

# Diagnostic analyses for mechanisms of self-discharge of electrochemical capacitors and batteries

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## Abstract

In the charged condition, electrochemical capacitors, like batteries, are in a state of high energy relative to that of the system in the discharged state. Hence there is a 'driving force', corresponding to the free energy of discharge, tending to spontaneously diminish the charge if some mechanism(s) of self-discharge exist. An ideally polarizable (chargeable) capacitor has no self-discharge or current-leakage pathway and hence can remain charged indefinitely. However, practical capacitors, like batteries, suffer appreciable self-discharge over periods of days or months so that this phenomenon is of major interest in evaluation of capacitor performance and choice of materials to minimize self-discharge. Several mechanisms of self-discharge are distinguished and the resulting forms of the change of potential on open-circuit with time or log time provide a means of identifying the type of self-discharge process that occurs. With  $\text{RuO}_2$ , some remarkable potential-recovery effects arise following discharge.

*Keywords:* Supercapacitors; Mathematical modelling

## 1. Introduction

As outlined above, charged capacitors, like charged batteries, are in a state of high free-energy relative to that of the discharged state, so there is a pseudo 'driving-force' for their 'self-discharge', as illustrated in Fig. 1, if appropriate mechanisms are available for passage of Faradaic currents. Similar considerations apply to battery systems. However, the electrochemistry of decline of charge in a double-layer capacitor electrode [1] is usually different from that at a bulk-phase battery electrode [2,3]. At the former, charge is lost by some thermodynamically allowed, direct Faradaic interphasial leakage while at the latter some anodic/cathodic mixed process, analogous to corrosion, must take place [2,3] since much more equivalent charge than that on the double-layer is generally lost.

## 2. Practical phenomenology of self-discharge

When capacitors or batteries are charged and then left on open-circuit, a certain degree of 'self-discharge' can set in depending on the chemistry and electrochemistry of the system, the purity of reagents and electrolyte, and the tempera-

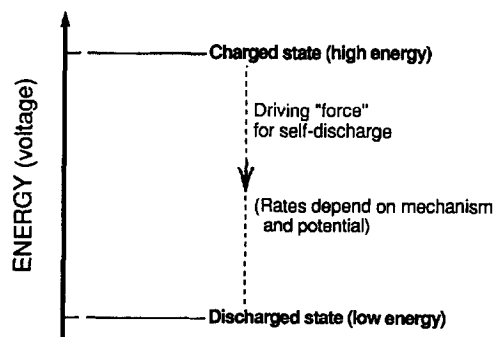


Fig. 1. Illustrating the Gibbs energy 'driving force' for self-discharge of a battery or capacitor.

ture. The rate of self-discharge, which usually diminishes with time, determines what is called the 'shelf-life' of batteries which is especially important in the case of primary cells which are sold in the charged condition and stored as inventory. Some battery systems have excellent shelf-life, e.g.  $\text{Li/SOCl}_2$  primaries, while others such as  $\text{NiOOH/Cd}$  or  $\text{NiOOH/Zn}$  have substantially poorer lifetime in the charged state due to self-discharge processes.

Similar self-discharge can arise in the case of electrochemical capacitors in the charged state but for somewhat different reasons, in detail, and with different mechanisms from those for the case of charged batteries. However, the practical result

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is the same: after some period of time on standing in the charged condition, charge may have become lost. Self-discharge causes a severe limitation to, or inconvenience in, the applications, performance and reliability of electrochemical capacitors, especially when capacitors are employed for 'standby' purposes.

In order to maintain 'full charge', a 'float current' of small magnitude can be applied to the charge storage system to balance the self-discharge rate. It measures the initial (highest) self-discharge rate. However, this adds technological and hardware complexity, so minimization of the intrinsic self-discharge rates is a desideratum to which research efforts are directed.

It must be emphasized that an ideal, non-leaky capacitance, corresponding to an 'ideally polarizable electrode' [1], never suffers self-discharge. Self-discharge can only occur if some Faradaic electron-transfer process(es) can take place at and below the maximum potential attained on charge or if some ohmic leakage between the electrodes arises due to faults in construction.

### 3. Self-discharge mechanisms

A capacitor or battery in the charged condition is in a state of high positive free-energy relative to that for the discharged or partially charged state (Fig. 1). Three kinds of self-discharge mechanism can then operate.

(i) If the capacitor (or battery cell) has been overcharged beyond the respective decomposition potential limit of the electrolyte, then the self-discharge corresponds to the spontaneous decline of the overvoltage,  $\eta$ , due to the overcharging current and arises on account of continuing discharge across the double-layer until  $\eta \rightarrow 0$ . The leakage process corresponds to a Faradaic charge-transfer reaction having a potential-dependent Faradaic resistance,  $R_F$ , operating in parallel across the double-layer capacitance, its value increasing with declining potential.

(ii) If the capacitor material and/or its electrolyte contain impurities that are oxidizable or reducible within the potential range corresponding to the potential difference across the capacitor on charge, then the capacitor becomes to some extent non-polarizable. If only low concentrations of impurities are present then the self-discharge redox process(es) is (are) diffusion-controlled. For some redox impurities, there is a 'shuttle' effect with 'red' and 'ox' species, e.g.  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{O}_2$ ,  $\text{H}_2\text{O}_2$ , interchanging and diffusing between the positively and negatively charged matrices of the electrochemical capacitor.

It is important to recognize that self-discharge processes in a 2-electrode configuration may not be identical to those at individual separate electrodes due to such 'shuttle' processes involving diffusion of impurities *between* the pair of electrodes.

In case (i), if  $\text{H}_2$  and  $\text{O}_2$  are generated due to adventitious overcharge at the polarized half-cell electrodes, then situation

(ii) can be set up with cross-diffusion of  $\text{H}_2$  (to the positive electrode) and  $\text{O}_2$  (to the negative one). At carbon, for example,  $\text{O}_2$  can be reduced to  $\text{H}_2\text{O}$  or  $\text{HO}_2^-$  ion (or  $\text{H}_2\text{O}_2$ ), which can then behave either as an oxidizing or reducing agent.

(iii) If the energy-storage device has internal ohmic leakage pathways, e.g. due to incomplete sealing of bipolar electrodes or inter-electrode contacts, self-discharge will take place through a 'Galvanic couple' effect.

### 4. Self-discharge by 'activation-controlled' Faradaic processes

This situation corresponds to case (i) above or to any electrochemical charge leakage process that is non-diffusion controlled. Then the kinetics of self-discharge are determined by an activation-controlled electrochemical reaction [2,3] that kinetically follows the Tafel equation which, in exp form, can be conveniently written as:

$$i(\eta) = i_o \exp[\alpha\eta F/RT] \quad (1)$$

where  $i(\eta)$  is the density of current in  $\text{A cm}^{-2}$  or  $\text{A m}^{-2}$  at an overcharge overvoltage of  $\eta$ ,  $i_o$  is the exchange current-density (i.e. the current passing reversibly in both anodic and cathodic directions, at equal values per  $\text{cm}^2$  or  $\text{m}^2$  at the reversible potential ( $\eta = 0$ ) for which  $i(\eta) = 0$ ) and  $\alpha$  is the so-called transfer coefficient characterizing the effect of electrode potential on the activation energy of the reaction.  $\alpha$  determines the slope of the (Tafel) relation between  $\eta$  and  $\log i$  and also that of the self-discharge relation (see below). In the simplest case, the self-discharge process is simply a continuation of the overcharge reaction which discharges the double-layer capacitance,  $C_{dl}$  until  $\eta \rightarrow 0$ .

If the rate of decline of  $\eta$  with time is  $-d\eta/dt$ , then using Eq. (1),

$$-C_{dl}(d\eta/dt) = i_o \exp[\alpha\eta(t)F/RT] \quad (2)$$

Two conditions may be discussed as follows, writing  $\eta$  more generally as  $V$ .

#### 4.1. Case 1. C constant with potential V

Upon commencement of self-discharge after termination of the polarization, the condition

$$-C dV/dt = i_o \exp(\alpha VF/RT) \quad (3)$$

obtains where the right-hand term is the Tafel function as in Eq. (1). After rearrangement and integration, Eq. (3) becomes

$$\frac{RT}{\alpha F} \exp(-\alpha VF/RT) = \frac{i_o}{C} t + \tau = \frac{i_o}{C} \left[ t + \frac{C\tau}{i_o} \right] \quad (4)$$

where  $\tau$  is an integration constant. Taking logs and with further rearrangement gives

$$V = -\frac{RT}{\alpha F} \ln \frac{\alpha F i_o}{RTC} - \frac{RT}{\alpha F} \ln \left[ t + \frac{C\tau}{i_o} \right] \quad (5)$$

Hence the potential  $V$  (or  $\eta$ ) declines with  $\ln t$  or  $\log t$  plus a term involving  $\tau$ . Note that the slope of this relation is the negative of the Tafel slope of the initial polarizing process,  $RT/\alpha F$ .

In the case where the Faradaic current is a parasitic current rather than an overcharge current the same analysis still applies so long as there is activation control in that impurity process, i.e. a Tafel relation obtains, but different from that for the Faradaic overcharging current.

The constant  $\tau$  follows from the initial condition,  $t=0$ , i.e.  $V=V_i$  and  $i=i_i$ , the initial polarization conditions. Then, noting  $i_i=i_o \exp(\alpha V_i F/RT)$  (cf. Eq. (1))

$$\tau = \left[ \frac{RT}{\alpha F} \right] \frac{i_o}{i_i} \quad (6)$$

which can be substituted in Eq. (5).

Empirical evaluation of the term  $C\tau/i_o$  in  $(t + C\tau/i_o)$  (Eq. (5)) then provides a way of determining the interfacial capacitance  $C$ .

#### 4.2. Case 2. $C$ varies exponentially with $V$

This condition can arise when a Faradaic self-discharge process, or the prior overcharge process, involves coverage by an intermediate, e.g. adsorbed H in the  $H_2$  evolution reaction, or OH and O in anodic  $O_2$  evolution (beyond  $\sim 1.3$  V in aqueous solution) that is potential-dependent. Then a pseudocapacitance,  $C_\phi$ , can arise which corresponds to the dependence of the coverage  $\theta$  of the Faradaically electro-sorbed species on potential,  $C_\phi = q_1(d\theta/dV)$  where  $q_1$  is the charge for formation or desorption of a monolayer of the intermediate.

Limitingly,  $C_\phi$  is dependent on potential as follows

$$C_\phi = K \exp(VF/RT) \text{ (low } \theta)$$

or

$$C_\phi = K \exp(-VF/RT) \text{ (high } \theta) \quad (7)$$

where  $0 < \theta < 1$ ; i.e. generally  $C_\phi = K \exp(\pm VF/RT)$ .

Introducing this  $V$ -dependent  $C_\phi$  in Eq. (3) instead of constant  $C$  gives

$$-K \exp(\pm VF/RT) dV/dt = i_o \exp(\alpha VF/RT) \quad (8)$$

where here  $\alpha_\phi$  may differ from  $\alpha$  of Case 1, depending on the mechanism of the Faradaic process. When the latter involves appreciable  $V$ -dependent coverage by the intermediate  $\alpha_\phi = 1 + \alpha$  for low  $\theta$  and  $\alpha_\phi \approx \alpha$  for  $\theta \rightarrow 1$ .

Rearranging Eq. (8) to combine the exp terms gives

$$-\exp(\pm 1 - \alpha_\phi) VF/RT dV = \frac{i_o}{k} dt \quad (9)$$

Integrating, as in Case 1, and taking logs again, gives

$$(\mp 1 + \alpha_\phi) VF/RT = -\ln(\alpha \mp 1) \frac{Fi_o}{RTK} - \ln \left[ t + \frac{K\tau}{i_o} \right] \quad (10)$$

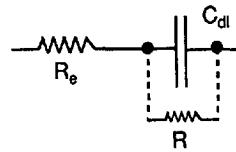
so that

$$dV/d \ln t = RT/(\pm 1 - \alpha_\phi)F \quad (11)$$

Two potential-decay slopes ( $-dV/d \log t$ ) can then arise: (i)  $-2.3 \times 2 RT/F = -120$  mV for small  $\theta$ , + sign, with  $\alpha_\phi = 3/2$ ; (ii)  $-2.3 \times 2 RT/3F = -40$  mV for large  $\theta$ , -ve sign, with  $\alpha_\phi = 1/2$ . Thus two self-discharge slopes in  $V$  versus  $\ln t$  are distinguishable, depending on whether  $C$  increases with  $V$  on potential-decay (small  $\theta$ ) or decreases ( $\theta \rightarrow 1$ ).

#### 5. Comparison with a capacitor discharging through an ohmic leakage resistance

The equivalent circuit for an ohmically leaky capacitor is simply (there may also be an equivalent series resistance, ESR,  $R_e$ ):



involving an ohmic load resistance,  $R$ . Its self-discharge characteristics will be determined then only by the  $CR$  product of the above combination. The 'self'-discharge behavior is then given by:

$$-C \frac{dV}{dt} = i \text{ through } R = \frac{V}{R} \quad (12)$$

since the potential across  $C$  is also, at any moment, equal to  $iR$ . Then

$$-C \frac{dV}{V} = \frac{dt}{R} \text{ or } -\frac{dV}{V} = \frac{dt}{RC} \quad (13)$$

Integration of this relation yields  $-\ln V = t/RC + \tau$ . When  $t=0$ ,  $V=V_i$ , as previously, so that  $-\ln V_i = \tau$  and then

$$V/V_i = \exp(-t/RC) \quad (14)$$

Hence it is  $\ln V$  that declines with  $t$  rather than  $V$  declining with  $\ln t$  as for a Faradaic, electrochemical leakage pathway. This is an important and fundamental difference between the two situations. The kinetics of potential decline are characterized by a time-constant,  $CR$ , which also determines the a.c. frequency response for this case.

#### 6. Self-discharge under diffusion-control

This case corresponds to practical examples where a capacitor is not overcharged to a potential difference beyond that for electrolyte/solvent decomposition but some depolarizing impurity is present that can undergo a Faradaic redox reaction *within* the potential range of charging and that for solvent stability. In this case the leakage current is not  $i_o \exp \alpha VF/RT$  but a diffusion-limited current

$$i_{\text{diff}} = zFD(dc_{\mathfrak{R}}/dx) \quad (15)$$

where  $c_{\mathfrak{R}}$  is the concentration of the diffusible redox species,  $\mathfrak{R}$ , and  $dc_{\mathfrak{R}}/dx$  is the gradient of concentration of  $\mathfrak{R}$  along direction  $x$  in the diffusion boundary layer near the electrode surface;  $D$  is the diffusion coefficient of  $\mathfrak{R}$  in solution. Then

$$-C \frac{dV}{dt} = zFD(dc_{\mathfrak{R}}/dx) \quad (16)$$

The solution of this type of equation is more difficult than for Case 1 since  $c_{\mathfrak{R}}$  and  $dc_{\mathfrak{R}}/dx$  are time-dependent but  $c_{\mathfrak{R}}$  and  $dc_{\mathfrak{R}}/dt$  can be obtained by solution of Fick's equations, say for semi-infinite diffusion to a plane capacitor electrode. Solutions for porous bodies or within a cylindrical pore are rather more complicated, but the diffusion path length will generally be small, on the order of microns, or less.

The time-dependence of  $c_{\mathfrak{R}}$  and  $dc_{\mathfrak{R}}/dx$  at a particular distance  $x$  from a plane electrode is generally square-root in  $t$ , so that integration of Eq. (16) will lead to a self-discharge relation for the  $t$ -dependence (decline) of  $V$  which can be distinguished from a log relation provided a sufficiently long range of  $t$  is covered. The course of diffusion is determined by Fick's two (related) laws. Solutions can be obtained by computational methods and are available in the literature, e.g. in the monographs by Crank or Carslaw and Jaeger on heat transfer and diffusion.

At smooth planar electrodes, concentration gradients can be recorded directly; unfortunately, in porous electrodes of practical significance in capacitor technology, only indirect electrochemical or analytical procedures are available. For the case of so-called semi-infinite linear diffusion the concentration,  $c$ , of a reacting diffusing substance at the electrode surface is given as a function of distance,  $x$ , and time,  $t$ , by

$$c(x,t) = c_0 \operatorname{erf} \left[ \frac{x}{2D^{1/2}t^{1/2}} \right] \quad (17)$$

where  $c_0 = c(x, t=0) = 0$  and  $\operatorname{erf}$  represents the error integral (also arising in statistics) and is to be found in tabulations of mathematical functions. The diffusion-controlled current under semi-infinite diffusion conditions at an electrode of area  $A$  is

$$I = iA = zFAD^{1/2}c_0\pi^{-1/2}t^{-1/2} \quad (18)$$

with  $I$  in A,  $F$  in coulombs,  $A$  in  $\text{cm}^2$ ,  $D$  in  $\text{cm}^2 \text{s}^{-1}$ ,  $c_0$  in mole  $\text{cm}^{-3}$  and  $t$  in s. The current is seen to be inversely proportional to the square-root of time. Hence, for the case of self-discharge associated with semi-infinite diffusion conditions

$$-C dV = zFAD^{1/2}c_0\pi^{-1/2}t^{-1/2} dt \quad (19)$$

where  $c_0$  is now the initial concentration in mole  $\text{cm}^{-3}$  of the depolarizing impurity.

Integration of the above equation leads to

$$C(V_i - V_t) = 2zFAD^{1/2}\pi^{-1/2}c_0t^{1/2} \quad (20)$$

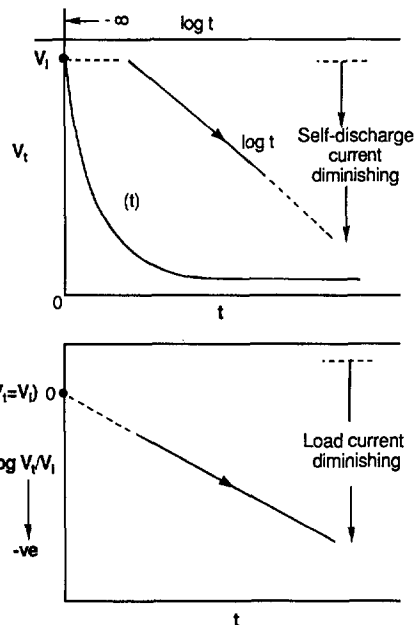


Fig. 2. (a) Time-dependence of potential on open-circuit self-discharge controlled by a Faradaic process: linear plot in the  $\log t$  or  $\log(t + \tau)$  variable (upper scale). (b) Time dependence of potential on open-circuit self-discharge when leakage is through an ohmic load resistance: linear relation in log plot of  $V_t/V_i$  vs.  $t$ .

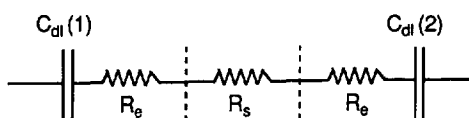
for self-discharge from an initial potential,  $V_i$ , under linear diffusion-controlled conditions. The mathematics for reaction at a cylindrical electrode can also be worked out and involves Bessel functions. This case is relevant to a porous fibrous electrode.

## 7. Slope parameters for decline of potential on self-discharge

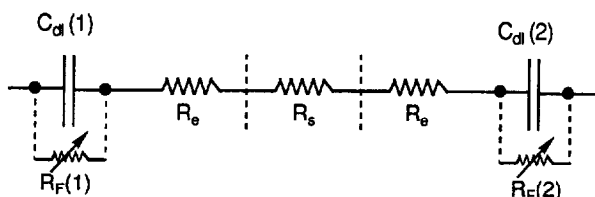
The above analyses show that three principal mechanisms of self-discharge can be distinguished by the forms of the decline of potential,  $V_t$ , in time: (i)  $V_t$  is log in  $t$  or  $(t + \tau)$ ; (ii)  $\log(V_t/V_i)$  is linear in time; (iii)  $V_i - V_t$  increases with  $t^{1/2}$  for activation-control, ohmic leakage and diffusion-control, respectively. The distinction between cases (i) and (ii) is illustrated in Fig. 2(a) and (b).

## 8. Self-discharge of double-layer type supercapacitors

Self-discharge of a double-layer type electrochemical capacitor arises in an essentially different way from that in a leaky regular capacitor because the former consists of two interfacial capacitances separated by an electrolytic resistance,  $R_e$ , plus (usually) a resistance (in series) due to the separator,  $R_s$ . The equivalent circuit is then:



Self-discharge processes can go on at either or both of the double-layer interphases depending on overcharge conditions or redox mechanisms. Thus, it is possible for asymmetric self-discharge to occur, e.g. across one double-layer or the other. Self-discharge would then be represented by an equivalent circuit involving two, possibly different, Faradaic leakage resistances, across each electrode interphase, thus:



This is an interesting and little understood situation since hitherto very little work has been done on self-discharge at 'half-cell' electrochemical capacitor electrodes.

## 9. Temperature effects in self-discharge

Self-discharge is a rate-process so is affected by temperature according to well known kinetic effects associated with activation energy,  $\Delta E^\ddagger$  in an Arrhenius relation. Then, since  $\Delta E^\ddagger$  is positive, self-discharge currents,  $i(T)$ , increase with temperature according to:

$$2.3 \log i(T) = 2.3 \log A - \Delta E^\ddagger / RT \quad (21)$$

so that  $\log i(T)$  is a linear relation in  $1/T$  the slope of which gives  $-\Delta E^\ddagger / R$ .

For Faradaically-controlled self-discharge processes,  $\Delta E^\ddagger$  is on the order of 40 to 80 kJ mol<sup>-1</sup> while, if it is diffusion-controlled,  $\Delta E^\ddagger$  is around 16 to 20 kJ mol<sup>-1</sup> corresponding to activated transfer of the depolarizing impurity or redox 'shuttle' species in the bulk of the solution, towards the electrode surface.

The important practical consequence of the temperature effect is that self-discharge of charged capacitors or batteries is a much more serious problem at 60–70°C than it is at 0–25°C. For a typical activation energy of 40 kJ mol<sup>-1</sup>, the ratio of self-discharge currents at say 70°C compared with 0°C is equal to 37 or 10<sup>1.56</sup>, a large increase. This is practically important for capacitor performance in elevated temperature environments, e.g. in torrid climates and/or under ICE-powered vehicle hoods.

## 10. Examples of experimental self-discharge behavior

Several electrochemical capacitor systems were experimentally studied with regard to the forms of self-discharge behavior they exhibited: one, a large 70 V propylene carbonate, double-layer type supercapacitor constructed in bipolar electrode configuration with high-area carbon fiber felt elec-

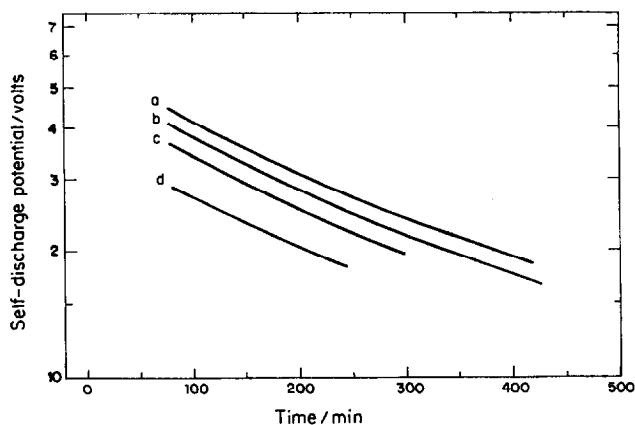


Fig. 3. Experimental data for self-discharge of the 70 V capacitor plotted as  $\log V_t$  as a  $f(t)$ . Initial potentials: a, 69.8; b, 60.4; c, 50.4; d, 39.8 V.

trodes. A second was a single electrode of the same carbon felt examined in a laboratory 3-electrode cell in 0.5 M aq. H<sub>2</sub>SO<sub>4</sub> at 298 K. The third was an RuO<sub>2</sub> oxide pseudocapacitor electrode [4] thermally formed on a Ti substrate.

Following charging to selected constant potentials (or cell voltage), the currents were interrupted by a relay and the decline of potential was digitally monitored through a high input impedance computer system over several decades of time. All solutions for the laboratory cell experiments were made up from high-purity 'Millipore' water and the purest H<sub>2</sub>SO<sub>4</sub> available, and solutions were outgassed by the bubbling of O<sub>2</sub>-free N<sub>2</sub> for an hour before experiments were commenced.

### 10.1. Behavior of the 70 V capacitor

This capacitor was a prototype constructed by Redox Corp. (Winchester, MA) to which we had access for self-discharge testing. The form of the decline of potential on self-discharge over several decades of time ( $t$ ) was examined by plotting  $V_t$  versus  $\log t$  or  $\log(t + \tau)$ ,  $\log(V_t/V_i)$  versus  $t$  and  $V_t$  as a function of  $t^{1/2}$ . The results are shown in Fig. 3; for this example, it was clear that the plot in  $\log(V_t/V_i)$  versus  $t$  applied best to the observed behavior indicating that the device suffered self-discharge through internal ohmic leakage possibly due to distributed shorts through the carbon fibers. The edge-seals of the bipolar electrodes were probably not electrolytically leaky owing to their method of construction.

### 10.2. Behavior of a single carbon-fiber felt electrode in a 3-electrode cell

Here a sample of the same high-area carbon-fiber felt electrode (Spectracorporation Spectracarb 2225) as that used in the 70 V capacitor was examined, on a small scale, in a laboratory 3-electrode cell, i.e. with a reference electrode. Here the solution was 0.5 M aq. H<sub>2</sub>SO<sub>4</sub> at 298 K. Self-discharge data were recorded over three decades of time from several initial polarizing (charging) potentials,  $V_i$ . In this case the  $V_t$  data plotted out as excellent linear relations to  $\log$

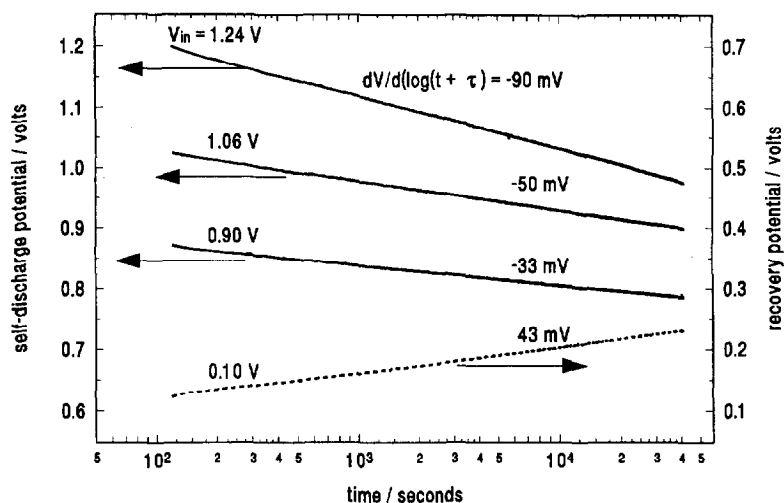


Fig. 4. Experimental data for self-discharge of the carbon fiber felt single electrode (Spectracorp Spectracarb 2225) plotted as  $V(t)$  as a log function of time  $t + \tau$  for transients taken from various initial potentials. Scale on r.h.s. is for potential recovery.

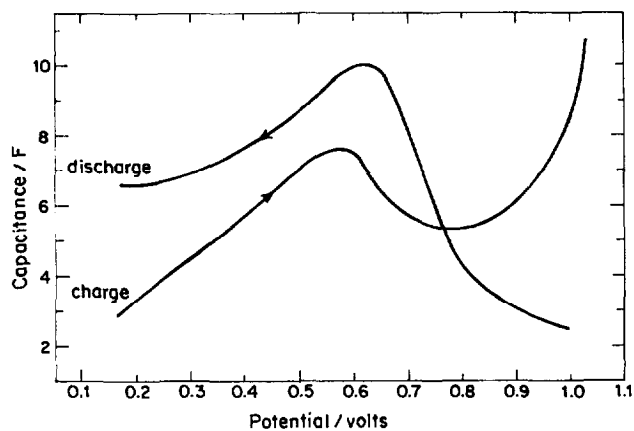


Fig. 5. Potential dependence of capacitance in F of the Spectracorp Spectracarb 2225 carbon-felt electrode (superficial area of the felt,  $\sim 0.14 \text{ cm}^2$ ) derived from galvanostatic charging at 0.8 mA.

( $t + \tau$ ) (Fig. 4) (cf. Eq. (5)) but from various  $V_i$  values separate, non-convergent, log time relations were observed having slopes dependent on  $V_i$ . This was probably due to the potential dependence of the double-layer capacitance of this electrode shown in Fig. 5. The direct relation of  $V_i$  to log of time clearly indicates a Faradaic process as the mechanism of self-discharge.

Interestingly, after imposed discharge at constant current, the potential *recovers*, also logarithmically in time (Fig. 4, scale on r.h.s.). This is probably due to non-uniform, i.e. incomplete, discharge in the porous carbon matrix which is followed, on conclusion of discharge, by relaxation (redistribution) of the charge distribution.

### 10.3. Behavior of the $\text{RuO}_2$ electrode

The  $\text{RuO}_2$  electrode was charged in 0.5 M aq.  $\text{H}_2\text{SO}_4$  at 298 K to various potentials (vs. RHE) in the range of 1.0 to 1.5 V, followed by digital recording of its potential on open-circuit. The behavior shown in Fig. 6 was observed. It was

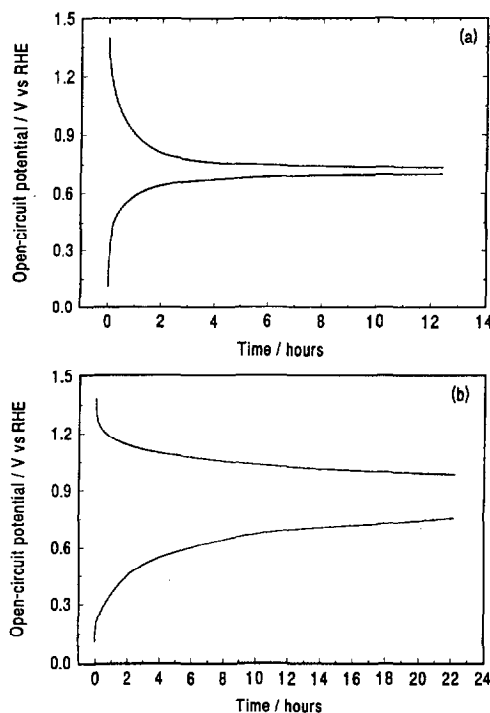


Fig. 6. Experimental self-discharge and recovery plots following forced charge and discharge of an  $\text{RuO}_2$  electrode in 0.5 M aq.  $\text{H}_2\text{SO}_4$ , at 298 K with attainment of a steady Nernstian potential: (a) thermally and (b) electrochemically prepared  $\text{RuO}_2$  films.

not fitted by either of the first two log relations tested above but rather by the time-dependence expected for a diffusion-controlled process. However, such a process is not due to any diffusion of impurity depolarizers and the potential always declined to a quasi-Nernstian value of  $0.70 \pm 0.02 \text{ V}$  (RHE). The potential was shown to follow a time-dependence well fitted by the equation for a semi-infinite diffusion process associated with *diffusion of oxidation state* due to non-uniform charging of the  $\text{RuO}_2$ , initially in the outer regions of the oxide film.

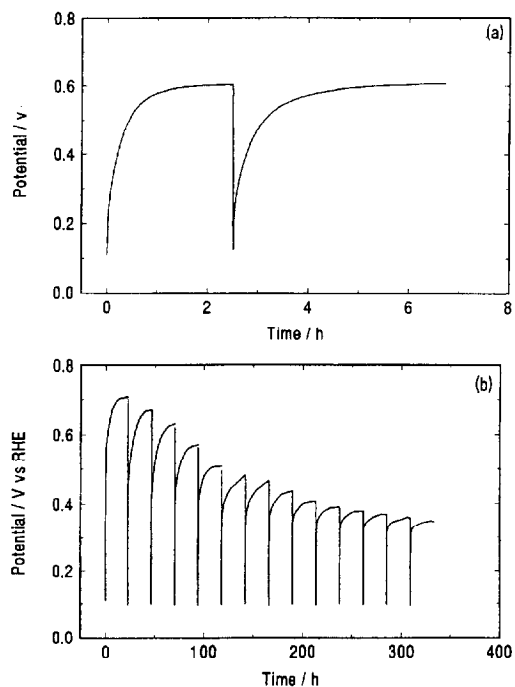


Fig. 7. Multiple potential recovery transients at  $\text{RuO}_2$  in aq.  $\text{H}_2\text{SO}_4$  at 298 K following successive galvanostatic discharges, without interim recharging; examples of successive recoveries of potential at: (a) a thick, thermally formed  $\text{RuO}_2$  film; (b) as in (a) but for a thin  $\text{RuO}_2$  film.

Correspondingly, potential recovery transients could be recorded (Fig. 6) after successive discharges and they also tended to the same 0.70 V potential which was therefore probably a well-defined Nernstian oxide redox potential. The recovery transients were also only fitted by diffusion kinetics.

An interesting and remarkable phenomenon was observed when the  $\text{RuO}_2$  electrode was cathodically discharged to 0.05 V; potential recovery towards 0.70 V took place, as described above, but a further cathodic discharge could be conducted which was followed again to recovery around 0.68 V. This behavior could be repeated a number of times, as shown in Fig. 7.

It must arise because the near-surface region of  $\text{RuO}_2$  is discharged first, followed, on recovery, by redistribution of oxidation state leading to replenishment of higher oxidation state in the surface region by proton and electron hopping.

## References

- [1] D.C. Grahame, *Chem. Rev.*, **47** (1947) 441.
- [2] H.B. Morley and F.E.W. Wetmore, *Can. J. Chem.*, **34** (1956) 359.
- [3] B.E. Conway and P.L. Bourgault, *Can. J. Chem.*, **40** (1962) 1690 and 1938.
- [4] S. Hadzi-Jordanov, B.E. Conway and H.A. Kozłowska, *J. Electrochem. Soc.*, **125** (1978) 1471.