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Determining Realistic Electrochemical Stability Windows of Electrolytes for Electrical Double-Layer Capacitors

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Electrical double-layer capacitors are a key building block for energy storage applications, including renewable energies, wherever high power is needed. Most research on electrolytes in this field focuses on improving their electrochemical stability. This improves the energy density as it scales with the square of the maximum operative voltage. However, the decisive criteria to assess the electrochemical stability window of electrolytes are unclear. Consequently, new electrolyte candidates are often presented with unrealistic high stability windows and their

performance is difficult to compare. In this Minireview, an overview of electrochemical stability window determination methods is presented. It is argued that constant voltage lifetime tests are needed to confirm the electrochemical stability window determined by any other method. Also, the importance of using realistic working electrodes, reference electrodes, and cycling protocols are highlighted. Finally, an industrial perspective on what is necessary to yield results relevant to applications is given.

1. Introduction

The high power of electrical double-layer capacitors (EDLCs) makes them important for many emerging applications in the vital effort to decarbonize the modern economy. While the total addressable market is expected to grow, their low energy density and related high cost per kWh are seen as key limits to be overcome.^[1] Increasing the maximum operative voltage allows more charge to be stored per unit mass or volume of activated carbon (AC) and this additional charge is also stored at higher voltage, i.e., more energy per unit charge. As a result, the total energy of an EDLC is proportional to the square of the voltage. Consequently, research efforts are focused on developing electrolytes that can withstand large positive and negative potentials, i.e., have a large electrochemical stability window (ESW). Here we take the ESW to be the absolute difference in Volt between the positive and negative stability potential limits (SPLs) in Volt measured vs. the potential of a reference electrode.

The potential at which a specific electrolyte is reduced or oxidized is in principle a thermodynamic property that is

independent of the electrode material. However, these values are not necessarily the most relevant for applications since, in practice, kinetics also play an important role. As reaction kinetics under many circumstances are slow, slightly exceeding the thermodynamic potential limit typically causes only negligible degradation currents to flow. What matters in an EDLC device is not the absence of any reactions, but their extent, be it due to decomposition of impurities, electrode materials or the electrolyte itself. How much can be tolerated is intrinsically a judgement call about whether the resulting life time and performance of the device will suffice for the application in the real world.

This means that practical SPLs are not hard thermodynamic quantities but soft kinetic limits, located beyond the thermodynamic stability window. Unfortunately, this additional leeway can lead to improper overestimation of SPLs due to unrealistic testing conditions and too lenient cutoff criteria. In addition, real active materials are vastly more complex than model surfaces often used in ESW determination (glassy carbon (GC), platinum, etc.). Thus, SPLs can only be valuable information if both the conditions of the experiment as well as the interpretation criteria are geared towards real applications. But even if criteria and conditions are well selected, differences in criteria can make comparisons difficult.

Therefore, in this minireview, an overview of SPL determination methods is given together with recommended experimental setups, including reference electrodes that can provide good initial SPL estimates. Furthermore, long term stability testing protocols are reviewed, which should always be used to verify the SPLs, highlighting the importance of proper mass balancing and voltage hold methods. It is expected that the adoption of these methods will enable better comparisons between results from different groups as well as higher relevance to industry.

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2. Electrochemical Stability Window Determination

2.1. Non-Porous Working Electrode Materials

Before discussing methods to determine SPLs, it is important to highlight the effect of the working electrode (WE) material. The standard approach to test the SPL of any electrolyte often is to employ linear sweep voltammetry (LSV) in three electrode cells employing an inert and planar WE, e.g., a Pt disk. The potential limit is then determined by setting an arbitrary current density cutoff. However, this setup neither provides realistic conditions nor is the determined limit in a useful relation to the observed kinetics.^[2–7] In fact, it has been shown in many studies that the WE material has a significant impact on the observed decomposition kinetics and, therefore, on the SPLs determined from LSV. For example, Borgel et al. found that ionic liquids (ILs) exhibited different onset potentials for decomposition on GC than on Pt. No clear trend in terms of higher or lower SPLs for any of the two materials was observed.^[8] Coustan et al. also measured hundreds of mV difference between the SPLs of water-in-salt electrolytes (WiSE) on Au, Pt and GC.^[9] These differences are attributed to catalytic effects of the WE material

that are highly dependent on the electrolyte studied. This means that SPLs determined on different WEs are not comparable. Furthermore, as none of these materials are typically found in EDLC devices, this information is not applicable in practice.

Differently, the reaction kinetics on materials that are in fact used in cell construction are highly relevant for applications. This is particularly important for aluminum current collectors. Aluminum is not an inert electrode material like GC or Pt, as it may undergo reactions itself, which might be seen as an additional complication. However, it is important to study these reactions if they occur, because a practical SPL has to take into account all reactions of all materials present in an EDLC. Although steel is too dense for industrial applications as current collector^[1] these points apply to it as well. Most lab scale cells contain steel parts like current collector pins, which can catalyze or undergo reactions. So the reactivity of aluminum or steel might be mistakenly attributed to interactions between the electrolyte and another WE material.

For many materials, the ESW of electrolytes in contact with the above-mentioned non-porous electrodes is larger than that of high surface area carbon (see Section 2.2.). In these cases, it is adequate to verify that the current collector itself does not interfere with the SPL determination on porous carbon with



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LSV. One should find a current onset at rather high and low potentials, respectively. However, it might be advisable to do repeated sweeps, i.e., use cyclic voltammetry (CV), as reactions in the first few cycles, like the oxidation of aluminum, can be transient in nature.^[10,11] If current collector stability is a concern, more precise measurements like chronoamperometry are recommended.^[12]

2.2. Porous Working Electrode Materials

Most important for the electrolyte ESW is the reactivity of the active material, i.e., the porous carbon. However, the high surface area of the carbon results in a non-faradic current hiding the onset of the faradic current associated with decomposition. Mousavi et al. claim that the SPLs determined on GC are similar to that of porous carbons,^[13] but they found up to 250 mV more negative cathodic limits on GC compared to porous carbons using their own LSV based SPL determination method (see supporting material).^[7] In addition, small current densities on low surface area WEs, which might be still acceptable in terms of ESW, would be greatly magnified on high surface area electrodes.^[14] Finally, it has been shown that functional groups present in ACs have a large influence on the long term stability of EDLCs, making it absolutely necessary to determine the SPLs on the specific AC with which the electrolyte is intended to be used.^[15–18] Consequently, any SPL determination method has to work with those porous materials and LSV based methods do not (see supporting material).

The inadequacy of the standard LSV approach on non-porous electrodes has been recognized by many authors, some of whom have suggested methods to standardize SPL determination and yield more informative SPLs.^[6,7,14,19–21] Some of the most commonly used ones will be reviewed in the next section.

2.3. Voltage Sweep-Based SPL Determination Methods

A very simple SPL determination method often employed is to simply set a coulombic efficiency ϵ (CE) cutoff criterion ranging from 99% to 97%.^[22,23] CV scans in three electrode cells are done with progressively more extreme vertex potentials. The SPL can be determined from the vertex potential where the CE of the respective cycle drops below the specified value. While straightforward, this method yields different results depending on the scan rate. In a fast scan, only little additional charge flows due to irreversible faradic reactions as the time spent near the vertex potential is relatively short. However, the charge related to non-faradic processes is independent of scan rate and is therefore approximately constant. In fast scans, this latter is proportionally much larger, resulting in high CEs.

Xu et al.^[14] developed a stability criterion based on analyzing the overall charge flowing in a CV cycle. They made the simplifying assumption that the overall charge in the charging sweep is due to non-faradic as well as faradic processes, while the discharging sweep only results from non-faradic processes. It was defined as

$$S_+ = Q_+/Q_- - 1 < 0.1; S_- = Q_-/Q_+ - 1 < 0.1$$

Where Q_{+-} is the charge passed due to positive and negative currents in the CV sweep, respectively.

This criterion would correspond to the ratio of faradic to non-faradic charge passed; under the assumption stated above. They suggested that it is independent of the electrode area and scan rate. The latter is not true, however, as the criterion can be simply converted to a CE cutoff criterion:

$$\epsilon_+ = Q_-/Q_+ = (S_+ + 1)^{-1}; \epsilon_- = Q_+/Q_- = (S_- + 1)^{-1}$$

Therefore, the same caveat as with CE-based criteria applies. Converting the limit of $S < 0.1$ to a CE criterion yields 0.91% CE, much lower than typically accepted for EDLCs. In fact, Moosbauer et al.^[24] pointed out this problem, suggesting a limit of $S < 0.02$ (98% CE) and Weingarth et al.^[19] presented a refined method based on the stability criterion of Xu et al. to address these issues. These authors argued that, if the kinetics of the decomposition reaction follow the Butler-Volmer equation, the faradic current increases exponentially and this can be used to detect the onset of decomposition. As they also kept the simplification made by Xu et al. (i.e., assuming faradic processes only occurring during charge), the extra charge from irreversible faradic processes increases S . While this is also true for constant background currents or linearly increasing leakage currents, they argued that $d^2S/dV^2 = 0$ for background and leakage currents but $d^2S/dV^2 \neq 0$ for exponentially increasing currents. Therefore, they set a new criterion of $d^2S/dV^2 < 0.05$ to mark the start of unacceptably high decomposition (Figure 1). Electrodes subjected to voltage hold life time tests at the SPLs determined in this way showed 80% capacitance retention after 500 h. A number of other authors have also adopted this method and applied it in their works.^[25–27]

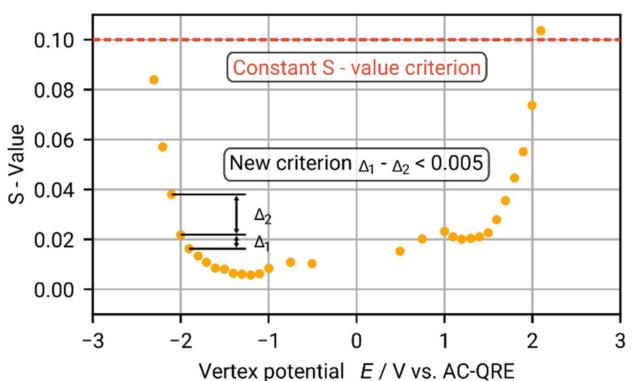


Figure 1. S-value criterion. CVs on AC in [EMIM][BF₄] with increasing vertex potential. A fixed S-value as Xu et al.^[14] suggested gives higher stability values than the criterion of Weingarth. The SPL is defined as $d^2S/dV^2 < 0.05$, therefore $\Delta_2 - \Delta_1 < 0.005$ for 100 mV vertex potential steps. Adapted from Ref. [19].

2.4. Leakage Current-Based SPL Determination Methods

All of the methods presented so far are based on voltage sweeps, but other approaches are also possible. In open circuit condition, charged EDLCs exhibit a voltage drop over time due to internal leakage currents, i.e., self-discharge. The resulting potential – time curve can provide information about the underlying mechanism. If the discharge is mainly due to low concentration impurities that undergo faradic reactions, these reactions are limited by the rate of diffusion of impurities. Thus, the voltage drop is proportional to $t^{1/2}$, i.e., the potential – time curve exhibits a linear shape on a E vs. $t^{1/2}$ plot. If the faradic self-discharge reaction involves species that are present in high concentration, such as for the decomposition of the electrolyte components, the reaction is activation controlled. In this case the voltage drop is proportional to $\ln(t)$ and consequently the shape of the potential – time curve is linear in a semi-log plot, after a plateau region.^[28]

Laheäär et al.^[20] studied the self-discharge behavior of EDLCs with various ILs and carbons in relation to the applied potential. They found that the shape of the self-discharge curves changed indicating diffusion control or activation control when the applied potential was higher or lower than a specific value (Figure 2A). Using this value as SPL for long term voltage hold tests, they could show that long life times were possible up to this value, i.e., stable operation was possible when self-discharge was diffusion controlled. Significant degradation occurred in those EDLCs that were charged above the voltage where self-discharge occurred through an activation controlled process. A significant advantage of this approach is the fact that additional relevant information about the self-discharge behavior is collected, which is rarely provided. Moreover, SPLs based on this data are intrinsically linked to the electrochemical processes occurring instead of subjective cutoff limit values. On the other hand, the discharge curves do not always neatly fit the theoretical expectation and the potential dependent shape change is quite gradual, leaving room for interpretation.

Self-discharge is also often studied in voltage hold measurements (also called floating test) by recording the leakage current required to keep the voltage constant.^[28] Le Fevre et al.^[29] employed this method after charging EDLCs to progressively higher/lower potentials and measured the leakage current after some dwell time at each potential. They found that, typically, the current nearly dropped to zero after a short time, but once a certain threshold potential was reached, it would rise significantly. In their study they set the threshold for significant current flow at ~ 1 mA, ($\sim 0.6 \text{ mA cm}^{-2}$), but selected SPL values that imply an actual threshold of $\sim 0.05 \text{ mA cm}^{-2}$. Because the current did always drop fast in the beginning of the test and would momentarily seem to completely subside, they also set a minimum dwell time of 10 minutes. This ensured to pick up delayed rise in current density. Despite the unclear current density threshold, their plot of $i_{10 \text{ min}}$ vs. E_{max} usually showed a very sharp increase, making the selection of the SPL relatively unambiguous (Figure 2B). Using this SPL, the authors then demonstrated stable operation of EDLCs in voltage hold

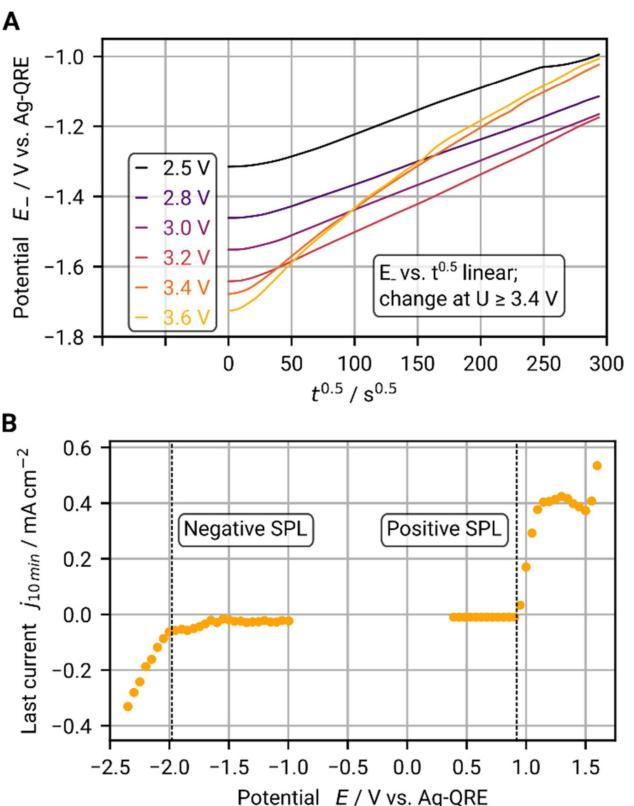


Figure 2. A) Self discharge mechanism change. AC in $[\text{BMIM}][\text{BF}_4]$. Potential vs. $t^{0.5}$ is linear for diffusion controlled faradic reactions causing self-discharge. The curve shape changes with increasing operative voltage. The switch from diffusion controlled (low concentration impurities) to activation controlled (electrolyte decomposition) is taken as SPL. Adapted from Ref. [20]. B) Leakage current increase. AC in 1 M $[\text{TEA}][\text{BF}_4]$ in ACN. The SPL is taken as the potential at which leakage current after 10 minutes is not yet increasing significantly. Adapted from Ref. [29].

tests. However, problems with this method could occur when comparing different cell types, which typically have different leakage currents, or when the rise of the leakage current with potential is more gradual.

It is probably not possible to give a definitive recommendation about which of these SPL determination methods should be used. It is, however, very noteworthy that almost all of the suggested methods are verified by their respective authors via some form of cycling lifetime test. While these methods all yield SPLs probably close to practical values, their predictions must always be verified. Only a cycling test that is designed to subject the EDLC to realistic conditions will actually provide convincing and useful SPL data. In that sense, the methods presented above should only be taken as preliminary experiment, while the true SPL determination is done with a voltage hold test. An overview of the best practices in this regard will be provided in Section 4.

Another commonality of the SPL determination methods presented above is that they should be done on individual electrodes in three electrode cells using a good reference electrode (RE). Some considerations and an overview about this topic are given in the next section.

3. Reference Electrodes

SPL determination can usually not be done using two electrode cells. Without a reliable RE, the immersion potential (IP), i.e., the potential of the electrodes before charge and, approximately, after discharge, is unknown. Also, as the specific capacitance of the negative and the positive electrode are often not equal, one cannot assume that the potential excursions for both electrodes are identical, despite using the same mass loadings. More importantly, ESWs are typically not symmetric with respect to the IP and, consequently, when any of the methods described before are applied on two electrode cells, it is not clear which of the electrodes is approaching its SPL. Using symmetric two electrode cells for ESW determination will almost always result in the underestimation of the ESW by stressing the electrolyte at one electrode first, while not using the full potential range of the electrolyte at the other electrode. A similar problem can occur in three electrode cells, when the counter electrodes are not significantly oversized. In two electrode cells, mass balancing can easily remedy this problem, by ensuring that both electrodes operate within their SPL (see Section 4). The potential excursion at the positive or negative electrode $V_{+/-}$ is dependent on the mass $m_{+/-}$, as $V_{+/-} = Q_{+/-}/m_{+/-}c_{+/-}$, with the charge Q and the specific capacitance c . But in order to use this relation to select the masses m_+ and m_- , the SPL (i.e. $V_{+/-, MAX}$) with respect to some potential scale needs to be known, not only the difference between the two SPLs, i.e. the ESW. Another way of saying this is that not only the size of the ESW is important, but also its position on the potential scale. Three-electrode measurements are therefore indispensable.

A thorough review of the field of reference electrodes for organic systems and ILs is beyond the scope of this minireview and has been done elsewhere.^[30–32] Here, a selection of the most commonly used REs is presented, especially highlighting those that are rather convenient to prepare and have been successfully applied.

3.1. Metallic Quasi-Reference Electrodes

The most widely used REs in organic media are Pt and Ag wires. These are, in fact, QREs, whose potential is often neither reproducible nor stable over time.^[30,32,33] SPLs determined with these QREs might well be shifted by several 100 mV upon repeating the experiment. Besides reproducibility issues, they can also experience potential drifts during the experiment. These aspects must not be overlooked as they can lead to largely over/underestimated SPLs. Prior to use, QREs must always be calibrated against a real RE, to locate their position on the potential scale, otherwise comparisons are impossible. Additionally, an internal standard such as ferrocene (Fc) or cobaltocenium (Cc^+) can be added to the electrolyte. In this way, the potential drift during the experiment can be monitored.

Metallic Li QREs are frequently used in Li battery research; however, the electrolyte has to contain Li ions at a fixed

concentration to yield a reasonably stable potential.^[34] This is not true in EDLC electrolytes where no ions of the metal electrode are present. Also, the use of Li metal QREs may lead to spontaneous reactions at the RE contaminating the electrolyte and, thus, interfere with the measurements at the WE. QREs based on the stable voltage plateau of partially delithiated Li-ion materials, e.g., LTO or LFP, are also employed. They seem more suitable than metallic Li, but require a rather complex preparation for each use due to the need for either lithiation (LTO) or delithiation (LFP).^[35]

3.2. Silver Reference Electrodes of the First and Second Kind

Although QREs are typically convenient, i.e., easy to prepare, and do not suffer from contamination or liquid junction potential problems, true REs offer stable and reproducible potential. The majority of designs for organic media involve a Ag wire in a compartment separated from the rest of the cell by a porous frit. The RE compartment contains Ag^+ ions dissolved in a solvent that can be identical to that in the cell electrolyte, or a liquid deemed compatible with it. This ranges from organic solvents to different ILs or mixtures thereof. The presence of Ag^+ ions at a defined concentration in the RE compartment electrolyte leads to a stable potential, due to the equilibrium of the Ag^+/Ag redox couple.

Electrodes of the first kind are realized immersing a silver wire in a defined concentration of a silver salt, with the anion often matched to the cell electrolyte. Examples include the works of Snook et al.^[36] (0.01 M silver trifluoromethanesulfonate ($AgOTf$) in 1-butyl-1-methyl-pyrrolidinium bis(trifluoromethane-sulfonyl)imide ($Pyr_{14}TFSI$)) and Saheb et al.^[37] (0.1 M $AgNO_3$ in the respective IL under study with 10 v/v% ACN).

For electrodes of the second kind, the Ag^+ concentration in the RE compartment is maintained by another equilibrium, which can be less sensitive to changes in the solution than in electrodes of the first kind. Saheb et al. also constructed a RE based on the low solubility of $AgCl$ in many organic solvents and ILs. The Ag^+ concentration is maintained constant by the presence of $AgCl(s)$ (usually coated ion the silver wire) and the Cl^- concentration in the RE compartment electrolyte, e.g., through dissolving 0.1 M Bu_4NCl . Lewandowski et al.^[38] used the complexation of Ag^+ with the cryptand 222 to maintain the Ag^+ concentration and thereby the potential of the RE. The Ag^+ can be introduced with a freely chosen silver salt dissolved in any organic solvent or IL. An advantage of this latter approach is that the RE is easier to construct (no need for depositing solid $AgCl$ onto the Ag wire) and, according to the authors, not sensitive light induced reduction of Ag^+ .

Unfortunately, all of these approaches suffer from at least four common practical problems. First, the requirement of a separate compartment means that it may not be easily integrated in the used cells. Second, for each new electrolyte it might be necessary to change the chemistry of the RE (salts and solvent). For example, $AgCl$ is quite soluble in some ILs. Third, the different electrolyte composition in the RE compartment and the cell will certainly cause a liquid junction

potential.^[32] Finally, problems may result from the leakage of the RE electrolyte into the cell electrolyte (and vice versa), causing their cross-contamination interfering with the measurements. Using salt bridges might limit the leakage into the main cell, but carries other problems due to construction complexity, additional problems with compatibility in terms of form factor and high junction impedance causing potentiostat instability.^[39]

3.3. Activated Carbon-Based Quasi Reference Electrodes

The determination of SPLs does not strictly require ± 1 mV accuracy like other quantitative electrochemistry work. Actually, RE potential variations within ± 10 mV are acceptable in most cases. Activated Carbon (AC)-based QREs easily provide this level of accuracy, while suffering from virtually none of the above mentioned inconveniences of REs and metal QREs. For the first time employed in the group of Kötz in 2005^[40] this type of QREs was further characterized in 2009 by Ruch et al.^[33] in organic media, and later by Weingarth et al.^[41] in ILs. The electrode construction is simple, employing polytetrafluoroethylene (PTFE) as binder, i.e., identical to those often used as WEs and oversized counter electrodes. The AC QREs are directly immersed in the electrolyte, but separated from the other electrodes with a conventional separator. The potential of the AC-QRE, measured over time against Fc^+/Fc , was found to drift less than 1 mV/day in most solutions and ILs, and was robust against Cl^- contamination (Figure 3). Interestingly, the potential was not very different between several ILs. Although there is no redox couple at equilibrium, the high electrode capacitance, resulting from the large surface area of AC, does not allow large potential shifts upon occasional charging events. This is obviously enabled by the high input impedance of modern potentiostats that allows only extremely small currents to flow.

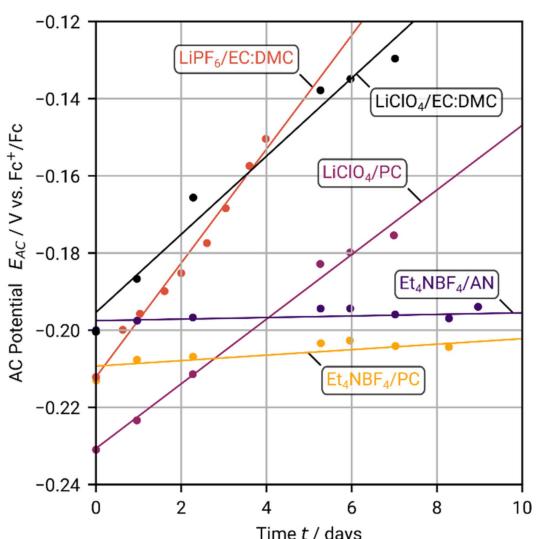


Figure 3. Potential of AC-QREs vs. time, measured vs. half-wave potential of Fc^+/Fc in various electrolytes. While relatively large drifts are observed in Li-based electrolytes, the electrode potential is very stable (<1 mV/day) in Li-free electrolytes. Adapted from Ref. [33].

However, Li^+ ions induce a steady upward drift of 10–20 mV/d of AC-QREs.^[33,42] An even stronger trend is found for Na^+ ions,^[43] but the study employed a low surface area carbon black and graphite composite electrode, which is likely the cause for the faster drift. According to Widmaier et al.^[42] a drift was also observed in LTO hybrid capacitors^[26] and in AC based EDLCs employing Li-salts.^[27] However, using a HNO_3 treatment to functionalize AC, Widmaier et al. were able to almost completely suppress the potential drift, i.e., to less than <1 mV/d. Lee et al.^[44] also validated AC-QREs for the use in aqueous electrolytes, where no increased drift in the presence of Li^+ or Na^+ was observed.

Although AC-QREs should always be characterized in terms of drift and reproducibility of the IP (e.g., versus Fc^+/Fc) when employed in new electrolytes, they certainly offer a rather wide application field. Their easy production from materials often used in EDLC research, shape flexibility and facile use without the problems associated with other REs, make AC-QREs the ideal reference electrode systems for the SPL determination methods described in Section 2.

In fact, besides the groups of Kötz and Presser, who continue to use AC-QREs after their efforts to develop them,^[45–51] these electrodes have recently been adopted by an increasing number of groups. The application areas include also post-Li batteries such as those using Ca ^[34] and Mg ,^[52] in-situ electrochemical STM studies,^[53] water purification^[54] and REs embedded in concrete for corrosion monitoring.^[55,56]

4. Life-Time Testing

4.1. Cycling and Voltage Hold Protocols

As mentioned in Section 2, SPLs determination methods are not enough to ascertain the ability of an electrolyte to tolerate a certain applied potential. Although time consuming, it is necessary to combine all the relevant materials under the envisioned conditions to elucidate all possible interactions among the cell components, the occurrence of long-term (slow kinetics) processes and other, unforeseeable problems. This means that long time testing of a complete EDLC within defined SPLs is the only way to ascertain its stability.

The two most common lifetime tests of EDLCs are galvanostatic charge-discharge cycles between predefined upper and lower voltage cut-off limits and voltage hold with regular testing of capacitance and equivalent series resistance (ESR) by short cycling. Weingarth et al.^[57] showed that this latter test is much more demanding when holding the cell voltage at the highest value of the former test procedure (Figure 4). In fact, upon continuous cycling the electrodes potentials are, for most of the time, rather far from the extreme values where the electrolyte decomposition may occur. This is even more true when high specific currents are applied, as the EDLC spends even less time per cycle at high voltage. Consequently, much longer test times are necessary until significant performance degradation occurs.

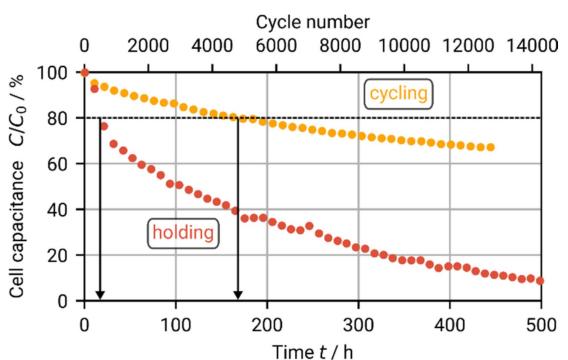


Figure 4. Comparison of voltage hold vs. cycling tests of symmetric EDLCs employing AC and 1 M [TEA][BF₄], within the operative voltage of 3.5 V. The cycling test reaches the end-of-life criterion (80% C retention) much later, due to slower aging. Adapted from Ref. [57].

The industrial standard IEC62391, see Section 5, defines the criteria for EDLCs' end of life to be 80% capacitance retention and ESR increase lower than 100%, which is widely used.^[57,20,58] However, what constitutes an acceptable lifetime is much less clear, although this is also specified to be 1500 h for voltage hold tests in the IEC standard. Despite the fact that commercial EDLCs are expected to operate for more than a million cycles under constant charge discharge cycling, frequently only a few tens of thousands cycles are reported. As that represents only a few percent of the actual lifetime, this is clearly insufficient.^[57] Nevertheless, high capacitance retention over such experiments is often presented as proof of stability.^[59–62] In contrast, as the voltage hold method generates faster performance decay, the length of most experiments of this kind is sufficient to reach end of life, or at least enable its more accurate estimation.^[29,63–65] In short, voltage hold tests yield a more complete picture faster, making this approach preferred with respect to galvanostatic cycling tests.

It has to be noted that the expected life of commercial EDLCs (1500 h) is rarely presented in typical research reports. On the other hand, the lifetime of commercial EDLCs refers to a rated capacitance that is typically lower than their maximum actual capacitance.^[66] Nonetheless, the lifetime is commonly tested at 65 °C to exacerbate the testing conditions. On the other hand, many research reports present data measured at room temperature only, although elevated temperature significantly reduces lifetime under constant voltage tests.^[63] That being said, discrepancies between small laboratory scale cells and larger industrial prototypes also come down to cell design. Swagelok and coin cells commonly used in research labs are more prone to electrode misalignment during assembly, high contact resistance or premature packaging failure.^[67] A possible approach is to validate first the reliability of a specific cell setup with standard materials employed in industry (e.g. TEA BF₄ in ACN and standard AC), whose SPL and lifetimes are well known. In this way, the extent of lifetime reduction compared to industrial values caused by the cell design can be roughly estimated. In any case, even with not entirely optimized cell setups, lifetimes of at least 250 h should be achievable.

Finally, a very important additional caveat is that commercial cells usually do not fail because of gradual performance decline. In fact, end of life is most often reached when the accumulation of gases from the electrolyte decomposition cause the cell's overpressure valve to open or when the electrode swelling generates mechanical damage.^[66] In most laboratory cells this condition is not verified due to the presence of a large dead volume or overly strong cell walls and rising internal pressure is not recorded. Thus a promising electrolyte candidate might be practically unsuitable despite its good performance data in laboratory cells. Gaseous decomposition products reported from common electrolytes include H₂, ethene, propene, CO, CO₂, metaboric acid and alkylboranes.^[40,68] While the last two are clearly related to the commonly used salt, [TEA][BF₄], the majority of gas evolution is actually due to solvent decomposition.^[69] Leakage currents are only in small parts related to gas evolution, but with rising proportion at more extreme potentials.^[70] However, the absolute amount of gas evolution strongly depends on the materials used, with, e.g., ACN being less prone to gas evolution than PC,^[71] and the surface functionalities of AC acting as catalytic sites or decomposing themselves.^[16] Thus, it is only possible to reliably judge the potential dependent gas evolution of an electrolyte with measurements directly probing the gas phase, or registering the internal cell pressure in some way. After promising electrochemical stability is proven, the gas evolution is certainly an important next step in evaluating an electrolyte candidate.

4.2. Mass Balancing in Full Cells

Although EDLCs are often described as "symmetric", the SPLs of the electrolyte at the negative and positive electrodes are rarely the same magnitude with respect to the potential at zero voltage (see Section 3), i.e., the potential of one of the electrodes reaches the corresponding electrolyte SPL first. However, many authors seem to be unaware of this fact as evidenced by many studies using symmetric mass loadings and operative voltages equal to the reported or presumed maximum ESW.^[60–62,72,58,73] For example, consider an aqueous EDLC with symmetric electrode mass loading, with relatively similar specific capacitance for positive and negative electrodes in a neutral electrolyte. It can be predicted to suffer almost exclusively from degradation related to the positive electrode. This is because the IP of carbon in aqueous electrolyte is about 0.440 V vs. NHE.^[44] At pH 7, the limit for the oxygen evolution reaction (OER) is at 0.816 V vs. NHE, while the corresponding limit for the hydrogen evolution reaction is at –0.414 V, i.e., more than 450 mV further away from the IP.^[74] The mass balancing to accommodate this asymmetry has been investigated since more than a decade ago^[75] and is used by many groups routinely.^[29,23,76] Despite this, several research reports appear in the literature highlighting the trivial performance improvement achieved switching from symmetric to properly mass balanced EDLCs.^[77–81] It should be rather clear to all that

electrode mass balancing is a must and not a discovery anymore.

In principle, SPL values determined according to any of the methods in Section 2 need to be verified with voltage hold tests in a way that ensures that this potential is actually kept by the electrodes under investigation for the time of the experiment. A straightforward way to verify their validity without taking care of the electrodes mass balancing is to individually test the negative and positive electrodes in three-electrode cells employing an RE and an oversized counter electrode. These tests, usually described as half-cell measurements, offer the advantage of granting a full control over the applied potential because only one electrode/electrolyte assembly is concerned. On the other hand, the stability of an EDLC might depend on the interactions between the two electrodes, e.g., the shuttling of decomposition products,^[20] and, in particular, progressive imbalance of the voltage excursions.^[82] The latter case occurs when the aging of the two electrodes, i.e., capacitance decay, does not occur evenly. Consequently, the electrode degrading faster will be subjected to a larger potential excursion, thus exceeding its SPL. These kind of phenomenon can only be investigated with two-electrode cell configurations.

Charge balance, i.e., $Q_+ = Q_-$, is the basis of the equation to determine the correct mass loading and optimal specific energy of two-electrode cells.^[75] The charge $Q_{+/-}$ is defined by the potential excursion from the IP to the SPL, denoted as $V_{+/-}$, and the capacitance of each electrode, calculated via its mass, $m_{+/-}$, and specific capacitance, $c_{+/-}$, according to $Q_{\pm} = m.c.V_{\pm} = m_{+/-}c_{+/-}V_{+/-} = Q_{+/-}$. Thus, $m_{+}/m_{-} = V_{+}/V_{-} = N.c_{+}/N.c_{-}$.

The calculated mass ratio is only theoretical, but it is usually applied directly. However, the uncertainty in the SPLs determination as well as differences between the extent of degradation upon cycling may require slightly different mass ratios to optimize the long-term performance. An approach to experimentally optimize the electrodes' mass ratio has been proposed by Cericola et al.,^[83] consisting in testing cells with a range of mass loadings around the theoretical one (Figure 5).

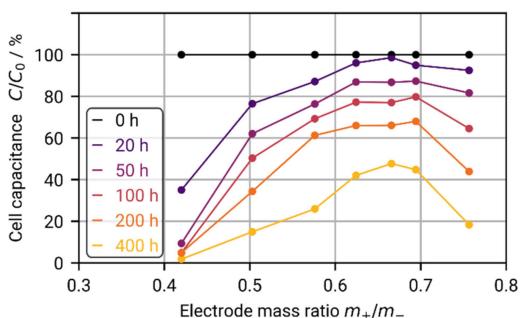


Figure 5. Differences in aging as a function of mass ratio. AC in 1 M [TEA][BF₄], operative voltage 3.5 V. Using different mass ratios around the calculated optimum, the most stable ratio can be found for a given operative voltage. Adapted from Ref. [83].

5. Impact on Industrial Applications

The elaborations on SPL and the methods of determination thereof are of critical importance for the application of electrolyte and carbon material research results in the EDLC industry.

From the industrial perspective, the most important characteristic of an EDLC is the customer benefit, which enables the producing company to sell their product in a large market. This benefit includes considerations on cost (the company has to make a profit) and performance (the application requirements need to be fulfilled). Standard characteristics for EDLC, such as capacitance, equivalent series resistance (ESR) or lifetime, are generally tested according to industry standards.

This results in clear requirements for the development of novel EDLC electrolytes, especially to exceed the current market standard operative voltage (2.85 V). As mentioned before, industrial EDLCs are generally tested according to IEC62391, which includes maximum voltage hold experiments at the maximum rated temperature, often 2.85 V and 65 °C. The cells are expected to last 1500 h at these conditions without their ESR increasing by more than 100% and their capacitance decreasing beyond 80% of the rated values.

Hence, only tests on two-electrode EDLCs in voltage hold conditions and elevated temperatures can be considered relevant for actual application/implementation.

Additionally, best practices in the SPL determination should include experiments at different temperatures as well as determination of the electrolyte degradation mechanisms and byproducts. This is especially relevant for gaseous byproducts, which lead to significantly shortened lifetimes in industrial devices.

A discussion on cost of materials and processing is needed in any case where a marketable application is considered, but the details of these discussions would go beyond the scope of this publication.

6. Summary and Outlook

In summary, the literature reporting on stability potential limit (SPL) determination methods based on voltammetry and leakage current measurements was reviewed. In these measurements, it is of utmost importance to employ for the WE the same materials implemented in real EDLCs to ensure the applicability of the results. Various reference electrodes for the SPL determination methods were discussed, highlighting the easy preparation and versatility of AC-QREs which show good stability in several EDLC electrolytes.

From the review of published results, it is evidenced that the voltage hold tests enable a faster detection of EDLCs lifetime, favoring a faster degradation than galvanostatic charge-discharge tests. The voltage hold tests allow reaching the EDLC end-of-life within a reasonable timespan, which is not possible when performing a limited number (e.g., 10000) of galvanostatic charge-discharge cycles.

For lifetime tests of two electrode cells it is important to use proper electrode mass balancing to avoid causing

premature aging of the EDLC due to degradation at only one electrode. Finally, the industrial perspective on the research efforts was reported, stressing the important factors for practical applications. For example, a certain EDLC's chemistry, including electrodes, electrolyte and inert components, should be considered a potential candidate for industrial application only if the SPL is confirmed by voltage hold experiments performed employing realistic cells. This is a mandatory requirement to ascertain the actual status of the development.

The optimized procedure to determine the ESW of a new electrolyte for EDLCs is proposed as follows:

- Calibrate and check stability of the RE (e.g., AC-QRE) in the new electrolyte employing the Fc^+/Fc redox reaction.
- Determine the limiting potentials of aluminum, steel and other "inert" cell materials by CV using the calibrated RE.
- Determine the limiting potential of the positive and negative electrodes, individually, by leakage current or voltammetry methods using the calibrated RE.
- Confirm the limiting potentials by voltage hold tests at those potentials, or below if needed. Use either three-electrode cells or two-electrode cells with a range of mass ratios above and below (e.g. $\pm 10\%$) the ideal ratio calculated with the formula $m/m_+ = V_+/c_+/V_-c_-$.
- Finally, discrepancies between indicative SPL determination techniques such as CV or self-discharge measurements and life time experiments should be clearly evidenced in research and industrial reports to enable a better understanding of the EDLC electrolyte degradation phenomena.

The experiments mentioned above should ideally be integrated with tests at elevated temperatures and investigations of gas evolution.

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Conflict of Interest

The authors declare no conflict of interest.

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