

The self-discharging of supercapacitors interpreted in terms of a distribution of rate constants

L.E. Helseth

Department of Physics and Technology, Allegaten 55, 5020 Bergen, University of Bergen, Norway

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ABSTRACT

Supercapacitors are prone to self-discharging, which is most often measured as a voltage decrease with time under open circuit conditions. It is of substantial interest to find simple and general methods to extract information about the processes going on in the supercapacitor during self-discharge. The current work fits a stretched exponential function to experimental data available in the literature, thus extracting parameters that allows one to probe the internal processes of the supercapacitor. In particular, experimental data related to charge holding time, charging rate before self-discharge and temperature dependence are investigated. It is demonstrated how the fitting data can be understood in terms of a kinetic model exhibiting a distribution of rate constants which are related to the fitting parameters. The current work therefore proposes a method that allows one to quickly map the internal processes of a self-discharging supercapacitors with only two variables, and might therefore become a useful tool.

1. Introduction

The Leyden jar was probably the first man-made capacitor, invented in 1745 [1]. Its ability to store electrical energy played a crucial role for the development of science and technology the following century. However, it was also known that the Leyden jar lost charge as time passed by. In 1854, Kolrausch investigated the decay of charge from a Leyden jar, and found that it did not follow a simple exponential decay law on the form $\exp(-t/\tau_1)$ with decay time τ_1 as one might expect [2]. Instead, he introduced a stretched exponential function on the form $\exp[-(t/\tau)^\beta]$ to explain the observed decay, where $0 < \beta \leq 1$ is a constant that sometimes has been denoted the Kolrausch parameter and τ is the decay time at which one has crossover from faster-than-exponential to slower-than-exponential decay. The stretched exponential function was 'reinvented' in 1949 by Förster to explain fluorescence resonance energy transfer [3] and then in 1970 by Williams and Watts to explain dielectric spectra [4]. Since then, the stretched exponential function has been used extensively to explain the behavior of glassy states, luminescence decay and electronic systems in terms of a distribution of relaxation times [5, 6]. However, it should be pointed out that also models not requiring a distribution of relaxation times have been developed which give rise to a stretched exponential function. These latter models are either based on intermediate kinetic steps [7] or time-dependent rate constants associated with rate laws [8] or the equations of motion [9,10].

An interesting and timely question is whether stretched exponential functions can provide useful information about the self-discharging of

supercapacitors. Supercapacitors were patented in 1957 and introduced to the commercial market in the late 1970s [11,12]. Supercapacitors utilize charge accumulation in dielectric double layers due to the use of appropriate electrolytes, combined with nanostructured surfaces to increase the area available to store charge. They can be modelled using either microscopic models [13–18] or equivalent circuits [19–33], where the latter often are preferred in practical applications due to the smaller computational load and complexity. The self-discharge of supercapacitors is a considerable problem, and is often observed as a time-dependent drop in voltage after charging. This experimentally observed self-discharge could be due to internal redistribution of charge along the electrode surface, redox reactions at the electrode surface, or leakage currents [34–47]. Blocking layers on the carbon electrodes are known to reduce the problem of self-discharge, but often at the cost of reduced capacitance and energy storage [48,49]. It has also been demonstrated that the self-discharge can be altered by controlling the surface chemistry of a carbon surface [39,50], although much remains to be understood. Self-discharge can be used as a diagnostic tool, and has been found to be faster than conventional tools such as potential floating when determining the stability of supercapacitors based on ionic liquids [51].

To date, neither timescale or the shape of the voltage-decay curve have been reproduced suitably well using microscopic models. Such models for charge distribution in porous structures often rely on a range of assumptions that are very challenging to verify experimentally. To improve and understand supercapacitors, one needs not only complex microscopic simulations, but also simple tools that allow quick and

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efficient mapping of crucial parameters. A stretched exponential function with $\beta=0.5$ was in Ref. [45] conjectured from diffusional dynamics and used to explain long-time self-discharging of supercapacitors. A further analysis of modelling self-discharge of supercapacitors using a distribution of relaxation times in an equivalent circuit network was given in Ref. [52], although no attempt was made to provide a systematic study of available data in the literature. The current study proposes the use of a kinetic model with a distribution of time-independent rate constants to fit to the experimental data for the self-discharge of supercapacitors. A systematic analysis of experimental data available in the literature for self-discharge of supercapacitors is made assuming that the voltage decay can be fitted to a stretched exponential function. Such a study is of interest as it allows one to quickly map some of the internal processes of a self-discharging supercapacitors with only two parameters.

2. Self-discharge due to a distribution of relaxation times

A kinetic model should be based on the features that are known to characterize supercapacitors. As shown in Fig. 1, it is known that the electrolyte penetrates in between carbon pores of a range of different sizes, where redox reactions or charge redistribution takes place. A possible scenario is that there are many decay constants, each corresponding to a set of sites or series of events each of a fixed decay constant.

Each local region has a large number of ions taking part in the charge transfer reaction, and is assumed to be governed by first-order kinetics of the type $dN_{fi}/dt = -k_{fi}N_{fi}$, where N_{fi} is the local density of charges at site i and $k_{fi} = k_{fi0}\exp(-\Delta E_i/k_B T)$ is the local decay constant at that site that is assumed to follow a Eyring or Kramers type of activation [53,54]. Here k_B is Boltzmann's constant and T is the temperature, while ΔE_i is the activation energy. This could be due to for example rearrangement of charge or redox-reactions, but here the detailed reaction mechanisms will not be required to develop the model. The charge then follows $Q_{fi} = Q_i(0)\exp(-k_{fi}t)$, where $Q_i(0)$ is the initial charge at the site. If we assume that the supercapacitor consists of a large number of sites that accumulate charge, and that each of these charges decay exponentially with time, the total charge is

$$Q(t) = \sum_{i=1}^N Q_i(0)e^{-k_{fi}t}. \quad (1)$$

As pointed out in Ref. [52], the voltage over a supercapacitor might be related to the charge by $V_c = \sum_{i=1}^N \frac{Q_i}{C_i} + R_s I$, where Q_i and C_i are the

charges and capacitances associated with particular site i , R_s is the series resistance and I the current through the supercapacitor. Since $R_s I$ is very small during self-discharge, it is convenient to write the voltage over the entire supercapacitor as

$$V_c(t) = \sum_{i=1}^N V_i(0)e^{-k_{fi}t}, \quad (2)$$

where $V_i(0) = Q_i(0)/C_i$ can be interpreted as a local voltage for a particular site as it occurs with a certain probability fraction γ_i . That is, if the initial voltage at $t=0$ is V_0 , then $V_i = \gamma_i V_0$ where $\sum_{i=1}^N \gamma_i = 1$. Therefore, one can write

$$V_c(t) = V_0 \sum_{i=1}^N \gamma_i e^{-k_{fi}t}. \quad (3)$$

If one assumes that the number N is very large, a continuous distribution can be assumed, such that the sum becomes an integral and

$$V_c(t) = V_0 \int_0^\infty P(k_f) e^{-k_f t} dk_f, \quad (4)$$

where V_0 is constant. Let us now define $s = k_f/k_{f0}$, where $k_{f0} = 1/\tau$ is a representative constant which the distribution of rate constants is distributed around. If one further defines $P(s) = k_{f0}P(k_f)$, eq. (4) can be written as

$$V_c(t) = V_0 \int_0^\infty P(s) e^{-\left(\frac{t}{\tau}\right)s} ds. \quad (5)$$

While the Laplace transform of eq. (5) can be fitted to any experimental self-discharge data, obtaining the corresponding $P(s)$ could be computationally challenging. However, one exception is the stretched exponential on the following form,

$$V_c(t) = V_0 e^{-\left(\frac{t}{\tau}\right)^\beta}, \quad (6)$$

where β and τ are used as fitting constants. Here β can tell us something about the distribution $P(s)$, in the sense that a small value of β gives a wide distribution whereas when $\beta=1$ represents a single decay rate. It should be emphasized that unless $\beta=1$, one cannot interpret τ as a representative or average decay rate [5]. In fact, τ should be understood as a fitting constant which provides information about the crossover from super-exponential to sub-exponential decay. The distribution of constants $P(s)$ can be found by requiring

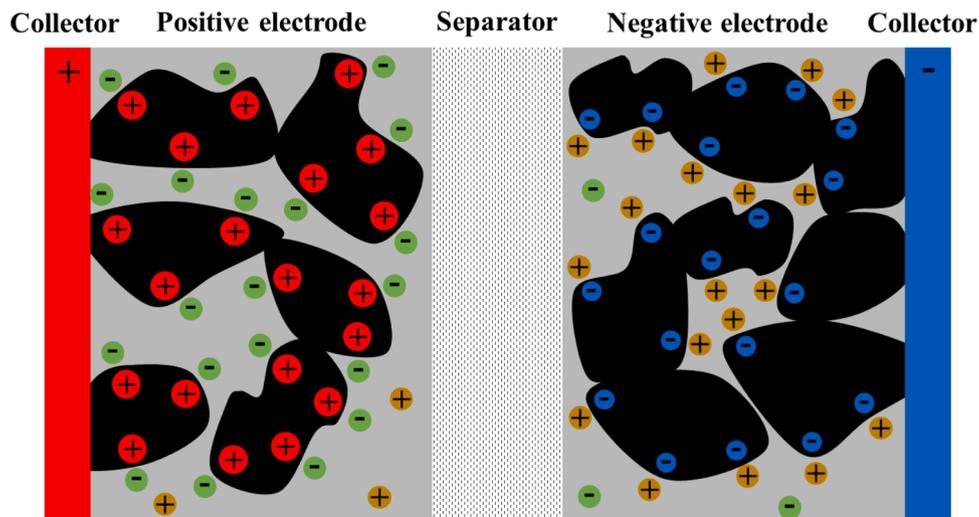


Fig. 1. Schematic drawing of the construction of a supercapacitor.

$$\int_0^{\infty} P(s)e^{-\left(\frac{t}{\tau}\right)^{\beta}} ds = e^{-(t/\tau)^{\beta}}, \quad (7)$$

where the condition $V(0)=V_0$ requires that $\int_0^{\infty} P(s)ds = 1$. It should be emphasized that tabulated tables are available for different values of β [55], thus making the extraction of $P(s)$ computationally very simple. The distribution function $P(s)$ is clearly linked to a distribution of rate constants. However, to link it directly to microscopical geometrical parameters of the pores of the supercapacitor would require microscopic measurements of the charge decay processes, which is a topic outside the scope of the current work. Nonetheless, one may be able to use the knowledge about the fitted constant β and the distribution function $P(s)$ as a diagnostic tool complementing already existing methods.

Some studies have already demonstrated that an empirical expression two exponential constants could be fitted to the experimental data [37,38,49]. The current work extends that approach to a distribution of constants. Given that there have been no systematic studies of how the stretched exponential can be used to fit the experimental data for self-discharge in the literature, it was in this study decided to extract some of the available data in order to find out what can be learned from a fit of eq. (6) to those data. In the current study the MatLab program `grabit.m` was used extract data from different published experimental self-discharge curves, and the MatLab function `nlinfit` was used to make nonlinear fits of eq. (6) to the experimental data.

2.1. Hold time

Figure 2 a) shows eq. (6) fitted to the experimental data in Fig. 2 of Ref. [36] for different hold times. The hold time is the time period over which the capacitor is held at a certain voltage after charging, such that

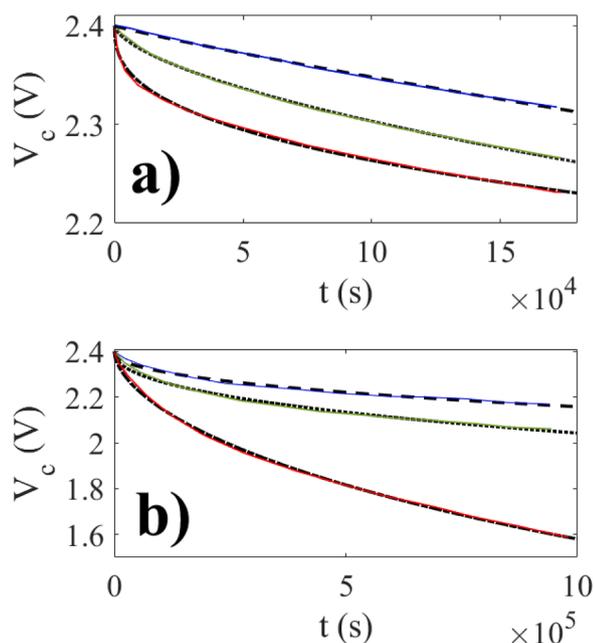


Fig. 2. In a) the experimental data are extracted from Fig. 2 in ref. [36] for the voltage over the supercapacitor during self-discharge for different hold times after charging. The red line is for 15 min hold time, with the dash-dotted line a corresponding fit using eq. (6). The green line is for 2 h hold time, with the dotted line a corresponding fit using eq. (6). The blue line is for 5 days hold time, with the dashed line a corresponding fit using eq. (6). In b) the experimental data are extracted from Fig. 5 in Ref. [36] for a self-discharging supercapacitor at $T=313$ K (red line), $T=296$ K (green line) and $T=256$ K (blue line). The dash-dotted, the dotted and the dashed lines are corresponding fits of eq. (6) to the experimental data. The experimental data are extracted from Ref. [36] and used with permission from Elsevier.

the charge has time to redistribute. In Fig. 2 a) the red line are data for a hold time of 15 min, and the corresponding dash-dotted line is a fit of eq. (6) with the parameters $k_{f0} = 1/\tau = 5.9 \cdot 10^{-9} \text{ s}^{-1}$ and $\beta=0.38$. The fit is good as indicated both visually and by the value $R^2=0.9969$. The green line is the experimental data for 2 h hold time, with the dotted line a fit of eq. (6) with $k_{f0} = 1/\tau = 5.8 \cdot 10^{-8} \text{ s}^{-1}$, $\beta=0.62$ and $R^2=0.9988$. The blue line corresponds to 5 days hold time, while the dashed line is a fit to eq. (6) with $k_{f0} = 1/\tau = 1.4 \cdot 10^{-7} \text{ s}^{-1}$, $\beta=0.90$ and $R^2=0.9986$. By comparing the three fits, it appears that both k_{f0} and β increase with the hold time, which is of interest as it suggests that these parameters are sensitive to the charge redistribution taking place in the supercapacitor.

To obtain further insight, eq. (6) was fitted to the self-discharge voltage decay the data in Fig. 2 in Ref. [36] and Fig. 7 in Ref. [40] to obtain values for β and $\tau=1/k_{f0}$, displayed in Fig. 3 a) and 3 b), respectively. The trend suggests that the stretching factor β increases with the hold time t_h , but appears to saturate close to single exponential decay behavior as β goes to 1. At holding times approaching 10^5 s there is a deviation in this trend obtained from the data in Ref. [40], but it does not alter the overall impression. On the other hand, the parameter τ appears to decrease with t_h , although one might speculate whether there is a limiting lower value based on the data. It should be emphasized strongly that τ is a fitting constant and cannot be associated with a decay constant in the same way as for single-exponential decay [5]. Thus, one cannot conclude from Fig. 3 b) that overall the decay constants decrease with the holding time. In fact, τ can only provide useful information about the crossover from super-exponential to sub-exponential decay, which means that the extracted parameters from Ref [36] in Fig. 3 b) suggests that the crossover happens more quickly as the holding time increases. The values of τ extracted from the data from Ref. [42] show significant fluctuations, and here one cannot clearly conclude whether there is indeed a decreasing trend similar to that obtained for the data from Ref. [36].

Since the trend in Fig. 3 a) is suggests strongly that β increases with the holding time, this should have implications for the distribution of rate constants $P(s)$. Figure 3 c) shows the distribution function $P(s)$ for $\beta=0.38$ (solid line), 0.62 (dashed line) and 0.90 (dash-dotted line), corresponding to the circles in Fig. 3 a). This distribution function might help us explain the results observed in Fig. 3 a). It is known that the fast charging and charge neutralization in the pores of a supercapacitor results in a non-equilibrium configuration of ions [56,57]. For small values of the holding time this results in a relatively fast self-discharge with a broad range of distributions constants, as seen in Fig. 3 c). As the holding time increases, the configuration of ions becomes more stable and possibly also reaching a larger range of the pores. This means that fewer of the decay modes are available for self-discharge, and in fact now the voltage follows more closely a single exponential decay curve.

For comparison, it should be mentioned that the original data obtained by Kolrausch can be fitted using $\beta=0.43$, and this particular value has found use in a range of systems [6]. However, in the case of supercapacitors the value of β varies according to the situation considered, and there is no unique or universal value.

2.2. Current

One interesting question is whether the observations of self-discharge decay for different holding times presented in Fig. 3 also coincide with the interpretation of other data available in the literature. In Ref. [25] it was systematically investigated how the voltage decay curve was influenced by the applied current I_0 during charging. The holding time was here assumed to be the same in all the experiments. Equation (6) has been fitted to the experimental voltage decay data in Fig. 11 in Ref. [25], and the extracted values for β and $\tau=1/k_{f0}$ are presented in Fig. 4. The fits were obtained with R^2 values 0.9984, 0.9941, 0.9942 and 0.9650 for $I_0=0.012$ A, 0.06 A, 0.3 A and 1.5 A respectively. Most of the fits are therefore rather good, perhaps except for the largest current, although the origin of the deviation is not known.

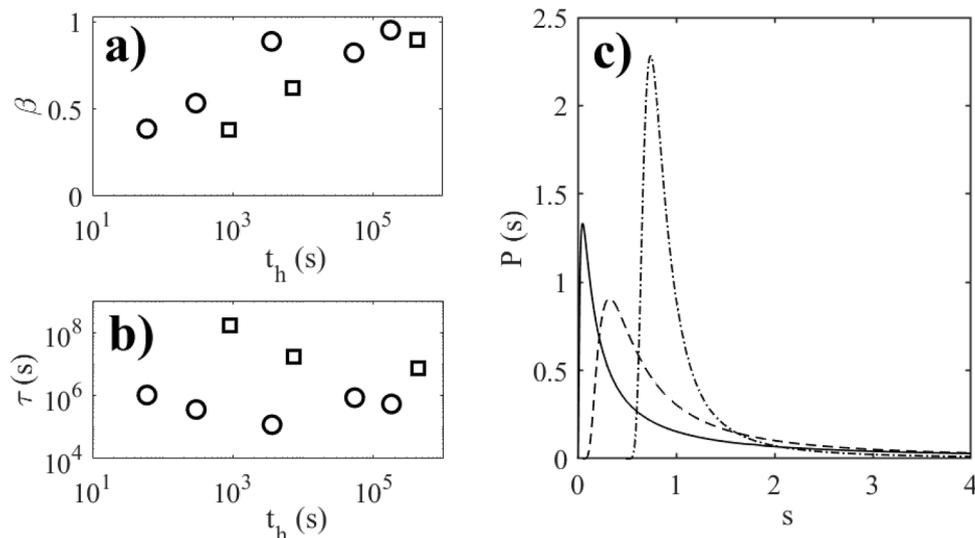


Fig. 3. The values of β (a) and τ (b) are extracted from the experimental data in Fig. 2 of Ref. [36] (squares) and Fig. 7 of Ref. [40] (circles). In c) the distribution of rate constants is shown for $\beta=0.38$ (solid line), 0.62 (dashed line) and 0.90 (dash-dotted line), corresponding to the three black boxes in a).

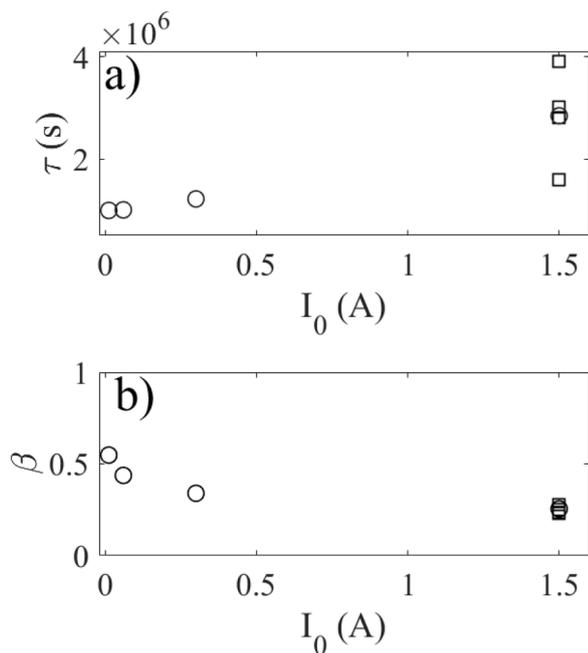


Fig. 4. The fitting parameters τ (a) and the β (b) as a function of current I_0 during charging to 2.7 V obtained fitting eq. (6) to the data in Ref. [25] and shown as circles. The black boxes are the values obtained when $I_0=1.5$ A was used to charge the supercapacitor to 1.2 V, 1.7 , 2.2 V and 2.7 V.

The squares in Fig. 4 correspond to the supercapacitor being charged by a current $I_0 = 1.5$ A to 1.2 V, 1.7 , 2.2 V and 2.7 V. From the data presented in Fig. 4 a), it is seen that the fitting constant τ increases with applied current I_0 during charging. It was found that τ decreases from $4 \cdot 10^6$ s for a final voltage $V_0=1.2$ V to about $2 \cdot 10^6$ s for a final voltage $V_0=2.7$ V for a constant charging current $I_0 = 1.5$ A. The data for the other values of V_0 (1.7 V and 2.2 V) appear to be clustered around $3 \cdot 10^6$ s. This suggest that the crossover from super-exponential to sub-exponential decay happens more slowly as the current I_0 increases, but is slowed down if the supercapacitor is charged for a longer time to higher final voltages. However, one should be extremely careful putting specific meaning to this, as it does not appear reasonable that merely altering the final voltage could change the crossover parameter τ . Most

likely further measurement data over a longer period are needed to be able to conclude on the behavior of τ for different voltages, but the author was not able to identify such data in the literature.

On the other hand, the Kolrausch parameter β decreases clearly with applied current, and appears to be independent of the final voltage V_0 for a given constant charging current. These observations suggest that as the current increases, the distribution of rate constants $P(s)$ gets broader thus exciting more decay modes as the system is brought further out of equilibrium.

2.3. Temperature

The voltage over a self-discharging supercapacitors as a function of temperature has been reported in several studies [24,35,36,58]. Figure 2 b) shows eq. (6) fitted to the experimental data in Ref. [36] for different temperatures. The red line is data for $T=313$ K, and the corresponding dash-dotted line a fit to eq. (6) with $k_{f0} = 1/\tau = 2.3 \cdot 10^{-7} \text{ s}^{-1}$ and $\beta=0.59$. The green line is the data for $T=296$ K, with the corresponding dotted line a fit to eq. (6) with $k_{f0} = 1/\tau = 1.8 \cdot 10^{-8} \text{ s}^{-1}$ and $\beta=0.46$. Finally, the blue line corresponds to experimental data taken at $T=256$ K, and the dashed line is a fit of eq. (6) with $k_{f0} = 1/\tau = 7.44 \cdot 10^{-9} \text{ s}^{-1}$ and $\beta=0.46$. All the fits in Fig. 2 b) appear to be good with values $R^2 > 0.994$. It is obvious from the difference in curve forms in Fig. 2 a) and 2 b), as well as the obtained fitted data, that the two parameters τ and β react differently to temperature and hold times.

To obtain further insight, eq. (6) was fitted to the self-discharge voltage decay the data in Fig. 5 in Ref. [36], Fig. 17 in Ref. [24] and Fig. 14 in Ref. [58] to obtain values for β and $\tau=1/k_{f0}$. The values for $\tau=1/k_{f0}$ and β are displayed in Fig. 5 a) and 5 b), respectively. The data in Fig. 5 a) appear to indicate that the value of τ decreases with increasing temperature, thus suggesting that the crossover from super-exponential to sub-exponential decay happens more quickly as the temperature gets higher. The value of β extracted from Refs. [28,36] display values close to 0.5 , consistent with a diffusional process as described in Ref. [45]. However, the value of β extracted from Ref. [58] is closer to 0.3 , thus suggesting an even wider distribution of rate constants. Interestingly, it is noted that in all the studies, β does not change much with temperature. Therefore, it is reasonable to conclude that the distribution of rate constants $P(s)$ does not change much when the temperature of the supercapacitor increases. However, the decay modes are pushed from super-exponential to sub-exponential more quickly as indicated by a decreasing τ .

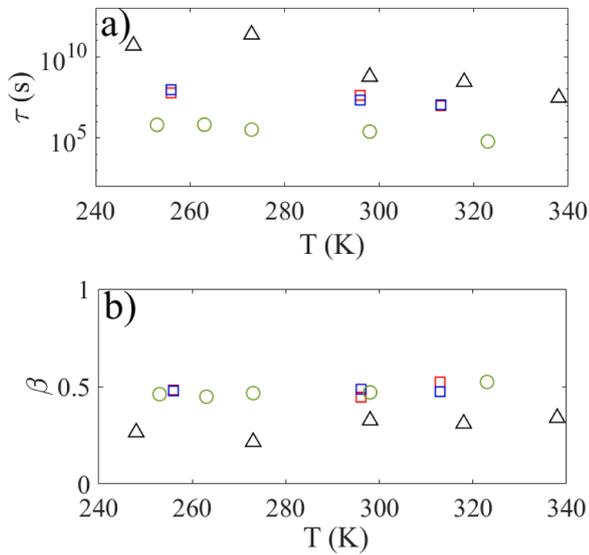


Fig. 5. The fitting parameters τ (a) and β (b) from the data in Ref. [35] (red boxes correspond to 1.3V, while blue boxes correspond to 2.7 V), the data from Ref. [24] (green circles) and the data from Ref. [58] (black triangles).

3. Self-discharge controlled by a single time-varying decay rate

In the previous section it was assumed that the voltage decay observed during discharging was due to a distribution of rate constants. The approach taken on in this work is different from that of numerous previous studies, where it has been assumed that one or two rate constants could be used to explain the results [33,35,48]. However, it is clear that if one is to interpret the self-discharge voltage in terms of a single exponential decay rate, this rate must be varying with time. At the same time, one should also note that experimental data at nominal [38] and excessive voltages indicate that activation takes place [59].

Let us see how an approach based on a single decay rate can be developed by redefining the basic assumptions. Assume now that all charges contribute, such that they are all in the final state and follow first order kinetics $dN_f(t)/dt = -k(t)N_f(t)$. We will also assume that the charges may dissociate from their position according to a Kramers - type thermal activation rate given by

$$k(t) = k_0 e^{-\frac{\Delta E(t)}{k_B T}}, \quad (8)$$

where k_0 is the dissociation rate in absence of forces, k_B is Boltzmann's constant and T is the temperature. Here $\Delta E(t)$ is the potential energy barrier which must be overcome to for the ions to dissociate. The energy barrier may change slowly with time as the charges are rearranged or driven from intermediate positions and into new positions where they cannot contribute to the charge effectively stored at the capacitor electrodes. The gradual dissociation of charges from the electrode is described by noting that each time a charge is removed, the energy ΔE decreases a little bit and therefore can be considered time-dependent if one view it over a longer time interval. From eq. (8) it is also seen that when the temperature increases or ΔE decreases, the rate k_f increases. If the elemental charge is q and we assume that $Q = qN_f$ with initial charge $Q_0 = qN_{f0}$, then

$$\frac{dQ(t)}{dt} = -k(t)Q(t), \quad (9)$$

which has a solution given by

$$Q(t) = Q_0 e^{-\int_0^t k(t) dt}. \quad (10)$$

In most cases the voltage is measured over a self-discharging supercapacitor, and it is therefore of interest to find its time-

dependency according to the theory presented here. Let us assume that the charge stored is proportional to the voltage according $Q(t) = C(t)V_c(t)$, where $C(t)$ is a time-dependent capacitance. The initial charge is $Q_0 = C_0 V_0$, where C_0 is the initial capacitance and V_0 is the initial voltage. Equation (10) then gives

$$V_c(t) = \frac{C_0 V_0}{C(t)} e^{-\int_0^t k(t) dt}. \quad (11)$$

If the capacitance remains approximately constant, one may write $C(t) \approx C_0$. In order to proceed, one needs to know the details of the interactions between the charges causing a specific time-dependence of the rate constant. In the special case that the decay rate follows a power law on the form $k(t) = k_0 t^{\beta-1}$, with k_0 a temperature-dependent constant, corresponding to a logarithmic time-dependency $\Delta E(t) = -k_B T \ln(k_0/k_{f0}) + k_B T(1-\beta) \ln(t)$, then the charge decay becomes a stretched exponential function

$$V_c(t) = V_0 e^{-\left(\frac{t}{\tau}\right)^\beta}, \quad \tau = \left(\frac{\beta}{k_0}\right)^{1/\beta} \quad (12)$$

This is the same as eq. (6), but with different interpretations of β and τ . The main difference between the two approaches is that while the theory behind eq. (6) assumes a distribution of rate constants, the theory behind eq. (12) assumes a time-dependent rate constant. Equation (9) states that this time-dependent constant $k(t)$ can be found according to

$$k(t) = -\frac{\frac{dQ(t)}{dt}}{Q(t)} = -\frac{I(t)}{\int_0^t I(t) dt}, \quad (13)$$

where $I(t)$ is the current. Thus, the charge Q stored by the capacitor or the current I due to charge rearrangement or redox-reactions can be used to evaluate the rate constant and the aggregated barrier energy ΔE . However, in most cases the voltage is measured over a supercapacitor, which complicates the determination of the rate constant. The rate constant is given by

$$k(t) = -\frac{\frac{d[C(t)V_c(t)]}{dt}}{C(t)V_c(t)} = -\frac{\frac{dV_c(t)}{dt}}{V_c(t)} - \frac{\frac{dC(t)}{dt}}{C(t)}, \quad (14)$$

such that only when $(dV_c/dt)/V_c \gg (dC/dt)/C$ the contribution from a changing capacitance can be neglected. Fortunately, the large capacitance C of many supercapacitors, combined with the relatively small change in capacitance with self-discharge, allows one to neglect the second term of Eq. (14), thus giving easier access to the rate constant $k(t)$ through voltage-time data.

The black triangles (Δ and ∇) in Fig. 6 a) are the rate $k(t)$ obtained from data of Fig. 14 in Ref. [58] for $T=248$ K (∇) and $T=338$ K (Δ). The dashed and dash-dotted lines are fits of eq. (12) these data with $k_0 = 1.5 \cdot 10^{-4} \text{ s}^{-1}$ and $\beta = 0.3386$ (value from Fig. 5) for $T=248$ K (Δ), and with $k_0 = 2.5 \cdot 10^{-3} \text{ s}^{-1}$ and $\beta = 0.2643$ (value from Fig. 5) for $T=338$ K (Δ). It is noted that the overall agreement appears reasonable, but the R^2 is low (<0.9) due to significant fluctuations in the extracted rate constants. The reason for these fluctuations, which occur particularly for small rate constants, is due to the sensitivity in the estimated rate constant to small changes in the extracted data for the voltage from the published figures. Direct extraction of voltage data, as in Fig. 2, do not show the same fluctuations, and analysis is easier to do on extracted data as used here.

The largest extracted rate constant which are the least influenced by the fluctuations associated with the extraction procedure, nominally $k(t \approx 0) = k_{fA}$, was plotted as a function of temperature for data obtained from Ref. [36] (blue squares), Ref [58] (green circles) and Ref. [24] (green circles). It is interesting to know whether the data for k_{fA} suggest Kramers-type activation barrier. To this end, eq. (8) was fitted to the blue squares (obtained from ref. [36]) to obtain $k_0 = 8.2 \cdot 10^{-4} \text{ s}^{-1}$ and $\Delta E = 0.16 \text{ eV}$ (dashed line). Similarly, a fit of Eq. (8) to the black triangles obtained from Ref. [58] gives $k_0 = 9.0 \cdot 10^{-3} \text{ s}^{-1}$ and $\Delta E = 0.20 \text{ eV}$ (dotted

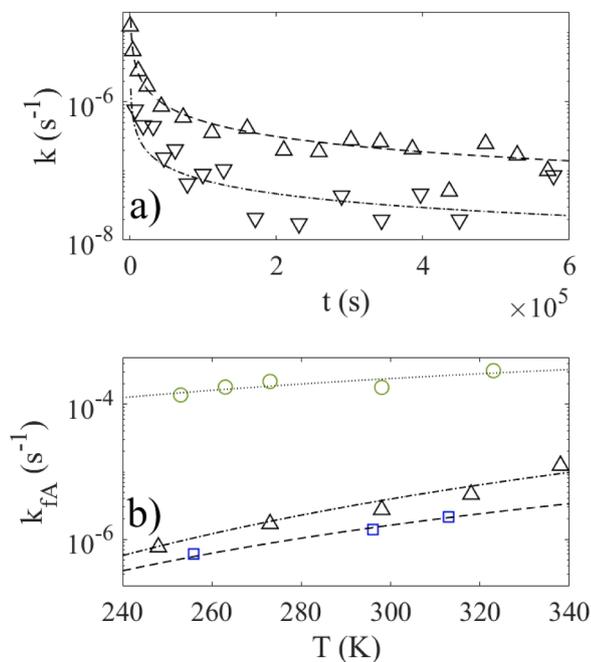


Fig. 6. In a) the time constant $k(t)$ is displayed as function of time for $T=248$ K (∇) and $T=338$ K (Δ) using the data from Ref. [58] (black triangles). The dashed and dash-dotted lines are fits of $k(t) = k_0 t^{\beta-1}$ to these data, respectively. In b) the maximum extracted rate constant k_{fA} is plotted as a function of temperature from the data in Ref. [36] (blue squares), the data in Ref. [58] (green circles) and the data in Ref. [24] (green circles). The dashed, the dotted and the dash-dotted lines are corresponding fits using eq. (8).

line), while a fit of Eq. (8) to the green circles obtained from Ref. [24] gives $k_0 = 3.3 \cdot 10^{-3} \text{ s}^{-1}$ and $\Delta E = 0.07 \text{ eV}$. It is seen that the fit of Eq. (8) represents the extracted rate constants rather well, although some outliers of unknown origin do appear. The initial rate constants obtained typically fall within the range 10^{-4} s^{-1} to 10^{-2} s^{-1} , while the energy activation barriers range are of the order 0.1 - 0.2 eV.

It is possible to connect the two theories leading to eqs. (6) and (12). Assuming that the kinetics follows eq. (14) with $(dV/dt)/V \gg (dC/dt)/C$, it is seen that $k(t) = -[dV_c(t)/dt]/V_c(t)$. Inserting eq. (4) for $V_c(t)$ gives

$$k(t) = \frac{\int_0^\infty k_f P(k_f) e^{-k_f t} dk_f}{\int_0^\infty P(k_f) e^{-k_f t} dk_f} \quad (15)$$

Thus, it is seen that the phenomenological rate constant $k(t)$ is given by the distribution of rate constants $P(k_f)$, although there might not be a unique correspondence. From eq. (15) it is also seen that $k(t=0) = \int_0^\infty k_f P(k_f) dk_f$. The observation that the parameter β , and therefore also $P(k_f)$, does not change much with temperature as seen in Fig. 5 b) may explain why k_{fA} can be modelled by a single Kramers-like activation barrier as seen in Fig. 6 b).

The results in this and the previous section are connected by the fact that the single time-varying decay rate can be deduced from a distribution of rate constants as in eq. (15). It should also be noted that the fact that the rate constant $k(t)$ decreases with time can be understood by considering the slowly rearranging charge which gradually alters the energy barrier as time passes.

4. Discussion

Based on what we know about activation, charge transfer and ion movement in carbon pores, the approach based on a distribution of constants appears reasonable to the author. However, it must be emphasized that direct evidence for a distribution of rate constants is lacking. The measurements needed to find such a distribution would

require local measurements of rate constants within the pores, and to the best knowledge of the author there are currently no systematic studies providing such information. With such data, the approach based on a distribution of rate constants may provide an additional source of information about the microscopic processes during self-discharge.

The values of β and τ can help us understand how supercapacitors behave under certain circumstances. It is for example noted that the value of β is about 0.5 for small currents in Fig. 4 b), as is also the case for small hold times in Fig. 3 a). This is also consistent with other literature, where a value of β close to 0.5 has been found in the cases where the supercapacitor is not driven too far from equilibrium before let alone to self-discharge [45,52]. However, perhaps more interesting for future applications is the relative change in the constants when parameters are altered. In Fig. 3 a), an increase in hold time appears to favor a narrower distribution of rate constants. This is probably due to a re-arrangement of charge such that the reaction sites become more uniform, thus favoring single-exponential decay. For applications, one might prefer the single-exponential decay to happen for shorter hold times. In Fig. 3 a) the data from ref. [40] (circles) appear to reach a narrow distribution of rate constants at much shorter hold times than the data from Fig. [36] (squares). However, from Fig. 3 b) it is also seen that the data from Ref. [40] (circles) exhibit a τ which is orders of magnitude lower than that of Ref. [36] (squares), which means that the self-discharge in the former is much faster despite the fact that a narrower distribution of rates is reached faster. A combination of both, i.e. β approaching 1 and a large τ , would be more optimal. In fact, much of the understanding of how to suppress self-discharge has been guided by single exponential decay models ($\beta=1$), and works to achieve this goal by altering the surface physics or chemistry has been discussed in Refs. [39,48–50].

The current study has demonstrated that also the distribution of rate constants plays a significant role in the self-discharge. For example, if the major goal is to keep the voltage constant for long-term storage, and a fast, initial voltage drop is of no concern, it would be beneficial to utilize a small β . A small β corresponds to a distribution peaking at small rates, but with a very extended tail at larger rates. Under such circumstances, there would be an initial rapid voltage drop to about 37 % (corresponding to $1/e$) of the maximum value when $t=\tau$, after which the voltage remains nearly constant. In many cases the distribution of rate constants that can be obtained under different charging conditions is governed mainly by the pore distribution near the electrodes. A small β could possibly be manufactured using a pore distribution peaking at small pores, but with an extended tail also at higher pore sizes. This would be different from the standard approach where the pores are made as small as possible with a more or less random distribution about a mean. In general, it is highly likely that putting more efforts into engineering pore size distributions would allow one to control the self-discharge behaviour in a more controlled way.

Another issue of interest is to design supercapacitors which work over extended temperature regions. The results presented in Fig. 5 show that the distribution of rate constants does not change noticeably with temperature, while the time for crossover from superexponential to subexponential decay decreases as the temperature increases. Under these conditions, the maximum rate constant k_{fA} in Fig. 6 b) exhibits a Kramers-type activation behaviour. In order to make the self-discharge of a supercapacitor even more temperature-independent, one solution would be to try to increase τ such that the crossover from superexponential to subexponential decay occurs as slowly as possible. However, this is a very challenging task requiring optimal combination of pore volume, surface physics and electrolyte chemistry. It might be easier to engineer β alone, as this parameter might be controlled more directly by charge-accessible pore size for the charge. Figure 3 a) implies that longer holding times allow charges to rearrange and access more of the pore volume. If one could design for example the temperature-dependency of the electrolyte or the pore size distribution itself such that charges could properly rearrange and access more of the pore volume with increasing temperature, then one might expect β to increase

with temperature giving rise to a slower self-discharge. However, obtaining such a result without a corresponding decrease in τ is a very challenging task that is far outside the scope of this work.

5. Conclusion

A stretched exponential function is fitted to the experimentally obtained voltages for self-discharging supercapacitors. The results are interpreted in terms of distribution of rate constants. In all the analyzed cases, a wide distribution appears to occur for supercapacitors that were initially quickly charged, whereas for slow charging a narrower distribution appears. If the charging conditions are kept constant, the temperature does not alter the relative distribution of rate constants noticeably, while at the same time the decay modes are pushed from super-exponential to sub-exponential more quickly with increasing temperature. The method presented here to analyze self-discharging data from a supercapacitor could provide a quick and easy method to access useful information that governs internal behavior during decay. As such, the method might therefore become a useful tool that complement existing techniques.

Declaration of Competing Interest

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

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