2.1 Samples Preparation

2.1.1 To determine which molecular weight group of chitosan will give a film with the highest electrical conductivity

Films of chitosan-acetic acid salt complexes were prepared by the solution cast technique. The chitosan powders from FLUKA of average molecular weight $2.0 \times 10^6$ g/mol (high molecular weight), $7.5 \times 10^5$ g/mol (medium molecular weight) and $7.5 \times 10^4$ (low molecular weight) were used to determine which molecular weight group will give a chitosan film with the highest electrical conductivity. 1.0 g of chitosan from each molecular weight group was dissolved in 100 ml of 1% acetic acid solution (Ajax Chemicals). The solutions were continuously stirred with magnetic stirrers for about 3 hours at room temperature. When complete dissolution is achieved, the solutions were then cast in different plastic petri dishes and the films were allowed to form at room temperature. The films take about 3 weeks to form. Six portions from each film were taken and the electrical conductivity was measured by impedance spectroscopy. The chitosan powder with the appropriate molecular weight from which the film giving the highest electrical conductivity was made will be used in the following studies.
2.1.2 To determine the better plasticizer between ethylene carbonate (EC) and propylene carbonate (PC) in enhancing electrical conductivity of chitosan acetate film

Having determined the choice of molecular weight, it is intended to investigate whether adding plasticizers can enhance the electrical conductivity of the chitosan-acetic acid salt complex. Two types of plasticizers will be used i.e. propylene carbonate (PC) and ethylene carbonate (EC). Two sets of solutions containing chitosan of the chosen molecular weight dissolved in 100 ml of 1-% acetic acid solution were prepared. The solutions were stirred thoroughly with a magnetic stirrer at room temperature for about 3 hours. For each set of solution different amounts of PC and EC were added. After complete dissolution of the plasticizers, the solutions were poured into different plastic petri dishes and left to dry at room temperature. By complex impedance spectroscopy the plasticizer containing film exhibiting the highest electrical conductivity will be determined.

2.1.3 To determine the salt content in a plasticized chitosan acetate film that gives the highest electrical conductivity

Another set of solutions containing the fixed amount of chitosan, acetic acid and the better plasticizer but different amounts of lithium triflate (LiCF₃SO₃) were then prepared in order to determine the chitosan acetate-plasticizer-salt film that exhibits the highest electrical conductivity. This film will be used in fabricating the lithium cells.
2.2 X-ray Diffraction (XRD)

Many researchers have used x-ray diffraction to study whether a material is amorphous or crystalline [50-51]. Some workers [52-53] have been successful in proving the occurrence of complexation between the salt and the polymer host although in PEO-AgSCN [54] it has been shown that XRD could not prove the existence of a new phase.

In polymers, conduction occurs in the amorphous regions. This has been reported by many workers [1]. The increase in electrical conductivity can therefore be partially understood if upon some modifications, say the addition of an inorganic salt to a polymer, makes the final material more amorphous than before any salt was added.

In this work XRD is used to determine the nature of the materials with the hope that it will give some light to understand other properties of the material in particular the electrical conductivity. X-ray diffraction was carried out using the Siemens D-5000 X-Ray Diffraction system at the Physics Department, University of Malaya. The films were adhered onto cleaned microscope slides and then placed in the sample chamber. The samples were scanned with a beam of monochromatic CuKα-X-radiation of wavelength \( \lambda = 1.5418 \text{ Å} \) between a 20 angle of 10° to 60°. To ensure that the noise level does
not enshroud any peak that could attribute the sample to be crystalline, the films were irradiated every 0.02° for 1.0 sec.

2.3 Infrared Spectroscopy (IR)

Infrared spectroscopy is widely used in the identification of polymeric materials. This technique involves the interaction between infrared radiation with various vibration modes of the molecules in the species concerned. According to Muzzarelli [39] the most important feature in determining whether chitosan has chelated a metal is the shift in the infrared band of O = C-NHR from 1650 to 1620 cm⁻¹, the shift in the band of –NH₂ from 1590 to 1575 cm⁻¹ and the shift in the band of -NH₃⁺ from 1560 to 1510 cm⁻¹. These shifts imply that not only –NH₂ or -NH₃⁺ groups but also the N-acetyl-amino groups remaining in the chitosan macromolecule have considerable interaction with the metal ions or metal salts themselves [39]. The metal ions will introduce modifications that depend on the nature of the metal ion, its concentration and also on its counter-anion. In this work, the infrared spectrum of LiCF₃SO₃ will be taken in order to distinguish bands due to the salt. The chitosan spectrum will also be taken to determine without ambiguity shifts in the bands that might be due to the acetic acid or the lithium salt interactions with the lone pair electron of the nitrogen atom in the amide group. The spectrum of the plasticizer containing film will also be taken to check if the spectrum is the same with the spectrum of the chitosan acetate
film without plasticizer. From these spectroscopic data we hope to determine whether complexation has taken place between the lithium salt and the lone pair electron of the nitrogen atom. Infrared spectroscopy was performed using the MAGNA-IR550 Spectrometer-Series II at the Physics Department, University of Malaya in the wavenumber region between 4000 – 400 cm$^{-1}$. The films, reasonably transparent and of ~0.02 mm in thickness were cut to suitable sizes and placed in the specimen holder of the spectrophotometer. A beam of infrared radiation penetrated the samples. The beam was split by KBr and detected by a DTGS KBr detector. To get a good impression the samples were scanned 100 times with an aperture of 100.

2.4 X-Ray Photoelectron Spectroscopy (XPS)

Suspecting that the shift in the $O = C-$ NHR, $-NH_2$ and $-NH_3^+$ bands in the infrared spectra could be caused by the interaction between these molecules and the acetic acid and not due to the interaction between the lithium salt, and the nitrogen atom of the amide group in chitosan, XPS was sought for to determine the binding energies of lithium and nitrogen. If interaction between the lithium salt and the lone pair electron of the nitrogen atom exist then it should be possible to deconvolute the lithium signal into two peaks with one peak at the binding energy of the lithium salt and the other at the binding energy of Li-N interaction. On the other hand, it should be possible to demonstrate that the nitrogen signal can be deconvoluted into three
peaks with binding energies representing that of the amide groups, the acetic acid-nitrogen interaction and the Li-N interaction.

The basic design of an X-ray photoelectron spectrometer requires an x-ray source, sample analyzer chamber, electron energy analyzer and detector, as shown schematically in Fig. 2.1

**Fig. 2.1: Schematic experimental arrangement for X-ray photoelectron spectroscopy of solid surface [55].**
The x-rays produced must have energy greater than 1 keV (sufficient enough to excite core-level electrons of all elements) and reasonably monochromatic with narrow line width and very few satellite lines. Mg K$_\alpha$ (1253.6 eV) or Al K$_\alpha$ (1486.6 eV) x-rays are usually used. The sample chamber is designed to hold a sample in the required physical state and is maintained at $10^{-9}$ torr to get a clean sample surface.

The energetic and monochromatic X-rays of energy $h\nu$ hit the sample to emit the core electron [56-57]. This energy is partially (a) absorbed by the core electron to overcome its binding energy with the surface atom, $E_b$; (b) absorbed by the core electron to overcome the work function of the material, $\phi_s$ and (c) converted into kinetic energy, $E_k$ of the photoelectron. Thus

$$h\nu = \phi_s + E_b + E_k \quad (2.1)$$

The binding energy of these electrons which reflect the attractive forces of the nucleus on the core electrons are characteristic of the type of atoms present in the sample surface. Since the binding energies of the elements have a specific value, thus by knowing the binding energy of a given photoelectron the element involved can be identified. Photoelectron emission is shown schematically in Fig. 2.2. A plot of intensity (counts per second-cps) versus kinetic energy (or binding energy) of the electron from the elements in the material makes an XPS spectrum.
The XPS studies in this work was carried out using a Kratos XSAM HS surface analysis spectrometer with an Mg K$_\alpha$ x-ray source (1253.6 eV) which is available at the Faculty of Physical and Applied Sciences, Universiti Kebangsaan Malaysia. The spectrum was taken at an operating current of 10 mA and an operating voltage of 14 kV. The spectrometer was calibrated using a clean Ag plate and the Ag3d$_{5/2}$ line was set at 368.25 eV. The C1s binding energy at 284.5 eV was used as a second reference. The solid polymer samples were mounted onto a standard stub holder using double-sided adhesive tape. The survey scan was recorded in the energy range between 10 eV to 1100 eV. The pass energy and step size energy was 160 eV and 1 eV
step⁻¹ respectively. Sweep time was set at 300 seconds per sweep. For the narrow scan, a smaller pass energy 20 eV with lower step size, 0.1 eV step⁻¹ were utilized. The sweep time was 59.898 seconds per sweep. Narrow scans were obtained for the C1s, O1s, N1s, F1s, S2p and Li1s regions. The sample analysis chamber was kept at ≈5.0 x 10⁻⁹ Torr or less during the scans. The Vision software provided by Kratos deconvoluted all core-level spectra into Gaussian component peaks. Charging effects were corrected for using the C1s binding energy at 284.5 eV. An example of a narrow scan spectrum consisting of photoelectron and satellite peaks is as shown in Fig.2.3.

![Graph showing the deconvoluted Cr2p peaks.](image)

**Fig. 2.3:** Narrow Scan of Cr sample [55].
2.5 Impedance Spectroscopy (IS)

When a monochromatic signal $v(t) = V_m \sin(\omega t)$ is applied to a sample [58-59], the resulting steady state current through the material is given by $i(t) = I_m \sin(\omega t) + \theta$. Here $V_m$ is the voltage amplitude, $\omega = 2\pi f$, $f$ being the single frequency (which is changed until the frequency range is completed) and $\theta$ is the phase difference between the voltage and the current. $\theta$ is zero for a purely resistive behaviour. The impedance can now be defined as $Z(\omega) \equiv v(t)i(t)$; its magnitude, $|Z(\omega)| = \frac{V_m}{I_m}$, and its phase angle $\theta(\omega)$.

Impedance is a more general concept than resistance because it takes phase differences into account. An impedance $Z(\omega) = Z_R + j Z_I$, where $Z_R$ is the real impedance and $Z_I$ is the magnitude of the imaginary impedance, is a vector quantity and may be plotted in the plane with either rectangular or polar coordinates. $Z_R$ and $Z_I$ are related to the magnitude of the complex impedance via the equations;

$$Z_R = |Z(\omega)| \cos \theta \quad (2.2)$$

and

$$Z_I = |Z(\omega)| \sin \theta \quad (2.3)$$
Other related functions besides impedance used in IS are complex admittance \( A(\omega) \), complex dielectric constant or complex permittivity \( \varepsilon(\omega) \) and complex dielectric modulus \( M(\omega) \). Any of these four basic response quantities; \( Z \), \( A \), \( \varepsilon \) and \( M \) can be denoted by a general term called immittance, \( I(\omega) = I_R + j I_I \). Table 2.1 shows the relations between the four basic immittance functions.

<table>
<thead>
<tr>
<th>( \mu )</th>
<th>( \mu Z )</th>
<th>( \mu A^{-1} )</th>
<th>( \varepsilon^{-1} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M )</td>
<td>( \mu Z )</td>
<td>( \mu A^{-1} )</td>
<td>( \varepsilon^{-1} )</td>
</tr>
<tr>
<td>( Z )</td>
<td>( \mu^{-1} M )</td>
<td>( A^{-1} )</td>
<td>( \mu^{-1} \varepsilon^{-1} )</td>
</tr>
<tr>
<td>( A )</td>
<td>( \mu M^{-1} )</td>
<td>( Z^{-1} )</td>
<td>( \mu \varepsilon )</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>( M^{-1} )</td>
<td>( \mu^{-1} Z^{-1} )</td>
<td>( \mu^{-1} M )</td>
</tr>
</tbody>
</table>

Here \( \mu = j\omega C_c \) where \( C_c = \varepsilon_o A/t \), \( \varepsilon_o \) = permittivity of free space, \( A \) is sample-electrode contact area and \( t \) is thickness of the sample. There are many ways IS data can be represented. In the IS field where capacitive (the phase angle \( \theta \) has a negative sign) rather than inductive (\( \theta \) is positive) effects dominate, conventionally one plots \(-Z_I\) on the y-axis and \( Z_R \) on the x-axis to give a
complex plane impedance plot. Such graphs are called the Cole-Cole plots. Another approach of plotting IS data is to use the Bode diagram where \[ \left[ Z(\omega) \right] \text{ or } \theta \] is plotted against log [f]. Alternatively, one can plot \( Z_R \) (or any \( I_R \)) or \(-Z_1 \) (or \(-I_1 \)) or the logarithms of these four basic quantities versus log [f]. The relationship between admittance and impedance can be given by

\[
A(\omega) = \frac{1}{Z(\omega)}
\]

\[
= \frac{1}{Z_R + jZ_1}
\]

\[
= \frac{1}{Z_R + jZ_1} \times \frac{Z_R - jZ_1}{Z_R - jZ_1}
\]

\[
= \frac{Z_R - jZ_1}{Z_R^2 - Z_1^2}
\]

\[
= \frac{Z_R}{Z_R^2 - Z_1^2} - \frac{jZ_1}{Z_R^2 - Z_1^2}
\]

\[\text{...............}(2.4)\]
Following Table 2.1 again, the relationship between \( \varepsilon \) and \( Z \) is given by;

\[
\varepsilon(\omega) = \frac{1}{\mu Z(\omega)}
\]

\[
= \frac{1}{j\omega C_c [Z_R + jZ_1]}
\]

\[
= \frac{1}{j\omega C_c Z_R - \omega C_c Z_1}
\]

\[
= \frac{1}{j\omega C_c Z_R - \omega C_c Z_1} \times -\frac{j\omega C_c Z_R - \omega C_c Z_1}{j\omega C_c Z_R - \omega C_c Z_1}
\]

\[
= -\frac{j\omega C_c Z_R - \omega C_c Z_1}{(\omega C_c Z_R)^2 + (\omega C_c Z_1)^2} \quad \frac{-j\omega C_c Z_R}{(\omega C_c Z_R)^2 + (\omega C_c Z_1)^2}
\]

\[
(2.5)
\]

Again following Table 2.1,

\[
M(\omega) = \mu Z
\]

\[
= j\omega C_c [Z_R + jZ_1]
\]

\[
= j\omega C_c Z_R - \omega C_c Z_1
\]

\[
= -\omega C_c Z_1 + j\omega C_c Z_R
\]

\[
(2.6)
\]
Upon conversion to the admittance formalism and plotting the imaginary admittance, $A_I$ versus real admittance $A_R$, the new reciprocal of the bulk impedance, $1/R_B$ may be easily obtained if the bulk impedance is difficult to determine from the complex impedance plots. Likewise converting the impedance data into the complex permittivity and electrical modulus formalisms enable the understanding of the conductivity mechanism that takes place in the samples [61-64]. The response of the circuit (Figure 2.4) consisting of a resistor and capacitor in series is a vertical spur when represented in the complex impedance plane (Figure 2.5). Representation in the complex admittance plane, Figure 2.6 shows the Debye nature of the material, where the shape of the complex immittance plot is a perfect semicircle.

![Diagram: Resistor and capacitor in series](image1)

**Fig.2.4:** Resistor and capacitor in series

![Diagram: A complex impedance plot](image2)

**Fig.2.5:** A complex impedance plot
The response of a circuit, Figure 2.7 consisting of a parallel resistor-capacitor combination in series with another capacitor is as shown by the dotted lines in Figure 2.8. In Figure 2.7, R is the bulk electrolyte resistance, $C_1$ is the geometric capacitance and $C_2$ is the charge transfer capacitance. The geometric capacitance is the capacitance that would arise if only air was present in the electrode gap [65]. However, this term remains even in the presence of the electrolyte. The circuit of Figure 2.7 is the simplest arrangement that will give the impedance plot shown.
The types of Cole-Cole plots often encountered in solid electrolyte studies are the inclined spur or spike and the depressed semicircle with and inclined spike as shown by the bold lines in Figure 2.8. No manipulation of series and parallel combinations of resistors and capacitors can give these "non-ideal" spectra [65]. To account for the depressed semicircle and spike inclination, a type of circuit element called the constant phase element (CPE) is required. The impedance of a CPE, $Z_{\text{CPE}}$ is given by:

$$Z_{\text{CPE}} = \kappa(j\omega)^{-\alpha}$$ \hspace{1cm} (2.7)

where $0 \leq \alpha \leq 1$. When $\alpha = 0$, $Z$ is independent of frequency and $\kappa$ is just the bulk resistance, $R_B$. When $\alpha = 1$, $Z = \kappa(j\omega)^{-1} = -j/(\omega \kappa^{-1})$. Here $(\omega \kappa^{-1})$ is capacitive reactance with $\kappa^{-1}$ corresponding to a capacitance $C$. The CPE exhibits mixed resistor-capacitor behaviour when $\alpha$ is between 0 to 1.
Incorporating the expression for $Z_{\text{CPE}}$, an equivalent circuit can be modelled and the complex plane plots be interpreted. Knowing the bulk resistance, the electrical conductivity of the sample can be calculated via the equation

$$\sigma = \frac{L}{R_b A}$$  \hspace{1cm} (2.8)

where $\sigma$ is the electrical conductivity, $L$ the sample thickness and $A$ is the surface area of contact. A micrometer screw gauge measures the thickness of the polymer film and the diameter of the film measured with a vernier caliper was 13.3 mm. The polymer film was placed in between two stainless steel pellets and placed in a conductivity mount as shown in Fig. 2.9.

![Diagram of conductivity measurement setup](image)

Fig. 2.9: Connections for conductivity measurement
The impedance was measured with a HIOKI 3531-01 LCR Hi-Tester that has been interfaced to a computer. This bridge has been set to measure the impedance and phase angle from 50 Hz to 5 MHz. The software controlling the measurement also calculates the real and imaginary impedance. The imaginary impedance is usually negative indicating the sample to be capacitive. A plot of negative imaginary impedance versus real impedance on a graph with horizontal and vertical axes having the same scale will give a semicircle if the sample has a Debye nature.

The conductivity measurements for each sample was also carried out at different temperatures up to 85°C (± 2°C) so as to be well below the glass transition temperature as reported in the literature [42]. In such a temperature regime the conductivity mechanism obeys a classical Arrhenius rule, given by the Eqn.(1.1) from which the activation energy can be calculated.

### 2.6 Ionic Transference Number Measurement

According to Linford [65] electron conduction can be neglected in polymer electrolytes. Thus the total current flowing in a polymer can be assumed to consist of cationic and anionic currents, i.e. \( i_T = i_+ + i_\) where \( i_+ \) is current due to cations and \( i_- \) is current due to anions. When the circuit is closed the ions will travel to the electrode connected to the terminal that has an opposite charge to that of their own charge. A back emf is produced and
polarization occurs. The experimental set up is shown in Figure 2.11. The polymer film is sandwiched between two zinc pellets. The applied voltage is ~ 1.5 V. The current value is taken every 15 seconds until a constant current attributable to cations was obtained. Blocking electrodes which do not allow ions to dissolve in them were used. Polarization concentration impedes the anionic current. Thus the cationic transference number \( t_+ \) is given by

\[
t_+ = \frac{i_{+\infty}}{i_T}
\]  

(2.9)

where \( i_{+\infty} \) is the cationic current saturation and \( i_T \) is the total current at the beginning of polarization.

Fig. 2.10: Ionic transference number measurement set up
2.7 Solid State Electrochemical Cell Fabrication

The polymer-plasticizer-salt complex film with the highest electrical conductivity was used as the electrolyte in the secondary electrochemical cell fabrication. Vanadium pentoxide (V$_2$O$_5$) was chosen as the cathode material since it is able to deliver a reasonably high voltage and high discharge capacity [66-67]. Lithium metal was used as the anode. The composite cathode was prepared by mixing 67 w/o V$_2$O$_5$, 0.5 w/o PVC, as a binding agent and 32.5 w/o electrolyte solution. 5 ml of acetone was added to the mixture and stirred with a magnetic stirrer to form a homogeneous mixture. After the acetone has evaporated, and the composite electrode has thoroughly dried, the mixture was grounded. The powdered composite cathode was distributed onto a copper mesh electron collector and pressed under a pressure of 20 000 kPa. The cell was assembled into the battery casing with the electrolyte sandwiched between the lithium anode and the composite cathode under argon atmosphere in a glove box.

In order to avoid the use of lithium metal, which is difficult to handle, another cell was fabricated using LiCoO$_2$ as the cathode material and V$_2$O$_5$ as the anode material. The preparation of the composite electrode V$_2$O$_5$ is the same as mentioned above. 70 w/o of LiCoO$_2$ was mixed with 19.5 w/o electrolyte solution, 9.5 w/o of carbon, 0.5 w/o PVC and 0.5 w/o LiCF$_3$SO$_3$. 

46
The composite electrodes were pelletized to form separate disks, i.e. a composite LiCoO$_2$ electrode and a composite V$_2$O$_5$ electrode.

2.7.1 Charge/Discharge Characteristics

As mentioned in Chapter 1, the discharge capacity, energy density and power density can be calculated from the charge/discharge characteristics. These characteristics were studied using the BAS LG50 computer-controlled galvanostat at the Institute of Postgraduate Studies and Research. Several charging and discharging currents were tried until the appropriate currents were selected. The cell Li/AC-EC-LiCF$_3$SO$_3$/V$_2$O$_5$ was charged with a constant current of 100 nA and discharged at 10 nA.

For the cell LiCoO$_2$/AC-EC-LiCF$_3$SO$_3$/V$_2$O$_5$, the charging current was 50 µA and the discharge current was 30 µA. By estimating the plateau time and knowing the mass of the cell and the voltage of the cell, the cell parameters of discharge capacity, power and energy densities can be calculated.