Chapter 7
Electromagnetic Energy Storage

7.1 Introduction

Several of the prior chapters in this text have shown that there is a wide range of energy storage needs with widely different time periods; some involve seasonal, weekly, and daily cycles, and others require energy intermittently, sometimes over much shorter time periods. A variety of different technologies are employed to meet these various requirements.

This chapter deals with two general mechanisms by which electrical energy can be stored. One involves capacitors, in which energy is stored by the separation of negative and positive electrical charges. The other involves the relationship between electrical and magnetic phenomena.

It will be seen that both of these mechanisms are most applicable to situations in which there is a requirement for the storage of modest amounts of energy under very transient conditions, for relatively short times and sometimes at high rates. Such applications, therefore, emphasize fast kinetics and high power, rather than focusing on the amount of energy that can be stored. A very large cycle life is also generally very important. It will be seen later that the amount of energy that can be stored by such methods is generally much less than can be stored by chemical and electrochemical methods.

The range of both current and potential future energy storage requirements and applications is very broad. In addition to the reduction in short-term transients in the large electrical power distribution grid system mentioned in Chapter 1, typical examples that are now highly visible include 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 hybrid vehicle traction applications, where the high power demand can extend from seconds up to minutes, and the ability to absorb large currents upon braking is also important.

R.A. Huggins, *Energy Storage*, DOI 10.1007/978-3-319-21239-5_7

There are two general approaches to the solution of these types of requirements. One involves the use of electrical devices and systems in which energy is stored in materials and configurations that exhibit capacitor-like characteristics. The other involves the storage of energy using electromagnets. These are discussed in the following sections.

7.2 Energy Storage in Capacitors

Energy can be reversibly stored in materials within electric fields and in the vicinity of interfaces in devices called capacitors. There are two general types of such devices, and they can have a wide range of values of the important practical parameters, the amount of energy that can be stored, and the rate at which it can be absorbed and released.

7.2.1 Energy in a Parallel Plate Capacitor

In a parallel plate capacitor, such as that shown schematically in Fig. 7.1, a dielectric material sits between two metallic plates. If an electrical potential difference is applied between the plates, there will be an electric field across the material located between them that causes local displacements of the negative and positive charges within it.

The energy stored W_C in a material between capacitor plates of area A separated by a distance d is given by

$$W_c = {}^1\!/_2 \varepsilon A \frac{V^2}{d} \tag{7.1}$$

where ε is the permittivity of the material between the plates, and V is the applied voltage.

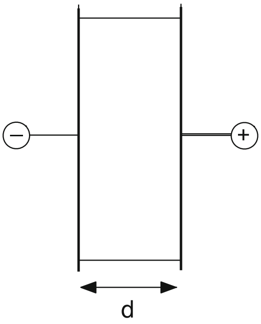

Fig. 7.1 Schematic view of a simple parallel plate capacitor

Table 7.1 Values of the relative permittivity of some materials at ambient temperature

Material	ε_r
Nylon	2.1
Teflon	2.6
Bakelite	4.9
Soft glass	6–7
Distilled water	80
High-permeability oxides	$10 \text{ to } 15 \times 10^3$

The capacity C of this configuration is given by

$$C = \varepsilon \frac{A}{d} \tag{7.2}$$

and

$$\varepsilon = \varepsilon_r \varepsilon_0 \tag{7.3}$$

where ε_r is the relative permittivity of the material, and ε_0 is the permittivity of a vacuum, 8.854×10^{-12} F per meter. The permittivity was sometimes called the dielectric constant in the past.

Values of the relative permittivity of several materials are shown in Table 7.1.

By substituting Eqs. (7.2) and (7.3) into Eq. (7.1), the energy stored in the capacitor can be written as

$$W_C = {}^1\!/_2 CV^2 \tag{7.4}$$

Since the charge stored in a capacitor, Q, is related to its capacitance and the voltage by

$$Q = CV \tag{7.5}$$

the stored energy can also be expressed as

$$W_C = {}^1\!/_2 QV \tag{7.6}$$

It is interesting that the amount of the energy stored in such a capacitor is inversely proportional to the volume of the dielectric material between the plates of the capacitor. This is counterintuitive, for we normally think that if a material carries energy, the greater the amount of the material, the greater amount of energy that it contains.

7.3 Electrochemical Charge Storage Mechanisms

The behavior of such a parallel plate configuration becomes very different if the space between the electrodes contains a material that has the properties of a liquid, or even a solid, electrolyte. In such a case the charge is stored in the interfacial region where the electronically-conducting material meets the ionically-conducting material. The physical separation between the positive and the balancing negative charges is then very small. This can be thought of as equivalent to a parallel plate capacitor with a thickness of the order of interatomic distances, and results in much greater amounts of charge storage per unit area.

Devices with this type of local structure are called electrochemical capacitors, and there are two general types. One involves the storage of charge in the electrical double-layer at or near the electrolyte/electronic material interface. Such devices are called *ultracapacitors*. The other type makes use of transient additional reversible absorption of atomic species into the crystal structure of the solid electronically-conducting electrode, and such devices are called *supercapacitors*. Both of these mechanisms can lead to much larger values of capacitance than capacitors with dielectric materials between their plates, as discussed above.

7.3.1 Electrostatic Energy Storage in the Electrical Double-Layer in the Vicinity of an Electrolyte/ Electrode Interface

As mentioned above, the interface between a chemically inert electronic conductor electrode and an adjacent electrolyte with mobile ionic charges can function as a simple capacitor with a very small distance separating two parallel plates.

The amount of charge that can be stored in such a configuration is generally of the order of 15–40 μF per cm^2 of interface [1–3]. Thus efforts are made to maximize the amount of interface in the device microstructure to produce the greatest amount of stored charge. 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. Typical values of specific capacitance, in Farads per gram, of a number of double-layer electrode materials are shown in Table 7.2.

Table 7.2 Characteristics of some double-layer electrode materials

Electrode material	Specific capacitance/F/g
Graphite paper	0.13
7.Carbon cloth	35
Aerogel carbon	30–40
Cellulose-based foamed carbon	70–180

The electrical potential difference that can be applied is limited by the decomposition voltage of the electrolyte, which is about 1.23 V for common aqueous electrolytes, but can be up to 4–5 V for some organic solvent electrolytes. The result is that the specific energies of simple aqueous electrolyte systems of this type are generally in the range of 1–1.5 Wh/kg, whereas those that use organic solvent electrolytes can be 7–10 Wh/kg.

A device in which this is the dominant charge storage mechanism will behave like a pure capacitor in series with its internal resistance. Its time constant is equal to the product of the capacitance and the series resistance. Thus it is important to keep the resistance as low as possible if rapid response is desired. Organic electrolytes characteristically have much lower values of ionic conductivity, and thus provide greater resistance, and longer time constants than aqueous electrolytes. The conductivity of acids, such as H_2SO_4, is somewhat greater than that of aqueous bases. Furthermore, the larger the capacitance, the greater the time constant, the slower the device, and the lower the power level.

Another important feature of devices that operate by the double-layer mechanism is that the amount of charge stored is a linear function of the voltage according to Eq. (7.5). The voltage therefore falls linearly with the amount of charge extracted. Thus voltage-dependent applications can only utilize a fraction of the total energy stored in such systems. The power supplied to resistive applications is proportional to the square of the instantaneous voltage, so this can be an important limitation.

Although there is some confusion in the literature about terminology, devices of this type that have been developed with large values of such capacitance have generally been called either EDLC (electrical double-layer capacitive) devices, or *ultracapacitors* [1–3].

Ultracapacitor devices utilizing the storage of charge in the electrochemical double layer have been developed and produced in large numbers in Japan for a considerable period of time [4]. These are primarily used for semiconductor memory backup purposes, as well as for several types of small actuators.

7.3.2 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 somewhat removed from those needed for the bulk deposition of a new phase. This results in the occupation of specific crystallographic sites on the surface of the solid electrode by species from the electrolyte. This mechanism typically results in only partial surface coverage, and thus the production of an *adsorption pseudo-capacitance* of some 200–400 mF/cm^2 of interfacial area [2]. This is significantly larger than the amount of charge stored per unit area in the electrochemical double layer. However, materials with which this mechanism can be effectively used are rare, and it is not common.

7.3.3 Faradaic Deposition that Results in the Three-Dimensional Absorption of the Electroactive Species into the Bulk Solid Electrode Material by an Insertion Reaction

As will be discussed in later chapters, many materials are now known in which atoms from the electrolyte can move into the surface of a solid electrode material, changing its local composition. These are called *solid solution electrodes*. In such cases, the *electroactive species* diffuses into and out of the interior of the crystal structure of the solid electrode as its potential is changed. Since the amount of energy stored is proportional to the amount of the electroactive species that can be absorbed by the electrode, this bulk storage mechanism can lead to much higher values of energy storage per unit volume of electrode structure than any surface-related process. Because it makes no sense to express this bulk phenomenon in terms of the capacitance per unit interfacial area, for it depends upon how far the material from the electrolyte penetrates into the solid, values of capacitance are generally given as *Farads per gram* in this case.

This mechanism was called *redox pseudo-capacitance* by the Conway group [1–3]. They also first started the use of the term *supercapacitors* to describe devices utilizing this type of charge storage. In this way, solid solution bulk storage *supercapacitors* can be distinguished from double-layer storage *ultracapacitors*, in which atoms from the electrolyte do not enter the solid electrode material.

The bulk storage *supercapacitor* mechanism is utilized in the devices that are most interesting for energy-sensitive pulse applications. Since the kinetic behavior of such devices is related to the electrolyte/electrode area, it is important that they also have very fine large surface area microstructures.

During investigations of the *dimensionally stable electrodes* that are used as positive electrodes in the *chlor-alkali process* it was noticed that RuO_2 seemed to behave as though its interface with the electrolyte had an unusually large capacitance. This swiftly led to several investigations of the capacitive behavior of such materials [5–8].

The possibility of the development of RuO_2-type materials as commercial supercapacitors began in Canada about 1975, the key players being D.R. Craig [9, 10] and B.E. Conway. This soon evolved into a proprietary development program at the Continental Group, Inc. laboratory in California, which subsequently was taken over by the Pinnacle Research Institute. The products that were initially developed and manufactured were all oriented toward the military market. This orientation is changing now, and activities are being undertaken by several firms to produce this type of product for the civilian market. Activities in this area have also been initiated more recently in Europe, including work at Daimler-Benz (Dornier) and Siemens in Germany, and at Thompson-CSF in France.

It was originally thought that charge storage in these materials is due to *redox reactions* near the interface between the electrolyte and RuO_2. Careful measurements showed that the capacitance is large, and proportional to the surface area [11].

It is now known, however, that the charge is stored by hydrogen insertion into the bulk of the RuO_2, and the capacitive behavior is not just on the surface [12]. At relatively short times the depth of hydrogen diffusion is limited, and the amount of charge stored in the bulk will not reach its ultimate saturation value.

Experiments [6, 13] showed that the chemical diffusion coefficient of hydrogen in bulk crystalline RuO_2 is about 5×10^{-14} cm^2/s. Thus the penetration into the bulk crystalline solid is rather shallow at the relatively high frequencies typically used in capacitor experiments. It was shown in later work [14] that the apparent hydrogen solubility is considerably higher in amorphous RuO_2 than in crystalline material. Experiments on hydrated RuO_2 [12, 15, 16] demonstrated that it has a substantially larger charge storage capacity than anhydrous RuO_2.

It has also been found [16] that the amount of charge that can be stored in hydrated RuO_2 is independent of the surface area, but proportional to the total mass. This is shown in Fig. 7.2. Over one hydrogen atom can be reversibly inserted into the structure per Ru atom [12]. The *coulometric titration* curve is shown in Fig. 7.3.

Crystalline RuO_2 is a very good electronic conductor, with an electronic resistivity of about $10^{-5}\,\Omega$ cm. This is about a factor of 100 lower than that of bulk carbons. The hydrated material, on the other hand, has a considerably higher resistivity, and it has been found to be advantageous to add some carbon to the microstructure in order to reduce the electronic resistance in that case.

Several other materials that are *electrochromic*, i.e., change color as charge is inserted or deleted, show similar pseudo-capacitive behavior. This clearly indicates the insertion of species into the bulk crystal structure. Materials such as NiOOH and IrO_2 thus could be used in supercapacitors.

Typical values of specific capacitance of a number of insertion reaction electrode materials are included in Table 7.3.

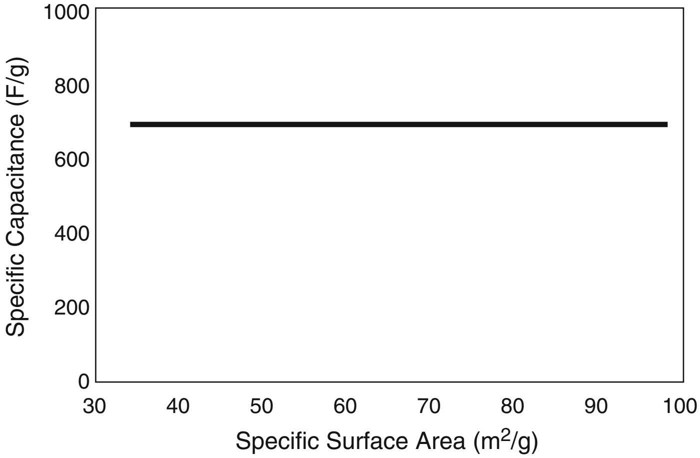

Fig. 7.2 Apparent capacitance of RuO_2 hydrate as a function of surface area [16]

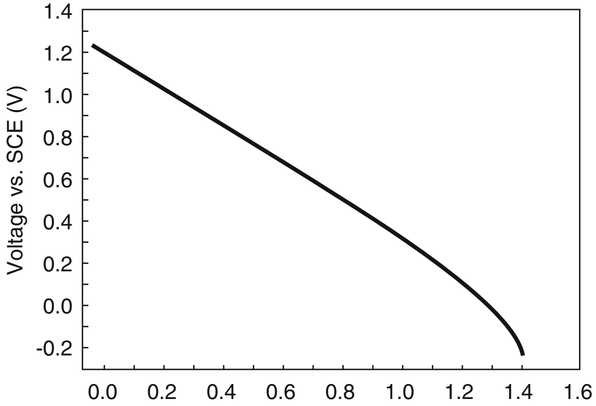

Fig. 7.3 Dependence of the potential of RuO_2 hydrate upon the amount of inserted hydrogen [12]

Table 7.3 Characteristics of some insertion reaction electrode materials

Electrode material	Specific capacitance/F/g
Polymers (e.g., polyaniline)	400–500
RuO_2	380
RuO_2 hydrate	760

The insertion of guest species into the host crystal structure in such insertion reactions generally results in some change in the volume. This can lead to morphological changes in electrodes, and a reduction in capacity upon cycling. The volume change is generally roughly proportional to the concentration of the guest species. As a result, it is often found that the magnitude of this degradation depends upon the depth of the charge-discharge cycles.

7.3.4 Faradaically-Driven Reconstitution Reactions

The electrodes in many battery systems undergo *reconstitution reactions*, in which new 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. As discussed elsewhere in this text, the amount of charge storage is determined by the characteristics of the related phase diagram, and can be quite large. 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, for 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 or reduced in certain cases has been proposed [17]. 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 small particles of the reactant phases.

7.4 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 results are shown schematically in Fig. 7.4, in which the relationship between the potential and the amount of charge delivered is plotted for three different types of systems, a double-layer electrode, an insertion reaction electrode, and a reconstitution reaction electrode. Electrodes that involve two-dimensional *Faradaic underpotential* deposition are not included, as they do 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, as shown on the left side of Fig. 7.4, the voltage falls off linearly with the amount of charge delivered.

A single-phase solid solution insertion-reaction type of electrode characteristically has a potential-charge relation of the type shown in the middle. The thermodynamic basis for this shape, in which the potential is composition-dependent, and thus state of charge dependent, will be discussed in Chap. 13.

The characteristic behavior of a reconstitution-reaction electrode system is shown on the right side. In this case, it is assumed that the temperature and pressure are fixed, and 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

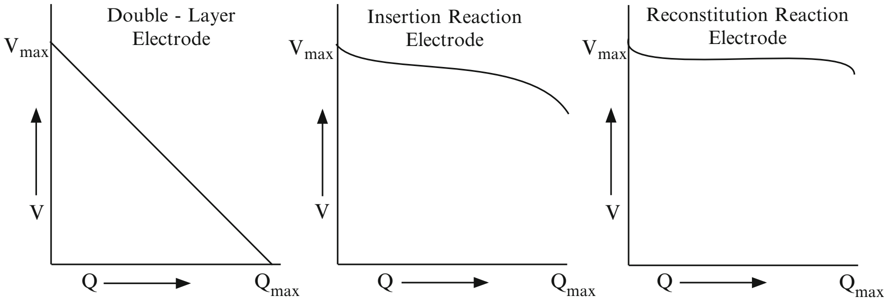

Fig. 7.4 Comparison of the variation of the potential with the amount of charge extracted for different types of energy storage mechanisms

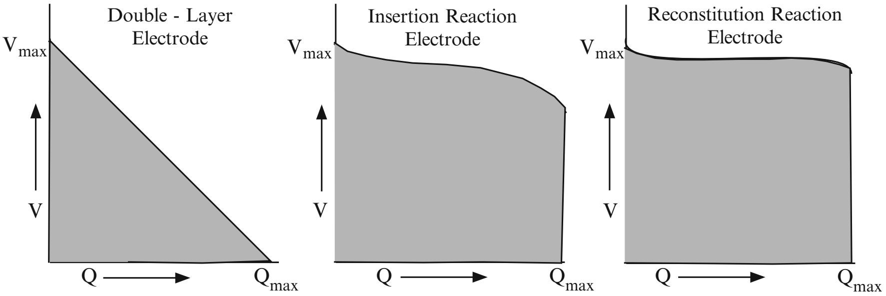

Fig. 7.5 The amount of energy available for materials with different types of storage mechanisms, indicated by the area under their curves

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.

As mentioned above, the maximum amount of energy that is available in each case is the area under the V/Q curve. This is indicated in Fig. 7.5 for the three cases of interest. It is seen that the maximum amount of energy that can be stored in an electrode that behaves as a capacitor is 1/2 $(V_{max})(Q_{max})$. 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.

7.5 Importance of the Quality of the Stored Energy

As mentioned earlier, 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 the temperature at which it is available.

One 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, the voltage at which it is available.

If this factor is taken into account, an additional difference between systems that utilize electrodes that operate by these three different types of mechanisms can be seen. This is indicated in Table 7.4, in which the amount of higher value energy available in the different cases is compared. In that case, only a simple distinction is used. Energy at a potential above $V_{max}/2$ is considered to be high value energy.

Thus there are a number of parameters that determine important properties of a transient energy storage system. These are listed in Table 7.5.

Table 7.4 Maximum amount of high-value energy available

Type of electrode	High-value energy/%
	Where ($V > V_{max}/2$)
Double-layer electrode	37.5
Insertion reaction electrode	About 80
Reconstitution reaction electrode	About 90

Table 7.5 Parameters that determine the values of maximum potential, maximum charge, and maximum energy stored

Type of electrode	V_{max} determined by
Double-layer electrode	The electrolyte stability window
Insertion reaction electrode	Thermodynamics of guest-host phase
Reconstitution reaction electrode	Thermodynamics of polyphase reactions
Type of electrode	Q_{max} determined by
Double-layer electrode	Electrode microstructure, electrolyte
Insertion reaction electrode	Mass of electrode, thermodynamics
Reconstitution reaction electrode	Mass of electrode, thermodynamics

7.6 Transient Behavior of a Capacitor

In addition to the question of the amount of energy that can be stored in a capacitor, consideration must also be given to the rate at which it can be obtained.

There is always some series resistance connected to a capacitor. This can be indicated for the case of a simple parallel plate capacitor and *ultracapacitors* in the simple equivalent circuit of Fig. 7.6. If one or both of the electrodes also undergo some insertion reaction, as is the case in *supercapacitors*, the kinetics become more complicated. The kinetic behavior in that case can be treated by the use of Laplace transform techniques, and will be discussed later in this chapter.

If such a capacitor is charged, and then shorted, which sets the external voltage V to zero, the voltage across the capacitor will be balanced by the voltage across the resistor, for

$$V = V_R + V_C \tag{7.7}$$

As the capacitor discharges, its voltage decreases, as does the voltage across, and thus the current through, the resistor.

The instantaneous current $i_{(t)}$ through the resistor decays exponentially with time according to

$$i_{(t)} = -i_0 \exp\left(-{}^{t}\!/_{RC}\right) \tag{7.8}$$

where i_0 is the initial current at the start of discharge.

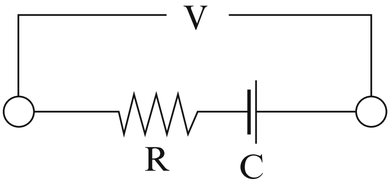

Fig. 7.6 Simple equivalent circuit of a capacitor and its associated series resistance

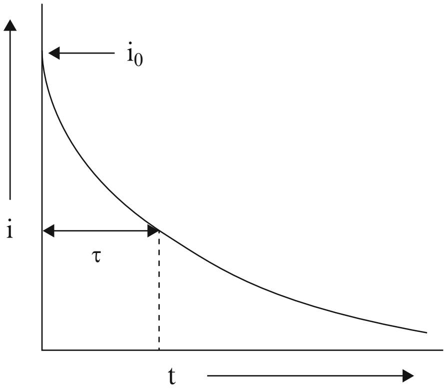

Fig. 7.7 Time-dependent current decay in a capacitor system

The product *RC* is called the *time constant*, τ. It is a useful parameter in understanding the rate at which energy can be obtained from capacitor-based systems.

Taking the logarithm of both sides of Eq. (7.8),

$$\ln\left({}^{i}\!/_{i_0}\right) = -{}^{t}\!/_{RC} \tag{7.9}$$

Thus the time *t* has the value of the time constant RC when

$$\left({}^{i}\!/_{i_0}\right) = \exp(-1) \tag{7.10}$$

The value of exp(−1) is approximately 0.3679.

In the case of a series arrangement of a resistor *R* and an inductance *L* the time constant is given by

$$\tau = {}^{R}\!/_{L} \tag{7.11}$$

The variation of the current through the resistor R with time in a capacitor system is shown in Fig. 7.7.

The rate at which energy can be stored—or supplied—is determined by the time constant. Therefore, it is desirable that the series resistance R is as small as possible.

But it is also obvious that if the capacitance C is large, the time constant will be large.

During operation some of the applied power goes into heating the resistor:

$$Power = i_{(t)}V_R = i_{(t)}^2 R \tag{7.12}$$

The maximum power is determined by the value of V^2/R, and can be very large for a short time, and values up to 10^9 watt/m^3 can be attained in some designs.

$$P = I_0^2 R = \left({}^{V}\!/_{R}\right)^2 R = {}^{V^2}\!\big/_{R} \tag{7.13}$$

7.7 Modeling Transient Behavior of Electrochemical Systems Containing Capacitive Components Using Laplace Transforms

7.7.1 Introduction

The quantitative understanding of the application of capacitive, or other, components in actual devices requires knowledge of the relationship between component properties and system behavior, for systems typically involve more than one component. As an example, in addition to the electrode impedances, there are almost always resistive, and/or capacitive, impedances present, both relating to internal phenomena in the device and to external factors.

It is often very useful to utilize *equivalent electrical circuits* whose electrical behavior is analogous to the behavior of physical systems as *thinking tools* to obtain insight into the important parameters and their interrelationships. This allows the use of the methods that have been developed in electrical engineering for circuit analysis to evaluate the overall behavior of interdependent physical phenomena.

A useful way to do this is based upon the simple concept of a relation between a *driving force* and the *response* of a device or system to it. This relation can be written very generally as

$$\text{Driving Function} = (\text{Transfer Function}) \times (\text{Response Function})$$

In an electrochemical system, the driving function represents the current or voltage demands imposed by the application, and the response function is the output of the electrochemical system in response to these demands. The key element of this approach is the determination of the (time-dependent) transfer function of the device or system, for that determines the relationship between application demand and system output.

7.7.2 Use of Laplace Transform Techniques

The general method that has been developed for electrical device and circuit analysis involves the use of *Laplace transform* techniques. There are several basic steps in this analysis. They involve:

1. The determination of the transfer function of the individual equivalent circuit components
2. The calculation of the transfer function of the total system
3. The introduction of the driving function determined by the application
4. The calculation of the system (energy source) output

Some readers of this chapter may not be familiar with Laplace transform methods. But they can be readily understood by the use of an analogy. Consider the use of logarithms to multiply two numbers, e.g., A and B. The general procedure is to find the logarithms (transforms) of both A and B, to add them together, and then to use antilogarithms to reconvert the sum of the logarithms (transforms) into a normal number.

This method has been applied to some simple electrochemical situations, including the influence of the presence of series resistance upon the rate of charge accumulation in an insertion reaction electrode [18] and the electrical response of electrochemical capacitors [11].

The calculation of the transient electrical response of an insertion, or solid-solution, electrode involves the solution of the diffusion equation for boundary conditions that are appropriate to the particular form of applied signal. In addition, the relation between the concentration of the electroactive mobile species and their activity is necessary. This approach has been utilized to determine the kinetic properties of individual materials by employing current and/or voltage steps or pulses.

But in real electrochemical systems or devices one has to consider the presence of other components and phenomena, that is, other circuit elements. As a simple example, there is always an electrolyte, and thus a series resistance, present, and the behavior of the electrolyte/electrode interface may have to be also considered. Thus the simple solution of Fick's diffusion laws for the electrochemical behavior of the electrode alone may not be satisfactory.

Examples of the Laplace transforms of several common functions are given in Table 7.6.

7.7.3 Simple Examples

To illustrate this method, several examples will be described; the response of an insertion electrode under both a step in potential and a step in current, as well as a system consisting of a simple series arrangement of a resistance and an insertion reaction electrode that has a diffusional impedance.

Table 7.6 Examples of Laplace transforms

Function	Laplace transform
General impedance function	$Z(p) = E(p)/I(p)$
Fick's second law	$pC - c(t = 0) = D\frac{d^2C}{dx^2}$
Current step d(t)	$I(p) = 1$
Potential vs. time	$E(p) = V(dE/dy)$
Impedance of insertion reaction electrode	$Z(p) = Q/Da$

where
$Q = \frac{V(dE/dy)}{nFs}$
$a = (p/D)^{1/2}$
dE/dy = slope of the coulometric titration curve
y = composition parameter
n = stoichiometric coefficient
F = Faraday constant
s = surface area
p = complex frequency variable
x = positional coordinate
ID="Par80">V = molar volume
$q(t)$ = charge accumulated in electrode
$i(t)$ = instantaneous current
$F(t)$ = instantaneous electrode potential

1. Upon the imposition of a step in potential F_0, the time dependence of the current i(t) is given by

$$i(t) = \frac{F_0}{Q}\left(\frac{D}{pt}\right)^{1/2} \tag{7.14}$$

2. The time dependence of the charge accumulated (or produced) $q(t)$ is

$$q(t) = \frac{2F_0}{Q}\left(\frac{t}{p}\right)^{1/2} \tag{7.15}$$

3. For the case of a step in current i_0, the time dependence of the electrode potential $F(t)$ is given by

$$F(t) = 2Q\left(\frac{t}{pD}\right)^{1/2} \tag{7.16}$$

4. The time dependence of the current after the imposition of a step potential of F_0 for the more complicated case of a resistance in series with an insertion reaction electrode is found to be

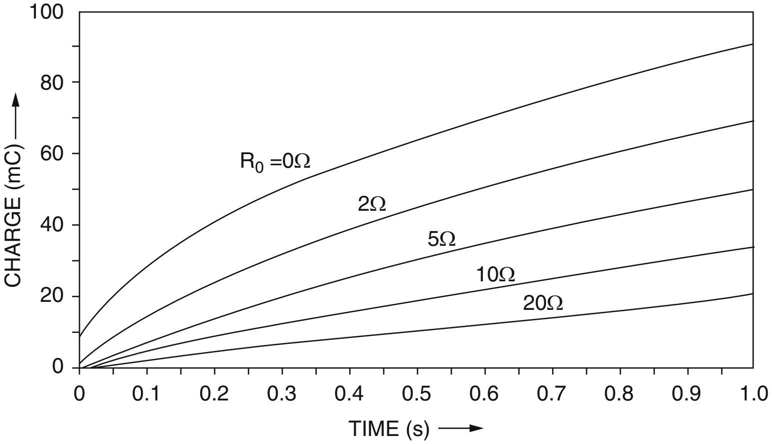

Fig. 7.8 The charge accumulated in an insertion reaction electrode as a function of time for various values of series resistance

$$i(t) = (F_0/R)\exp\left[\left(\frac{Q}{R}\right)^2 t\right] erfc\left[\frac{Qt^{1/2}}{R}\right] \tag{7.17}$$

5. The charge accumulated (or produced) in the case of this series combination is found to be

$$q(t) = \frac{F_0 R}{Q^{1/2}}\left[\exp\left[\left(\frac{Q}{R}\right)^2 t\right] erfc\left[\frac{Qt^{1/2}}{R}\right] - 1\right] + \frac{2F_0}{Q}\left(\frac{t}{p}\right)^{1/2} \tag{7.18}$$

The influence of the value of the series resistance can readily be seen in Fig. 7.8 [19].

The parameters used in the calculation illustrated in Fig. 7.8 are

$$Q^{-1} = 6.33 \text{ ohm sec}^{-1/2}$$

derived from $D = 10^{-8}$ cm^2/s, $V_m = 30$ cm^3/mol, $dE/dy = -2$ V, $s = 1$ cm^2 and $n = 1$.

The applied voltage step was 0.5 V.

Examination of the solutions for the behavior of single components under the first two sets of conditions obtained by this method shows that they are equivalent to those for the analytical solution of the diffusion equation under equivalent experimental conditions.

The impedance of an insertion reaction electrode alone under an AC driving force has also been described in [19].

This Laplace transform procedure is thus an alternative to the more conventional analytical approach. But the real value of the Laplace transform approach becomes clearer, however, under more complex conditions, such as when more than one component is present, and in which the normal procedures become quite cumbersome.

7.8 Energy Storage in Magnetic Systems

The energy storage capability of electromagnets can be much greater than that of capacitors of comparable size. Especially interesting is the possibility of the use of superconductor alloys to carry current in such devices. But before that is discussed, it is necessary to consider the basic aspects of energy storage in magnetic systems.

7.8.1 Energy in a Material in a Magnetic Field

It was shown earlier in this chapter that the energy stored in a parallel plate capacitor with spacing *d* and area *A* when a voltage *V* is applied across it can be written as

$$W_C = {}^1\!/_2 \varepsilon A \frac{V^2}{d} = {}^1\!/_2 C V^2 \tag{7.19}$$

ε is the *permittivity*, a measure of the polarization of the material between the plates by the electric field, and *C* the *capacitance*.

Energy can also be stored in magnetic materials and systems. The analogous relation is

$$W_M = {}^1\!/_2 \mu H^2 \tag{7.20}$$

where *H* is the intensity of a *magnetic field*, and μ is the *permeability*, a constant that is dependant upon the material within the field, analogous to the *permittivity*. The magnetic field *H* is sometimes called the *magnetizing field*, or the *magnetizing force*.

There is also a relation equivalent to that in Eq. (7.3):

$$\mu = \mu_r \mu_0 \tag{7.21}$$

where μ_r is called the *relative permeability* of the material present in the magnetic field, and μ_0 the *permeability of vacuum*, 1.257×10^{-6} Henries per meter.

When a material is placed in a magnetic field, an internal magnetic field will be induced within it whose magnitude depends upon the material's permeability μ. This internal *induced magnetic field*, B, which is sometimes called the *magnetic induction*, or the *magnetic flux density*, is thus related to the external field H by

$$B = \mu H \tag{7.22}$$

Equation (7.20) can therefore be rewritten in terms of the *induced magnetic field* B inside the material instead of the external field H as

$$W_M = \frac{1}{2\mu} B^2 = {}^1\!/\!_2 BH \tag{7.23}$$

Equation (7.22) can be rewritten to show the separate influence of the external field and the internal properties of the material as

$$B = \mu_0 H + \mu_0 M \tag{7.24}$$

M is called the *magnetization*, and $\mu_0 M$ is the additional induced magnetic field due to the properties of the solid. The *magnetization* can also be expressed as

$$M = \frac{(\mu - \mu_0)H}{\mu_0} = \frac{\mu H}{\mu_0} - 1 = \mu_r H - 1 \tag{7.25}$$

The magnetic properties of the solid can also be expressed in terms of the *susceptibility*, X, which is dimensionless, where

$$\mathrm{X} = \frac{M}{H} = \frac{\mu - \mu_0}{\mu_0} = \frac{\mu}{\mu_0} - 1 = \mu_r - 1 \tag{7.26}$$

and

$$B = \mu_0 (H + M) \tag{7.27}$$

One way to generate a magnetic field H is to pass current through a nearby electrical conductor. In the case of a wire shaped into a spiral, or helix, the value of the H field inside it is

$$H = 4\pi n l \tag{7.28}$$

where n is the number of turns per unit length of the spiral, and I is the magnitude of the current. The direction of this field is parallel to the length of the spiral. This is shown schematically in Fig. 7.9.

The H field is continuous through the material, as well as in its external environment, whereas the B field is only within the solid.

Since magnetic units and their dimensions may not be as familiar to many people as electrostatic units, a list of some of them is given in Table 7.7.

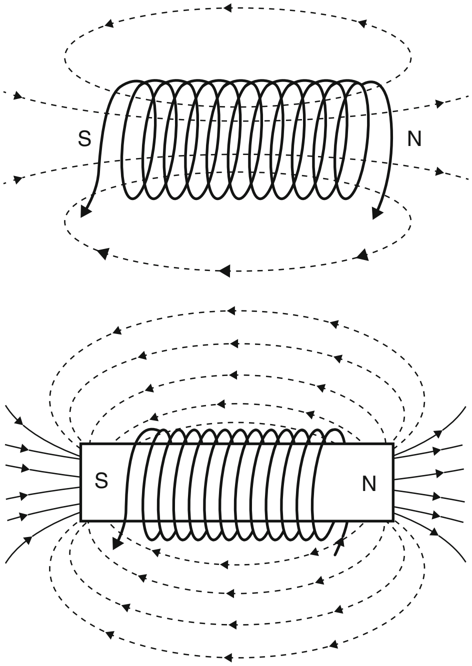

Fig. 7.9 Schematic representation of the *H* field in the vicinity of a linear helix. It is seen that the presence of the material with a high value of susceptibility amplifies the external *H* field

Table 7.7 Magnetic quantities, units, and dimensions

Quantity	Unit	Symbol	Dimensions
Magnetic field	Henry	H	A/m
Magnetic induction	Tesla	B	$\mathrm{Wb/m^2 = Vs/Am^2}$
Permeability		μ	Vs/Am
Energy product		BH	$\mathrm{kJ/m^3}$
Magnetization per unit volume		$\mathrm{M_v}$	A/m
Magnetization per unit mass		$\mathrm{M_m}$	$\mathrm{Am^2/kg}$
Magnetic flux	Weber	Wb	Vs
Inductance	Henry	L	Wb/A = Vs/A

The unit of permeability in the SI system is the Henry. One Henry has the value of 1 Wb per Amp, and is the *inductance* that produces one volt when the current in a circuit varies at a uniform rate of one ampere per second.

It was shown in eqn. 7.23 that the energy in an electromagnet is proportional to the product of *B* and *H*. These quantities are related to each other by the value of the magnetization *M*, or the relative permeability, μ_r. There are two general classes of magnetic materials, one group are generally described as *soft magnetic materials*, and the other are called *hard magnetic materials*. Samples of the latter

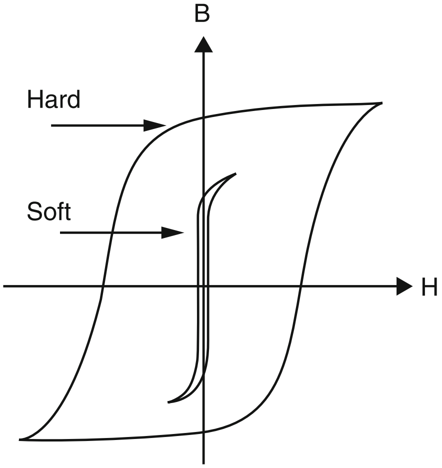

Fig. 7.10 Schematic B–H curves for soft and hard magnetic materials

Table 7.8 B–H products of several hard magnetic materials

Material	(BH)max/Wb-A/m3
Alnico	36,000
Platinum–cobalt	70,000
Samarium–cobalt	120,000

are also often named *permanent magnets*. Their characteristics are shown schematically in Fig. 7.10.

It can be seen that these are very different. The major difference is the large area in the case of the hard material. If such a material is magnetized by increasing *H*, and then H is reduced to zero, *B*, and thus the magnetization, remains at a high value. In order to reduce *B*, or the magnetization, to zero, a large negative value of *H* is required. Thus the material tends to remain magnetized, i.e., is “hard.” The magnitude of this reversed *H* field that is necessary to demagnetize this material is called the *coercivity*. Thus such a material stores a lot of magnetic energy, but it is very difficult to get it out. The area inside the B–H curve, a measure of hysteresis, represents the energy lost each time the magnetization is reversed. Data on several hard magnetic materials are included in Table 7.8.

It can be seen that the area within the curve for the soft magnetic material in Fig. 7.10 is much smaller than that for the hard magnetic material. It is soft, rather than hard, magnetic materials that are used to reversibly store energy in electromagnetic systems under transient conditions. For this type of application the energy loss due to hysteresis (the area inside the B–H curve) should be as small as possible. Data on the magnetic properties of several types of soft magnetic materials are shown in Table 7.9.

Table 7.9 Data on some soft magnetic materials

Material	Composition/wt%	Relative permeability	Resistivity/Ω-m
Commercial cast iron	99.95 Fe	150	1×10^{-7}
Oriented silicon iron alloy	97 Fe, 3 Si	1,400	4.7×10^{-7}
Permalloy	55 Fe, 45 Ni	2,500	4.5×10^{-7}
Supermalloy	79 Ni, 15 Fe, 5 Mo	75,000	6×10^{-7}
Ferroxcube A	48 MnFe2O4, 52 ZnFe2O4	1,400	2,000
Ferroxcube B	64 ZnFe2O4, 36 NiFe2O4,	650	107

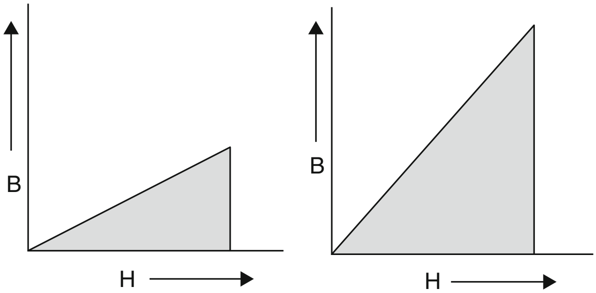

Fig. 7.11 Areas indicating the amount of stored energy for two materials with different values of relative permeability up to the same value of *H* field

Because they have a large influence over the efficiency, a considerable amount of work has been done over many years to optimize soft magnetic materials for their different uses. An important step forward was the development of iron–silicon alloys with relatively high electronic resistivity, thus reducing the hysteresis losses due to induced *eddy currents*. Processing these materials so that they develop a preferred crystallographic orientation also increases their permeability appreciably, as does annealing them in moist hydrogen to reduce the amount of carbon impurity present. These alloys are now commonly used as insulated laminated sheets in transformers for the transmission of moderate to large amount of electrical power.

Another class of soft magnetic materials includes the nickel–iron *permalloy* type of alloys. These materials have very large values of permeability, and are generally used in very low power applications that require large changes in magnetization with relatively small applied fields.

A third class of soft magnetic materials includes transition metal oxide ceramics called ferrites. Because they have very high values of electronic resistivity, and thus have no appreciable eddy current loss, they can be used in electronic equipment at very high frequencies.

According to Eq. (7.23) the energy stored in a magnetic material is one half the product of *B* and *H*, and therefore the area under a plot of *B* versus *H*. From Eq. (7.22) the slope of such a curve is the material's permeability. This is shown in Fig. 7.11 for two soft magnetic materials with different values of relative permeability in the same *H* field.

In this case, it is assumed that there is very little hysteresis, so that the data measured when the H field is increased are essentially the same as those when the H field is decreased.

This is analogous to the energy under a stress/strain curve in mechanical materials systems, and the energy stored under the voltage/composition curve in electrode materials in electrochemical systems.

7.8.2 Energy Storage in Superconducting Magnetic Systems

The magnetic energy of materials in external H fields is dependent upon the intensity of that field. If the H field is produced by current passing through a surrounding spiral conductor, its magnitude is proportional to the current according to Eq. (7.28). It is obvious that high currents are desirable if one wants to store large amounts of energy.

However, the passage of current through a metal wire causes Joule heating according to Eq. (7.29):

$$\text{Heat} = I^2 R \tag{7.29}$$

Thus it is desirable to consider the use of a superconducting material that has essentially no resistance to carry the current. Such systems are generally designed with the high permeability soft magnetic material within a superconductor coil in the shape of a toroid.

Energy can be fed into such a system by use of a DC power supply. Once the current is established in the superconductor, the power supply can be disconnected. The energy is then stored in the magnetic material inside the superconducting coil, where it can be maintained as long as desired without the need for further input.

The transmission of energy to and from the DC superconductor electromagnetic storage system requires special high power AC/DC conversion rectifier, inverter, and control systems. Such a power conditioning system typically causes a 2–3 % energy loss in each direction.

An additional feature that must be taken into account is the generation of large mechanical forces acting on the materials by the large magnetic fields present. The mitigation of this can add considerably to the cost of the whole system.

Superconductor materials have to be maintained below a so-called material-specific *critical temperature*. The maintenance of the required low temperature by the use of a cryostatic refrigerator requires energy, of course. There is another complication in that superconducting materials lose their superconductive property if the value of the surrounding H field is above a critical value, called the *critical field*. Since the field is caused by the current in the superconductor, another way of looking at this limitation is in terms of a *critical current*, rather than a *critical field*.

Such systems are generally used for short-term energy storage, such as improving the power quality and stability of a transmission distribution system, where the rapid response and high short-term power available can be a distinct advantage.

There is a serious potential danger if either the temperature or the field becomes too high, so that the material is no longer superconducting. Its resistance then becomes "normal." This can result in very large, and dangerous, amounts of Joule heating. Safety considerations related to superconducting energy storage devices of any appreciable magnitude generally involve their being placed in caverns deep underground.

7.8.3 Superconductive Materials

The phenomenon of superconductivity was discovered in 1911 by H. Kammerlingh Onnes [20]. He found that the electrical resistance of solid Hg disappeared below about 4 K. Research and development activities aimed at finding materials that remain superconducting to higher temperatures has been vigorously pursued over many years. Several groups of metals and alloys with higher critical temperatures were gradually found. Intermetallic compounds containing niobium have been shown to have attractive properties. The gradual improvement in the superconducting transition temperature resulting from the development of different alloys is shown in Fig. 7.12.

During the 1970s and 1980s it was generally concluded from both experimental and theoretical work that the maximum possible temperature for superconductivity was about 24 K. Then, in 1986, J.G. Bednorz and K.A. Müller showed that superconductivity could remain present in a ceramic oxide material, lanthanum barium yttrium oxide, up to 35 K [21]. A discussion of their work leading to this discovery can be found in [22].

A frantic effort was undertaken in many laboratories to confirm this surprising result, and investigate the possibility that superconductivity could be extended to even higher temperatures in other non-metallic materials. An important step was

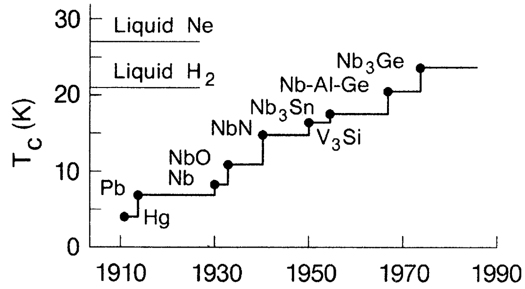

Fig. 7.12 The time-dependent increase in the superconducting transition temperature resulting from the development of new materials

Table 7.10 Values of the critical temperature and critical field of some superconducting materials

Material	Critical temperature/K	Critical field/Tesla
Nb-Ti	10	15
Nb_3Al	18	?
Nb_3Ge	23.2	37
Nb_3Sn	18.3	30
NbTi	10	15
MgB_2	39	74
$YBa_2Cu_3O_7$	92	?

the discovery that the phase yttrium barium copper oxide, $YBa_2Cu_3O_7$, remains superconducting up to 93 K [23]. This discovery was particularly important, for this temperature is above the boiling point of relatively inexpensive liquid nitrogen, 77 K. The details of the synthesis of this material have a large influence upon its properties. Particularly important is the oxygen content [24].

Another quite different material that has recently been found to be superconducting is magnesium diboride, MgB_2 [25]. Although its critical temperature is only 39 K, it may become important for some applications, for it is quite inexpensive and relatively easy to make into wires or other shapes.

Data on the properties of some of the important superconductive materials are included in Table 7.10.

All of the higher temperature oxide superconductors are inherently brittle. It has proved to be difficult to find a way to make these materials into the long lengths necessary to make magnetic coils. As a result, the wires used in electromagnets are now typically made from the alloys that have lower critical temperatures. Nb–Ti alloys, that have a ductile BCC crystal structure, and can be formed into wires and made into coils are commonly used for this purpose. Fibers of this material can be imbedded in an aluminum or copper matrix for structural purposes.

However, they cannot withstand as high a magnetic field intensity as the more expensive Nb_3Sn, which is harder to use. Nb_3Sn is very brittle, and cannot be drawn into a wire shape. To overcome this problem, a composite microstructure containing ductile precursor phases can be formed, with separate alloys of Nb, Cu, and Sn. After the material is made into wire and worked into the final shape, it is heat treated, during which the Sn reacts with the Nb to form the Nb_3Sn phase. Because of its high critical field, this material is preferred for the production of high-power magnets and electrical machinery.

$YBa_2Cu_3O_7$, is also brittle, and cannot readily be formed into wires and other shapes. It is expected that this problem can also be circumvented, however, by forming it in situ within other materials that can be readily shaped, and a considerable amount of development effort is currently aimed in this direction.

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