POROUS ACTIVATED CARBONS AND ELECTRIC DOUBLE LAYER CAPACITANCE

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INTRODUCTION

Activated carbons (AC) are technically important materials. Although activated carbons have been used in industries for more than one century [1], recent interests using AC as the electrode materials in the electric vehicle oriented electric double layer capacitors (EDLC) ignite another worldwide investigation on their porous structures and electrochemical behaviors [2]. A crucial factor that will influence the electrochemical performance of an AC based EDLC is AC's pore size and porous surface distribution. In order to make high energy and high power EDLC, one needs to maximize the surface area with high double layer capacitance and average pore size without losing surface area. Therefore, the accurate characterization of pore size and surface area of AC is extremely important for selecting a better carbon material used in EDLCs.

However, to characterize AC's porous structures precisely is not an easy job due to its extreme complicated structures. Conventionally, pores in AC can be divided into three groups by size, that is, micropore (pore width less than 20 Å), mesopore (between 20 and 500 Å) and macropore (larger than 500 Å) [3]. The macropore contribution to total surface area on most of activated carbons is usually negligible (less than 2 m^2/g). Micropores have molecular dimension in which volume filling of pores occurs (TVFM of Dubinin) rather than capillary condensation of mesopore[4]. Furthermore micropore surface behaves differently for storing charges on the surface other than mesopore surface (external surface area) Both micropore and mesopore sizes and surface areas can be determined by gas adsorption experiment with the aid of various empirical or computer-aid simulation models. The capacitance of an AC based capacitor can be measured using standard electrochemical dc or ac methods.

EXPERIMENTAL

Activated carbon fibers, fabrics and powders used in this work were mainly obtained from Spectracorp (USA). The pore structures were investigated by Micromiritics ASAP 2000 porosimeter. Nitrogen gas was used as probing gas and liquid nitrogen chosen as the cold bath. All ACs were degassed on ASAP 2000 degas port for over night before the measurement started. The equilibrium time between each gas dosing was set at 1 minute to insure a good equilibrium before two consecutive doses. Typically about 50 data points were collected for an isothermal curve with nitrogen relative pressure p/p_0 ranged from 10^{-6} to 1 where p_0 is the saturation pressure of nitrogen gas. A typical whole data collection takes about 1 day, which varies according to the degree of the material's porosity. All the data then were analyzed by using a home made gas analysis software based on two-term DR and a-plot models and a Mircomiritics gas analysis software based on density functional theory (DFT). The porous structural parameters then were extracted and compared.

The DC capacitance of activated carbons were measured using a home made reassemble test cell [5]. The constant current discharge (about 5 mA/cm^2) was used for calculating the slope and DC capacitance. The electrolyte used was 30% weight KOH aqueous solution. For each AC material, three tests with slightly different electrode masses were carried out and an average specific capacitance were used in the analysis. The specific capacitance (single electrodes) then were obtained by dividing the total capacitance by 4 times total active materials. For some of activated carbons, an independent electrochemical ac impedance measurement was carried for detail investigation of the accessibility of micropores. An AC impedance fitting program based on well-known network distribution model was developed and used for estimating distributed percentage capacitance and accessing time etc..

RESULTS AND DISCUSSION

Various surface areas were calculated based on different gas adsorption models. Figure 1 shows three different surface areas obtained from BET, two-term DR and DFT models respectively. DFT

gives a close surface area numbers to that of the conventional Dubinin model, which has become a standard model in investigating gas adsorption of microporous materials. Obviously, BET is not suitable for these high surface area ACs. A detail analysis and comparison of the micropore surface area, external surface area and corresponding pore size distribution between these models have been done. The results show that DFT and classic two-term Dubinin model are quite consistent as far as the extracted microporous parameters considered.

The specific double layer capacitance were calculated based on the weight of active mass and its DFT surface area. One of the interesting results is that the specific capacitance is not only dependent on the surface area but also strongly dependent on the porous structure and surface morphology, such as, the surface functional groups and external or micropore surface etc.. Micropore surface contributes different specific double layer capacitance than external surface area does.

The micropore accessibility is also investigated by using ac impedance and DFT pore size distribution data. Figure 2 shows a comparison study between these two independent measurement. It shows that the micropore is main limiting factor for quick energy taking and putting and most of micropore is accessible to KOH electrolyte under certain conditions. The best balance conditions between pore size and surface area is still needed to be further studied and it is the key to choose the right AC for EDLC.

CONCLUSIONS

The porous structures of over 50 different activated carbons were investigated by using nitrogen gas adsorption method and computer modeling software. The double layer capacitance on the different AC surface in aqueous KOH electrolyte is studied as well. The results show that (1) DFT model is a good model for studying the pore structure of AC materials and (2) AC's double layer capacitance strongly depend on different surface and related surface morphology.

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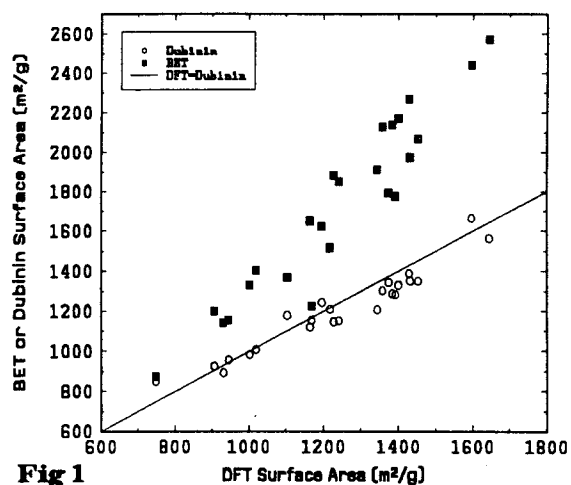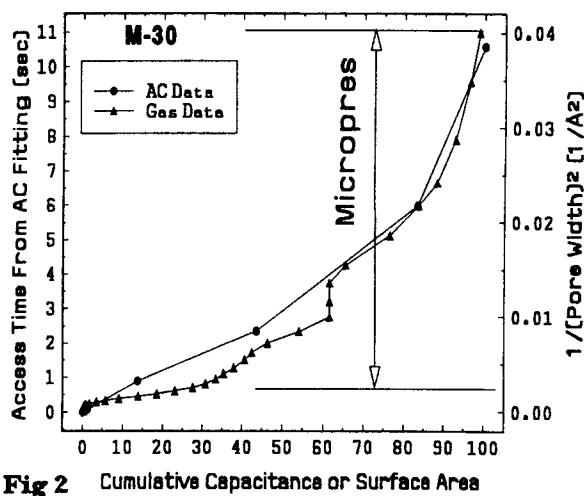
Fig 1

Fig 2 Cumulative Capacitance or Surface Area