Chapter 14. Electrical properties

Engineering materials are important in everyday life because of their versatile structural properties. Other than these properties, they do play an important role because of their physical properties. Prime physical properties of materials include: electrical properties; thermal properties; magnetic properties; and optical properties. The electrical behaviors of engineering materials are diverse, and so are their uses in electrical applications. Few examples of electrical applications: copper and aluminium wires used in power transmission; amorphous silicon in solar cells; LEDs; gallium-arsenide chips used in modern day computers, cell phones, digital assistants; etc.

This chapter shall describe electrical properties and behavior of engineering materials in electrical applications. First, basic electrical property, electrical conductivity, will be described followed by different types of electrical conduction including semi- and super-conductivities. Some peculiar phenomena like ferro-electricity and peizo-electricity are explained in addition to electrical insulation.

14.1 Electrical conduction

Electrical conductivity of a material is defined in terms of ease with which a material transmits an electrical current. Electrical current ($I$) is flow of electrons, and driving force for the flow of electrons is called voltage ($V$). Ohm’s law relates these parameters as follows:

$$V \propto I$$

$$V = IR$$

where $R$ – is the materials resistance to flow of electrons through it.

$V$, $I$, and $R$ respectively have units as volts, amperes, and ohms ($\Omega$).
Electrical resistance of a material is influenced by its geometric configuration; hence a new parameter called *electrical resistivity* \( \rho \) is defined such as it is independent of the geometry.

\[
\rho = \frac{RA}{l}
\]  

where \( A \) – cross-sectional area perpendicular to the direction of the current, and \( l \) – the distance between points between which the voltage is applied. Units for \( \rho \) are ohm-meters (\( \Omega \)-m).

Reciprocal of the electrical resistivity, known as *electrical conductivity* \( \sigma \), is used to express the electrical behavior of a material, which is indicative of the ease with which a material allows of flow of electrons.

\[
\sigma = \frac{1}{\rho} = \frac{l}{RA}
\]

Electrical conductivity has the following units: \((\Omega \cdot \text{m})^{-1}\) or mho/meter.

*Resistivity or conductivity* does not depend on the dimensions of the material. These properties are microstructure-sensitive instead, like many other intrinsic properties, for example yield strength. Thus either of it (usually conductivity) allows us to compare different materials. Solid engineering materials exhibit very wide range of electrical conductivity (about 27 orders of variation). Hence the materials for electrical applications are classified according to their electrical conductivity as: *conductors*, *semiconductors* and *insulators/dielectrics*. Metals are conductors having conductivities in range of \(10^7\) \((\Omega \cdot \text{m})^{-1}\), while semiconductors have conductivities in range from \(10^{-6}\) to \(10^4\) \((\Omega \cdot \text{m})^{-1}\), and materials with conductivity lower than \(10^{-10}\) \((\Omega \cdot \text{m})^{-1}\) are termed as insulators.

In components designed to conduct electrical energy, minimizing losses is important to conserve energy as well as minimize heating. The electric power \(P\) lost when a current flows through a material is given by:

\[
P = VI = I^2R
\]

Electrical losses are also known as Joule heating losses.

Second form of Ohm’s law can be obtained by combining the equations (3) and (4) to give:

\[
\frac{I}{A} = \sigma \frac{V}{l} \Rightarrow J = \sigma E
\]

where \(J\) – current density \((\text{A/cm}^2)\), \(E\) – electric field strength \((\text{V/cm})\).
Current density can be defined in different terms as

\[ J = n.q \bar{v} \]  

where \( n \) – number of charge carriers \((1/cm^3)\), \( q \) – charge on each carrier \((1.6 \times 10^{-19} C)\), \( \bar{v} \) - average drift velocity \((cm/s)\), which occurs as a result of an applied electric or magnetic field.

The term ‘\( \bar{v}/E \)’ is called mobility, \( \mu \) \((cm^2/V.s)\) of the carriers, thus

\[ \sigma = n.q.\mu \]  

From the above equation, the following can be concluded: electrical conductivity of a material can be controlled by (i) controlling number of charge carriers, \( n \) or (ii) controlling the mobility of the carriers, \( \mu \). Mobility is important for metals or electrical conductors, whereas number of carriers is important for semi-conductors and insulators.

Electrons are charge carriers in metals. In ionic materials (for example ionic ceramics), conduction is result of net movement of charged particles (cations and anions) in addition to any electron motion. However, both electrons and holes are charge carriers in semiconductors and in doped conductive polymers. Thus equation 7 can be written as follows:

for metals : \[ \sigma = n_e q_e \mu_e \]  

for semiconductors : \[ \sigma = n.q.\mu_n + n.q.\mu_p \]  

for ionic materials : \[ \sigma_{\text{total}} = \sigma_{\text{electronic}} + \sigma_{\text{ionic}} \]  

In all conductors, semiconductors, and many insulating materials, only electronic conduction exists i.e. electrons are the only charge carriers. Ionic conduction results because of net motion of charged ions. Movement different particles in various materials depend on more than one parameter. These include: atomic bonding, imperfections, microstructure, ionic compounds, diffusion rates and temperature. Because of these, electrical conductivity of materials varies tremendously.

In metals not all electrons will accelerate in the presence of an electric field. Instead the number of charge carriers is dependent on the arrangement of electron states/levels with respect to energy, and the manner in which these states are occupied by electrons. Electrons in metals are arranged into shells and sub-shells in accordance with Pauli exclusion principle. Each of these shells / sub-shells is distinguished from every other by their energy state/level. Basic existence of metals is dependent on metallic bond where large groups of atoms come together and share valence electrons in what is called metallic bond. Thus there are \( \bar{N} \) atoms in the lattice with \( N \) atomic orbitals and \( N \)
molecular orbitals, many of which are of same energy. This leads to bands of electrons. The electrons not involved in bonding remain in what is called the core band, whereas the valence electrons that form the electron gas enter into the valence band. The remaining un-filled orbitals form higher-energy bands, called conduction band. It is the conduction band that gives metals and alloys the ability to freely conduct electrons.

Four different types of band structures are possible at 0 K: (1) Where one outermost band is only partially filled with electrons. The energy corresponding to the highest filled state at 0 K is called the Fermi energy, \( E_f \). (2) There is overlap of an empty band and a filled band. (3) and (4) One filled band (valence band) and an empty band (conduction band) are separated by an energy band gap which lies between them. These are schematically shown in the figure 14-1.

![Figure 14-1](image)

Band structures (1) and (2) are found in metals / conductors. Band structures (3) and (4) are distinguished by the size of energy band gap. Narrower energy band gap i.e. size < 2 eV, is found in semiconductors, while the broader energy band gap i.e. size > 4 eV, is found in insulators. Fermi energy for these two band structures lies within the band gap near its center.

Metals have high conductivities because of the large number of free electrons that have been excited into empty states above the Fermi energy. If the metal crystal lattices were perfect and there are no lattice vibrations, the electrons would pass through the lattice un-scattered, encountering no resistance. However, lattice vibrations and phonon scattering play a role in disrupting the mean free path of electrons. In addition, crystalline defects and impurity atom affect the conductivity. These scattering mechanisms act independently on one another. Thus the effective resistivity of metals can be represented as follows:
\[ \rho = \rho_{\text{thermal}} + \rho_{\text{residual}} \]  

Equation 11 is sometimes known as Mathiessen’s rule. With increase of temperature, thermal vibrations increase so the resistivity, and vice versa. In the same manner, with increase of either defects or impurities, resistivity increases. Thus, in general, for pure metals, the resistivity approaches zero at absolute zero temperature.

Some metals, however, such as Pb, lose all resistivity abruptly and completely at some low temperatures. This phenomenon is called superconductivity, and the materials that exhibit it are called superconductors. The temperature at which the resistivity vanishes is called the critical transition temperature, \( T_c \). Many elemental metals, solid-solution alloys, some ceramics and intermetallic compounds exhibit superconductivity. For example: Ti, V, Zn, W, Al, Hg, NbTi, Nb₅Sn, MgB₂, La-Sr-Cu oxide, YBa₂Cu₃O₇₋ₓ, carbon nanotubes, etc. BCS (Bardeen, Cooper and Schrieffer) theory explains that the superconductivity is caused by electron-lattice interaction and that the superconducting electrons consist of paired ordinary electrons called a Cooper pair.

14.2 Semiconductivity

Conductivity of semiconductors is not as high as metals / conductors. However, their electrical properties are unique, in the sense that their electrical properties are extremely sensitive to even minute concentrations of impurities. For intrinsic semiconductors, their electrical behavior is based on inherent electronic structure of the pure material. On the other hand, if the electrical properties are dominated by impurities, they are called extrinsic semiconductors.

Intrinsic semiconduction: Energy band gap between the valence and conduction bands can be used to classify materials as conductors, insulators, and semiconductors. The magnitude of the band gap is characteristic of the lattice alone, and varies widely for different crystals. In semiconductors, the valence and conduction bands do not overlap as in metals, but they possess enough electrons in the valence band that can be promoted to the conduction band at a certain temperature. Promotion of electrons leaves behind positively charged holes in the valence band which maintain the charge neutrality. These holes can be regarded as moving positive charges through the crystal with a charge magnitude and ass as that of an electron. Conduction that arises from thermally / optically excited electrons is called intrinsic semiconduction. It usually takes place at elevated temperatures since sufficient thermal agitation is necessary to transfer a reasonable number of electrons from the valence band to the conduction band. At still higher temperatures, the concentration of thermally excited electrons in the conduction band becomes so high that the semiconductor behaves more like a metal. The elements capable of intrinsic conduction are limited, and include: Si, Ge, Sn, Pb, etc.
In intrinsic semiconductors, the number of holes equals the number of mobile electrons. The resulting conductivity can be expressed as

$$\sigma = n_e q_e \mu_e + n_h q_h \mu_h = n_e q_e (\mu_e + \mu_h) \ldots \ldots (12)$$

as $n_e = n_h$, and both electron and hole possess equal magnitude of charge.

The mobility of holes is always less than those of electrons i.e. $\mu_h < \mu_e$. In Si and Ge, the ratio $\mu_e / \mu_h$ is approximately three and two respectively.

**Extrinsic semiconduction:** The charge carrier density can also be increased by adding impurities of either higher or lower valence. This addition of impurities is known as doping, and impure atoms in the element are called donor atoms.

When a pentavalent substitutional atoms like P, As, or Sb are placed into a covalently bonded tetravalent materials such as Si or Ge, only four of their five valence electrons are required to participate in covalent bonding, while the fifth electron remains weakly bound to the donor atom. However, this binding energy is in order of 0.01 eV, much less than that of a covalently bonded electron. The energy state of this electron is indicated as $E_d$. Energy gap between the donor and conducting bands is much smaller than that between the valence band and conduction band, $E_g$. Thermal agitation, even at room temperature, is good enough to excite this electron to the conduction band, leaving behind a positively charged hole in the donor band. Conductivity is due to motion of negatively charged electrons in the conduction band, and so the material is called *n-type semiconductor*. Fermi level ($E_f$) of *n*-type extrinsic semiconductor is higher than that of intrinsic semiconductor i.e. it shifted upward in the band gap, to within the vicinity of the donor state; and its exact position is a function of both temperature and donor concentration.
Other possibility of substitution involves impurity with lower valence. For example, trivalent elements like B, Al, Ga, In, Th doped to Si or Ge. Since the donor atoms are deficient in bonding electrons, one of their bonding orbitals will contain a hole that is capable of accepting an electron from elsewhere in the crystal. Binding energy is small, and promotion of an electron from the valence band to the acceptor band, $E_a$, leaves a positively charged hole in the valence band that can act as a charge carrier. Materials with this p-type extrinsic semiconduction are called p-type semiconductors. Fermi level ($E_f$) for p-type semiconductors is positioned within the band gap and near to the acceptor level.

For an n-type semiconductor, electrons in the conduction band are charge carriers and holes participate in bonding, whereas for a p-type semiconductor, the electrons participate in bonding, and the holes are the charge carriers. Conductivity equations for these extrinsic semiconductors are written as:

$n$-type semiconductor: \[ \sigma \equiv n.q.\mu_e \quad \ldots\ldots (13) \]

$p$-type semiconductor: \[ \sigma \equiv n.q.\mu_h \quad \ldots\ldots (14) \]
In both types of extrinsic semiconductors, the doping elements are chosen so that both acceptor and donor levels are located closer to the corresponding energy bands and only a small energy gap in involved when exciting electrons. Intrinsic semiconductors are pure to the order greater than $10^7$, while extrinsic semiconductors are made with impurity levels in order of 1-1000 ppm.

In intrinsic semiconductors, the conductivity is dominated by the exponential relation between temperature and band-gap. However, the conductivity of extrinsic semiconductors is governed by competing forces: charge carrier density and charge carrier mobility. At low temperatures, the number of charge carriers initially increases with temperature. At intermediate temperatures, for $n$-type extrinsic semiconductor, most of the donor electrons have been promoted and the number of charge carriers is nearly independent of temperature in what is known as the exhaustion range. At higher temperatures, the number of valence electrons excited to the conduction band greatly exceeds the total number of electrons from the donor atoms, and extrinsic semiconductor behaves like an intrinsic semiconductor. That is, at low temperatures the conductivity varies with temperature as the charge carrier concentration, at higher temperatures the charge carrier mobility dominates and the conductivity decreases with temperature, and at still higher temperatures the extrinsic semiconductor behaves like an intrinsic semiconductor.

14.3 Electrical conduction in ionic ceramics and in polymers

In addition to the conduction of charge via electrons, charge can be conducted via ions. Ions are present in most crystalline ceramic materials such as oxides and halides. This process is called ionic conduction, and may occur either in conjunction with or separately from electronic conduction.

Several types of compounds show exceptionally high ionic conductivity. Such phases fall into three broad categories: halide and chalcogenides of silver and copper; oxides with β-alumina structure; and oxides of fluorite structure. Conductivity of halides and chalcogenides is result of larger number of available sites than the number of cations. In oxides with β-alumina structure (AM₁₁O₁₇) monovalent cation A (such as Na, K, Rb, Li) is mobile. High dopant levels in the fluorite-type solid solutions leads to large defect concentrations and vacancy ordering which results in rapid oxygen migrations. This is the base for development of high-temperature superconductors. For example: La$_2$CuO$_4$ ($T_c = 30$ K), YBC compounds – yttrium doped perovskite structure, YBa$_2$Cu$_3$O$_7$ ($T_c = 92$ K).

Although ceramics are insulators, by properly engineering the point defects in ceramics, it is possible to convert them into semiconductors. For example: Indium tin oxide (ITO) is used as a transparent conductive coating on plate glass, and also for tough screen displays; Yttria-stabilized zirconia (YSZ) is used as solid electrolyte in solid oxide fuel cells; Lithium cobalt oxide is used as solid electrolyte in lithium ion batteries.

Polymers have a band structure with a large energy gap leading to low conductivity because their valence electrons are involved in covalent bonding. Hence polymers are used
frequently in applications that require electrical insulation. In some cases however, low conductivity is undesirable. For example; static electricity can accumulate on housing for electronic equipment making the polymer vulnerable to electromagnetic radiation that damages the internal devices. These problems can be solved in two approaches: (1) introducing an additive to the polymer to improve conductivity, and (2) creating polymers with inherent conductivity.

Adding ionic compound to the polymer can reduce resistivity because the ions migrate to the polymer surface and attract moisture, which in turn, dissipates static charges. Introducing conductive fillers such as carbon black can also dissipate static charges. Some polymers inherently have good conductivity as result of doping or processing techniques. When acetal polymers are doped with agents such as arsenic pentafluoride, electrons or holes are able to jump freely from one atom to another along the backbone of the chain, increasing the conductivity to near that of metals. However, unlike semiconductors, the dopant atoms or molecules do not substitute for or replace the polymer atoms. Other polymers include polyparaphynylene, polypyrole, and polyaniline. Some other polymers such as polyphthaocyanine can be cross-linked by special curing processes to raise its conductivity.

14.4 Dielectric behavior

A dielectric is a material separating two charged bodies. For a material to be a good dielectric, it must be an electrical insulator. Thus, any insulator is also called a dielectric. Dielectric materials are used in capacitors, devices used to store the electric energy.

When a voltage is applied between two parallel plates in a vacuum, one plate becomes positively charged and the other negatively charged, with corresponding field directed from the positive to the negative. Then the energy stored, $Q$, is given by:

$$Q = CV$$

where $C$ is the capacitance (units: coulombs per volt or farads [F]). It is dependent on the geometry of plates as follows:

$$C = \varepsilon_0 \frac{A}{l}$$

where $A$ – area of the plates, $l$ – distance between them, and $\varepsilon_0$ – permittivity of vacuum ($8.85 \times 10^{-12}$ F/m). If a dielectric material is inserted between the plates,

$$C = \varepsilon \frac{A}{l}$$

$\varepsilon$ – permittivity of the medium, which will be greater in magnitude than $\varepsilon_0$. The relative permittivity $\varepsilon_r$, also called dielectric constant, is defined as
\[ \varepsilon_r = \frac{\varepsilon}{\varepsilon_0} \]  \hspace{1cm} (18)

which is greater than unity, and presents the increase in charge storing capacity by insertion of the dielectric medium between the plates. This is result of polarization – orientation of permanent or induced dipoles under externally applied electric field. Polarization causes positive charge to accumulate on the bottom surface next to the negatively charged plate, and causes negative charge to accumulate toward the positively charged plate on the top. This tends to decrease the effective surface charge density on either plate. The expected decrease in effective charge corresponds to the polarization, of the material which equals the induced dipole moment per unit volume of polarizable material. The magnitude of the charge per unit area on either plate, called the dielectric displacement or flux density or surface charge density, \( D \), is defined as:

\[ D = \varepsilon \xi \]  \hspace{1cm} (19)

where \( \xi \) – electric field strength,

\[ \xi = \frac{V}{l} \]  \hspace{1cm} (20)

In the presence of the dielectric, surface charge density can also be presented as

\[ D = \varepsilon \xi = \varepsilon_0 \xi + P \]  \hspace{1cm} (21)

where polarization is defined as,

\[ P = \varepsilon_0 (\varepsilon_r - 1) \xi \]  \hspace{1cm} (22)

the increase in charge density above that for a vacuum because of the presence of the dielectric.

Figure 14-5: Schematic representation of capacitor and polarization phenomenon.
The polarization may also be thought of as the total dipole moment per unit volume of the dielectric material or as a polarization electric field within the dielectric that results from the mutual alignment of the many atomic or molecular dipoles. Polarization of a dielectric material may be caused by at least one of four major types of polarization: electronic, ionic (atomic), orientation, and space charge (interfacial).

Electronic polarization arises because the center of the electron cloud around a nucleus is displaced under an applied electric field. Ionic polarization occurs in ionic materials because an applied field acts to displace cations in the direction of the applied field while displacing anions in a direction opposite to the applied field. Orientation polarization can occur in materials that possess permanent electric dipole moments. These permanent dipoles tend to become aligned with the applied electric field, but entropy and thermal effects tend to counter this alignment, thus it is highly temperature dependent. Space charge polarization results from the accumulation of charge at structural interfaces in heterogeneous materials. Such polarization occurs when one of the phases has a much higher resistivity than the other.

The total polarization subjected to an alternating electric field depends upon the ease with which the permanent or induced dipoles can reverse their alignment. The time required for dipole reversal is called the \textit{relaxation time}, and its reciprocal is called the \textit{relaxation frequency}. As the frequency of the applied electric field approached the relaxation frequency, the polarization response increasingly lags behind the applied field. The reorientation of each type of dipole is opposed by internal friction, which leads to heating in the sample and power loss. The power loss depends on the degree to which the polarization lags behind the electric field. This is also called \textit{dielectric loss}, and a low dielectric loss is desired at the frequency of utilization.

At high enough frequencies, the dielectric will experience electrical breakdown initiated by the field-induced excitation of a number of electrons into the conduction band, and the insulator become a conductor. The magnitude of the electric field required to cause dielectric breakdown is called the \textit{dielectric strength} or \textit{breakdown strength}.

Many ceramics and polymers are utilized as insulators and in capacitors. For example: glass, porcelain, stealite, mica. These have dielectric constants within the range of 6-10. Typical applications: electrical insulation, switch bases, light receptacles. Dielectric constant for most polymers lies in the range of 2-5, less than that for ceramics, since the later exhibit greater dipole moments. Typical applications: insulation for wires, cables, motors, generators, some capacitors.

\subsection*{14.5 Ferro-electricity and Piezoelectricity}

Two peculiar phenomena related to electric dipoles are \textit{ferro-electricity} and \textit{piezoelectricity}. Ferro-electricity is defined as the spontaneous alignment of electric dipoles by their mutual interaction in the absence of an applied electric field. This arises from the fact that the local field increases in proportion to the polarization. Thus, ferro-electric materials must possess permanent dipoles. Ex.: BaTiO$_3$, Rochelle salt
(NaKC₄H₄O₆.4H₂O), potassium dihydrogen phosphate (KH₂PO₄), potassium niobate (KNbO₃). These materials have extremely high dielectric constants at relatively low applied field frequencies. Thus, capacitors made from ferro-electric materials are smaller than capacitors made of other dielectric materials.

Piezo-electricity, or pressure electricity, is defined as polarization induced by the application of external force. Hence, by reversing the direction of external force, direction of the field can be reversed i.e. the application of an external electric field alters the net dipole length and causes a dimensional change. This property is characteristic of materials having complicated structures with a low degree of symmetry. Thus, piezo-electric materials can be used as transducers – devices that convert mechanical stress into electrical energy and vice versa. Application for these materials includes microphones, ultrasonic generators, sonar detectors, and mechanical strain gauges. Ex.: Barium titanate, lead titanate, lead zirconate (PbZrO₃), ammonium dihydrogen phosphate (NH₄H₂PO₄), and quartz.

References