CHAPTER VI

SOLID STATE COULOMETER (TIMER)
6.1 Introduction

Coulometer is one of the useful application of solid electrolyte cell. Coulometer means coulomb + meter i.e. measurement of charge accumulating at one electrode when constant current flows through electrolyte. For liquid electrolytes, Faraday's law of electrolysis states that the mass deposited at the cathode or charge flowing through the electrolyte is proportional to the current passing through the electrolyte and the time for which the current flows. This law holds good for solid electrolyte cells also. If the current, which flows through the electrolyte is kept constant, the amount of charge or mass deposited at the electrode due to flow of charge, can be used to 'time' a circuit. The device (coulometer) based on above mentioned principle is called 'timer'. Liquid electrolyte systems usually based on silver, have a long record of satisfactory use in such applications under normal ambient conditions. However, at extremes of temperature or where the application demands unusual ruggedness, reliability and accuracy, it is desirable not to rely on liquid electrolyte system. Therefore solid electrolytes are suitable for fabrication of timer. These timers are used as timing devices for ordnance fusing. They are also used for commercial purposes such as engine and equipment maintenance, warranty monitoring and virtually any other area where timing or integration of electrical signal is required.
5.2 Principle of Coulometer Timer:

The principle of coulometer timer is very simple. One of the electrodes is made up of the same material as the nature of the mobile ion species in the electrolyte. The other electrode, which is also called indicator electrode, is made up of the material which is non-reactive or insoluble to the moving ions. If electrolyte is silver ion conductor (i.e., AgI, NH$_4$Ag$_4$I$_5$, RbAg$_4$I$_5$, AgBr, KAg$_4$I$_5$ etc.), the mobile ions are silver ions then one electrode will be made up of silver and the other electrode (indicator electrode) may be of gold or graphite. Chandra 3 and Kennedy et al. 4,5 have reviewed solid electrolyte coulometer timer. Kennedy et al. 4,5 reported a thin film coulometer timer Ag/RbAg$_4$I$_5$/Au. Vacuum evaporation technique is used for film formation. They operated coulometer at current density of 10 μA for charge time 20 to 250 sec. accurately. The accuracy is lowered at current density of 1 μA. A schematic representation of solid electrolyte coulometer timer is shown in Fig. 5.1. During charging or 'Set' operation, gold or graphite electrode is kept at the negative potential and silver electrode at positive. The amount of charge passed through it is given by:

\[ q = \int_{0}^{t \text{ charge}} i \, dt \]

At the end of charging time, $t_{\text{charge}}$, the quantity of this charge determines the mass of silver deposited on the gold or graphite.
electrode (according to Faraday's law of electrolysis). During discharge or 'stripping' operation, the silver which was deposited during charging, is transferred back to the silver electrode by reversing the polarity of the current. The time $t_{\text{strip}}$ in which all the silver deposited on gold or graphite electrode is stripped completely depends on stripping current $i_{\text{strip}}$ which is given by:

$$\int_{0}^{\text{charge}} i_{\text{strip}} dt = t_{\text{strip}}$$

At the completion of charging, silver deposited or plated on gold or graphite indicator electrode, forms silver/electrolyte/silver cell until all the silver is anodically stripped from indicator electrode. The open circuit voltage (OCV) of this cell is zero and the applied voltage during stripping remains close to zero with just IR drop and electrode polarization contributions. As the silver is stripped from indicator electrode the voltage starts to rise due to decrease of silver activity on one side of the electrolyte. When the silver is stripped off completely, the voltage rises steeply to the mark where gold itself oxidizes or the decomposition voltage of electrolyte is reached. This sudden rise in voltage during stripping can be used to activate a trigger circuit or intervals between voltage surges can be used for timing purposes. The typical shape of time Vs. voltage across the coulometer behaviour during
stripping is shown in Fig. 5.2(a) and cyclic waveform obtained during multiple charging and stripping of a coulometer is shown in Fig. 5.2(b).

For a silver ion conducting coulometer, the reactions at the anode and cathode are given below:

<table>
<thead>
<tr>
<th>Coulometer cell</th>
<th>Electrolyte</th>
<th>M (Au or C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Charge or 'Set' Ag → Ag⁺ + e⁻</td>
<td>(Ag X)</td>
<td>Ag⁺ + e⁻ → Ag</td>
</tr>
<tr>
<td>(b) Discharge or strip Ag⁺ + e⁻ → Ag</td>
<td></td>
<td>Ag → Ag⁺ + e⁻</td>
</tr>
<tr>
<td>(c) Cut off or end point Ag⁺ + e⁻ → Ag</td>
<td></td>
<td>M⁺nX⁻ → MXn + ne⁻ or X → X + e⁻</td>
</tr>
</tbody>
</table>

For perfect operation of the timer, the basic conditions are that (i) the number of coulombs (charge) used for stripping and setting must be equal, (ii) all of the plated silver be available for subsequent stripping and (iii) the faradaic impurities be excluded from the system. The other parameters, such as electrolyte resistance, electrode-electrolyte interface resistance, indicator electrode cut off characteristics, coulometric accuracy including the time delays between setting and stripping operation and operating temperature range also affect the performance of coulometer. The third condition is important for small coulombic charges or when it is required that the device has an extended stand-life in the pre-set condition. To avoid 'loss' of silver which is apparent in
FIG. 61—SCHEMATIC REPRESENTATION OF A SOLID ELECTROLYTE COULOMETER TIMER
FIG. 6-2- STRIPPING ACTION OF A COULOMETER

(a) TYPICAL SURGE OF VOLTAGE OBTAINED IN A COULOMETER AFTER CERTAIN STRIPPING TIME.

(b) CYCLIC WAVE FORM DURING MULTIPLE CHARGING AND STRIPPING.
poor coulombic efficiency, it is essential that, when the device is fabricated good electrode/electrolyte contact is established. At poor contact region silver can become detached from ionic or electronic contact at the interface and will not be available for oxidation. In this chapter coulometer timer using \( \text{NH}_4\text{Ag}_4\text{I}_5 \) pellets is presented.

6.3 Preparation and Experimental Arrangement for Coulometer-Timer Action Studies:

\( \text{NH}_4\text{Ag}_4\text{I}_5 \) is prepared as described in Chapter II. Pellets of 0.7 gm of \( \text{NH}_4\text{Ag}_4\text{I}_5 \) are pelletized at a pressure of 2.5 tons/1.33 cm\(^2\) because such pellets have maximum electrical conductivity as discussed in Chapter III. These pellets are annealed at 150\(^\circ\)C for 3 hrs. A silver powder pellet, pelletized at a pressure of 5 tons/1.33 cm\(^2\) is pressed at one side of annealed electrolyte pellet. Fine graphite powder pellet, pelletized at a pressure of 2.5 tons/1.33 cm\(^2\) is pressed at the other side of annealed electrolyte pellet. We use graphite because it is easily available, low cost and its pellet is easily formed. Thus the following coulometer is fabricated:

\[ \text{Ag} / \text{NH}_4\text{Ag}_4\text{I}_5 / \text{C} \]

A constant current source, fabricated in laboratory as shown in Fig. 2.3 in Chapter II, is used for constant current charging. A microammeter (0-100 \( \mu \text{A} \)) is used for measurement of current. For measurement of voltage across the terminals of coulometer
FIG.- 6.3- EXPERIMENTAL ARRANGEMENT FOR CHARGING AND STRIPPING OF A COULOMETER TIMER.
DC microvoltmeter PP 9004 is used. The experimental arrangement for charging and stripping is shown in Fig. 5.3. The coulometer timer is charged or set at different time intervals by passing constant current through electrolyte. During charging or setting silver electrode is kept at positive potential and graphite electrode at negative. Silver ions are transported through the electrolyte and deposited on graphite electrode according to cell reaction discussed in section 5.2. At strip or discharge action, the polarity of constant current source is reversed. During discharging or stripping the silver deposited on graphite electrode is transported back to silver electrode through electrolyte. The voltage across the cell suddenly surge when all the silver is stripped.

6.4 Studies of Characteristics of Coulometer Timer:

The following characteristics of the coulometer $\text{Ag/Ag}_{2}\text{I}_{3}/\text{C}$ are studied.

1) Stripping action - The coulometer cell is charged at 100 $\mu$A current for 240 sec. charge time and is stripped at 100 $\mu$A current at 40°C. The stripping action is shown in Fig. 5.4. The stripping actions are observed by varying charging and stripping current from 20 to 100 $\mu$A for 50 sec. charge time and then for other charge time between 50 to 240 sec. also.
**FIG. 6.4 - STRIPPING OF COULOMETER Ag/NH₄Ag₄I₅/C**

CHARGE 240 SEC AT 100 μA, STRIP 100 μA.
(ii) Maximum Stripping Voltage Vs. Stripping Current Characteristics.

At the end of a stripping cycle, the maximum voltage across the terminal of coulometer is observed by varying charge-discharge current from 20 to 100 μA for 50 sec. charge time at 40°C. The curve for the above is shown in Fig. 6.5.

(iii) Cut off time Vs. Number of Stripping Cycles Characteristics.

The coulometer is charged and stripped successively up to 40 cycles at 50 μA charge-discharge current for 50 sec. charge time. In each stripping cycle, cut off time is observed for cut off voltage 0.45 V at 40°C and 80°C. Variation of cut off time with number of stripping cycles are shown in Figs. 6.7 and 6.8. In Fig. 6.9 the same characteristic is shown when coulometer is operated at 100 μA charge-discharge current for 240 sec.

(iv) Stripping Voltage Vs. Time Characteristics.

There is successive charging and discharging of the coulometer up to 40 cycles at 50 μA charge-discharge current for 50 sec. charge time. Variation of stripping voltage across the terminals of coulometer with time is observed in 1st, 10th, 20th, 30th and 40th cycle at 40°C and 80°C taking cut off voltage to be 0.45 V. The characteristics at 40°C and 80°C are shown in Figs. 6.10 and 6.11 respectively.
FIG. 6.5- CUT OFF TIME VS STRIPPING CURRENT.
CHARGE 60 SEC. CUT OFF VOLTAGE 0.45V
TEMPERATURE 40°C.
**Fig. 6.6**—Maximum terminal voltage vs stripping current. Charge 60 sec, temperature 40°C
FIG. 6.7 - CUT OFF TIME VS NUMBER OF STRIPPING CYCLES
CHARGE 60 SECONDS, TEMPERATURE 40°C.
CHARGING CURRENT 500 mA, STRIPPING CURRENT 500 mA.
Fig. 6.8 - Cut off time vs number of stripping cycles
Charge 60 seconds, temperature 80°C.
Charging current 50 μA.
Stripping current 50 μA.
**FIG. 6-9** - CUT OFF TIME VS NUMBER OF STRIPPING CYCLES. CHARGE 240 SEC. TEMPERATURE 40°C CHARGING CURRENT 100 µA. STRIPPING CURRENT 100 µA.
FIG. 6.10 - STRIPPING VOLTAGE VS TIME

STRIPPING CURVES FOR 1st(a), 20th(b), 30th(c), & 40th (d) CYCLE.

CHARGE 60 SEC. AT 50μA.

STRIP 50μA - CUT OFF 0.45 V.

TEMPERATURE 40°C.
STRIPPING CURVE

- 1st — ○
- 10th — □
- 20th — △
- 30th — ●
- 40th — ◆

+ 0.45 V CUT OFF

STRIPPING VOLTAGE (VOLTS)

10 20 30 40 50 60

TIME (SECONDS)

FIG. 6.11 — STRIPPING VOLTAGE VS TIME.

CHARGE 60 SEC. AT 50μA. STRIP 50μA.

TEMPERATURE 80°C.
Charging Voltage Vs. Number of Charging Cells Characteristics.

The coulometer cell is charged and discharged successively up to 40 cycles at 50 μA charge-discharge current for 60 sec. charge time. At the end of each charging cycle, charging voltage is observed across the terminals of coulometer.

6.5 Results and Discussion:

During stripping when all the silver plated on indicator electrode is transferred back to silver electrode, the voltage across the terminals of coulometer rises suddenly. Sharpness in the rise of voltage is the measurement of sensitivity of coulometer-timer. The stripping action of coulometer-timer Ag / NH$_4$AgI$_5$ / C is shown in Fig. 6.4. The final rise in this voltage Vs. time curve is sharp. The sensitivity of the coulometer also depends on its capacitance value which is determined by:

\[
C = \frac{1}{\frac{dv}{dt}} \quad (6.1)
\]

This is not true capacitance due to faradaic effects which include oxidation of impurities at indicator electrode and oxidation of indicator electrode itself at high voltages. The apparent capacitance calculated by formula (6.1) from Fig. 6.4 comes to be 1535 μF/cm$^2$ which is very high. This higher value of capacitance may be due to silver residing in the graphite grains boundaries being oxidized at higher voltages.

For cut off voltage 0.45 V, variation of cut off time with
charging stripping current is shown in Fig. 6.5. From this figure it is seen that cut off time increases sharply for lower stripping currents and remains nearly constant at higher stripping currents (more than 80 μA). The main function of coulometer is to store charge in the form of silver atoms on the indicator electrode and to determine this charge by anodic stripping. Low cut off time at lower currents may be due to storage of very small amount of silver atoms at graphite electrode during charging. This small amount of silver is anodically stripped in short time from graphite electrode and stripping voltage rises early. The cut off time is small at lower currents due to low efficiency of coulometer. Kennedy et al.\textsuperscript{4,5} also reported the low efficiency of coulometer at lower currents.

Variation of voltage across the terminals of coulometer at the end of stripping cycle with charging-discharging currents is shown in Fig. 6.6. It is observed that this maximum voltage increases with increase in charging stripping currents. At lower currents, rise in maximum stripping voltage is faster while at higher currents, it is constant. At lower currents, at the completion of stripping cycle, there is a possibility of some quantity of silver residing on graphite electrode. The final voltage rise is small due to silver activity of residing silver at one side of electrolyte. With the increase of charging stripping currents the quantity of residing silver decreases and the voltages across the terminals of coulometer increases and at
higher currents (more than 30 μA) the voltages remain constant. In other words we can say that efficiency of the coulometer increases with increase of charging discharging currents and above 30 μA its efficiency is good.

Variation of cut off time with number of stripping cycles at 50 μA charging discharging current for 50 sec. charge time is shown in Fig. 6.7 at 40°C and in Fig. 6.8 at 80°C. The same at 100 μA charging discharging current for 240 sec. charge time at 40°C is shown in Fig. 6.9. The errors in cut off time are within 04-20% of true value in Fig. 6.7, 13-37% of true value in Fig. 6.8 and 06-35% of true value in Fig. 6.9. In all the operations, errors are negative. These negative results obtained may be attributed to the migration of silver ions into graphite grain boundaries to become essentially 'lost'. It is seen from Fig. 6.7 that cut off time increases with number of stripping cycles up to 20 cycles, then it remains nearly constant. During observation it is seen that charging voltage remains constant throughout the charging in each cycle in multiple charging discharging up to 40th cycle. It means that silver electrode is not polarized. The increase in cut off time may be due to (a) polarization of graphite electrode, (b) saturation of accessible sites in graphite electrode. At lower number of stripping cycles accessible sites are unsaturated so that cut off time is low. As number of stripping cycles increases, accessible sites may approach
saturation. So cut off time increases and increase in cut off time is slow with increase in number of stripping cycles. After 20th cycle, due to complete saturation of accessible sites of graphite electrode, cut off time is large and remains constant with increase in number of stripping cycles. At temperature 80°C, the cut off time increases up to 30 cycles and then it becomes constant. The accuracy is poor at this temperature than at 40°C. This may be due to presence of some electronic conducting impurity. In this case at higher temperature a solid electrolyte would exhibit a small residual current i.e., a steady state current flows when a constant voltage below the decomposition potential is applied and it would effect the cut off time. This will not effect the cut off time at 40°C due to very low electronic contribution. At higher charging discharging current (100 μA) the increase in cut off time is uniform up to 15 cycles and then it remains nearly constant as seen from Fig. 6.9 but at 50 μA charging discharging current, the cut off time first increases rapidly and then uniformly (Fig. 6.7). This may be due to increase in efficiency of coulometer with increase in charging discharging current as discussed earlier (Fig. 6.5).

Variation of stripping voltage across the terminals of coulometer with time for 1st, 20th, 30th and 40th cycle at 40°C is shown in Fig. 6.10 and at 80°C in Fig. 6.11. It is observed
from these figures that sudden rise of stripping voltage decreases with increase in number of charging discharging cycles. If we calculate the capacity for electrolyte/graphite interface for 1st, 20th, 30th and 40th cycle, using formula (6.1) it comes out to be 45, 1023, 1125 and 1324 μF/cm² respectively. This shows that graphite electrode is polarizing with increase in charging discharging cycles due to silver residing.

During multiple charging discharging cycles of coulometer maximum charging voltage across the terminals of coulometer is observed at the end of each charging cycle up to 40 cycles. It is seen that maximum charging voltage remains the same at the end of each charging cycle in all 40 cycles. It proves that silver electrode is not polarized during multiple charging discharging cycles.

This solid electrolyte coulometer with graphite indicator electrode is giving negative error in cut off time. Its graphite electrode is polarized with increase in number of charging discharging cycles but silver electrode remains unpolarized. The favourable result is that its stripping curve or cut off curve is very sharp.

Note: A paper entitled "An Electrochemical cell with solid superionic NH₄Ag₄I₆ as the electrolyte" (Paper No. 3.4) was presented at the Symposium held on Solid State Electrochemistry and Electrophysics on 31-3-94 at Central Electrochemical Research Institute, Karaikudi, Tamilnadu.
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2. Electronics, 40, No. 7, 186 (1967).

