



# Impedance analysis of porous carbon electrodes to predict rate capability of electric double-layer capacitors



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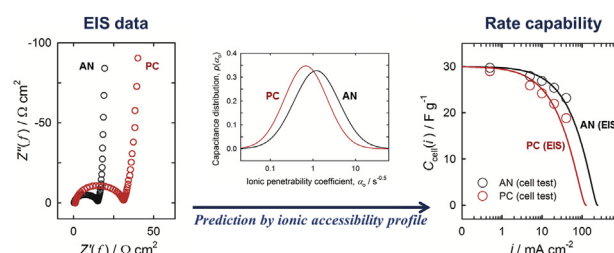
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## HIGHLIGHTS

- Rate capability of EDLC was quantitatively predicted by an impedance measurement.
- Ohmic resistance and pores' ionic accessibility were factorized by EIS.
- From the two factors, ohmic voltage drop and utilizable capacitance was derived.
- A key formula was devised to correlate the ac with dc information of EDLC.
- Thus predicted rate capabilities were verified by comparing with cell test results.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Electrochemical impedance analysis is performed to predict the rate capability of two commercial activated carbon electrodes (RP20 and MSP20) for electric double-layer capacitor. To this end, ac impedance data are fitted with an equivalent circuit that comprises ohmic resistance and impedance of intra-particle pores. To characterize the latter, ionic accessibility into intra-particle pores is profiled by using the fitted impedance parameters, and the profiles are transformed into utilizable capacitance plots as a function of charge–discharge rate. The rate capability that is predicted from the impedance analysis is well-matched with that observed from a charge–discharge rate test. It is found that rate capability is determined by ionic accessibility as well as ohmic voltage drop. A lower value in ionic accessibility for MSP20 is attributed to smaller pore diameter, longer length, and higher degree of complexity in pore structure.

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## 1. Introduction

Electric double-layer capacitors (EDLCs) have been used as a high-power energy storage device due to their unique characteristics of high rate capability (<1 min charge–discharge) and long

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cycle life (>100,000 cycles). At present, activated carbons are the most popular EDLC electrodes due to their high electrical conductivity, large surface area and wide pore size distribution [1].

In general, the rate capability of activated carbon electrodes is governed by two factors: 1) ohmic resistance that determines the ohmic voltage drop and thus working voltage, and 2) ionic accessibility into pores, by which utilizable capacitance is determined. Commonly, dc methods are employed to assess the rate capability; for instance, galvanostatic charge–discharge cycling with varied current density. Here, the ohmic resistance ( $R_{ohm}$ ) can be estimated from the voltage drop at the beginning of current reversal, whereas the ion accessibility can be estimated from the delivered capacitance values. Even if the dc methods can give general information on EDLC parameters, ac methods such as electrochemical impedance spectroscopy (EIS) can provide more detailed information; for instance, pore structure of electrode materials and kinetics in double-layer charging/discharging processes [2]. In the previous works, ac impedance analysis based on transmission-line model with pore size distribution (TLM-PSD) was successfully utilized to assess the pore structure of carbon materials [3–5]. Later on, the concept of TLM-PSD has been incorporated into complex capacitance analysis, which allows a graphical analysis on capacitance, rate capability, and leakage current [6–15]. Especially, it was demonstrated that the effect of pore structure, electrode potential, and electrode thickness on rate capability can be easily evaluated by comparing the peak frequency on imaginary capacitance plots.

The primary objective of this work is to establish an analytical method to correlate the ac method (impedance analysis) with dc method (galvanostatic charge–discharge cycling) for the prediction of rate capability of EDLC systems. To this end, experimental ac impedance data are analysed to obtain ohmic resistance and ionic accessibility for activated carbon electrodes. Then, the utilizable capacitance is calculated as a function of operating time ( $t_{op}$ ) or current density ( $i$ ) by using correlation functions between ac and dc variables. Finally, the transform technique is validated by comparing the rate capability predicted from two methods.

## 2. Experimental details

### 2.1. Material characterizations

The samples were characterized by using a field-emission scanning electron microscope (FE-SEM, JEOL JSM-6700F), nitrogen adsorption (Micromeritics, ASAP 2010), and small angle X-ray scattering (SAXS, Bruker GADDS,  $CuK\alpha$ ,  $\lambda = 0.154056$  nm). The nitrogen adsorption data was analysed by Barret–Joyner–Halenda (BJH) and modified micropore (MP) [16,17] methods to characterize mesopores and micropores, respectively.

### 2.2. Electrode preparation

For the electrochemical tests, the composite electrodes were prepared by coating the slurry of active material (RP20 or MSP20), polytetrafluoroethylene and carboxyl methyl cellulose (PTFE + CMC, 6:4 in mass ratio) binder, and conductive carbon (Super-P) (8:1:1 in mass ratio in deionized water) on a piece of Al foil (thickness = 21  $\mu$ m). The electrode plates were dried in vacuum oven at 120 °C for 12 h without pressing process. The resultant thickness of the coated film was approximately  $40 \pm 2$   $\mu$ m with the active mass loading of  $1.5 \pm 0.1$  mg on the electrode area of 0.95  $cm^2$ .

### 2.3. Electrochemical measurements and impedance fitting

For a 3-electrode cell test, a home-made cell comprising polyether–ether–ketone (PEEK) body and stainless steel (316L) current

collectors was used. A spring was attached to a current collector to keep the positive, negative, and reference electrodes be tightly contacted to the current collectors. O-rings (Viton®) were used to ensure the sealing at the joints of current collectors and cell body. Positive and negative electrodes were positioned to exactly confront each other, and the reference electrode was just beside them. Two pieces of separator was put between positive, reference, and negative electrodes for all the electrodes to be insulated one another. Activated carbon (RP20) were utilized to prepare a reference electrode [18] (coated film on Al foil, 1 mg on 0.6  $cm^2$ , 50  $\mu$ m thickness) and a counter electrode (sheet-type, 30 mg on 1.8  $cm^2$ , 400  $\mu$ m thickness). A porous glass fibre was used as the separator. The electrolytes were 1 M tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) in acetonitrile (AN) or propylene carbonate (PC). Impedance was measured at 0.0 V vs. carbon over the frequency range of 2 mHz–100 kHz (Zahner, Im6e) with a root mean square (rms) amplitude of 5 mV. For the complex nonlinear least squares (CNLS) fitting of the impedance data, the TLM-PSD was coded in FORTRAN to run in LEVM 8.09 software [19]. Modulus weighting (with respect to calculated values) was adopted for the CNLS fitting.

For rate experiment, symmetric 2-electrode (CR2032 coin type) cells were assembled by sandwiching two identical electrodes and operated in 0–3.5 V. Experimental conditions are same with the 3-electrode experiments, except for the electrode area (2.27  $cm^2$ ). Galvanostatic charge–discharge cycling was made with a WBCS-3000 battery cyler (Wonatech Co.). Both of charging and discharging current densities were varied from 0.5 to 40  $mA\ cm^{-2}$ .

## 3. Results and discussion

### 3.1. Characterization of activated carbons

As the EDLC electrodes, two different activated carbons were used; RP20 (Kuraray Chemical Co.) and MSP20 (Kansai Coke and Chemicals Co.). The former is produced by physical steam activation, whereas the latter by chemical activation using potassium hydroxide (KOH). As shown in the FE-SEM images (inset of Fig. 1a), RP20 has a rougher morphology as compared with that for MSP20. It is known that steam activation (RP20) leads to more severe morphological change as compared with KOH activation (MSP20) [20]. The particle diameter is similar for two carbons (~5  $\mu$ m).

From the nitrogen adsorption isotherms, total pore volumes ( $V_{total}$ ) are calculated to be 0.77  $cm^3\ g^{-1}$  (RP20) and 0.98  $cm^3\ g^{-1}$  (MSP20) (Table 1). The adsorption–desorption isotherms (Fig. 1a) also show that RP20 has a larger portion of mesopores and macropores, while the micropores are dominant in MSP20. The BET surface area ( $S_{BET}$ ) is larger for MSP20 due to the higher population of micropores. In the BJH pore size distribution (Fig. 1b), RP20 shows a larger portion of meso- or macropore volume between the diameters of 4–300 nm. The meso- and macro-pore volume at  $D > 2$  nm are 0.17  $cm^3\ g^{-1}$  for RP20 and 0.15  $cm^3\ g^{-1}$  for MSP20, which is 22% and 15% of  $V_{total}$ , respectively. Accordingly, the average mesopore diameter ( $D_{meso}$ ) is calculated to be larger for RP20 (4.9 nm) as compared with that for MSP20 (2.8 nm). When the micropore region ( $D < 2$  nm) is analysed by the modified MP method (Fig. 1c), larger portion of micropore volume is calculated for MSP20 (0.83  $cm^3\ g^{-1}$ , 85%) compared to RP20 (0.60  $cm^3\ g^{-1}$ , 78%).

Pore complexity is compared for two activated carbons by using SAXS technique (Fig. 1d). In the Porod region, the slope in logarithmic scale (Porod slope,  $z$ ) is related with the fractal dimension ( $d$ ) of pores by: Intensity ( $q$ )  $\sim q^{-(6-d)} = q^{-z}$ . The theoretical Porod slope is 4 for an ideal flat surface, but the slope gradually decreases to approach 1 with an increase in pore complexity [21]. From the Porod slopes in this work (ca. 2.2 for RP20 and 1.4 for MSP20), it can be assumed that MSP20 has a more complex pore structure.

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