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Double-layer and pseudocapacitance types of electrochemical capacitors and their applications to the development of hybrid devices

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Abstract The basis of the complementary use of electrochemical capacitors (so-called supercapacitors) in hybrid electric power generation by rechargeable batteries and fuel cells is explored. Electrochemical capacitors are of two types: one where the interfacial double-layer capacitance of high specific area carbon materials is the basis of electric charge storage (as ions and electrons); and the other where pseudocapacitance, associated with electrosorption and surface redox processes at high-area electrode materials, e.g. RuO_2 , or at conducting polymers, provides the basis of charge storage. The former, double-layer, type of capacitance stores charge non-faradaically while the latter type, pseudocapacitance, stores charge indirectly through faradaic chemical processes but its electrical behaviour is like that of a capacitor. Two types of hybrid battery/capacitor system are recognized: one based on combination of an electrochemical capacitor cell with a rechargeable battery or a fuel cell in a load-leveling function, e.g. in an electric vehicle power train; and the other based on combination of a faradaic battery-type electrode coupled internally with a capacitive electrode in a two-electrode hybrid module (termed an asymmetric capacitor). Optimization of operation of such systems in terms of balancing of active masses, of power and charge densities, and choice of maximum but limited states-of-discharge, is treated.

Keywords Double-layer capacitance · Electrochemical capacitors · Pseudocapacitance

Dedicated to Prof. Wolf Vielstich on the occasion of his 80th birthday in recognition of his numerous contributions to interfacial electrochemistry.

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Introduction

While the concept of fuel cells originated with Sir William Grove [1] in England in 1839 as his “gas” battery, the field experienced a lengthy period of gestation until the commencement of the pioneer work of Bacon in the 1940s, with its extension to the USA soon after through Pratt and Whitney and its associate company, Leesona Moos. Parallel activities were developing in Germany by Justi and at other companies in the US in the 1950s and 1960s, e.g. Sun Oil and American Cyanamid, that pioneered the use of flexible Teflon-bonded carbon electrodes with Pt loading. A major development arose with the invention of the ion-exchange Nafion polymer electrode, coated with Pt and other activating metals, e.g. Ru, in the PEM technology by General Electric in the Gemini Project [2].

In the earlier and ensuing years of fuel-cell development, Vielstich made major contributions to this field, especially in the direction of fundamental work in the area of so-called “electrocatalysis”, a term coined by Grubb and Niedrach of the GE group [2]. Historically, it is of interest that Frumkin, in 1939, recognized catalysis in electrode processes at a conference lecture in Leningrad [3]. A first and perceptive definition of electrocatalysis seems to be that given by Busing and Kauzman [4] in terms of promotion of rates of the rate-determining step in an electrode process by the electrode material involved. The publication of Vielstich’s monograph, “Brennstoff Elemente” [5], in 1965, provided a much needed crystallization of the literature (in relation to his own researches) at that time and became the workbook of the field.

Following a gap of some years, rejuvenation of the field of fuel-cell research and technology, and related battery and electrochemical capacitor technology [6], has taken place during the past 10 years in work by Ballard in Canada and at the centre for electrochemical energy research at Ulm, Germany, as well as by Stonehart Associates in collaboration with United

Technologies and by Ross and coworkers at Lawrence-Berkeley Laboratory. This renewed effort has been driven by the perceived requirement for urgent development of emission-free electric vehicles (EVs) to meet environmental concerns arising from the generation of “greenhouse gases” and nitrogen oxides, “NOX”, by vehicles burning carbonaceous fuels.

Recent electrochemical engineering concepts envisage EVs being powered by rechargeable batteries (lead acid or nickel/metal-hydride) coupled advantageously with a supercapacitor [6], operating in a load-leveling function to improve up-hill driving or acceleration performance. This concept arises from the perceived capability of electrochemical capacitors of operating at high power densities (PDs) (compared with those of batteries), albeit at relatively low energy densities (EDs); the hybrid combination then has an overall PD/ED specification better than either component alone [7].

In the context of the present article, similar advantages accrue from operation of a fuel cell coupled in a parallel, but electronically interfaced way, with a supercapacitor. As for the battery hybrid case, this enables the fuel-cell unit of an EV power system to operate under more steady conditions than would otherwise arise in operation of a stand-alone cell. Such a hybrid configuration offers the advantages of minimizing fluctuations of fluxes of produced water and anode/cathode pH differences, as well as of non-steady H₂ and O₂ gas flux demands in the two porous electrode structures, in the case of the H₂/O₂ fuel cell.

In this article, in the section entitled “Battery, or fuel-cell/electrochemical capacitor hybrid concept, for electric vehicles”, we give a brief review of the basis and principles of operation of two kinds of electrochemical supercapacitor device that can be used in the above manner: (1) the double-layer capacitance type and (2) the pseudocapacitance type, based on surface redox processes at conducting metal oxides, e.g. RuO₂ or conducting polymers. Both depend on establishing capacitative charge-storage processes at high specific area electrodes (1000–2000 m² g⁻¹ of active material), leading to capacitor devices having practical capacitance densities of ca. 100–200 F g⁻¹ or cm⁻³ [6]. In the section “Coupling of capacitor/battery electrodes in an asymmetric single cell” we describe a relatively new but different concept in hybridization, viz. where a non-faradaic, double-layer type of capacitor electrode (e.g. high specific-area carbon) is worked against a rechargeable, faradaic battery-type of electrode in a single-cell configuration.

First we describe the nature of the double-layer type of electrochemical capacitor.

Double-layer electrochemical capacitors

General basis of double-layer charge storage

The interfacial specific double-layer capacitance at electrode interfaces usually depends appreciably on electrode

potential and the physicochemical nature of the electrode surface (especially in the case of carbon materials, depending on their provenance, conditioning treatment and extent of graphitization [6]). The “reference example” is usually the Hg/solution interface, the double-layer capacitance of which varies substantially through the potential of zero (surface) charge (p.z.c.) densities and depends much on the nature of the anions of the electrolyte which can be adsorbed at Hg, and on the dipolar nature, the electron-donor number of the solvent and its solvating power for anions and cations of the electrolyte solute.

At solid, especially noble, metals, again the double-layer capacitance depends appreciably on the chemical identity of the metal and especially whether the metal bears a thin surface-oxide film (e.g. Pt or Au) and at which surface plane of single-crystal electrodes, e.g. Au, the capacitance is measured. At such electrodes, the p.z.c. is specific to the Miller index orientation of the surface plane and is directly related to the electron work-function of that plane.

The concept of a capacitor device, utilizing the interfacial double-layer capacitance of a high-area porous electrode structure, seems to have originated in the patent of Becker (US Pat. 2,800,616) in 1957 to General Electric. However, understandably, this first embodiment of the concept was rather crude and inadequately described, leading to subsequent misunderstandings of the difference in function between electrochemical capacitors and faradaic battery systems (cf. [8] and chapter 2 in [6]). A later 1970 patent (US Pat. 3,536,963) to Standard Oil (D.L. Boos) disclosed a pasted carbon double-layer capacitor operating in a non-aqueous, aprotic solvent such as propylene carbonate containing a tetraalkylammonium salt as electrolyte. This enables a substantially higher voltage of ca. 3.5 V on charge to be realized with a correspondingly higher energy density of some 8.5 times that for an aqueous system where the thermodynamic maximum voltage on charge is the decomposition potential of water, 1.23 V. The energy density of a capacitor is, of course, $(\frac{1}{2})CV^2$ or $(\frac{1}{2})qV$, where q is the density of charge accommodated at voltage V . Comparatively, for a battery cell, the energy density for the same q and V is qV , twice that for corresponding conditions for a capacitor.

Porous electrode limitation to double-layer capacitance behaviour

The experimentally measurable capacitance behaviour of carbon electrodes for supercapacitors is determined in a major way by the porosity of the electrode material, which is necessarily related to the requirement of high specific area in order to manifest large capacitance densities on the order of 100 F g⁻¹ or more. The porosity relevant to the development of high capacitance is itself not a simple parameter and involves pore sizes

and pore-size distribution for a given overall specific area ($\text{m}^2 \text{g}^{-1}$) of the material.

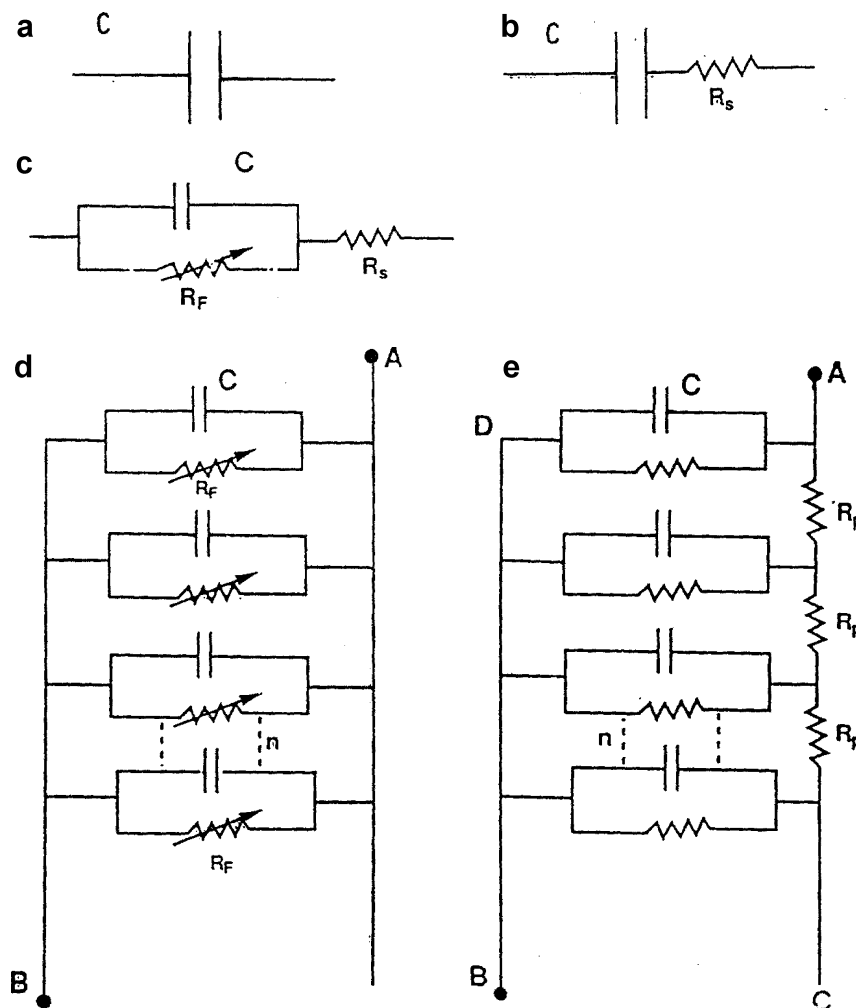
The dynamical electrochemical behaviour of a porous electrode is determined by its "equivalent circuit", which is usually represented by a "ladder" arrangement of series/parallel RC elements representing the distribution of resistive (ohmic) elements, R , coupled with charge-storage elements, C , down the pores of the electrode structure. The impedance and dynamical charging behaviour of a pore has been treated in detail by de Levie [9, 10] and, later, in some more specific detail regarding pore shapes by Keiser and co-workers [11]. With respect to response to an admitted time-dependent modulation signal (AC or DC pulse), the matrix offers a distribution (spectrum) of RC time constants determining the response (or "transfer") function for the pore or pore matrix. The resulting behavior is characterized by a power spectrum in the electrical response. These effects are quantitatively related to the so-called "penetration length" (de Levie [9, 10]) of the modulating signal down the pore, from its opening into the bulk solution, and across any remaining resistance (so-called equivalent series resistance, ESR) of the electrode to the current collector of the device.

The equivalent circuit of a porous electrode, according to the model of de Levie, is shown in its simplest configuration in Fig. 1 and corresponds to that of a transmission line. Its behaviour can be well simulated by a "brush electrode" made up of a multitude of linear wires, e.g. Au, Pt, Ag, constrained in an open-ended glass or plastic tube (cf. [9, 10] and [12]). The important impedance characteristic of a transmission line is the observation of a 45° phase angle, independent of frequency, as is observed experimentally at a porous carbon electrode and with the metal-wire brush electrode [9, 10].

Battery, or fuel-cell/electrochemical capacitor hybrid concept, for electric vehicles

We have referred to this concept in relation to improvement of the performance of battery or fuel-cell powered EVs achieved by electrical coupling between such primary sources of electrochemical energy and power, and non-faradaic electrochemical capacitors. For optimized engineering and sizes of such hybrid capacitor/battery devices, account must be taken of the differences

Fig. 1 Hierarchy of equivalent circuits of increasing complexity for capacitors and electrochemical capacitors, through to the de Levie [9, 10] transmission line model: (a) simple capacitor; (b) capacitor with equivalent or real series resistance; (c) capacitor with series resistance and potential-dependent faradaic leakage resistance, R_f ; (d) parallel combination of n C and R_f leakage elements. Overall " RC " constant is $R_f/n \times nC = R_f C$ for the single element; (e) (de Levie transmission line model) parallel C , R_f elements, R_p related to transmission line, constant phase element but with R_f leakage pathways



of attainable mass and volumetric charge densities of the capacitor material relative to that of the battery component in order to achieve the most favourable optimized conditions. For the highest specific-area carbon materials, viz. on the order of $2000 \text{ m}^2 \text{ g}^{-1}$ or $2 \times 10^7 \text{ cm}^2 \text{ g}^{-1}$ (e.g. "Spectra" woven carbon fibre cloth), the capacitance density for a double-layer capacitance of, say $20 \text{ } \mu\text{F cm}^{-2}$, will be 400 F g^{-1} . At full state of charge, say at 1 V, the stored charge would be 400 C or ca. $400/10^5$ Faradays g^{-1} , i.e. $12 \times 4 \times 10^{-3}$ Faradays per g mole of carbon (atomic weight = 12). Thus, the effective equivalent weight of the carbon forming the matrix of the capacitor would be $12/0.048 = 250 \text{ g}$.

Three aspects of the above estimate of energy densities require special comment. (1) The series relation between the required two electrodes of a symmetrical capacitor device necessarily gives rise to half the capacitance of each electrode, owing to the well-known reciprocal relation between the overall capacitance of the device and that of each of its two individual electrodes. (2) The specific capacitance of high-area carbon electrodes in most non-aqueous solutions is significantly lower than that of the same electrodes in aqueous solution, owing to the lower dielectric constant of the for which gives rise to lower energy densities. (3) The practical operating voltages of carbon double-layer capacitors are higher than those that might otherwise be supposed, based on known evolution of CO_2 at some carbon materials, prior to O_2 evolution on overcharge or of H_2 on over-discharge. This favourable feature arises on account of the appreciable overvoltages that arise in anodic O_2 evolution or cathodic H_2 evolution at carbon, which gives some advantageous overcharge protection. In non-aqueous systems, of course, higher operating cell voltages can be achieved owing to less facile and electrochemically different decomposition processes with organic solvents and electrolytes.

In hybrid operation with, say, a lead-acid cell (PbO_2 and Pb , after charge) for EV load-leveling, the above equivalent weight has to be balanced with that for the battery couple which, for the lead-acid case is (theoretically) ca. $239/2 = 119$. Hence the theoretically required mass of the carbon double-layer capacitor cell would be more than twice that for the battery electrode component for full state-of-charge. Of course, the above calculated equivalent weight for both the lead-acid battery cell and the coupled electrochemical capacitor module assume 100% depth of discharge of active materials, and are based on their masses alone (i.e. without packaging burden). In fact, practically, especially for the lead-acid cell, if the latter is to have maximized cycle-life, the depth of discharge should be restricted on cycling to substantially less than "100%", e.g. ca. 66% [13], i.e. the whole system must be limited by the capacity of the capacitor-device component. According to Linden [14], the theoretical energy density, based on the mass of electrode materials alone, for a lead-acid battery is 228 Wh kg^{-1} ; the theoretical energy density, based on mass of all battery components, including electrolyte,

separator, etc., is ca. 75 Wh kg^{-1} , and the realizable energy density is only ca. 35 Wh kg^{-1} . These figures significantly reduce the ratio of carbon mass/battery mass for optimization. However, account must be taken of the desired or anticipated power levels of operation of hybrid-device charge-storage systems. Thus, supercapacitor-type cells are usually perceived [6, 8] as being capable of operation at substantially greater levels of power density than are battery electrodes of comparable faradaic charge capacity. However, this perception requires some qualification since porous carbon double-layer capacitor electrodes experience the de Levie [9, 10] "porous electrode effect" due to distributed capacitance and electrolytic resistance that gives rise to a *power spectrum* limitation referred to in the previous subsection.

Furthermore, importantly, the capacitor load-leveling component does not have to match the whole potential faradaic charge but only up to some arbitrary practical limit, e.g. of ca. 10–20% during transient high-load periods, depending on the power requirements in such loads. Nevertheless, eventually, the battery component has to recharge the capacitor component of the EV, which has its (required) maximum power density availability at full state-of-charge.

In the case where the capacitor component is coupled with a fuel cell, e.g. in an EV application, the above limitation does not arise since the fuel cell can provide controlled or programmed capacitor recharge indefinitely, since a fuel cell has no state-of-charge limitation of the kind arising with batteries or electrochemical capacitors, though it does have power profile limitations which, coupling with a supercapacitor, can be avoided. Thus a fuel cell, more so than a battery, is best operated under conditions involving minimization of substantial changes of power drain, a situation that avoids problems of water-balance and gas-flow variations as a result of load variations.

Coupling of capacitor/battery electrodes in an asymmetric single cell

A different, and now important, type of hybrid charge and electrical energy storage device, that is multiply rechargeable, has recently been investigated by various workers [13, 15, 16], including the present authors [17]. This type of system is based on the concept of combining a non-faradaically (or pseudo-faradaically [6]) rechargeable electrochemical capacitor type of electrode with a faradaically rechargeable battery-type electrode, e.g. acid $\text{PbO}_2/\text{PbSO}_4$ or alkaline $\text{NiOOH}/\text{Ni}(\text{OH})_2$ internally in a single-cell module, and is generally termed an "asymmetric capacitor device". Such a system combines the high operating power density advantage of the capacitor component with the good energy density of the battery electrode component and especially, for the $\text{PbO}_2/\text{PbSO}_4$ electrode, the relatively constant electrode potential of the latter with diminishing state-of-dis-

charge down to ca. 90% discharge. This leads to an important advantage with respect to availability of charge from the non-faradaic electrode, namely that its initial full charge is available on discharge against the faradaic electrode compared with effectively (cf. [18]) only one quarter of full charge in conventional double-layer capacitor devices, where: (1) one carbon electrode is worked against another similar one (charged in the opposite direction) in a so-called "symmetrical capacitor" series configuration and (2) at zero charge, the overall cell voltage has declined by *twice* that at each of the pair of electrodes.

Formally, the first point follows from the simple, reciprocal, relation for the overall capacitance, C , in terms of the individual capacitances, say C_1 and C_2 , in series. Thus:

$$\frac{1}{C} = \frac{1}{C_1} + \frac{1}{C_2} \quad (1)$$

First, when $C_1 \equiv C_2$ (symmetrical combination), the observable, measured C would be *half* the value of each

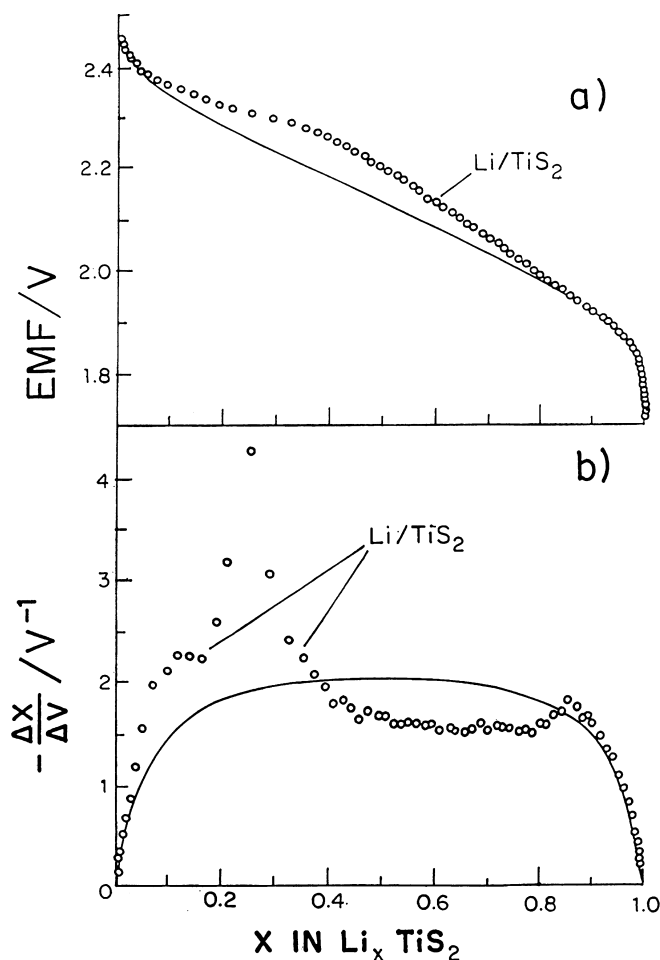


Fig. 2 Illustrating potential dependence of state-of-charge, X , of Li/TiS₂ intercalation electrode, corresponding to pseudocapacitance behavior. Lower curve represents differential plot, $\Delta X/\Delta V$, of the data for the upper curve, corresponding to potential-dependent pseudocapacitance

of the components. If "2" refers to a faradaic electrode, C_2 is essentially infinity, so $C \equiv C_1$ and the full charge stored on C_1 is hence available for discharge, as C , against the faradaic electrode.

The only interesting and significant exception to this would be for the case of the capacitor electrode being combined with a Li-ion intercalation electrode which exhibits, formally, a pseudocapacitance (cf. [8] and [19]) as, for example, the case of Li/TiS₂. Then Eq. 1 would apply to the combination. This situation arises with a number of Li intercalation battery electrodes formally for the reason that the state-of-charge/discharge is substantially dependent (see Fig. 2) on the electrode potential in the discharging or recharging processes; hence the charge q has a differential coefficient with respect to the potential which corresponds to a large differential (pseudo-) capacitance, dq/dV , or an equivalent integral capacitance over the potential range, ΔV , for charge or discharge.

The above behaviour for the asymmetric capacitor/battery electrode cell has been discussed by Beliakov [13] and is illustrated in Fig. 3, based on his paper.

In considering conditions for coupling capacitors with battery-type electrodes, as well as comparing capacitor discharge with battery electrode discharge curves, the most important aspect is that capacitor discharge follows an almost linear decline in voltage with decreasing state-of-charge, while faradaic-type electrodes exhibit a more constant electrode potential during discharge (with the exception of Li intercalation electrodes). This implies that asymmetric-type cells have an

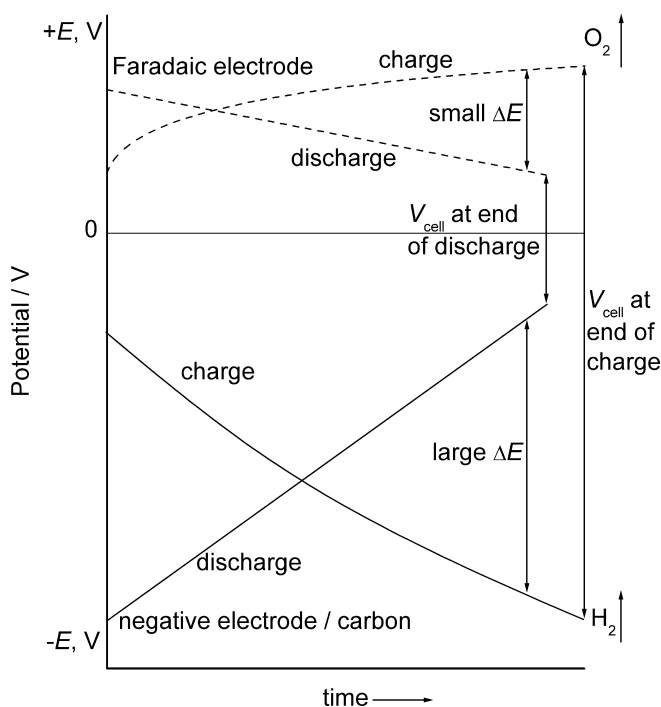


Fig. 3 Dependence of voltage on state-of-charge for a battery/capacitor electrode hybrid cell (schematic, after Beliakov [15])

energy- and power-density dependence on state-of-charge that has to be factored into performance specifications and choice of applications.

Pseudocapacitance and its significance for electrochemical capacitor development

Definition and significance of pseudocapacitance

At the beginning of renewed interest in supercapacitor development in 1990, as represented, for example, by the commencement of the Florida Educational Seminar Series on Double-Layer Capacitors and Related Devices [7, 15] in 1991 (continuing until the present time [17]), the distinction between pseudocapacitance and double-layer capacitance was not well understood in the field of applied electrochemistry. However, in more fundamental electrochemistry it was a common concept much earlier and a key bridging paper was that of Buzzanca and Trasatti [20], in which they recognized that the cyclic voltammetry behavior of RuO₂ DSA electrodes, developed as stable anodes for commercial Cl₂ production, had the form corresponding to the response of a capacitor under linear voltage sweep modulation. Pseudocapacitance, associated with the underpotential deposition of adatoms of H (and later of metal atoms), was also already treated in detail by Conway and Gileadi in 1962 [19].

As noted earlier, when the extent of faradaic charge (q) passed, e.g. in an electrosorption process or even in a quasi-two-dimensional intercalation process, or in a

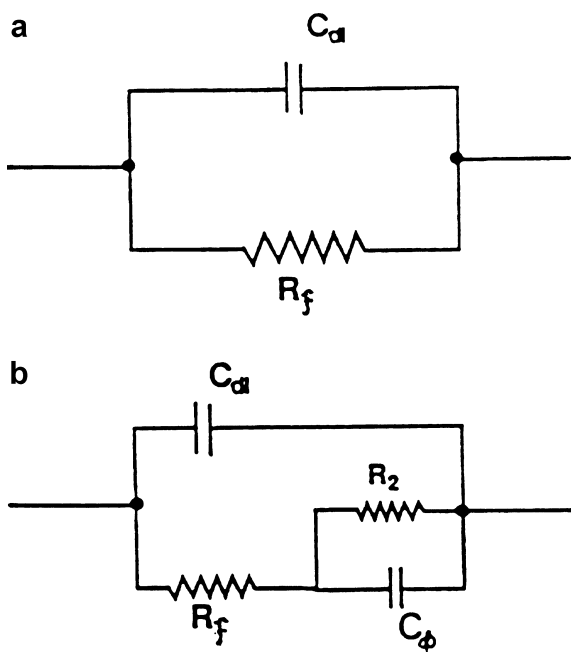


Fig. 4 Equivalent circuits for: (a) charging a pure capacitance through a series resistance; (b) charging of a pseudocapacitance, C_ϕ , in parallel with a double-layer capacitance, through a faradaic resistance, R_f , with charge leakage through a parallel resistance, R_2

surface redox process as with RuO₂, is a function of electrode potential, then a derivative, dq/dV , arises that has the significance of a capacitance and is measurable as such. Importantly, this kind of capacitance is faradaic in origin, rather than being associated with potential-dependent accumulation of electrostatic charge, as in a double layer, corresponding to double-layer capacitance; hence it is referred to as *pseudocapacitance*, the charging of which is faradaic. Then its equivalent circuit is that shown in Fig. 4b, where R_f is a faradaic resistance in series with C_ϕ , the pseudocapacitance, both being in parallel with the double-layer capacitance, C_{dl} . R_2 is a potential-dependent leakage resistance. Note that C_{dl} is always a component in the representation of all interfacial electrode processes (Fig. 4a) or equilibria which may or may not involve C_ϕ and R_f components.

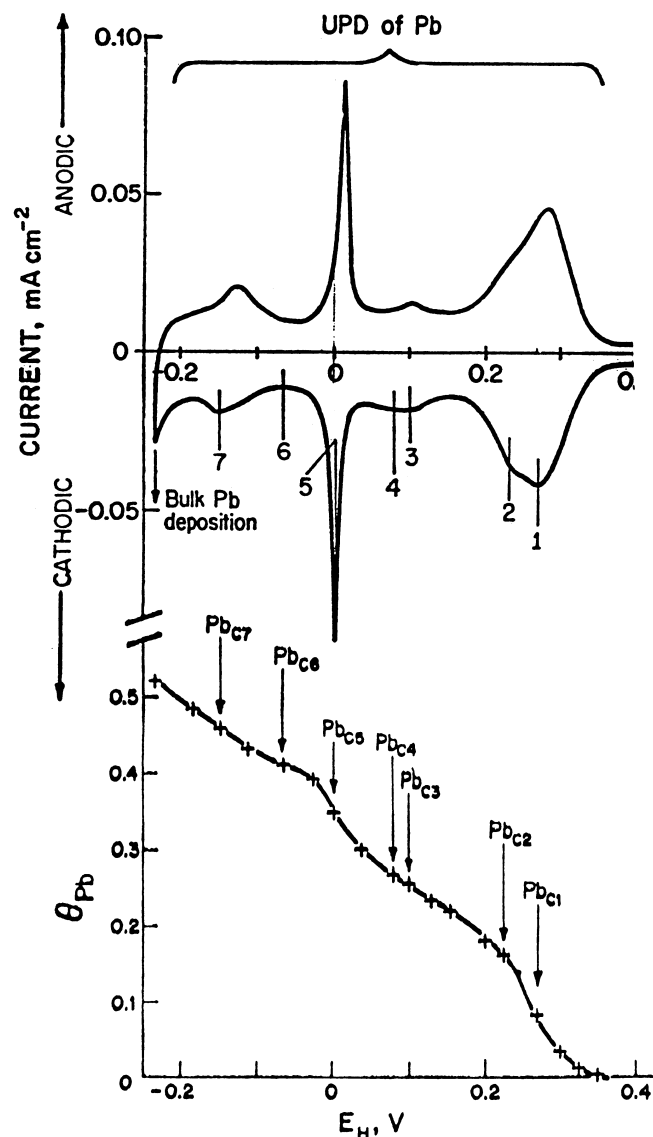


Fig. 5 Cyclic voltammetry profile for UPD of Pb adatoms on polycrystalline Au from aq. HClO₄ solution, exhibiting seven distinguishable states below a monolayer. Lower curve is integral of cathodic sweep profile. Sweep rate, 50 mV s⁻¹; 298 K

Because of the above representation of the charging process for C_ϕ , its impedance spectrum is quite different and distinguishable from that for C_{dl} , e.g. at the Hg electrode or at C. In certain redox-oxide porous electrodes, where large C_ϕ values can arise as at RuO_2 , IrO_2 , Co_3O_4 , etc. [21], the C_ϕ and R_f components are distributed down or amongst pores so the equivalent circuit (Fig. 1) and the resulting impedance spectra can become quite complex.

Contrast between double layer and pseudocapacitance

In concluding this section, we illustrate in Figs. 4, 5, 6 the fundamental contrast between cyclic voltammograms for well-defined pseudocapacitance behaviour as

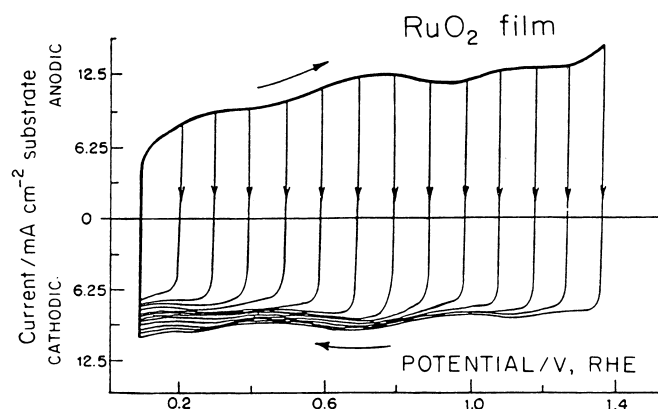
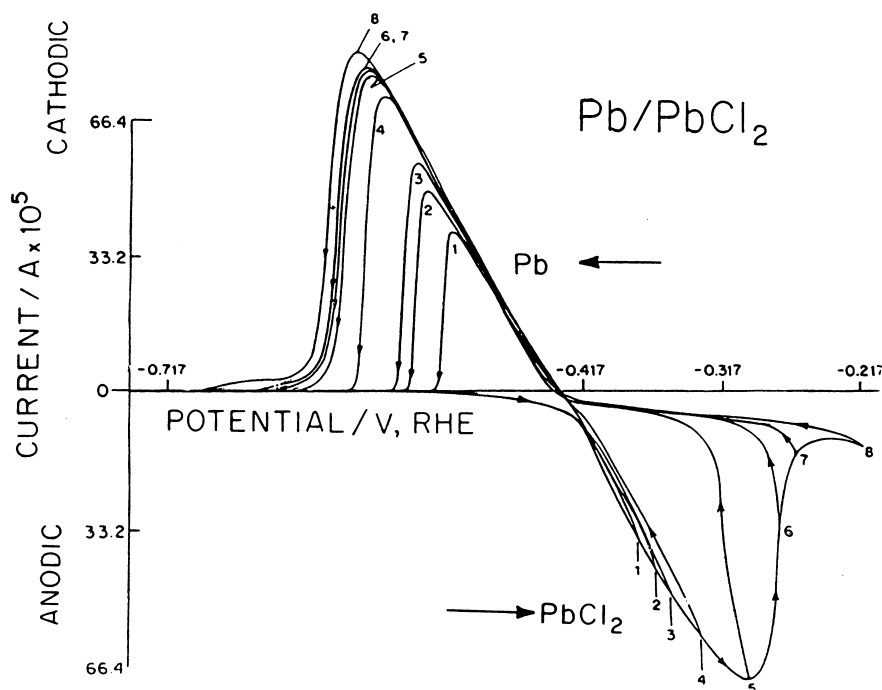


Fig. 6 Cyclic voltammetry profiles for RuO_2 in aq. 0.1 M H_2SO_4 taken to a successive series of positive electrode potentials relative to RHE. Sweep rate, 50 mV s^{-1} ; 298 K

Fig. 7 Cyclic voltammograms for formation and reduction of PbCl_2 at Pb, showing complete irreversibility between the anodic and cathodic response currents. Sweep rate 50 mV s^{-1} ; 298 K



exhibited, for example, by Pb^{2+}/Pb underpotential deposition at Au (Fig. 5) and by RuO_2 (Fig. 6), where surface redox couples are the origin of the large C_ϕ over a range of potential of 1.4 V, and, in contrast, the cyclic voltammograms for a regular, bulk faradaic, type of battery electrode process: $\text{Pb} \rightarrow \text{PbCl}_2$ (Fig. 7). The lead-acid anode process, $\text{Pb} \rightarrow \text{PbSO}_4$, behaves similarly.

The important and principal difference between the above two faradaic behaviours is that the pseudocapacitance charging and discharging processes, e.g. for UPD of H or Pb, or for RuO_2 , are quite reversible over an appreciable voltage range (and, significantly, then, the anodic and cathodic voltammograms are almost mirror images of one another, as they are for a pure capacitance). In contrast, the bulk phase Pb/PbCl_2 voltammograms (taken to successively changing potentials in Fig. 7) are completely *irreversible*. This is typical of battery-type, bulk, electrode materials except for Li-ion hosts [8], and arises because major three-dimensional (3D) phase-changes are usually involved in the discharging/recharging processes. Overall, however, the chemical and stoichiometric changes of the electroactive species involved remain reversible.

Another system exhibiting pseudocapacitance arises from electrochemical generation of conducting polymers at carbon fibre or Au substrates by means of voltage cycling in the positive direction. With aniline, reversible positive charge generation on the anodically formed polyaniline chains [22] takes place with the appearance of electronic conductivity. The charge accommodation can be regarded as charging of a linear double layer or as a Lewis acid/base oxidation of centres on the chains. With (*p*-fluorophenyl)thiophene, charging can be

Table 1 Correlation of types of systems giving rise to pseudocapacitance with application to electrochemical capacitors^a

System type	Essential relations
(a) Redox system: $\text{Ox} + ze^- \rightleftharpoons \text{Red}$ and $\text{O}^{2-} + \text{H}^+ \rightleftharpoons$ in lattice	$E = E^\circ + \frac{RT}{zF} \ln \frac{R}{1-R}$ $R = [\text{Ox}] / ([\text{Ox}] + [\text{Red}]); R/(1-R) = [\text{Ox}]/[\text{Red}]$
(b) Intercalation system: Li^+ into “MA ₂ ”	$E = E^\circ + \frac{RT}{zF} \ln \frac{X}{1-X}$ $X =$ occupancy fraction of layer lattice sites (e.g. for Li^+ in TiS_2)
(c) Underpotential deposition of metal adatoms, $\text{M}^{z+} + \text{S} + ze^- \rightleftharpoons \text{SM}$ (S = surface lattice sites) or $\text{H}^+ e^- + \text{S} \rightleftharpoons \text{SH}$.	$E = E^\circ + \frac{RT}{zF} \ln \frac{\theta}{1-\theta}$ $\theta =$ two-dimensional site occupancy fraction

^aNote that (b) and (c) can be regarded as mixing of occupied (X or θ) sites with unoccupied sites, $(1-\theta)$ or $(1-X)$

Table 2 Double-layer capacitance and pseudocapacitance compared

Double-layer capacitance	
1.	Non-faradaic
2.	20–50 $\mu\text{F cm}^{-2}$
3.	C fairly constant with potential, except through the p.z.c.
4.	Highly reversible charging/discharging
5.	Has restricted voltage range (contrast non-electrochemical electrostatic capacitor)
6.	Exhibits mirror-image voltammograms
Pseudocapacitance	
1.	Involves faradaic process(es)
2.	2000 $\mu\text{F cm}^{-2}$ for single-state process; 200–500 $\mu\text{F cm}^{-2}$ for multi-state, overlapping processes
3.	C fairly constant with potential for RuO_2 ; for single-state process, exhibits marked maximum
4.	Can exhibit several maxima for overlapping, multi-state processes, as for H at Pt
5.	Quite reversible but has intrinsic electrode-kinetic rate limitation determined by R_f
6.	Has restricted voltage range
7.	Exhibits mirror-image voltammograms

accomplished in both positive and negative directions [23], giving a wide voltage range for development of pseudocapacitance. Conducting polymer materials can be easily and cheaply made in high-area forms, giving rise to materials having large specific electrochemical capacitance, capable of cycle lives on the order of several thousand.

It is useful to compare the three distinguishable types of pseudocapacitance: bulk and surface redox, 2D electrosorption (UPD) processes and quasi-2D intercalation; Table 1 shows the thermodynamic equations for dependence of electrode potential on logarithmic activity functions for a surface process, a redox reaction and an intercalation process. Reciprocals of the differentiated equations in this table lead to respective pseudocapacitance relations having similar mathematical forms. Table 2 compares the essential features of double-layer capacitance behaviour with that of pseudocapacitance.

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