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A new formula for the faradaic fraction used to estimate the coulombic hysteresis in the charge/discharge profiles of electrochemical energy storage systems

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Abstract

The present work is concerned with the charge hysteresis frequently observed in the charge/discharge profiles of electrochemical capacitors (ECs) at the full charge voltage. In energy storage applications, the concept of operating potential window (OPW), envisioned as the potential window in which ECs are not deteriorated, is a key parameter for addressing the problems of both the life cycle and the energy density, but its determination remains arbitrary in nature due to its experimental determination based on kinetic parameters. For ECs, it was proposed to define the OPW as the closed gap in potential limited by a preset faradaic fraction at both ends of the stability window to ensure that the faradaic degradation of the electrode/electrolyte interface is commensurate with the charge stored in the electrochemical double layer. By implication, the potential limits so obtained are closely related to the potential range covered to reach a preset value of the faradaic fraction, so that the initial potential from which the stability is evaluated is expected to have an impact on the OPW. Here, this source of error was explored in detail and a voltage-correction is proposed to make the faradaic fraction less sensitive to the initial potential.

1. Introduction

In electrochemical operations, extreme positive and negative potentials beyond which the electrode/electrolyte interface is degraded set boundaries for the stability window envisioned as the potential domain where no faradaic current flows in absence of electroactive solutes. For ECs,

an accurate determination of the electrochemical stability window identifies a viable operating potential window (OPW) compatible with a long life cycle, while high-voltage cell systems are the best avenue for improving the energy density [1-4]. Therefore, the assessment of the largest potential range useable is a key parameter in the description of ECs, but remains elusive in nature because of their experimental determination. In practice, a cyclic voltammogram (CV) is recorded from a potential value where no redox reaction occurs to a positive or negative potential where the electrode/electrolyte interface is electrochemically degraded. Therefore, an estimate of the stability window of the interface is obtained by minimizing the irreversible faradaic processes to approach the potential limit at which just a purely capacitive current is obtained [5]. With non-porous working electrodes, potentials at which a preset cut-off current density is obtained give a realistic estimate of the stability window, since the faradaic current can be approximated to the observed current as the capacitive current is negligible [6,7]. However, nonsensical results are obtained with porous electrodes for which the capacitive current cannot be neglected [8]. For this reason, Xu et al. proposed to use a stability factor R suitable for porous electrodes, expressing the faradaic charge consumed in the electrode/electrolyte degradation as a fraction of the capacitive charge stored in the electrochemical double layer during the potential excursion [9,10]. By using the cyclic voltammetry technique, the potential of individual electrodes is scanned from the open circuit potential (OCP) to a variable vertex value, separately in the positive and negative direction, and the viable potential range for the cell corresponds to the largest potential domain within which R , calculated from the integrated positive and negative charges of the CVs, remains below a preset threshold value. Since, in the R -voltage method, the faradaic charge is commensurate with the capacitive charge stored in the double layer, the determination of the potential limits at both ends of the stability window depends, strictly speaking, to the potential range scanned to reach a faradaic charge satisfying the preset R value, so that the initial potential

from which the stability of the electrode/electrolyte interface is evaluated is expected to have an impact on the determining of the OPW. As before the initial potential is ignored to be an important variable, the question arises to what extent the initial potential have an impact on the OPW.

At this stage, it is important to note that other efficiency metrics of the charge/discharge performances, such as energy efficiency, can be used to evaluate the state-of-health of ECs or assess their OPW [11], but the ultimate objective of this article is to propose a voltage-corrected formula to make the faradaic fraction less affected by the initial potential and ensure a more accurate determination of the OPW, not to extend its value. This is achieved by identifying the initial potential that is to be used in the opening cyclic voltammetry experiments to avoid making an error on the assessment of the stability window by under- or over-estimating one of the two degradation phenomena. In a first part, the impact of the initial potential on the actual method of determining the OPW based on the R-voltage method was evidenced. In a second part, a voltage-corrected faradaic fraction S was proposed in order to take account of the difference in sensitivity of the electrode towards the anodic and cathodic decomposition processes and so obtain realistic values of the faradaic fraction suitable for a correct assessment of the stability window.

2. Experimental results

2.1. Electrode fabrication and cell assembling

Electrodes were prepared by mixing the YP80F activated carbon (from Kuraray) with poly(vinylidene fluoride) and carbon black (superior graphite) with a ratio of 80:10:10 (w:w:w) 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 μ L of carbon ink was spread on a gold surface consisting in a disk of 18 mm diameter. After drying at 60 °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 μm , guaranteeing that the entire depth of the carbon coating was soaked by electrolyte. Porous carbon electrodes served as both working and counter electrodes. The supercapacitor cells were assembled in a 3-electrode configuration by compressing two carbon electrodes of approximately the same mass separated by a 0.5 mm thick glassfiber separator (purchased from Whatman) impregnated with 1 M H_2SO_4 . A silver wire served as quasi reference electrode.

2.2. Electrochemical measurements

Electrochemical experiments were performed with a VMP-Biologic potentiostat and were monitored by the ECLab software. In all cases, before performing the cyclic voltammetry measurements, 300 pre-conditioning cyclic voltammograms at 10 mV/s were recorded over a potential range of 0.5 V in a potential domain where no degradation of the electrode/electrolyte interface takes place. Next, the window opening cyclic voltammetry experiments were performed at 10 mV/s from 0 V vs Ag to a final negative or positive potential, first in 0.1 V decrement/increment and then in 0.05 V decrement/increment when approaching the onset of the electrode/electrolyte interface degradation. Noted that six successive cyclic voltammograms (CVs) were recorded for each value of the vertex potential (only the sixth one was used for the calculation). Importantly, a fresh carbon electrode was used for each window opening cyclic voltammetry measurements. Experiments were conducted in a 3-electrode configuration and with symmetric configurations (mass loading of about 0.8 mg/cm^2) to assess separately the stability window of the electrode/electrolyte interface in the negative and positive potential domains. 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.

3. Results and discussion

The OPW of an electrochemical capacitor is related to its voltage robustness expressed as the faradaic charge fraction responsible to the electro-degradation of the electrode/electrolyte interface during the charge process. Strictly speaking, a preset value of the faradaic charge in absolute term is sufficient to delimit the electrochemical potential window, but the sole mention of the faradaic charge is not specific enough for energy storage applications. The main reason is because the electrochemically accessible surface of porous electrodes to ions and their impact on the electrochemical degradation of electrolytes may differ substantially depending on their textural properties, making the electrode sensitivity towards the electrolyte degradation potentially different from one porous carbon to another [12]. To address this issue, Xu et al. first proposed to express the faradaic charge as a fraction of the delivered charge as in the equation (1) [9]. In the present study, the “CE” subscript is a reminder that R is reliable to the coulombic efficiency:

$$R_{CE} = \frac{Q_{ch} - Q_{dis}}{Q_{dis}} = \frac{1}{CE} - 1 \quad (1)$$

Where Q_{ch} and Q_{dis} refer to the electrical charges for the charge and discharge steps at the forward and backward branches of the CV, as illustrated in the Figure 1a. Noted that all values are used in absolute terms to be valid both for positive and negative potential excursions. In this approach, it is implicitly assumed that Q_{dis} can be identified with the non-faradaic charge, Q_{nF} , originating from the purely electrostatic storage in the electrochemical double-layer, so that its subtraction to Q_{ch} leads to the irreversible faradaic charge, Q_F , lost during the charge process. It is

important to note that the electrode material cannot always be regarded as inert towards the electro-degradation of the electrolyte. Here, because of the susceptibility of the carbon to be oxidized in aqueous acidic electrolytes [13,14], Q_{ch} and Q_{dis} include a pseudocapacitance in addition to the double-layer capacitance as evidenced by the broad anodic and cathodic peaks observed at around 0.2 V vs Ag in the Figure 1b. Similarly, it is worth noting that the irreversible charge Q_F is of a more complex nature and can also result from linkage current. If such phenomenon is mainly experienced by ECs while stored in the charged state and can be assumed to be negligible in the duration of a charge/discharge cycle, the linkage current problem is becoming more significant in high voltage and low discharge rate conditions and can be aggravated by using a high-surface area electrode material [15]. In addition, it was claimed that surface functionalities and dissolved gases providing from water decomposition, are expected to increase the linkage current [16-18].

Since the capacitive charge accumulated at the electrode/electrolyte interface depends to the potential domain covered during the charge period, the faradaic fraction R_{CE} is dependent on the initial potential E_i from which the potential excursion starts, as evidenced by equation (2), where C refers to the capacitance, while E_m represents the voltage measured between E_i and E_{vx} (Figure 1a).

$$R_{CE}^{E_i} = \frac{Q_F}{Q_{nF}} = \frac{1}{E_m} \times \frac{Q_F}{C} \quad (2)$$

In the remainder of the study, a distinction will be made between an arbitrarily selected preset faradaic fraction value, termed R_{CE} , and the function $R_{CE}^{E_i}(V_{vx})$ where the initial potential E_i used to determine the voltage dependence of the faradaic fraction will be specified in superscript. Compared to the voltage dependence of R_{CE}^0 determined by starting the CVs at 0 V (Figure 1b), an increase of the initial potential by 0.1 V led to a more pronounced evolution of the faradaic

fraction $R_{CE}^{0.1}$ with the voltage in the anodic potential domain, because of the comparatively smaller capacitive charge accumulated in the interface for reaching a given vertex potential (Figure 1c). In the same time, a lower evolution of the faradaic fraction is noticed in the cathodic potential domain, due to the comparatively higher capacitive charge stored in the interface for reaching a given negative vertex potential. For this reason, a shift of the initial potential towards the positive potential caused a decrease of both the anodic and cathodic potential limits (Figure 1d), since a lower anodic faradaic charge is needed to keep the faradaic fraction at its preset value, while a higher faradaic charge, in absolute terms, must be consumed at the cathode for maintaining R_{CE} at its reference value. Noted that a decrease of E_i (see $R_{CE}^{-0.05}$ vs R_{CE}^0 in Figure 1c) has the opposite effect, causing a positive shift of both $E_{lim,Red}$ and $E_{lim,Ox}$. Importantly, the shift in potential needed to adjust the anodic and cathodic faradaic charges for satisfying the preset value of R_{CE} at both ends of the stability window do not necessarily offset each other. Indeed, because of the exponential dependence of the faradaic current with the potential, the shift in the potential limit on the side of the nearest decomposition process (relative to the initial potential) is not necessarily compensated by that of the potential limit on the side of the more distant decomposition process. As the initial potential is approaching the threshold value of the anodic (cathodic) decomposition process, the negative (positive) shift in potential to decrease the anodic (cathodic) faradaic charge in order to keep the faradaic fraction at its reference value becomes more important because of the more gradual increase of the anodic (cathodic) faradaic current with the potential at the beginning of the anodic (cathodic) decomposition process. In the same time, the initial potential becomes far from the threshold value of the cathodic (anodic) decomposition process and a small negative (positive) shift in potential is sufficient to maintain

the faradaic fraction at a constant value, owing to the accelerating increase of the cathodic (anodic) faradaic current with the potential.

It follows from the above that the R_{CE} -voltage method is becoming more and more sensitive to the nearest degradation process, and is becoming less and less sensitive to the more distant degradation process. Between those two extremes, there is a “pivotal” initial potential, $E_{i,p}$, from which the stability of the electrode/electrolyte interface is evaluated with the same relative sensitivity to the anodic and cathodic decomposition processes (Figure 1d). Around this intermediate initial potential, infinitesimal variations of E_i produced equal changes of the cathodic and anodic potential limits, so that the gap between them does not varies any more, corresponding to a maximum value of the OPW. This “pivotal” initial potential is found in the Figure 1d at the abscissa value where the partial derivatives of the potential limits with respect to the initial potential are crossing. Note that, in the present study, the “pivotal” initial potential is approximately equidistant to both decomposition phenomena. This latter observation has kinetic implications, which will be discussed in a subsequent publication.

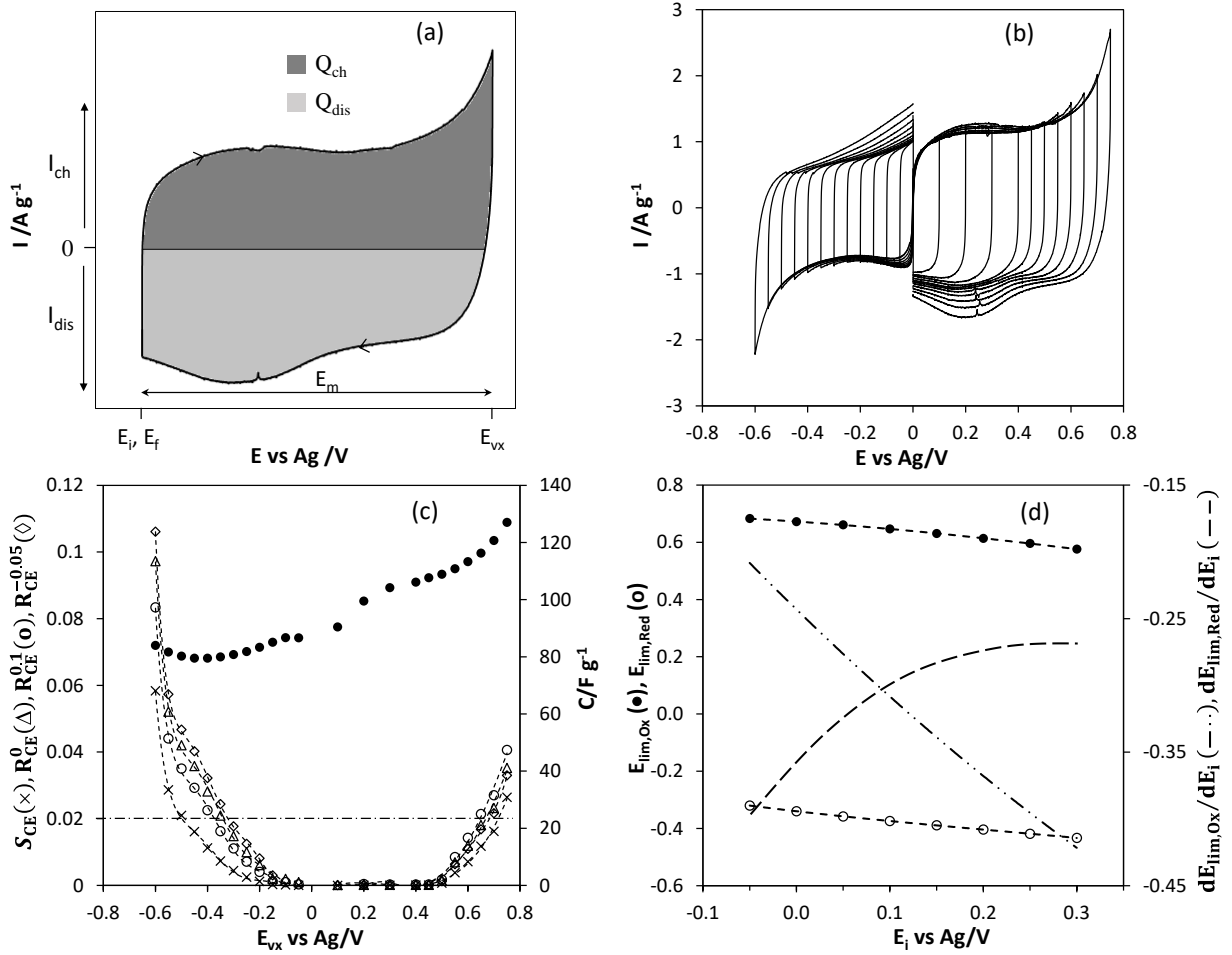


Figure 1 : (a) Schematic description of charge and discharge charges in a cyclic voltammogram helpful in the quantification of the electrolyte stability window on porous electrodes. (b) Series of CVs recorded at 10 mV s^{-1} in H_2SO_4 1M from 0 V to a variable vertex potential comprised between -0.6 V and 0.75 V. (c) Potential dependence of the stability factors S_{CE} and R_{CE} calculated for different initial potentials. The horizontal solid line intercepts the stability curves at anodic and cathodic potential limits for a faradaic fraction of 0.02. The secondary y-axis shows the specific capacitance averaged between 0 and the vertex potential. (d) Impact of the initial potential on the potential limits. The secondary y-axis shows the derivatives of the potential limits with respect to the initial potential.

An attempt to make the faradaic fraction $R_{CE}^{E_i}$ independent from the initial potential is to propose a voltage-corrected faradaic fraction S_{CE} defined as the product between the voltage excursion and $R_{CE}^{E_i}$:

$$S_{CE} = (E_{vx} - E_i) \times R_{CE}^{E_i} = \frac{Q_F}{C} \quad (3)$$

At this stage, it is worth noting that such a voltage correction does not make the faradaic fraction (now envisioned as a faradaic-charge/capacitance ratio) rigorously E_i -independent, but only less sensitive to the initial potential, because of the potential dependence of the capacitance (see Figure 1c). Nevertheless, assuming that the possible values for the initial potential can only be in a narrow potential range around the open circuit potential, the impact of a change in E_i on the specific capacitance averaged over the measured voltage is negligible.

As noted above, the R_{CE} -voltage method gives a realistic estimate of the OPW only if the anodic and cathodic potential limits corresponding to the preset R_{CE} value are reached from a “pivotal” initial potential $E_{i,p}$. By implication, the question of the OPW raises the problem of how determine the “pivotal” initial potential.

At this stage, it is important to note that the dimensionless ratio R_{CE} is replaced by S_{CE} expressed in Volt that represents the voltage required to accumulate in the electrochemical double layer a capacitive charge equivalent to the irreversible charge loss during the charge period. Consequently, another way to represent the charge hysteresis of the charge/discharge process is to show the voltage dependency of a theoretical voltage E_{th} needed to store in the electrochemical double layer a charge equivalent to the sum of the reversible capacitive charge Q_{nF} and the irreversible faradaic charge Q_F . Figure 2a represents the voltage dependency of the theoretical voltage for a zero E_i . Noted that the arbitrary choice of a preset R_{CE} value in the R_{CE} -voltage method is replaced in the S_{CE} -voltage method by a linear equation used as a valuation line, Y_{val} , whose slope is related to CE (or R_{CE}) and intercept depends on E_i (Figure 2b). In this representation, the OPW corresponds to the segment on the x-axis delimited by the abscissa of the two points of intersection of E_{th} and Y_{val} , as defined by equation (4) where S_{CE} can be regarded as the sensitivity of the electrode towards the degradation processes.

$$OPW(R_{CE}, E_i) = E_{m,Ox} - E_{m,Red} = \frac{1}{R_{CE}} \times [S_{CE}(E_{lim,Ox}) - S_{CE}(E_{lim,Red})] \quad (4)$$

Where $E_{m,Ox}$ and $E_{m,Red}$ represent the potential domain scanned from the initial potential to reach the anodic and cathodic potential limits. It result from the above that an increase of the OPW is obtained when the electrode is becoming less sensitive towards the cathodic and anodic degradation of the interface (i.e. when S_{CE} more gradually increases with the electrode potential, so that E_{th} intercepts Y_{val} at higher potential limits in absolute terms). Interestingly, this can either result from a decrease of Q_F or from an increase of C . In aqueous electrolytes, the first situation corresponds to the well-known overpotential effect recently explored to expand the voltage range of supercapacitors by pushing the dihydrogen evolution potential away from its thermodynamic value under neutral pH conditions [19,20]. The second situation could open up new avenues for the enhancement of the OPW by increasing the electrode (pseudo)capacitance, without the kinetic of the degradation process being significantly affected. In this connexion, it might be anticipated that the high voltage value reported by Lebègue et al. in propylene carbonate with carbon electrodes grafted with redox molecules might be ascribed to the addition of a large pseudocapacitance to the double-layer capacitance of the carbon [21].

In the Figure 2a, the graphic display of the evolution of the OPW with E_i is possible by dragging the valuation line inside the stability window without changing its slope (thin dotted line vs. thick dotted line in Figure 2b). An equivalent way of showing the E_i dependency of the OPW is to plot the E_{vx} dependency of the characteristic equation $E_{th} - Y_{val} = 0$ and to identify the OPW to the potential range on the x-axis between its two roots. Figure 2c shows the graph of the characteristic equation for a zero E_i and a R_{CE} value equal to 0.02. As above, by assuming that S_{CE} is E_i independent, the OPW associated to a given initial potential corresponds to the potential range between the two zero x values for a x-axis that intersects the y-axis at $-E_i \times R_{CE}$. For a set

of possible values for the initial potential, sets of anodic and cathodic potential limits associated to a preset R_{CE} value can be extracted from Figure 2c, allowing to trace the evolution of the OPW with the initial potential (Figure 2d). Noted that Figure 2c can be conveniently used for the determination of the “pivotal” initial potential, since it corresponds to the initial potential from which the OPW segment on the x-axis is delimited by a pair of parallel tangent lines to the curve. This can be inferred from the equation (4) and on the basis of the definition of the “pivotal” initial potential (equality of the rate change of the potential limits with respect to E_m), since where these conditions are met, the derivative of the OPW function with respect to E_m is null at the “pivotal” initial potential, as resumed in equation (5).

$$\left[\frac{d(OPW)}{dE_m} \right]_{E_{i,p}} = 0 = \frac{1}{R_{CE}} \times \left[\frac{dS_{CE}(E_{lim,Ox})}{dE_m} - \frac{dS_{CE}(E_{lim,Red})}{dE_m} \right]_{E_{i,p}} \quad (5)$$

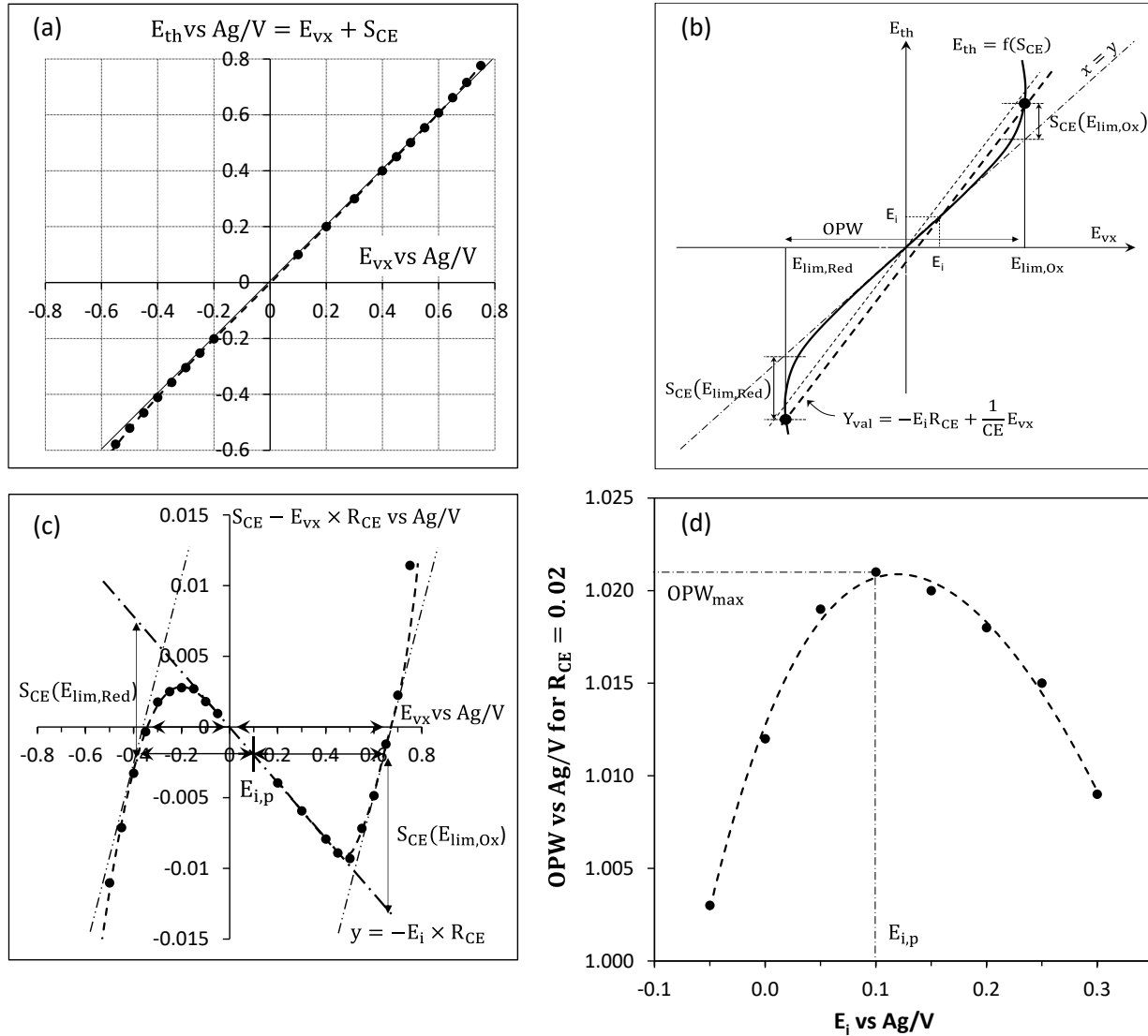


Figure 2 : (a) Representation of the theoretical voltage as a function of the vertex potential. (b) Illustration of the impact of the initial potential and the arbitrary choice of CE (or R_{CE}) on the OPW. (c) Graphic display of the E_i dependency of the OPW. (d) Evolution of the OPW of the H_2SO_4 1M electrolyte on a YP80F supercapacitor electrode with the initial potential used in the opening cyclic voltammetry experiments.

As reflected in Figure 2d, a small change in E_i around the “pivotal” initial potential has no effect on the OPW because it produces the same variation, in absolute terms, of the anodic and cathodic potential limits and the result is a maximum value for the OPW. In other words, the differential sensitivity $\frac{dS_{CE}}{dE_m}$ of the porous electrode towards the anodic and cathodic

decomposition of the electrode/electrolyte interface is the same when E_m is measured from the “pivotal” initial potential, and the irreversible charges lost in the anodic and cathodic decomposition processes at both ends of the OPW during the charge period are commensurate with the capacitance of the electrode in the anodic and cathodic potential domains, respectively, so that no decomposition phenomenon is under- or over-estimated in comparison with the other. In these conditions, the gap in potential around the “pivotal” initial potential closed by potential limits at which the equality of the differential sensitivity of the electrode towards the anodic and cathodic decomposition processes is verified, gives a more realistic value of the OPW than that deduced to the R_{CE} -voltage method.

It is important to emphasize here that the exclusive concern of this work is to eliminate the voltage dependence of the faradaic fraction R_{CE} . In particular, neither the optimization of the OPW nor the increase of the cyclability was an objective of the present work. In fact, the purpose of this study is on the methodology used for the determination of the faradaic fraction and its impact on the OPW, not to enlarge the OPW for high-voltage supercapacitors. Again it should be emphasised that other metrics, such as energy efficiency, can be used for quantifying the hysteresis between charge and discharge processes, especially for large scaled energy storage systems such as lithium-ion batteries in electric vehicles or for high power storage systems for which high current rates give large voltage hysteresis [22]. For these reasons, it would be interesting to explore other systems with large voltage windows such as organic electrolytes or ionic liquids and to discuss the problem of the energy and voltage efficiencies in a similar formalism as the one applied to CE. These issues will be addressed in a subsequent publication.

4. Conclusion

As demonstrated above, the stability window determined by the R_{CE} -method depends to the initial potential from which the stability of the electrode/electrolyte interface is evaluated. The origin of this voltage effect lies in the non-linear variation of the faradaic current with the potential. As the initial potential changes, shift in the potential limits at both ends of the stability window are required to adjust the faradaic charge for keeping constant the preset faradaic fraction. Because of the exponential increase of the faradaic current with the potential, the amplified change, in absolute value, of the potential limit on the side of the nearest (relative to E_i) decomposition process produced by a change in the initial potential, is not compensated by the lesser change, in absolute value, of the potential limit on the side of the more distant (relative to E_i) decomposition process. Importantly, for a “pivotal” initial potential, the potential limits shift in the same extent to adjust the cathodic and anodic faradaic charges for keeping constant the preset R_{CE} value, leading to a realistic estimate of the OPW. As an attempt to make the R_{CE} -voltage method independent from the initial potential, a voltage-correction leads to a novel formula for the faradaic fraction S_{CE} now envisioned as the sensitivity of the electrode towards the decomposition process and defined as the ratio between the irreversible faradaic charge and the electrode capacitance. Here, the voltage-corrected faradaic fraction S_{CE} , coupled with the concept of “pivotal” initial potential ensured a more realistic determination of the OPW.

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