

Peculiarities and requirements of asymmetric capacitor devices based on combination of capacitor and battery-type electrodes

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Abstract

New concepts have arisen in recent years concerning configurations of the so-called hybrid charge-storage devices in which a faradaic, rechargeable battery-type electrode is combined with a non-faradaic, electrochemical, double-layer type of electrochemical capacitor electrode, the combination now being referred to as an “asymmetric” device. Other hybrid systems combine a double-layer electrochemical capacitor device with a fuel-cell or a separate rechargeable battery.

Following a discussion of dependence of cell voltage of regular, two-electrode, non-faradaic electrochemical capacitors on state-of-charge (SOC), comparisons are made with recently conceived hybrid combinations of a battery-type rechargeable electrode with a double-layer capacitor-type electrode. Advantages, disadvantages and requirements of such hybrid systems over regular electrochemical supercapacitors or batteries are discussed and critically examined in regard to available energy- and power-densities, energy and coulombic efficiency, cycle-life, voltage profiles on discharge, and self-discharge behaviour.

Emphasis is given to importance of using a third electrode, as reference, especially in evaluations of discharge/recharge behaviour of each electrode of an hybrid pair having very different electrochemical characteristics, one faradaic, the other non-faradaic. Use of a reference electrode also provides the opportunity of following self-discharge behaviour of the individual electrodes independently.

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1. Introduction: the hybrid device concept

In recent years, several types of the so-called hybrid electrochemical charge storage and delivery systems have been conceived and operated: (a) an hybrid system combining an electrochemical supercapacitor device [1], based on double-layer capacitance [1,2] or redox-oxide pseudocapacitance [3], interfaced with a fuel-cell or a faradaically rechargeable battery system, e.g. for electric-vehicle motive power. In such an application, the capacitor device provides a load-levelling function, smoothing the power demand from the battery or fuel-cell component [4]. (b) Use of a battery or capacitor device, supported by an internal combustion engine (ICE); here the ICE serves to maintain charge of the electrochemical components and itself operates in a smoother and more efficient manner than in a vehicle directly powered by an ICE (cf. the diesel–electric system powering railway trains). The third type of hybrid electrochemical system, (c) involves hybridisation of a faradaically rechargeable battery-type electrode,

e.g. Pb/PbO₂ or Ni(OH)₂/Ni-O-OH, with a non-faradaically rechargeable supercapacitor electrode system. Such systems have been conceived in recent years and their behaviour has been reported [5–9]. A different type of hybrid capacitor device is that described by Evans [10] in which RuO₂ is used as a capacitive electrode (cathode) conjugate to a Ta₂O₅ electrolytic capacitor anode, achieving improved energy-density and charge capacity.

In the present paper, we discuss the requirements for effective operation of an hybrid rechargeable system of type (c) and some peculiarities of its electrochemical behaviour in relation to experimental evaluation tests made on a Pb/PbO₂ cathode combined with an highly reversible carbon double-layer capacitor device (cf. Refs. [5,6–9]). This type of two-electrode system is now being referred to as an “asymmetric” capacitor device, since only one of the electrodes is charged non-faradaically, the complementary electrode being charged and discharged faradaically. The above term usefully distinguishes the device of type (c) from the regular type of electrochemical capacitor comprising two reversibly chargeable double-layer or pseudocapacitance electrodes of the *same type* but being charged one against the other in opposite directions, i.e. “symmetrically.

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The term asymmetric device derives from the US Patent 6,222,723 titled “Asymmetric Electrochemical Capacitor and Method of Making” by Razoumov et al. [11] (cf. Ref. [9]). In the continuing text of the paper we shall refer to this hybrid type electrode configuration as an “asymmetric capacitor” device in order to avoid confusion with other types of hybrid system referred in this section.

Traditionally, double-layer [1,2] and redox-oxide [3] types of electrochemical capacitors have been designed and operated in a “symmetrical” mode, i.e. the same type of capacitor material, e.g. high-area C or RuO₂, has been employed for both the positively and negatively polarised electrodes of the capacitor device, configured in a single cell. This does not, however, mean that the charging curves for each of the pair of electrodes, studied individually versus an inert counter-electrode with electrode potential being measured against a (third) reference electrode, will actually be identical. This, in fact, will not normally be the case since the positive electrode (referred to the potential of zero charge, p.z.c.) usually experiences strong anion adsorption from the electrolyte compared with weaker cation adsorption at the negative electrode, as is well known for the seminal case of the Hg electrode [1,12] where this can lead to a difference of specific capacitance (with respect to the p.z.c.) which can be as large as a factor of 2 [12].

This implies that the capacitance or accessible charge-density per cm² of the positive electrode of an electrochemical capacitor can be appreciably greater by ca. 30–50% than that of a negative electrode of the same real area. Thus an intrinsic asymmetry of electrochemical capacitors tends to arise for fundamental reasons unless the mass of the positive plate is adjusted relative to that of the negative plate to balance the densities of anodic and cathodic charge storage or delivery.

Additionally, at porous C electrode materials, the double-layer capacitance is rarely constant (as is the case also at Hg [12]) over the operating range for charging and discharging, e.g. as demonstrated by Blurton [13] and reviewed in Ref. [1, Chapter 9], and in Ref. [14]. However, even though differential capacitance curves often exhibit humps and minima [1,14], the corresponding charging curves tend to be smoother and more continuous since they are the integral of the differential capacitance response with respect to changing electrode or cell potential.

Examination of the literature, e.g. from Ref. [1], and of seminar presentations (e.g. Ref. [15]), indicates that the above factor of intrinsic asymmetry has been little addressed, though it is not difficult to evaluate. However, a cell symmetrically balanced initially, for charge acceptance/delivery, may not retain the initially designed symmetry after extensive cycling, so the overall charging efficiency can decline.

The above considerations apply mainly to the double-layer (d.l.) type of electrochemical capacitor and any degree of asymmetry due to disbalance of intrinsic charge capacity between the positive (p) and negative (n) pair of electrodes in a single cell will result in the overall capacitance of

the device being determined by the electrode that has the *smaller* capacitance density. Thus, the net overall capacitance density (on a cm² basis), C_T, in relation to the individual electrode capacitance densities, C_p and C_n will be

$$\frac{1}{C_T} = \frac{1}{C_p} + \frac{1}{C_n} \quad (1)$$

so that C (or average C) is determined mainly by the *smaller* of the two capacitances when they are substantially unequal or, if they are approximately equal, it is seen that the overall C of any “symmetric” capacitor is only *half* that of the individual capacitance densities (Farads cm⁻²), of each of the electrodes of the cell pair. This is a quite general result of combining capacitative elements in series and has to be taken into account in device design to optimise performance specifications and delivered efficiency, as discussed below.

A further practical point, emphasised by Miller [16], is that the effective limit of useful charge availability (in terms of useable energy-density) is at SOC of only 0.5 (50%). This arises on account of the energy-density (ED) of a charged capacitor being determined by

$$ED = \frac{1}{2} CV^2 \quad (2)$$

where V is the potential difference (voltage on charge) across the device when it has been charged to a voltage of V, i.e. ΔV between the plates. Hence, for V being, say, 0.5 (SOC 50%) of the full-charge voltage, the remaining ED (from Eq. (2)) is 25% of its initial value (0.5² = 0.25); and the usable energy-density is only 75% of the initial value. Then, with the consequence of Eq. (1) for two capacitative electrodes in series, the device ED is only 3/8th (on a cm² basis) and 3/16th (on a mass basis) of that of its individual electrodes!

Although this conclusion follows from simple principles, it seems not to have been widely appreciated, nor its negative consequences in ED specifications emphasised. The ED limitation on the restricted effective availability of energetically useful charge can, however, be modified in an important favourable direction by combination of an electrochemical-capacitor type electrode (double-layer or redox-oxide (RuO₂, conducting polymer, etc., pseudocapacitance element [1,3]) with a rechargeable battery-type electrode, e.g. (see below and Refs. [5,6–9,11]) Pb/PbO₂/PbSO₄ lead-acid, or Ni·O·OH [9,17] with Cd or Zn, or an “MH” alkaline type of anode material). This concept is the essence of the material given in the present paper.

As we noted above, such a system is then termed an “asymmetric” (capacitor) device and, importantly, combines the advantages of a non-faradaic charge-storage component (the capacitor electrode) with those of the battery-element which operates on the principle of faradaic charging or discharging. The chief advantage of such a system is that the conditions for which Eq. (1) applies become quite different since the faradaic electrode has effectively *infinite capacitance* so that C → C_{d.l.} of the high-area double-layer charging electrode and consequently the full charge capacity of the “double-layer” component electrode is then utilisable. In

the (d.l.) capacitor electrode component, the charge is stored *electrostatically* across the double-layer interphase at the interface of a large specific-area electrode (C fibres, aerogels, nanotubes, etc.) in a direct manner while, at the battery electrode component, charge is stored indirectly in a *chemical way* and becomes available as the Gibbs (free) energy of an electrochemical reaction involving faradaic electron transfer and electrochemical phase-transformation of the battery reagent materials, e.g. in the lead-acid cell, $\text{PbO}_2 \rightarrow \text{PbSO}_4$ (cathode process) coupled with $\text{Pb} \rightarrow \text{PbSO}_4$ (anode process), on discharge.

The use of d.l. or oxide-redox (e.g. RuO_2) pseudocapacitance-type [1,3] electrochemical capacitors for electrical energy and charge storage is usually predicated on the assumption (not always valid for certain conditions) that (a) they can be operated at high power-densities and (b) that such operations can be conducted largely reversibly over long cycle-lives, $\geq 10^5$ cycles. If these two desirable performance features are to be successfully retained in an asymmetric combination with a faradaic, battery-type, second electrode, then the choice and operating conditions of the latter electrode have to be carefully evaluated and selected so that the performance of the faradaic electrode does not impair that of the (usually highly reversible) conjugate capacitive electrode in the overall, two-electrode device.

2. Candidate systems for the battery electrode component (charge capacity and equivalent weight)

The pre-eminent systems for the rechargeable faradaic electrode components are the $\text{PbO}_2/\text{PbSO}_4$ and the $\text{Ni}\cdot\text{O}\cdot\text{OH}/\text{Ni}(\text{OH})_2$ materials [5,17]. The lead dioxide electrode is a two-electron cathode having equivalent weight of ca. 119 g while the nickel oxide electrode is a one-electron cathode at ordinary temperatures (>1 at low temperatures) having an equivalent weight of ca. 92 g. Of course these are the material weights for faradaic storage, or provision of 1 F or 96,450 C of electric charge, i.e. equivalently 6×10^{23} electrons per mole, not including packaging mass. Li intercalation compounds have recently been considered as the negative faradaic electrode in an asymmetric capacitor device [18–20]. Other hybrid technologies are discussed in the literature [21,22]. Zheng has evaluated the maximum theoretical energy density of several asymmetric capacitor systems including carbon/LiPF₆ ethylene carbonate:dimethyl carbonate (EC:DMC)/Li_xTi₅O₁₂, carbon/LiPF₆ EC:DMC/WO₂, and $\text{Ni}(\text{OH})_2/\text{KOH H}_2\text{O}/\text{carbon}$ [23].

For a non-faradaic capacitor electrode based, say, on porous C material having $2000 \text{ m}^2 \text{ g}^{-1}$ and specific double-layer capacitance of, say, $20 \mu\text{F cm}^{-2}$ at C, the specific capacitance would be 400 F g^{-1} (theoretical), i.e. 400 C g^{-1} at nominal 1 V charge. This would correspond 4800 C per gram atomic weight, 12, of carbon. On a real-area basis for C having $2 \times 10^7 \text{ cm}^2 \text{ g}^{-1}$ (as used in some of our

previous work), this area corresponds to ca. 2.0×10^{15} C atoms per cm^2 . Per atom of C, this figure is equivalent to a charge of $(20 \times 10^{-6}/10^5)(6 \times 10^{23}/2.0 \times 10^{15})$ electrons per atom, i.e. 0.06. The effective equivalent weight (i.e. weight per Faraday of charge) is hence $12/0.06 = 200 \text{ g (mol e)}^{-1}$. This is to be compared with the faradaic equivalent weight of, e.g. PbO_2 (119) or $\text{Ni}\cdot\text{O}\cdot\text{OH}$ (92). The figure of 0.06 electrons per C atom is probably a minimum as it depends on the assumed inter-C atom spacing in the surface of the C electrode structures.

It is hence seen that the same orders of magnitude for specific charge storage capacitatively by porous C, as by PbO_2 or $\text{Ni}\cdot\text{O}\cdot\text{OH}$, can arise if sufficient mass of porous C is provided for charge balance to be achieved in the combined, two-electrode system.

Note that the effective equivalent weight of the capacitor electrode depends on charge-density at maximum attainable voltage, i.e. just prior to onset of over-charge. Of course, the effective equivalent weight continuously increases with declining SOC.

Usually the faradaic electrode has the following disadvantages relative to the capacitive electrode:

- (i) It has less potential power-density (but usually much better energy-density).
- (ii) It has less cycle-life.
- (iii) Its cycle-life depends materially on operating rates of discharge and recharge.
- (iv) Its cycle-life depends substantially on depths-of-discharge which determine the effective, available energy-density.
- (v) The performance of the faradaic electrode over a range of temperatures will usually be different from that of the capacitive electrode since different energies of activation and temperature-dependent degradation processes are usually involved.
- (vi) The capacitor electrode component is normally much more reversible, both kinetically and with respect to phase-interconversions, than battery-type processes where the latter phase changes are often major and slow. Phase changes do not have to take place in capacitor electrode discharge/recharge processes so the latter are intrinsically much more reversible and can be conducted at substantially higher C-rates.

The faradaic electrode has the following advantages relative to the capacitive electrode:

- (i) It has substantially better energy density. Normally charge acceptance per mole of battery-type electrochemical reagents is larger (theoretically) by a factor of 5 or more than that stored in C-type double-layer capacitors per gram atom of C as treated quantitatively in Section 4. Hence a chemical stoichiometric balance must be made gravimetrically in fabricating capacitor/battery electrode asymmetric capacitor devices to ensure appropriate conditions for charge and discharge,

i.e. avoiding overcharge or overdischarge of one or other of the conjugate pair in a cell. Also, allowance must be made in charge-capacity matching for the anticipated depth-of-discharge limitation in operation of the faradaic electrode, required for preservation of its long cycle-life (see below).

- (ii) It has (generally) a relatively flat discharge profile, quite unlike that of a capacitor electrode; exceptions are Li-intercalation electrodes.

3. The electrochemical behaviour of capacitor/battery asymmetric device systems for electrical energy, and charge storage and delivery

This combination of non-faradaic and faradaic charge-storage elements into a single two-electrode device brings together separate advantages of each component but unavoidably introduces, synergistically, some weaknesses. We list the former in note format:

- (i) The high degree of reversibility of the non-faradaic component (10^5 – 10^6 cycles) is retained at one electrode; this does not imply that an asymmetric device would cycle reversibly 10^5 times; rather, device cycle life would likely be limited by the faradaic electrode. However, the replacement of one of the faradaic electrodes with an intrinsically more reversible capacitive electrode provides advantageous opportunity for optimisation of device cycle life.
- (ii) Hence high power-density at that (capacitive) electrode is retained; then, again, the power capability of an asymmetric device would be determined, of course, by the electrode (faradaic or non-faradaic) having the lower power-density.
- (iii) The disadvantage of relatively low ED of the capacitive electrode is compensated by:
- (iv) The advantage of relatively high ED of the rechargeable faradaic electrode; thus an asymmetric device would have effective ED intermediate between that of the faradaic and capacitive electrodes, i.e. as noted by Zheng [24]; asymmetric devices involving one electrode of high-area carbon and the other a faradaic one have substantially improved ED over that of a symmetric carbon/carbon d.l. capacitor.
- (v) The disadvantage of the two capacitive electrodes in a regular symmetric electrochemical capacitor device, each having a voltage on discharge that declines almost linearly with state of discharge, is halved since the faradaic electrode, especially $\text{PbO}_2/\text{PbSO}_4$, has relatively constant electrode potential down to ca. 10% SOC. Thus, the discharge voltage curve is asymmetric (see below) with respect to state of discharge.
- (vi) Related to point (v), the accessible ED is larger than that for a symmetric configuration since the asymmetric device capacitance is twice that of a

two-capacitive electrode device (Eq. (1)); asymmetric device: $C_p = \infty$, $C_n = C$ and net total capacitance, $C_T = C$; two-capacitive electrodes: $C_p = C_n = C$ and $C_T = C/2$. Furthermore, with a fortuitous choice of faradaic electrode, the voltage profile on discharge may be “lifted” with respect to that of a capacitive device (window of voltage operation for a two-capacitive electrode device in aqueous electrolyte is 1.2–0 V, while for a PbO_2/C device discharge can be achieved between 2.1 and 0.9 V).

- (vii) Self-discharge (SD) behaviour, which arises at both electrodes of a symmetric capacitor cell, becomes modified since the SD is now determined by one electrode (see Section 8) more than the other and the net result is usually an improvement.

The above factors will determine how the faradaic electrode component *should be matched* with the capacitive, second, electrode in a cell in order to optimise the performance of the combined pair in an operating asymmetric device cell.

The following two points need to be addressed to ensure the device operates optimally:

- (a) The cell charge-capacity (Ah) must be limited by the “capacitive electrode”, so that the faradaic-type battery electrode is operated down to an *appropriate* SOC so as to optimise the cycle life and ED of the resulting device. For a d.l./ PbO_2 type asymmetric device, the faradaic electrode should be cycled upon discharge such that not less than 50–66% of its total capacity remains at the end of cell discharge (evaluated for a given rate or corresponding power-density), i.e. it is protected from deep depth-of-discharge or over-discharge, conditions that are well known to be undesirable for long-life performance. In fact, the patent referred to earlier in this text teaches that the capacitor electrode should be operated preferably with, at the most, one third of the charge capacity of the faradaic electrode, i.e. under conditions of “anode limitation”. This, of course, increases the effective equivalent weight of the cathode in relation to that of the coupled C-capacitor anode. For a d.l./Ni-O-OH type asymmetric cell, on the other hand, the device must be designed so as to operate at nearly 100% of the rated capacity of the faradaic electrode so as to prevent memory effect, but with sufficient control that overcharge/discharge of the Ni-O-OH does not occur. Manganese dioxide and lithium type asymmetric capacitors are also subject to design limitations as prescribed by the faradaic electrode cycle-life and charge capacity behaviours.
- (b) For a faradaic cathode electrode, such as $\text{PbO}_2/\text{PbSO}_4$ [5], the discharge/recharge rates should not exceed ca. $C/4$, as, for example, specified by Linden [25] for general lead-acid battery operation; higher rates of discharge/recharge are possible for Ni-O-OH faradaic cathode electrodes (up to, in some cases, ~ 1 C rate) [25].

4. Active mass, charge balance and state-of-charge (SOC) in design specifications for asymmetric capacitor cells

The above considerations imply that, for a given ampere-hour charge capacity, the active masses of each of the cathode or anode electrodes should be calculated on the basis of conditions (i) and (ii) in Section 2, and (a) and (b) in Section 3 in terms of effective “equivalent weights” based on Faraday’s laws for the faradaic electrode and on measured specific capacitance C (F g^{-1} or F kg^{-1}) for the capacitor electrode component, taking account of the desired “anode limitation” (expressed for the direction of discharge of the initially fully charged cell, e.g. PbO_2 or $\text{Ni}\cdot\text{O}\cdot\text{OH}$ at the cathode and the fully negatively charged C double-layer at the anode) identified in condition (a) in Section 3.

The effective equivalent weight of the C double-layer electrode depends on its specific capacitance (as defined above) and the maximum voltage to which it can be charged before any significant onset of electrolyte solution decomposition sets in (over-charge). This is effectively $\sim 1.2\text{ V}$ for aqueous media or $3.0\text{--}3.5\text{ V}$ for non-aqueous, aprotic, solvent electrolytes. In the latter case, of course, the anode capacitance has to be worked against a non-aqueous “Li-ion” cathode, e.g. Li/CoO_2 in PC in a Li^+ -ion electrolyte [17–19]. In that case, the capacitive, negative electrode would be Li/high-area C, which would be equivalent to a Li rocking-chair battery system. (Elsewhere [26], we have noted the equivalence of such phase-transfer, electrochemical systems, to pseudocapacitors [1,3].)

The operational voltage range ΔV (ca. 1.2 V for aqueous and ca. 3 V for organic electrolyte) of the C capacitor electrode determines its charge-density, q , both on a mass basis, as

$$q (\text{C g}^{-1}) = C \Delta V \quad (3)$$

if C is in F g^{-1} , and an “electron per atom” basis (as calculated in Section 2) to ca. 0.06 per C atom (aqueous) or 0.18 per C atom (organic solvent) depending, of course, on the specific C value.

This is to be compared with 1 or 2 electrons per molecule for most faradaic electrode reagents. Thus, although C has a low atomic weight, this electron per atom factor above makes its effective equivalent weight about 200, thus determining its real energy-density in an asymmetric device. Furthermore, the theoretical value of the equivalent weight, given by Eq. (3) is usually appreciably greater, also for other reasons, than the apparently available value due to restriction of access of electrolyte to the finest pores of the porous-electrode matrix. Also, in pulsed or AC modulation, another restriction arises due to the de Levie signal penetration effect [27] associated with the distributed RC network (equivalent to a transmission line) that represents the equivalent circuit of the micro-structure of the C electrode matrix (or of other systems such as high-area RuO_2 [3,28]). Thus, the effective

energy-density of a double-layer capacitor electrode may also show a dependence on discharge/recharge rate [29].

As remarked earlier in this article (Section 3 (a)), for a PbO_2 based asymmetric device, the practical charge capacity of the faradaic electrode should be some 33–50% greater than the practical charge capacity of the C double-layer electrode in order to maintain anode limitation and good cathode rechargeability. In this regard, note that the effective charge capacity of faradaic cathode materials is usually appreciably dependent on *rate* of operation, i.e. operating power-density, so that this behaviour has to be factored into mass and charge balance calculations for optimisation of the asymmetric, two-electrode, combination in a cell module.

Note also that achievable EDs at faradaic electrodes are usually substantially lower than the theoretical ED, and depend on operating power levels (Ragone plot behaviour).

5. Power balance

Electrochemical capacitor electrodes are generally perceived to be capable of substantially higher levels of power operation than faradaic electrodes of comparable charge capacity (subject to the limitations, discussed in Ref. [30], of the distributed RC network [27] referred to above). Hence, combination of the latter type of electrode with the former can inhibit the potentiality for high-power operation of that capacitor electrode unless allowance is made for such power-density differences.

Under operation, the power dissipation (rate of energy consumption or delivery) in a cell applies communally to both electrodes. However, the *power-density* in operation of each electrode at a common current has to be adjusted in terms of active mass and real surface area of each electrode in the design of the cell, according to the principles stated above. This amounts to optimising current-densities at each electrode of the asymmetric device.

Individual electrode specifications, according to the optimisation factors listed earlier, are of much more importance in the design of asymmetric hybrid cell types than for symmetric capacitor cells of the conventional kind, made from two C double-layer capacitor electrodes, worked one against the other. However, even then some adjustments have to be made to allow for the usually different specific capacitance of high-area C exhibited on positive polarisation from that on negative polarisation, as for the case of Hg noted earlier (Section 1).

6. Form of discharge curves

It is useful to discuss the forms of discharge curves for a symmetrical electrochemical capacitor in comparison with those of an asymmetric faradaic/non-faradaic device.

The primary difference between an asymmetric capacitor/battery electrode combination over a two-electrode,

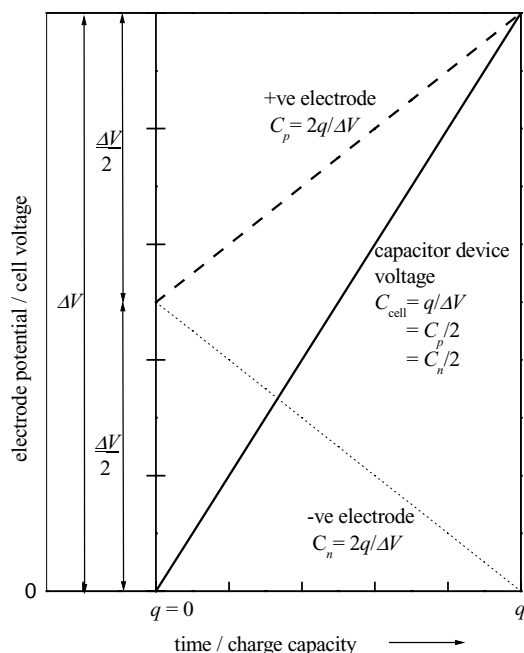


Fig. 1. Schematic voltage profiles for charging of a symmetric double-layer capacitor; (---) positive electrode and (···) negative electrode potential, (—) cell voltage.

double-layer capacitor is that the non-faradaic capacitor electrodes have *intrinsically declining* electrode potentials on discharge determined by the relation between capacitance C , charge q and voltage, ΔV , across the capacitor (Eq. (3)), or generally

$$C = \frac{q}{V} \quad (4)$$

so that V or ΔV is proportional to accumulated charge, q while, ideally at least, for battery-type electrodes based on two well-defined phases at equilibrium overall states-of-charge, an electrode potential is exhibited that is (ideally) independent of SOC and determined by the thermodynamics of the electrode reactions.

Fig. 1 shows the normal (ideal) course of potential change of each electrode of a two-electrode double-layer capacitor device exhibiting half the theoretical capacitance of each electrode measured separately due to the series combination (Eq. (1)). Fig. 1 also shows the resulting, two-electrode cell voltage, ΔV , as a $f(\text{SOC})$ or charge capacity and is drawn schematically for the case where the specific capacitance C per cm^2 is the same for positive as for negative polarisation. In this case the device capacitance is half that of either of the positive or negative electrodes.

More commonly C is different for positive (p) compared with negative (n) polarisation, as referred to in Section 3. The charging profiles for the individual electrodes and resulting cell voltage for a two-electrode device having capacitance of the positive (C_p) greater than that for the negative electrode (C_n) (as found at Hg [12]) by an arbitrary factor ‘ x ’ ($x > 1$) are shown in Fig. 2a. For such a device, substitution

of the individual electrode capacitances ($C_p = xC_n$ and C_n) into Eq. (1) results in an overall cell capacitance of $C_T = (x/(x+1))C_n$. The cell capacitance is intermediate between that for a single electrode (i.e. C_n) and that shown schematically in Fig. 1 ($C_n/2$). In Fig. 2b is shown the complementary example in which the negative electrode capacitance is greater than the positive electrode capacitance ($C_n = xC_p$).

More generally still, C is commonly not constant with changing electrode potential or cell voltage (cf. Refs. [1,12,14]) as found for various C materials depending on their provenance and pretreatment conditions [14].

In the case of combination of a capacitor-type electrode with a faradaic battery-type electrode, the principal difference, ideally, is the relative lack of decline of electrode potential of the faradaic electrode with its state-of-charge until towards the end (~ 5 , or 0% ideally) of the discharge half-cycle, exemplified here with the $\text{PbO}_2/\text{PbSO}_4$ half-cell electrode (cf. Ref. [5]) and schematically illustrated in Fig. 3 for combination with an half-cell electrode (Fig. 1) of the capacitor type.

From Fig. 3 it is seen that the decline of cell voltage, ΔV , with diminishing SOC is, of course, mainly due to decline of the electrode potential of the capacitor electrode component rather than in *both of them* as in a symmetric electrochemical capacitor (Fig. 1). This means, importantly, that all of the energy-density and accumulated charge stored in the d.l. capacitor half-cell element is relatively accessible since it is combined, effectively, with the infinite capacitance of the battery element. Hence the accessible C , as given by Eq. (1), is $C_{\text{d.l.}}$ (with $C_p = \infty$ and $C_n = C_{\text{d.l.}}$) rather than $0.5C_{\text{d.l.}}$ for a symmetric capacitor device. The whole of the capacitance of the d.l. capacitor, half-cell electrode is therefore available for energy and charge storage and delivery, giving a higher ED for the negative electrode. The result of this situation is shown in Fig. 3, as has been illustrated in a presentation by Beliakov [6].

The reduced energy and power of the asymmetric and symmetric capacitor devices with respect to the maximum energy E_{cmax} ($= CV_{\text{cmax}}^2/2$) and maximum power P_{cmax} ($= IV_{\text{cmax}}$) of a single double-layer capacitive electrode (i.e. E/E_{cmax} and P/P_{cmax}) are plotted as a function of reduced time t/t_m (where t_m is the time to fully discharge the capacitive electrode at current I , and the subscript cmax refers to the maximum in E , P or V for a single capacitive electrode) in Fig. 4 for the asymmetric capacitor having a faradaic positive electrode. The defining equations for these plots are presented in Table 1. The effects of IR, Tafel and concentration polarisation (cf. Ref. [29]) are not considered in these calculations. Both energy and power capabilities of the asymmetric device are superior to the two-electrode symmetric capacitor device (provided, of course, a suitable faradaic electrode is chosen such that the operating voltage of the asymmetric device is ‘‘raised’’ as compared to the two-electrode symmetric and single electrode cases). The calculation also assumes that the device is operating at discharge current-densities below any limits imposed by power

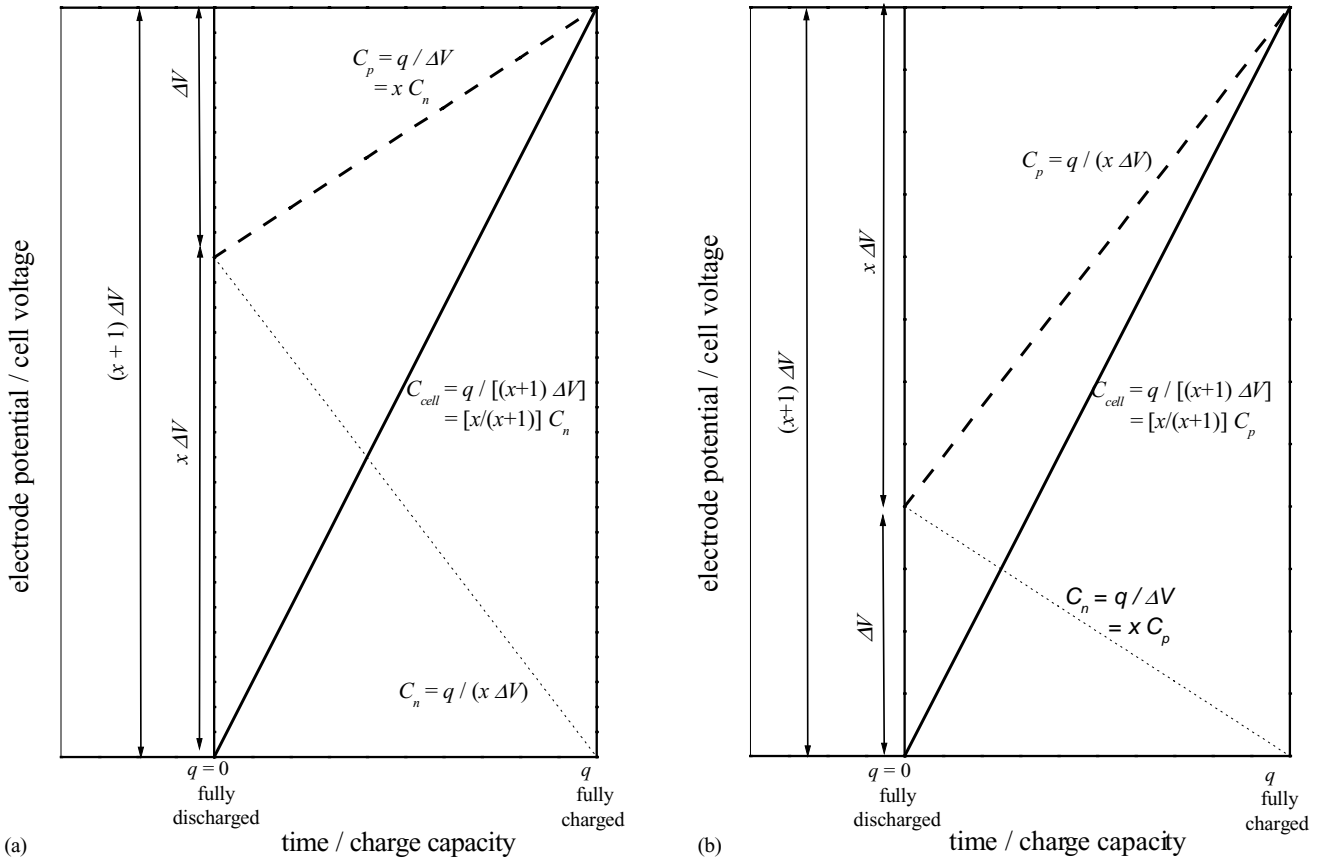


Fig. 2. As in Fig. 1 but for an asymmetric double-layer capacitor having different specific C values for the positive and negative electrodes: (a) $C_p = xC_n$ and $C_T = (x/(x + 1))C_n$; (b) $C_n = xC_p$ and $C_T = (x/(x + 1))C_p$; where x is an arbitrary constant >1 ; (---) positive electrode and (···) negative electrode potential, (—) cell voltage.

restrictions at either the capacitive or faradaic electrodes. Clearly the asymmetric capacitor device offers potential advantages over the symmetric device.

Other significant points are as follows:

- (i) The rate of decline of voltage on diminishing SOC upon discharge is only about half that which would arise in the overall discharge of a symmetrical capacitor cell having both electrodes the same (cf. curves in Fig. 4a).
- (ii) The operating voltage of the asymmetric combination of electrodes hence remains higher through discharge

and remains longer (Figs. 3 and 4) than for the symmetric capacitor (Fig. 2) (provided, of course, again that a suitable faradaic electrode is chosen); hence the operating power- and energy-densities can remain higher through most of the discharge half-cycle.

- (iii) A residual, finite voltage remains across the device as $SOC \rightarrow 0$ upon completion of discharge ($t/t_m = 1$) of the anode-limiting capacitor electrode, but is not accessible to discharge except through other short-circuiting conditions and associated processes. This residual voltage is an interesting feature of discharge of asymmetric

Table 1
Defining equations for Fig. 4

Single capacitor electrode	Two electrode capacitor device	Asymmetric capacitor device
$\frac{E_{max}}{E_{cmax}} = 1$	$\frac{E_{max}}{E_{cmax}} = \frac{1}{2}$	$\frac{E_{max}}{E_{cmax}} = \frac{2V_f}{V_{cmax}} - 1$
$\frac{E}{E_{cmax}} = \left(1 - \frac{t}{t_m}\right)^2$	$\frac{E}{E_{cmax}} = \frac{1}{2} \left(1 - 2\frac{t}{t_m}\right)^2$	$\frac{E}{E_{cmax}} = \left(\frac{t}{t_m}\right)^2 + \frac{2V_f}{V_{cmax}} - \left(\frac{2}{V_{cmax}}\right) \left(\frac{t}{t_m}\right) - 1$
$\frac{P_{max}}{P_{cmax}} = 1$	$\frac{P_{max}}{P_{cmax}} = 1$	$\frac{P_{max}}{P_{cmax}} = \frac{V_f}{V_{cmax}}$
$\frac{P}{P_{cmax}} = \left(1 - \frac{t}{t_m}\right)$	$\frac{P}{P_{cmax}} = \left(1 - 2\frac{t}{t_m}\right)$	$\frac{P}{P_{cmax}} = \frac{V_f}{V_{cmax}} - \frac{t}{t_m}$

V_{cmax} , E_{cmax} , P_{cmax} are, respectively, the maximum voltage, energy and power of a single capacitive electrode; V_f is the constant discharge voltage of the faradaic electrode and t_m is the time to fully discharge the capacitive electrode.

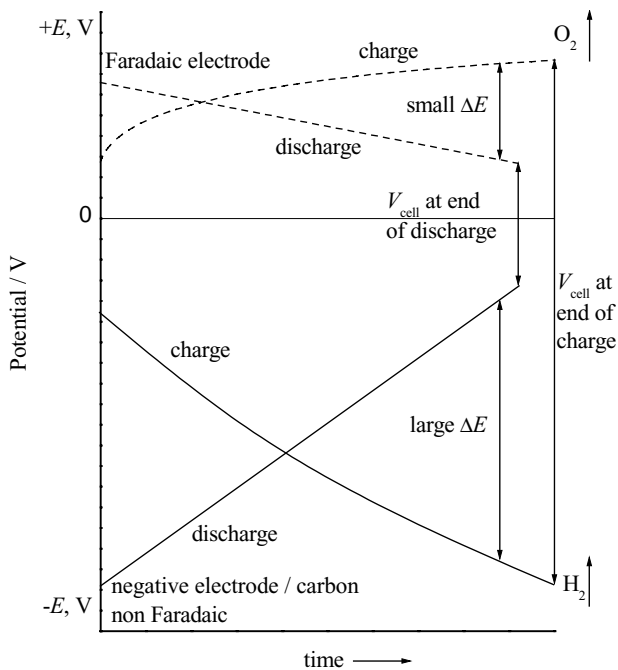


Fig. 3. Voltage profiles for each of the two electrodes of an asymmetric double-layer capacitor electrode combined with a typical faradaic, battery-type electrode showing residual cell voltage after discharge.

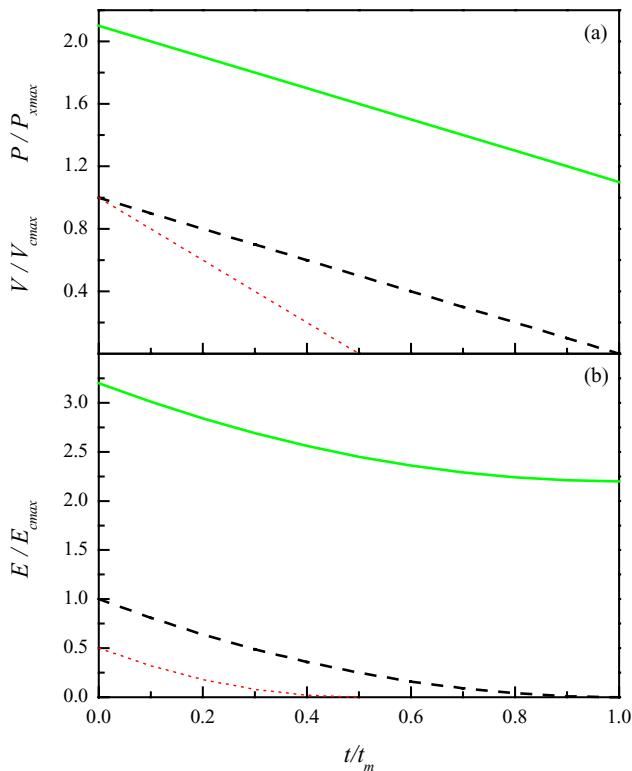


Fig. 4. Energy, E , power, P , and voltage, V , for each of a single capacitor electrode (---), a symmetric two-electrode capacitor (···) and an asymmetric capacitor device (—) plotted as E/E_{cmax} , P/P_{cmax} and V/V_{cmax} as a function of the reduced time, t/t_m ; where E_{cmax} , P_{cmax} and V_{cmax} are the maximum voltage, energy and power of a single capacitive electrode and t_m is the time to fully discharge the capacitive electrode.

devices and may have some specific advantages in special applications.

- (iv) Self-discharge behaviour of the combined but different electrodes will differ from that for the symmetric cell comprised of two non-faradaic electrodes.
- (v) The cell voltage may be used as an accurate indication of SOC due the voltage of the capacitive electrode being dependent on charge capacity (SOC).

7. Exemplification by evaluation of electrochemical behaviour of a $PbO_2/PbSO_4$ —C double-layer asymmetric capacitor system

7.1. System studied

Asymmetric cell modules, comprised of $PbO_2/PbSO_4$ positive-plate electrodes of the type used in “lead-acid” batteries, worked against high specific-area carbon powder electrochemical-capacitor electrodes, were provided by C and T Laboratories, Toronto. The electrolyte was “lead-acid” battery aqueous sulphuric acid. Modules were initially sealed cells having 0.15–0.2 Ah charge capacity. The relative charge-capacities of the anode/cathode pairs were adjusted to meet the requirement of cathode (i.e. capacitor electrode) limitation according to the condition stated in Section 3 (a), applied to maintain good cyclability (see below) of the $PbO_2/PbSO_4$ positive electrode.

7.2. Charge/discharge regime

A modified constant current charging regime was applied to the cells. The cells were charged sequentially at 1.95, 1.50, 1.0, 0.5 and 0.2 A steps each to a maximum cut-off voltage of 2.3 V. A constant discharge current of 0.35 A was applied immediately following the charge schedule. The discharge cut-off voltage was set to half the maximum voltage on charge (i.e. 1.15 V). After completion of the discharge, prior to recharge, the cells were left on open-circuit for a 30 min rest period. Monitoring of the open-circuit potential during this “rest” period was useful in assessing the “health” of the cell.

7.3. Cyclability and efficiency

Charge/discharge cycling was carried out following the regime described in Section 2. Excellent reproducibility of the forms of the cathode/anode half-cycle was maintained over an extended period of time (up to the date of submission of this paper, 10,000th cycle, from December 2001) as seen in the solid line from the 3097th cycle compared with the dotted line for the 6325th cycle (Fig. 5). The detailed reproducibility of charge/discharge is illustrated for a sample of 11 cycles shown in Fig. 6.

The coulombic efficiency for discharge/recharge as a function of cycle-number, from 500 to 7100, is shown in

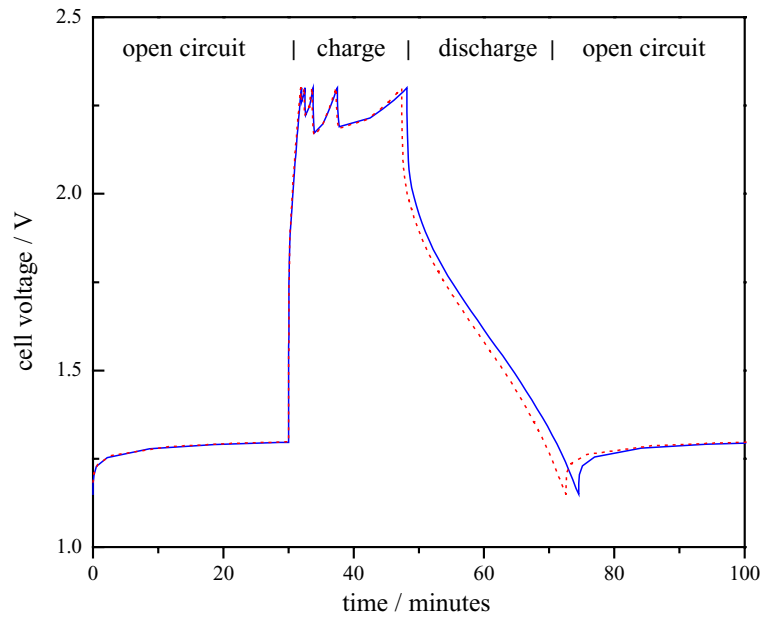


Fig. 5. Recharge/discharge profile as a function of time for an asymmetric capacitor; (—) 3097th cycle; (···) 6325th cycle.

Fig. 7, (□) and a performance figure of ca. 90–95% has been maintained over most of the above cycle life, to date. This figure also shows the dependence of charge-capacity (■) as a function of the cycle-number.

Additionally, the *energy-efficiency* was evaluated through the period of cycling and is also presented in Fig. 7. The energy efficiency was in the range of 63–67%. For comparison, energy and coulombic efficiencies for lead-acid and

Ni-based battery systems are presented in Table 2, based on data in Ref. [25].

Energy efficiencies are significantly lower than are the coulombic efficiencies as they include the effects of IR polarisation, Tafel and concentration polarisation [30]. The net result of these effects is that the voltage applied during charge is significantly higher than that delivered on discharge, as is usually and unavoidably the case. Generally, energy

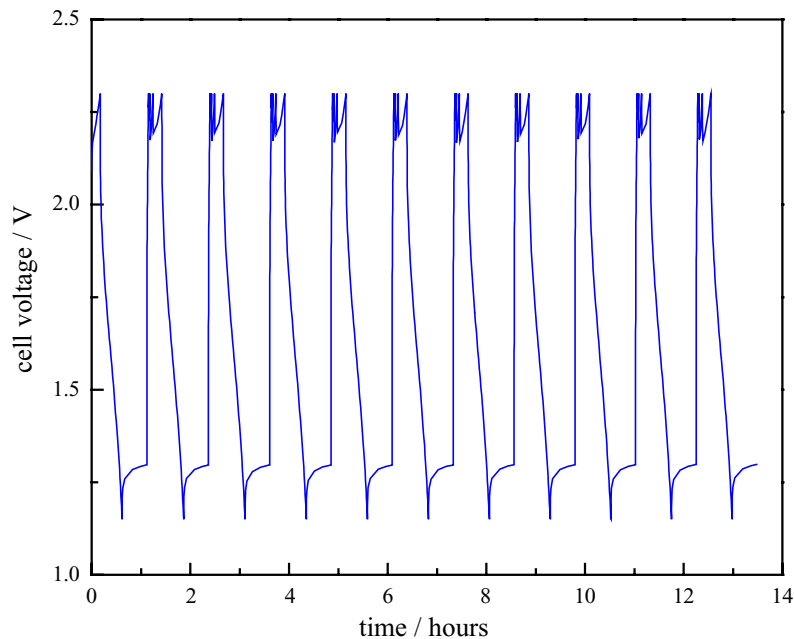


Fig. 6. Detailed recharge/discharge voltage profiles for a sample of 11 cycles for an asymmetric capacitor device.

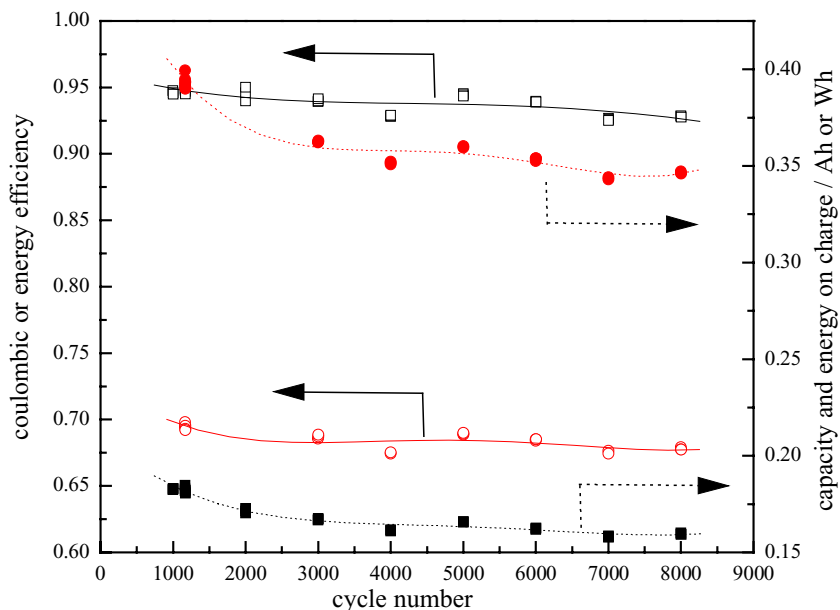


Fig. 7. Coulombic (\square) and energy (\circ) efficiencies and capacity (\blacksquare) and energy (\bullet) on charge as a function of cycle number (1000–8000 cycles) for discharge/recharge of an asymmetric capacitor device.

efficiency will be a function of recharging/discharging rate and will decrease as the rate of recharge/discharge increases.

7.4. Single-electrode behaviour on discharge and recharge, using a “third” electrode as reference

Most cycling data on practical batteries is obtained from charge/discharge curves obtained in terms of the charge and discharge currents evaluated as a function of changes of the overall battery anode-to-cathode voltage but rarely of single-electrode potentials.

However, from a more fundamental point of view, it is desirable to be able to record the electrode-potential changes at single electrodes (anode or cathode) as a function of charging or discharging currents. This requirement is specially important for the asymmetric type of cell examined in the present work where the anode and cathode electrodes

behave, electrochemically, in quite different ways in the “asymmetric” device.

In the present work, we have recorded anode and cathode potentials separately as a function of SOC, versus a Hg/Hg₂SO₄ reference electrode external to the cell but communicating with it electrically via an electrolyte capillary probe or a wetted wick having access to an otherwise sealed cell via a small hole drilled through its case at an appropriate point between anode and cathode.

Sample results of such measurements are shown in Fig. 8 for a single PbO₂/PbSO₄—C d.l. cell where overall cell voltage (—) and cathode (---) potential changes for a single charge–discharge cycle. By this means, specific differences of the charge/discharge half-cycles can be directly and easily perceived.

We believe this is an important and significant aspect of the experimental procedures employed here, and should be more widely used. It is also an essential aspect of recordings of self-discharge of electrochemical power sources where self-discharge mechanisms (cf. our previous work in Ref. [31]) are usually different at anode and cathode electrodes. This is specially the case where asymmetric devices are concerned involving electrodes of very different types, viz. faradaic and non-faradaic.

Table 2

Energy and coulombic efficiencies of various electrochemical charge storage devices

System	Efficiency (%)	
	Coulombic (Ah)	Energy (Wh)
Lead-acid		
Pasted, Planté	90	75
Tubular	80	70
Nickel–cadmium		
Pocket vented	70	60
Sintered vented	70–80	60–70
Sealed	65–70	55–65
Nickel/metal hydride	65–70	55–65
Asymmetric C/PbO ₂	90–95	63–67

8. Self-discharge behaviour

The overall self-discharge behaviour of a two-electrode cell is ideally the sum of the individual profiles of self-discharge which takes place in opposite directions at the individual electrodes recorded against a reference electrode. A practical exception arises when products of one

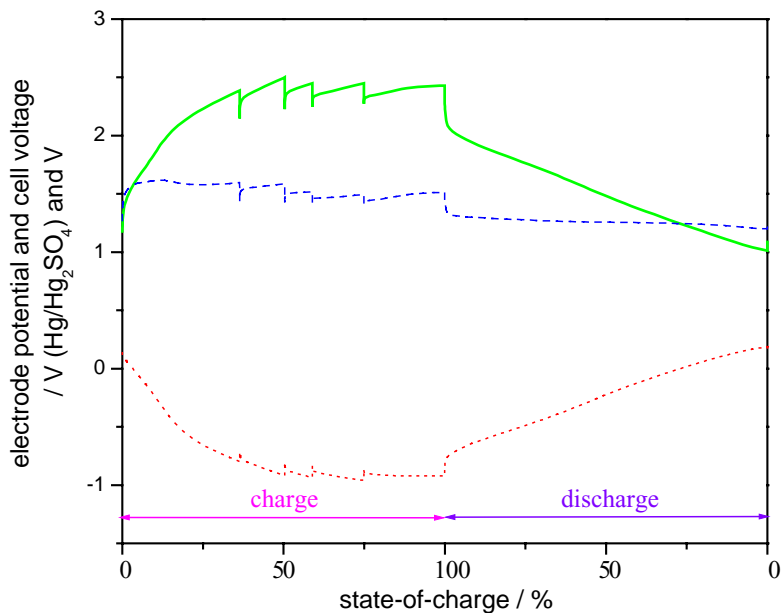


Fig. 8. Cell voltage (—), anode (···) and cathode (---) potential with respect to a stable reference electrode as a function of time for recharge and discharge of an asymmetric capacitor.

electrode process can diffuse and depolarise the other, e.g. as in nickel-oxide/zinc cells or Zn/Br₂ cells. In the case of a C double-layer anode coupled with a PbO₂/PbSO₄ cathode (on discharge), it is likely that the ideal additive self-discharge behaviour will be approached but this has to be experimentally verified. It will depend, for example, on whether any carbonaceous impurities arise from the high-area C electrode and diffuse to the cathode or whether any lead ions (very slightly soluble) change the specific capacitance of the C, in time on open-circuit. Arguably, the overall self-discharge of the asymmetric capacitor cell can be significantly less since faradaic electrodes, the potentials of which are thermodynamically based, are usually more stable than charged capacitor electrodes that have no thermodynamically defined electrode processes that would be self-stabilising. Thus, the overall self-discharge rates may, therefore, be determined effectively by only one electrode, rather than both (Fig. 2) in opposite directions—hence an advantageous situation.

A final practical point is that if one electrode of a couple self-discharges at an appreciably greater rate than the other, then, upon recharge, the latter electrode could suffer overcharge in the next recharge half-cycle.

Substantially more work has to be done on the above aspects of asymmetric-cell behaviour and is in progress in our laboratory.

9. Conclusions

A series of recommendations can be made for the design and operation of the so-called asymmetric capacitor electrochemical power sources in which a faradaic, battery-type electrode is coupled with a non-faradaic, electrochemical

supercapacitor-type electrode. The charging characteristics of such electrodes are very different, so special conditions have to be adopted for the operation of the pair in order to optimise their overall performance in the asymmetric device with respect to factors such as: (a) long cycle-life; (b) balanced charge capacities, taking into account effective equivalent weights; (c) choice of anode limitation conditions to ensure good cycle-life of the faradaic-type cathode material and (d) to ensure optimal power-density of the cathode process (on discharge and recharge).

Experimental aspects of operation of a PbO₂/PbSO₄—carbon double-layer capacitor type of rechargeable electrochemical asymmetric capacitor power source are described and demonstrate excellent reversibility of discharge/recharge cycling and very good associated coulombic efficiency.

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