However, the certainty that all insulators are experimentally found being charged by metals has steadily drawn the researchers into the information on the nature of electron states in insulator. This has subsequently led to an assumption that the insulators have electron energy levels or electron sites within their energy gap, which can be the result either of impurities and imperfections or of surface states. In case that an insulator is negatively charged, electrons from a contacting metal must reach the acceptor-like sites in the insulator, which should lie below the Fermi level of the contacting metal, by tunnelling, so only the real surface states or the bulk impurity sites which are by chance very close to the surface will take up electrons. Note that there is also the opposite situation in which the insulator consists of the full donor-like states lying above the Fermi level of the contacting metal. In that case, the insulator can lose electrons to the metal and becomes positively charged. The assumption has been experimentally confirmed by a number of investigators (i.e. Lowell, 1976, Duke and Fabish, 1978). The charge transfer between a metal and an insulator has been proved by them to be the result of the electrons tunnelling between the metal and the electron states in the insulator, both on the surface and in the bulk. Those electron states are within a narrow range of energy near the metal Fermi level. The tunnelling hypothesis can also be used to explain why the charge transferred between metal and insulator are found depending on the work function of the metal, as the thermodynamic equilibrium ordinarily does so. The information about the electron states in solids has been applied to the investigation of the role of surface states in the contact electrification. It is observed that the charge transferred to the surface states of an insulator by a contacting metal depends also on whether the density of the surface states is small or large.

In the surface state theory (see more details in Lowell and Rose-Innes, 1980), states deep within the bulk of an insulator are unconvincing to play any part in the charging mechanism since they are too far for electrons from the contacting metal to access. Nonetheless, it is contrary for bulk states that appear to lie very close to the surface which electrons from the metal can tunnel with a short distance into the insulator. The theory has two limits designated as the low surface state density and the high surface state density limits. Consider only negative charging. When a charge passes from the metal to the insulator surface, it commonly sets up an electric field between the insulator and the metal. In high-density limit, the density of acceptors in the insulator is so large that, when they are filled by the electrons
from the contacting metal, the resulting electric field between the metal and the insulator is significant. The electron transfer will then cease as soon as the resulting potential step across the interface has increased to such a value that the energy of the acceptor-like sites reaches the metal Fermi level. In the low-density limit, the density of the sites in the insulator is so low that, even if they have all taken up electrons, the resulting electric field across the interface is still so small that there is a negligible increase in their energy. The magnitude of the contact charge, therefore, will be limited by the density of states in the insulator.

In general, the surface state theory has been alternatively proposed to explain the experimental observations of the dependence of contact charge on metal work function. It states that the charge transferred between the insulator and the contacting metal is in proportion to the difference between the effective or surface work functions of the two materials. Note that this theory can apply equally to electron or ion transfer. The fact that an insulator may be charged negatively when touched by a metal of smaller work function (high Fermi energy), but positively when touched by a metal of higher work function (lower Fermi energy), implies that such an insulator consists of both empty acceptor states and filled donor states.

Turning now back to the ordinary thermodynamic equilibrium theories of electron transfer. The general principle of these theories is described in such a way that: when contact between an insulator and a metal is made, the charge transfer is assumed to be determined by the condition that the Fermi levels in both materials become coincident. The Fermi level in the insulator is known to differ from that in metal (Figure 1.7). In the case that electrons pass from the metal to the insulator when the contact are made, a dipole is created and, in equilibrium, the potential difference across this dipole will be $V_c$, which is sufficient to raise the Fermi level of the insulator into coincidence with that of the metal. Then the charge density in the insulator can be determined or predicted because the energy of electrons occupying states depends on the potential and the distribution of charge in the insulator.

The fact that the charge transferred to an insulator from a metal is often dependent on the metal work function has influenced most of the published theories of contact electrification of insulators by
metals to be based on an assumption that thermodynamic equilibrium is achieved during contact. The calculations or predictions of the charge transfer for this case are, however, not the same as for metals, though they are obviously on the basis of the contact electrification of metal.

Unquestionably, the correlation between the contact charge and the metal work function is of great importance for the mechanism of the contact electrification, and numerous experiments have been conducted in connection with that point. As a result, there is disagreement about the relationship of the contact charge to the work function of the contacting material. For example, some investigators have found a nearly linear relationship whereas the others have reported the contact charge to be independent of the contacting metal work function. In accordance with the results obtained by many researchers, four major theories have been proposed to interpret the experimental relationships and predict the charge density of the insulator.

The first theory considers an insulator with \( n_A \) empty acceptor-like states per unit volume above its Fermi level, and suppose for the time being that these states lie at the same energy \( E_A \) (Figure 1.8 (a)). Suppose further that the Fermi level of this insulator lies below that of the contacting metal, and assume that the charge transferred to the insulator by the metal is contained entirely in the acceptor-like states. The charge density is then given by

\[
\sigma \approx - \left\{ 2\varepsilon_r \varepsilon_0 n_A kT \exp \left( - E_A / kT \right) \right\}^{1/2} \exp \left( eV_c / 2kT \right),
\]  

where \( \varepsilon_r \) is the permittivity of the insulator and \( V_c \) is the contact potential difference (which is intimately related to the work function of the metal). The equation above (1.3.9) predicts an exponential dependence of the contact charge on the contact potential difference and therefore the work function of the contacting metal.
Figure 1.7. Evidence that contact charging of insulators by metals is determined by the energy difference between the metal Fermi energy and some energy $E_0$ characteristics of the insulator. (a) Energy levels in a metal and an insulator. (b) Contact charging of Nylon 66 by various metals (reference with gold for contact potential difference, cpd). (c) Contact charging by Zinc of a range of salicylaldehyde anils. (after Lowell and Rose-Innes, 1980)
Secondly, unlike the situation above, this theory presents the incident in which the electron energies of the insulator are not discrete but spread over a wide band with an exponential tail (Figure 1.8). If the equilibrium is reached when the insulator and the metal are brought into contact, the bands of the insulator must bend as shown in Figure 1.8 (b) and (c), depending on whether the localized states in the insulator are initially above or below the metal Fermi level. Suppose further that the insulator contains both acceptor-like and donor-like states. The density of the donors \( n_D \) is greater than the density of the acceptors \( n_A \) and the donor level lies much more than \( kT \) above the acceptor level. For that reason, the donor level is partly occupied, containing \( n_D - n_A \) full states and \( n_A \) empty states per unit volume. The Fermi level will be very close to the donor level, unless \( n_D \) and \( n_A \) are almost equal. If the Fermi level of the contacting metal lies above the donor level, electrons can then pass from the metal to the empty donor states; and if below, electrons from the occupied acceptor states can pass to the metal. The charge density for this case is given by

\[
\sigma = - \left\{ 2\varepsilon_r \varepsilon_0 n_A eV_c \right\}^{1/2}, \quad V_c \geq 0 \quad \text{and}
\]

\[
\sigma = + \left\{ 2\varepsilon_r \varepsilon_0 (n_D - n_A ) eV_c \right\}^{1/2}, \quad V_c \leq 0. \quad [1.3.10]
\]

(as long as the metal Fermi level is above the acceptor level)

In this case, the quadratic dependence of the charge density on the metal work function is expected in agreement with the equation (1.3.10). Moreover, the equation (1.3.10) also suggests that the charge density for a given \( V_c \) should, in general, be completely different in magnitude to the charge density for \(-V_c\).

Nevertheless, in the equation (1.3.10), all the donor states accountable for the contact electrification are assumed to have the same energy, whereas they may be distributed over a wide range of energy in practice. Interestingly, it seems that the latter gives much more credible results than the former, according to the experimental data.
Figure 1.8. Contact between a metal and an insulator or semiconductor containing localized states. (a) shows the energy states before contact. If equilibrium is reached when the metal and insulator are in contact, the bands of the insulator must bend as shown in (b) and (c). To explain the experimental results, it is necessary to suppose that the insulator contains both acceptor-like and donor-like states (d).
It is concluded that the relationship between the charge density and the contact potential difference should be linear, or nearly linear, if the insulator states are spread over a wide range of energy. To explain the experimental results, it is necessary to suppose that the insulator consists of both acceptor-like and donor-like states (Figure 1.8 (d)), and the densities of donor and acceptor states are approximately equivalent so that the Fermi level falls near $E_0$, the energy level characteristics of the insulator. If there are $n_0 dE$ states per unit volume in the energy range $E$ to $E + dE$ ($n_0$ = constant), the charge density is therefore given by

$$\sigma = (n_0 e^2 \varepsilon_r \varepsilon_0)^{1/2} V_c.$$  \[1.3.11\]

Definitely, it seems unlikely that $n_0$ would be independent of energy. The Gaussian distribution of states focused on an energy $E_0$ is then introduced,

$$n(E) = \left( \frac{n}{\Delta\sqrt{\pi}} \right) \exp\left\{ - \frac{(E - E_0)^2}{\Delta^2} \right\},$$  \[1.3.12\]

which represents a total of $n$ states per unit volume with an energy distribution of a half-width equal to 0.5 eV. Furthermore, the linear relationship between the contact charge and the work function of the contacting material can also be explained on the tunnelling hypothesis, if the states which are filled on contact are distributed over a wide range energy: electrons transfer only into the states below the metal Fermi level, so the total charge transferred depends on the Fermi energy of the metal.

Finally, there is also compelling evidence that the thermodynamic equilibrium may never be reached or achieved for some kinds of insulator, particularly the insulators with a wide energy gap in relation to $kT$, because charge cannot penetrate deep into the insulator. The charge transferred between the insulator and the contacting metal for this case is suggested to go only into surface states. Moreover, a limited equilibrium may be accomplished in such a way that electrons in the metal are in equilibrium with the surface states of the insulator, but the electrons in the metal are not in equilibrium with the bulk states. As mentioned earlier, electrons may tunnel into the insulator, but only to the traps and those bulk states that happen to be very close to the surface of the insulator. It is unlikely that the thermodynamic
charge is established by tunnelling. If traps in the insulator below the Fermi level of the contacting metal are filled by tunnelling, the change in the energy of the traps is then not significant. For this reason, the charge density happens to be very small. Accordingly, if traps occur at a single energy, the contact charge would be definitely independent of the work function of the contacting metal. This circumstance has occurred to some experiments (Elsdon and Mitchell, 1976; Cottrell, et.al., 1979).

The details of all calculations will be provided in the Appendix.

iii) Insulator-Insulator Contacts

The most spectacular cases of contact electrification appear when two insulators are brought into contact with each other. However, such cases have not been so profoundly studied because at present little is known about the electronic nature of insulators. Whether the transfer of charge from one insulator to another occurs by a similar mechanism, or whether absolutely different processes are implicated, remains the subject researchers want to learn. A number of impressive reviews of this phenomenon have been provided in the literature. In particular, the reviews made by Harper (1967), Lowell and Rose-Innes (1980), Cross (1987), and most recently by Lee (1994) and Castle (1997), present detailed discussions and excellent summaries of the work relevant to the contact charging between insulators (dielectrics).

There is some experimental evidence that the contact electrification of insulator-insulator is indicated by the similar basic mechanism to that of metal-insulator contacts, and that the charge transferred between the two insulator samples can be predicted from the knowledge of the charge acquired by each of these insulators on contact to a metal. Davies (1970) has found that the charge transfer between two insulators is correlated with their energy characteristics ‘Fermi levels,’ $E_0$. It appears that electrons pass from the insulator with the higher ‘Fermi level’ to the one with the lower, resulting in the sign of the charge existed on the insulators. More recently, Duke and Fabish (1978) have extended their assumption of metal-insulator electrification to the case of contact charging between insulators. As noted earlier, the charge transfer between a metal and an insulator has been claimed to be
the result of the electrons tunnelling between the metal and the electron states in the insulator which are within a narrow range of energy near the metal Fermi level (Duke and Fabish, 1978). Their proposed mechanism for the case of insulator-insulator electrification is principally the same to some extent. The only exception is that the range of energy is much wider because, in insulators, the strong energy-dependence of the density of the states will counterbalance the strong energy-dependence of the tunnelling matrix element. Based on this information, they predicted the charge transfer between two polymers from the density of states in each, which is assumed from metal-insulator charge transfer measurement. It is apparent that the mechanisms proposed by Davies (1970) and by Duke and Fabish (1978) are different, although both have shown the interdependence between the contact electrification of two insulators and the charge acquired by such insulators by contact with metals. It should be pointed out, though, that most of the experimental work on contact electrification of insulators has been conducted on organic polymers.

For many years, the charge transfer between two insulators was believed to be a result of electrons transferring. Until recently, it has been well documented that ions and material mass transfer may also contribute to the charge transfer mechanism. Surprisingly, in some special cases, all three of these mechanisms: i.e., electron, ion, and material transfer, may take place altogether (Castle, 1997). However, the transferring of electrons is preferably credited as the dominant mechanism for charge transfer between two insulators.

Certainly, the concept of contact electrification of insulators has been extended from the theory applied to metal-insulator contact. It has been proposed that electron states of the polymer (insulator) are present in the forbidden gap but are localized at the surface of the material, so that the charge can transfer rapidly as observed in experiments. Therefore, the theory of an effective work function associated with an insulator, as described in previous section, may be considered to be a surface property rather than a bulk property, which is generally associated with metals and semiconductors. This is known as the surface state theory, which offers the model for charge transfer in the contact electrification of two insulators. As the surface state theory has already been described in the section of metal-insulator contacts, it is therefore unnecessary to repeat it here. However, it should be noted that
the charge, in general, is transferred between the two insulators so that the resulting energy occurred by 
the charge transfer offsets the difference in work functions at interface (Castle, 1997).

In addition, it is a common experience that identical insulators may charge one another by 
rubbing together, and ice is a notably important example of this circumstance. The electrification of ice 
crystals in clouds by collision with each other is believed to give rise to the strong electric fields that 
consummate in lightning. It appears likely that the charge transfer between two identical insulators when 
they are rubbed together can occur as a result of temperature difference between the contacting 
surfaces (Thomson effect); as rubbing usually introduces local heating. However, it has not been 
established whether the electrification of identical insulators can be found upon normal contact.

1.4. Triboelectric Charge Measurement and Experimental Method

Any discussion of the nature of triboelectrification must be based on experimental evidence and 
so the experimental techniques for measurement of such phenomenon are vital in the investigation. As in 
all fields of experimental study, irreproducible and incorrect results have been accumulated because of 
the failure to recognize some ill-defined experimental techniques. In the area of electrostatics, it needs to 
be remembered that the technique of measurement does involve the small quantities of charge and may 
be difficult to promise the absolute result. Hence, it is necessary to be prepared to re-evaluate the 
observations with an alternative approach when making the charge measurement.

The first task of a careful experimentation is to measure the charge on a specimen that has been 
touched by, or made contact with, another specimen. However, it is important to bear in mind that, in 
general, the charging apparatus and the charge measuring technique are always related firmly to each 
other. Therefore, one often sees a new approach to triboelectric charge measurement being developed 
on the basis of the mechanism or behavior of charging, and it is impractical to discuss them separately.
While charge is one of the key criterions in the electrostatic separation systems, it is not always convenient for a direct measurement. On the contrary, an associated parameter such as an electric field rarely bears that difficulty. Electrostatic charge is usually measured by induction. There are fundamentally two alternative standard techniques, which are of service to the basis for nearly all charge measuring devices in use today. The first of these techniques is the “Faraday pail” (or “Faraday cage”) technique. The principle of this technique is classically simple and it offers the absolute value of the charge. It is even mentioned as a standard method of measuring charge by use of a Faraday cage or pail coupled to a suitable monitoring circuit. As illustrated in Figure 1.9 (a), the charged specimen is put into a metal cage that is almost closed, or at least very deep. The charge $+Q$ on the specimen induces charge $-Q$ on the surrounding cage and, when the cage is connected to a qualified electrometer of input capacitance $C_E$, the electrometer will register a voltage:

$$V = \frac{Q}{C_1 + C_E}$$  \hspace{1cm} [1.4.1]

where $C_1$ is the capacitance of the cage to ground. With this arrangement, the charge induced on the inner walls of the cage is equal in magnitude but opposite in sign to the introduced charge, and the charge of the same magnitude and sign appears on the outside of the cage, or is transferred to the monitoring circuit.

Despite its serviceability, the Faraday pail method can only be used if the charged specimen is allowed to move thoroughly into the cage. However, there is another associated technique in which the charge can be measured without the necessity of moving the charged specimen. Although in an ideal case a Faraday pail should completely enclose the charged specimen whose charge is being measured, but in practice it is not always required to do so. As shown in Figure 1.9 (b), an accurate charge measurement can be alternatively done by merely placing the specimen (I) on a metal sheet (M) which is connected to ground through an electrometer. If M is the only metal that is close to I, the electrometer will then indicate the charge induced on M that is equal to the charge on I.
The second standard method of measuring the charge on a specimen is called a “proof-plane” technique. The principle is simple: a metal plate (or a proof plane), which is connected to an electrometer, is brought intimately to the charged specimen and the potential of the metal plate is measured. The potential of this proof plane is developed by the field from the charge on the specimen; or simply put, the potential is due to the charge induced on the proof plane. In the event shown in Figure 1.9 (c), the charged specimen sheet I is placed on the top surface of an earthed metal sheet G and a proof plane P connected to an electrometer is brought over I to detect the charge occurred by contact electrification on the upper surface of it. By using this technique, the specimen needs not to be moved, resulting in the more convenience. Unfortunately, this advantage is shadowed by the technique’s shortcoming. The method itself can not give the absolute value of charge. If the absolute charge is needed, the calculations based on the geometry of the arrangement must be made. It is found that: if the ‘relative permittivity’ of the specimen (insulator) is $\varepsilon_r$, a charge $+Q$ on the surface of the insulator will induce a voltage $V$ on the proof plane, which is given by

$$V = -\frac{Q}{(C_E + C_G)(1 + \varepsilon_r d/t)},$$

where $C_E$ is the input capacitance of the electrometer, $C_G$ is the capacitance to ground of the proof plane, $d$ is the distance between P and the upper surface of I, and $t$ is the distance between the upper surfaces of I and G. It should be noted, however, that for many insulators, the relative permittivity $\varepsilon_r$ (in equation (1.4.2)) is rather ill-defined.

The proof plane technique has been variously modified for other measuring purposes, aside from measuring the surface charge density of insulators (Davies, 1964). One example is that the proof plane P may be periodically vibrated to moderate $d$ (Englehardt, et.al, 1977; Flasson and Harris, 1977), whereby the a.c. signal is created. If the charge $Q$ is small, it may be inevitable to allow for signals owing to the difference in work function between the proof plane P and the rest of apparatus. This finding performs as a basis for making work function measurements of various materials in many works.
Up to the present, the existing charge measuring devices developed for the triboelectrostatic separation systems are mostly based on the principle of the “Faraday pail”, although they are distinctive according to the applications for the particular tribocharging systems. Reviews of the charge measuring systems have been well established in recent years by a number of authors: for instance, by Davies (1974), Haase (1977), Bright and his coworkers (1978), Secker (1980), and Secker and Chubb (1984). For the following recounts, the intention is to present the reference only in which it is concerned as a background for the experimental part of this dissertation.

An inductive, non-intrusive method for measuring an electric charge of charged bodies when at rest or moving relatively slow has been proposed by Gajewski (1987), with mathematical and physical description included. The principle of the measurement is based on the difference of electrical potentials between any two points in the field of a point charge: for instance, the surface charge of dielectric and conducting spheres, cylinder, or flat surfaces. The theoretical considerations involve the use of a cylindrical capacitor and an arrangement of electric circuit for non-interfering measurements of electric charge generated on surface of various bodies. In the measurement, two coaxial light-wall cylinders of conducting materials were formed with radii \( r_1 \) and \( r_2 \) \((r_1 < r_2)\) and with length \( l \) \((l >> r_1 \text{ and } r_2)\) to be a cylindrical capacitor, for which capacitance and potential difference are given by

\[
C = 2 \pi \varepsilon_0 l \left( \ln \frac{r_2}{r_1} \right)^{-1}, \text{ and} \tag{1.4.3}
\]

\[
U = V_1 - V_2 = Q \left( 2 \pi \varepsilon_0 l \right)^{-1} \ln \frac{r_2}{r_1}, \tag{1.4.4}
\]

where \( Q \) is an electric charge, or a point charge. If an electric charge \( Q_1 \) is put in the geometrical center of the capacitor and by grounding the outer cylinder, charge \( Q_2 \) induced in the inner cylinder is zero as a result of the same value, but opposite sign, of charge on both sides of the cylinder (Figure 1.10). Still, the potential or voltage \( V_2 \) is, at the same time, non-zero and it is thus defined. Charge \( Q_3 \) induced in the internal surface of the outer cylinder is also non-zero and its absolute value is equal to \( Q_1 \) but opposite sign, \( Q_3 = -Q_1 \), when charge \( Q_1 \) is surrounded by the cylinder. As shown in Figure 1.11, the
measurement of the potential $U_{20}$ is of particular interest because it allows one to obtain the magnitude and sign of an unknown charge $Q_1$. According to the electric circuit arrangement of the measuring system shown in Figure 1.11, the analysis made by the authors shows that:

$$U_{IN}(\infty) = U_{20}(\infty) = \frac{C_{12}}{C_{12} + C_{20} + C_{IN} + C_V},$$  \[1.4.5\]

$$Q_1 = \left[ C_{10} + C_{20} + C_{IN} + C_V + \frac{C_{10}(C_{20} + C_{IN} + C_V)}{C_{12}} \right] U_{IN}, \text{ and}$$  \[1.4.6\]

$$Q_2 = 0.$$  \[1.4.7\]

Or the equation (1.4.6) may be written in a general form,

$$Q_1 = k C' U_{IN},$$  \[1.4.8\]

where $k$ is correction factor obtained in process of calibration of a measuring system, and $C'$ is the resultant capacitance as given in equation (1.4.6). It is apparent that this charge measuring device shares the same characteristic with a Faraday pail.

A unique method for measuring the charge tendency of large particles by using a rotating cylinder, including the earlier works in the related area, has been described by Peterson (1954). Years later, Kittaka and his group (1976), at Science University of Tokyo, modified their charge measuring device based on the same principle, but concerning with the particles of low gravity. The major parts of their charge measuring system included a metal charging cylinder (in which the particles are charged frictionally), a source of compressed air, a modified Faraday cage, and a vacuum pump.