

A New Empirical Equation for Estimating Specific Surface Area of Supercapacitor Carbon Electrode from X-ray Diffraction

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Abstract. The current trend of increasing research interest in supercapacitor is due to high demands for an energy storage device that can work in systems that require either low or high power-energy usage. In a supercapacitor using porous carbon electrodes, the energy storage mechanism involves the electrolyte ions in electrode pores and electronic charges in electrodes to form electric double layers at the electrode-electrolyte interface without undergoes any chemical reaction. The specific surface area of porous electrodes, which affect the performance of supercapacitor, have been widely investigated by many researchers using the nitrogen adsorption-desorption measurement. However, despite its simplicity, the X-ray diffraction method is rarely found being used to determine the specific surface area of porous electrodes. Therefore, in the present paper, we propose a new equation which expressed the specific surface area of electrodes as a function the electrode structural parameters obtained from the X-ray diffraction data, and duration of activation time employed during the electrode preparation. This equation is found to produce a satisfactory result and is expected to be beneficial for studying supercapacitor electrode materials.

Introduction

Supercapacitor is an energy storage device whose ranges of energy and power lie between that of conventional capacitor and battery. Its application as high power-energy storage devices can be found, for example, in space flight system, electronic military devices, automotive and public transports, and as low power-energy storage devices one can find its application in printers, photographic flashes, game consoles and portable media players [1]. Basics components of a supercapacitor are electrode, electrolyte, current collector and separator. Current trend indicates that electrode materials such as carbon nanotubes [2], carbon aerogels [3], graphene[4], metal oxide [5], conducting polymers [6], composite materials [7] and activated carbon [8-10] have been widely studied and developed. Among those electrode materials, activated carbon still remains a popular choice of supercapacitor electrode material because of its advantages in terms of higher surface area, chemical stability, low cost material and wider availability, simpler and cheaper to produce.

The overall supercapacitor performance is partly determined by its capacitance value and it is well known that the capacitance of a supercapacitor electrode critically depends on the pore structure and surface chemistry of the electrode. This dependency is associated with the energy storage mechanism which involved the electrochemical double layer formed by ionic and electronic charges at the interface of electrolyte and pore-wall surface in the electrode. In general, electrode having higher surface area with pore sizes network compatible with the sizes of electrolyte ion will

have higher capacitance value [11]. Therefore, there have been numerous studies to optimize the pore characteristic of activated carbon electrode [12], and the most widely used methods of optimization are chemical and/or physical activation using different types of chemical modifiers such as KOH [13], H₂SO₄[14], ZnCl₂[15] and CO₂[16]. The interest of researcher to use the specific surface area (SSA) in the study of supercapacitor performance is widely found in the literature because the specific surface area is directly related to the specific capacitance (C_{sp}) by an equation $C_{sp} = C_{dl} \times SSA$, where C_{dl} is the electric double layers capacitance. In general, the SSA from the nitrogen adsorption-desorption experiment is widely used.

In our recent studies, both chemical and physical activations have been used and significantly improved pore characteristics have been obtained [17, 18, 19], however the analysis that relates the capacitance of electrode to the electrode surface area determined from the X-ray diffraction data has not been tested in such studies. It is apparent in the literature that there has been very limited number of study that deal with the quantitative analysis involving the use of empirical formulas in describing the relationship between the capacitance and surface area of electrode, particularly the SSA determined from the X-ray diffraction data [20, 21, 22]. In view of this trend, the present paper reports the result of reanalyzing the structural and porosity results of supercapacitor electrodes reported in reference [18] in the context to test and modify the formula in reference [21], which expressed the surface area of electrode as a function structural parameters, and also express the specific capacitance as a function of the surface area of electrode. The aim of the present paper is to propose a more accurate empirical formula that can estimate the carbon electrode SSA from the X-ray diffraction data. This approach could be an alternative choice to the nitrogen adsorption-desorption experiment which is more time consuming compared to the X-ray diffraction experiment, and consequently there would be more researchers interested in using X-ray diffraction data to obtain the SSA for describing the behaviour of electrode specific capacitance.

Materials and Methods

The material we used as precursor to produce supercapacitor activated carbon electrodes was fibers of oil palm empty fruit (EFB) bunches. Summary of properties and availability of EFB fibers can be found elsewhere [23, 24, 25, 26]. The EFB fibers were first carbonized at low temperature to produce pre-carbonized EFB fibers, followed by grinding, milling and sieving to produce self-adhesive carbon grains (SACG) [27]. SACG can be chemically treated, pelletized, carbonized (under N₂ environment) and activated (under CO₂ environment) to produce activated carbon pellets or monoliths [28, 29]. These monoliths were polished to desired thickness suitable to be used as electrodes in a symmetrical supercapacitor cell [17, 18,19].

The prepared activated carbon monoliths were characterized by an X-ray diffraction technique for it structural property and by nitrogen adsorption-desorption technique for it porosity property [18]. The X-ray data were processed using a standard method to determine the interlayer spacing (d_{002}), stack width (L_a) and stack height (L_c) of graphitic microcrystallites in activated carbon electrodes. The nitrogen adsorption-desorption data were also processed using a standard method to determine the SSA of activated carbon electrodes. The relationship of the stack height of the graphitic microcrystallite and the SSA of the material is given by [20, 21],

$$SSA_{xrd} = 2/(\rho_{xrd}L_c) \quad (1)$$

where ρ_{xrd} is the X-ray density, which is given by $\rho_{xrd} = \{d_{002}(\text{graphite})/d_{002}\}\rho(\text{graphite})$, and $d_{002}(\text{graphite})$ and $\rho(\text{graphite})$ are 0.33354 nm and 2.268 g/cm³, respectively. As can be seen in Eq. 1, the size, mutual orientation and stacking of the microcrystallites are strongly associated with the microporosity and the high surface area, indicating that a small microcrystallite height and short range ordering between microcrystallites are required to produce super high surface area activated carbon [30].

Results and Discussion

For convenient in reporting the results, the structural parameter data determined from X-ray diffraction study and the SSA_{bet} data determined from nitrogen adsorption-desorption data for supercapacitor electrodes previously reported by our group are shown in Tables 1 and 2 respectively [18]. The SSA_{xrd} values estimated from the structural parameter data in Table 1 using Eq. 1 [20, 21] are also shown in Table 2.

Table 1. Interlayer spacing, microcrystallite parameter, ratio of L_c/L_a and L_c/d_{002} [18]. K1- K5: Activated carbon monolith at different activation time; L_a : Stack width; L_c : Stack height

Sample	d_{002} (nm)	L_c (nm)	L_a (nm)	L_c/L_a	L_c/d_{002}
K1	3.711	9.50	52.81	0.1799	2.5600
K2	3.692	10.09	51.77	0.1949	2.7329
K3	3.701	10.48	48.33	0.2168	2.8317
K4	3.695	9.05	49.73	0.1820	2.4493
K5	3.695	8.47	52.22	0.1622	2.2923

Table 2. Specific surface area x and y are from [18], and z is present work. K1-K5: Activated carbon monolith at different activation time; SSA: Specific surface area

Sample	$^xSSA_{bet}$ (m^2/g)	$^ySSA_{(xrd)}$ (m^2/g)	$^zSSA_{(xrd-m1)}$ (m^2/g)
K1	723	1033	851
K2	1100	967	1005
K3	1704	934	1322
K4	1219	1080	921
K5	1279	1155	705

The estimated SSA_{xrd} values shown in Table 2 are in the same order of magnitude compared with that of the SSA_{bet} values, but with a noticeable disagreement in terms of their trend and magnitude. This result seems to indicate that the presence of only L_c in Eq. 1 is inadequate to represent the pore structural characteristic of the electrodes. Therefore, it is appropriate to include other structural parameters in Eq. 1. Here, we therefore propose Eq. 2, which is the modified version of Eq. 1,

$$SSA_{xrd-m1} = SSA_{xrd} (L_c/L_a)^\alpha (N_{fl})^\alpha \quad (2)$$

The purpose of this modification is to ensure that both the trend of change and magnitude in SSA_{xrd-m1} are in satisfactory agreement with that of the SSA_{bet} for all the tested electrode samples. The term (L_c/L_a) was included because it was found that L_c/L_a and SSA_{bet} peak values are at a common activation time, h value (3 hours) but the L_c/L_a curve was less sharpen than that in SSA_{bet} curve. Therefore we need to introduce the power (α) to the term L_c/L_a , which can be adjusted so that the estimated SSA_{xrd-m1} may fit the SSA_{bet} curve. The normalization factor N_{fl} was also introduced in the equation so that the magnitude of SSA_{xrd-m1} can be scaled to the SSA_{bet} values. As shown in Figure 1, the overall curve shape of the SSA_{xrd-m1} and SSA_{bet} appeared to be similar but the former curve lacked of asymmetric feature in the region of higher time of activation compared to the later curve.

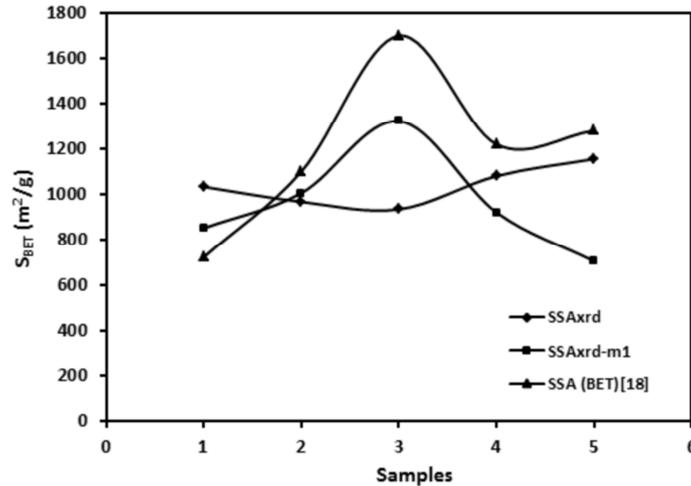


Fig. 1. Specific surface area of samples 1 to 5 ($\alpha = 2.9$, $N_{f1} = 5.2$)

These results suggested that further modification to Eq. 2 must be made in order to include the experimental condition or factor that significantly influence pore characteristic of electrodes such as shape, size distribution and volume of pores. Since the activation time contributes such a significant influence, we therefore proposed the following equation,

$$SSA_{xrd-m2} = SSA_{xrd} (L_c/L_a)^\alpha (1 + h/h_m)^{\text{sqrt}(\alpha)} (N_{f2})^\alpha \quad (3)$$

where h is the activation time and h_m is the maximum activation time, N_{f2} is the normalization factor, and α is the fitting parameter that determine the degree of contribution from these terms to SSA_{xrd-m2} values. As can be seen in Figure 2, for $\alpha = 2.9$ and $N_{f2} = 4.3$, the SSA_{xrd-m2} results are in satisfactory agreement (standard deviation, $\sigma = 120 \text{ m}^2/\text{g}$) with the SSA_{bet} data both in shape and magnitude, indicating the applicability of this newly proposed equation.

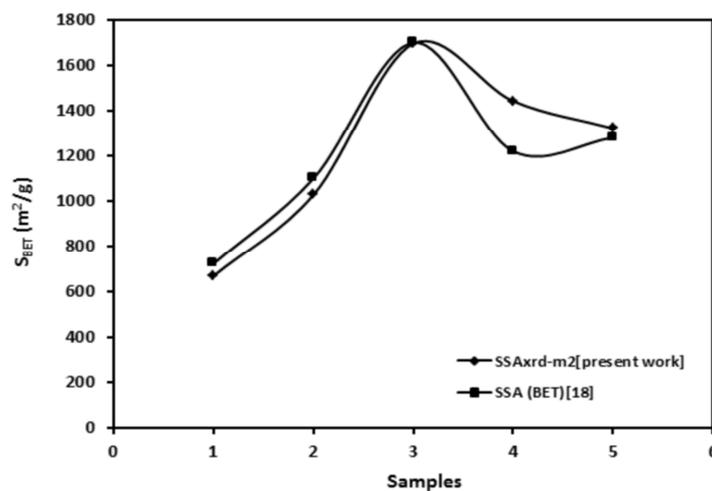


Fig. 2. Specific surface area of samples 1 to 5 ($\alpha = 2.9$, $N_{f2} = 4.3$)

Conclusion

In conclusion, this study observed an inaccurate prediction of the SSA of supercapacitor electrodes by an equation reported in the literature which relates SSA to the structural parameter, namely X-ray density and microcrystallite stack height of the electrode material, whose values are concluded that this equation was too simple and a

modification was necessary to be made by including the ratio between microcrystallite stack height to its stack width, ratio of activation time to maximum activation time, and also normalization factors in the equation. With this modification, the predicted values of the specific surface area of supercapacitor electrodes from X-ray diffraction data was found in satisfactory agreement with that of the nitrogen adsorption-desorption experiment. Although the basis for such a modification appears lacking theoretical input or consideration, the modified equation is expected to be useful for further development of quantitative procedure and theoretical framework to explain the relationship between the specific surface area and structure of carbon electrode, which then may contribute to a better understanding of the supercapacitor performance dependency on the pore and surface characteristic of the electrode materials.

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