ORIGINAL PAPER

# RF oxygen plasma treatment of activated carbon electrodes for electrochemical capacitors

**Chuen-Chang Lin · Chia-Cheng Yen**

**Abstract** Activated carbon modified by Radio Frequency (RF) plasma at different power levels, times and volume flow rates of oxygen was prepared for activated carbon electrodes. Electrochemical characterization of different activated carbon electrodes was carried out using cyclic voltammetry (CV) with different electrolytes at a concentration of 0.1 M. A maximum capacitance of 38.9 F $g^{-1}$ was obtained in a 0.1 M $H_2SO_4$ solution for the activated carbon (precursor material: coconut shell made in Japan) with plasma treatment conditions: power = 300 W, time = 3 min, and volume flow rates of oxygen = 45 sccm (standard cubic centimeter per minute). In addition, specific surface areas/pore-size distributions, functional groups, and surface morphologies of activated carbon with/without plasma treatment were examined by gas adsorption meter, Fourier transform infrared spectroscopy (FTIR), and scanning electron microscope (SEM), respectively.

**Keywords** RF plasma · Activated carbon · Fourier transform infrared spectroscopy · Electrochemical capacitors

## 1 Introduction

Electrochemical capacitors are charge-storage devices which possess higher power density and longer cycle life than batteries [1, 2]. Their applications include hybrid power sources, backup power sources, starting power for fuel cells, and burst-power generation in electronic devices [3–7]. Electrochemical capacitors are classified into two types, electric double layer capacitors (EDLC) and pseudo-capacitors according to the energy-storage mechanisms. The capacitance of an EDLC arises from the separation of charge at the interface between the electrode and the electrolyte. However, pseudocapacitance arises from redox reactions of electroactive materials with several oxidation states [1, 8–12].

The specific surface areas and pore size distributions of activated carbon influence the capacitance [13–15]. In addition, functional group distributions on the surface of activated carbon also affect the capacitor performance [15]. For example, the modification of activated carbon fiber cloth (ACFC) electrodes was performed by cold plasma in Ar–$O_2$ atmosphere and the effect of its cold plasma treatment on the capacitor performance was discussed according to functional groups and pore size distributions of the ACFC surface [15]. Furthermore, Cascarini De Torre et al. [16] stated that graphitized carbon black was oxidized in a cool oxygen plasma and this treatment changed graphitized carbon black surfaces from hydrophobic to hydrophilic. Li and Horita [17] mentioned that the carbon black surface was modified by low temperature oxygen plasma, it changed from hydrophobic to hydrophilic and its functional groups containing oxygen increased. Thus, in this research, a Radio Frequency (RF) oxygen plasma was used to modify the surface properties (specific surface areas, pore size distributions, and functional groups, etc.) of activated carbon without changing its bulk properties.

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## 2 Experimental methods

About 25 g of activated carbon powder was evenly spread on the bottom of a vessel (height: 4.9 cm, inside diameter: 4 cm,

**Table 1** Size distributions, specific surface areas, and specific capacitance (in a 0.1 M $H_2SO_4$ solution) of activated carbon prepared with different precursor materials

| Activated carbon | Size distribution (%) | Specific surface area ($m^2 \ g^{-1}$) | Specific capacitance ($F \ g^{-1}$) |
|---|---|---|---|
| *Precursor material* | | | |
| Coconut shell made in Japan | Macropore: 34 | 1,419 | 29 |
| | Mesopore: 45 | | |
| | Micropore: 21 | | |
| Wood | Macropore: 38 | 1,183 | 23.1 |
| | Mesopore: 43 | | |
| | Micropore: 19 | | |
| Coconut shell made in USA | Macropore: 52 | 709 | 13.7 |
| | Mesopore: 34 | | |
| | Micropore: 14 | | |
| Coke made in Japan | Macropore: 46 | 989 | 19.4 |
| | Mesopore: 36 | | |
| | Micropore: 18 | | |

and outside diameter: 8.3 cm) of stainless steel. The vessel was placed into a reaction chamber (85 $cm^3$) for plasma treatment (frequency: 13.56 MHz and maximum power: 1,000 W). The chamber was degassed to $10^{-5}$ torr. Finally, oxygen gas was introduced to the chamber and the activated carbon powder was modified by RF plasma at different power levels (100–500 W), times (1–5 min) and volume flow rates (30–60 sccm) of oxygen. The resulting modified activated carbon power was incorporated into electrodes.

About 1.7 g of the plasma treated activated carbon was completely mixed with 0.3 g of poly-vinylidenefluoride (PVDF) binder and 3.5 mL of NMP (*N*-methyl-2-pyrolidinone) solvent for 10 min and then shaken ultrasonically for 20 min to completely remove any bubbles formed by stirring. The mixed sludge of electrode material was then homogeneously spread on stainless steel mesh (about 1 $cm^2$) by means of a knife blade to an approximate thickness of 1 mm. The mesh had previously been rinsed ultrasonically with acetone, etched in 6 M aqueous HCl for 30 min at 75 °C to increase its surface roughness, rinsed ultrasonically with deionised water and then dried in air and weighed. Finally, the prepared electrodes were dried for 8 h at 90 °C and weighed.

Specific surface areas and pore-size distributions of activated carbon were analyzed using a gas adsorption meter (Autosorb-1, Quantachrome). In addition, functional groups of activated carbon with/without plasma treatment were analyzed by Fourier transform infrared spectroscopy (FTIR) (Perkin Elmer LEE-59). Furthermore, surface morphologies of activated carbon with/without plasma treatment were conducted by scanning electron microscope (SEM) (JOEL 5410LV, Japan).

The electrochemical measurements for the prepared electrodes were performed using an electrochemical analyzer (CH Instruments CHI 608B, USA). The three-electrode cell consisted of Ag/AgCl as the reference electrode, Pt as the counter electrode and the prepared electrodes as the working electrode. The electrolytes were degassed with purified nitrogen gas before voltammetric measurements and nitrogen was passed over the solution during all the measurements. The solution was maintained at 25 °C by means of circulating water thermostat (HA-AKE DC3 and K20, Germany). The CV was undertaken with different electrolytes ($H_2SO_4$, $Na_2SO_4$, KCl, NaCl, and LiCl) at a concentration of 0.1 M. A CV scan rate of 25 mV $s^{-1}$ in the range 0–1 V was used in all measurements except where stated. Specific capacitance ($F \ g^{-1}$) is normalized to 1 g of activated carbon except where stated.

## 3 Results and discussion

Table 1 shows that the lower the percentage of the macropore size distribution, the higher the specific capacitance; and the higher the specific surface area, the higher the specific capacitance. The reason behind this behavior may be that the lower the percentage of the macropore size distribution, the higher the specific area, leading to higher specific capacitance. Thus, the activated carbon whose precursor material is coconut shell made in Japan was chosen for plasma treatment due to its highest capacitance.

Figure 1 shows the effect of different electrolytes at a concentration of 0.1 M on the specific capacitance of activated carbon; this reached a maximum with $H_2SO_4$. This may be because $H_2SO_4$ has the smallest hydration cation ($H^+$) diameter (1.916 Å) and smaller hydration anions ($HSO_4^-$ and $SO_4^{2-}$) diameter (5.84 Å and 5.33 Å), respectively (See Table 2) and thus its ions more easily penetrate the 21% micropore (pore diameter < 20 Å) of the activated carbon (See Table 1, precursor material: coconut shell, Japan). In addition, a pore size of around two to three

**Fig. 1** Effect of different electrolytes at a concentration of 0.1 M on the specific capacitance [A (NaCl): 24.3 F g$^{-1}$, B (Na$_2$SO$_4$): 26.8 F g$^{-1}$, C (H$_2$SO$_4$): 29 F g$^{-1}$, D (LiCl): 21.6 F g$^{-1}$, and E (KCl): 27.5 F g$^{-1}$] of activated carbon whose precursor material is coconut shell made in Japan
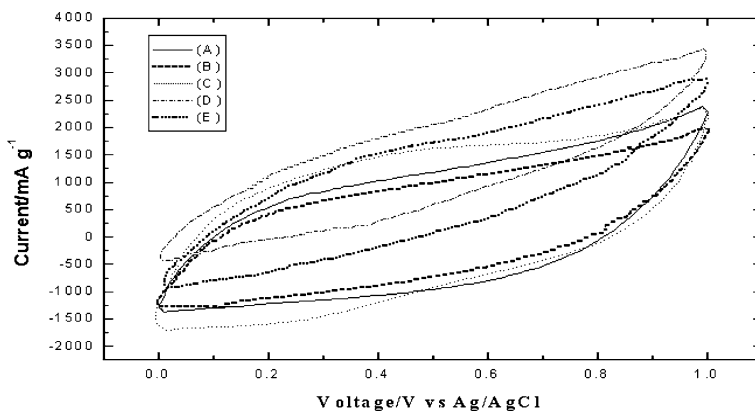


**Table 2** Hydration ion diameters of different electrolytes [7, 18–20]

| Electrolytes | LiCl | Na$_2$SO$_4$ | KCl | NaCl | H$_2$SO$_4$ |
|---|---|---|---|---|---|
| Cation | Li$^+$ | Na$^+$ | K$^+$ | Na$^+$ | H$^+$ |
| Hydration cation diameter | 7.64 Å | 7.16 Å | 6.62 Å | 7.16 Å | 1.916 Å |
| Anion | Cl$^-$ | SO$_4^{2-}$ | Cl$^-$ | Cl$^-$ | HSO$_4^-$ (SO$_4^{2-}$) |
| Hydration anion diameter | 6.64 Å | 5.33 Å | 6.64 Å | 6.64 Å | 5.84 Å (5.33 Å) |

times larger than the hydration ion diameter of the electrolyte has been considered as the most suitable pore size for allowing good capacitance [19].

Figure 2 shows the effect of the power on the specific capacitance, which reached a maximum at 300 W. This phenomenon is attributable to variations in oxygen functional groups on the surface at different power levels. Figure 3 reveals that the higher the power, the more numerous the oxygen functional groups at lower power (100, 200, and 300 W), which in turn leads to higher specific capacitance. However, it shows that the higher the power, the less numerous the oxygen functional groups at higher power (400 and 500 W), which leads to lower

specific capacitance. Moreover, the surface morphologies of activated carbon without plasma treatment and with plasma treatment at the conditions 300 W, 3 min and 45 sccm of oxygen are shown in Fig. 4a, b, respectively. Figure 4b reveals more numerous pores due to etching with plasma treatment.

Figure 5 shows the effect of the time (1, 3, and 5 min at 300 W and 45 sccm of oxygen) on the specific capacitance, which reached a maximum (38.9 F g$^{-1}$) at 3 min. Further, Fig. 6 shows the effect of the volume flow rates of oxygen (30, 45, and 60 sccm at 300 W and 3 min) on the specific capacitance, which reached a maximum (38.9 F g$^{-1}$) at 45 sccm of oxygen, but showed only a small difference.

**Fig. 2** Effect of the power of plasma treatment (1 min and 45 sccm of oxygen) on the specific capacitance [A (400 W): 9 F g$^{-1}$, B (500 W): 6 F g$^{-1}$, C (300 W): 33.4 F g$^{-1}$, D (100 W): 28 F g$^{-1}$, and E (200 W): 30 F g$^{-1}$] in a 0.1 M H$_2$SO$_4$ solution
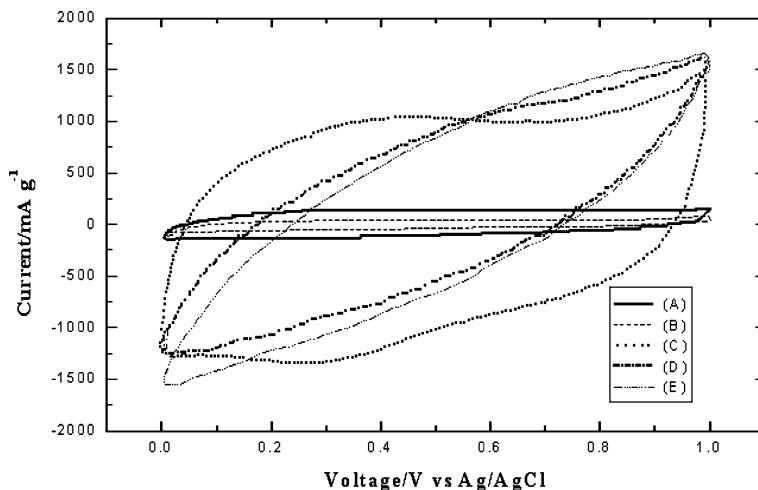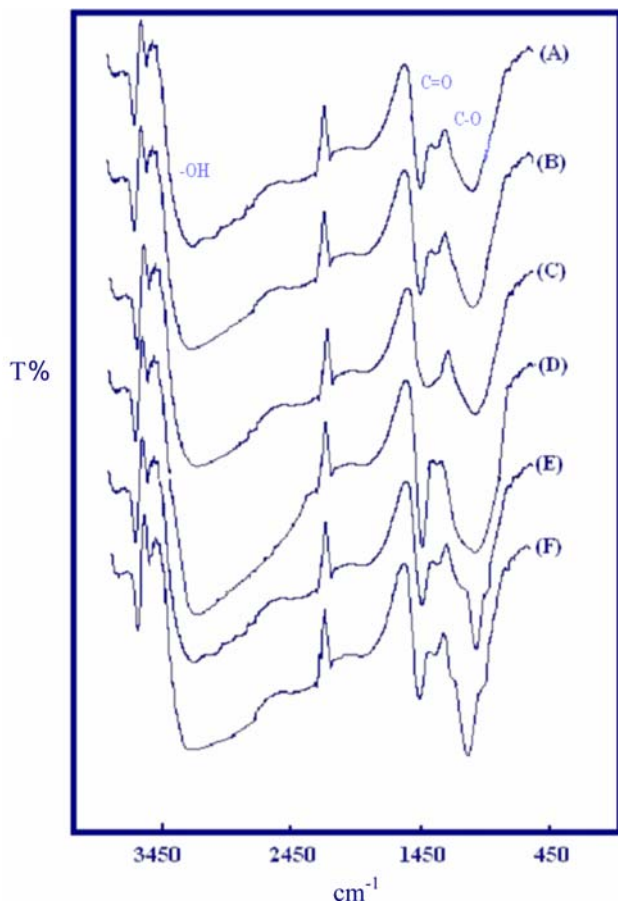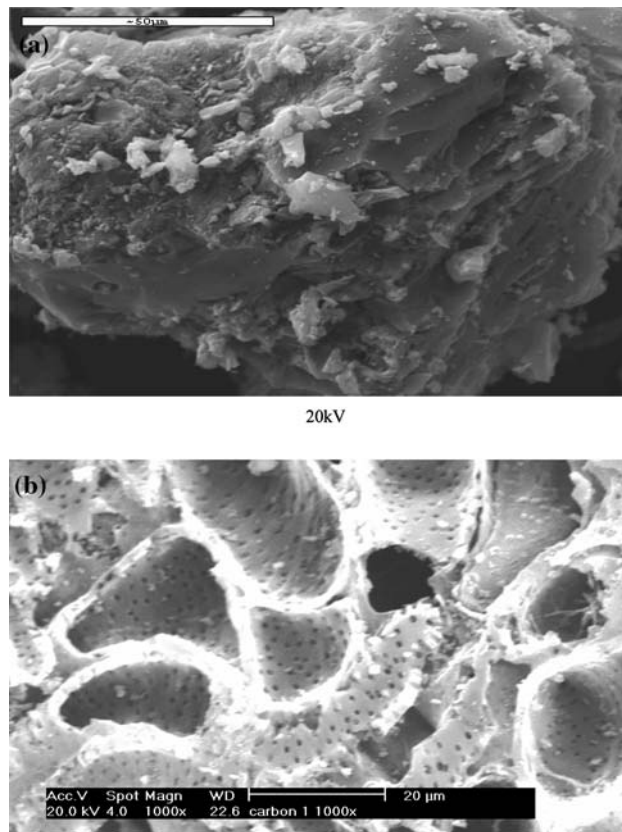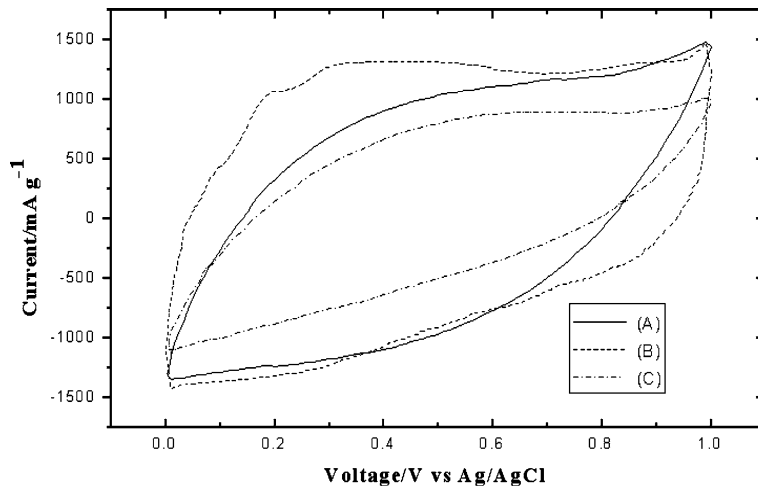
**Fig. 3** FTIR spectrum of activated carbon with plasma treatment (3 min and 45 sccm of oxygen) at various power levels [100 W (B), 200 W (C), 300 W (D), 400 W (E), and 500 W (F)] and activated carbon (A)

## 4 Conclusion

A maximum capacitance of 38.9 F g$^{-1}$ was obtained in a 0.1 M H$_2$SO$_4$ solution for the chosen activated carbon with



**Fig. 4** (**a**) SEM micrograph of activated carbon without plasma treatment. (**b**) SEM micrograph of activated carbon with plasma treatment at the conditions (300 W, 3 min, and 45 sccm of oxygen)

the following plasma treatment conditions: power = 300 W, time = 3 min, and volume flow rate of oxygen = 45 sccm. In addition, FTIR revealed that the higher the power, the more numerous the oxygen functional groups on the surface of activated carbon at lower power (100, 200, and 300 W), thus leading to higher specific capacitance.
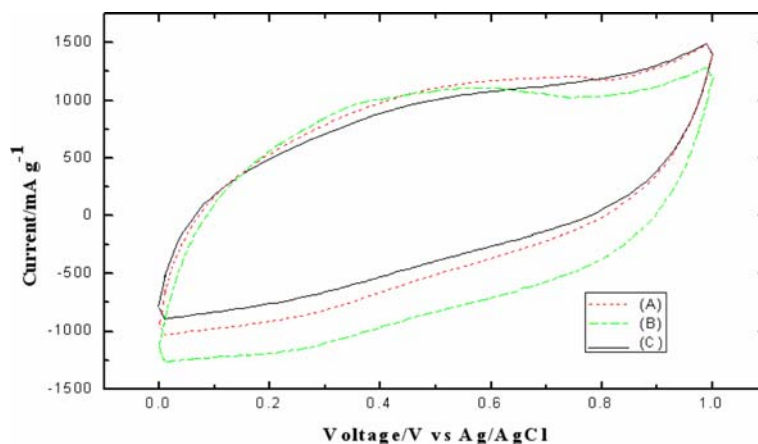
**Fig. 5** Effect of time of plasma treatment (300 W and 45 sccm of oxygen) on the specific capacitance [A (1 min): 33.4 F g$^{-1}$, B (3 min): 38.9 F g$^{-1}$, and C (5 min): 27 F g$^{-1}$] in a 0.1 M H$_2$SO$_4$ solution

**Fig. 6** Effect of $O_2$ volume flow rate (300 W and 3 min) on the specific capacitance [A (30 sccm): 36.5 F $g^{-1}$, B (45 sccm): 38.9 F $g^{-1}$, and C (60 sccm): 35.1 F $g^{-1}$] in a 0.1 M $H_2SO_4$ solution



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