INTRODUCTION

It has been true throughout human history that knowledge has given rise to practical results and practical results have given rise to knowledge. Similarly we say science contributes to technology and technology to science. In the modern world there is most urgent need for better and cheaper technology to satisfy the ever increasing demands for energy. Technology since its inception has been associated with coal, then with oil and coal and more recently with oil natural gas and coal. Eventhough energy is a natural resource, energy crisis due to exhaustion and escalating cost of these sources leads to new sources which are abundant, clean and cheap. The other sources are atomic, solar, wind, tide and geothermal and hydrogen. Present resource consuming economy will bring many more difficulties in the future. Energy and economy are closely connected, eventhough there is difference in different countries. Insight and estimation of every demand and resource need national, international plans and programmes to improve the quality of life of vast majority of the people in the world. There is no single simple answer to the energy problem we face today. The complexity of the energy issue and its importance to society compel us to explore the options seriously, carefully and with attention to the consequences. The total energy that we use to sustain our present civilisation amounts to barely 1/600000 of the solar energy that reaches the earth. This shows the tremendous potentiality of this inexhaustible energy source. To conserve
such energy to use at high altitudes, remote places and arctic regions we are bound to create new battery technology.

1.1. History of battery

Development of the battery system began undoubtedly with Volta's experiments about 200 years ago (1791). He combined metals like copper, silver as positive with zinc, tin as negative electrodes in simple salt electrolytes. His remarkable discovery gave high currents in the order of amperes and produced high voltages by combining cells into piles. Modifications and improvements of Volta's cell were carried out by many innovators like Daniel, Grove and Bunsen. In 1860 Leclanche [1] constructed the first cell with restricted electrolyte using MnO$_2$ as positive electrode and zinc as the negative electrode. Gaston Plante [2] built a true secondary acid battery using lead and sulphuric acid. In the year 1881 the origin of alkaline battery started using zinc and copper oxide as electrode materials and KOH/NaOH as electrolytes. In 1893 zinc/CuO, known as Waddel-Entz battery, was used in New York to power a trolly car line [3]. Then battery scientists like Ruben, Edison, Jungner and others brought out more reversible, highly reliable, high energy and high power systems. After 1970 new lithium batteries, sealed Ni/Cd, lead/acid and zinc chloride systems appeared. The stringent performance and reliability requirments for modern weapons, equipment for present and future have led to the development of new systems and improvement of established systems.
1.2. Types and classification of batteries [4-7]

The word battery, originally used for the assembly of cannons and for the apparatus obtained by capacitor connections, was applied first for the array of galvanic cells by Humphry Davy in 1801. Figure 1.1 and 1.2 illustrate the scenario of the developments of various electrochemical systems.

The concept of electrochemical energy conversion from chemical energy can be accomplished by a suitable choice of a battery system. Batteries are unique in many ways. They are "living dynamic systems that respond to the environment in ways not commonly observed with other electrical components. A multiplicity of coupled chemical reactions transform chemical energy into electrical energy inside the battery whenever connected to a load. Batteries are available in many different shapes and sizes. They can be classified into many ways depending on their nature or on their operating temperature or on the electrolyte used, positives used and high power and low power applications. Table 1.1 [8] illustrates the classification of batteries based on the electrolyte used. However, in general, batteries can be classified under four major heads as given below.

1.2.1. Primary batteries

These are designed for single discharge but not for recharge. Generally, they have good energy density and good shelf life. Primary batteries are widely used in small to big sizes. They are Zn, Mg, Li anodes based batteries.
Fig. 4.1 Scenario of the development of various electrochemical power sources.
Fig. 1. 2. SCHEME OF THE DEVELOPMENT OF VARIOUS ELECTROCHEMICAL POWER SOURCES.
### TABLE 1.1

Battery systems based on electrolytes

<table>
<thead>
<tr>
<th>Acid</th>
<th>Neutral</th>
<th>Alkaline</th>
<th>Non-aqueous Solvents</th>
<th>Solid Electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn/HCl₂</td>
<td>Sn/AgCl</td>
<td>Sn/KOH</td>
<td>Li/MnO₂</td>
<td>Li/LiCl-KCl/FeS</td>
</tr>
<tr>
<td>Pb/H₂SO₄</td>
<td>Pb/Ag₂O</td>
<td>Sn/KOH/Fe</td>
<td>Li/SO₂</td>
<td>Na/β-Alumina/S</td>
</tr>
<tr>
<td>Fe/HCl₂</td>
<td>Mg/Ag₂O</td>
<td>Sn/KOH/HgO</td>
<td>Li/SOCl₂</td>
<td>Ag/RbAgI₂</td>
</tr>
<tr>
<td>Mg/Mg(ClO₄)₂/m-DNB</td>
<td>Zn/KOH/NO</td>
<td>Fe/KOH/NiO</td>
<td>Li/FeS</td>
<td>etc.</td>
</tr>
<tr>
<td>Zn/KOH/Air</td>
<td>Ni/KOH/H₂</td>
<td>Zn/KOH/NiO</td>
<td>Li/(CF)n-</td>
<td></td>
</tr>
<tr>
<td>Cd/KOH/NiO</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni/KOH/H₂</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
1.2.2. Secondary batteries

Batteries designed for many recharges to save cost are known as secondary batteries. Common examples are lead acid, alkaline Ni/Cd and non-aqueous Li batteries.

1.2.3. Mechanically rechargable batteries

In these batteries after discharge one of the electrodes namely anode is renewed. Advantage of this type is rapidity of recharge over conventional secondary batteries. Examples are Al/air and Zn/air.

1.2.4. Hybrid batteries

This battery includes a cathode which consumes gas like fuel cell, while the anode used is itself consumed. Examples of hybrid batteries are Zn/bromine, Zn/air and the latest Zn/lead dioxide.

1.3. Concepts of battery

Battery consists of two or more cells, connected in series or parallel or both depending on the desired output voltage and capacity.

- Anode or negative electrode is the reducing or fuel electrode which gives up electrons and is oxidised during the reaction.

- Cathode or positive electrode is the oxidising electrode which accepts electrons.

- Electrolyte is an ionic conductor which provides the media for transfer of electrons as ions within the cell between anode and cathode. It is a liquid such as water or other solvents with dissolved salts or acids or alkalis to impart ionic
conduction. Some batteries use solid electrolytes which are conducting at optimum temperature of the cell.

A good anode should be an efficient reductant, or electron donating, with good conductivity, should be stable and suitable for easy fabrication. A good cathode should have efficient electron accepting property, good stability, low cost, and useful voltage. The cell discharge reaction in a system can be schematically represented by the Figure 1.3. The left side electrode or anode is getting oxidised yielding electrons while the right side electrode is getting reduced accepting electrons. After the discharge of the cell or as the result of electrochemical reaction, the change in volume of the negative and positive electrode material is represented by the Figure 1.4. Batteries are fabricated in different shapes and configurations depending upon the needs and requirements. Battery configurations are cylindrical, flat and prismatic with venting or without venting.

1.4. Thermodynamics of battery system

A battery comprises anode and cathode which participate in the cell reaction. The anode generates electron and the cathode accepts the generated electrons. The flow of electrons takes place through the external load and the ionic conduction through the electrolyte. To understand the thermodynamics of the battery system, the first invented Daniel cell can be considered.

Anodic reaction at the zinc anode:

\[ \text{Zn} \rightarrow \text{Zn}^{2+} + 2\text{e}^- \]  

\[ \text{1.1} \]
Fig 1.3 SCHEME OF AN ELECTROCHEMICAL CELL
(DISCHARGE REACTION)
Fig. 1.4  VOLUME CHANGE DURING DISCHARGE
Cathodic reaction at the copper cathode:

\[ \text{Cu}^{2+} + 2e^- \rightarrow \text{Cu} \]  \hspace{1cm} \text{1.2}

Overall reaction in the Daniel cell:

\[ \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Zn}^{2+} + \text{Cu} \]  \hspace{1cm} \text{1.3}

The enthalpy change for the reaction at 25°C is

\[ \Delta H^o = -227 \text{ kJmol}^{-1} \]

During the cell reaction, heat will be released and energy will be dissipated in the load. This is expressed as the equation

\[ -\Delta H = -q + VdQ \]  \hspace{1cm} \text{1.4}

Here \( V \) is the cell voltage and \( Q \) is the electrical charge. At equilibrium, no current passes and \( V \) assumes maximum equal to \( E_{th} \), \(-q\) reaches its minimum value of \( T\Delta S \) where \( T \) is the absolute temperature and \( \Delta S \) is the entropy change in the reaction.

\[ -\Delta H = -T\Delta S + E_{th} nF \]  \hspace{1cm} \text{1.5}

where the charge \( Q \) is given as the product of \( n \) (number of \( \text{mol} \) of electrons passed) and \( F \) is Faraday (the charge per electron). The latter is equal to 96487 C mol\(^{-1}\) and \( E_{th} \) of Daniel cell is 1.12V if all the cell components are at unit activity. The maximum electrical work available is:

\[ -\Delta G = nE_{th} F \]  \hspace{1cm} \text{1.6}

Where \( \Delta G \) is the Gibbs free energy change of the reaction, in

\[ \Delta G = \Delta H - T\Delta S \]  \hspace{1cm} \text{1.7}
The potential of 1.12 V generated at equilibrium by the Daniell cell can be expressed as the difference between the individual potentials associated with the electrode reactions given by equations 1.1 and 1.2. As it is impossible to measure individual electrode potentials in an absolute sense, they are each measured with reference to another electrode which is used as a standard. The electrode normally chosen for this purpose is the standard hydrogen electrode (SHE) which in practice is usually composed of a platinum black foil immersed in a solution of hydrogen ions of unit activity and saturated with hydrogen gas at a partial pressure of 1 atm. With this electrode as reference and assuming electrolytes are at unit activity, the zinc electrode reaction, equation (1.1), produces an electrode potential $E_{Zn/Zn^{++}}$ of $-0.76\, V$, and the copper electrode reaction, equation (1.2), gives a potential $E_{Cu^{++}/Cu}$ of $+0.36\, V$. It is possible to calculate the overall theoretical cell potential, $E_{th}$, by subtracting the anode electrode potential, $E_{anode}$, from the cathode electrode potential, $E_{cathode}$, giving the expression

$$E_{th} = E_{cathode} - E_{anode} \quad \cdots \cdots \cdots \cdots 1.8$$

In the case of the Daniell cell this becomes the equation

$$E_{th} = E_{Cu^{++}/Cu} - E_{Zn/Zn^{++}} \quad \cdots \cdots \cdots \cdots 1.9$$

When the cell components possess activities of unity

$$E_{th} = 0.36 - (-0.76) \quad \cdots \cdots \cdots \cdots 1.10$$

$$= 1.12\, V.$$ 

If the direction of equation 1.3 is reversed, denoting a cell charging reaction, the cell voltage, by this convention, would be
This example of Daniell cell for thermodynamics of battery system is given in the Modern Battery Technology by C.D.Tuck.

1.5. **Effect of temperature and temperature co-efficient of voltage**

The capacity and voltage characteristics of battery system are affected by the temperature at which the battery is discharged. At lower temperature the ionic mobilities are decreased leading to an increase in internal resistance of the battery. As the operating temperature of battery is lowered, cell capacity is reduced and the slope of the discharge curve increases indicating the increase in internal resistance of the battery.

At higher temperature also, there is loss of cell capacity due to rapid chemical deterioration during discharge. The extent of deterioration depends on the temperature of battery system. The cell voltage decreases as the rate of discharge increases. This rate of cell voltage decrease is usually more rapid at the lower temperature.

According to the Gibbs-Helmholtz equation the heat content change (H calories) in a reaction is given by

\[
\Delta H = -nFE + nFT\frac{dE}{dT}
\]

where \( \Delta H \) is the heat content change, 'n' is the number of
electron involved in the reaction (the no of equivalent of chemical reaction), \( F = 96,500 \text{C} \), \( T \) is the temperature in Kelvin, \( (dE/dT)_p \) is the temperature coefficient of the cell EMF (E) at constant pressure P, 4.18 is the conversion factor from international Joule to calories.

1.6. Electrochemical Techniques used for Battery Development

Electrochemical techniques used for the electrochemical investigation can be applied for studying the properties of battery materials. If the single electrode is effectively studied, battery couple can be assembled and tested and studied using the above techniques. Partly or fully assembled battery electrodes are subjected to the electrochemical techniques to understand the secondary phenomena like size effects, electrode morphology and potential distribution.

1.6.1. Single Electrode Study

Simple D.C. technique is to use three electrodes namely working, counter and non polarisable reference electrodes. The reference electrode is connected to the working electrode through a narrow electrolyte-filled luggin capillary. These three electrodes are immersed in the particular battery electrolyte using a special electrical circuit. In a battery mode a constant current is passed and the potential between working and reference electrode is recorded. The potential drop due to the use of luggin capillary is given as

\[ V_{iR} = \frac{id}{k} \] \( \text{(1.12)} \)

where 'i' is the operating current, \( k \) is the distance between the specimen and the tip of the capillary and 'd' is the effective distance at which the potential is measured.
Galvanostatic and potentiostatic measurements made on negative electrodes, are useful to characterise single battery electrodes.

1.6.2. Two Electrodes Study

To study the cell performance and energy availability, the cell is simply discharged at constant load or with an applied constant current. Figure 1.5. shows the nature of discharge as the result of the effect of constant load and constant current modes of discharge. The regions of discharge denoted by A, B, C, reveal the polarisation of the electrodes. In the constant current discharge mode the initial fall (A) in voltage due to electrochemical polarisation is gradual. When the dissolution of the electrode material takes place, the internal resistance increases gradually bringing the gradual decline of the voltage as shown by B. When the depletion of active material leads to enormous increase of internal resistance, the final voltage falls rapidly as shown by C. But constant load drain leads to high initial current and low final current as a result of initial high voltage. Discharge nature varies depending upon the conductivity change of the electrolyte or that of reduction products like magnesium\silver chloride system.

1.6.3. Cyclic Voltammetry

Linear sweep voltammetry is a simple potential sweep technique which involves sweeping the electrode potential between limits of $E_i$ and $E_f$ at a known sweep rate $v$.

In a rechargeable system cyclic voltammetry is a useful technique in determining oxidation and reduction reactions. In this case the potential sweep may be halted, again reversed
Fig. 1.5 The typical voltage versus current behaviour observed for cells discharged under constant load and constant current conditions.
alternatively continued to the required potential. In cyclic voltammetry the current recorded is the function of voltage applied.

For a reaction

\[ 0 + n \text{e} \rightarrow R \] \hspace{1cm} 1.13

The important parameters that can be derived from Linear sweep voltammetry (LSV) and CV are the magnitudes of peak current \( (i_p) \), number of electrons, reactant molecule, rate constant, diffusion coefficient and electrochemical reversibility.

The peak current \( (i_p) \) for a reversible system is described by the Randles-Severk equation

\[ i_p = 2.69 \times 10^5 \ A \ n^{3/2} \ D^{1/2} \ v^{1/2} \ c \]

where 'A' is the area of the electrode, 'n' is the number of electrons involved in the process, 'D' is the diffusion coefficient of the species, 'v' is the sweep rate and 'c' is the concentration of the species \( \text{mol cm}^{-3} \). According to this equation \( i_p \) is directly proportional to concentration and \( v^{1/2} \).

In the case of reversibility of the system, the peak current is proportional to the scan rate when \( v \) the peak potential is independent of the scan rate. The peak width is given by the equation

\[ E_P - E_P/2 = 59\ n \text{mV} \] \hspace{1cm} 1.14

\[ (25^\circ \text{C}) \]

For reversible reaction, \( I_{pa} \) is equal to \( I_{pc} \) and peak separation \( E_P \) is given by an expression

\[ E_P = E_{pa} - E_{pc} = 59\ n \text{mV} \] \hspace{1cm} 1.15
The criteria for the completely reversible, quasi reversible, irreversible processes followed or preceded by chemical reaction are described in literature.

1.6.4. A.C. Techniques

A.C. Technique known as impedance spectroscopy can be applied to single electrode or full cells. Impedance data obtained from single electrode are useful and from cell is more useful and significant for better understanding of battery conditions and performance.

As in the case of D.C. signal, when A.C. signal is applied to the interface ohms law is applied. The impedance measured thus is given by

\[ Z = V_p / I_p \]  \hspace{1cm} 1.16

where \( V_p \) is the peak voltage and \( I_p \) is the measured peak current.

A Nyquist plot (plot of \( Z' \), the real component vs \( Z'' \) the imaginary component) of impedance spectroscopic data gives a semi circle with a radius of \( R_{ct} \sqrt{2} \) where centre lies on the \( Z' \) axis at \( R_s + (R_{ct}/2) \) where \( R_s \) is the electrolyte solution resistance and \( R_{ct} \) is the charge transfer resistance.

The apex of the semicircle is \( w_{z'' \text{max}} = \frac{1}{C_{dl} R_{ct}} \)

\( w_{z'' \text{max}} \) is the frequency at which \( z'' \) is maximum and \( C_{dl} \) is the double layer capacitance of the interface. Bode plots (log-log plots of the phase angle and absolute value of \( Z \) vs the A.C. frequency) are sometimes better suited for quantitative analysis.
of processes with short time scales. In spite of the complicating phenomena like roughness, porosity, adsorption of reactants and intermediates, A.C. techniques can be used to monitor battery state of charge or extent of depth of discharge in different battery systems.

1.7. **Physical Techniques Used**

In a battery system when the discharge continues, the chemical reaction takes place at or near the solid electrodes mainly. Due to this the solid electrodes face or undergo the physical changes which finally control the reaction path or ultimately the performance. Therefore in the development of a battery system the physical techniques have become essential to study surface morphological and composition changes.

1.7.2. **Electron Microscopy**

In this technique two methods used are transmission electron microscopy (TEM) and scanning electron microscopy (SEM). SEM is more widely used for battery development. A beam of electrons is manipulated electrically and electronically to produce images to analyse the surface. The secondary electrons emitted give an image to examine the specimen surface morphology and structure. TEM employs a beam of high energy electrons to penetrate the specimen and thus internal structure, grain boundary, crystal dislocation etc can be studied.

1.7.2. **X Ray Diffraction And Neutron Diffraction**

Information about the crystalline size, nature of the crystal, concentration of different phases can be studied by this technique. Neutron diffraction is more suitable for light and magnetic materials [9-10].
1.7.3. Electron Spectroscopy

This technique [11-12] comprising ultra model photo electron spectroscopy, (UPS)X ray photo electron spectroscopy (XPS) and Auger electron spectroscopy (AES) is used to enable surface element mapping with good resolving power.

1.7.4. I.R. and Raman Spectroscopy

To study non aqueous battery, identify species in battery electrolytes, polymer battery materials, I. R. and Raman spectroscopy [13-17] have been used. Surface films on lithium in non aqueous solvents are studied mainly by I.R. spectroscopy whereas Raman spectroscopy is highly useful in the study of solute molecules and adsorbed solvent as well as decomposition products in non aqueous electrolytes.

1.7.5. Thermo gravimetric analysis (TGA) and Differential thermal analysis (DTA)

These techniques [18-19] study the thermal properties of substances which are heated or cooled in a controlled manner. DTA is more refined technique which records the peak changes at characteristic temperature with respect to a reference sample. This method is used to study the behaviour of beta manganese dioxide and other battery materials.

1.7.6. Analysis of particulate battery material

Surface area of particles, [20-22] porosity and density of the porous battery material have significant effect on both physical, chemical and catalytic properties. Pore size and pore
size distribution measurements are also important for understanding the performance. Brunauer, Emmet and Teller (BET) [23-24] method which measures the quantity of adsorbate gas at equilibrium pressure is used for measuring surface area. Mercury porosimetry which measures the volume of mercury which enters the pores gives the analysis of micro and macro pores and porosity measurement.

1.7.7. Particle sizing and counting

Irregularly shaped particles are used as battery materials. To have better understanding of size effect on the performance, optical microscopy and advanced electron [25-26] microscopy are helpful for determining the number and size of particles suspended in a suitable electrolyte. Laser diffraction [27-28] technique is the latest one in this area.

1.8. Battery inefficiency

1.8.1. Self discharge

When a battery is discharged the electrode materials change to give or generate external current. In addition to the main reaction side reaction occurs. In aqueous electrolytes hydrogen is produced at the anode as side reaction. This hydrogen evolution reaction at anode is due to the presence of noble element impurities which have low hydrogen overvoltage. In addition it depends on the dissolution rate and solubility of the reaction products. In the case of secondary batteries, self discharge occurs at fairly high rate (2 to 5% per week). In the case of primary batteries self discharge rate is very low, for example leclanche dry cells gives 90% of its original capacity.
even after their storage for one year at room temperature. This corresponds to a self discharge rate of 0.2 % per week.

1.8.2. Passivation

When the battery electrode reacts with the battery electrolyte the surface of the electrode is passivated due to film formation. This passivation reduces the battery voltage and leads to difficulties in achieving the required voltage level immediately upon switch on. In magnesium batteries magnesium hydroxide film is coated on the anode. This film is beneficial for storage but causes a voltage delay effect when the battery is activated. In lithium batteries also this type of porous passive film is formed in non aqueous electrolytes. This film displays properties possessed by solid electrolytes having high resistivity. Since the films act as separating media between the metal and electrolyte, they are called solid electrolyte interface.

1.8.3. Dendrite growth and shape change.

In secondary batteries like silver oxide-zinc and lithium batteries, the dissolved anode material is getting redeposited during charging. Dissolution and deposition processes continue during cycling of the battery. As a result of the above process dendrites are formed on the negative electrodes and the deposit is uneven. Finally the shape of electrode also changes.

1.9. Inorganic Positives

Most of the inorganic depolarisers are non conducting salts or oxides. Some of them are used for primary, secondary or
for both. Since conductivity and rigidity of the electrodes are important for better performance, these cathode materials are mixed with conducting materials like carbon or acetylene black and binders like carboxy methyl cellulose or polyvinyl alcohol. Cathodes prepared as mentioned above are used for fabrication of cells or batteries. Even though many cathode materials like oxides, peroxides, persulphates, halides, sulphides and sulphur are available, four important positive materials are copper oxide, manganese dioxide, silver oxide and nickel oxide. Details of these extensively used positives are reported below.

1.9.1. Copper oxide

Copper oxide is the first positive active material used in the first alkaline zinc secondary battery in 1882 [29]. This old system was used in railway signalling devices. When copper oxide is reduced, it is not reduced directly to copper state because cuprous oxide is formed by the combination of copper oxide with copper. Since cuprous oxide is highly non conducting, the reduction efficiency and operating voltage is low. Addition of sulphur improves both voltage and efficiency [30].

1.9.2. Manganese dioxide

This cathode material is cheap and extensively used in the well known Leclanche system and later in alkaline system. The discharge reaction indicates two levels of discharge corresponding to \( \text{MnO}_2 \) to \( \text{MnO}_1.5 \) and \( \text{MnO}_1.5 \) to \( \text{MnO}_1 \) [31]. There are different forms of manganese oxide (alpha, beta, gamma and delta) differing in structure and performance. This cathode material gives higher capacity in the acidic aluminium chloride
electrolyte than in neutral electrolyte and it corresponds to two electron transfer as shown below[32].

$$\text{MnO}_2 + 4\text{H}^+ + 2\text{e}^- \rightarrow \text{Mn}^{2+} + 2\text{H}_2\text{O}$$

Depending upon the anode materials coupled like zinc, magnesium, aluminium and titanium, the theoretical capacity of these couples varies from 616 Wh/kg to 880 Wh/kg. The concentration of electrolyte, current density and other discharge conditions play important role on the performance capacity, and voltage of the systems. The reversibility of manganese dioxide positive is partial because complete reduction to $\text{Mn}_2\text{O}_3$ will not be reversible. Zinc alkaline manganese dioxide secondary is to be improved still to perfect the system.

### 1.9.3. Silver oxide

Silver oxide is an attractive inorganic positive active material used in high energy primary and secondary batteries. The standard potential of $\text{Ag}\text{Ag}_2\text{O}$ and $\text{Ag}\text{AgO}$ are $+0.342V$ [33] and $+0.599V$ [34] and the theoretical capacity of $\text{AgO}$ and $\text{Ag}_2\text{O}$ are $0.438 \text{Ah/g}$ and $0.244\text{Ah/g}$, respectively. Silver oxide has three different modifications namely monoclinic [35-36], tetragonal [37] and cubic [38]. The conductivity of $\text{Ag}_2\text{O}$ is lower than $\text{AgO}$. In alkaline solution $\text{AgO}$ decomposes slowly due to stable $\text{Ag}_2\text{O}$ formation and high oxygen overvoltage[39]. Discharge of silver oxide zinc batteries show two plateaus corresponding to the formation of $\text{Ag}_2\text{O}$ and $\text{Ag}$ at low current drain. For specific use this can be avoided by the use of additions like lead and palladium or at the loss of capacity. In silver oxide batteries high rate discharge is possible. But low rates of charge (10 to
20 hour rate) are necessary for good performance of the system.

1.10. Choice of battery anodes

Although a wide variety of anodes has been used in primary battery systems, relatively few have achieved practical success. Important and attractive anodes which offer the advantages of good shelf life, reasonably high power density, energy density, acceptable cost and reliability are zinc, magnesium, aluminium and lithium. A comparison of the commercially used anodes of primary batteries is shown in Table 1.2 [40].

1.10.1. Zinc

The most widely used battery material is zinc which is employed in Ruben cell, Leclanche cell, alkaline Leclanche cell and silver zinc cell. This material is more active than cadmium, cheaper and lighter. This anode is usually amalgamated to improve stability to decrease hydrogen evolution and to increase anodic efficiency. Alloying additions such as lead and cadmium improve mechanical properties and decrease corrosion respectively. Dry cells and acid electrolyte cells employ massive or sheet zinc electrodes. In alkaline electrolyte, zinc powder or zinc oxide stabilized in a gel structure forms the anode.

In the Leclanche cell, zinc dissolves anodically, then forms complexes with the electrolyte, the type of complex depending upon the solution composition on continued anodic discharge. Zinc build up in solution side leads to the formation
### TABLE 1.2

Comparison of commonly used anodes in Primary Cells

<table>
<thead>
<tr>
<th>Anode metal</th>
<th>$E^*$ at 25°C (V)</th>
<th>Density (g/cc)</th>
<th>Theoretical capacity (Ah/g)</th>
<th>Compatible</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>-0.76</td>
<td>7.14</td>
<td>0.82</td>
<td>Acid, Neutral, alkali</td>
</tr>
<tr>
<td>Al</td>
<td>-1.66</td>
<td>2.69</td>
<td>2.98</td>
<td>Neutral, alkali, nonaqueous solvents, fused salt</td>
</tr>
<tr>
<td>Mg</td>
<td>-2.38</td>
<td>1.74</td>
<td>2.20</td>
<td>Neutral, nonaqueous solvent, fused salt</td>
</tr>
<tr>
<td>Li</td>
<td>-2.43</td>
<td>0.54</td>
<td>3.86</td>
<td>Nonaqueous solvent, fused salt</td>
</tr>
<tr>
<td>Pb</td>
<td>-0.13</td>
<td>11.34</td>
<td>0.26</td>
<td>Acid</td>
</tr>
</tbody>
</table>
of insoluble products. On light discharge the compound ZnCl₂ 4Zn(OH)₂ is formed, while on heavy discharge the compound Zn (NH₃)₂Cl₂ is formed.

In alkaline cells zinc hydroxide and zinc oxide are formed during discharge. The product is converted to zinc during charging process. Changes in the morphology of zinc electrodes severely limit the cycle life of the battery. Shape change and dendrite formation are the difficulties faced in this case resulting in lower efficiency. Dendrite formation can be minimised by the use of additives such as lead, emulphogene and tetrabutyl ammonium chloride.

1.10.2 Aluminium

The half cell reaction for the anode discharge of aluminium are as follows [41]:

\[
\begin{align*}
\text{Al}^{3+} + 3e & \rightarrow \text{Al} \quad E^0 = -1.66V \quad \ldots \ldots \ldots \ldots \ldots 1.18 \\
\text{Al(OH}_3\text{)} + 3e & \rightarrow \text{Al} + 3\text{OH}^- \quad E^0 = -2.31V \quad \ldots \ldots \ldots \ldots \ldots 1.19 \\
\text{H}_2\text{AlO}_3^- + \text{H}_2\text{O} + 3e^- & \rightarrow \text{Al} + 4\text{OH}^- \quad E^0 = -2.35V \quad \ldots \ldots \ldots \ldots \ldots 1.20
\end{align*}
\]

High theoretical potential, low equivalent weight, availability and low cost are the attractive features of aluminium anode. The limitations of this anode are more corrosion, passivation and delayed action. These challenges are to be met to use aluminium as attractive useful anode. Aluminium is used for reserve batteries employing sodium hydroxide electrolyte. Another electrolyte used is aluminium chloride with chromate inhibitor. The anode efficiency varies with the current drain. Corrosion of aluminium is minimised by alloying with zinc
Lithium is very active, light and attractive anode dominating in the battery field in recent years. It is employed in non-aqueous electrolytes because of its reactivity with water [44-47]. High electrode potential, high energy density and compatibility with various cathode depolarisers brought out a number of primary and secondary systems. It is harder than other alkaline metals but softer than lead. Lithium reacts vigorously with oxygen and nitrogen and hence dry room facilities are essential for the assembly of lithium cells. Inspite of many advantages lithium possesses some demerits. They are the voltage delay on high temperature storage due to passivation [48-49] and the safety hazards associated with some lithium systems. Glove box facility is essential for research and development of lithium battery which is expensive.

Magnesium

The standard potential of magnesium is -2.34 V. However, the steady state working potential is generally in the order of 1.45 V [50] which is due to the magnesium hydroxide film formation over magnesium. The hydroxide film keeps the magnesium surface in passive state and it controls of corrosion and discharge.

The effect of pH on the corrosion rate of magnesium as well as magnesium alloy in acid and alkaline solutions has been studied by several authors. Below pH 3 corrosion increases, but
above pH 3 corrosion decreases and above pH 11.5 corrosion ceases due to the film formation. At lower pH, magnesium hydroxide film is very thin or penetrated due to lesser OH⁻ concentration, but at high pH values high concentration of OH⁻ ions precipitates Mg²⁺ on the anode forming thick magnesium hydroxide film. This film results in low potential, low corrosion and high polarisation. In the case of neutral magnesium salts, chloride ions are more corrosive than bromide ions. The shelf life and anode efficiency of magnesium [51] are greater in magnesium perchlorate than in magnesium chloride and magnesium bromide electrolytes. Anode efficiency is above 70% in magnesium perchlorate solution. But even in less corrosive magnesium perchlorate solutions more heat is evolved at high current drain. This disadvantage leads to lower capacity and designing difficulty of magnesium batteries. At low temperature this becomes advantageous. In organic salt electrolytes it gives more coulombic capacity with good voltage. In inorganic electrolyte the corrosion of magnesium anode increases with current density. This is known as negative difference effect. Intensive corrosion around the grain boundaries is known as chunk effect. These lead to premature cell failure due to non-uniform corrosion.

To minimise corrosion of magnesium anode, impurities like iron, copper and nickel have to be avoided in the electrolyte used and suitable inhibitors like lithium chromate and barium chromate [52-55] can be added to the electrolyte. The stability of this anode can be increased by adding some alloying agents like Al, Pb, Zn and Mn [56-58]. Film formation and
corrosion are controlled by the addition of these elements. Table 1.3 presents composition of major constituents in different magnesium alloys in percentage [59].

1.10.5. Titanium, Manganese and Indium

Inspite of oxide film formation on titanium, titanium is used as battery negative electrode with MnO₂ as positive using fluoride electrolyte. Its OCV is 1.75V [60] Ti/lead dioxide cell system shows higher potential of 2.2 to 2.7V. It is used as reserve cell using fluoborate as electrolyte. Alloying elements like Ni, V and Mo [61-62], improved the performance of this anode. Indium is a soft and light metal. Indium is alloyed with 1% Bi. Addition of lithium improves its capacity [63]. Indium/AgO system with alkaline solution is reported.

Manganese can be used as a negative electrode in reserve batteries like Mn/AgCl[64] using NaCl, CaCl₂ and perchloric acid.

1.11. Cathode materials in Magnesium batteries

Magnesium anode has been employed with different types of cathodes and shows different operating voltages(Table-1.4)[65]

Various versions of magnesium cells viz.reserve, wet and dry are known to exist. Most of these types of cells employ aqueous medium during discharge operations whilst a new trend has now begun with non-aqueous electrolyte systems for the futuristic magnesium secondary batteries.

1.11.1. Magnesium dry cells

Magnesium dry cells are fabricated by using magnesium alloy(AZ 31, AZ61, AP65) as anode, manganese dioxide as cathode
<table>
<thead>
<tr>
<th>Alloys of Magnesium</th>
<th>Al</th>
<th>Pb</th>
<th>Zn</th>
<th>Tl</th>
</tr>
</thead>
<tbody>
<tr>
<td>AZ 31</td>
<td>2.5-3.5</td>
<td>--</td>
<td>0.7-1.3</td>
<td>--</td>
</tr>
<tr>
<td>AZ 31 B</td>
<td>2.5-3.5</td>
<td>--</td>
<td>0.6-1.4</td>
<td>--</td>
</tr>
<tr>
<td>AP 65</td>
<td>6</td>
<td>5</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>AZ 61</td>
<td>6</td>
<td>--</td>
<td>1</td>
<td>--</td>
</tr>
<tr>
<td>MTA 75</td>
<td>5</td>
<td>--</td>
<td>--</td>
<td>7</td>
</tr>
<tr>
<td>Cathode materials</td>
<td>Operating voltage (V)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiO</td>
<td>2.0 to 1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgO</td>
<td>1.7 to 1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>HgO</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>MnO₂</td>
<td>1.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgCl</td>
<td>1.6 to 1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbCl₂</td>
<td>1.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cu₂Cl₂</td>
<td>1.1 to 1.3</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>m-DNB</td>
<td>1.1 to 1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi₂O₃</td>
<td>1.1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuO</td>
<td>1.0 to 0.9</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
and magnesium perchlorate as electrolyte. The basic cathodic reaction is:

\[
\text{MnO}_2 + H_2O \rightarrow \text{Mn(OH)}_2 + \text{Mn}_2\text{O}_3 \quad \text{1.21}
\]

A kraft paper separator keeps the anode and cathode apart but still permits ionic conduction. The cell container made from the rolled magnesium itself serves as the anodic material of the dry cell device. The cells are basically similar to the conventional carbon-zinc dry cells. Presently the magnesium dry cell is considered as one of the important power sources for military communication equipments. Yet the utility distribution for the civilian market is awaited.

Magnesium dry cells possess several advantages like high energy density, high cell voltage, good low temperature performance, good capacity retention even under high temperature storage and low cost.

1.11.3. Reserve battery

Reserve battery is one which is kept in reserve and operates when it is activated with its electrolyte. To increase the shelf life of a primary battery, self discharge has to be minimized. This is done by separation of electrode and electrolyte. The configuration of reserve cells depends upon the application whether they work for short period of time varying from minutes to hours or days. The efficiency of the system, operating voltage and stability of discharge voltage depend upon the nature of cathode materials used [66-67]. Magnesium reserve batteries find use in applications such as torpedoes, sonobouy, beacons, pagers, lifejackets, weather ballons, oceanographic
equipment and other weapon systems. Lozier studied a number of cathode materials of high potential with magnesium anode in neutral magnesium perchlorate electrolyte. Operating voltages of different types of magnesium batteries are given in Table 1.4.

Cupric oxide has also been shown to be practicable both in conventional wet cells [68-70] and in sea water batteries but is seldom used because of high cost and low operating voltage.

Air depolarised cathodes [71-74] with magnesium anodes have shown higher operating potential than with zinc.

Magnesium-chlorine system has been studied and it has intrinsically high voltage of 2.8V to 2.9V as compared with 2.05V of its zinc counterpart. Magnesium with mercurous chloride, mercuric oxide,[75] and mercurous sulphate has been investigated. Mercurous chloride system can be drained at high current density with good efficiency.

The chlorides of lead, copper, silver, and silver sulphate have been used as cathode materials[76-79] in water activated batteries. Magnesium-manganese dioxide dry cell system has been used in the military communication equipments.

1.12. State of the Art of Organic active materials for Batteries

Energy economics and organic fuel conservation stimulate greater interest in new galvanic power sources including exploitation of all types of organic materials[80-82] in small and larger systems. Development of synthetic organic chemistry and new analytical techniques and depletiopn of primary resource like manganese dioxide ore have turned battery man’s attention to organic compounds. Generenally organic
compounds possess electrochemically and commercially attractive features: 1) relatively high coulombic capacity, 2) reasonably useful range of operating potential 3) acceptably low polarization loss and flat discharge voltage levels, 4) competitive cost and 5) availability in the country.

These are the factors which answer the question why organic depolarizer is used in batteries. Inspite of their defects like low conductivity, high complexity of reaction, and solubility and low specific gravity, organic compounds are gaining more importance in the recent years as primary cathode material and secondary positive electrodes.

During the last two decades, there has been an amazing spurt of activity in the development of primary cells with organic cathode materials. The reasons for this are: the depletion of the resources of high grade manganese ore and the rapid development of organic synthesis technology making possible large scale production of relatively cheap organic oxidants.

Rapid strides have been made in the field as shown by the astonishing number of organic raw materials proposed as cathode materials. A host of organic materials such as nitro and halogen substituted organic compounds and quinones have been used. Arsem in 1942 [83] widely expanded the patented organic depolarisers to include neutral, acid and alkali electrolytes as well as nitro compounds and their reduction products, positive halogen types and quinone compounds [84]. In 1951 Bloch described the use of quaternary alkyl halide derivatives while
Sargent in the same year reported the use of aluminium anodes with organic cathodes.

Morehouse and Glicksman in 1958-60 [85] and later Lozier of RCA studied the use of Mg anode in a series of galvanic cell systems employing many organic cathode depolarisers such as aromatic nitro compounds, aromatic nitroso compounds, nitroalkanes, azo compounds, quinone compounds, nitro-pyridine, heterocyclic compounds, and N-halogen compounds [86-88]. Subsequently the dry cells containing aromatic nitro compounds, aromatic nitroso-compounds, heterocyclic compounds and N-dichloro-p-toluene sulphonamide were developed by them.

The cathodic depolarisers were formulated by the RCA investigators who also described the screening test for a number of anodic compounds including hydrazine, hydroxylamine, hydroxy- and aminophenol.

A number of studies were carried out with quinone compounds. At first in 1957, cells with quinones were developed. Later Morehouse and Glicksman studied a system containing p-benzoquinone dioxide and quinone compounds with magnesium anode. Then in 1969, Alt et al patented chloroanil, iodonil and fluoronil in lithium battery with lithium perchlorate-methylcyanide electrolytes. In 1972 they reported the use of quinone compounds in lithium battery employing lithium propylene carbonate and LiClO₄ electrolyte. In the same year Alt published another paper with quinone/NH₄Cl secondary battery and quinone/zinc/H₂SO₄ system and a few more papers with quinone were also published. Quinone compounds yielded promising results and a host reports was published on chloroanil-anthraquinone system.
Subsequently in 1976, magnesium-di-chloro dicyanobenzoquinone system was reported. Recently napthoquinone-alkali anodes, pyrene-quinone, benzoquinone or its derivatives have been investigated [89-90].

Nitro-compounds are yet another class of compounds which have manifested superior performance. Stephen J.Bartosch patented m-dinitrobenzene and magnesium system in 1962 [91]. m-Dinitrobenzene has also been studied with magnesium anode in magnesium perchlorate electrolyte as dry cell, reserve battery and galvanic cell, with zinc anodes and with liquid NH$_3$KSCN electrolyte. Besides, susbstituted compounds of m-dinitrobenzene such as chloro-2,4-dinitrobenzene[92] and 2,4-dinitrophenol[93] have also been reported.

Other types of compounds such as azodicarbonamide, biurea [94] azobis [95] formamides, nitrothiazole, benzofuran oxide, polynuclear aromatic charge transfer complex, benzopheroximine thiazole and redox polyester[96] polymers have also been tried as possible cathode active materials. The classification of these organic compounds can be made arbitrarily as cathode and anode based on the functional groups. Table 1.5[97] presents the classification of organic compounds into anodic and cathodic materials.

1.12.1. Secondary organic cathode materials

Some of the organic compounds which are reversible in particular electrolytes are coupled with zinc and used as secondary organic positives. They are biurea and tetra chloroquinon1. The reversible characteristics of these compounds
TABLE 1.5

Classification of organic cathodes and anodes based on the functional groups

<table>
<thead>
<tr>
<th>Cathodes</th>
<th>Anodes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nitro group and related types</td>
<td>Phenols and related types</td>
</tr>
<tr>
<td>Positive halogens</td>
<td>Substituted ammonium compounds</td>
</tr>
<tr>
<td>Quinonoids</td>
<td>Alcohols</td>
</tr>
<tr>
<td>Per-bond, perox types, etc</td>
<td>Carbohydrates</td>
</tr>
<tr>
<td>Halogenoids</td>
<td>Carbonyls</td>
</tr>
<tr>
<td>Carbonyl groups</td>
<td>Hydrocarbons</td>
</tr>
</tbody>
</table>
have been studied already.

Biurea is very stable on storage so that prolonged storage in the discharge condition is possible. Rechargeable cells of these systems start with the discharged biurea product. In the case of chloroanil the flat discharge voltage is obtained in an electrolyte of 3N sulphuric acid. If pH of electrolyte is increased the discharge behaviour of chloroanil differs.

1.13.2. Nitro compounds

The best organic depolarisers are generally one of four types: Nitro compounds, positive halogen compounds, halogen addition compounds, and peroxide. All except nitro compounds have limited capacity due to two electron transfer and limited stability in aqueous solution. Nitro compounds have average voltage, but higher coulombic capacity and efficiency.

In addition to the established meta-dinitrobenzene as attractive cathode depolariser, other nitrocompounds are 2,5-dinitrobenzoic acid, 3,6-dinitrophthalic acid, 1,3,5-dinitrobenzene, and 2,4,5-trinitro toluene [98]. Among them, meta-dinitrobenzene is dominating as the organic depolariser due to practical advantages over other nitro compounds. One of the three factors controlling the reduction efficiency of meta nitrobenzene is pH of the electrolyte. In acid electrolyte like HBr, MgBr₂ it is reduced the efficiently. But this acid electrolyte cannot be used for batteries since the anodes will not withstand in acid electrolytes. In neutral electrolytes like MgBr₂, MgCl₂, Mg(ClO₄)₂, efficiency of cathode is comparatively less, but as a battery electrolyte Mg(ClO₄)₂ is
more suitable due to high anodic efficiency of Mg anodes. Moreover, it is better than MgBr\(_2\) because its salting in effect over metadinitrobenzene is higher than MgBr\(_2\). The solubility of metadinitrobenzene in different concentration of Mg(ClO\(_4\))\(_2\) has been found out by spectrophotometric and polarographic techniques. It is more soluble in 3M Mg(ClO\(_4\))\(_2\). since the pH of it is higher. lower concentration with good conductivity is preferred for better performance.

Electrochemical reduction of m-DNB is stepwise in the mildly acid to alkaline solution. The discharge capacities and the formation of products depends upon the pH of the electrolyte, operating potential or current drain and the catalytic nature of the current collector. As reported earlier the pH of electrolyte plays an important role in the reduction of m-DNB. The formation of intermediate products and the rapidity of reduction of the intermediate compounds are controlled by the shift of pH during the course of reduction. The potentiostatic reduction of m-DNB at the stationary graphite confirmed the easily achievable two four electron stages. Reduction in the lower pH in the aqueous electrolyte is found to form metanitro phenyl hydroxyl amine and 1,3-diamino benzene. Stephene J. Batosh patented meta dinitrobenzene and magnesium system in 1962 [99] and N.Muniyandi et al., [100] have patented magnesium/m-DNB system. Among the several substituted nitrocompounds, m-DNB based system has been studied much more extensively as dry cell [101-102] or as a reserve battery employing either magnesium [103-107] or zinc [108] as anodic material and also liquid NH\(_3\)-KSCN electrolyte
based wet cells were reported in the literature [109-112]. Besides, substituted compounds of m-DNB such as chloro-2,4-dinitro benzene [113-115], 2,4-dinitro toluene [116], 2,4-dinitrophenol [117] and para-nitroaniline [118] have also been investigated by several workers. Table 1.6 [119] shows the list of the theoretical capacities of different depolarisers. Attractive high capacity of m-DNB brings down the unit cost of nitro compounds. Organic electrophores in nitro compounds serve the function of electron sinks for the cathode current collector sources. Thus, electric charge transfer occurs and electrode products are formed. This occurrence is studied well to understand the mechanisms and technology. Attractive aspects of m-DNB are discussed below.

1) High theoretical capacity. As given in the table 1.6 the theoretical capacity is 1.92 Ah/g. This is due to the transfer of 12 electrons during the reduction process and is attractive both on volumetric and gravimetric basis.

2. Low cost: Even though the cost of some nitro compounds is high due to synthesis problems when compared with synthetic MnO₂ depolariser. The cost of m-DNB is comparatively low due to low production cost and high electron transfer.

3. Steady operating voltage. Mg/m-DNB cell shows steady voltage of 1.1 V during discharge unlike Mg/MnO₂. This is due to the solubility of reduced product of m-DNB and easy availability high energy depolariser at reaction sites.

The above analysis on the informations available about the utility of organic depolariser materials, in place of established low energy inorganic cathode materials, particularly
### TABLE 1.6
Comparison of cathode active materials

<table>
<thead>
<tr>
<th>Cathode material</th>
<th>Electrons transferred</th>
<th>Theoretical capacity (Ah g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td>1</td>
<td>0.18</td>
</tr>
<tr>
<td>PbCl₂</td>
<td>2</td>
<td>0.19</td>
</tr>
<tr>
<td>Chloroanil</td>
<td>2</td>
<td>0.22</td>
</tr>
<tr>
<td>PbO₂</td>
<td>2</td>
<td>0.22</td>
</tr>
<tr>
<td>CuCl</td>
<td>1</td>
<td>0.27</td>
</tr>
<tr>
<td>NiO₂</td>
<td>1</td>
<td>0.30</td>
</tr>
<tr>
<td>MnO₂</td>
<td>1</td>
<td>0.31</td>
</tr>
<tr>
<td>AgO</td>
<td>2</td>
<td>0.43</td>
</tr>
<tr>
<td>P-benzoquinone</td>
<td>2</td>
<td>0.50</td>
</tr>
<tr>
<td>CuO</td>
<td>2</td>
<td>0.67</td>
</tr>
<tr>
<td>m-dinitrobenzene</td>
<td>12</td>
<td>1.91</td>
</tr>
</tbody>
</table>
in the context of m-DNB has facilitated the following class of organic materials towards furthering their potentialities in the development of practically viable reserve battery system.

The effective utilization of electro-reduction behaviour of particularly organic nitro compounds has not been understood in the context of methods of enhancing its reduction behaviour for energy storage process. This indeed opened up avenues of probing different approaches wide the choice of grid material, nature of cathode mix and their respective understanding with choice of anode material and electrolyte composition. The understanding of the above issues also depends on their integrated behaviour in total battery systems as its components through capacity evaluation, optimization of current drain rate while delivering the required energy and its utility over wide temperature range. Such investigations are expected to provide a better understanding on the design and development of practically viable magnesium organic reserve battery with high energy density about which this thesis concerns.
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