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## Exploring the interdependence between the coulombic, voltage and energy efficiencies

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### ABSTRACT

Recently, a consensus emerges on the relevance of using the energy efficiency (EE) as a metric to evaluate the operational potential window (OPW) of the electrochemical energy storage systems. Unfortunately, EE alone is not comprehensive enough to provide a full understanding of the electrochemical degradation at the electrode/electrolyte interface since both the coulombic efficiency (CE) and the voltage efficiency (VE) have an impact on EE. Here it is proposed to deconvolute EE into its CE and VE contributions by plotting the variations of CE with VE after their Neperian logarithmic transformation ( $\text{Ln}$ ) in a polar coordinate system ( $\rho$ ,  $\alpha$ ) where the modulus  $\rho$  can be approximated to  $\text{Ln}(\text{EE})$  and the argument  $\alpha$  represents the relative importance of the individual contributions of CE and VE. In the present case, results obtained with YP80F based electrodes in 1 M  $\text{H}_2\text{SO}_4$  electrolyte demonstrate that the decrease in EE at both ends of the OPW is different in nature depending on whether the electrode serves as positive or negative electrode.

### 1. Introduction

With the advent of large scaled energy storage systems such as lithium-ion batteries in electric vehicles or energy storage technologies for high-power applications such as electrochemical capacitors (ECs), a consensus emerges on the use of the EE instead of the CE for determining the OPW [1,2]. For an ideal capacitor capable of operating at high scan rates, the charge/discharge process is only limited by the equivalent series resistance, which can be put forward to estimate the EE [3]. But for real ECs based on porous activated carbons with inhomogeneous pore sizes, power limitations arise from the distributed resistance of electrolyte inside pores, to which may be added the reaction kinetics of redox surface groups and the electrolyte degradation when potential limits are approached [4,5]. Thus, when charge transfer reactions occurs at the electrode/electrolyte interface of ECs, as with any degradation reactions, EE is much more sensitive to their cycling performances than CE, because of the cumulative effect of CE and VE [6].

It is well-known in literature that the decomposition of the electrolyte can result in the electrode passivation by accumulation of insoluble side-products in the porosity or in the chemical modification of the carbon electrode, so that a strong interdependence between CE and VE exists [7,8]. An immediate corollary is that an equal value of EE may be different in nature depending on whether it is mainly impacted by CE or VE, so that it becomes equally important to know EE than the importance of the individual contributions of CE and VE. In the present paper, the variations of CE, VE and EE were evaluated for YP80F based electrodes working in 1 M sulfuric acid electrolyte over a wide potential

window with special attention placed on the interdependence between CE and VE as the potential limits are approached.

### 2. Experimental

#### 2.1. Electrode fabrication and cell assembling

Working and counter electrodes were prepared by mixing the YP80F activated carbon (from Kuraray) with poly(vinylidene fluoride) and carbon black (superior graphite) with weight ratios of 80:10:10 in THF (the product loading was 16.7 mg/mL). The mixture was stirred for several hours until a homogeneous carbon ink was obtained. 150  $\mu\text{L}$  of the carbon ink was spread on a gold surface consisting in a disk of 18 mm diameter. After drying at 60  $^\circ\text{C}$  under vacuum for one night, thin films of 2–3 mg were obtained, which ensures that the carbon film thickness does not exceed 50  $\mu\text{m}$ , guaranteeing that the entire depth of the carbon coating was soaked by electrolyte. Electrodes were assembled in a 3-electrode cell with a symmetric configuration to assess separately the stability window of the electrode/electrolyte in the negative and positive potential domains. Glass fiber separators (purchased from Whatman) of 0.5 mm thickness were used and a silver wire served as quasi reference electrode.

#### 2.2. Electrochemical measurements

CE, VE and EE were determined from cyclic voltammograms (CVs) recorded at 10  $\text{mV}\cdot\text{s}^{-1}$  from 0 V to a variable vertex potential comprised between  $-0.6$  V and 0.75 V, first in 0.1 V decrement/increment

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and then in 0.05 V decrement/increment when approaching the onset of the electrolyte degradation. Noted that, before performing the cyclic voltammetry measurements, 300 pre-conditioning CVs at  $10 \text{ mV}\cdot\text{s}^{-1}$  were recorded over a potential range of 0.5 V in a potential domain where no electrolyte degradation takes place. Next, six successive CVs were recorded for each value of the vertex potential and only the sixth one was used for the calculation. Importantly, a fresh carbon electrode was used for each window opening cyclic voltammetry measurements. Noted that galvanostatic measurements are often preferred because they give a more realistic description of the device, but the cyclic voltammetry technique is well-suited for a fundamental study since it is more sensitive to the faradaic current and permits to finely discriminate the capacitive and faradaic contributions to the charge storage.

### 2.3. Calculation methods

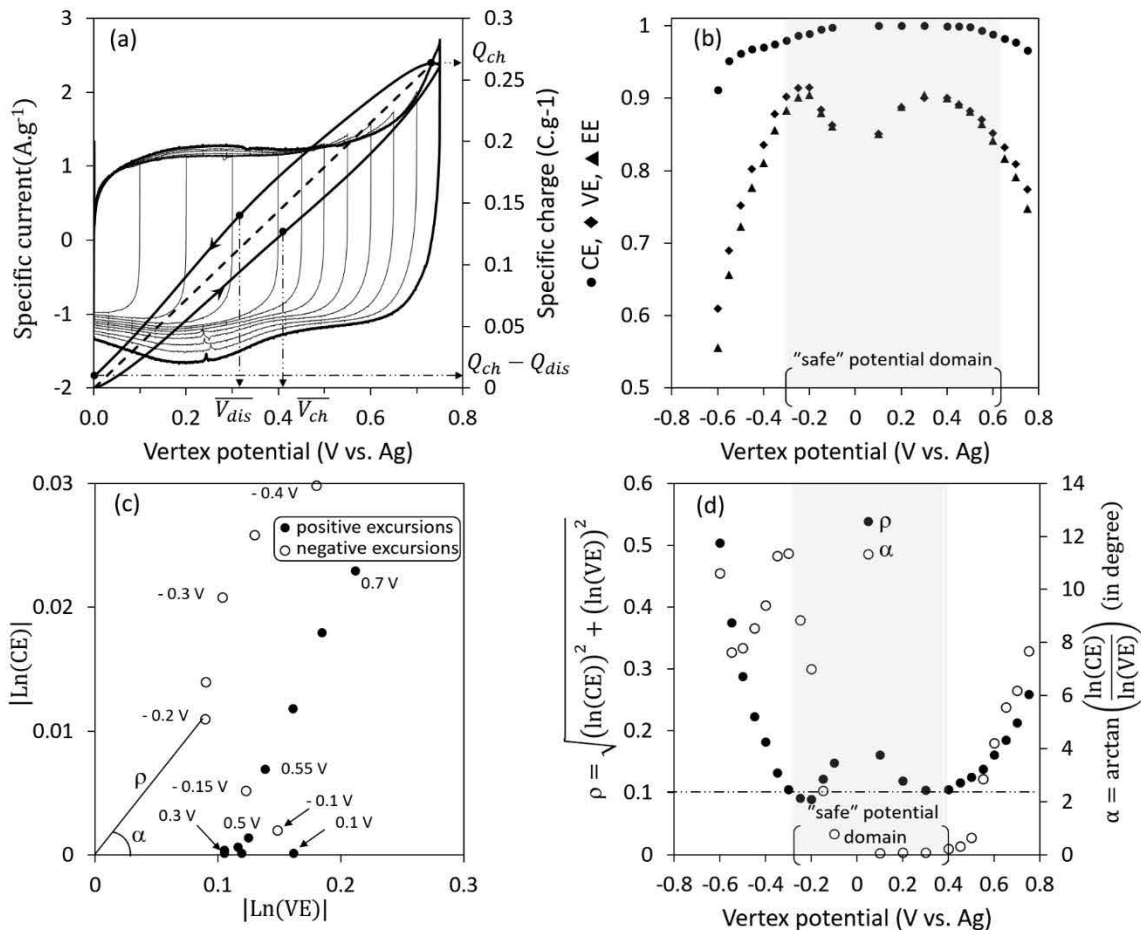
By definition, CE is a measure of the reversibility of the charge/discharge process and is expressed as the ratio of the amount of discharge electricity  $Q_{\text{dis}}$  to the amount of charge electricity  $Q_{\text{ch}}$ , both determined by integrating the CVs. VE is a measure of the deviation of the average discharge potential from  $\bar{V}_{\text{dis}}$  the average charge potential  $\bar{V}_{\text{ch}}$  and EE is defined as the ratio of the discharge energy  $\xi_{\text{dis}}$  to the charge energy  $\xi_{\text{ch}}$ . Importantly, VE and EE were obtained from the integrated cyclic voltammetry data as recommended when non-linearity appears in the charge/discharge curves [9]. The equations used to obtain CE, VE and EE are presented below and the critical parameters on

which they depend are identified in the Fig. 1a for the anodic part of the window opening cyclic voltammetry experiments.

$$CE = \frac{Q_{\text{dis}}}{Q_{\text{ch}}}; VE = \frac{\bar{V}_{\text{dis}}}{\bar{V}_{\text{ch}}} = \frac{\frac{1}{Q_{\text{dis}}} \int_{q \leq 0} V dq}{\frac{1}{Q_{\text{ch}}} \int_{q \geq 0} V dq}; EE = \frac{\xi_{\text{dis}}}{\xi_{\text{ch}}} = \frac{\int_{q \leq 0} V dq}{\int_{q \geq 0} V dq} = CE \times VE$$

### 3. Results and discussion

Because EE can be expressed by the product of CE and VE, there is a growing body of literature that propose to use EE to provide a more realistic assessment of the OPW [10], claiming that EE is the most sensitive indicator to the electrolyte decomposition, especially for high power storage systems for which high current rates give large voltage hysteresis (i.e. low VE) even when CE is close to 100%, as it can be verified in the Fig. 1b. Over the potential window where the electrostatic charge process is found to be reversible, EE and VE are quite similar and follow the same trend, first increasing with the potential window before decreasing sharply as an additional charge is consumed in the decomposition of the electrolyte (i.e. when CE starts to decrease). The main reason of the first increase of VE in the potential domain of the charge storage reversibility is because the ohmic drop represents an increasingly low fraction of the potential window as the vertex potential increases, so that the ratio of the average discharge voltage to the average charge voltage tends to unity as long as CE is equal to 100%. EE



**Fig. 1.** (a) Series of CVs recorded at  $10 \text{ mV}\cdot\text{s}^{-1}$  in 1 M  $\text{H}_2\text{SO}_4$  from 0 V to a variable vertex potential up to 0.75 V. The specific charge-potential curve superimposed corresponds to the largest potential window cyclized in bold line (the dotted straight line separate the integrations of the positive and negative parts of the CV). (b) CE, VE and EE variations with the vertex potential. The "safe" potential window is delimited at both ends by CE equal to 0.98. (c) Variations of  $\text{Ln}(\text{CE})$  with  $\text{Ln}(\text{VE})$ . (d) Representation of the data points of the Fig. 1c in a polar coordinate system ( $\rho$ ,  $\alpha$ ) as illustrated in the Fig. 1c for the data point at  $-0.2 \text{ V}$ . The "safe" potential window is delimited at both ends by  $\text{Ln}(\text{EE})$  equal to 0.1.

and VE reach a maximum value when the electrode potential approaches the anodic and cathodic potential limits beyond which the decomposition of the electrolyte starts. Above these limits, CE have a growing impact on EE that gradually differs from VE, so that the extent of the decrease of EE is greater than those of VE and CE alone (Fig. 1b). Such an impact can be aggravated by kinetic polarization effects and passivation effect, to which may be added an increase of the internal ohmic drop as the faradaic current exponentially increases [4]. Nevertheless, the knowledge of EE alone is not comprehensive enough to provide a full understanding of the individual contributions of both CE and VE. For example, in the Fig. 1b, at both ends of the “safe” potential domain established from a preset value of CE equal to 0.98, a lower EE is obtained at the anodic potential limit compared to that of the cathodic potential limit, implying that EE is differently impacted by VE depending on whether the electrode serves as positive or negative electrode. This is originating from the complex nature of VE, which depends on factors such as the electrode resistance, bulk electrolyte resistance, charge transfer resistance and mass transfer resistance [11]. Considering that electrode passivation, porous obstruction or chemical modification of the carbon electrode may be caused by the decomposition of the electrolyte, a strong interdependence between CE and VE is expected [7,8]. It results to the above that it is equally important to know EE than the relative importance of the individual contributions of CE and VE to make EE a meaningful indicator of the state-of-health of the electrode/electrolyte interface. To address this point, the Fig. 1c shows the variations of CE with VE after their Neperian logarithmic transformation (Ln). Noted that this transformation makes possible the conversion of Cartesian coordinates into polar coordinates well-suited for functions depending on the relative importance of two parameters. In this new polar representation shown in the Fig. 1d, each data points can be described by a modulus  $\rho$  that can be identified to Ln(EE) and an argument  $\alpha$ , giving the relative importance of Ln(CE) and Ln(VE) on Ln(EE), as illustrated in the Fig. 1c. Interestingly, the absolute value of Ln(CE) gives a good approximate of the faradaic fraction R proposed by Xu et al. as long as  $CE = 1/(1 + R)$  remains close to unity [12]. By analogy, Ln(VE) and Ln(EE) can be approximated to  $R_{VE}$  and  $R_{EE}$ , which reflect the voltage and energy dissymmetry of the charge/discharge process in a fraction of the average discharge voltage and the discharge energy. Noted that in this formalism, the faradaic fraction should be better renamed  $R_{CE}$ .

As it was obtained in the Fig. 1c, Ln(VE) gradually decreased (i.e. VE approaches to unity) for positive potential excursions up to 0.3 V and for negative potential excursions up to -0.2 V because the ohmic drop becomes rapidly negligible against the potential window, as it was previously discussed. As the vertex potential becomes higher than 0.3 V and lesser than -0.25 V, an increase of Ln(VE) along with an increase of Ln(CE) is obtained, corresponding to a concomitant decrease of CE and VE. Importantly, in a first step, both in the anodic and cathodic branches of the potential window, Ln(CE) is increasing faster than Ln(VE), leading to an increase of  $\alpha$  in the polar representation (Fig. 1d). This means that, at the beginning of the anodic and cathodic decomposition processes, CE plays a prominent role in EE compared to VE. Remarkably, the Fig. 1c shows that in the very beginning of the anodic decomposition process (in the potential range 0.3 V - 0.5 V), the increase in Ln(VE) is accompanied by a small increase of the anodic faradaic fraction (approximated by Ln(CE)), while a comparatively higher cathodic faradaic fraction as that consumed in the potential range of -0.1 V to -0.20 V is accompanied by a decrease of Ln(VE). These results implies that EE is differently impacted by CE and VE in these potential domains.

The polar coordinates system ( $\rho$ ,  $\alpha$ ) presented in the Fig. 1d is most appropriate to analyse the interdependence between CE and VE and their impact on EE, because the modulus  $\rho$  provides information on EE and  $\alpha$  gives the relative importance of CE and VE on EE. In the cathodic part of the graph,  $\alpha$  increases quickly before reaching a maximum at -0.3 V, and then sharply decreased to rise again from -0.55 V, implying

that CE and VE alternatively play a prominent role in EE depending on the electrode potential. Basically, the increase of  $\alpha$  at the very beginning of the cathodic degradation process and from -0.55 V implies that CE plays a prominent role on EE compared to VE in these potential domains. Interestingly, the decrease of  $\alpha$  between -0.3 V and -0.55 V reveals that VE contributes significantly to EE in this narrow potential domain that it would have been difficult to diagnose otherwise. This may be possibly due to several causes related to an alteration of the electrolyte or the electrode material, without possibility to clearly address the issue. In contrast, in the anodic part of the Fig. 1d, a smaller and more gradual increase of  $\alpha$  from 0.4 V paired with a significant change of the modulus, implies that EE is less impacted by CE, as it can be verified in the Fig. 1b, revealing that EE is close to VE during the anodic degradation process. This demonstrates that the energy and power limitations of the electrode can have different causes at both ends of the OPW. By referring to EE at the maximum of  $\alpha$  to delimit the OPW, with a limit value of c.a. 0.1 for Ln(EE) that represents roughly a loss of energy during the charge equal to 10% of the discharge energy, a narrower “safe” potential domain marked in the Fig. 1d is obtained. The large difference in the  $\alpha$  values at both ends of this potential domain illustrates that the equal EE values delimiting the OPW are fundamentally different in their origin. On the cathodic side of the OPW, EE is mainly controlled by CE, while on the anodic side, EE is predominantly impacted by VE. In the present study, the discussion was illustrated with results obtained in 1 M H<sub>2</sub>SO<sub>4</sub> because, in this electrolyte, carbon is differently impacted by cathodic and anodic treatments so that EE was expected to be different in nature depending on whether the electrode serves as positive or negative one, but it would be interesting to explore this approach in a subsequent study relative to other systems with large voltage windows such as organic electrolytes and ionic liquids.

#### 4. Conclusion

In this paper, the interdependence of CE and VE is significantly recognized, and evidence was made for the existence of different EE regimes for ECs, depending on whether power limitations is under CE or VE control. This study was an opportunity to take a critical look at using EE without a full understanding of the individual contributions of CE and VE. It was demonstrated that the power limitation of YP80F based electrodes working in 1 M H<sub>2</sub>SO<sub>4</sub> is different in nature depending on whether the electrode serves as positive or negative electrode. The cycling performances evaluated in the negative potential window show that the decrease in EE at the beginning of the degradation process is mainly originating from a decrease in CE, while in the positive potential domain a decrease in EE is obtained even when CE is close to 100%, because of a strong impact of VE.

#### CRedit authorship contribution statement

**Charles Cougnon:** Conceptualization, Data curation, Formal analysis, Investigation, Methodology, Supervision, Validation, Writing - original draft, Writing - review & editing.

#### Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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