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Comment to the letter to the editor from Costentin et al. Entitled “Ohmic drop correction in electrochemical techniques. Multiple potential step chrono-amperometry at the test bench”

We have read with a lot of interest the Letter to Editor from Costentin et al., where the authors claim that the MUSCA method we reported (Shao et al, Energy Storage Materials 18 (2019) 456 461) [1] is not applicable and could lead to artefacts in the interpretations of electrochemical data. The MUSCA method is a step potential method to reconstruct cyclic voltammetry of an electroactive electrode for energy storage applications, by decreasing the ohmic drop contributions, following pioneer work from Donne et al. for instance [2 4].

After careful reading and analysis of the Letter from Costentin et al., we strongly disagree with their conclusions and reaffirm in a constructive way the validity of the MUSCA method and the results presented in [1].

First, the plots presented by Costentin et al. in the Figure 2 of their paper are wrong since the curvature of the cyclic voltammetry plots cannot decrease when increasing the potential scan rate. Another error in the same Figure 2 and in Figure 3 of their paper lies on the choice of the potential step (25 mV), since we evidenced in [1] that such a potential step is too small to be used. Furthermore, the same calculations done with a potential step of 200 mV or 100 mV such as defined in [1] leads to a mean current value $\frac{i_{\text{m}}}{C_{\text{d},v}}$ up to 98% of the total current in Figure 2. Hopefully, these are the only errors in the paper from Costentin et al.

More important, the mathematical model proposed by Costentin et al. describes an ideal case which does not take into consideration the volume distribution of the reactive sites inside the bulk of the electrode. Indeed,

electrodes used for energy storage applications are constituted by a current collector covered with tens of micrometer thick porous films. As a result, there is a potential distribution within the volume of these porous, thick electrodes which drives the electrochemical performance (see Fig. 1 below). Differently, the set of equations proposed by Costentin et al. only applies to an ideal case, i.e. a flat 2D metallic electrode surface uniformly accessible to the ions, with uniform potential distribution. Such an ideal situation is unlikely to occur in thick, porous (bulk) electrodes used for energy storage applications and the set of equations they propose is too simplistic to correctly describe such a complex situation. Instead, the constant uncompensated resistance R_u and constant capacitance C used by Costentin et al. in their equations should be replaced with a variable resistance R_{var} and a non constant capacitance C_{var} both depending on the potential scan rate to depict the situation in a realistic way.

Finally, the MUSCA method has never been presented as a universal method allowing the reconstruction of “ohmic drop free CV response”, such as written by Costentin et al. The MUSCA method relies on minimizing the potential distribution inside the volume of the electrode during the step, to reach homogeneous state of charge at the end of each potential step. Then, potential step height and step time have to be carefully selected [1] to get reliable and valid results; once that done, MUSCA tool offers interesting ways to build back CVs from realistic experiments.

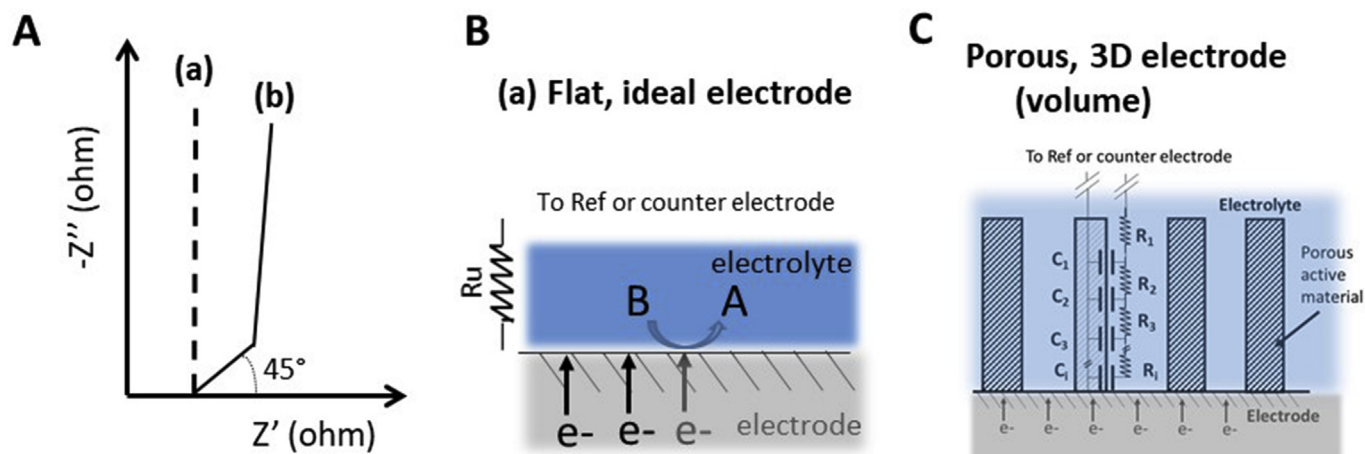


Fig. 1. (A) Electrochemical impedance plot for a capacitive, flat electrode (a), and a porous, carbon electrode (b). B) Schematic of a fast surface redox reaction on active sites located on the 2D electrode surface and C) Schematic of a porous electrode with active sites in the volume of the electrode. The porous structure of the electrode leads to the existence of series R,C circuits to depict the local conductivity and site accessibility for electrolyte ions. Adapted from [5,6]. Such a simplified model of porous structure also applies to MXene electrode [1], where 2D flakes of MXene forms slit pores.

Hopefully, this should close endless and unfruitful discussions that were ignited by a gap between experimentalists and theorists.

References

- [1] H. Shao, L. Zifeng, P.L. Taberna, P. Simon, *Energy Storage Mater.* 18 (2019) 456–461.
- [2] M.F. Dupont, S.W. Donne, A step potential electrochemical spectroscopy analysis of electrochemical capacitor electrode performance, *Electrochim. Acta* 167 (2015) 268–277.
- [3] M.F. Dupont, S.W. Donne, Charge storage mechanisms in electrochemical capacitors: effects of electrode properties on performance, *J. Power Sources* 326 (2016) 613–623.
- [4] M. Forghani, S.W. Donne, Method comparison for deconvoluting capacitive and pseudo-capacitive contributions to electrochemical capacitor electrode behavior, *J. Electrochem. Soc.* 165 3 (2018) A664–A673.
- [5] B. Conway, *Electrochemical Supercapacitors; Scientific Fundamentals and Technological Applications*, Springer, 1999, pp. 377–416.
- [6] B. Conway, W. Pell, Power limitations of supercapacitor operation associated with resistance and capacitance distribution in porous electrode devices, *Electrochemical Supercapacitors*, *J. Power Sources* 105 (2002) 169–181.

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