2.1 Thin films: introduction

Thin films have been used in the study of the relationship between the structure of solids and their physical properties. Thin films are formed by depositing material onto a clean supporting substrate to build up films thickness, rather than by thinning down bulk material. “Any solid or liquid object with one of its dimensions very much less than that of the other two is called thin films”. The mechanical properties of thin films are quite different from those of the bulk material. An electronic effect of thinness is observed in very thin dielectric films as an abrupt change in the conductance at constant field as the thickness is reduced below some finite dimension. With dielectric films thicker than about 100 Å, the field required to cause a given current to flow is generally independent of films thickness. Thinner films, however exhibit a large increase in current density due to “tunneling”. This is because the probability of an electron with a given energy penetrating the potential barrier presented by the dielectric increases exponentially with decreasing thickness. Thinness results also in a marked change in the conductivity of metallic films as films thickness becomes of the same order as, or smaller than the electron mean free path. When this occurs, scattering of electrons at the films surface becomes a significant factor and the effective conductivity is reduced. Observations of films resistivity as a function of thickness thus provides one means of estimating the electron mean free path. This method has been found different in practice, since films of a high degree of perfection are required. The resistivity of metal films may be separated into thermal motion and another caused by scattering at lattice imperfections. The imperfections in deposited metal films result in resistivities higher than those observed for bulk metals. The effect of temperature on the two modes of scattering is not same and this result in differences between the temperature coefficients of resistance of bulk metals and
those of polycrystalline metallic films. The magnitude of this difference may be used to infer the degree of imperfection in films [65-67].

The emerging technology needs various types of thin films for variety of applications because of their potential technical value and scientific curiosity in their properties such as; a) particle size b) particle shape c) size distribution d) particle composition, and e) degree of particle agglomeration. Many novel as well as traditional chemical routes of synthesis (bulk/thin films) allow materials to be in the nanocrystalline form. The required properties and versatility can be obtained by choosing proper method of thin films deposition. Thin films deposition methods can be broadly classified as either physical or chemical.

Under physical methods, we have vacuum evaporation and sputtering, where the deposition takes place after the material to be deposited has been transferred to a gaseous state either by evaporation or an impact process. Under chemical methods, we have the gas phase chemical processes such as conventional chemical vapor deposition (CVD), laser CVD, photo CVD, metal organo-chemical vapor deposition (MOCVD) and plasma enhanced CVD. Liquid phase chemical methods include electrodeposition, chemical bath deposition (CBD), modified chemical bath deposition (M-CBD), successive ionic layer adsorption and reaction (SILAR), spray pyrolysis, liquid phase epitaxy etc. The broad classification of liquid phase thin films deposition techniques is outlined in Chart 2.1
2.2 Theoretical background of chemical deposition methods

2.2.1 Dip coating method

Dip-coating method is found to be a relatively simple and reliable method for the fabrication of thick and thin films at room temperature with controllable thickness. In this method, the highly polished stainless steel substrates are dipped into the suspension of more dispersed solution containing the desired material and then dried immediately in dry air. The schematic of this method is as shown in Fig.2.1.

![Cycle repeat diagram](image.png)

**Fig 2.1 Deposition of MWNTs on stainless steel substrate.**

The thickness and size of the films can be controlled by the repetitive dipping of the substrates in the suspension solution. Films can be coated on large area, on both sides of the substrates, on any irregular surface, cylindrical substrates or spherical substrates by making use of Dip-coating technique. High quality superconducting, conducting, or insulating thin films, nanowires and nanoparticles can be coated by using these chemical methods with uniform surface and thickness. The hydrophobic and hydrophilic nature of substrate plays crucial role while coating the materials. In order to coat, surface passivation, activation and nuclear center formation are required in some cases.

2.2.2 Chemical bath deposition (CBD) method

The CBD method is presently attracting considerable attention as it does not require sophisticated instrumentation like vacuum system and other expensive equipment. Simple equipment like hot plate with magnetic stirrer is needed. The schematic of the method is shown in Fig.2.2.
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The theoretical background of chemical deposition methods, thin films characterization techniques and supercapacitance studies

2.2.2.1 Basics of CBD

(A) Concept of solubility and ionic product

Sparingly soluble salt \(AB\), when placed in water, a saturated solution containing \(A^+\) and \(B^-\) ions in contact with undissolved solid \(AB\) are obtained and equilibrium is established between the solid phase and ions in the solution as

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The starting chemicals are commonly available and cheap. With CBD method, a large number of substrates can be coated in a single run with a proper jig-jag design. Electrical conductivity of the substrate is not the necessary requirement. Any insoluble surface to which the solution has a free access will be a suitable substrate for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical bath deposition results in pin hole free and uniform deposits since the basic building blocks are ions instead of atoms. The preparative parameters are easily controllable and better orientations and improved grain structure can be obtained. A number of review articles discussing the status of CBD have been appeared in the literature [68, 69]. The details of CBD method, mechanism of films formation etc. have been greatly described in the review by Mane et al.[70].

2.2.2.1 Basics of CBD

(A) Concept of solubility and ionic product

Sparingly soluble salt \(AB\), when placed in water, a saturated solution containing \(A^+\) and \(B^-\) ions in contact with undissolved solid \(AB\) are obtained and equilibrium is established between the solid phase and ions in the solution as
\[ AB(S) = A^+ + B^- \]  

(2.1)

Applying law of mass action to this equilibrium,

\[ K = \frac{C_A^+ C_B^-}{C_{AB}(S)} \]  

(2.2)

where, \( C_A^+ \), \( C_B^- \) and \( C_{AB} \) are concentrations of \( A^+ \), \( B^- \) and \( AB \) in the solution, respectively. The concentration of a pure solid phase is a constant number i.e.

\[ C_{AB}(S) = \text{constant} = K' \]  

(2.3)

\[ K = \frac{C_A^+ C_B^-}{K'} \]

or

\[ KK' = C_A^+ C_B^- \]  

(2.4)

Since, \( K \) and \( K' \) are constant, the product \( KK' \) is also constant, say \( K_S \), therefore equation (2.4) becomes,

\[ K_S = C_A^+ C_B^- \]  

(2.5)

The constant \( K_S \) is called solubility product (SP) and \((C_A^+ C_B^-)\) is called as the ionic product (IP). When the solution is saturated, the ionic product is equal to the solubility product. But when IP exceeds the SP i.e. \( IP/SP = S > 1 \), the solution is supersaturated \((S = \text{degree of supersaturation})\), precipitation occurs and ions combine on the substrate and in the solution to form nuclei. Solubility product is affected by temperature, solvent and particle size [71-73].

\textbf{(B) Formation of precipitate in the solution}

The particle size of precipitate is determined to some extent by the experimental conditions, prevailing at the time of its formation. The temperature, rate of mixing of reagents, concentration of reagents and the solubility of precipitate are the variables affecting the particle size. All of these can be related to the relative supersaturation of a system. A state of supersaturation may be achieved by lowering the temperature of an unsaturated solution of the solute. For any precipitate, there is some minimum number of ions or molecules required to produce a stable second phase in contact with a solution is called as ‘nuclei’. The rate at which nuclei form in a solution, is dependent on the degree of supersaturation. The rate of nucleation increases exponentially in higher supersaturated solution.

\[ \text{Rate of nucleation} = K_0 (Q - S)X \]  

(2.6)
provided that $X > 1$, where $Q$ is the concentration of solute in solution and $K_o$ and $X$ are constants.

In the second step, growth of particles already present in the solution. This begins when nuclei or other seed particles are present. In the case of ionic solid, the process involves deposition of cations and anions on appropriate sites \[ (AB)_n + A^+ + B^- \rightarrow (AB)_{n+1} \] \[ (AB)_{n+1} + A^+ + B^- \rightarrow (AB)_{n+2} \]

where, $n$ is the number of $A^+$ and $B^-$ required for giving stable phase $(AB)_n$. The rate of growth is directly proportional to the supersaturation \[ \text{Rate of growth} = K_o' a (Q - S) \]

where, $a$ is the surface area of the exposed solid and $K_o'$ is the constant which is a characteristic of the particular precipitate. If the supersaturation is maintained at low level throughout the precipitation, relatively few nuclei formed will grow to give a small number of large particles. With high supersaturation, many more nuclei are formed initially and nucleation may occur throughout the precipitation process. As a result, there is large number of centers upon which growth process can take place, none of the particles grow very large and a colloidal suspension is formed. The colloidal suspension consists of finely divided solid particles in a liquid phase with diameter of 0.01 to 0.1 micron. Under some circumstances, colloidal particles can come together and adhere to one another and the resulting solid is called colloidal precipitate. This process of formation is called agglomeration. Colloidal particles when agglomerated are quite different from a crystalline solid, since the particles are arranged irregularly.

### 2.2.2.2 Effect of preparative parameters

The rate of deposition and terminal thickness depend upon the number of nucleation centers, supersaturation of the solution (defined by ratio of IP/SP) and rate of stirring. The growth kinetics depends on the concentration of ions, their velocities and nucleation and growth processes on immersed substrates. The effect of various deposition conditions on these parameters are discussed below \[75\]:

- **pH:**

  The reaction rate as well as rate of deposition depends on the supersaturation condition: the lower the supersaturation, the slower the formation of MX (where $M$ and $X$ is the number of metals and chalcogenides ions, respectively). If the concentration of $OH^-$ ion in the solution is higher, the $M$ ion concentration will lower
and the reaction rate will be slow. With an increase in pH as the M ion concentration decreases, the rate of formation decreases. At a certain pH, the concentration of M ion decreases to a level such that the ionic product of M and X becomes less than the solubility of MX and a film will not be formed.

- **Complexing Agent:**
  The rate of release of metal ion concentration decreases with increase in concentration of complexing agent. Consequently, the rate of reaction and hence precipitation is reduced leading to larger terminal thickness of the films.

- **Temperature:**
  The dissociation of complex and the anion of the compound (X compound) depend on the temperature. At the higher temperatures, the dissociation is greater and gives higher concentrations of M and X ions that result in higher rates of deposition.

  The thickness increases or decreases with increase in the bath temperature depending on the condition under which films are prepared. At low pH values, supersaturation is high even at low temperature and increase further with increasing in temperature. This results in formation of precipitation and consequently lower thickness is obtained. At high pH values, precipitation is limited due to the low supersaturation and most of the product is formed on the substrate surface. Further, the thermal dissociation of the complex and anion compound is increased at higher temperature so that more M and X are available for MX formation and thus higher thickness is obtained.

- **Substrate:**
  Films formation takes place only under certain conditions i.e. either under optimum conditions for MX formation or when the substrate has special properties facilitating for the formation of single crystal films. The second condition favors the formation because when the lattice of the deposited material matches well with that of the substrate, the free energy change is smaller, thereby facilitating nucleation.

- **Doping:**
  Doping in the starting material can be incorporated into the films only if the impurities form insoluble oxides under the same condition of the deposition and provided that corresponding ionic product is greater than solubility product. The doping affects films thickness and properties.
2.2.3 Successive ionic layer adsorption and reaction (SILAR) method

In the CBD method, the films formation on substrate takes place when ionic product exceeds solubility product. However, this results into precipitate formation in the bulk of solution, which cannot be eliminated. In order to avoid such unnecessary bulk precipitation and hence the loss of material, CBD is modified and known as successive ionic layer adsorption and reaction (SILAR) method shown schematically as in Fig.2.3.

![Schematic diagram of successive ionic layer adsorption and reaction](image)

**Fig.2.3** Schematic diagram of successive ionic layer adsorption and reaction

In this modification, thin films are obtained by immersing the substrate into separately placed cationic and anionic precursors and rinsing between every immersion with ion-exchanged water. The SILAR method is mainly based on the adsorption and reaction of the ions from the solutions and rinsing between every immersion with double distilled water to avoid homogeneous precipitation in the solution. The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. The term adsorption can be defined as the interfacial layer between two phases of a system. Adsorption may be expected when two heterogeneous phases are brought in contact with each other. Hence, gas-solid, liquid-solid and gas-liquid are three possible adsorption systems. In SILAR method, we are concerned with adsorption in liquid-solid system. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attractive force between ions in the solution.
and surface of the substrate. These forces may be cohesive or Van-der Waals. Atoms or molecules of substrate surface are not surrounded by atoms or molecules of their kinds on all sides. Therefore, they possess unbalanced or residual force and hold the substrate particles. Thus, adsorbed atoms (ad-atoms) can be holding on the surface of the substrate. The factors like temperature of solution, pressure, nature of the substrate, concentration of the solution, area of the substrate etc. affect the adsorption process. The reaction of newly adsorbed anions with pre-adsorbed cations forms thin films of the desired material [74, 77].

2.2.3.1 Basics of SILAR:

The SILAR method is capable of forming thin nanocrystalline compact as well as porous layer of zinc oxide on glass substrate, without the requirement of controlling atmosphere. Similar to CBD method, SILAR method has the following advantages:

1. The thickness and morphology of the films can be easily controlled by preparative parameters.
2. Relatively uniform films can be obtained on substrates of complex shape.
3. The equipment needed is not expensive and does not require sophisticated instrumentation and vacuum.
4. SILAR method has usually low operating temperature. Apart from the obvious advantages in terms of energy saving, the low deposition temperature avoids high temperature effects such as inter diffusion, contamination and dopant redistribution. Even with above advantageous points, SILAR has interesting feature and additional advantage over CBD method is that, SILAR method saves material cost due to non-formation of precipitate in solution. SILAR method can be used for deposition from aqueous or non-aqueous baths and it can be employed as one of the steps in the preparation of semiconductors or oxides.

SILAR growth consists of at least four different steps. 1. Adsorption, 2. Rinsing (I), 3. Reaction and 4. Rinsing (II).

- Adsorption:

In this step, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. This layer is composed of two layers: first, the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative forms the counter ions of the cations.
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- **Rinsing (I):**
  
  In this step, excess unadsorbed ions $pK^{a+}$ and $aX^p$ are rinsed away from the diffusion layer. This results into saturated electrical double layer.

- **Reaction:**
  
  In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of the material $K_pA_a$ a solid substance is formed on the interface. This process involves the reaction of $pK^{a+}$ surface species with the anionic precursor $A^p$.

- **Rinsing (II):**
  
  In last step, the excess and unreacted species $A^p$, $X$, $Y$, and the reaction byproduct from the diffusion layer are removed. By repeating above cycles, a thin layer of material $K_pA_a$ can be grown.

  Following the above-mentioned steps, the maximum increase in films thickness per one reaction cycle is theoretically one monolayer. This results into a solid layer of the compound $K_pA_a$. Dividing the measured overall films thickness, nominal films thickness by number of reaction cycles growth rate can be estimated. This gives a numerical value for growth rate under the given conditions. If the measured growth rate exceeds the lattice constant of the material, a homogeneous precipitation in the solution could have taken place. In practice the thickness increase is typically less than or greater than a monolayer. Thus, the process involves an alternate immersion of the substrate in a solution containing a soluble salt of the cation of the compound to be grown. The substrate supporting the growing films is rinsed in highly purified double distilled water after each immersion.

  The factors affecting the growth phenomena are the purity of the precursor solutions, their pH values, concentrations, counter ions, individual rinsing and dipping times. In addition, complexing agent and pretreatment of the substrate have been shown to affect the SILAR growth.

2.3 Thin films characterization techniques

Before using the films in application, one has to characterize the films to achieve optimum performance of the films prepared [78]. It is an important step in the development of alien materials. The complete characterization of any material consists of phase analysis, compositional analysis, structural identification, micro-structural analysis and surface characterization which have strong bearing on the
properties of materials. This has led to the emergence of variety of advanced techniques in the field of materials science. In this section, different analytical instrumental techniques used for thin films characterization are described with relevant principles of their operation and working.

2.3.1. Thickness measurement

The thickness of films is the most significant parameter that affects the properties of the thin films.

Thickness by gravimetric method

One of the most convenient and reliable method for determining films thickness is gravimetric method. In this method, area and weight of the films are measured. The thickness is obtained by using the formula [14]

\[ t = \frac{M}{A} \]  

\[ M = m_1 - m_2 \]  

where, \( t \) is films thickness, \( M \) is mass of the films material, \( A \) is area of the films, \( m_1 \) is mass of the substrate with films, \( m_2 \) is mass of the substrate without films. In order to get more accurate results, one should measure thickness by using the films with maximum area, so that weight difference is accurately measurable. In case of porous thin films, the density of deposited material will not be well defined so thickness of thin films can be calculated in terms of deposited mass per unit area of the material only so the equation (2.10) becomes.

\[ t = \frac{M}{A} \]  

2.3.2 X-ray diffraction technique

X-ray diffraction is a very powerful and suitable technique for characterizing the phase identification and microstructure of thin films. The schematic of this technique is as shown in Fig. 2.4. It is non-destructive, non-contact and provides useful information, such as presence and composition of phases, films thickness, grain size, orientation and strain state [79, 80]. In general, diffraction of X-rays occurs only when the wavelength of the wave motion is of the same order of magnitude as the repeat distance between scattering centers. This condition of diffraction is nothing but Bragg’s law [81] and is given as

\[ 2d \sin \theta = n\lambda \]
Where, \( d \) = interplaner spacing, \( \theta \) = diffraction angle, \( \lambda \) = wavelength of X-ray, 
\( n \) = order of diffraction.

**Fig. 2.4 Schematics of X-ray Diffractometer**

In crystalline solids, atoms are arranged in regular and three dimensional geometric patterns. A smallest group of atoms which is building block of the crystal is called as unit cell. The interplaner spacing of the atomic planes is comparable to the wavelength of X-rays (0.5 to 2.5 Å). Hence, crystals are the best diffraction grating to study diffraction of X-rays. The directions of diffracted X-rays give information about the atomic arrangements and hence the crystal structure and phase formation can be confirmed by X-ray diffraction studies. The way of satisfying Bragg’s condition is devised and this can be done by continuously varying either \( \lambda \) or \( \theta \) during the experiment.

According to Bragg’s law for the particular \( d \) value, the constructive interference of X-rays should occur only at particular \( \theta \) value i.e. Bragg’s angle and for all other angles there should be destructive interference and intensity of diffracted beam will be minimum. However, if the size of the diffracting tiny crystal is small, there is no more complete destructive interference at \( \theta \pm d \theta \), which broadens the peak corresponding to diffracted beam in proportion to the size of the tiny crystal. This can be used to calculate the particle size. The relation for the same is given by Debye Scherrer formula [82] and formulated as:

\[
t = \left( \frac{0.9\lambda}{\beta \cos \theta_B} \right)
\]  

(2.14)
where, \( t \) = crystallite size, \( \theta_B \) = diffraction angle, \( \lambda \) = wavelength of X-rays and \( \beta \) line broadening at full width at half maxima (FWHM).

### 2.3.3 FTIR spectroscopy

Studies of the spontaneous orientation of dipole moment in semiconductors are carried out with a non-destructive tool of analysis by infrared spectroscopy which can give information on atomic arrangement and inter atomic forces in the crystal lattice itself. It is possible to investigate how the infrared vibrational frequencies and thus the inter-atomic forces are affected by the onset of the semiconductor states. If the two energy levels \( E_1 \) and \( E_2 \) are placed in an electromagnetic field and the difference in the energy between the two states is equal to a constant \( h \) multiplied by the frequency \( \nu \) of the incident radiation, a transfer of energy between the molecules can occur, giving therefore

\[
\Delta E = h\nu \tag{2.15}
\]

where, the symbols have their usual meanings. When the \( \Delta E \) is positive the molecule absorbs energy; when \( \Delta E \) is negative, radiation is emitted during the energy transfer and emission spectra are obtained. When the energies are such that the equation (2.15) is satisfied, a spectrum unique to the molecule under investigation is obtained. Fig. 2.5 shows the schematic representation of FTIR. The spectrum is usually represented as a plot of the intensity Vs the frequencies and peaks occur when the condition

---

**Fig. 2.5 Schematic of typical FTIR spectrometer**

(equation 2.15) is satisfied. Frequency ranges that can be encountered in this spectrum
vary from those of Gamma rays, which have wavelength of about $10^{10}$ cm to radio waves which have wavelength of $10^{10}$ cm.

The most of spectroscopic investigation are carried out in a relatively small portion of spectrum close to visible light. This region includes UV, visible and IR regions and is arbitrarily defined as being between wavelength of $10^{-6}$ cm and $10^{-3}$ cm. Both the atoms and molecules give rise to spectra but they differ from each other. The difference between the atomic and molecular spectra lies in the nature of energy levels involved in the transitions. In the atom, the absorption represents transition between the different allowed levels for the orbital electrons. In case of molecules, however, the atoms within the molecules vibrate and the molecule as a whole rotates and the total energy contributions are represented by the equation [83-85].

$$E_{tot} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$$  \hspace{1cm} (2.16)

where, $E_{elec}$ is the electronic energy, $E_{vib}$ is the vibrational energy, $E_{rot}$ is the rotational energy and $E_{trans}$ is the translation energy. The separate energy levels are quantized and only certain transitions of electronic, vibrational and rotational energy are possible. Translational energy is usually sufficiently small to be ignored. The vibrational spectrum of a molecule is considered to be a unique physical property and is a characteristic of the molecule. As such, the infrared spectrum can be used as a fingerprint for identification, in support of X-ray diffraction technique for the purpose of characterization.

2.3.4 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces. The SEM uses electrons for imaging, such as a light microscope uses visible light. The advantages of SEM over light microscopy include much higher magnification (>100000 X) and greater depth of field up to 100 times than that of light microscopy [86]. The SEM generates a beam of incident electrons in an electron column above the sample chamber. The electrons are produced by a thermal emission source, such as a heated tungsten filament, or by a field emission cathode. The energy of the incident electrons can be as low as 100 eV or as high as 30 KeV depending on the evaluation objectives.

The electrons are focused into a small beam by a series of electromagnetic lenses in the SEM column. Scanning coils near the end of the column direct and position the focused beam onto the sample surface. The electron beam is scanned in a raster pattern over the surface for imaging. The beam can also be focused at a single
point or scanned along a line for X-ray analysis. The beam can be focused to a final probe diameter as small as about 10 Å. The incident electrons cause electrons to be emitted from the sample due to elastic and inelastic scattering events within the sample’s surface and near surface material. High-energy electrons that are ejected by an elastic collision of an incident electron, typically with a sample atom’s nucleus, are referred to as back scattered electrons. The energy of backscattered electrons will be comparable to that of the incident electrons.

The lower-energy emitted electrons resulting from inelastic scattering are called secondary electrons. The energy of secondary electrons is typically 50eV or less. To create an SEM image, the incident electron beam is scanned in a raster pattern across the sample's surface. The emitted electrons are detected for each position in the scanned area by an electron detector. The intensity of the emitted electron signal is displayed as brightness on a cathode ray tube (CRT). By synchronizing the CRT scan to that of the scan of the incident electron beam, the CRT display represents the morphology of the sample surface area scanned by the beam. The schematic of SEM is as shown in Fig. 2.6 as follows:

Fig.2.6 Schematic diagram of (a) collision between electron and sample surface produces secondary electrons, backscattered electrons, X-rays, cathode luminescence, auger electrons (b) Crust produces higher and trough produces lower number of
2.3.5 Study of transmission electron microscopy (TEM)

Microstructural characterization has become very important for all types of materials in recent times. Microstructural information is required for structure property correlation and for carrying out basic and applied research in materials. TEM is a tool which can provide the above-mentioned information at nano-level [87]. It comprises an electron gun, a vacuum system, electromagnetic lenses, high voltage generator, recording devices and associated electronics. All TEMs need a source of electrons in order to illuminate the specimen. The microscope column is maintained at very high levels of vacuum to prevent the scattering of the electrons by the atmosphere inside the microscope. The electrons are focused by set of electromagnetic lenses on to specimen, which has been made electron transparent by special specimen preparation techniques. The special preparation techniques involve thinning the specimen either by electrochemical dissolution or by bombardment with ions. The typically specimen thickness is in the range of 50 to 100 nm for it to be electron transparent. The set of lenses used for the focusing the beams on to the specimen are not the image forming lenses. These lenses are for illuminating the specimen from one side. A set of lenses are used instead of one lenses to provide a variety of illuminating conditions like parallel beam illumination, nano-beam illumination and convergent beam illumination. This allows a better control on the size of the beam. The first image-forming lens is the objective lens. The image formed by the objective lens acts as an object for the next lens and so on. Typically, a modern day TEM has about five to six image forming lenses. The final image is projected on the screen.

2.4 Introduction and backgrounds of supercapacitor

In response to the changing global landscape, energy has become a primary focus of the major world powers and scientific community. There has been great interest in developing and refining more efficient energy storage devices. One such device, the supercapacitor has matured significantly over the last decade and emerged with the potential to facilitate major advances in energy storage. Supercapacitors, also known as ultracapacitors or electrochemical capacitors, utilize high surface area electrode materials and thin electrolytic dielectrics to achieve capacitances several orders of magnitude larger than conventional capacitors [88-91]. In doing so,
supercapacitors are able to attain greater energy densities while still maintaining the characteristic high power density of conventional capacitors.

The first electrochemical capacitor device was disclosed in a General Electric Co. patented in 1957 to Becker but was of a crude nature, employing porous carbon. In 1969, Sohio described a so-called "electrokinetic capacitor" utilizing porous carbon in a non-aqueous electrolyte which enabled it to be charged up to about 3V, though the operation of the device was not "electrokinetic" in nature [92]. In 1971, Trasatti and Buzzanca [93] recognized that the electrochemical charging behaviour of ruthenium dioxide films was like that of capacitors. Between 1975 and 1980, the present author and his co-workers from Continental Group Inc., carried out extensive fundamental and development work on the ruthenium oxide type of electrochemical capacitor which behaves as a surface-redox pseudo capacitance [94].

2.4.1 Theoretical background of supercapacitor

We know that, conventional capacitors consist of two conducting electrodes separated by an insulating dielectric material. When a voltage is applied to a capacitor, opposite charges accumulate on the surfaces of each electrode. The charges are kept separate by the dielectric, thus producing an electric field that allows the capacitor to store energy. Capacitance ‘C’ is defined as the ratio of stored (positive) charge $Q$ to the applied voltage $V$:

$$ C = \frac{Q}{V} \quad (2.17) $$

For a conventional capacitor, $C$ is directly proportional to the surface area $A$ of each electrode and inversely proportional to the distance $d$ between the electrodes:

$$ C = \frac{\varepsilon_0\varepsilon_r A}{d} \quad (2.18) $$

The product of the first two factors on the right hand side of the last equation is a constant of proportionality where $\varepsilon_0$ is the dielectric constant (or permittivity) of free space and $\varepsilon_r$ is the dielectric constant of the insulating material between the electrodes. The two primary attributes of a capacitor are its energy density and power density. For either measure, the density can be calculated as a quantity per unit mass or per unit volume. The energy $E$ stored in a capacitor is directly proportional to its capacitance:

$$ E = \frac{1}{2}CV^2 \quad (2.19) $$
In general, the power $P$ is the energy expended per unit time. To determine power for a capacitor, though, one must consider that capacitors are generally represented as a circuit in series with an external “load” resistance $R$, as is shown in Fig. 2.7.

The internal components of the capacitor (e.g., current collectors, electrodes, and dielectric material) also contribute to the resistance, which is measured in aggregate by a quantity known as the ‘equivalent series resistance’ (ESR). The voltage during discharge is determined by these resistances. When measured at matched impedance ($R = ESR$), the maximum power $P_{\text{max}}$ for a capacitor [91, 92] is given by:

$$P_{\text{max}} = \frac{V^2}{4 \times ESR}$$ (2.20)

This relationship shows how the ESR can limit the maximum power of a capacitor. Conventional capacitors have relatively high power densities but relatively low energy densities when compared to electrochemical batteries and fuel cells.

That is, a battery can store more total energy than a capacitor, but it cannot deliver it very quickly, which means its power density is low. Capacitors, on the other hand, store relatively less energy per unit mass or volume, but what electrical energy they do store can be discharged rapidly to produce a lot of power, so their power density is usually high. Supercapacitors are governed by the same basic principles as conventional capacitors. However, supercapacitors incorporate electrodes with much higher surface areas $A$ and much thinner dielectrics that decrease the distance between the electrodes. Thus, Eq. 2.20 leads to an increase in both capacitance and energy. Furthermore, by maintaining the low ESR characteristic of conventional capacitors, supercapacitors are also able to achieve comparable power densities [92].
2.4.2 Classification of supercapacitors

Based on the current research trends, supercapacitors can be divided into three general classes: electrochemical double-layer capacitors, pseudocapacitors, and hybrid capacitors. Each class is characterized by its unique mechanism for storing charge. These are non-Faradaic, Faradaic, and a combination of the two. Faradaic processes, such as oxidation-reduction reactions, involve the transfer of charge between electrode and electrolyte. A non-Faradaic mechanism, by contrast, does not use a chemical mechanism, rather charges are distributed on surfaces by physical processes that do not involve the making or breaking of chemical bonds. A graphical classification of the different classes and subclasses of supercapacitors is presented in Chart 2.2.

Chart 2.2 Graphical classification of the different classes and subclasses of supercapacitors

Although capacitance is directly proportional to surface area, empirical evidence suggests that, for activated carbons, not all of the high surface area contributes to the capacitance of the device [95-98]. This discrepancy is believed to be caused by electrolyte ions that are too large to diffuse into smaller micropores, thus preventing some pores from contributing to charge storage [99-100]. Research also suggests an empirical relationship between the distribution of pore sizes, the energy density, and the power density of the device. Larger pore sizes correlate with higher...
power densities and smaller pore sizes correlate with higher energy densities. As a result, the pore size distribution of activated carbon electrodes is a major area of research in EDLC design [101]. In particular, the optimal pore size for a given ion size and upon improving the methods used to control the pore size distribution during fabrication.

2.4.3 Electrochemical double-layer capacitors

Electrical double layer results from strong interactions between the ions/molecules in the solution and the electrode surface. At a metal-solution interface, there is a thin layer of charge on the metal surface, which results from an excess or deficiency of the electrons. On the other hand, in the vicinity of the electrode surface, there is an opposite charge in solutions due to an excess of either cations or anions. Thus, the electrical double layer is made of whole array of charged species and oriented dipoles existing at the metal-solution interface [102].

The electric double layer capacitance is generally a function of potential, which is different from a standard capacitor. Several models, such as Helmholtz model [103], Gouy-Chapman model [104], and Stern model [105] have been proposed to explain the behaviour observed for electrodes under potentiostatic control in solution. The electric double layer can be characterized by several layers [102] as shown in the Fig.2.8. The inner layer closest to the electrode, also called compact, Helmholtz or Stern layer, consists of solvent molecules and sometimes other specifically absorb ions or molecules. The inner layer can be divided into inner Helmholtz plane (IHP) and outer Helmholtz plane (OHP). The IHP is (Fig.2.8.c), where the electrical centers of the specifically adsorbed ions are located, while the OHP is which represents the closest distance that the solvated ions can approach metal or starting point of a diffused layer.

These solvated ions are non-specifically adsorbed since the interaction between solvated ions and charged metals involves. Due to thermal agitation, the nonspecifically adsorbed ions are distributed from the OHP into the bulk of the solution and form a three dimensional diffused layer, whose thickness is determined by the total ionic concentration in the solution. In the double layer, the total charge density on the solution is made from specifically adsorbed ions in the inner layer, and a total excess charge density in a diffused layer [88]. Hence, the capacitance of the double layer \( (C_{dl}) \) includes Helmholtz type compact double layer capacitance \( (C_H) \) and
diffused region of the double layer capacitance \( (C_{diff}) \), and a total layer capacitance is given by equation [88]:

Utilization of the capacitance of the double-layer at electrode interfaces for electrical energy storage is the basis of so-called 'double-layer capacitors' (DLC) or supercapacitors, developed first (in principle) by Becker [106] and by Crooke et al [107] using high-area carbon powder materials and tetraalkyl ammonium salt as an electrolyte.

\[
\frac{1}{C_{dl}} = \frac{1}{C_H} + \frac{1}{C_{diff}}
\]  

(2.21)

A double-layer capacitor (DLC) consists of two porous polarizable electrodes. The energy-saving process in DLC is realized by means of the division of the charge on two electrodes with a sufficiently large potential difference between them. The electric charge of a DLC is determined by the EDL capacitance. The electrochemical process in DLC may be represented as equation [108]

On the positive electrode:

\[ E_{S_1} + A^- \leftrightarrow E_{S_1}^+ // A^- + e \]  

(2.22)

On the negative electrode:

\[ E_{S_2} + K^+ + e^- \leftrightarrow E_{S_2}^- // K^+ \]  

(2.23)

And the overall reaction

Fig.2.8 Models of the electric double layer at the positive charged surface
(a) Helmholtz model (b) Gouy-Chapman model (c) Stern model

Theoretical background of chemical deposition methods, thin films characterization techniques and supercapacitance studies
where, ‘$E_{S1}$‘ and ‘$E_{S2}$‘ represents the electrode surface; ‘///’ is EDL where the charge is stored on its either side; $K^+$ and $A^-$ are cations and anions of electrolyte, respectively. During a charging process, the electrons are transferred from the positive electrode to the negative electrode through an external current source. Ions from the volume of electrolyte move towards electrodes. During a discharging process, the electrons shift from the negative electrode to the positive electrode through a load and ions return from surface into the volume of electrolyte. During both a charging process and a discharging process, the charge density at interface and the electrolyte concentration remains constant. In other words, no charge transfer takes place across the interface and the current observed during this process is a displacement current due to the rearrangement of charges (conventionally described as an ideally polarized electrode). Therefore, this process is non-faradaic in nature [109]. Energy is stored in the double-layer capacitor as charge separation in the double-layer formed at the interface between the solid electrode material surface and the liquid electrolyte in the micropores of the electrodes [110]. In the past years, major works have been focused on the application of activated carbons as the electrode material for double-layer capacitors because of their accessibility, an easy process ability and relatively lower cost.

2.4.4 Pseudocapacitors

The pseudocapacitors store electric charge at the expense of a faradaic pseudocapacitance of sufficiently reversible redox reactions and the EDL capacitance. Pseudocapacitance arises at electrode surface where a completely different charge storage mechanism applies. It is faradaic in origin, involving the passage of charge across the double layer, as in battery charging or discharging, but capacitance arises on account of the special relation that can originate for thermodynamic reasons between the extent of charge acceptance ($\Delta q$) and charge of potential ($\Delta E$), so that a derivative $d(\Delta q)/d(\Delta E)$ or $dq/dE$, which is equivalent to the capacitance. The capacitance exhibited by such systems is referred to as pseudo-capacitance since it originates in a quite different way from that corresponding to classical electrostatic capacitance of the type exhibited mainly by double layer capacitors.

For devices that utilize pseudo-capacitance, most of the charge is transferred at the surface or in the bulk near the surface of the solid electrode material. In this case, the interaction between the solid material and the electrolyte involves faradaic
reactions, which in most cases can be described as charge transfer reactions. The charge transferred in these reactions is voltage-dependent resulting in the pseudo-capacitance \( C = dQ/dV \) also being voltage-dependent. Three types of electrochemical processes have been utilized in the development of ultracapacitors using pseudo-capacitance. These are surface adsorption of ions from the electrolyte, redox reactions involving ions from the electrolyte, the doping and undoping of active conducting polymer material in the electrode. The first two processes are primarily surface reactions and are highly dependent on the surface area of the electrode material. The third process involving the conducting polymer material is more of a bulk process. The specific capacitance of the material is much less dependent on its surface area although relatively high surface area with micropores is required to distribute the ions from the electrodes in a cell. In all cases, the electrodes must have high electronic conductivity to distribute and collect the electron current. An understanding of the charge transfer mechanism can be inferred from \((CV)\), which is often determined by using cyclic voltammetry.

For assessing the characteristics of devices, it is convenient to use the average capacitance \( C \),

\[
C = \frac{Q_{tot}}{V_{tot}}
\]  

(2.25)

where, the \( Q_{tot} \) and \( V_{tot} \) are the total charge and voltage change for a charge or discharge of the electrode. This permits a determination of the average specific capacitance of the material for the electrolyte of interest. The specific capacitance of pseudo-capacitance materials is much higher than that of carbon materials. It is thus expected that the energy density of devices developed by using the pseudo-capacitance materials would be higher.

2.4.5 Hybrid capacitors

Hybrid capacitors attempt to exploit the relative advantages and mitigate the relative disadvantages of EDLCs and pseudocapacitors to realize better performance characteristics. Utilizing both Faradaic and non-Faradaic processes to store charge, hybrid capacitors have achieved energy and power densities greater than EDLCs without sacrifices in the cycling stability and affordability which limited the success of pseudocapacitors. Research has been focused on three different types of hybrid capacitors, distinguished by their electrode configuration: composite, asymmetric and battery type.
a) Composite:

Composite electrodes integrate carbon-based materials with either conducting polymer or metal oxide materials and incorporate physical and chemical charge storage mechanisms together in a single electrode. The carbon-based materials facilitate a capacitive double-layer of charge also provide high-surface-area backbone that increases the contact between the deposited pseudocapacitive materials and electrolyte. The pseudocapacitive materials are able to further increase the capacitance of the composite electrode through Faradaic reactions [111,112]. Composite electrodes constructed from carbon nanotubes and polypyrrole, a conducting polymer have been particularly successful. Several experiments have demonstrated that this electrode is able to achieve higher capacitances than either a pure carbon nanotube or pure polypyrrole polymer-based electrode. This is attributed to the accessibility of the entangled mat structure, which allows a uniform coating of polypyrrole and a three-dimensional distribution of charge. Moreover, the structural integrity of the entangled mat has been shown to limit the mechanical stress caused by the insertion and removal of ions in the deposited polypyrrole. Therefore, unlike conducting polymers, these composites have been able to achieve a cycling stability comparable to that of EDLCs [113].

b) Asymmetric:

Asymmetric hybrids combine Faradaic and non-Faradaic processes by coupling an EDLC electrode with a pseudocapacitors electrode. In particular, the coupling of a negative activated carbon electrode with a positive conducting polymer electrode has received a great deal of attention. The lack of an efficient negatively charged conducting polymer material has limited the success of conducting polymer pseudocapacitors. The implementation of a negatively charged, activated carbon electrode attempts to circumvent this problem. While conducting polymer electrodes generally have higher capacitances and lower resistances than activated carbon electrodes, they also have lower maximum voltages and less cycling stability. Asymmetric hybrid capacitors that couple these two electrodes mitigate the extent of this trade off to achieve higher energy and power densities than comparable EDLCs. Also, they have better cycling stability than comparable pseudocapacitors [114-116].

c) Battery type:

Like asymmetric hybrids, battery-type hybrids couple two different electrodes; however, battery-type hybrids are unique in coupling a supercapacitor electrode with
a battery electrode. This specialized configuration reflects the demand for higher energy supercapacitors and higher power batteries, combining the energy characteristics of batteries with the power, cycle life, and recharging times of supercapacitors. Research has focused primarily on using nickel hydroxide, lead dioxide, and LTO (Li$_4$Ti$_5$O$_{12}$) as one electrode with activated carbon as the other [117, 118]. Although, there is less experimental data on battery-type hybrids than on other types of supercapacitors, the available data suggests that these hybrids may be able to bridge the gap between supercapacitor and batteries. Despite the promising results, the general consensus is that more research will be necessary to determine the full potential of battery-type hybrids [119, 120].

2.5 Supercapacitor characterization through electrochemistry

![Fig. 2.9 Schematic representation of an EDLC](image)

As shown in the Fig 2.9, besides the two electrodes, the electrolyte, which resides inside the separator as well as inside the active material layers, is one of the most important electrochemical supercapacitor (ES) components. The requirements for an electrolyte in ES include: wide voltage window, high electrochemical stability, high ionic concentration and low solvated ionic radius, low resistivity, low viscosity, low toxicity, low cost and availability at high purity. The electrolyte used in an ES can be classified into 3 types:

1. Aqueous Electrolytes
2. Organic Electrolytes
Chapter 2

3. Ionic Liquids

a) Aqueous Electrolytes:

Compare with organic electrolytes, aqueous electrolytes (such as H$_2$SO$_4$, KOH, Na$_2$SO$_4$ and NH$_4$Cl aqueous solution and so on) can provide higher ionic concentration and lower resistance. ES containing aqueous electrolyte may display higher capacitance and higher power than those with organic electrolytes, probably due to higher ionic concentration and smaller ionic radius. Unfortunately, a large disadvantage of aqueous electrolyte is there small voltage window as low as about 1.2V, much lower than those of organic electrolytes.

b) Organic Electrolytes:

Compared to aqueous electrolytes, organic electrolytes can provide a voltage window as high as 3.5 V. This is a large advantage of organic aqueous electrolytes. Among organic electrolytes, acetonitrile and propylene carbonate are the most commonly used solvents.

c) Ionic Liquids:

A salt may be melted, namely, ‘liquefied’, by providing heat to the system to counter balance the salt lattice energy. Such a system is called molten salts or ionic liquids. Ionic liquids can exist in liquid form at desired temperatures. Their desirable properties such as low vapor pressure, high thermal and chemical stability, low flammability, wide electrochemical stability window make them promising candidate for ES electrolytes. The main ionic liquids studied are imidazolium and pyrrolidinium.

2.5.1 Cyclic voltammetry

Cyclic voltammetry is a method for investigating the electrochemical behaviour of a system. It was first reported in 1938 and described theoretically by Randles [121]. In this technique, current flowing between the electrode (whose potential is monitored with respect to a reference electrode) and a counter electrode is measured under the control of a potentiostat. The cyclic voltammogram determines the potentials at which different electrochemical processes occur. The working electrode is subjected to a triangular potential sweep, whereby the potential rises from an initial value $E_i$ to a final value $E_f$ then returns back to the start potential at a constant potential sweep rate. The sweep rate applied can vary from a few millivolts per second to a hundred volts per second. The current measured during this process is often normalized to the electrode surface area and referred to as the current density.
The current density is then plotted against the applied potential, and the result is referred to as a cyclic voltammogram. A peak in the measured current is seen at a potential that is characteristic of any electrode reaction taking place. The peak width and height for a particular process may depend on the sweep rate, electrolyte concentration and the electrode material [122].

Cyclic voltammetry makes possible the elucidation of the kinetics of electrochemical reactions taking place at electrode surfaces. In a typical voltammogram, there can be several peaks. From the sweep-rate dependence of the peak amplitudes, widths and potentials of the peaks observed in the voltammogram, it is possible to investigate the role of adsorption, diffusion, and coupled homogeneous chemical reaction mechanisms [123]. The reaction taking place between the electrode surface and species within the solution can proceed through two different processes, which are either Faradaic or non-Faradaic [88, 124]. Faradaic processes are non-adsorptive processes arising from electron transfer across the metal/electrolyte interface. The resulting redox reaction of solution species that takes place is controlled by Faraday’s laws, i.e., the amount of electricity passed (charge) is proportional to the number of moles of reactant converted. Electrode surfaces where Faradaic processes take place are classified as charge transfer electrodes, since the extent of reaction depends on the measured charge passing through the electrode surface. When the electron transfer rate in both the forward and reverse directions at the electrode is high, the reduction is described as reversible, and the cathodic and anodic peaks are separated by a potential.

The standard cell configuration consists of three electrodes immersed in the electrolyte: the working electrode (WE), counter electrode (CE), and reference electrode (RE). The potential at the WE is monitored and controlled precisely with respect to RE. While the current flowing between the working electrode and counter electrode is measured and the resulting I/V trace is then plotted out as current (I) vs. potential (V). A CV curve generally has a rectangular shape when the capacitance merely originates from the electric double layer and there are no Faradaic reactions between the active materials and the electrolyte. The specific capacitance is estimated from the current at the middle point of potential range (I) and scan rate (\( v \)) according to the equation:

\[
C = \frac{I}{m v}
\]  

(2.26)
where v is scan rate, I is the peak current and m is the mass of active material. With respect to pseudocapacitor, the pseudocapacitive behaviour usually leads to the presence of redox peaks with a deviation from the rectangle shape. Thus, the average specific capacitance is calculated using the voltammetric charge integrated from the CV curve according to the following equation:

\[ C_{f/g} = \frac{q}{2mv} = \frac{1}{2mVv} \int_{v_b}^{v_a} I(v)dv \]  

(2.27)

where q is the total charge obtained by the integration of positive and negative scans in a CV curve, m is the mass of the active material in two electrodes, v the scan rate, and \((V = V_a - V_b)\) represents the potential window.

In present thesis, CV technique is used qualitatively to investigate the potential window and electrochemical processes of the system. Ag/AgCl reference electrode is used in all the three-electrode tests. Further, quantitative analyses are carried out with CV technique to estimate the capacitance of the system. Finally, CV is employed to examine the stability of the systems within the potential window by cyclic tests.

### 2.5.2 Galvanostatic charge-discharge techniques

Different from cyclic voltammetry, galvanostatic charge-discharge techniques records the potential response of a controlled current excitation. Galvanostatic charge-discharge techniques are also called ‘Chronopotentiometric’ techniques, as a small constant current is applied to study the potential as a function of time. Galvanostatic charge-discharge is commonly applied to investigate the charge capacitance and stability of power sources, e.g. batteries, fuel cells and electrochemical capacitors. In the application of electrochemical capacitors, the capacitance can be calculated by:

\[ C = \frac{\Delta q}{\Delta E} = \frac{It}{\Delta E} \]  

(2.28)

where, \(I\) is the constant current applied, \(t\) is the charge or discharge time and \(\Delta E\) is the cut-off potential setting during the examination. It’s worth mentioning that an ohmic drop (IR)drop is commonly observed in such experiments due to the resistance within the solution, electrode and connection interface. In the work of developing energy storage devices, the existence of IR drop complicates the potential profiles and should be eliminated if possible. In this thesis, constant current chronopotentiometry is applied to examine the performance of cells and to determine the equivalent series resistance of the cells. Coulomb efficiency (\(\eta\)), specific power
(SP) and specific energy density (SE) are three important parameters to evaluate the
capacitive performance of a supercapacitor cell. The energy density is the capacity to
perform work, whereas the power density exhibits how fast the energy is delivered.
The Coulomb efficiency of a capacitor was determined based on ratio of the discharge
and charge time as

$$\eta = \text{Coulomb efficiency (\%) = } \frac{t_D}{t_C} \times 100$$ (2.29)

where \(t_D\) and \(t_C\) are the discharging and charging time, respectively. The values of
specific power (W/kg) and specific energy density (Wh/kg) for a supercapacitor cell
were also calculated from the charge-discharge data[88] by using the following
equations.

**Specific Power (SP)**

$$\text{Specific Power (SP)} = \frac{VI}{m}$$ (2.30)

**Specific Energy (SE)**

$$\text{Specific Energy (SE)} = \frac{VI t_D}{m}$$ (2.31)

where \(V\) is voltage (excluding the IR drop occurring at the beginning of the
discharge) and \(t_D\) is the discharge time. The specific capacitance of the cell depends
extensively on the electrode materials. Hence, a broad operating cell voltage, a large
capacitance, and minimum ESR are essential for a supercapacitor with good
performance. In present investigation, different small constant current are applied to
study the potential as a function of time.

**2.5.3 Electrochemical impedance spectroscopy**

Electrochemical impedance spectroscopy (EIS) is a powerful tool to
investigate electrochemical systems. The advantage of EIS is that it is generally non-
destructive system. EIS is the most common method for measuring the equivalent
series resistance (ESR) of electrochemical capacitors. It also allows creating methods
to describe underlying reaction mechanisms. Normally, EIS is conducted at the open-
circuit voltage (OCV) by applying a small amplitude of alternative potential (5 ~ 10
mV) in a range of frequency (generally 0.01 to 100Hz). The resistance \((Z)\) is defined
as \(Z = Z' + jZ''\), where \(Z'\) and \(Z''\) are the real part and the imaginary part of
impedance, respectively. The specific capacitance is calculated from the imaginary
part \((Z'')\) of the collected EIS data according to the equation:

$$C = -\frac{1}{2\pi f z'' m}$$ (2.32)
where, \( f \) (in Hz) is the frequency and \( m \) is the mass of electrode materials.

The important form for EIS is plot of \( Z' \) against \( Z'' \) to obtain a so-called Nyquist plot. The impedance curve exhibits a semicircle over the high frequency range, followed by a linear part in the low frequency region. It is notable that a large semicircle observed from a Nyquist plot is an indicative of high charge-transfer resistance, contributing to the poor electrical conductivity of materials, whereas a more vertical the line is more closing to an ideal capacitor. In characterizing systems with capacitive behaviour, it is suggested that the frequency range can be divided into three regions: high-frequency region, medium frequency region and low frequency capacitive region [87,123]. The high-frequency and medium frequency is divided by the knee frequency. The low-frequency region is characterized by a slope of -1 in Bode plot; ideal capacitive behaviour can be observed at the frequency \( f_0 \) at which phase-angle = -45°, and the reciprocal of \( f_0 \) is defined as characteristic response time (\( \tau_0 \)). Obviously, we can see that smaller the \( \tau_0 \), faster the response would be and thus better pulse power performance. The quantitative data for these parameters can be obtained by fitting the impedance spectra using the electrical equivalent circuit. The double-layer capacitance is usually substituted with the constant phase elements in order to better fit the high-frequency capacitive loop.

In this thesis, EIS measurements are conducted in frequency range between 10 mHz and 1M Hz with an AC signal of 10 mV. EIS is applied to give an insight into the mechanism of the electrode processes and to confirm the capacitance of the system calculated from cyclic voltammetry results. In addition, impedance models of electrode processes are built with equivalent circuits to gain a deeper understanding of the electrochemical processes that could be beneficial in improving the cell performance.

2.6 Prospectus on the future of research on supercapacitor

Over the last several years, supercapacitor has focused upon efforts to increase the capacitance of electrode materials and to develop improved quantitative models. However, recent research trends suggest that new areas may be rising to the forefront of supercapacitor. In particular, researchers efforts concerning hybrid capacitors, equivalent series resistance, electrolyte optimization, and self-discharge are likely to expand and enable major performance advances in supercapacitors. ESR prevents supercapacitors from achieving power densities closer to the theoretical limits. Thus,
determining how to lower the ESR of supercapacitors is becoming an important area of research. Several methods for reducing the ESR already have been developed, including polishing the surface of the current collector, chemically bonding of the electrode to the current collector and using colloidal thin films suspensions. In addition, there has been research in defining the relationship between pore size and ESR in electrode materials and determining the intrinsic ESR of various electrolytes [125]. In the scientific literature, electrolyte optimization has been emphasized consistently as the critical step towards improving supercapacitor performance. While the resistance of an electrolyte can limit power density, its ion concentration and operating voltage can limit the energy density of a supercapacitor. Despite the impact of electrolyte properties on supercapacitor performance, researcher’s efforts toward improving electrolytes have yet to become as rigorous or to be as fruitful as the comparable efforts towards improving electrodes.

Another step that needs to be taken for supercapacitors to fulfill their promise is to ameliorate their tendency to self-discharge. Because charged supercapacitors are in a higher state of potential energy than discharged supercapacitors, there is thermodynamic pressure for a supercapacitor to discharge. This pressure sometimes manifests itself in the undesirable phenomenon known as self-discharge, which occurs when a capacitor discharges internally on an open circuit. Self-discharge is intrinsic to all electrochemical energy storage systems including batteries as well as capacitors. However, it occurs at a higher rate for supercapacitors. Hence, self-discharge tends to be more detrimental for them. This is because there is not an intrinsic barrier to the supercapacitor operating in reverse as there is in the case of systems based upon chemical reactions in which the reverse process often is retarded by thermodynamic or kinetic barriers in the absence of an external connection between the electrodes. Also, in supercapacitors the potential difference between the electrodes often is very large and the distance is very small. As a result of these several factors, the potential difference within an EDLC can be much more difficult to maintain than that within a battery. There are number of different mechanisms for self-discharge but they commonly result from uncontrollable Faradaic reactions, such as the reduction and oxidation of impurities in the electrode material. Thus, improving material purity has been identified as one way to decrease the rate of self-discharge in supercapacitors.