performances at different current density in short cycles for bare-AC and steam-treated AC electrodes and (b) recyclability performances at 1.0 A/g current density for EDLCs with bare-AC and steam-treated AC electrodes after 1000 cycles.

~92% of initial capacitance after 1000 cycles in comparison with bare AC electrode. The advancement in stability of EDLC with steam-treated AC electrode is attributed to the intensified surface characteristics such as surface area, mesopores, and pore volume. These factors are substantial for steam-treated AC electrode to produce more adsorption sites for the accommodation of organic electrolyte ions through the mesoporous entrances at low current density. This performance clearly shows the importance of pore volume and surface characteristics by steam pretreatment in AC for better EDLC performance.

4. Conclusions

Surface properties such as surface area, pore distribution and pore volume were improved by highly controlled steam pretreatment on AC materials at 700 °C followed by H$_2$ gasification and employed as electrode materials for EDLCs. The significant decrease in the hydroxyl groups of AC by steam pretreatment followed by H$_2$ gasification. After the steam pretreatment at 700 °C, the electrocatalytic activity of AC materials was considerably enhanced which resulted in the improvement of the electrochemical and capacitive properties of AC electrode. A high specific capacitance of 187.2 F/g was recorded by the EDLC based steam-AC/700 °C electrode and EDLC based on bare AC electrode exhibited low capacitance of 155.2 F/g. The steam pretreatment on AC materials significantly elevated the electrode properties, resulting in the excellent stability by persisting ~92% of initial capacity after 1000 cycles.

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