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Impact of the scan rate on the stability window of an electrical double-layer capacitor

Charles Cougnon

Abstract: Because of the intermittent nature of renewable energy sources, such as solar or wind power, energy storage is becoming strategic for securing the energy transition. In this context, energy storage technologies must become robust, secure and efficient, so that they become attractive and competitive solutions. For these reasons, the stability of storage systems is a matter which must concern us. In the supercapacitor community, methodologies used to evaluate the stability window are widely discussed and debated, but the way it is impacted by the charge regime is rarely investigated. This question is even more important as the stability window is only valid for the current rate at which it was determined. In this study, the impact of the charge regime on the stability window was investigated both qualitatively and quantitatively by cyclic voltammetry. Results clearly demonstrate that the stability window reduces as the charge regime decreases. This is because degradation processes can be viewed as the result of irreversible electrochemical processes. In severe cases, this reduction in stability is such that it can be fatal for the supercapacitor if such a change in the charge regime has not been anticipated.

Keywords: Energy storage; supercapacitors; stability window; charge regime

1. Introduction

The supercapacitor community has not aligned on a standardized method to assess the stability window envisioned as the potential domain in which the electrode-electrolyte interface is inert towards oxidation and reduction [1-3]. The main difficulty is to deconvolute the observed current into its capacitive and faradaic components, because in the immediate vicinity of the threshold potential from which the degradation of the electrified interface proceeds, the capacitive current and the observed current cannot be distinguished as the faradaic current is low. This problem is exacerbated by the use of supercapacitor electrodes due to the very high specific capacitance values obtained and the possible presence of a pseudocapacitance behavior commonly attributed to surface redox functionalities in native porous carbons or emerging during cycling [4], bearing in mind also that both the textural characteristics and surface chemistry of carbons can have an impact on stability [5,6]. Practically, the evaluation of the stability is based on cyclic voltammetric or galvanostatic potential window opening experiments from the open circuit potential to a progressively increased potential limit [7-9]. The determination of the extra charge consumed during the charge period compared to the discharge period is indicative of the irreversibility of the complete charge-discharge cycle and is commonly attributed to the faradaic charge loss in the electrochemical degradation reactions. Noted that in these experiments, cyclic voltammetry is preferred for distinguishing between faradaic and capacitive currents, while galvanostatic experiments are recommended for more realistic charge-discharge conditions [10].

Roughly speaking, for storage applications there are two completely different approaches to delimit the stability window. The first one, and most commonly used, is to take the coulombic efficiency CE (or equivalently the faradaic fraction R_{CE}) as cut-off criterion for setting the degradation tolerance level at the interfaces of positive and negative electrodes [11,12]. Noted that the cut-off CE method is derived from the ancient cut-off current (or current density) method and was established to consider the very large capacitive current of porous carbon-based supercapacitors electrodes. This is equivalent to make the comparison between the electrical charge stored during the charge period and that delivered during the discharge period. This method, also called the capacity-based electrochemical method, has been subject of corrections to consider the small irreversibility of the purely capacitive process [13], mainly caused by the electronic leakage current, and to rectify the potential dependence of the capacitive charge [14].

The second approach, known as the "linear fits method", consists to envision the potential limit with that coinciding with the interception of two separate linear fits of the current–potential curve in potential domains where capacitive current and electrolyte migration dominate the cyclic voltammetry

response [15]. This approach is an attempt to subtract the impact of the interfacial kinetics on the stability window to make possible the determination of the "true" threshold potential of the electrochemical decomposition. Such a method is based upon the assumption that in common liquid electrolytes with fast diffusion mass transportation, the electrolyte migration becomes rapidly the dominant mass transport when the threshold potential is exceeded, so that a linear increase of the current-potential curve is expected. In these liquid electrolytes, linear extrapolations of the current-potential curve on both sides of the potential limit in the cyclic voltammogram allow to intercept the potential axis at a value close to the threshold potential. Interestingly, the minor effect of the scan rate on the negative potential limit found in propylene carbonate + 0.3 M NBu_4I with a glassy carbon electrode by the linear fits method demonstrates the validity of this approach for electrolytes enabling fast ion diffusion [16]. But reservations can be made concerning solid electrolytes and polymer electrolytes having low diffusion coefficients [13], and by extension, in pure ionic liquids or in general, in all media where a rapid ion motion is not guaranteed.

Regarding the two methods presented above, the arbitrariness of the first one has been widely criticized as the cut-off criterion is chosen by the experimenter, and the second one must be used with caution because it is only valid in electrolytes ensuring a fast ion diffusion. At this stage of the discussion it is important to note that even the linear fits method remains arbitrary in nature, because instructions on how to perform the linear fits were chosen by the experimenter [16], but it is indicative on the way by which the interfacial kinetics impacts the stability of the electrochemical interface. On this important point, the pioneering study of Nicholson and Shain on the linear sweep cyclic voltammetry technique, and especially the section about the irreversible electrochemical processes, is extremely informative [17]. Authors demonstrated that for a diffusional irreversible electrochemical process, the faradaic charge consumed by exceeding the threshold potential increases when the scan rate decreases. Based on this, it appears that the stability window is only valid for the charge regime at which it was determined, so that the stability of an electrified interface should preferably be explore at different rates to have a more realistic view of stability [18-20]. This, and the fact that increasing the charge rate makes the ohmic drop increase, we can conclude that an optimal charge rate exists which minimizes the sum of thermal and chemical energy losses for the charge period [21]. Unfortunately, the effect of the charge rate on the stability window is rarely examined, and even more rarely quantified. In this work, the impact of the scan rate in window opening cyclic voltammetric experiments was explored in detail to quantify how the stability window becomes narrower as the scan rate is decreasing. This study is illustrated by results obtained with a microporous carbon-based supercapacitor tested in a three-electrode cell configuration in aqueous acidic electrolyte, but importantly, the main conclusions can interest other storage communities, as a loss in stability is often due to irreversible electrochemical reactions.

2. Materials and methods

2.1. Electrode fabrication, cell assembling and electrochemical measurements

Working and counter electrodes were prepared mixing YP80F activated carbon (from Kuraray), poly(vinylidene fluoride) and carbon black (superior graphite) using a previously published method [14]. Supercapacitor cells were assembled from two carbon-based electrodes of the same mass separated by a glassfiber impregnated with 1 M H_2SO_4. Supercapacitors were tested in a three-electrode configuration using a silver wire as quasi reference electrode. Electrochemical experiments were performed with a VMP-Biologic potentiostat and were monitored by the ECLab software. The stability of supercapacitors was examined by cyclic voltammetry based on potential window opening experiments using a methodology previously described [14]. In the present study, the window opening cyclic voltammetry experiments were performed at different scan rates (2 mV s^{-1} , 5 mV s^{-1} , 10 mV s^{-1}, 15 mV s^{-1} , 20 mV s^{-1} and 30 mV s^{-1}) from the open-circuit potential to a gradually increased final negative or positive potential. Noted that fresh carbon electrodes were used for each scan rate, and also to explore the stability both in the positive and negative potential direction, separately.

2.2. Calculation methods for CE, VE, EE, R_{CE} and S_{CE}

The current metrics for exploring the stability of electrochemical charge storage systems are the coulombic efficiency (CE), the voltage efficiency (VE) and the energy efficiency (EE). By definition, CE is a measure of the reversibility of the charge-discharge process and is expressed as the ratio of the

delivered electrical charge Q_{dis} to the charge stored Q_{ch}. VE is a measure of the deviation of the average discharge potential $\overline{V_{dis}}$ from the average charge potential $\overline{V_{ch}}$, and EE is defined as the ratio of the discharge energy ξ_{dis} to the charge energy ξ_{ch} [22,23]. Importantly, CE, VE and EE were obtained by integrating the cyclic voltammograms (CVs) as recommended when the charge-discharge curves deviate from a purely capacitive behavior [24]. The equations used to obtain CE, VE and EE are presented below:

$$\mathrm{CE} = \frac{Q_{dis}}{Q_{ch}};\ \mathrm{VE} = \frac{\overline{V_{dis}}}{\overline{V_{ch}}} = \frac{\frac{1}{Q_{dis}}\int_{q\leq 0} V dq}{\frac{1}{Q_{ch}}\int_{q\geq 0} V dq};\ \mathrm{EE} = \frac{\xi_{dis}}{\xi_{ch}} = \frac{\int_{q\leq 0} V dq}{\int_{q\geq 0} V dq} \tag{1}$$

In a pioneering work [11], K. Xu and R. Jow propose to handle CE as a fraction defined by the ratio of the charge loss during the charge period, ΔQ, to the delivered charge Q_{dis}:

$$\mathrm{R_{CE}} = \frac{Q_{\mathrm{ch}} - Q_{\mathrm{dis}}}{Q_{\mathrm{dis}}} = \frac{\Delta Q}{Q_{\mathrm{dis}}} = \frac{(1-\mathrm{CE})}{\mathrm{CE}} \tag{2}$$

Originally named R, we have recently renamed this ratio $\mathrm{R_{CE}}$ to remind that this fraction is related to the coulombic efficiency [25]. In spite of its complex nature, ΔQ is most often identified with the irreversible faradaic charge consumed to degrade the electrode-electrolyte interface, so that this ratio can be regarded as a "faradaic" fraction. $\mathrm{R_{CE}}$ has recently undergone adjustments to correct the voltage dependence of the capacitive charge Q_{dis} [14]. It was proposed a "faradaic-charge"/capacitance fraction $\mathrm{S_{CE}}$ as voltage-corrected "faradaic" fraction:

$$\mathrm{S_{CE}} = \frac{\Delta Q}{C} = \mathrm{R_{CE}} \times V_m, with\ V_m = \left(E_f - E_i - iR\right) \tag{3}$$

Where C is the electrode capacitance, R is the electrical resistance, i corresponds to the measured current and V_m represents the measured voltage, which is equal to the voltage excursion between final and initial potentials (E_f and E_i) minus the ohmic drop iR.

3. Results and discussion

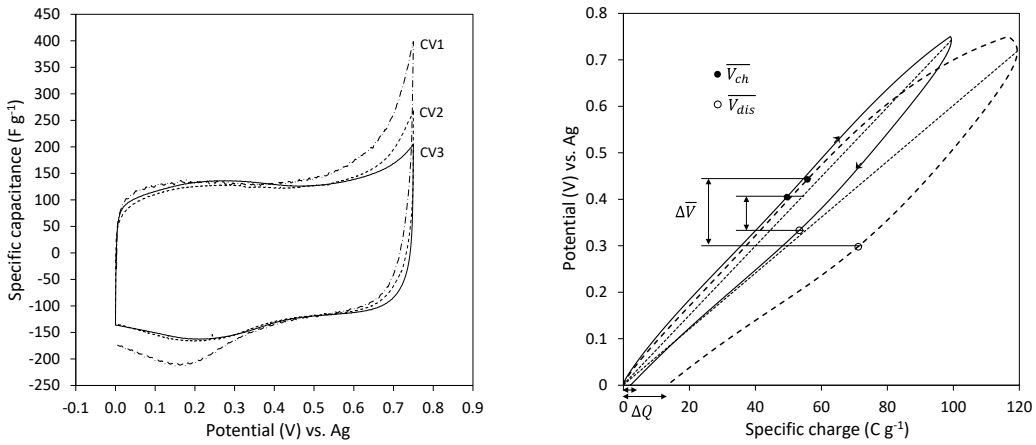
Exploring the stability of electrified interfaces in electrolytes remains a scientific and technological challenge, because of its direct impact on the attractiveness and competitiveness of storage solutions [26]. The difficulty is to find a realistic stability criterion, as the stability depends on many parameters such as voltage, charge rate, temperature, not to mention the electrolyte, electrode materials, as well as the way in which the cell was assembled and tested. It is so broad a problem that it can appears intractable. To give the best chance to succeed, we have recently suggested to change our perspective on stability to replace the kinetics of the electrodegradation reaction at the center of the debate on stability [25]. In this approach, the problem could become part of the solution, because this would no longer the experimenter who decides by choosing arbitrarily the cutoff criterion to use for delimit the stability domain, but it could be the interfacial dynamics that alerts the experimenter when the degradation is becoming fatal for the interface. It is important to make clear here that “degradation” refers to all phenomena that make the charge stored larger than the charge delivered, so that in this perspective, the direct result of the degradation is that the charge-discharge process becomes unbalanced, disregarding chemical and structural changes in electrolyte and electrode materials. For this reason, with the current metrics (CE, VE and EE), the stability refers to the reversibility of the charge-discharge cycle and gives no indication about the fatigue of the components of the energy storage system, while it is clear that there is a link between stability and ageing [27,28]. It results to the above that a decrease in stability may not be associated to apparent physical or chemical degradation of the electrode material, so that in the present study, the stability of the electrified interface, envisioned as a charge hysteresis, is disconnected from the manner in which the interface is affected by this loss of reversibility.

One way to illustrate how the heterogeneous kinetics impacts the stability window is to investigate the stability on different time scales by using dynamic electrochemical techniques such as cyclic voltammetry at different scan rates. This later technique is preferred to other such as galvanostatic methods because the effect of the kinetics of electrodegradation reactions, envisioned as irreversible

electrochemical processes, on the current-potential curves obtained is fully understand and was equated for a long time [17]. In the following two sections, the impact of the interfacial dynamics on the stability of an electrified interface will be examined by charging at different scan rates a carbon-based supercapacitor electrode up to a fixed full charge potential that exceeds slightly the threshold potential of degradation, so that an irreversible charge loss exists. We will see how this charge loss evolves with the scan rate, and how it affects the coulombic efficiency and the energy efficiency. Importantly, it should be emphasized that the scan rate effect reported here is an opportunity to highlight the entanglement between interfacial dynamics and stability, and the ensuing difficulties in determining a realistic stability domain instead of the determination of the largest operational potential domain.

3.1. Qualitative examination of the effect of the scan rate on CE, VE and EE

Figure 1a shows superimposed CVs recorded at different scan rates from 0 V, where a capacitive behavior dominates, to 0.75 V, where the electrodegradation is featured by a positive current leap corresponding to the very beginning of an irreversible anodic peak. Noted that, in Figure 1a, the current was divided by the scan rate to highlight differences between CVs. As it is well known since the pioneering work of Nicholson and Shain [17], a decrease in the scan rate makes the irreversible anodic peak move towards less positive potentials. Noted that for one-electron transfer processes the potential limit shifts by $(RT/(2\alpha F))\ln 10$ per decade of scan rate. In this equation, α is the transfer coefficient and R, T and F have their usual meaning. At 298 K and for α equal to 0.5, it corresponds to a shift of about 59 mV, but low α values can be obtained when reactions occur within a porous electrode structure [29], so that porous carbons can become very sensitive to the scan rate. Based on the Figure 1a, we can observe that when the scan rate is decreasing from 20 mV s^{-1} (curve 3) to 2 mV s^{-1} (curve 1), the irreversible system ascribed to the anodic degradation of the interface starts earlier so that a huge increase in the faradaic current appears at the end of the forward scan. By implication, the effect of the ohmic drop on the CV becomes more visible at the beginning of the backward scan. As a result, the charge loss in the degradation at extreme potentials makes the average charge potential increase, and the missing charge due to the ohmic drop makes the average discharge potential decrease. A graphical display of how the average potentials are evolving with the scan rate is given in the Figure 1b, which shows a potential-charge representation of the CV1 (in dotted line) and CV3 (in solid line) presented in the Figure 1a. Noted that, in our conditions, the decrease of the average discharge potential at low scan rate is aggravated by the occurrence of a reduction wave during the backward scan at around 0.15 V that can be attributed to the redox behavior of the decomposition products.



(**a**) (**b**)

Figure 1. Cyclic voltammograms (CVs) at different scan rates: (a) CVs recorded in 1M H_2SO_4 with a YP80F carbon-based supercapacitor electrode at 2 mV s^{-1} (CV1), 10 mV s^{-1} (CV2) and 20 mV s^{-1} (CV3). (b) Potential-charge representation of the CVs recorded at 20 mV s^{-1} (solid line) and 2 mV s^{-1} (dotted line) with mention of their corresponding average charge potentials (solid symbols) and average discharge potentials (open symbols). The dotted straight lines separate the positive and negative parts of the CVs.

It results to the above that the average charge and discharge potentials move away from each other as the scan rate decreases, causing an increase of the voltage loss $\Delta\overline{V}$. Interestingly, the energy loss $\Delta\xi$ can be expressed from the average charge potential and the average discharge potential, so that we can conclude that a growing distance between them makes the energy cost of the degradation increase:

$$\Delta\xi = \xi_{ch} - \xi_{dis} = Q_{ch} \times \overline{V_{ch}} - Q_{dis} \times \overline{V_{dis}} \tag{4}$$

Equation (5), directly obtained from the equation (4), gives an indication of the energy cost of the storage of Q_{dis} in the double layer:

$$\frac{\Delta\xi}{Q_{dis}} = \left(\frac{\overline{\mathrm{V}_{ch}}}{\mathrm{CE}} - \overline{\mathrm{V}_{dis}}\right) \tag{5}$$

Noted that when no degradation occurs, the voltage loss corresponds just to the ohmic drop (i.e. $\Delta\xi/Q_{dis}\ (V) = iR$ when $CE = 1$).

Figure 2 presents the evolution of the ratio above for scan rates between 30 mV s^{-1} and 2 mV s^{-1}. It is clear from the results that the reversibility of the charge-discharge cycle suddenly deteriorates when the scan rate becomes less than 15 mV s^{-1}. This scan rate can be identified with a critical charge regime below which the charge loss becomes large enough so that its impact on $\Delta\overline{V}$ cannot be ignored, producing an accelerated increase of the energy loss during the charge period. In one respect, it resembles a resonance phenomenon where two quantities lost (ΔQ and $\Delta\overline{V}$) aggravate each other. Noted that $\overline{V_{ch}}/\mathrm{CE}$ in the equation (5) is a measure of this cooperative effect. The direct consequence is that the energy cost of the degradation increases in an accelerated manner for scan rate lower than 15 mV s^{-1}. By contrast, in the high scan rate domain, $\Delta\xi/Q_{dis}$ reaches a plateau because the charge loss becomes lower so that CE tends to unity, implying that $\Delta\xi/Q_{dis}$ can be approximated by the ohmic drop. Remarkably, results demonstrate that at 2 mV s^{-1}, the impact of the kinetics on the charge loss contributes more to the energy loss than the ohmic drop.

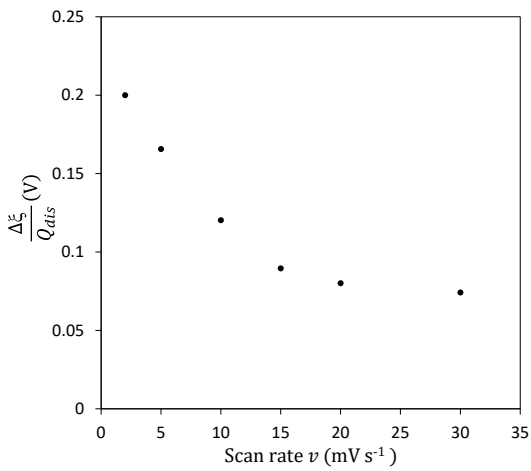


Figure 2. Scan rate dependence of $\Delta\xi/Q_{dis}$.

The impact of the charge regime on both charge and energy losses discussed above can be regarded as a consequence of the interdependence between CE, VE and EE [30]:

$$\mathrm{EE} = \mathrm{VE} \times \mathrm{CE} \tag{6}$$

In that perspective, Figure 3 shows that, keeping constant the potential limit at 0.75 V, the charge consumed during the charge period rapidly deviated from the capacitive charge as the scan rate decreases, causing a progressive fall in CE from 0.99 at 30 mV s^{-1} to 0.89 at 2 mV s^{-1}. At the same time, the energy efficiency decreases from 0.82 at 30 mV s^{-1} to 0.6 at 2 mV s^{-1}. Especially, EE decreases faster at scan rates lower than 15 mV s^{-1}, because in these conditions, the charge loss has a non-negligible and growing impact on the voltage loss that control the energy cost of the degradation, as clearly demonstrated in Figure 2.

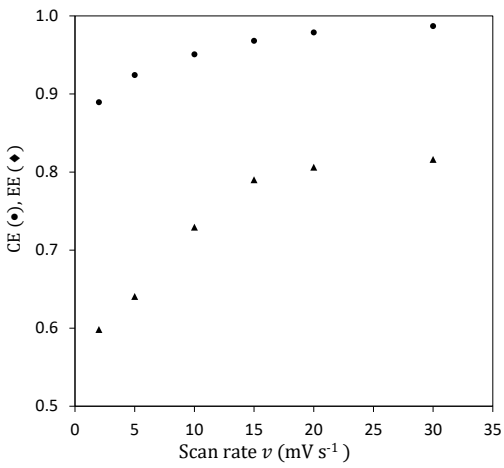


Figure 3. Scan rate dependence of the coulombic and energy efficiencies deduced to CVs recorded from 0 V to 0.75 V.

At this stage it becomes evident that potential limits (most often envisioned as potentials corresponding to a preset value of CE) are closely related to the interfacial dynamics of the degradation process. The corollary is that the electrodegradation processes occurring at the positive and negative electrodes can affect differently the evolution of CE with the scan rate, due to different kinetic properties for the anodic and cathodic degradation processes. This can become a real problem for the determination of the stability window if kinetic parameters are significantly different, so that positive and negative electrodes feel a different scan rate effect towards degradation.

3.2. Quantitative examination of the scan rate effect on the stability window of a carbon-based supercapacitor working in aqueous acidic electrolyte

Actually, in supercapacitor application, CE (or equivalently the faradaic-charge/capacitive-charge fraction R_{CE}) is most often used as cut-off criterion to assess the stability window. In practice, the stability window is bordered by two identical values of CE (or R_{CE}) at positive and negative electrodes, corresponding to equal charge losses in the anodic and cathodic degradation. But as discussed above, such a stability window is valid only for the scan rate at which it is determined. Strictly speaking, the stability window should be determined at different scan rates to identify the most appropriate charge regime. As an example, Figure 4 presents the superimposition of stability-potential curves deduced to window opening cyclic voltammetry experiments performed at different scan rates in the negative and positive potential directions from the open circuit potential. Noted that in the present study, S_{CE} is preferred to the faradaic fraction R_{CE} for estimating the coulombic hysteresis over a complete CV, because it allows to correct the voltage dependence of the capacitive charge that is source of errors in the calculation of R_{CE}, as indicated in the *Materials and methods* section (for further details see Ref. 14). In any case, as S_{CE} represents the faradaic-charge/capacitance fraction, considerations on R_{CE} and S_{CE} point to the same conclusion.

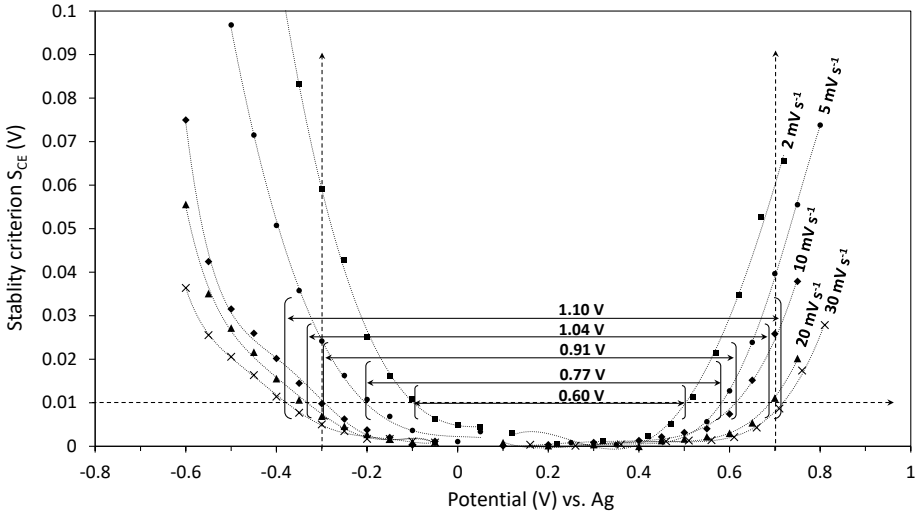
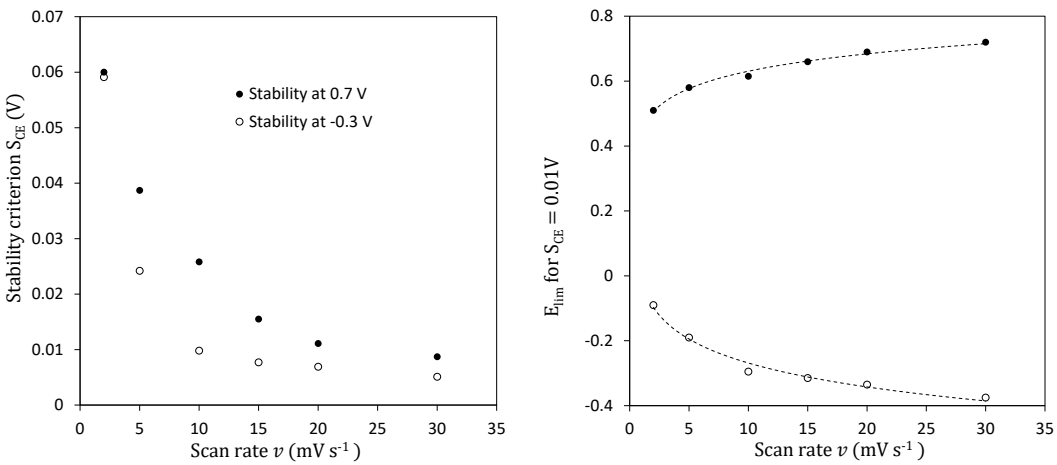


Figure 4. Effect of the scan rate on the evolution of the stability factor S_{CE} with the electrode potential. The horizontal dotted line intercepts the stability curves at anodic and cathodic potential limits for a preset value of S_{CE} equal to 0.01 (the corresponding stability windows are showed in square brackets), and the two vertical dotted lines allow to visualize the scan rate dependence of S_{CE} at -0.3 V and 0.7 V.

The results demonstrated that the stability window strongly decreases as the scan rate becomes lower, going from 1.1 V at 30 mV s^{-1} to 0.6 V at 2 mV s^{-1}. This is because the electrochemical degradation processes at both ends of the stability window are very sensitive to the scan rate, undergoing an exaltation at lower scan rate, so that a more and more important irreversible charge ΔQ is consumed at these extreme positive and negative potentials by decreasing the scan rate. At fixed potential limits of -0.3 V and 0.7 V, corresponding roughly to the two ends of the stability window at 30 mV s^{-1} for a preset S_{CE} value of 0.01 V, a decrease of the scan rate thus causes an exponential increase of S_{CE}, as illustrated in the Figure 5a. Noted that in our conditions, at 0.7 V a significant increase in S_{CE} is felt when the scan rate is below 20 mV s^{-1}, while at -0.3 V an increase in S_{CE} is felt when the scan rate is below 10 mV s^{-1}, corresponding to different kinetic properties for the anodic and cathodic degradation processes. Reciprocally, the preset S_{CE} value of 0.01 V, corresponding roughly to potential limits equal to - 0.3 V and 0.7 V at 30 mV s^{-1}, is attributed to declining potential limits in absolute terms when scan rate decreased (Figure 5b).



(**a**) (**b**)

Figure 5. (a) Effect of the scan rate on the stability criterion S_{CE} at -0.3 V and 0.7 V. (b) Scan rate dependence of the anodic and cathodic potential limits corresponding to a preset value of S_{CE} equal to 0.01 in absolute term.

Interestingly, as equal S_{CE} values correspond to charges losses proportionated to the electrode capacitances, potential limits at which they correspond are presumed to coincide with equally degraded electrodes, since the capacitance reflects the electrochemically active surface area. In other word, using S_{CE} as cut-off value is the same as choosing equal surface charge loss density at both electrodes, so that a different impact of the scan rate on the potential limits reflects different kinetic properties for the anodic and cathodic degradation. Over one decade of scan rate from 20 mV s^{-1} to 2 mV s^{-1}, the anodic potential limit decreased by 0.18 V and the cathodic potential limit shifts towards the negative potential by 0.245 V, corresponding to transfer coefficients equal to 0.16 and 0.12, respectively, for one-electron transfer processes at 298 K. Noted that these values were deduced to equations therorized by Nicholson and Shain for purely diffusional electrochemical processes [10], which are only valid in our case if electrolyte migration can be neglected and just at the beginning of the electrodegradation where there is no significant depletion of ions inside the porous carbon. Interestingly, authors have recently demonstrated that comparable α values can be obtained when reactions occur within a microporous electrode [29]. Figure 6 shows that it corresponds to a decrease of the stability window of around 0.4 V when the scan rate decreases from 20 mV s^{-1} to 2 mV s^{-1}, which can be fatal for the supercapacitor if such a change in the charge regime has not been anticipated.

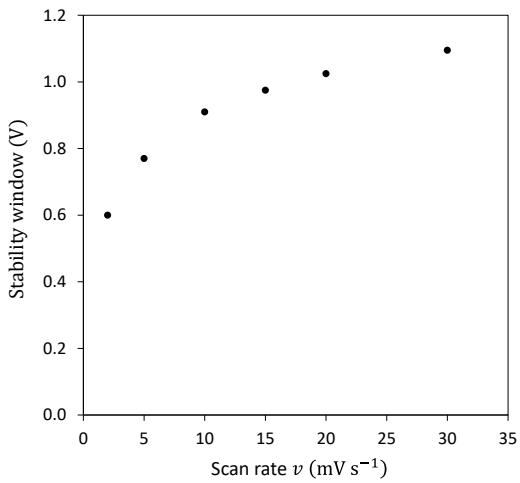


Figure 6. Effect of the scan rate on the stability window delimited at both ends by a preset value of S_{CE} equal to 0.01 in absolute term.

As previously discussed, the heightened sensitivity of both electrodes towards electrodegradation processes when the scan rate becomes lower than 15 mV s^{-1} makes the stability window decrease faster below this scan rate. This critical scan rate value makes the transition from a "high" scan rate domain where the charge loss is still too low to have a significant impact on the energy loss, to a "low" scan rate domain where the charge loss becomes large enough to have an aggravated impact on the energy loss. For scan rates large than the critical one, we can approximate that the charge loss is very mildly affected by the scan rate, so that CE varies only slightly. It results that by using $S_{CE} = 0.01\ V$ as cut-off criterion, the stability window should preferably be determined at 15 mV s^{-1} and used at a greater or equal scan rate.

4. Conclusions

The present study explores the impact of the charge regime on the stability window of the electrode-electrolyte interface of a carbon-based supercapacitor electrode working in aqueous acidic electrolyte. The stability window is determined by opening cyclic voltammetry experiments, so that the charge regime corresponds to the scan rate. The justification for this study is the determination of the charge regime range for which a stability window is secured, recognizing that a stability window is only valid for specific charge-discharge conditions. Results showed that beyond threshold potentials where electrochemical degradation reactions occurred, a decrease in scan rate causes an increase of the electrical charge loss consumed during the charge period. Such an effect is becoming very significant

below a critical scan rate, making the stability window rapidly declining. Such a critical charge regime is closely related to the heterogeneous kinetics of the electrochemical degradation reaction and corresponds to a charge rate below which the charge loss has an aggravated impact on the average charge potential, thereby increasing the energy cost of the degradation. Conversely, at scan rates higher than such a critical scan rate, the stability window becomes less sensitive to the charge regime, so that the stability window should preferably be determined at the critical scan rate and used at equal or greater scan rates in order to minimize the impact of the charge regime on the stability.

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Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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