

**Effects of Functional Groups of Activated Carbon Electrode on Electric Double Layer Characteristics**

A. Yamashita and H. Oda

Faculty of Engineering, Kansai University  
3-3-35 Yamate-cho, Suita, Osaka 564-8680, Japan

**1. Introduction**

Various carbon materials are used as electrodes in electric double layer capacitors (EDLC). The chemical characteristics of electrode materials, such as surface oxygen functional groups, can affect EDLC performance but this has rarely been discussed quantitatively in the literature<sup>1)</sup>. In this study, we prepared activated carbon fibers (ACFs) with various amounts of functional groups from the same ACF by a redox method. The ACFs were used as electrodes for EDLCs. In this study, we attempted to understand quantitatively the effect of a functional group on capacitance using X-ray photoelectron spectroscopy (XPS) analysis. In addition, activated carbon powder (AC) was employed in the study for comparison.

**2. Experimental**

A commercial ACF (C) (B.E.T. surface area: 1550 m<sup>2</sup>/g; acidity: 0.17 mmol/g) was used. To prepare ACFs with different amounts of functional group, C was liquid-phase oxidized with 0.1 mol/l HNO<sub>3</sub> for 1 h (C-Ox) and electrically oxidized with 0.1 mol/l HNO<sub>3</sub> by an applied voltage of 3 V for 1 h. To increase the hydrophobic property, C was reduced at 1173 K under a hydrogen atmosphere for 1 h (C-Re).

The activated carbon powder (AC) (B.E.T. surface area: 2280 m<sup>2</sup>/g; acidity: 1.30 mmol/g) was also heat-treated at 873 K or 1173 K for 1 h (AC-873HT and AC-1173HT, respectively) and reduced at 873 K under a hydrogen atmosphere for 1 h (AC-873Re). The amount of functional group on the ACFs and ACs was evaluated by the back titration method. In addition, quantitative fractionation of functional groups was studied using XPS (JEOL, JPS-9000MX). Capacitance was determined using a two-electrode cell by the constant current method. For the aqueous electrolyte, 1.0 mol/l H<sub>2</sub>SO<sub>4</sub> was used, and for the organic electrolyte, 0.5 mol/l LiClO<sub>4</sub>/PC was used.

**3. Results and discussion**

**Table 1** shows the characteristics for each sample. The amount of functional group on ACFs after oxidation treatment was increased by five times for C-Ox and 10 times for C-EO. **Table 2** shows XPS analysis results for the ACFs. With C-Ox there is little variation in the O-C=O bond attributed to the carboxyl group, and the O-C bond attributed to the phenolic hydroxyl group was increased by 1.7 times. Also for C-EO, the O-C=O bond was increased by 1.8 times while the specific surface area decreased by 10%. Thus it was found that a mild oxidation which does not cause the destruction of the carbonaceous matrix will form phenolic hydroxyl group, while a severe oxidation will mainly form a carboxyl group.

We next examined the effects of the functional group on capacitance. In the case of the aqueous electrolyte, the capacitance of both the ACFs and ACs increased proportionally with the amount of functional group. It is considered that a greater amount of functional group promotes the wettability of electrodes leading to an increase in capacity. **Fig. 1** shows for each functional group the relationship between capacitance and ratios to the C-C bond from XPS analysis. This allows us to identify the effective functional group. The O-C=O bond has a higher correlation therefore, the carboxyl group is more effective for capacitance.

In the case of the organic electrolyte, **Fig. 2** shows the relationship between capacitance and functional group. Conversely to the aqueous electrolyte, these results show that a greater amount of functional group leads to a decrease in the wettability of electrodes for the organic electrolyte. Therefore, in case of the ACFs, capacitance decreased with an increased in the amount of the functional group. ACs, however, exhibited an almost constant capacitance irrespective of the amount of functional group. It is considered that ACs have a meso pore volume (with a pore diameter of no less than 2 nm, nor more than 50 nm) 10 times that of the ACFs, and ACs have a wide range of pore size distribution.

**4. Conclusion**

In the case of the aqueous electrolyte, the carboxyl group is more effective for increasing capacitance. On the other hand, in the case of the organic electrolyte, pore structure seems to be a more dominant factor than functional group.

**5. References**

- 1) D. Lozano-Castello, D. Cazorla-Amoros, A. Linares-Solano, S. Shiraishi, H. Kurihara and A. Oya, *Carbon*, **41**, 9 (2003) 1765-1775

**Table 1** Characteristics of ACF samples

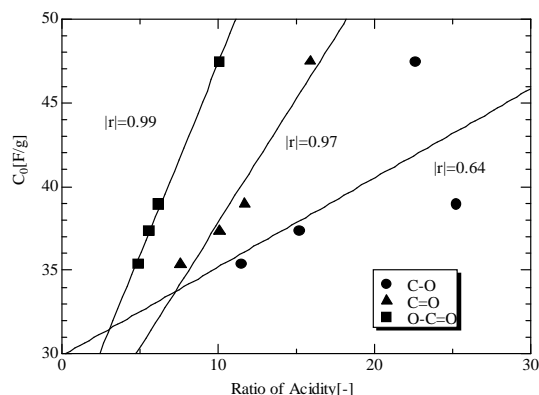
|           | S.B.E.T. [m <sup>2</sup> /g] | V <sub>micro</sub> [ml/g] | Total Acidity* [mmol/gACF] |
|-----------|------------------------------|---------------------------|----------------------------|
| C         | 1550                         | 0.62                      | 0.19                       |
| C-Ox      | 1550                         | 0.62                      | 0.79                       |
| C-EO      | 1400                         | 0.55                      | 1.76                       |
| C-Re      | 1665                         | 0.66                      | 0.10                       |
| AC        | 2280                         | 1.05                      | 1.30                       |
| AC-873HT  | 2280                         | 1.08                      | 0.89                       |
| AC-1173HT | 2060                         | 0.98                      | 0.47                       |
| AC-873Re  | 2400                         | 1.16                      | 0.53                       |

\* Back titration method

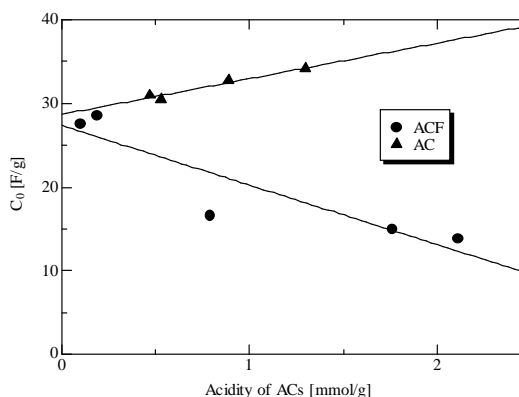
**Table 2** XPS analysis of C<sub>1s</sub> spectra of ACF C

|      | C-C<br>(284.7eV) | C-O<br>(286.3eV) | C=O<br>(287.5eV) | O-C=O<br>(289.0eV) |
|------|------------------|------------------|------------------|--------------------|
| C    | 100              | 15.2             | 10.1             | 5.6                |
| C-Ox | 100              | 25.2             | 11.7             | 6.2                |
| C-EO | 100              | 22.6             | 15.9             | 10.1               |
| C-Re | 100              | 11.5             | 7.6              | 4.9                |

X-ray Source : MgKα



**Fig. 1** Relationship between functional group and capacitance



**Fig. 2** Relationship between amount of functional group and C<sub>0</sub> (Electrolyte : 0.5mol/l LiClO<sub>4</sub>/PC)