CHAPTER VII

ELECTROCHEMICAL CAPACITOR
Use of solid electrolyte in power sources is of great interest. The solid electrolytes, $\text{MAg}_4\text{I}_5$ (where $M = \text{K}, \text{Rb}$, $\text{NH}_4$) have high ionic conductivity.\textsuperscript{1,2} In these compounds and also in parent compound, silver iodide conduction occurs solely by the movement of silver entities through the crystal lattice. It is therefore interesting to obtain more basic information on the nature and kinetics of electrochemical processes which can occur in solid state systems.

An electrochemical capacitor is formed in the form of double layer which exists at electrode/electrolyte interface. The capacitance of this electrochemical capacitor, that can be achieved are thus intrinsically higher than those in which a dielectric layer is employed. The disadvantage of elimination of separate dielectric layer is that the maximum voltage per cell is considerably reduced below the electrolyte decomposition voltage (i.e., in practice $< 0.5$ V for $\text{RbAg}_4\text{I}_5$ because the carbon electrode ceases to behave capacitively at higher potentials). This feature, clearly, has a strong influence on circuit design, although it is not a major shortcoming because the waveform can be readily amplified.

Space charge polarization in solid and liquid systems has
been reported by number of workers. They studied diffuse double layer and tried to explain frequency dispersion. Macdonald \(^8\) reported that as charge is injected onto an ideally polarizable electrode, it is possible for a static concentration gradient of an ionic species of a given sign to be established which extends to a significant extent into the bulk electrolyte. Friauf \(^9\) studied Ag / AgBr /Ag and Au / AgBr/ Au arrays between temperature 200° and 300°C and reported about their frequency dependent resistance and capacitance effects. The capacitance value was of the order of 100 \(\mu F/cm^2\). Raleigh \(^10\) and Wagner and Wagner \(^11\) modified the above array in the following way. One of the electrodes is reversible to one of the electrolyte components, while the other electrode is inert. At the inert electrode, there will exist a potential range over which no steady state current will flow but a transient faradaic current is possible which according to the Nernst equation, will tend to readjust the activity of each of the electrolyte components at the inert electrode according to applied d.c. potential. In the system Ag / AgI / M (where M is inert electrode), the activity 'a' of Ag and I\(_2\) at the M / AgI interface is given by :

\[
\text{For Ag } \quad a_{Ag} = \exp \left( - \frac{FE}{RT} \right) \quad (7.1)
\]

\[
\text{and for I}_2 \quad a_{I_2} = \exp \left[ - \frac{2F(E_D - E)}{RT} \right] \quad (7.2)
\]

where \(E_D\) is the decomposition potential of the electrolyte.
the potential of $M$ with respect to $Ag\ /\ AgI$, the other terms have their usual significance. For a given change in the inert electrode potential $E$, both $a_{Ag}$ and $a_{I_2}$ readjust by faradaic process.

Raleigh reported double layer behaviour of interface formed between single crystal of silver bromide with graphite, platinum and gold electrodes in the temperature range 244-292°C. He showed that the response of such interfaces to potential step perturbations could not be represented by simple RC series network.

Interface double layer capacitance has been measured by a number of workers. They used silver as reversible electrode, graphite and platinum as inert electrode and $AgI$ and $AgBr$ as solid electrolyte. They reported that the interface ($AgBr/C$ or $AgBr/Pt$) capacitance was low and independent of bias voltage.

Commercial double layer capacitor was formed by Sakido et al. recently. They used mixture of graphite and solid electrolyte as polarization electrode, mixture of solid electrolyte with a compound containing Cu and Cu$_2$S or TiS$_2$ as non-polarization electrode and solid electrolyte $K_xRb_{1-x}Cu_4I_yCl_{5-y}$ where $x = 0.1 - 0.25$ and $y = 1.25 - 1.67$.

7.2 Principle of Electrochemical Capacitor

In the electrochemical capacitor left side electrode
is composed of the parent metal M(s) of an electrolyte for the conduction of a certain species M⁺. As both M(s) and M⁺ are present at this electrode interface, the following equilibrium is maintained:

\[ M(s) \rightleftharpoons M^+ + e^- \]

Thus this electrode behaves as ideally reversible electrode. The right hand side electrode metal, M⁺ must be such that it will not react with electrolyte. At suitable cathodic potentials the metal M(s) can be electrodeposited on its surface while some anionic species can be discharged at the sufficiently high anodic potentials. In the intermediate range of applied voltage ion discharge is not possible and these ions accumulate at electrode surface. For a given solid electrolyte, the intermediate range of applied voltage is determined by the free energy connected with the formation of electrolyte. Thus this electrode behaves as an ideally polarizable electrode. The cell having reversible and polarizable electrode is shown in Fig. 7.1.

When a polarizing voltage is applied to the cell a double layer capacitor is formed at the electrolyte/C interface. A diffuse space charge layer, which is formed due to steady state field created by polarizing bias, is defined by Pissou-Boltzmann distribution of positive (interstitial) and negative (vacancy) carriers in the electric field which are truncated at a distance 'dₑ', the distance of closest approach of the mobile
Fig. 7.1 - Behavior of solid electrolyte between two electrodes as capacitor.

M - reversible ion electrode.
M' - polarized electrode of metal.

M + electrolyte + M'
species to the electrode surface. This truncation has the
effect of placing a parallel plate 'inner layer' capacitor.
The plates of this inner layer capacitor are separated by a
distance $d_c$. This inner layer capacitor and diffused space
charge layer capacitor are in series. Thus double layer
capacitor is formed. The capacitance per unit area ($C_i$) of
inner layer, is independent of defect concentration and voltage
and it is given by:

$$C_i = K \varepsilon_0 / d_c$$ (7.3)

where $K$ is effective dielectric constant, $\varepsilon_0$ is the permittivity
of free space. If $d_c$ is the radius of charge carrying ions
($Ag^+$ ions), its value will be 1-3 Å. If $K = 1$, the value of
capacitance from Eqn. (7.3) comes to 3-9 $\mu$F/cm$^2$. The diffuse
layer capacitance depends on bulk defect concentration and
voltage. In the solid electrolyte in which all the mobile ions
are of one type, diffuse layer is not detected.

Various polarizing potentials are applied to the cell and
charge storage characteristics at electrolyte/C interface are
studied. A small step voltage is applied to the cell and current
$i(t)$ and its time integral $Q(t)$ corresponding to the recharging
of interface capacitance is determined. The other method for
determining storage capability of electrolyte/C interface is by
measuring the a.c. cell impedance as a function of applied d.c.
biased potential.
7.3 Types of Electrochemical Capacitor:

The electrochemical capacitor are of two types.

(i) Polar - This type is represented by cell

\[ \text{Ag} / \text{RbAgI}_3 / \text{C} \]

In this cell silver electrode is ideally non-polarizable electrode while carbon (graphite) electrode is capacitive.

(ii) Non-Polar - This type is represented by cell

\[ \text{C} / \text{RbAgI}_3 / \text{C} \]

In this cell both are carbon electrodes. The advantage of being non-polar results from absence of the silver electrode which can limit the useful life of the non-polar as a result of dendrite growth and the development of poor silver utilization i.e., the silver electrode ceases to become ideally non-polarizable.

7.4 Experimental Arrangement:

Ammonium silver iodide is prepared as described in Chapter II. 0.7 gm of \( \text{NH}_4\text{AgI}_3 \) is used for preparation of each pellet which is pelletized at a pressure of 2.5 tons/1.33 cm\(^2\) as the ionic conductivity of such pellets are maximum as described in Chapter III. Some pellets are annealed at 190°C for three hours. Silver powder pellet, pelletized at a pressure of 5 tons/1.33 cm\(^2\), is pressed on one side of \( \text{NH}_4\text{AgI}_3 \) pellet as one
electrode (reversible electrode). Graphite powder pellet is pressed on the other side of solid electrolyte pellet as second electrode (polarizable electrode). Thus the following polarizable cell is studied.

\[ \text{Ag} / \text{NH}_4\text{AgI}_3 / \text{C} \]

\[ \text{NH}_4\text{AgI}_3 / \text{C} \] interface capacitance is measured with Radart LCR Bridge when d.c. bias is applied from constant voltage source fabricated in the laboratory, keeping a.c. signal very low (nearly 30 mV). The experimental arrangement is shown in Fig. 7.2.

This electrochemical capacitor is in polar form. During charging of the cell referred above, Ag\(^+\) ions migrate from right to left and discharge to form a layer of silver metal at the bulk silver electrode/electrolyte interface. The voltage change at this electrode is negligible compared with the voltage change at graphite electrode. Therefore, it can be considered to have infinite capacity. The voltage change of the carbon electrode is nearly linear at constant current corresponding to an applied voltage between 0 and 0.45 V. During the discharge, exactly reverse takes place, the silver metal is oxidized to Ag\(^+\) ions and the double layer at carbon electrode is discharged. Above 0.5 V electrolyte decomposition takes place.
FIG. 7.2 - EXPERIMENTAL ARRANGEMENT FOR MEASUREMENT OF ELECTROCHEMICAL CAPACITANCE.
7.5 Characteristics of Electrochemical Capacitor:

The following characteristics are studied.

(i) Variation of capacitance as a function of bias voltage -

A d.c. bias voltage is applied to the cell Ag / NH$_4$Ag$_3$I$_5$ / C in such a way that the imposed voltage would be retained under open circuit condition indefinitely. Thus the graphite / NH$_4$Ag$_3$I$_5$ interface appears to be polarized interface in the solid state system. The cell current under d.c. bias is allowed to settle to a steady state value before starting measurements. A.C. capacitance of the interface at 1 KHz is measured by varying bias voltage between 0.05 to 0.5 V. This characteristic is studied at 40°, 80° and 140°C with annealed electrolyte pellets.

(ii) Variation of Capacitance with Frequency at different d.c. bias Voltage -

A d.c. bias of 0.05V is applied to the cell Ag / NH$_4$Ag$_3$I$_5$ / C with annealed electrolyte pellet. A.C. capacitance is measured as a function of frequency from 300 Hz to 20 KHz. The same is repeated at different bias between 0.05 to 0.5 V. These characteristics at temperature 40°, 80° and 140°C are shown in Figs. 7.4, 7.5 and 7.6 respectively.
FIG. 7.3 - VARIATION OF CAPACITANCE OF CELL Ag/NH\textsubscript{4}Ag\textsubscript{4}I\textsubscript{5} / C WITH BIAS VOLTAGE AT 1 KHZ.
Fig. 7.4 - Variation of capacitance of cell Ag/NH$_4$Ag$_4$I$_5$/C with frequency at different bias voltages.
FIG. 7.5 - VARIATION OF CAPACITANCE OF CELL Ag/NH₄Ag₄I₅C WITH FREQUENCY AT DIFFERENT BIAS VOLTAGES.

ANNEALED TEMPERATURE 80°C

- 0.1 V
- 0.2 V
- 0.3 V
- 0.4 V
Fig. 7-6 - Variation of capacitance of cell Ag/NH$_4$Ag$_4$$_{15}$/C with frequency at different bias voltage.
Temperture 40°C.

Fig. 7.7 - Comparison of capacitance of cell Ag/NH₄Ag₄I₅/C as a function of bias voltage at 1 kHz.
Fig. 7.8 – Comparison of capacitance of cell $\text{Ag/NH}_4\text{Ag}_4\text{I}_5/\text{C}$ as a function of bias voltage at 1 kHz.
Fig. 7.9 - Comparison of capacitance of cell Ag/NH₄Ag₅I₅/C as a function of bias voltage at 1 kHz
(iii) Comparison of Capacitance of the cell Ag / NH₄Ag₄I₅ / C using annealed and unannealed pellets of Electrolyte at different temperatures.

The cells with annealed and unannealed pellets are prepared. The capacitance of both types of cells at 1 KHz is measured as a function of d.c. bias voltage between 0.05 to 0.5 V. The comparisons corresponding to temperatures 40°, 80° and 140°C are shown in Figs. 7.7, 7.8 and 7.9 respectively.

7.6 Results and Discussion : 

The variation in a.c. capacitance with applied bias voltage at different temperatures is shown in Fig. 7.3 at 1 KHz. The a.c. capacitance remains nearly constant for applied d.c. bias between 0.2 to 0.5 V at all temperatures. Below 0.2 V capacitance increases. It is also observed from the Fig. 7.3 that capacitance increases with increase of temperature. When d.c. bias is applied, a double layer capacitor is formed at NH₄Ag₄I₅ / C interface. This consists of inner layer capacitor, which is independent of voltage and defect concentration and diffused layer capacitor which depends on voltage and defect concentration as reported by Armstrong and Mason. Therefore double layer capacitor also depends on voltage and defect concentration. The defect concentration is very high in the electrolyte NH₄Ag₄I₅. When low d.c. bias voltage (0.05V) is
applied, the number of mobile ions are less in diffused layer so capacity is large. Number of mobile ions increases in diffused layer when d.c. bias increases up to 0.2 V, so the capacitance decreases. Above 0.2 V bias voltage, the defect concentration is maximum in diffused layer and so the potential drop across the diffused layer remains constant or diffused layer becomes undetectable. Therefore the interface capacitance becomes independent of bias voltage. This variation of capacitance, between 0.05 to 0.2 V bias voltage, decreases as temperature increases i.e., it is lesser at 80°C and least at 150°C as shown in Fig. 7.3. As the mobility of ions increases with rise of temperature, more Ag⁺ ions will reach to graphite electrode, forming diffused layer when low bias voltage is applied. Thus, with the increase of bias voltage the variation of potential drop across the diffused layer is less. It results in less variation of interface capacitor with increase of temperature at low bias voltage range (0.05 to 0.2 V).

From the Fig. 7.3 it is also observed that interface capacitance increases with temperature. Raleigh⁹ for AgBr/C interface and Oxley²⁰ for RbAg₄I₅/C interface also reported the increase of capacitance with temperature. When temperature of polarizable cell is increased, pressed powder NH₄Ag₄I₅ exhibits grain growth. Thus growth of large grains at the expense of small ones appears to enlarge grain dimension without filling the
space left by the digested grains. This process enhances porosity in electrolyte pellet and roughening of NH₄Ag₄I₅ / C interface. With the increase of temperature, gradual expansion and outgassing of air, entrapped in the electrolyte pellet during the pressing process, also produce a stable roughening of interface. This results in an increase in capacitance of interface.

Figs. 7.4, 7.5 and 7.6 show the frequency dispersion of the capacitance at temperatures 40°, 80° and 150°C respectively. A low frequency dispersion in capacitance is observed between the frequencies 300 Hz to 20 kHz at all temperatures. This low frequency dispersion behaviour is in contrast to the behaviour reported for graphite-silver bromide interface at the temperature close to the melting point of electrolyte (Raleigh 10). As graphite acts as an ideally polarized electrode over the potential range +0.45 to -0.03 V, the effect of presence of diffused double layer is expected. This effect is considered to be simply capacitance one. Diffused layer capacitance C_d is a lumped parameter showing no spatial dependence. 21 This indicates that the presence of diffused double layer results in frequency dispersion with respect to a simple RC series circuit model. Hull and Pilla 12 explained for AgI/C interface by a simple calculation that the concentration potential gradient of Ag⁺ extending in the bulk is virtually nonexistent and therefore the diffused
double layer should act as a lumped parameter in the overall series RC equivalent circuit. For solid electrolyte where conduction is by thermally generated bulk lattice defects, the concentration of current carriers is low enough to anticipate diffused double layer effect. For NH$_4$Ag$_4$I$_5$ solid electrolyte where all the mobile ions are of same type, the large value of defect concentration assures that there is no detectable diffused layer capacitance and hence no frequency dispersion.

Comparison of capacitance of cell Ag/NH$_4$Ag$_4$I$_5$/C with annealed and unannealed pellets of electrolyte at temperatures 40$^\circ$, 80$^\circ$ and 160$^\circ$C is shown in Figs. 7.7, 7.8 and 7.9 respectively. It is observed from the figures that capacitance for annealed pellet cell is less than that for unannealed pellet cell. It is attributed that high capacitance value for unannealed pellets are due to small crystallites i.e., their large real interface area. After annealing size of crystallites increases and hence interface area decreases.

The electrochemical capacitor formed at NH$_4$Ag$_4$I$_5$/C interface is poor but it is temperature sensitive. Its value increases with rise of temperature. There is low frequency dispersion.
REFERENCES


