

Linear and non-linear pseudocapacitance with or without diffusion control

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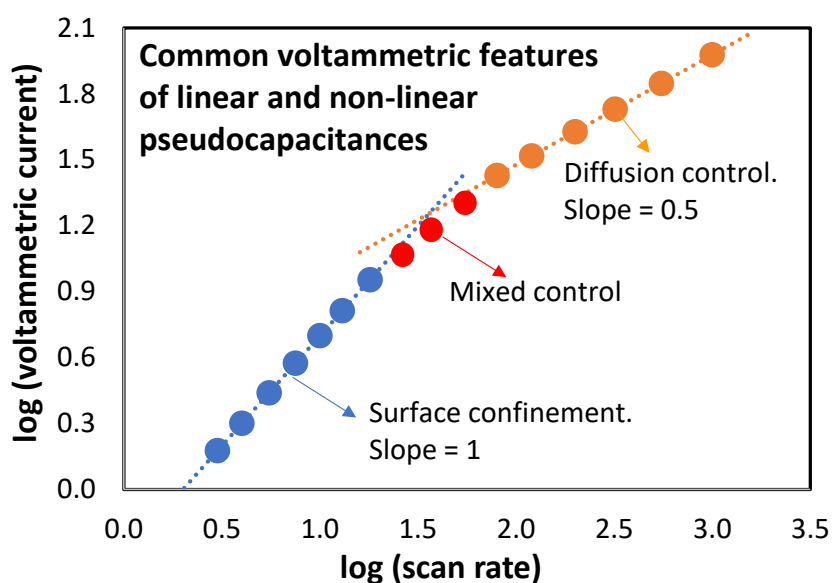
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Highlights

1. A redox active material electrode stores charge via either linear or non-linear pseudocapacitance or their combinations.
2. Pseudocapacitance, either linear or non-linear, can be influenced or controlled by diffusion through the redox material electrode.
3. Linear pseudocapacitance is featured by rectangular cyclic voltammograms in a wide potential range, contributing wholly or partly to energy storage in supercapacitors.
4. Nonlinear pseudocapacitance may lead to peak-shaped cyclic voltammograms in a narrow potential range, corresponding to rechargeable batteries and some supercapatteries.

ToC graphic and text



Capacitive redox active materials for supercapacitors exhibit linear pseudocapacitance, whilst Nernstian materials used in rechargeable batteries and some supercapatteries present non-linear pseudocapacitance. The voltammetric currents from both types of pseudocapacitance can vary linearly with either the potential scan rate or the square root of scan rate at relatively low or sufficiently high scan rates, respectively.

Abstract

Pseudocapacitance is an important reversible charge storage mechanism in many electrode materials. Although the concept was first proposed in early 1960s, it has been more widely studied following the observation of rectangular cyclic voltammograms (CVs) when testing some transition metal oxides and electronically conducting polymers, and the association with supercapacitor. However, interpretation of pseudocapacitance is inconsistent in the literature. Although all agree that materials are pseudocapacitive if they undergo Faradaic reactions and exhibit rectangular CVs, some have regarded any surface confined Faradaic reactions which may present non-rectangular or even peak-shaped CVs to be pseudocapacitive. In the case of rectangular CVs, the amount of charge stored in the electrode is a linear function of the electrode potential, whilst for non-rectangular or peak-shaped CVs, the relationship is non-linear. It is shown in this article that only **linear pseudocapacitance** is of relevance to supercapacitor, but **non-linear pseudocapacitance** may find applications in rechargeable battery and supercapattery. Further, it is clarified that the equation $i = k_1V + k_2V^{1/2}$ is useful in analysis of electrode kinetics in terms of surface confinement and diffusion control. However, this kinetic equation is blind to the thermodynamically determined charge storage mechanisms as shown by experimental evidence, and should not be used to differentiate non-capacitive Faradaic processes from pseudocapacitance, either linear or non-linear.

Keywords: Pseudocapacitance; Cyclic voltammetry; Galvanostatic charging and discharging; Supercapacitor; Rechargeable Battery; Supercapattery

1. Basics of electrode processes

In textbooks of electrochemistry, two basic electrode processes are commonly explained: (1) charging and discharging of the interface between the electrode and electrolyte in association with the concept of electric double layer (EDL) and the EDL capacitance, and (2) redox or Faradaic reactions on electrode that involve electron transfer crossing an interface and formation of new phases or new chemical species [1-4]. The EDL dis-/charging is widely regarded as physical changes in nature, whilst redox reactions on electrode are unambiguously chemical processes.

Traditionally, the interface refers to the “electrode | electrolyte” interface where electrode is usually an electronic conductor and electrolyte an ionic conductor. In many cases, electrode is a solid and electrolyte a liquid, but it is also possible, for example, to form an interface between a liquid metal and a solid electrolyte. There are more complicated interfaces, such as the “current collector (solid) | redox active material (solid)” interfaces that are present in an electrode loaded with mixed redox active material and conductive additive. In the latter case, the interfaces include those between the redox material and conductive additive, and also between the solid phases and the liquid electrolyte.

Electron transfer crossing an interface causes chemical changes plus an electric current flowing through the electrode, and is also known as a Faradaic process because the amount of electric charge transferred by electrons is proportional to the amount of chemical conversion in, on or near the electrode surface according to Faraday’s law for electrolysis. Historically, those Faradaic processes with appreciable reversibility were broadly represented by peak-shaped cyclic voltammograms (CVs) and plateau-shaped galvanostatic charging-discharging plots (GCDs) [1-4], and can generally be described according to the Nernstian equation. Such Nernst equation governed Faradaic processes are responsible for the discharging and charging reactions in conventional rechargeable batteries, and are termed as Nernstian reactions or processes [5,6].

However, as it is known now, Faradaic processes can also result in rectangular CVs,

resembling the property of an electronic capacitor [7-10]. This behaviour has been observed in a large number of transition metal oxides (TMOs), electronically conducting polymers (ECPs), and other semi-conducting redox materials [6-12]. Such capacitive Faradaic processes have been linked to the concept of pseudocapacitance that was however originally proposed to account for some experimental observations linked to electro-adsorption [13-16] which is irrelevant to supercapacitor.

On the other hand, the processes of EDL dis-/charging (or more generally the de-/adsorption of charged species or ions on the electrode surface) can also lead to a transit current flow without electrons transfer crossing the electrode/electrolyte interface. Such electrode processes are featured by either the absence of formation of new phases or atomic or molecular species, or the chemical change, if any, being likely potential dependent, instead of current driven. In other words, these processes do not follow Faraday's law and hence are non-Faradaic. The CVs and GCDs of EDL dis-/charging are rectangular and linear or triangular, respectively, exhibiting the same or comparable features as those of an electric capacitor.

It should be pointed out that both the EDL dis-/charging and Faradaic processes induce mass transport in the electrolyte to or from the electrode, which is undertaken by natural or forced convection, migration of charged species in the electric field between the positive and negative electrodes, and diffusion under a concentration gradient caused by composition changes near or inside the electrode. Of these three mass transport processes, the convection is ineffective in a sufficiently thin layer of solution next to the electrode surface or inside the pores of a porous electrode, whilst migration is minimised by using a sufficiently concentrated supporting electrolyte. Therefore, diffusion plays the major role of mass transport near the electrode surface or inside the layered or channelled pores of a porous electrode. When the composition variation near or inside the electrode is faster than what can be supplied by diffusion, the overall electrode process becomes limited or controlled by diffusion whose effect will be discussed later.

2. Confusion on pseudocapacitance

In principle, electrochemical energy storage (EES) can be achieved through any or a combination of the above mentioned reversible electrode processes for dis-/charging, but excludes irreversible (and poorly reversible) electron transfer reactions even though they are also Faradaic. Supercapacitors based on either or both of EDL capacitance and Faradaic capacitance, and rechargeable batteries utilising Nernstian reactions are good examples for EES. A more recent EES development is supercapatteries which include various ion capacitors, aiming to combine the merits of both capacitive and Nernstian processes [6].

Capacitive electrode processes can proceed via EDL dis-/charging without invoking electron transfer reactions, or be Faradaic in nature. The observation of capacitor-like or capacitive behaviour, i.e. rectangular CVs of many redox active materials such as hydrous RuO₂ and polypyrrole is of unambiguously Faradaic relevance [7,11,12]. The capacitance derived from capacitive Faradaic processes (in contrast to Nernstian Faradaic processes) should have been termed as **Faradaic capacitance**. Unfortunately, confusion started when the effort to understand such capacitive Faradaic processes was directed to "pseudocapacitance" that was originally proposed in place of "pseudocapacity" resulting from some reversible electro-adsorption processes which are typically featured by peak-shaped CVs [13-17]. In these early studies, the amount of charge, Q , passing through the electrode was plotted and analysed as a function of the electrode potential, E , in different electrolytes. The differentiation, dQ/dE , was used as an indicator for comparison. Because dQ/dE has the unit of capacitance ($C/V = F$), it is widely termed as **differential capacitance**, C_{dif} , in many electrochemical literatures [1-3]. These early studies also found that in the presence of electro-adsorption, the values of C_{dif} increased significantly in comparison with the EDL capacitance

values in the absence of electro-adsorption at the same potentials. To reflect this electro-adsorption caused change, pseudocapacity [13-15] and later **pseudocapacitance** or **adsorption pseudocapacitance**, C_{ads} were used to differentiate them from the true EDL capacitance [15-21]. A very important feature of C_{ads} is that it is an upward peak-shaped function of electrode potential, as shown in **Figure 1**, for a simple electro-adsorption reaction, $A^+ + e \rightleftharpoons A$, where A is adsorbed on electrode. Similar but downward peak-shaped profiles can be derived for electro-desorption. The combined profile of electro-adsorption and -desorption corresponds to a peak-shaped CV [15-21].

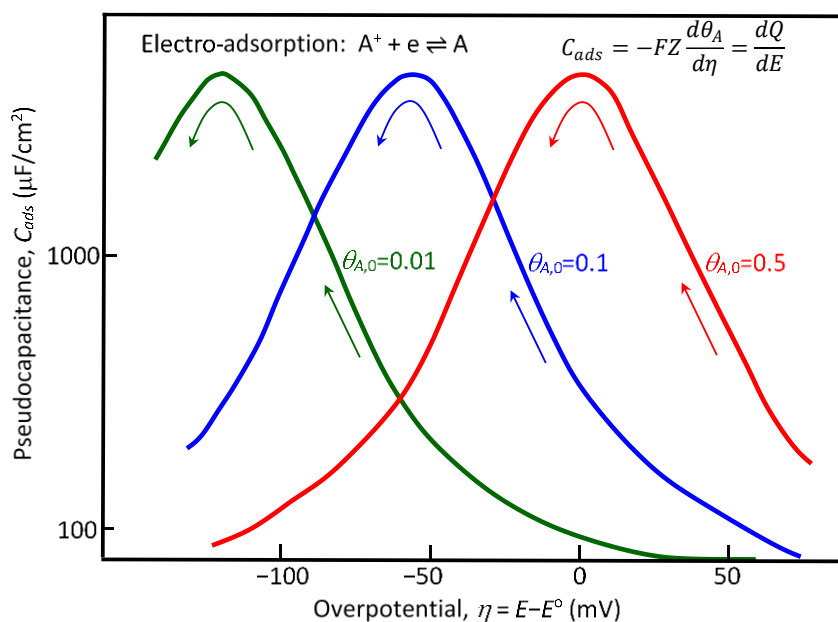


Figure 1 Profiles of pseudocapacitance of electro-adsorption, C_{ads} , versus electrode overpotential, $\eta = E - E^\circ$, according to the Bockris-Kita model [15] for a simple electro-adsorption reaction, $A^+ + e \rightleftharpoons A$, at different values of equilibrium adsorption coverage, $\theta_{A,0}$, as indicated. $C_{ads} = -FZ(d\theta_A/d\eta) = dQ/dE$ where the minus sign is because θ_A increases as η (or E) shifts negatively; F is the Faraday constant; Z the total number of reaction sites on electrode surface; θ_A the coverage of A adsorbed on electrode; $Q = ZF\theta_A$ the charge passed through electrode for $A^+ + e \rightleftharpoons A$. E and E° are the applied and equilibrium electrode potentials, respectively. (Redrawn according to reference [15])

In fact, the observations of capacitive or rectangular CVs of hydrous RuO_2 , polypyrrole and other redox materials [11,12, 18-23] are largely irrelevant to electro-adsorption, and the areal capacitance values (e.g. 1.0 F/cm^2) derived from these rectangular CVs are also much larger than the reported peak values of C_{ads} (e.g. 10^{-3} F/cm^2), although both have Faradaic origins. In order to differentiate the capacitive behaviour of these unique redox active materials from those in rechargeable batteries, and also those in EDL supercapacitors, the term pseudocapacitance was first, but unfortunately, linked to supercapacitor in early 1990s [21]. It must be acknowledged that the use of pseudocapacitance as a charge storage mechanism in supercapacitor has made great positive impacts on the development of supercapacitor electrode materials. This is evidenced by several high profile review articles on the topic of pseudocapacitance. However, the interpretations are not all consistent in terms of, for example, historical development, experimental observations and values of pseudocapacitance [7-10]. In the literature, all agree on that pseudocapacitance is non-EDL and results from Faradaic reactions. The main issue is that if pseudocapacitive materials should present

rectangular or peak-shaped CVs.

An early publication in which, for example, theoretically calculated peak-shaped CVs of “a single-state **surface process**” were attributed to pseudocapacitance [21]. This correlation was apparently based on that between reversible electro-adsorption on electrode and pseudocapacity or pseudocapacitance [13-16]. However, in the same paper [21], rectangular and approximately rectangular CVs with small-and-broad peaks were attributed to capacitance and pseudocapacitance, respectively, against poorly reversible peak-shaped CVs for battery electrode behaviour [21]. It was also suggested that “pseudocapacitance arises when, for thermodynamic reasons, the charge required for the progression of an electrode process is a continuously changing function of potential”, pointing out a deviation from EDL capacitive behaviour by showing remarkable “reversible redox peaks connected with pseudofaradaic reactions” [21,22].

A later and more widely used description is that pseudocapacitance results from “fast, reversible redox reactions at the surface of active materials”, in which successive electron transfer steps in a certain range of distributed potentials define the rectangular CVs similar to that of the EDL capacitance [23]. The emphasis on surface reactions was considered to be unnecessary, if the overall electrode process were not limited by “solid-state ion diffusion”, whilst causes for pseudocapacitance could be either intrinsic or extrinsic of the material [7]. It was also shown that combining the successive electron transfer steps with the respective Nernst equations could result in a broader current peak, but not a rectangular CV as that of the EDL capacitance. This theoretical analysis then led to a surprising claim that the so called pseudocapacitance was simply enhanced EDL capacitance when the active electrode material gained sufficiently high electronic conductivity upon a small amount of Faradaic reaction [24,25]. However, this claim is contradictory to previous studies revealing redox change in pseudocapacitive materials that were subjected to dis-/charging in the capacitive potential range (CPR). For example, RuO₂ and IrO₂ thin films were observed undergoing simultaneous electrochromic changes during potential cycling, indicating the variation of oxidation state [26]. Analyses of ECPs during potential cycling in the CPR by *in situ* electron spin resonance spectroscopy also provided clear evidence of electron transfer reactions [27-30].

The confusion on pseudocapacitance as mentioned above has been widely recognised [6,8,21,30-32]. Specifically, it was long ago pointed out that correlating a peak-shaped CV with pseudocapacitance and using the “charge/potential-range” ratio derived from the CV as capacitance are “not very useful or informative, and would be misleading” [21]. There were later efforts to clarify the differences between peak-shaped and rectangular CVs concerning pseudocapacitance, and to indicate the errors in energy calculations based on the “charge/potential-range” ratio of peak-shaped CVs [8,31].

However, these clarification efforts have achieved only a limited impact. For example, in a review published in 2020, it was stated that “pseudocapacitive materials store charge through battery-like redox reactions but at fast rates”, and often show “broad Faradaic charge-transfer peaks superimposed over a box-like” CV [33]. Similarly, in 2021, another high profile journal published a research article in which peak-shaped CVs and plateau-shaped GCDs were used to obtain the “charge/voltage-ratio” as the pseudocapacitance that reached 2568 F/g in a potential range as narrow as 0.375 V [34]. If a symmetrical supercapacitor were built from this material, the specific capacitance of the cell would be 642 F/g, corresponding to a specific energy value of 45.1 J/g = 12.5 Wh/kg. This energy capacity, assuming it could be practically achievable, is far from being a commercial interest. On the other hand, if one considers the charge capacity, instead of capacitance, the claimed maximum capacitance of 2568 F/g in 0.375 V is equivalent to a fairly decent charge capacity of 963 C/g or 268 mAh/g, whilst values over 400 mAh/g are not uncommon amongst recently reported new positive electrode materials.

3. Capacitive discharging and charging

The continuation of inconsistent interpretation of pseudocapacitance may have multiple causes, but it is mainly because pseudocapacitance has been classified, repeatedly in some influential publications, into the following three different sub-mechanisms [7,9,21,34,35]:

- (1) electro-adsorption and, a special case, underpotential deposition,
- (2) intercalation, and
- (3) surface redox reactions.

In fact, these three mechanisms are all well reported for electron transfer reactions on electrode and identified in the literature of electrochemistry. However, their scientific and more importantly technological links are absent or very weak to supercapacitor as explained below.

The most important difference between supercapacitor and rechargeable battery is that the former can be assessed by both capacitance and charge capacity, but the latter only by charge capacity. By definition, a supercapacitor is still a capacitor and capable of dis-/charging in the same way as a conventional electronic or electrolytic capacitor, i.e. **capacitive dis-/charging**, but the capacitance, C , and energy capacity, W , of the supercapacitor is much larger than that of the conventional capacitor by several orders of magnitude. According to basic capacitor physics [5,6], W , is linked to C and the maximum working voltage, U_{max} , of the supercapacitor (a two-electrode cell) by the simple equation (1).

$$W = \frac{CU_{max}^2}{2} \quad (1)$$

The validity of equation (1) is based on at least three criteria or requirements as listed below, which can be applied to judge if a device is or is not a supercapacitor.

(i) C is a constant and independent of the cell voltage, U , that varies between 0 and U_{max} during dis-/charging [5,35].

(ii) Because $C = Q/U$ by definition, where Q is the amount of charge stored in or discharged from the supercapacitor, the ratio of Q/U must also be constant and independent of U .

(iii) The independence of C on U is equivalent to high reversibility of the respective electrode processes, which is the fundamental cause for supercapacitor to have fast dis-/charging rates, long cycle life, and high energy efficiency.

In experimental terms, the requirement of constant capacitance by equation (1) dictates that a supercapacitor must exhibit rectangular CVs. This is because the constant capacitance, C , dictates a constant current, i , on the CV of a capacitor or supercapacitor according to equation (2).

$$C = \frac{Q}{U} = \frac{dQ/dt}{dU/dt} = \frac{i}{v} \quad (2)$$

where v and i are the voltage scan rate and the current on the CV, respectively. Note that in equation (2) the signs of v and i must be the same to maintain a positive value of C . In other words, a positive v (i.e. the scan increases the voltage) leads to a positive i , but when the scan direction is reversed to give a negative v (decreasing voltage), the current jumps from positive to negative as well, which results in the sharp current drop at the high voltage end of the CV. The opposite occurs during the negative voltage scan. Also, in the CV experiment, v is constant which means i must also be constant because C is constant. These two features of equation (2) lead to a rectangular CV.

Equation (2) also governs the features of the galvanostatic charging-discharging plot (GCD).

In a GCD measurement, the current, i , is constant which means $v = dU/dt$ must also be constant because C is constant, dictating a linear voltage-time profile on which the gradient (dU/dt) is positive for charging (increasing voltage) or negative for discharging (decreasing voltage) of the supercapacitor. The overall profile from consecutive dis-/charging is therefore triangular in shape. These features on the CV and GCD of a supercapacitor as dictated by equations (1) and (2) are rarely observed in the CV and GCD measurements of conventional rechargeable batteries [6,8], but may or may not be seen in those of supercapatteries which are hybrid devices combining supercapacitor and battery electrodes [6,30].

Because equation (1) is not applicable to peak-shaped CVs and non-linear or plateau-shaped GCDs, such as those from rechargeable batteries and some supercapatteries [6], calculations of the energy capacity of the respective devices have to use the general equations (3) and (4) below for the charging sections of CVs and GCDs, respectively.

$$W = \int_0^{U_{max}} i(t)U(t)dt = v \int_{U_0}^{U_{max}} i(t)tdt \quad (\text{CV}) \quad (3)$$

$$W = \int_0^{U_{max}} i(t)U(t)dt = i \int_0^{U_{max}} U(t)dt \quad (\text{GCD}) \quad (4)$$

It is worth noting that equation (1) can be derived from either equation (3) for a rectangular CV or equation (4) for a linear GCD because in both cases $i(t)$ is a constant, and $U(t) = (dU/dt)t = vt$ is a linear function of time, t , which means $i/(dU/dt) = i/v = C = \text{constant}$ [35]. However, for a peak-shaped CV, equation (3) does not give a simple solution, whilst for a non-linear GCD, the result from equation (4) is proportional to the area under the plot.

Figure 2 illustrates two commonly reported non-linear GCDs in comparison with the linear GCDs that are expected from ideal supercapacitors. The two non-linear GCDs are very much the same as the respective experimentally recorded GCDs [36,37]. For the supercapacitor GCDs, the maximum cell voltage and the dis-/charging times are taken to be the same as the counterparts of the respective non-linear GCDs.

It should be pointed out that in these GCD experiments, discharging has reached 0 V, which results from the use of an externally forced discharging method as a common practice in laboratory. However, discharging to 0 V is in fact not possible nor recommended for most, if not all, electrochemical energy stores in practical uses. This is because, for example, a minimum amount of energy must be left in the store to drive the assisting electronic accessories. Also, rechargeable batteries will undergo irreversible electrode reactions if discharging reaches below a minimum voltage which is, for example, about 3.0 V for a lithium ion battery.

Figure 2a shows a commonly reported GCD from an asymmetrical supercapacitor tested beyond the maximum voltage [36]. It can be estimated that the discharging charge, Q_d , which is proportional to the discharging time, is about 72% of the charging charge, Q_c , which means a columbic or charge efficiency of $(Q_d/Q_c) \times 100\% = 72\%$. More importantly, the charging area is more than twice larger than the discharging area, indicating an energy efficiency of less than 50%. If one uses the Q/U ratio ($Q = it$) of the charging section as the capacitance, and equation (1) to calculate the energy input during charging, the result is in fact the area of the triangle on the left side. This is a significant underestimate of the actual energy input. Similarly, if one uses the Q/U ratio of the discharging section as the capacitance, the energy output according to equation (1) is the area of the triangle on the right side, which is an obvious overestimate of the true energy output.

The GCD in **Figure 2b** represents a special case of supercapattery with a battery positrode (= positive electrode) and a supercapacitor negatrode (= negative electrode) [37]. Again, it can be estimated from this GCD that the columbic efficiency is about 69%, whilst the energy efficiency is lower than 50%. Using the Q/U ratio as the capacitance, and equation (1) to calculate the energy

capacity, the results are the areas of the two triangles. It can be seen that in this case the areas under the non-linear GCD for both charging and discharging are larger than those of the two triangles, suggesting serious underestimates of the actual energy input and output of the cell.

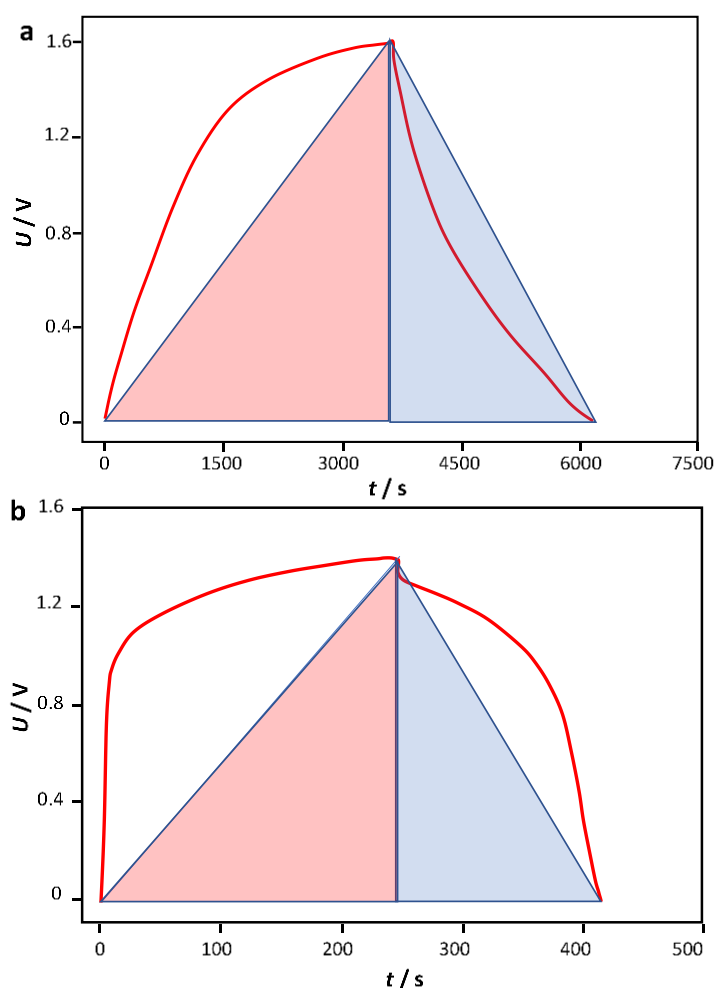


Figure 2 GCDs of (a) an asymmetrical supercapacitor [36] and (b) a supercapattery [37]. The area of shaded triangle is the energy input (light red) or output (light blue) predicted by equation (1) using the charge / voltage ratio as the cell capacitance. (Redrawn according to references [36, 37].)

In both examples of **Figure 2**, the columbic efficiency is higher than the energy efficiency. This is in fact very common for all types of electrochemical energy stores that exhibit non-linear GCDs. In externally forced dis-/charging experiments such as the GCD test, it is possible to achieve high columbic efficiency, approaching 100% in properly designed and constructed supercapacitors and batteries. High columbic efficiency often translates to high energy efficiency in supercapacitors in which the electrode processes are highly reversible. However, the same does not apply to rechargeable batteries in which the reversibility of electrode reactions is often compromised by kinetic complications. For supercapacitors, it is common for the energy efficiency to be higher than 90%, but batteries can rarely reach beyond 70% in energy efficiency.

In summary, equation (1) is only valid for capacitive dis-/charging which can only occur in materials that can exhibit rectangular CVs and linear or triangular GCDs. If one uses the Q/U ratio derived from peak-shaped CVs or non-linear GCDs as the capacitance, the use of equation (1) for the

calculation of energy capacity can lead to significantly erroneous and misleading results.

4. Single electrode analysis

Equation (1) is not directly applicable to a single electrode, even if the cell voltage, U , is replaced by the electrode potential change, ΔE . This is because although an electrode can store electric charge, the stored charge is only able to do work, i.e. to store or release energy, when it flows through an external circuit driven by a voltage against another electrode. In electrochemical measurements, the behaviour of a single electrode, i.e. the working electrode, is explored against the counter and reference electrodes in the so called three-electrode cell. In this way, the potential of the single or working electrode, E , is controlled against the reference electrode, but the current flowing through the working electrode is controlled against the counter electrode. As a result, the potential change of the working electrode against the reference electrode has a different value from that against the counter electrode. More importantly, in principle, the potential change of the working electrode is accompanied by a near-zero current flowing through the reference electrode, and hence near-zero energy is stored or released between these two electrodes. Between the working and counter electrodes, there is a current flow, but the voltage between these two electrodes is not known or uncontrolled. Further, the counter electrode is usually inert and enables whatever electrochemical change possible in the electrolyte to maintain the current flow. Of course, it is possible to make the counter electrode from a charge storage material, but this approach requires more complicated instrumental set up [38].

Nevertheless, replacing U by ΔE enables equation (2) to suit a single electrode. If C_+ and C_- denote the capacitances of positive and negative electrodes, respectively, in a supercapacitor, they should allow the calculation of the supercapacitor capacitance, C , and energy capacity, W , according to equations (5) and (1), respectively.

$$\frac{1}{C} = \frac{1}{C_+} + \frac{1}{C_-} \quad (5)$$

Equation (5) is simple but powerful for judging if an electrode material can be used or more suitable for making supercapacitor or superbattery or battery. This is because equation (5) applies a clear and strict requirement on the correlation between individual electrode capacitances and the cell capacitance, and hence the energy capacity of a supercapacitor. The argument is straightforward: if either or both of C_+ and C_- are variable with electrode potential, C is most likely variable with the cell voltage according to equation (5). A variable or voltage dependent C cannot satisfy equation (1) and the respective device is not a supercapacitor. (It is acknowledged that mathematically, the variations of C_+ and C_- may be coordinated in such a way, e.g. $C_+ = CC_-/(C_- - C)$, that equation (5) produces a constant C , but such a situation is almost impossible in practice.) Therefore, for assembling a supercapacitor, equation (5) excludes any type of electrode on which the ratio of $Q/\Delta E$ changes significantly upon potential variation. Peak-shaped CVs and plateau-shaped GCDs represent significant variation or dependence of $Q/\Delta E$ upon potential change, which is why such electrochemical features are regarded non-capacitive, and the respective electrode materials are not suitable or qualified for use in supercapacitor [8,21,31].

With the restrictions of equations (1) and (5) as explained above, it is clear why rectangular CVs and linear or triangular GCDs are crucial to judge if an electrode material is capacitive and if it is suitable for supercapacitor application. These restrictions, however, do not affect using those materials exhibiting peak-shaped CVs and non-linear GCDs for making the electrodes in batteries or superbatteries. Many such redox active or Nernstian materials are capable of fast dis-/charging

and long time cycling in comparison with traditional battery electrode materials. They also work well when coupled with capacitive materials in supercapatteries. It is just that they are non-capacitive and hence not suitable for use in supercapacitors. The device made from these materials are better called battery or supercapattery, but not supercapacitor.

Because electro-adsorption (including underpotential deposition) processes are featured by their peak-shaped CVs and non-linear GCDs, they are Nernstian but non-capacitive, and hence cannot be used for making supercapacitors. The association of electro-adsorption with pseudocapacitance has its historical reason as discussed above, but such defined pseudocapacitance is irrelevant and meaningless to supercapacitors. Particularly, it is confusing and misleading to associate the Q/U ratio of the overall process of electro-adsorption with the concept and unit of capacitance in the context of electrochemical energy storage.

The same issue applies to the claimed **intercalation pseudocapacitance**. Intercalation refers originally to the reversible insertion of ions between the layers of a layer-structured material, such as TiS_2 , graphite and LiCoO_2 , to maintain electric neutrality in the electrode when it is dis-/charged upon electro-oxidation or -reduction. However, also due to the electric neutrality principle, reversible ion insertion also occurs in non-layer or -channel structured or even amorphous redox active materials on electrode, such as hydrous RuO_2 and polypyrrole. In the latter cases, intercalation has also been used commonly (along other terms, e.g. doping), although the mechanism for ion insertion differs significantly from the original proposal. For example, graphite and LiCoO_2 are very selective or preferable for Li^+ ions to intercalate, and the Li^+ ions in the layered structure are de-solvated. However, the insertion of proton into RuO_2 is facilitated by the water molecules in the hydrous oxide phase, whilst polypyrrole and other conducting polymers are much less selective and allow the reversible insertion of almost all sorts of small anions.

Nevertheless, if one only considers the claim of intercalation pseudocapacitance in relation with layered or channelled structures of transition metal compounds [7,35], the respective CVs are peak-shaped and GCDs are plateau-shaped as confirmed by both experimental tests and theoretical simulations [39-43], which are typical Nernstian features. **Figure 3a** shows simulated CVs of differently sized LiMn_2O_4 particles with clear current peaks [43], and **Figure 3b** compares the GCDs of bulk and nanoparticulate LiCoO_2 samples of which most show a potential plateau [40]. It is worth mentioning that lithium ion intercalation occurs in a large number of layer- or channel-structured materials without changing the structure or phase of the host material. In other words, intercalation is a homogeneous reaction which can fit well with the Nernst equation.

The research [40] also found that the GCDs changed from plateau-shaped (Nernstian) to linear (capacitive) when the LiCoO_2 samples changed from crystalline bulk to nanoparticles, see **Figure 3b**. However, EDL contribution was excluded as the cause according to estimated specific surface of the samples. This apparent Nernstian to capacitive transition was accompanied by a significant loss in discharging potential and capacity, whilst similar transitions were also observed when larger particles were discharged at higher rates (currents) [40]. It was attributed to the different structures (larger interlayer gaps) and compositions (ratio of $\text{Li}/\text{Co} > 1$) in the surface layers of the LiCoO_2 samples, whilst the effect of such differences increases with decreasing the particle size [40]. Therefore, it is more likely that the apparent capacitive behaviour could have resulted from the loss of intercalation, instead of intercalation pseudocapacitance.

Interestingly, on the contrary, the CVs in **Figure 3a** show an opposite phenomenon with the current peaks becoming sharper, i.e. more Nernstian, when decreasing the nanoparticle size. Therefore, it remains inconclusive that reducing the nanoparticle size of a lithium ion intercalation host material or other types of charge storage material could cause the so called extrinsic pseudocapacitance [7,10,23,33].

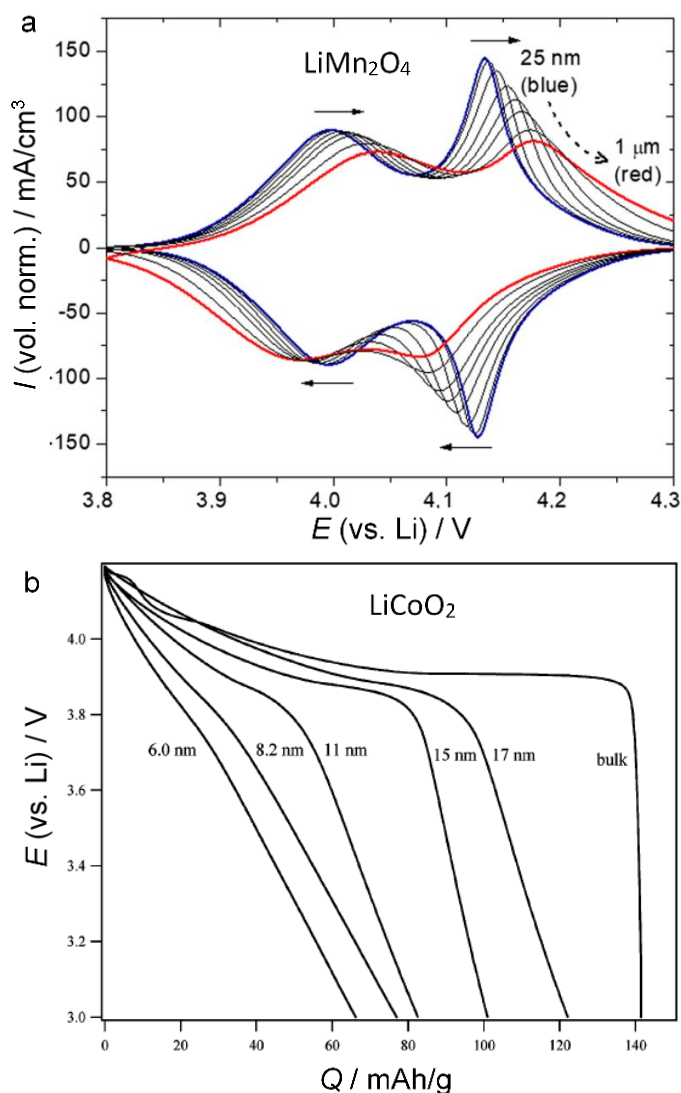


Figure 3 (a) Simulated CVs of differently sized nanoparticles of LiMn_2O_4 (the current is normalised over the nanoparticle volume) [43] and (b) experimentally recorded GCDs of differently sized nanoparticles of LiCoO_2 [40]. Note the gradual increase of the Nernstian feature, i.e. the current peaks on the CVs of LiMn_2O_4 , but the opposite transition, gradual disappearance of the potential plateau, on the GCDs of LiCoO_2 when the size of the respective nanoparticles decreases. (Adopted with modification from references [43] and [40] with permission from Springer Nature and the American Chemical Society, respectively.)

5. Surface confined and diffusion controlled processes

The association of pseudocapacitance with surface redox reactions is highly ambiguous because the definition of surface can vary. Underpotential deposition can surely be seen as a surface redox reaction if the surface refers to that of the electrode substrate (or current collector), but it is however non-capacitive as discussed above. The surface may refer to the “interface” between the liquid electrolyte and the active material attached to the electrode substrate. Apparently, intercalation occurs from the “interface” into the body of the active materials with layered or channelled structures, and hence should not be regarded as surface redox reactions. More importantly, in many widely recognised pseudocapacitive metal oxides and conducting

polymers, redox reactions occur not only on the surface (or “interface”) but also throughout the body of the material, accompanied by reversible insertion of charge balancing ions.

The association of pseudocapacitance with the surface reaction was re-interpreted recently to state that the surface restriction is unnecessary as long as the overall electrode process is not limited by “solid-state ion diffusion” [10]. The emphasis on solid-state diffusion or diffusion in general might have evolved from the use of one of the two equivalent equations (6) and (7) below to differentiate between pseudocapacitance (claimed to be surface confined) and non-capacitive Faradaic charge storage (diffusion controlled) mechanisms in redox active materials whose CVs are typically non-rectangular or peak-shaped [10,33,34].

$$i = k_1 v + k_2 v^{1/2} \quad (i/v^{1/2} = k_1 v^{1/2} + k_2) \quad (6)$$

$$i = a v^b \quad (\log i = \log a + b \log v) \quad (7)$$

where i is the current on, and v the potential scan rate of the CV. k_1 , k_2 , a and b ($= 0.5$ to 1.0) are constants and can be derived from plotting experimental data according to the rearranged forms of equations (6) and (7) as shown in the brackets. As a matter of fact, these two equations have long been established for analysis of complex electrode processes involving parallel surface confined ($k_2 = 0$ or $b = 1$) and diffusion controlled ($k_1 = 0$ or $b = 0.5$) electron transfer processes [44-48]. These two parallel processes can be Faradaic or non-Faradaic, and may be different processes, or the same reaction at different sites on/in the electrode. In particular, the electrode is coated with a porous or permeable film with or without redox activity, and investigated by cyclic voltammetry in a sufficiently wide range of potential scan rates. When $k_2 = 0$ or $b = 1$, the electrode process is surface confined or controlled by electron transfer at the electrode | electrolyte interface, or within the surface coating. If $k_1 = 0$ or $b = 0.5$, the electrode process is diffusion controlled. In some cases, both terms of equation (6) are present to form a mixed control of the electrode process, which is equivalent to a value of b between 0.5 and 1 .

Of many redox active coatings on electrode, the CVs show surface confined currents at low potential scan rates, and then transit to diffusion controlled currents at high scan rates. **Figure 4a** presents an example of peak-shaped CVs from a Nernstian organic-inorganic hybrid coating on electrode [45]. The inset in **Figure 4a** plots the peak current, $I_{p,a}$, against v on the logarithmic scale, revealing clearly the transition from surface confinement at low scan rates ($b = 0.98$) to mainly diffusion control ($b = 0.55$) at higher scan rates. Apparently, deviation of b from the ideal values of 1.0 and 0.5 reflects the minor contribution of diffusion and surface process to the overall current on the CVs. It is noted that this transition occurs to the same Nernstian (= non-capacitive Faradaic) reaction inside the coating. A question is what relation could be between these CVs and pseudocapacitance, or if this material should be regarded as being pseudocapacitive. However, it is clear that this ferrocene containing material is non-capacitive and cannot be used for making a supercapacitor.

As explained above, equations (6) and (7) apply to any electrode process that may involve either or both of surface confined and diffusion controlled contributions. The Nernstian process is shown clearly by **Figure 4a** to suit well equations (6) and (7). For the capacitive process, **Figure 4b** confirms the co-existence of surface confinement and diffusion control in the composite film of a conducting polymer, poly[3,4-ethylene-dioxythiophene] (PEDOT), with nanostructured carbons [48]. In this case, near-ideal rectangular CVs were recorded on the symmetrical cells of the composite in a cell voltage window of 0.5 V.

Obviously, dis-/charging of the composite films should include both EDL capacitance (e.g. from the nanostructured carbon) and capacitive Faradaic reactions (in PEDOT). As expected, the analysis of the current on the rectangular CVs at different scan rates according to equation (6)

revealed a notable diffusion contribution to the overall capacitive current on the rectangular CV. In **Figure 4b**, it is also interesting to note that extracted non-diffusion CV seems not to be as rectangular as the overall CV. This observation makes it unreasonable to claim the diffusion contribution to be from the non-capacitive Faradaic or battery behaviour [33].

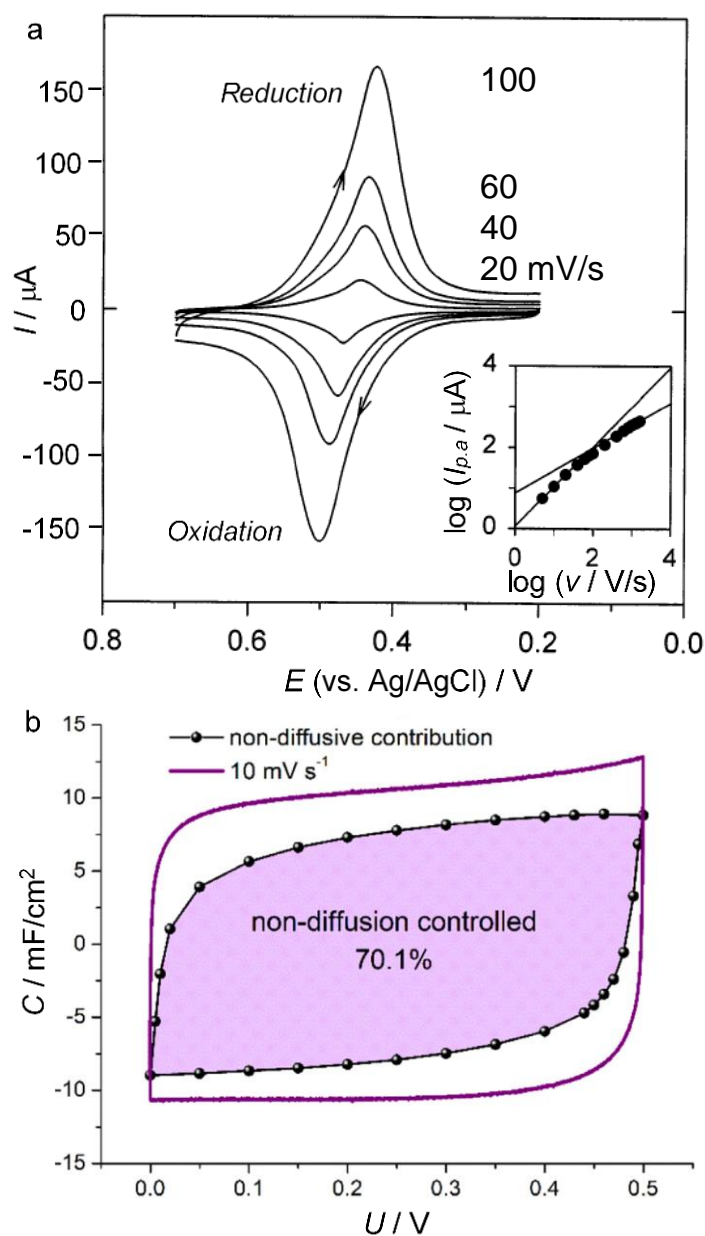


Figure 4 (a) CVs of a ferrocene containing organic-inorganic copolymer film in aqueous 0.1 mol/L KNO_3 , pH 4 at indicated potential scan rates [45]. The inset plots the peak current vs. potential scan rate at the logarithmic scale. (b) A CV of the symmetrical supercapacitor cell of a composite film of PEDOT and nanostructured carbon in aqueous 0.5 mol/L MgSO_4 [48]. The shaded area (labelled with non-diffusion controlled) is calculated according to equation (6). (Adopted with modification from references [45] and [48] with permission from Elsevier.)

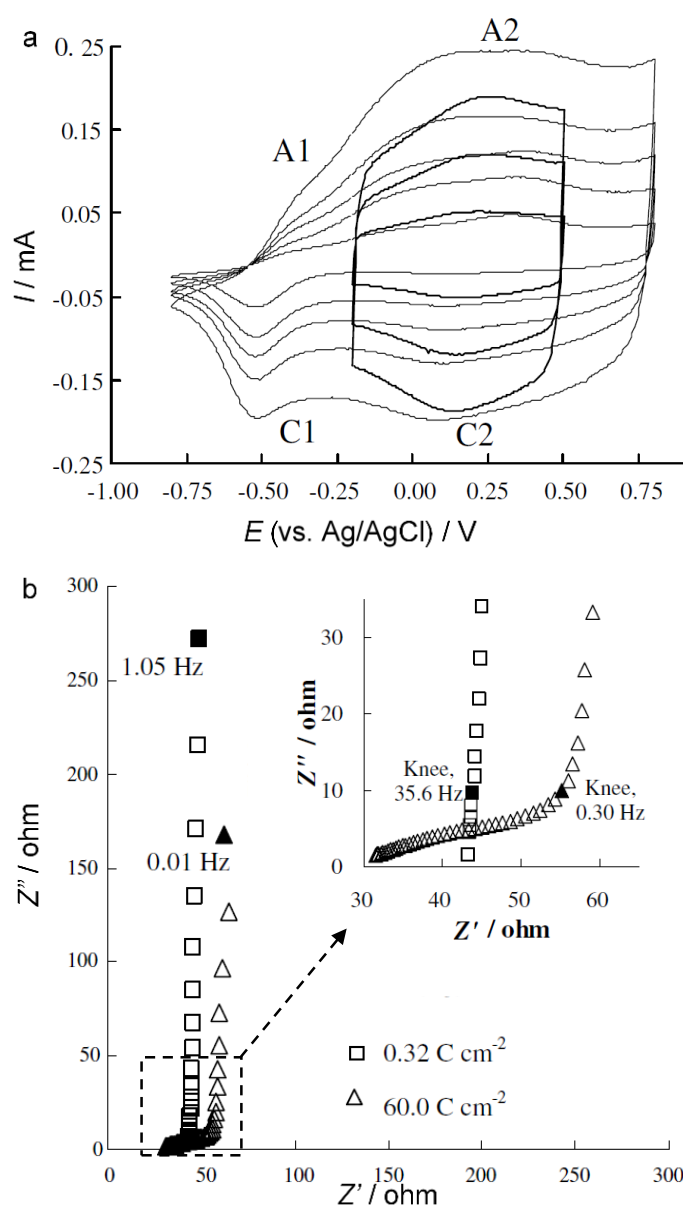


Figure 5. (a) CVs of an electrodeposited thin PEDOT film (deposition charge: 0.32 C/cm^2) recorded in a wide potential range (300, 150, 100, 50 mV/s) and a narrow potential range (300, 200, 100 mV/s) in an acetonitrile solution of 0.5 mol/L LiClO_4 . The currents on both sets of CVs increased linearly with potential scan rate. (b) EIS plots of the PEDOT film in (a) and a much thicker one (deposition charge: 60 C/cm^2) in an aqueous 0.5 mol/L KCl. The inset in (b) is an expanded view of the section at high frequencies. (Adopted with modification from reference [49] with permission from Elsevier.)

The transition from surface confinement to diffusion control can also occur when the coating becomes thicker due to the increased length and time for charge balancing ions to transport through the coating. This change is not convenient to demonstrate by CVs, but can be easily identified by electrochemical impedance spectrometry (EIS) or AC impedance analysis. **Figure 5a** presents the CVs of a thin coating of PEDOT in a wide potential window and a narrow one. The currents on both sets of CVs were proportional to the scan rate, indicating no or little diffusion influence. However, only the narrow window CVs were sufficiently rectangular.

Figure 5b compares the AC impedance plot of the thin coating with that of a much thicker one. Both coatings showed a low frequency vertical line resulting from capacitive dis-/charging, but the thick coating also exhibited a sloped and approximately linear region that is indicative of mixed control of ion transfer crossing the PEDOT | electrolyte interface and diffusion within the PEDOT coating at high frequencies [49]. However, this diffusion controlled process is simply a part of the capacitive dis-/charging of the thick PEDOT film and has no relevance to battery-like behaviour.

The above discussion suggests that equations (6) and (7) are useful in the kinetic analysis of electrode processes in terms of surface and diffusion controls. Results from such analyses can also be used to infer, for example, the porous structure or permeability of the electrode coating and the size and solvation of the insertion or intercalation ions. However, equations (6) or (7) alone cannot tell which of the electrode processes is capacitive or non-capacitive, or EDL or Nernstian.

6. Origin of pseudocapacitance

Research efforts are continuing to clarify the confusion around the concept and causes of pseudocapacitance. Whilst all agree that redox active materials exhibiting rectangular CVs are pseudocapacitive, some have claimed the three sub-mechanisms as discussed in Section 3. Of these two opinions, the one that emphasises rectangular CVs and linear or triangular GCDs needs a convincing explanation for the origin [5,6,8,23,50-57]. A plausible hypothesis is that pseudocapacitance could have originated from partially or zone delocalised valence electrons that exist in many semiconducting materials whose properties are governed by the band model [6,50-52]. Localised valence electrons exist in molecules and ions dissolved in solution, and in insulating redox active materials. They have the same singular or widely separated energy levels, relating to one or a few particular redox potentials and hence single or multiple current peaks on CVs. On the contrary, delocalised valence electrons are present in semiconducting materials such as transition metal oxides and electronically conducting polymers. They possess a large number of closely spaced energy levels that join into a band, corresponding to a wide potential window in which electron transfer occurs consecutively and continuously, leading to the constant current on a rectangular CV [6]. Studies on different heteroatoms doped graphenes by DFT modelling provided strong evidence supporting the delocalisation hypothesis [53-55]. The delocalisation hypothesis was also considered in a recent successful modelling study of the rectangular CVs of pseudocapacitance in terms of multiple redox reactions [56]. In fact, multiple redox reactions were previously considered to be responsible for the rectangular CVs of pseudocapacitance [23] and supported by modelling studies, for example, of manganese dioxide [57]. Continuing and supporting these modelling efforts are very much needed for better understanding of pseudocapacitance so that design and synthesis of the respective materials can truly benefit the development of high energy density supercapacitors.

On the other hand, it should be acknowledged that materials exhibiting peak-shaped CVs with improved dis-/charging rate and cycling stability are equally, if not more, important than those showing rectangular CVs for electrochemical energy storage. It is however more appropriate to evaluate such materials by specific charge capacity (mAh/g or C/g) for application in battery or supercapattery. Also, some materials exhibiting non-rectangular or broad-peak-shaped CVs in a wide potential window may show rectangular CVs in a narrower window as evidenced in **Figure 5a** for PEDOT. Similar changes were also observed in other redox active materials, such as NiO [58], MnO₂ [59] and polyaniline [60], emphasising the importance to relate capacitive properties with the CPR, capacitive potential range.

Last, but not the least, to avoid future confusion, it may be worth a terminological differentiation between the pseudocapacitance associated with rectangular CVs and that with non-rectangular or peak-shaped CVs. As indicated by the title of this article, the author would like to

propose **linear pseudocapacitance** for the former, and **non-linear pseudocapacitance** for the latter. This is because the charge capacity varies linearly with electrode potential for the former, but not for the latter. Strictly speaking, only materials of linear pseudocapacitance can be used to make a supercapacitor with equations (1) and (5) as the criteria. For the measurement of the overall performance, the various units for capacitance, e.g. F, F/g and F/cm², can be used for linear pseudocapacitance. However, for non-linear pseudocapacitance, it is more appropriate to use the charge capacity units, such as C, Ah and mAh/g. Table 1 compares the main features of linear and non-linear pseudocapacitances.

Table 1. Comparison between linear and non-linear pseudocapacitances

Categories	Linear pseudocapacitance	Non-linear pseudocapacitance
Charge	Linear dependence on potential	Non-linear dependence on potential
CV shape	Rectangular	Non-rectangular or peak-shaped
GCD shape	Linear or triangular	Non-linear or plateau-shaped
Example units	F, F/g, mF/cm ²	C, Ah, mAh/g
Mechanism	Capacitive charging and discharging	Nernstian charging and discharging
History	Supercapacitor development, 1970s	Reversible electro-adsorption, 1950s
Terminology	Capacitor-like behaviour, redox capacitance, pseudocapacitance, electrochemical capacitance.	Battery-like behaviour, pseudocapacity, (adsorption) pseudocapacitance, electrochemical capacity.
Application	Supercapacitor or supercapattery	Rechargeable battery or supercapattery

7. Summary

A supercapacitor is still a capacitor and stores electric charge and energy according to the same principle. It is widely accepted that supercapacitor can be based on two different types of capacitance: non-Faradaic electric double layer capacitance and pseudocapacitance which is Faradaic in nature. A widely accepted and un-argued interpretation is that pseudocapacitance is a Faradaic process that exhibits capacitor-like features, typically rectangular CVs and linear or triangular GCDs. The other interpretation is linked with not only capacitor-like, but also battery-like performances, including peak-shaped CVs and plateau-shaped or non-linear GCDs. To avoid confusion, it is proposed to use **linear pseudocapacitance** for rectangular CVs and linear GCDs, and **non-linear pseudocapacitance** for non-rectangular CVs and non-linear GCDs.

The concept of pseudocapacitance has indeed been used by many authors (but not all) to describe some surface confined electron transfer reactions, starting from reversible electro-adsorption in the 1960s, although a recently recommended restriction states the “absence of solid state diffusion” influence. This restriction basically makes pseudocapacitance the same as what is known as surface confined processes, e.g. Faradaic reactions in a thin coating on electrode. Note that thin coating here means the absence of diffusion influence. However, because many surface confined processes are Nernstian in nature, and exhibit peak-shaped CVs and non-linear GCDs, using the corresponding $Q/\Delta E$ ratio as the electrode capacitance may lead to erroneous calculation of the energy capacity of a cell with one or two such electrodes. It is particularly misleading when ΔE is very narrow (< 0.5 V), and used together with small to moderate charge capacity to achieve very high $Q/\Delta E$ ratios as electrode capacitance and then to claim applicability in supercapacitor.

The correlation between pseudocapacitance and surface confined process is still problematic in the context of supercapacitor. Exclusion of diffusion contribution from capacitive

charge storage does not agree with the working principle of supercapacitor. This is because diffusion control and surface confinement are both kinetic phenomena, but specific capacitance, like specific charge, has a thermodynamic origin. In other words, diffusion can influence on, but not be excluded from capacitive charge storage measurements. In line with this understanding, the kinetic equation, $i = k_1v + k_2v^{1/2}$, is blind to thermodynamic properties, and should not be used to differentiate capacitive and non-capacitive contributions to the overall dis-/charging current on an electrode. There is a plenty of experimental evidence showing diffusion controlled or influenced capacitive charge storage, and surface confined battery behaviour [46-49,60,61]. Also, diffusion control is inevitable when dis-/charging EDL electrodes of thick layers of nanostructured carbons [62,63].

It is acknowledged that the accuracy of a practical measurement of any thermodynamic property always depends on the conditions that affect the kinetics of the process on which the measurement is based. The same applies in measurements of the specific charge capacity or specific capacitance of any charge storage material coated on electrode. It is always possible to enhance either surface confined or diffusion controlled contribution by varying, for example, the coating thickness, the speed of dis-/charging, or even the electrolyte composition. This practicality does not change the thermodynamic nature of specific capacity or capacitance, but it should be included in consideration of kinetic effects on the measured thermodynamic values.

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