Performances of Electrical Double-layer Capacitors Composed of Pitch-based Activated Carbons

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The ACS-series activated carbons with specific surface areas were produced from coal tar pitch by an alkali-activation program at China Steel Chemical Corporation. The surface area, porosity characteristics, and ash content of the activated carbons were characterized and compared with those of the coconut shell based activated carbons. The electrochemical performance of the electrode materials made of the activated carbons were investigated with a radical-type Electrical Double-Layer Capacitor (EDLC) assembly. The volumetric capacitance and specific energy of the electrodes were found to increase with the porosity of micropores, while the Dc resistance and leakage current had showed an opposite trend. The electrode consisting of energy-type activated carbon ACS15 or ACS20 could reach a maximum volumetric capacitance of 67 F/cc, and its specific energy was larger than 1.68 Wh/kg. The electrode made of activated carbon ACS25 had the advantage of power performance and exhibited a specific power higher than 4000 Wh/kg. Due to the low ash content, the EDLCs consisting of ACS-series activated carbons had shown an excellent electrochemical reliability under aging or cyclic charge-discharge conditions.

Keywords: Coal tar pitch, Activated carbon, Electrical double layer capacitor

1. INTRODUCTION

Highly porous activated carbons are the crucial material for Electrical Double Layer Capacitors (EDLCs). The capacitance of EDLC is dominated by the electrically active surface within the micro-scale porous structure, and hence the pore size should be accessible for ionic charge-complexes of the electrolyte[1-3]. The specific pore characteristics of activated carbons are highly relative to the natural structure of its precursor, and the activation engineering.

Biomass materials are the principal source of the activated carbons that commercial EDLCs generally use, e.g. the coconut shell[4]. For the coconut shell based activated carbons, the carbonaceous porous structure is derived from the mesocarp of coconut using the steam activation and the micropores are created externally during steam-etching. However, the biomass precursor also contains a large amount of residual impurities, and the electrochemically active impurities generally cause irreversible reaction and strongly impact the reliability of ELDC performances.

Activated carbons can also be obtained from coal tar pitch, petroleum pitch, and some of the artificial resins[4]. Their porous structure and impurity can be precisely controlled to fit the requirement of EDLC applications. Particularly, the pitch precursors belong to soft carbon, and therefore the resulting carbon materials can achieve much higher electrical conductivity than artificial resins and biomass materials.

ACS-series activated carbons from China Steel Chemical Corporation (CSCC) are produced from coal tar pitch using an alkali-activation program. Depending on the recipe and procedures, the pitch-based activated carbons can be obtained with their individual Brunauer-Emmett-Teller (BET) surface area, microporosity, and pore size distribution. Three products of ACS-series activated carbons, ACS15, ACS20 and ACS25 were categorized by the BET surface area.

In this study, the correlation between the material characteristics and the electrochemical performances of ACS-series activated carbons was investigated. The coconut shell based activated carbons were also used for comparison.

2. EXPERIMENTAL

2.1 Characterization of activated carbons

Three ACS-series activated carbons, ACS15, ACS20 and ACS25 from CSCC were used as electrode materials of EDLCs. Two coconut shell-based activated carbons, C1 and C2, were the comparison samples

which were produced by steam-activation. Specific surface areas and pore volumes of these five activated carbons were determined by an isothermal N_2 adsorption and desorption at 77 K using the BET and t-plot methods, respectively. The amount of N_2 adsorbed at relative pressures near unity was employed to determine the total pore volume[5], and the microporosities were represented via the ratio of micropore volume and the total pore volume. The median pore widths were calculated using the Horvath-Kawazoe method.

To examine the ash content, 5 g of the activated carbons were oxidized at 900°C in an air atmosphere, the weight fraction of the remaining substance was represented as the impurity.

2.2 Preparation of electrical double layer capacitors

Radical-type EDLCs were prepared to examine the electrochemical performance of activated carbon samples. Firstly, the single-side-coated electrodes were fabricated by coating an activated carbon slurry layer upon a surface-etched aluminum foil strip. The aqueous slurry used was prepared by mixing activated carbon, conductive carbon (SuperP Li®), binder latex, and DI-water with the weight ratio of 20:2:3:75. The slurry coated on the aluminum foils were then dried at 80°C to form laminated electrode sheets. After a subsequent rolling step, the activated carbon layer was adjusted to have a thickness of approximately 100 μm.

To assemble the EDLCs, the laminated electrode sheets were wound as a jellyroll with a cellulous separator in between, and then dried under vacuum at 110°C for 12 h to remove the residual water. After being submerged with an electrolyte of 1.0 mol $TEABF_4$ (tetraethylammonium tetrafluorobornate) / AN (acetonitrile), the jellyrolls were then assembled as the radical-type EDLCs. The standard ratings for the radical-type EDLCs are shown in Table 1.

2.3 Electrochemical measurements

The initial electrochemical characteristics of the electrode materials of the activated carbons were measured at room temperature. The measurements included capacitance, DC resistance, and leakage current, and were carried out according to the international standard IEC 62391-1[6]. For the power-type applications of EDLCs, the capacitance and DC resistance were measured from 2.7 to 1.35 V with the testing current of 0.1 A, the leakage current was detected after floating at the testing potential of 2.7 V for 12 h. The volumetric capacitance, specific energy density, and specific power density of each kind of electrode material were compared with those of other materials in this study. The volumetric capacitance (C_v) was calculated as Eq.(1):

$$C_V = \frac{4 \times 0.1 \times t}{\Delta V \times VO2.} \quad \text{.....(1)}$$

where C_v is in the unit of F/cc, t (in second) is the endpoint time of discharging, ΔV (in voltage) is the voltage gap between the IR drop and the bounce-back voltage[7], *Vol*. is the sum of the volumes of activated carbon layers of positive and negative electrodes. The DC resistance (R_{Dc}) is the value of ΔV dividing by the testing current of 0.1 A. The specific energy density (E_{max}) and the specific power density (P_{max}) were calculated as Eqs (2) and (3), respectively.

$$E_{\max} = \frac{1/2 \times C \times V^2}{3600 \times mass} \quad \text{.....(2)}$$

$$P_{\max} = \frac{V^2}{4 \times R_{Dc} \times mass} \quad \text{.....(3)}$$

where C is the real capacitance value (in F) , V is the rated voltage of 2.7 V, *mass* is the value of radical-type EDLC.

The electrochemical reliability of the electrode material of each activated carbon was evaluated via the aging testing at 65°C with the floating potential of 2.7 V for lasting 1344 h. The projected lifetime ($LIFE_{DC}$) can be expedited as Eq.(4).

$$LIFE_{DC} = T \times 2.89 \exp\left(\frac{65°C - 25°C}{10}\right) \quad \text{.....(4)}$$

where *T* is the test duration (in hour).

Compared with the commercial radical-type EDLCs, the electrochemical reliability of electrode materials was also evaluated by the cyclic charge-discharge operation at room temperature with the potential range of 1.35 to 2.7 V.

3. RESULTS AND DISCUSSION

3.1 Porous characteristics of the activated carbons

Figure 1 shows the results of isothermal N_2 adsorption and desorption of five activated carbons.

Table 1 Standard ratings of the radical-type EDLCs used (8 mm diameter, 12 mm in length)

Rated capacitance (F)	DC resistance (mΩ)	Leakage current (μA, @ 12 h)	Specific energy (Wh/kg)	Specific power (W/kg)
1	700	25	0.92	2367

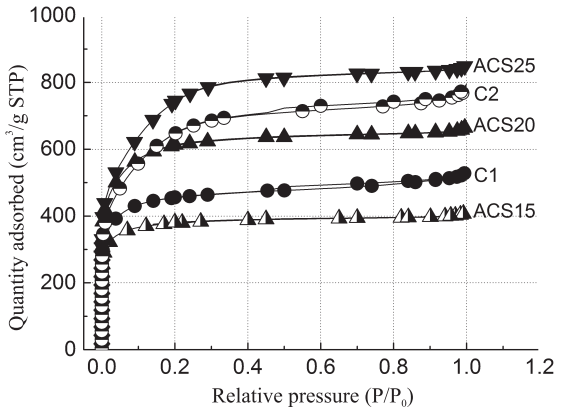

Fig.1. The isotherms of N_2 on activated of ACS-series and C-series activated carbons at 77 K.

According to the Brunauer, Deming, Deming and Teller classification[8], all the isotherms have the typical Type I behavior, which discloses that the surface resides almost exclusively within the micropores. In contrast with the ACS series activated carbons, the coconut-shell based activated carbon C1 and C2 had a clear hysteresis loop in the high relative pressure region, indicating the coconut-shell based samples had more complex porous structure due to their intrinsic porous texture.

The results of detailed porous analyses of the activated carbons are shown in Table 2. The pitch-based activated carbons, ACS15, ACS20, and ACS25 were produced with the programmed alkali-activation level of 15, 20 and 25 respectively. The BET surface areas of these activated carbons were in the range of 1,400-2,500 m^2/g and the pore volume in the range of 0.60-1.3 cm^3/g. It can be seen that the BET surface area increased with increasing the alkali-activation level, however the percentage of micropore revealed a reverse trend.

The activated carbon C1 and C2 for comparison had their BET surface area value falling in the range of those of ACS15, ACS20 and ACS25. Activated carbon C1 had the microporosity of 70% which is between those of ACS15 and ACS20, but its median pore width of 0.61 nm was the same as that of ACS20. Activated carbon C2 had the microporosity of 20% and its median pore width of 0.65 nm was close to as that of ACS25.

The ACS-series activated carbons from CSCC were well developed electrode materials for EDLCs, and their microporosity and median pore width were finely adjusted to fit the electrochemical-accessed demands for aqueous, organic and ionic-liquid based electrolyte systems. In this study, the electrochemical performance of the ACS-series activated carbons have been demonstrated only with the organic based $TEABF_4$/AN electrolyte.

3.2 Initial electrochemical performances

Initial electrochemical performances were evaluated using the radical-type EDLC of 40 pieces for each activated carbon electrode material. The normal distribution of capacitance, DC resistance, and leakage current are represented with box-and-whisker plots as shown in Fig.2. The bottom and top of the box are indicators of the first and the third quartiles, and the band inside the box is the median. Furthermore, the ends of the whiskers represent the upper and lower quartiles.

According to the median value of capacitance, the electrode materials can be categorized as three levels of high, middle and low group, as shown in Fig.2(A). The electrodes of ACS15 and ACS20 both had the highest median capacitance value of 1.44 F with their normal distributions 16% higher than the Upper Specification Limit (USL) of 1.2 F. For the middle group, the electrode ACS25 and C1 had the same median capacitance value of 1.16 F, slightly below the USL. The electrode C2 gave a relative lower median capacitance value of 0.95 F, but its normal distribution still stood above the Lower Specification Limit (LSL). The resulting volumetric capacitance, specific energy, and specific power of EDLC for the electrode materials made of ACS-series and C-series activated carbons are given in Table 3. The electrodes of ACS15 and ACS20 showed an advantage from the largest volumetric capacitance of 67 F/cc, which can offer the maximum specific energy of 1.68-1.70 Wh/kg, almost 10% higher than practical application demands[3].

Table 2 The characteristics of ACS-series and C-series activated carbons

Acitvated carbons	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Percentage of micropore (%)	Median pore width (nm)	Ash content (wt%)
ACS15	1427	0.63	80	0.58	0.05
ACS20	1978	1.02	60	0.61	0.03
ACS25	2503	1.30	20	0.64	0.03
C1	1578	0.81	70	0.61	0.25
C2	2393	1.19	20	0.65	0.40

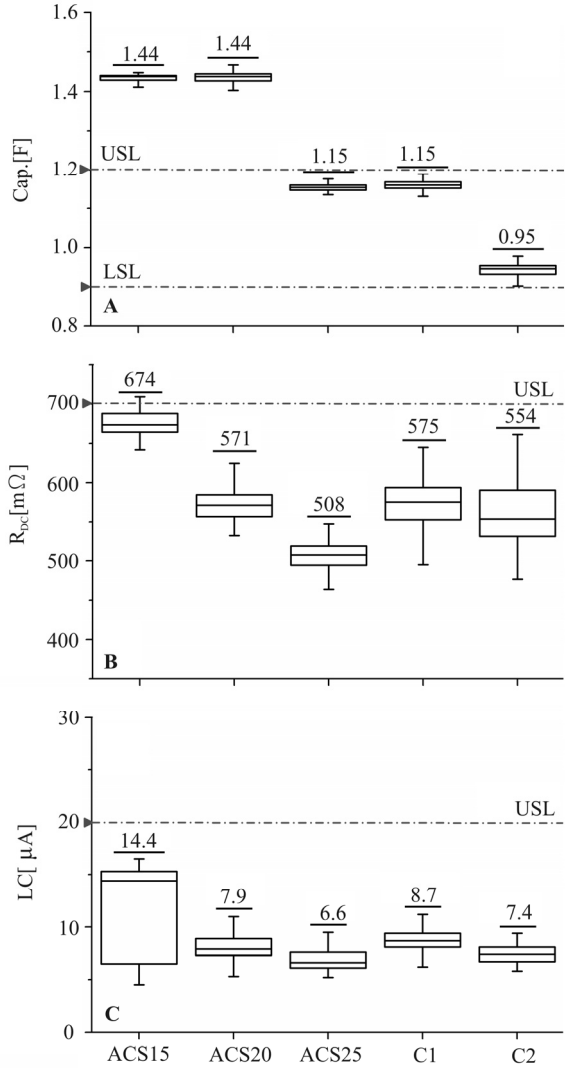

Fig.2. The initial capacitance (A), DC resistance (B) and leakage current (C) of EDLC of the electrode materials made of ACS-series and C-series activated carbons.

Figure 2(B) shows the DC resistance for each activated carbon electrode. It has an interesting trend between the DC resistances and the median pore width listed in Table 2; the larger the median pore width, the lower the DC resistance. The electrode ACS25 showed the lowest dc resistance of 508 mΩ, which could provide the specific power of more than 4200 W/kg. As a power-type product of ACS-series, the activated carbon ACS25 is a promising material for power application demands.

For the electrodes of ACS20, C1 and C2, they had a similar level of dc resistance around 550-580 mΩ, which the specific power could be in the range of 3500-3800 W/kg. The electrode of ACS15 had the highest DC resistance of 674 mΩ, but it could have the greatest specific energy and also a very competitive material-cost advantage over other four electrodes. The activated carbon ACS15 and ACS20 are both categorized as the energy-type product of ACS-series. However, the activated carbon ACS20 has the optimum performance between the specific energy and specific power, which could be a reliable choice of electrode material for either the high energy or the high power applications.

The leakage currents of activated carbon electrode materials are shown in Fig.2(C). The electrode of ACS15 had the highest median value and a broader normal distribution of leakage current, but still far below the USL of 20 uA. The result is due to the porosity nature of activated carbon ACS15. For the electrodes of ACS20, ACS25, C1 and C2, their interquartile ranges (25-75%) of normal distribution were all under 10 uA.

3.3 Aging and cyclic charge-discharge performances

As the assembly design of 1F radical-type EDLCs, the projected lifetime ($LIFE_{DC}$) is set to be at least 10 years at 25°C, with performance specifications of capacitance change less than 30% (versus the initial value) and dc resistance change less than 200% (versus the rated value of 700 mΩ). In this study, the radical-type EDLCs were used to evaluate the electrostatic reliability of each activated carbon electrode material.

Figure 3 shows the aging testing results of (A) capacitance change and (B) DC resistance change for the electrodes of ACS20, ACS25, C1 and C2. Typically, the capacitance decreased and DC resistance increased during aging. Both of the ACS-series electrodes had shown very steady performances of DC resistance

Table 3 The electrical properties of EDLCs of the electrode materials made of ACS-series and C-series activated carbons

Electrodes	Volumetric capacitance of electrode (F/cc)	Specific energy of EDLC (Wh/kg)	Specific power of EDLC (W/kg)
ACS15	67	1.70	3109
ACS20	67	1.68	3667
ACS25	54	1.39	4275
C1	54	1.33	3589
C2	44	1.09	3762

change in the whole testing duration. For the final duration of 1344 h, the electrode ACS20 and ACS25 had the capacitance change and DC resistance change less than 25% and 50%, respectively. Compared with the electrode of ACS20, the ACS25 electrode exhibited a relatively larger capacitance decay due to its higher BET surface area.

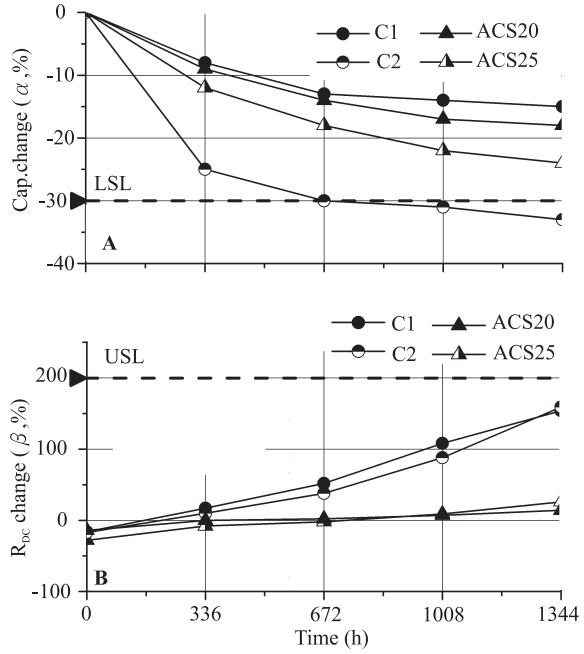

Fig.3. The aging performances of EDLCs of the electrode made of ACS-series and C-series activated carbons.

However, the C-series electrodes could not perform as well as the ACS-series. At the 1344 h aging test, both of the C-series electrodes had the largest decay in DC resistance, and the electrode of C2 had a sharp decreasing rate of capacitance change. Except that the electrode material was different, these four electrodes were fabricated under the same composition and procedures. Hence, it is reasonable that the material characteristics dominates the decay phenomenon.

It should be a good point to compare the ash content and the electrochemical reliability of the ACS-series and C-series materials. The ash content of the C-series activated carbons was roughly one order higher than those of ACS-series activated carbon, as indicated in Table 2. An activated carbon is a good catalyst carrier which could provide active sites to catalyze chemical or electrochemical reaction. Reasonably, with a higher impurity level, the C-series electrodes would have a higher chance of the occurrence of faradic reaction. The unexpected faradic reaction would consume the electrolyte, and then caused the rapid decay of electrochemical performances during aging.

Figure 4 shows the cyclic charge-discharge test results of capacitance change and DC resistance change of two EDLC samples. One was made with the ACS20 electrode, and another commercial EDLC sample was purchased from market. According to the charge-discharge test of 250000 cycles in our lab, these two EDLCs had a similar capacitance change of 18%, however the EDLC consisting of the ACS20 electrode had a relative steady performance of DC resistance change of 21%, which is better than that of the commercial sample.

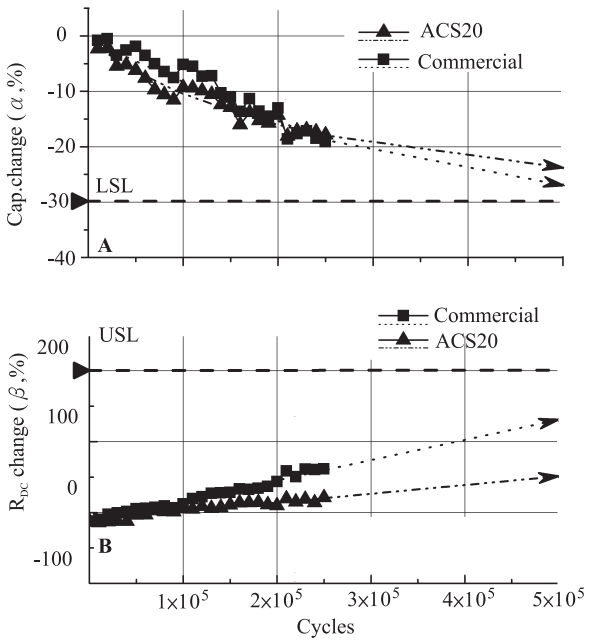

Fig.4. The cyclic charge-discharge performances of EDLC of the electrode made of activated carbon ACS20, and those of a commercial EDLC.

4. CONCLUSION

ACS-series activated carbons from CSCC were produced from the coal tar pitch by an alkali-activation program. The surface area, pore volume, microposity, and median pore width of the ACS-series activated carbon could be precisely controlled upon the alkaliactivation level. For example, a maximum BET surface area of 2500 m^2/g of the activated carbon ACS25 could be achieved with the highest alkali-activation level of 25. For all the ACS-series products, they had a very low ash content, less than 0.05 wt%, which was much lower than those of the coconut shell based activated carbons.

The electrodes of EDLCs made of ACS-series activated carbons were also found with the advantages of both energy and power applications. By using the 1M $TEABF_4$/AN as electrolyte, the energy-type electrodes of ACS15 and ACS20 had a relatively high volumetric capacitance of 67 F/g and their specific

energy could reach 1.68-1.70 Wh/kg. Moreover, the power-type electrode of ACS25 had the lowest DC resistance, and its specific power could achieve more than 4000 W/kg. Due to the advantage of low ash contents, the EDLCs made of the ACS-series products exhibited excellent electrochemical reliability under the aging condition. According to the results of the cyclic charge-discharge test, EDLC consisting of activated carbon ACS20 also revealed a steady performance with a cycle life of at least 250000 cycles.

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