



## Discussion

## Reply to comments on “Intrinsic limitations of impedance measurements in determining electric double layer capacitances” by H. Wang, L. Pilon [Electrochimica Acta 63 (2012) 55]

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## ABSTRACT

In the commentary to our paper [Electrochimica Acta 63 (2012) 55], Roling and Drüschrler raised a very important issue regarding the measurements and comparison of the differential and integral capacitances retrieved using electrochemical impedance spectroscopy (EIS). They clearly explained that EIS measures differential capacitance rather than integral capacitance. The present letter aims to correct our previous study. It also clarifies the fact that cyclic voltammetry (CV) and galvanostatic methods can measure both differential and integral capacitances. Similar confusion exists in the literature on electrical energy storage devices and may explain discrepancies reported when measuring the capacitances of supercapacitors using EIS, CV, or galvanostatic methods. Finally, our original paper, for the first time, solved a modified Poisson–Nernst–Planck model with a Stern layer for simulating EIS. It also presented an interpretation of “capacitance dispersion” and a scaling analysis of electric double layers in EIS simulations. The model, scaling analysis, and the associated results were not affected by the confusion pointed out by Roling and Drüschrler.

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### 1. Introduction

In the commentary to our paper, Roling and Drüschrler [1] pointed out that we trivially compared the *differential capacitance* retrieved from electrochemical impedance spectroscopy (EIS) simulations with the theoretical *integral capacitance*. We agree with Roling and Drüschrler that we inappropriately compared these two different capacitances in our original paper [2]. However, we feel that several important issues were not appropriately clarified in both our original paper [2] and the commentary [1]. The present letter aims to clarify the capacitances measured using not only EIS but also cyclic voltammetry (CV), and galvanostatic charge/discharge.

### 2. Analysis and discussion

#### 2.1. Definitions

The areal differential capacitance  $C_{\text{diff}}$  and integral capacitance  $C_{\text{int}}$  (both in F/m<sup>2</sup>) are respectively defined as

$$C_{\text{diff}} = \frac{dq_s}{d\psi_s} \quad \text{and} \quad C_{\text{int}} = \frac{q_s}{\psi_s} \quad (1)$$

where  $q_s$  and  $\psi_s$  represent the surface charge density and the surface electric potential, respectively. Note that these definitions are independent of experimental measurements.

#### 2.2. Capacitances measured using different techniques

In their commentary, Roling and Drüschrler wrote that “It is important to note that both methods (EIS and CV) measure a differential capacitance [...]” [1]. We would like to point out that this statement is not quite accurate. In fact, it should be noted that CV measurements can be used to retrieve both the differential and integral capacitances depending on how the experimental data are analyzed. First, EIS measures the differential capacitance through the following formula [3,4],

$$C_{\text{diff}} = \frac{-1}{2\pi f Z''} \quad (2)$$

where  $f$  and  $Z''$  are the frequency of the applied electric potential signal and the out-of-phase component of the measured impedance, respectively. In addition, the differential capacitance  $C_{\text{diff}}$  [5–7] and integral capacitance  $C_{\text{int}}$  [6–12] can be computed from CV measurements according to,

$$C_{\text{diff}} = \frac{j_s}{\nu} \quad \text{and} \quad C_{\text{int}} = \frac{1}{\psi_{\text{max}} - \psi_{\text{min}}} \oint \frac{j_s}{2\nu} d\psi_s \quad (3)$$

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**Table 1**  
Calculation formula of the differential or integral capacitances using EIS, CV, and galvanostatic charge/discharge methods (N/A: not available).

Capacitance	EIS	CV	Galvanostatic
$C_{\text{diff}}$	$\frac{-1}{2\pi f Z''}$	$\frac{j_s}{\nu}$	$\frac{j_s}{d\psi_s/dt}$
$C_{\text{int}}$	N/A	$\frac{\int_{\psi_{\text{min}}}^{\psi_{\text{max}}} \frac{j_s}{2\nu} d\psi_s}{\psi_{\text{max}} - \psi_{\text{min}}}$	$\frac{j_s \Delta t}{\psi_{\text{max}} - \psi_{\text{min}}}$

where  $j_s$  and  $\psi_s$  represent the measured current density and the imposed surface electric potential, respectively. The scan rate is denoted by  $\nu$  while  $\psi_{\text{max}}$  and  $\psi_{\text{min}}$  are the maximum and minimum values of the imposed electric potential  $\psi_s$ , respectively.

Similarly, the galvanostatic charge/discharge method can be used to measure the differential capacitance [3,7] as well as the integral capacitance [5,7–9,13–15] through,

$$C_{\text{diff}} = \frac{j_s}{d\psi_s/dt} \quad \text{and} \quad C_{\text{int}} = \frac{j_s \Delta t}{\psi_{\text{max}} - \psi_{\text{min}}} \quad (4)$$

where  $\Delta t$  is the time for varying the electric potential from  $\psi_{\text{min}}$  to  $\psi_{\text{max}}$  or vice versa under imposed current  $j_s$ . Note that in galvanostatic measurements, the differential and integral capacitances calculated using Eq. (4) are identical only when the measured electric potential varies strictly linearly with time. This condition could be met near zero surface potential [16]. It is also important to note that the integral capacitance rather than the differential capacitance is typically reported for supercapacitors when using galvanostatic charge/discharge method [5,7–9,13–15]. This may be due to two reasons: (i) the integral capacitance directly represents the total charge storage performance of supercapacitors and (ii)  $\psi_s$  in Eq. (4) is the variable directly measured in the galvanostatic method unlike  $d\psi_s/dt$ . Table 1 summarizes whether the EIS, CV, and galvanostatic charge/discharge methods can measure the differential and integral capacitances and gives the associated expressions.

### 2.3. Differential capacitance under equilibrium conditions

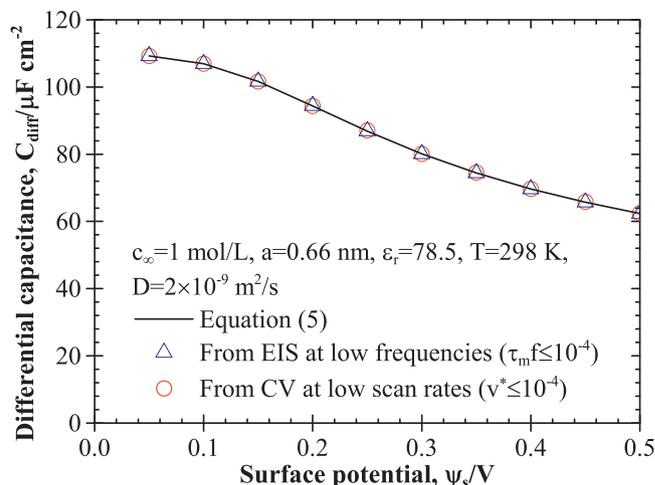
Under equilibrium conditions, the differential double layer capacitance  $C_{\text{diff}}$  is given by [16,17],

$$\frac{1}{C_{\text{diff}}} = \frac{1}{C_{\text{diff}}^{\text{St}}} + \frac{1}{C_{\text{diff}}^{\text{D}}} \quad \text{with} \quad C_{\text{diff}}^{\text{St}} = \frac{\epsilon_0 \epsilon_r}{H} \quad (5a)$$

where  $C_{\text{diff}}^{\text{St}}$  and  $C_{\text{diff}}^{\text{D}}$  denote the differential Stern layer and diffuse layer capacitances, respectively. Here,  $\epsilon_0$  and  $\epsilon_r$  are the free space permittivity and relative permittivity of the electrolyte, respectively. As pointed out by Roling and Drüscher [1], the diffuse layer differential capacitance accounting for finite ion size is expressed as [16,17],

$$C_{\text{diff}}^{\text{D}} = \frac{\frac{\epsilon_0 \epsilon_r}{\lambda_D} \sinh\left(\frac{ze\psi_D}{k_B T}\right)}{\left[1 + 2\nu \sinh^2\left(\frac{ze\psi_D}{2k_B T}\right)\right] \sqrt{\frac{2}{\nu} \log\left[1 + 2\nu \sinh^2\left(\frac{ze\psi_D}{2k_B T}\right)\right]}} \quad (5b)$$

where the valency of the symmetric electrolyte is denoted by  $z$ , while  $T$  is the temperature,  $c_\infty$  is the bulk molar concentration of electrolyte,  $e$  is the elementary charge,  $N_A$  and  $k_B$  are the Avogadro constant and Boltzmann constant, respectively. The packing parameter is defined as  $\nu = 2a^3 N_A c_\infty$  where  $a$  is the effective ion diameter. The electric potential at the Stern/diffuse layer interface is denoted by  $\psi_D$ . Note that  $\psi_D = \psi_s$  for simulations without Stern layer. It is also important to note that in the presence of the Stern layer, the value of  $\psi_D$  in Eq. (5b) is unknown. In fact,  $\psi_D$  varies



**Fig. 1.** Predicted differential capacitance  $C_{\text{diff}}$  from EIS and CV simulations at low frequencies or scan rates as a function of surface potential ranging from 0.05 to 0.5 V. Results were obtained by numerically solving the MPNP model with Stern layer along with the equilibrium differential capacitance given by Eq. (5) with  $c_\infty = 1$  mol/L,  $H = a/2 = 0.33$  nm,  $\epsilon_r = 78.5$ , and  $D = 2 \times 10^{-9}$  m<sup>2</sup>/s.

significantly with varying  $\psi_s$ . Its value must be determined numerically by solving the equilibrium modified Poisson–Boltzmann model with the Stern layer [12,16,18,19].

In their commentary, Roling and Drüscher [1] compared the relative difference  $|\delta = 1 - C_{\text{EIS}}/C_{\text{int}}|$  from our original paper with that defined by  $|\delta^* = 1 - C_{\text{diff}}/C_{\text{int}}|$ . Here,  $C_{\text{EIS}}$  is the differential capacitance retrieved from EIS simulations using Eq. (3) in Ref. [2]. Identical results between  $\delta$  and  $\delta^*$  were shown in Fig. 1 [1]. However, it is not clear how Roling and Drüscher obtained the values of  $\psi_D$  for cases with the Stern layer in order to compute  $C_{\text{diff}}$  and  $C_{\text{int}}$  and compare the relative difference shown in Fig. 1 of the commentary [1]. To clarify this important point and to make a direct comparison, we computed  $C_{\text{diff}}$  retrieved from EIS and CV simulations using Eq. (2) and (3), respectively.

Fig. 1 shows  $C_{\text{diff}}$  predicted using EIS and CV simulations of a planar electrode as a function of the surface potential ranging from 0.05 to 0.5 V. Results were obtained by solving the MPNP model with the Stern layer [Eq. (4) in Ref. [2]] at low dimensionless frequencies ( $\tau_m f \leq 10^{-4}$ ) or low dimensionless scan rates  $\nu^*$  ( $= \nu \tau_m F / R_u T \leq 10^{-4}$ ). The parameters were chosen as  $c_\infty = 1$  mol/L,  $H = a/2 = 0.33$  nm,  $T = 298$  K,  $\epsilon_r = 78.5$ , and  $D = 2 \times 10^{-9}$  m<sup>2</sup>/s. Numerical details can be found in Refs. [2,12]. Fig. 1 also shows the theoretical equilibrium differential capacitance predicted by Eq. (5). Here, the values of  $\psi_D$  in Eq. (5) were computed by solving the equilibrium modified Poisson–Boltzmann model with the Stern layer [16,19]. Fig. 1 demonstrates that EIS and CV simulations predicted the same values of  $C_{\text{diff}}$  at low frequencies and low scan rates, respectively. This capacitance was identical to the equilibrium differential capacitance predicted by Eq. (5). Consequently, the apparent relative difference shown in Fig. 7 of our original paper [2] was indeed due to the inappropriate comparison between  $C_{\text{diff}}$  retrieved using EIS and the theoretical integral capacitance, as pointed out by Roling and Drüscher [1]. Therefore, EIS and the associated equivalent RC circuit have no “intrinsic limitations” in measuring the double layer differential capacitance as mistakenly claimed in Section 4.3 of Ref. [2].

### 2.4. Approach reported in the literature

EIS, CV, and galvanostatic charge/discharge methods have been extensively used to measure the capacitances of various electrical energy storage devices. However, the measured capacitances

using these techniques have typically been reported and compared without any discrimination between differential and integral capacitances in the literature [9,15,20–26]. For example, the differential capacitance of various supercapacitors estimated from EIS or CV measurements have been compared with their integral capacitance measured using CV or galvanostatic charge/discharge method in Refs. [9,15,20–24]. However, it is evident from Table 1 that such a comparison is inappropriate. Roling and Drüscher's commentary [1] highlights the widely spread confusion in the way the capacitances are calculated and reported in the literature. We regret that we also felt victim to this confusion and inappropriately compared the differential capacitance retrieved using EIS simulations and the theoretical integral capacitance in our original paper (e.g., Fig. 7) [2]. We expect that the confusion between  $C_{\text{diff}}$  and  $C_{\text{int}}$  could explain some of the reported discrepancies between EIS and CV or galvanostatic/discharge measurements of the capacitances of supercapacitors [9,15,20–24].

Finally, it is important to note that, despite this confusion, the other results reported in Ref. [2] remain correct. First, no previous studies had simulated EIS measurements under both large electrolyte concentrations and electric potential other than by using RC circuits or transmission line models [2]. By contrast, our original paper [2] proposed a modified Poisson–Nernst–Planck (MPNP) model with a Stern layer for simulating EIS measurements. Second, the “capacitance dispersion” phenomenon observed experimentally was numerically reproduced in Ref. [2] by simulating ion transport dynamics. It also established that the “capacitance dispersion” at high frequencies can be attributed to the fact that ion transport cannot follow the rapid variation in the electric potential [2]. Moreover, a scaling analysis governing EIS measurements for planar electrodes were identified. For example, a characteristic time for ion diffusion  $\tau_m$  was identified as  $\lambda_m^2/D$  where  $\lambda_m$  is the Debye length based on the maximum ion concentration [2]. For a given concentration, the predicted differential capacitance and the phase shift of surface charge density plotted versus dimensionless frequency  $\tau_m f$  for various values of diffusion coefficient  $D$  and Debye length collapsed on a single line. This was true for all models considered with or without Stern layer [2].

### 3. Conclusions

This letter corrected and clarified our previous studies thanks to Roling and Drüscher's commentary. It also summarized the differential and integral capacitances measured using electrochemical impedance spectroscopy, cyclic voltammetry, and galvanostatic charge/discharge methods. In addition, numerical results of the

differential capacitance predicted by EIS and CV simulations at small dimensionless frequencies or scan rates are presented. First, EIS and CV measurements were found to predict the same differential capacitance at low frequencies or scan rates corresponding to equilibrium conditions. Moreover, confusion between  $C_{\text{diff}}$  and  $C_{\text{int}}$  could explain some of discrepancies reported in the literature when measuring the capacitances of supercapacitors using EIS or CV and galvanostatic methods. This indicates that distinction should be made between the differential and integral capacitances when reporting the electrical energy storage performances of different electrode materials or devices. Finally, other results, scaling analysis, and conclusions reported in Ref. [2] remain valid.

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