Supercapacitors [and Discussion]

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Supercapacitors

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There is increasing interest in energy sources that are optimized to provide electrical energy at high power levels for short times. Applications include the very short pulses used in digital electronic devices, the longer power pulse demands of heart defibrillators and other implantable medical devices, and the much larger transient power requirements for electric vehicle traction.

The various mechanisms that can be used to provide pulsed energy in electrochemical systems, as well as their fundamental characteristics and applicability to the different types of pulse output requirements, are discussed.

The most favourable materials operate by means of topotactic insertion reactions. Four different electrochemical methods can be used to evaluate their critical parameters.

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1. Introduction

There are a number of applications that require electrical energy in the form of relatively short pulses. Thus devices are needed that are designed to maximize their short-term power output, independent of their total energy content. The range of both current and potential future requirements is very broad, including digital communication devices that require pulses in the millisecond range, implanted medical devices that require pulses with characteristic times of the order of seconds and vehicle traction applications where the high power demand can extend from seconds up to minutes. These all require output characteristics that are different from those that are normally considered for electrochemical systems, which are typically oriented more toward energy storage and output at lower power levels.

Because of the great variation in the requirements for transient power sources, it is unrealistic to assume that any one type of device, or any one design, will be able to optimally fulfil such diverse needs. It is now quite common to think in terms of hybrid systems that include components that can meet two different types of needs: a primary energy source and a supplementary source that can meet the transient needs for higher power levels than can be handled by the primary source.

A possible strategy is to use a high-energy system that operates at a relatively high voltage when the power demand is low. The output voltage of such energy sources typically falls off as the output current is increased. If a second high-power, but lower-energy source that operates at a lower voltage is placed in parallel, it will come into play under conditions that drive the output voltage of the primary high-energy system down into its range of operating voltage, and meet the high-power demand for a limited period. When this demand is no longer present, the voltage

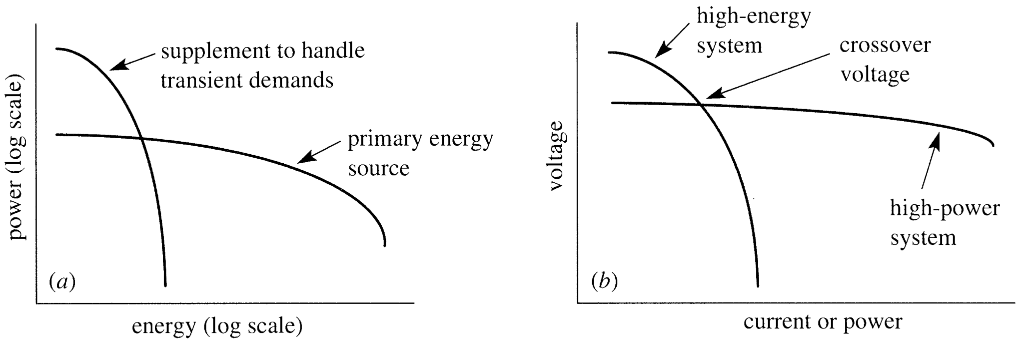

Figure 1. Desired characteristics of hybrid system: (*a*) power–energy characteristics; (*b*) desired voltage–power relationship.

will again rise, and the high-power component of the system will be recharged by the higher-energy component. The characteristics of such a hybrid combination are shown schematically in figure 1.

In order to approach the development of useful devices for this type of application one should consider the various types of charge storage mechanisms that can be employed and their thermodynamic and kinetic characteristics, as well as the relationships that determine system performance.

2. Electrochemical charge storage mechanisms

There are four basic types of charge storage mechanisms in electrochemical systems.

(*a*) *The storage of charge in the electrical double layer within the electrolyte in the vicinity of the electrolyte–electrode interface*

In this approach the electrode is considered to be chemically and electrochemically inert. The amount of charge that can be stored in the electrolyte double layer is typically of the order of 15–40 $\mu F\ cm^{-2}$ of interface (Conway 1991, 1993). Thus one tries to optimize the amount of interface in the device microstructure. Techniques have been devised to produce various types of carbon, as well as some other electronically conducting, but chemically inert materials in very highly dispersed form, leading to very large interfacial areas.

An electrode in which this is the dominant charge storage mechanism will behave like a pure capacitor in series with its internal resistance.

Devices using the storage of charge in the electrochemical double layer generally employ aqueous electrolyte cells with carbon electrodes with extremely large surface areas. They have been developed and produced commercially in large numbers in Japan for a considerable period of time. These are primarily used for semiconductor memory back-up purposes, as well as to power several types of small actuators.

(*b*) *Underpotential Faradaic two-dimensional adsorption on the surface of a solid electrode*

Due to the characteristics of the electrolyte–electrode surface structure and its related thermodynamics, it is often found that modest amounts of Faradiac electrodeposition can occur at potentials different from those needed for the bulk formation of a new phase, i.e. at potentials more positive than the bulk deposition potential for cathodic processes, and more negative than the potential necessary for bulk deposition in the case of anodic processes. This can involve the selective occupation of specific crystallographic sites on the solid surface. In such a case, it results in only partial surface coverage. In other cases, up to a complete monolayer can be deposited. This mechanism can produce an 'adsorption pseudo-capacitance' of some 200–400 μF cm^{-2} of interface (Conway 1993). This is significantly larger than the amount of charge that can be stored per unit area in the electrochemical double layer.

(*c*) *Faradaic deposition that results in the three-dimensional absorption of the electroactive species into bulk solid electrode material by an insertion reaction*

Many materials are now known that can act as solid solution electrodes. In such cases, the electroactive species diffuses into the interior of the crystal structure of the solid electrode after it is deposited from the electrolyte. This mechanism has sometimes been called 'redox pseudo-capacitance' (Conway 1991, 1993).

Since the amount of energy stored is proportional to the amount of the electroactive species that can be absorbed by the electrode, this three-dimensional storage mechanism can lead to much higher values of energy storage per unit volume of electrode structure than can result from any surface-related process. Because it makes no sense to express this bulk phenomenon in terms of the capacitance per unit interfacial area, values are generally given as Farads per gram. As the kinetic behaviour of such electrodes is related to the electrolyte–electrode area, it is also useful to have very fine microstructures in such devices.

In contrast to the Japanese development and commercial production of double-layer storage devices, work on devices that use this three-dimensional charge storage mechanism has been much less visible. This has been at least partly due to the proprietary nature of the major development activities, as well as their orientation toward the military market. The electrode materials that are most commonly used in this case are based upon either ruthenium oxide or its hydrate.

(*d*) *Faradaically driven reconstitution reactions*

The electrodes in many battery systems undergo polyphase reconstitution reactions, in which some phases form and others are consumed. In accordance with the Gibbs phase rule, this often results in an open-circuit electrode potential that is independent of the state of charge. The amount of charge storage is determined by the characteristics of the related phase diagram, and can be quite large—comparable to those obtainable with insertion reactions.

Some reactions of this type can also have relatively rapid kinetics. However, there is a potential difficulty in the use of this type of reaction in applications that require many repeatable cycles, as they generally involve microstructural changes that are not entirely reversible. Thus the possibility of a cycle-life limitation must be kept in mind.

A special strategy whereby this microstructural irreversibility may be avoided in certain cases has been proposed (Boukamp *et al.* 1981). This involves the use of an all-solid electrode in which a mixed-conducting solid matrix phase with a very high chemical diffusion coefficient surrounds the reactant phases.

One approach to the use of reconstitution reactions for applications requiring high power levels for limited periods of time is the recent development by the Bolder Tech-

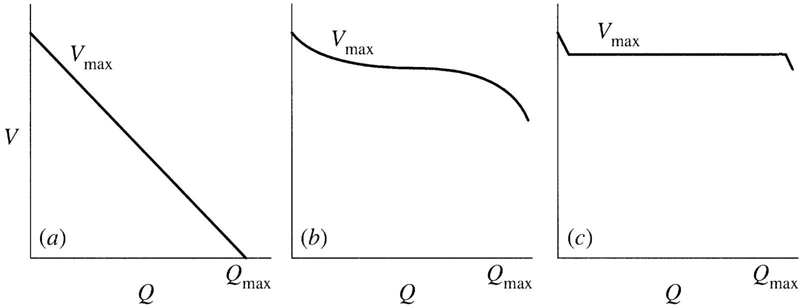

Figure 2. Relationship between potential and charge delivered for three different types of energy storage mechanisms: (*a*) electrical double-layer system; (*b*) insertion reaction system; (*c*) reconstitution reaction system.

nologies Corporation of very thin layer cylindrical lead–acid cells with an unusually low internal impedance.

3. Comparative magnitudes of energy storage

The maximum amount of energy that can be stored in any device is the integral of its voltage–charge product, and cannot exceed the product of its maximum voltage and the maximum amount of charge it can store. On this basis, we can make a simple comparison between these different types of energy storage mechanisms.

The relationship between the potential and the amount of charge delivered is plotted in figure 2 for three different types of systems: a double-layer electrode, an insertion-reaction electrode and a reconstitution reaction electrode. The storage of charge by two-dimensional Faradaic underpotential deposition is not included, as it does not constitute a practical alternative.

In the case of a true capacitor, the amount of charge stored is a linear function of the applied voltage. Thus the voltage falls off linearly with the amount of charge delivered.

A single-phase solid-solution insertion-reaction-type electrode characteristically has a potential–charge relation of the type shown in figure 2*b*. The thermodynamic basis for this shape, in which the potential is composition-dependent, and thus state-of-charge-dependent, will be discussed below.

In the case of the reconstitution–reaction electrode system it has been assumed that the number of components is equal to the number of phases, so that from a thermodynamic point of view there are no degrees of freedom. This means that all of the intensive variables, including the electrode potential, are independent of the overall composition, and thus independent of the amount of charge delivered. Thus the discharge characteristic consists of a voltage plateau.

The maximum amount of energy that is theoretically available in each case is the area under the V/Q curve. The actual amount of available energy will, of course, depend upon the power level, due to unavoidable losses, such as that due to the inevitable internal resistance of the system.

4. The concept of energy quality

The quality of heat is a commonly used concept in engineering thermodynamics. High-temperature heat is generally much more useful than low-temperature heat.

Thus, in considering a practical thermal system one has to consider both the amount of heat and its quality (the temperature at which it is available).

We can consider an analogous situation in the application of energy storage devices and systems. In such cases, in addition to the total amount of energy that can be stored, one should also consider its quality, i.e. the voltage at which it is available. Low-voltage energy is of little use.

If we take this factor into account, we see an additional important difference between systems that utilize electrodes that operate by these three different types of mechanisms. If we consider high-value energy to be that which is available at voltages above $V_{\max}/2$, we see that this is only 37.5% of the total theoretical energy in the case of double-layer capacitors, but can be some 80–90% of the theoretical energy in the other two cases.

5. The influence of composition on the potential of insertion-reaction electrodes

Materials in which the charge is stored by the use of solid state topotactic insertion reactions can be useful for applications in which both the amount of energy stored and the cycle life are important.

The composition dependence of the potential of such materials, commonly known as the coulometric titration curve when measured under quasi-open circuit conditions, is determined by the electrochemical potential of the electroactive guest species in the host solid crystal structure. This can be formally divided into two components, the contribution due to the electron energy band structure of the host material, and that due to the enthalpy and entropy values of the guest ions.

In the case of a random solid solution the major contributions are thus the contribution from the Fermi level of the degenerate electron gas that is characteristic of such mixed conductors, and that due to the configurational entropy of the guest ions in the host crystal lattice (Raistrick *et al.* 1981).

If we assume that the electrons can be treated as fully degenerate, the chemical potential of the electrons is directly related to the Fermi level, E_{F}, which can be written as

$$E_{\mathrm{F}} = \text{const.} \times (x^{2/3}/m^*),$$

where m^* is the effective mass of the electrons.

The configurational entropy of guest ions, assuming random mixing, and a concentration x, statistically distributed among x_0 lattice sites of equal energy, is

$$S = -R \ln[x/(x_0 - x)].$$

Thus the electrode potential can be written in a general form as

$$E = \text{const.} \times (x^{2/3}) - (RT/nF) \ln(x/(1-x)).$$

This relationship is illustrated in figure 3, which also shows the influence of the value of the electron effective mass upon the general slope of the titration curve. Larger effective masses make the potential less composition-dependent.

As mentioned earlier, the amount of energy stored is the integral of the voltage–charge product. The slope of the titration curve determines the range of potential at which the electrochemically stored charge, and thus the energy, is available. This information can be obtained by integration of the current as a function of the potential. This is a type of electrochemical spectroscopy, and the theoretical results for

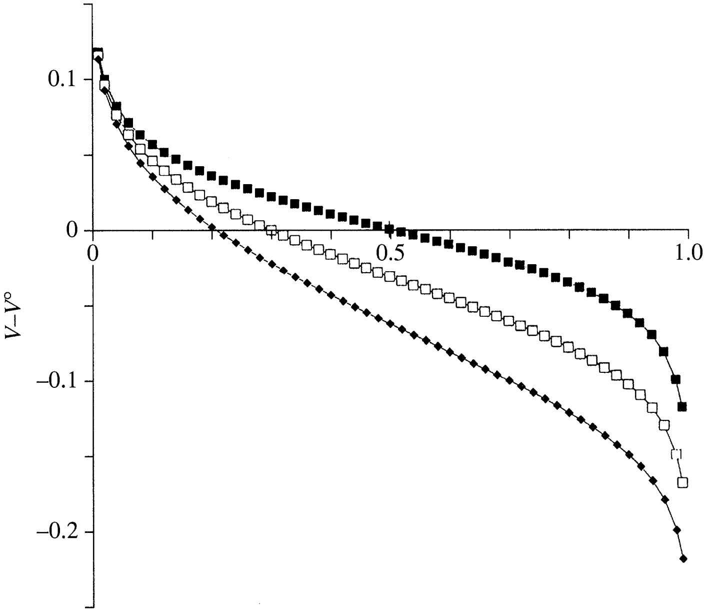

Figure 3. Dependence of the potential upon the extent of reaction in the case of an insertion-reaction electrode for three different values of the electron effective mass. The value of $V°$ is the potential determined by enthalpy factors alone for the case where the electron effective mass is unity.

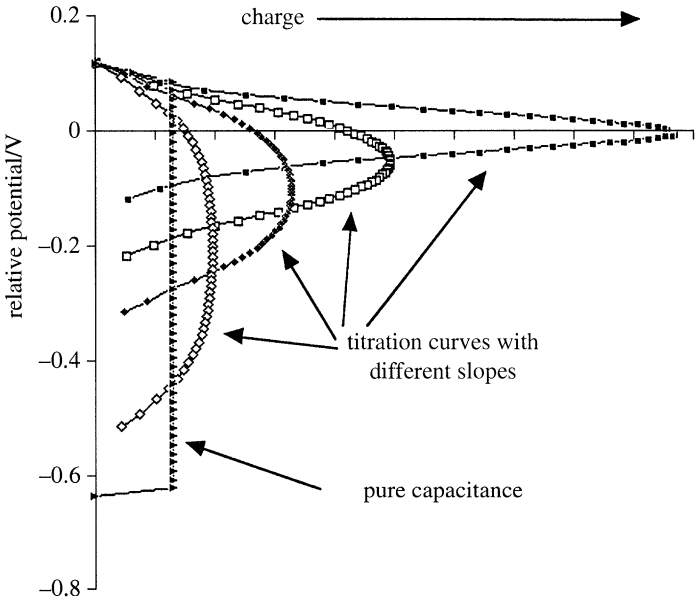

Figure 4. Theoretical relationship between the charge available and the potential for materials with titration curves with different slopes. Also shown is the behaviour of a pure capacitance with the same total energy content, assuming a maximum voltage of about 0.61 V.

titration curves with various slopes are shown in figure 4. Also shown is the behaviour of a pure capacitance with the same energy content.

It is seen that as the slope of the titration curve increases the energy becomes available over a wider range of potential, and the behaviour of an insertion-reaction electrode approaches that of a pure capacitance, except that the magnitude of the stored energy is very much greater in the three-dimensional storage mechanism case. Relatively flat titration curves give energy of a higher quality.

6. Experimental determination of the critical properties of insertion-reaction electrode materials

In order to determine the response of electrodes to different requirements one needs to have basic information about the relevant parameters of the electrochemically active materials involved. The most important properties of electrode materials are:

(i) the potential, and its dependence upon the state of charge;

(ii) the capacity, i.e. the maximum amount of charge that can be stored or supplied; and

(iii) the kinetic behaviour under various conditions.

The actual behaviour of electrodes may deviate from the properties of their electrochemically active components, of course. This may be due to non-uniform reaction under dynamic conditions or microstructural inaccessibility of the active material due to the presence of blocking constituents, for example. Thus information about the basic properties of the electroactive components themselves represents the most favourable limiting case. Actual performance may be less attractive.

The most important parameter relating to the transient behaviour of a solid material that operates by an insertion-reaction mechanism is the chemical diffusion coefficient. This quantity can be much greater than the self-, or component-diffusion coefficient that is often evaluated by the use of radiotracer or nuclear magnetic measurement techniques because of the enhancement factor W. This factor results from the influence of a concentration gradient upon the interaction between the different particle fluxes involved in the mass transport process in the solid. This will not be discussed here, as it can be readily found elsewhere (Wagner 1953; Weppner & Huggins 1977). The important point is, however, that W can be very large in some mixed conductors, so that one has to be careful about using data obtained by the use of experimental methods that do not employ concentration gradients. In one example, it was shown to reach values of about 70 000 (Weppner & Huggins 1977).

Several electrochemical methods have been developed by which information about insertion-reaction electroactive components can be obtained. These include:

(i) the galvanostatic intermittent titration technique (GITT) (Weppner & Huggins 1977);

(ii) the potentiostatic intermittent titration technique (PITT) (Weppner & Huggins 1978);

(iii) the Faradaic intermittent titration technique (FITT) (Weppner & Huggins 1978); and

(iv) the alternating current (Wechselstrom) intermittent titration technique (WITT) (Ho *et al.* 1980).

In each case, stepwise measurement of the electrochemical titration curve is accompanied by an evaluation of the kinetic behaviour after each step. Thus one can obtain simultaneously both thermodynamic and kinetic information as a function of electrode composition (the extent of reaction).

The kinetic measurement parts of these four methods, which are based upon the analytical solution of the diffusion equations under various relevant initial and bound-

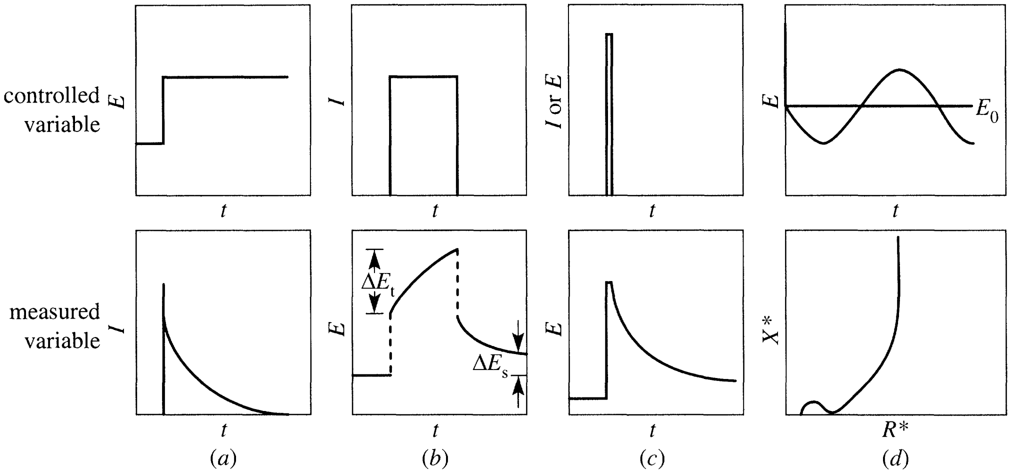

Figure 5. Schematic representation of the time dependence of the potential and current when using different techniques to evaluate chemical diffusion in a solid electrode: (*a*) GITT, (*b*) PITT, (*c*) FITT and (*d*) WITT.

ary conditions, have been discussed in detail elsewhere (Weppner & Huggins 1978; Wen *et al.* 1981) and can be represented schematically as shown in figure 5 (Wen *et al.* 1981), in which the controlled (independent) variables, and the type of response of the relevant dependent variables, are shown.

In the GITT method, the time dependence of the potential after a current step can be expressed as

$$\frac{\mathrm{d}E}{\mathrm{d}t^{1/2}} = \left[\frac{2IV_\mathrm{m}}{zFSD^{1/2}\pi^{1/2}}\right]\left[\frac{\mathrm{d}E}{\mathrm{d}y}\right], \quad \text{if } t \ll (x^2/D).$$

Here, V_m is the molar volume, z the charge carried by the electroactive species, F the Faraday constant, y the stoichiometric parameter and S the surface area.

Alternatively, D may be evaluated from an experiment in which a current step of finite length is applied, using the simplified expression

$$D = \left[\frac{4x^2}{\pi t}\right]\left[\frac{\Delta E_\mathrm{s}}{\Delta E_\mathrm{t}}\right]^2, \quad \text{if } t \ll (x^2/D),$$

where t is the time duration of the current step, ΔE_s is the change in the equilibrium open circuit voltage resulting from the current pulse and ΔE_t is the total transient voltage change, after eliminating the IR drop.

For a fixed value of $(\mathrm{d}E/\mathrm{d}y)$, the dependence of E on t will be linear at long times and the diffusion coefficient can be evaluated from

$$E - E(t=0) = \frac{IV_\mathrm{m}}{zFS}\frac{x}{3D}\left[\frac{\mathrm{d}E}{\mathrm{d}y}\right], \quad \text{if } t \gg (x^2/D).$$

In the case of the PITT method, the current varies with time after the imposition of a potential step. At short times, the time dependence of the current can be approximated by

$$I = \frac{QD^{1/2}}{2x\pi^{1/2}}[t^{-1/2}], \quad \text{if } t \ll (x^2/D),$$

where Q is the total charge passed following the potential step and x is the distance

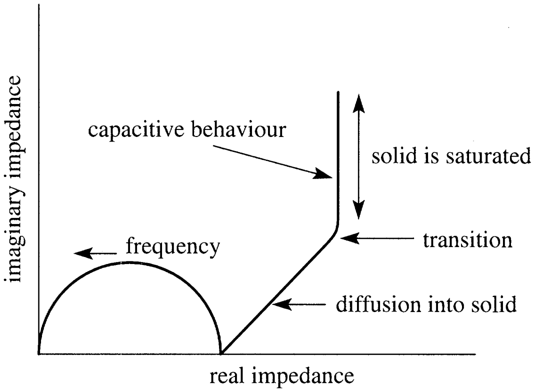

Figure 6. Schematic representation of the frequency dependence of the complex impedance in the case of an insertion-reaction electrode.

parameter into the solid. At long times it becomes

$$I = \frac{2QD}{x^2} \exp\left[\frac{\pi^2 Dt}{4x^2}\right], \quad \text{if } t \gg (x^2/D).$$

In the FITT method, a given amount of electroactive solute material is deposited onto, or into, the surface of the electrode material. As it diffuses into (or out of) the underlying bulk material under open circuit conditions, the surface composition will gradually approach the value characteristic of a uniform solute distribution. The time dependence of the potential is thus

$$\frac{\mathrm{d}E}{\mathrm{d}(t^{-1/2})} = \frac{QV_\mathrm{m}}{zFSD^{1/2}\pi^{1/2}}\left[\frac{\mathrm{d}E}{\mathrm{d}y}\right], \quad \text{if } t \ll (x^2/D).$$

The WITT method involves the use of small-signal alternating current methods to evaluate diffusion in a solid. Without going into the details of the method, which can be found elsewhere (Ho *et al.* 1980; Wen *et al.* 1981), the type of result that is obtained is illustrated in figure 6.

Under ideal conditions and one-dimensional diffusion into a semi-infinite solid, the response is dominated by the diffusional admittance at low frequencies. In the case of thin films, the range of frequency over which diffusion dominates the observed behaviour can be limited. At even lower frequencies, below a critical value given by

$$\omega = 2D/x^2,$$

where D is the chemical diffusion coefficient and x the dimensional parameter, there is sufficient time for the solid composition to stay saturated at the value related to the imposed time-varying potential. When that is the case, the sample electrode has the characteristics of a capacitor, since its composition varies with the applied potential.

The analytical solution to this problem has been obtained for two important cases, one-dimensional diffusion in a slab whose thickness is large compared to the depth of penetration of the diffusion profile, i.e. $x^2 \gg D/\omega$ and one-dimensional diffusion into a thin layer of material under conditions where compositional saturation is achieved, i.e. $x^2 \ll D/\omega$.

In the first (thick-layer) case, the phase difference between the current and the potential is independent of the frequency, and is equal to 45°. The impedance related to diffusion of the electroactive species is then

$$|Z| = \left| \frac{V_\mathrm{m}}{zFSD^{1/2}} \frac{\mathrm{d}E}{\mathrm{d}y} (\omega^{-1/2}) \right| .$$

In the thin layer case the current is 90° out of phase with the potential, and is independent of the diffusion coefficient. The real part of the complex impedance (R) is

$$R = \frac{|Z|\omega x^2}{3DS}$$

and the imaginary part (X) is

$$X = |Z| = \left| \frac{V_\mathrm{m}}{zF\omega xS} \frac{\mathrm{d}E}{\mathrm{d}y} \right| .$$

The limiting low-frequency capacitance C_l and resistance R_l are given by

$$C_\mathrm{l} = \omega X = \omega |Z|$$

and

$$R_\mathrm{l} = \left| \frac{V_\mathrm{m}}{zFS} \frac{1}{3D} \frac{\mathrm{d}E}{\mathrm{d}y} \right| .$$

The good correspondence obtained by the use of these four different methods is shown in figure 7, in which the composition dependence of the measured values of the chemical diffusion coefficient in the phase ‘LiAl’ is plotted.

The response of insertion-reaction electrodes and simple systems under various conditions by the use of Laplace transform techniques have been presented (Raistrick & Huggins 1982).

7. Summary

The use of electrochemical devices and systems under conditions that require pulse output imposes requirements that are quite different from those typical of other, more traditional, applications.

Consideration has been given to the question of the most appropriate general strategy to follow to select and evaluate materials for this type of application. It was shown that there are three principal choices: materials that act as double-layer capacitors, materials that undergo insertion reactions and reconstitution-reaction systems.

Those that act as double-layer capacitors represent a relatively unattractive option for applications that require a substantial output of high-quality energy. Reconstitution reactions, which involve a change in the phase constitution of the microstructure, may present problems in applications in which a long cycle life is required. Insertion-reaction materials thus represent the best general approach, and are used in the devices based upon materials that presently show the best performance.

The critical materials properties include the thermodynamic parameters that determine the potentials and capacities, evaluated experimentally in terms of the coulometric titration curve, and kinetic parameters, the most important of which is the chemical diffusion coefficient. In a number of cases the analytical solutions to the diffusion equation also require information about the local slope of the titration curve.

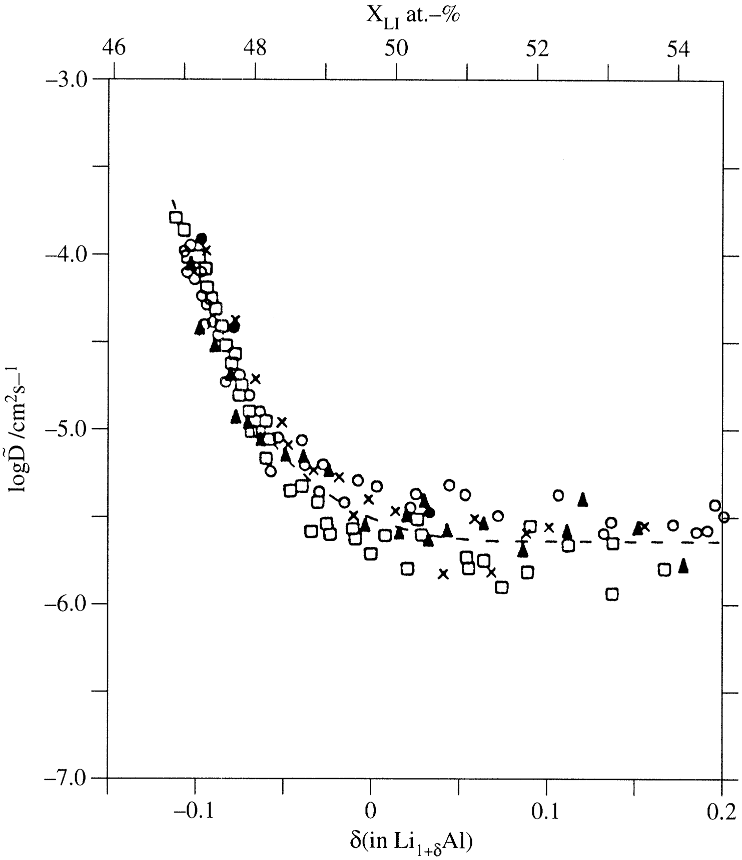

Figure 7. Composition dependence of the chemical diffusion of lithium in the phase 'LiAl' as evaluated by the use of four different experiment methods (Wen *et al.* 1981): ▲, PITT method; ☐, ○, GITT method; ×, FITT method; ●, WITT method.

Four different types of experimental methods have been developed to obtain quantitative data about these basic properties of potential materials. A series of investigations has demonstrated the very consistent results that can be obtained from these different techniques, as well as their good correspondence with theoretical expectations.

If one has information about the chemical diffusion coefficient for a given material, its kinetic properties as an electrode reactant can be calculated using the appropriate analytic solution of the diffusion equation. Alternatively, one can use computer spreadsheet methods to obtain numerical solutions under various initial and boundary conditions.

Actual devices, however, generally consist of several components, and the overall kinetic behaviour is dependent upon their interaction. Either analytical or Laplace transform methods can be utilized for this purpose.

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Discussion

R. Parsons (*Department of Chemistry, University of Southampton, UK*). What distinguishes an intercalation supercapacitor from an intercalation electrode for a battery system? Is it just a question of timescale?

R. A. Huggins. There is, in principle, no difference. In the case of batteries optimized for maximum energy storage, the area under the titration curve is of most concern. For supercapacitor applications the kinetic issues are generally more important.