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A NEW CIRCUITRY MODEL FOR ELECTRIC DOUBLE LAYER CAPACITOR

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ABSTRACT

A new circuitry model, which consists of constant phase elements is proposed to simply describe the charge storage mechanism of an electric double layer capacitor (EDLC). The model is developed based on previously reported experimental data of cellulose- and glass wool-based capacitors measured by electrochemical impedance spectroscopy. As a result, with a considerably small normalized error, the proposed model fitted the experimental data well for the whole frequency range (from mHz to kHz). The model is capable of providing beneficial information on the charge storage mechanism inside the tested capacitors for each frequency region; low, medium and high frequency region separately. Interestingly, the fitted parameters from the model are consistent with the static EDLC parameters; in particular, the specific capacitance (corresponds to double layer capacitance) and internal resistance values attained from dc properties characterization.

1. INTRODUCTION

Electric double layer capacitor (EDLC) stores charges electrostatically onto its high surface area active electrodes (activated carbon) in a form of sub-nanometer layer, creating excellent double layer capacitance effect (Beguin, et al., 2013). Taking advantages of its high power density and comparable energy density to battery, EDLC has been widely applied in various modern applications such as in electric/hybrid vehicle (normally coupled with lithium ion battery), heavy lifting crane, emergency door of airplane, street lighting, and renewable energy system (Kotz, et al., 2000 & Miller, et al., 2008).

In order to have better illustration on the charge storage mechanism, many approaches including *RC* ladder, *RC* transmission line and fractional circuits; have been used in modeling an EDLC for the past decade (Conway, et al., 2002, Jang, et al., 2006, and Martin, et al., 2008). Among these models, the fractional circuit, which typically uses the so-called Warburg element and constant phase element, provides the best fitting data to the experimental (Martin, et al., 2008). Nonetheless, in most cases, the circuit parameters obtained from the fitted data do not have any relationship to the essential dc properties characterization of an EDLC to confidently justify the fitting reliability.

This paper proposes a new circuitry model that consists of resistance and constant phase elements to not only simply describe the charge storage mechanism but also justify the dc properties of cellulose- and glass wool-based capacitors.

2. EDLC MODELING

2.1 General Model

Figure 1(a) represents general electrical model in modeling an EDLC by describing the separator-electrolyte layer with bulk solution resistance R_s and the carbon electrodes (charge accumulation area) with parallel-connected double layer capacitor C_{dl} and leakage current R_l. The model can be simply deduced as in Figure 1(b).

2.2 Proposed Circuit

Generally, a constant phase element Q (Ω) is expressed as (Abouzari, et al., 2009),

$$Q = 1/Y(j\omega)^n \quad (1)$$

where ω is angular frequency while Y and n are the pre-factor and exponent of the constant phase element, respectively. Constant phase element Q describes an element that behaves in between capacitor and resistor whereby an ideal capacitor has unity n value with Y is identified as a capacitor C (F).

Previously published data of cellulose- and glass wool-based capacitors were used to develop (from electrochemical impedance spectroscopy) the proposed circuitry model (Noorden, et al., 2013). The tested capacitors were constructed by sandwiching the electrolyte-containing separator (cellulose or glass wool)

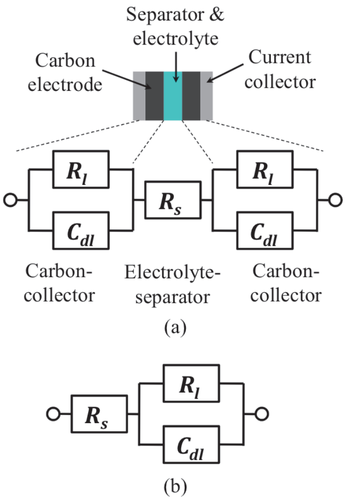

Fig. 1 General circuitry model of an EDLC; (a) cross-sectional area with corresponded elements, and (b) simplified circuit.

with two activated carbon sheets. A solution of 1M sulfuric acid (H_2SO_4) was used as the electrolyte.

As shown in Figure 2, a new circuitry was proposed on the basis of the Nyquist plot (measured ac impedance data) in Figure 3. Each element in the circuit was pre-determined in accordance to these observations (refer Figure 2 and 3);

1) solution bulk resistance R_s due to the highest frequency plots do not lies at the origin (shifted to the right side),
2) suppressed semi-circle behavior at medium/high frequency region (corresponded to carbon-collector resistance) described by a resistor R_{cc} connected in parallel to a constant phase element Q_{cc}, and
3) another parallel connected of constant phase element Q_{dl} and leakage resistor R_l (corresponded to double layer capacitance characteristic) that explains the near-vertical lines at low frequency region.

3. RESULTS AND ANALYSIS

The fitted Nyquist plots of the cellulose- and glass wool-based capacitors in 1M H2SO4 can be referred to Figure 4. The curve-fitting calculation of the measured impedance data was carried out using EIS Spectrum Analyzer software. Table 1 summarizes the fitted parameters including normalized fitting error σ^2, the pre-factors Y_{cc} and Y_{dl} of the constant phase elements Q_{cc} and Q_{dl}, respectively and their exponents n_{cc} and n_{dl}. The

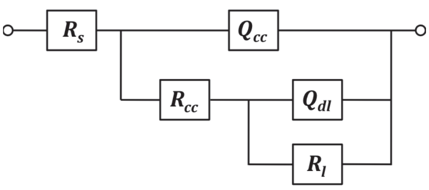

Fig. 2 Proposed circuit.

fitting error values were calculated based on the following equation,

$$\sigma^2 = \sum_{i=1}^{n}[(Z_{rei} - Z_{reic})^2 + (Z_{imi} - Z_{imic})^2] \quad (2)$$

where Z_{rei} and Z_{imi} are the measured impedance data for i-th data, Z_{reic} and Z_{imic} represent the fitted impedance values, n is the number of points and m is noted as number of fitted parameters. Referring to Figure 3(a)-(d), it can be seen that the calculated impedance values are well-fitted the measured data with the considerably small fitting errors.

Referring to Table 1, the solution bulk resistances R_s for both capacitors are close to the solution resistances R_{sol} obtained from the impedance data (Noorden, et al., 2013). The latter also agrees for the corresponding resistances to the semi-circle appearance R_{cc} that describe the cell resistance R_{cell} values (associated by contact resistance of the test cell) (Noorden, et al., 2013). In addition, as frequency changed towards lower frequency region, so-called 'real' capacitance C_{dl} (F/g) (that correspond to the electric double layer capacitance) for both capacitors can be estimated from the constant phase element Q_{dl} and the leakage resistor R_l by the following equation (Abouzari, et al., 2009),

$$C_{dl} = R_l^{\frac{1-n_{dl}}{n_{dl}}} . Y_{dl}^{\frac{1}{n_{dl}}} \times \frac{4}{m} \quad (3)$$

Interestingly, as tabulated in Table 1, these 'real'

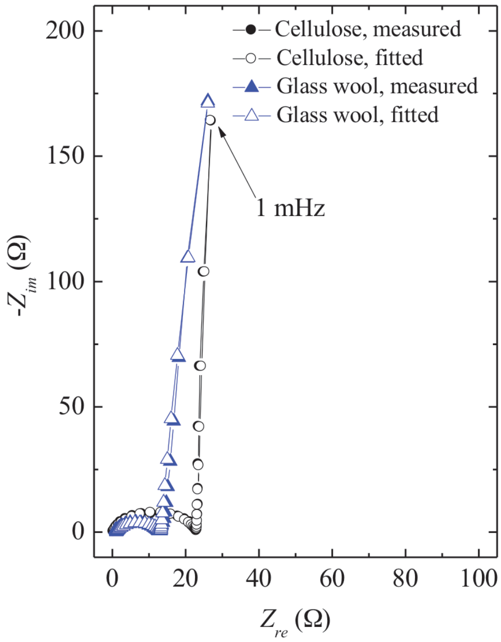

Fig. 3 Measured and fitted Nyquist plot for cellulose- and glass wool-based capacitors in 1M H_2SO_4.

capacitance values C_{dl} are identical to that of specific capacitance obtained from cyclic voltammetry and galvanostatic tests (Noorden, et al., 2013). The finding suggests the good reliability of the proposed circuit and the curve-fitting calculation in evaluating the tested capacitors' properties. The proposed circuit is capable of justifying the dc properties of the tested capacitors.

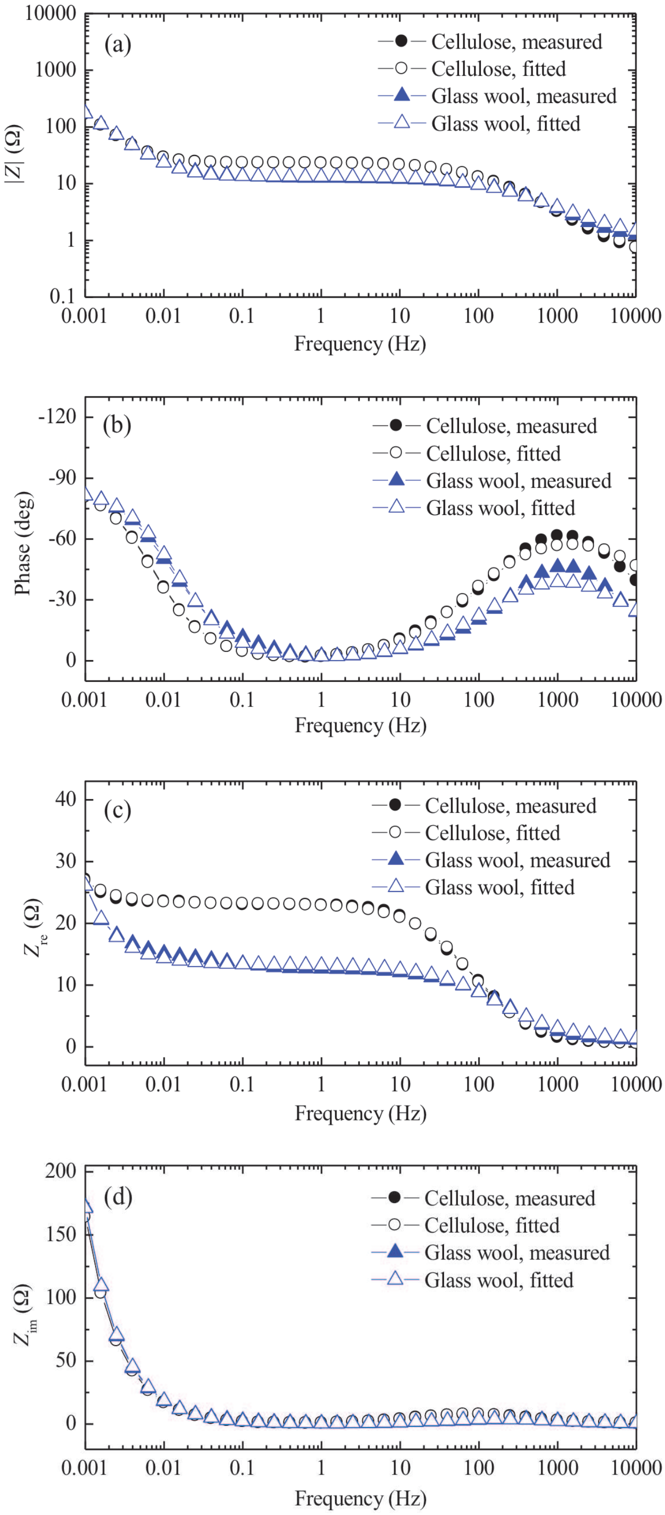

Fig. 4 Variation of measured and fitted (a) impedance $|Z|$, (b) phase, (c) real impedance Z_{re}, and (d) imaginary impedance Z_{im} for cellulose- and glass wool-based capacitors in 1M H_2SO_4.

Table 1 Fitted parameters for cellulose- and glass wool-based capacitors in 1M H_2SO_4.

Parameter	Fitted		Measured	
	Cellulose	Glass wool	Cellulose	Glass wool
σ^2	0.132	0.428	-	-
R_s (Ω)	0.5	1	0.6[1]	1.2[1]
R_{cc} (Ω)	22.7	12.3	19[2]	13[2]
R_l (kΩ)	28.6	9.2	-	-
Y_{cc} ($\mu s^n \Omega^{-1}$)	372	577	-	-
n_{cc}	0.77	0.70	-	-
Y_{dl} ($\mu s^n \Omega^{-1}$)	0.92	0.77	-	-
n_{dl}	0.99	0.96	-	-
C_{dl} (F/g)	118	129	118[3]	129[3]

[1]Values obtained from electrochemical impedance spectroscopy, [2]values calculated from galvanostatic test and [3]average values computed from cyclic voltammetry and galvanostatic tests (Noorden, et al., 2013).

Referring to Figure 3 and 4, in accordance to the well-fitted circuit, the charge storage mechanism within the tested capacitors can be summarized as follows (from high to low frequency);

1) at high frequency region, ions (H^+ and SO_4^{2-}) in the electrolytes start to move towards the opposite electrodes with solution resistance R_s,

2) small capacitance (corresponded to Q_{cc}) builds up immediately at high-medium frequency region associated with resistance R_{cc} (creating half semicircle behavior),

3) at medium-low frequency region, ions start to penetrate into the pores of carbon electrodes, resulting the built-up capacitance less dominant compared to the resistance component (completing the another half semicircle behavior); and,

4) as the frequency approaching 1 mHz from 1 Hz, complete ions penetration into the porous carbon electrodes is expected and double layer capacitance (corresponded to Q_{dl}) eventually grows associated with leakage resistance R_l, describing the non- ideal capacitance behavior (the presence of nearly vertical line).

CONCLUSION

The proposed new circuitry is not only capable of fitting the experimental data well to describe the charge storage mechanism, but also capable of justifying the dc properties of cellulose- and glass wool-based capacitors. The finding provides useful information in correlating the ac impedance, fitting data and dc properties of EDLC.

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