

# Corrosion in Batteries

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A comprehensive coverage of corrosion in batteries is rendered difficult by the wide choice of materials, environments and physical features as obtained in practical settings. Understanding of the complex processes that occur in these electrochemical systems gets clearer as new theoretical approaches backed by sophisticated analytical and characterization techniques continue to provide valuable insights which aid in controlling/mitigating wasteful corrosion reactions which affect battery shelf-life, cycle life, rate capability and capacity. In the light of the above, I limit myself to a discussion on corrosion aspects in representative system such as conventional Leclanche, lead-acid battery and magnesium batteries, and advanced lithium systems.

**Keywords** : *Corrosion, Leclanche cell, lead-acid battery, nickel-metal hybride battery, lithium battery*

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## 1. Introduction

Corrosion is the destructive effect of parasitic chemical and electrochemical reactions that occur on metallic and other materials in contact with a variety of environs. Different forms of wet corrosion by liquid/solid electrolyte media such as pitting corrosion, uniform surface corrosion, erosion corrosion, stress corrosion, high temperature corrosion and hydrogen embrittlement manifest singly or in combination in battery systems. Since Volta's cell of 1800, a burgeoning variety of battery chemistries have emerged catering to such needs of a fleet-footed society as consumer electronics, telecommunications, defence, transport, space, information technology and medicine. Batteries may broadly be classified as

- aqueous systems (acidic electrolyte based ones such as the lead-acid battery, neutral electrolyte systems such as Leclanche and alkaline ones such as nickel- and silver-based cells)
- non-aqueous systems (lithium and lithium-ion batteries employing organic aprotic liquid electrolytes)
- solid electrolyte systems (polymer electrolyte based ones such as lithium/polymer batteries)
- high temperature cells (like the zebra cells and sodium-sulfur batteries with beta-alumina solid electrolyte)
- thermal batteries (such as those based on calcium and lithium)
- activated batteries or reserve batteries (in which the electrolyte is introduced at the time of use)
- fuel cells with acid, alkaline, molten carbonate or solid polymer electrolyte.

Given the combination of highly reactive materials in such systems, the active materials are prone to deteriorate in corrosive electrolyte media even under open-circuit conditions adversely influencing performance features such as shelf-life. Moreover, the corrosion resistance of container materials and other hardware such as bus bars can affect both shelf-life and service life of power sources. A comprehensive coverage of corrosion in batteries is rendered difficult by the wide choice of materials, environments and physical features as obtained in practical settings. Understanding of the complex processes that occur in these electrochemical systems gets clearer as new theoretical approaches backed by sophisticated analytical and characterization techniques continue to provide valuable insights which aid in controlling/mitigating wasteful corrosion reactions which affect battery shelf-life, cycle life, rate capability and capacity. In the light of the above, I limit myself to a discussion on corrosion aspects in representative system such as conventional Leclanche, lead-acid battery and magnesium batteries, and advanced lithium systems.

## 2. Leclanche cell

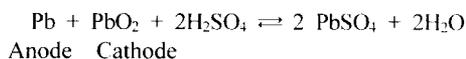
The oldest and the most popular primary cell is Zn-NH<sub>4</sub>Cl-MnO<sub>2</sub>-graphite cell. The shelf-life of this cell is determined by the extent of corrosion of the zinc anode. Chloride is a very aggressive ion. If zinc is impure, local cell action would lead to pitting and puncturing of the zinc anode bobbin. Uniform corrosion is observed with homogeneous alloys or pure metal. Inhibitors may help

in prolonging the shelf-life by reducing corrosion, but their use is generally not resorted to because they will increase the time-lag, i.e., current will not be generated instantaneously if inhibitors are present; in most crucial moments, such time-lags can be a nuisance and even be dangerous. Similar and more severe time-lags have been observed in the case of magnesium-based and aluminium-based primary cells.

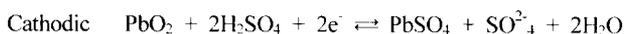
In Leclanche cells, the corrosion of zinc has been reduced considerably and the performance improved by the following steps: (a) coating the inside portion of the zinc can with an emulsion of starch and a water-insoluble high polymer, which acts as a separator, and (b) use of non-aqueous solvents.<sup>1)</sup>

### 3. Lead acid battery

The oldest and still the most popular secondary cell is the lead acid battery. The essential cell reaction is<sup>1)</sup>:



Both the anodic and cathodic reactions produce PbSO<sub>4</sub> as the product.



In order to minimize corrosion of lead without impairing the physical properties, several alloy compositions have been developed, e.g., lead-antimony, with low (3 to 7%) antimony content but with additional elements such as As, Ag, Cd, Co, Cu, Se, Sn or Te. Corrosion of pure metals is different from that of the alloys, and the corrosion of homogeneous (single phase) alloy is different from that of heterogeneous alloys. Alloying invariably strengthens the metal, and lead-antimony is stronger than pure lead.

When an alloy corrodes, both components need not corrode at the same rate. Sometimes one of the components leaches out faster as in dezincification of brasses. Here antimony is leached out faster from the lead-antimony grid alloy. This increases the rate of self-discharge, both at the negative and positive plates. In addition, antimony has a low hydrogen overvoltage. Hence, if antimony is allowed to accumulate on sponge lead electrode, hydrogen evolution would take place during charging and instead of the PbSO<sub>4</sub> reduction. Sometimes poisonous SbH<sub>3</sub> gas is also evolved.

### 3.1 VRLA batteries

Value regulated lead acid batteries meant for minimum maintenance and long cycle life should have less corrosion in order to avoid gas evolution due to chemical corrosion. Therefore suitable grid material has to be used. The influence of calcium and tin in the place of antimony on lead grid alloy was studied to understand the corrosion phenomena. The results indicate that a combination of a low calcium (0.07%) and a high tin (0.7%) content in the alloy yields low growth rates that are accurate for long life (3-6% growth in 54 weeks at 60°C). The microstructure of the alloy and the number of grain boundaries per unit volume is reported to determine the extent of corrosion. Lead-calcium-tin alloys with a composition of 0.07 % calcium and 0.7% tin are reported to have a lower number of grain boundaries when compared with alloys of same system with 0.9% calcium and 0.3% tin. However the performance of the alloys in VRLA battery is reported to be far superior to that of lead-0.9% calcium-0.3% tin alloy.<sup>2)</sup>

The role of tin on the passivation phenomenon has been reported.<sup>3)</sup> The influence of bismuth addition on age hardening and grain size of the grids has also been studied.<sup>4)</sup> Addition of bismuth up to 0.09% is known to have no major effect on the self-discharge behaviour.

Lead-calcium alloy is the most successful rival to lead-antimony alloys. For some types of services it is even superior. Unfortunately calcium has a very limited solid solubility, amounting to 0.1% at the peritectic temperature and 0.01% at room temperature. Lead-calcium alloys containing more than 0.01% calcium, therefore, corrodes faster. But at this composition, it shows less tendency to recrystallize at room temperature leading to less intergranular attack. The alloy shows much lower self-discharge rates and hence requires less water and has lower gassing rate. Calcium is relatively cheap (and only 0.01% required) and more plentiful than antimony.

Excessive rapid freezing of lead-calcium alloys results in abnormal microstructure and hence rapid corrosion and abnormal rate of growth. Service predictions for lead-calcium (0.01%) alloy ranges from 20 to 50 years of life: less self-discharge means less water and lower gassing rate. Hence lead-calcium alloy seems to be the likely grid material for use in non-spillable cells for portable equipment in maintenance-free batteries.

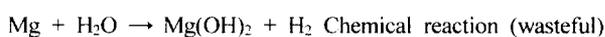
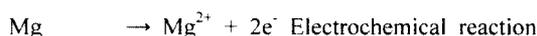
Much more data on structure and phase relations, precipitation-hardening and passivation behaviour, calcium sulphate precipitation and other secondary corrosion effects need to be studied before considering lead-calcium (0.01%) alloy as a candidate for maintenance-

free lead acid batteries.

#### 4. Magnesium reserve battery

Reserve batteries are those which are kept idle without contact with electrolyte and which operate when activated by adding suitable electrolyte. Among reserve batteries are magnesium based ones like Mg/MnO<sub>2</sub>, Mg/CuO, Mg/HgO, Mg/AgCl, Mg/Cu<sub>2</sub>Cl<sub>2</sub> and Mg/*meta*-dinitro benzene. These batteries are used for naval, meteorological and defence applications. All the above systems except Mg/HgO have been developed at CECRI.<sup>5)</sup> A special high energy 200 Ah magnesium/*meta*-dinitrobenzene (organic) battery was developed at CECRI for defence application.

Anodic reaction of Mg



The electrolyte used in this system is a less corrosive and low freezing magnesium perchlorate solution. Other electrolytes used are magnesium chloride, magnesium bromide, or their mixtures. The corrosion observed is of the pitting type. The rate of corrosion depends upon three factors, namely

- rate of discharge
- nature of electrolyte (pH) and
- amount of catalyst in the cathode

During the chemical reaction, heat is generated along with hydrogen generation. One gram of magnesium dissolution liberates 3.3 kcal of heat. This heat generation affects battery performance at room temperature and above room temperature but it can be used advantageously for low temperature operations.

The standard potential of magnesium is -2.34V. However, the steady- working potential is only +1.45V. This is due to the formation of Mg oxide/Mg hydroxide film on the active anode surface. This passive film is helpful in controlling further corrosion and self- discharge.

##### 4.1 Corrosion measurements<sup>6)</sup>

To minimize corrosion of the magnesium-anode, impurities like iron, copper, and nickel have to be avoided in the electrolyte. Alloying of Mg with Al, Zn, Pb and Mn reduces corrosion in different media like MgCl<sub>2</sub>, MgBr<sub>2</sub>, and Mg(ClO<sub>4</sub>). Among the above electrolytes, Mg(ClO<sub>4</sub>) is the best one; the other two are more corrosive. The corrosion difference is due to the nature of anions namely Cl<sup>-</sup>, Br<sup>-</sup>, ClO<sub>4</sub><sup>-</sup>, etc. Another way of controlling corrosion of is addition of suitable inhibitors like lithium

**Table 1. Corrosion rate measurements of magnesium and its alloys in 2M Mg(ClO<sub>4</sub>)<sub>2</sub>, 2M MgBr<sub>2</sub> and 2M MgCl<sub>2</sub>**

Electrolyte	Corrosion rate (mg cm <sup>-2</sup> min <sup>-1</sup> )			
	Alloys			
	AZ61	AP65	AZ31	Mg
2M Mg(ClO <sub>4</sub> ) <sub>2</sub>	0.0041	0.0445	0.0031	0.0873
2M MgBr <sub>2</sub>	0.00875	0.0951	0.0792	0.162
2M MgCl <sub>2</sub>	0.1651	0.1940	0.1505	0.259

**Table 2. Anode efficiency of magnesium alloys at different current densities**

Electrolyte	Current density (mA/cm <sup>2</sup> )	Alloys		
		AP65	AZ61	AZ31
2M Mg(ClO <sub>4</sub> ) <sub>2</sub>	5	55	60	71
	10	60	70	75
	20	64	72	78
	30	65	72	79
	40	65	72	79
2M MgBr <sub>2</sub>	5	46	50	60
	10	50	55	63
	20	55	60	68
	30	58	63	70
	40	59	63	71
2M MgCl <sub>2</sub>	5	40	45	52
	10	43	50	55
	20	50	54	60
	30	56	60	65
	40	57	62	66

chromate, barium chromate to the electrolyte. Both chromates convert magnesium surface to magnesium chromate which prevents further corrosion. Magnesium metal and its alloys, AZ31, AZ61 and AP65, were evaluated for their corrosion behaviour in various electrolytes<sup>6-8)</sup> using both weight loss method and gasometric method. The latter method gave a more accurate value for the weight loss due to metal dissolution. Tables 1 and 2 show, respectively, the corrosion rate and anodic efficiency measured in different electrolytes.

#### 5. Nickel-metal hydride batteries

Nickel plays a primary role in the composite surface oxide layer formed on the surface of the metal hydride electrode. It has also been reported that nickel-rich surface layer on alloy particles is expected to improve the performance of metal hydride electrode. Based on microscopic and Raman results it has been reported that lanthanum, cobalt, manganese and other alloy components segregated and enriched progressively in the alloy surface

layer due to their affinity with water and subsequently produced oxides in charge-discharge processes. The improvement in the bulk properties of alloy particles is a way suggested to increase the cycle life of metal hydride electrodes.

The corrosion study of  $MmNi_{3.55}Co_{0.75}Mn_{0.4}Al_{0.3}$  alloy in aqueous KOH electrolyte has been undertaken<sup>9)</sup> to better understand the decrease in storage capacity of AB<sub>5</sub> type alloys in rechargeable nickel/metal hydride batteries undergoing repeated charge/discharge cycles. In this study a combination of SEM, TEM and high resolution electron microscopy has been used to understand the local structure, chemistry, morphology and distribution of the corrosion products of MmNi alloy which had been exposed to air and to aqueous KOH had been cycled in a model battery. In air a thin nanocrystalline scale of metal (Ni, Co) solid solution, rare earth oxide  $Mm_2O_3$  and mixed oxide  $NiMn_2O_4$  are reported to be formed. After exposure to KOH or cycling in a battery hollow and solid needles of mixed rare earth hydroxide  $Mm(OH)_3$  on top of a continuous nanocrystalline corrosion scale composed of metal (Ni, Co) solid solution, oxide (Ni, Co) solid solution and rare earth hydroxide are found on a Mm-depleted alloy substrate.

A model has been proposed and as per this short-term corrosion is said to be controlled by  $Mm(OH)_3$  needle growth and long-term corrosion is reported to be controlled by the growth of the continuous corrosion scale. The short-term corrosion is said to follow a parabolic rate law whereas the long-term corrosion is reported to follow linear growth behaviour.

## 6. Corrosion in lithium batteries<sup>10)</sup>

Advanced rechargeable lithium ion batteries are attractive for use in consumer electronic and electric vehicle applications. Higher reliability and possibly longer service life are required for military and aerospace applications. For these applications long term chemical degradation of the cell hardware materials is the main concern because it affects the electrical performances capacity, life and safety. Potentially severe corrosion problems have been reported in primary lithium batteries. Environmentally assisted cracking (EAC) has been reported to occur at highly stressed portions of the nickel current collector grid in Li/SOCl<sub>2</sub> cells and in the nickel plated carbon steel material used in Li/SO<sub>2</sub> cells.<sup>11)</sup>

In lithium secondary batteries, lithium is so reactive in most organic solvents and lithium cells operate at a high working potential that a number of inherent or adverse problems such as electrolyte decomposition, electrode

dissolution and cell corrosion are observed in lithium batteries. These are attributed to be the major reasons for bubble formation, electrolyte leakage, capacity loss over cycling and unexpected battery failure. In most cases, cell corrosion is the result of bad electrical contact between the electrode and electronic contact.<sup>12)</sup>

The primary current collector materials being used in lithium ion cells are susceptible to environmental degradation, aluminium to pitting corrosion and copper to environmentally assisted cracking.

Localized pit-like corrosion of aluminium positive electrode current collectors occurs at the highly oxidising potentials that exist in charged condition. The corrosion mechanism appears to be different from that observed in aqueous systems probably because of the organic electrolyte and the imposition of electrical cycling. Under these conditions, each corrosion site was filled with a corrosion product that formed mounds or nodules. Electrochemical impedance spectroscopy was used as a tool and the results can be summarised as

- In the first few hundred cycles, a PC:DEC electrolyte formulation was reported to be less corrosive than the one composed of EC:DMC solvent.
- The general electrochemical behaviour was reported to be not a function of the extent of electrical cycling or metallurgical purity.
- When charging potential is increased the corrosion resistance was found to decrease.
- Lithium was the predominant surface species that was reported on the surface of the electrodes.

The copper negative current collector was reported to be susceptible to environment cracking at or near the potential. To understand the corrosion of copper current collectors potentiodynamic anodic and cathodic polarisation studies cyclic voltammetry and electrochemical impedance spectroscopy were carried out at CECRI.<sup>13)</sup>

Results of cyclic voltammetric studies on copper in EC:DMC (1:1) solvent mixture in LiAsF<sub>6</sub> and LiPF<sub>6</sub> are given in Table 3. Linear polarisation results on copper in

**Table 3. Results of Cyclic Voltammetry studies on copper in EC : DMC (1:1) solvent mixture in LiAsF<sub>6</sub> and LiPF<sub>6</sub>**

Electrolyte	E (V)	I (mA)
LiAsF <sub>6</sub> (1 Cycle)	3.464	- 0.0538
	3.342	0.3216
	3.228	0.3240
After 5 Cycles in LiAsF <sub>6</sub>	3.448	-0.0762
	3.404	0.2590
	3.198	1.032
LiPF <sub>6</sub>	3.31	1.92

**Table 4. Linear polarisation studies on copper in EC:DMC (1:1) in LiAsF<sub>6</sub> and LiPF<sub>6</sub>**

Electrolyte	E <sub>corr</sub> V	I <sub>corr</sub> A cm <sup>-2</sup>	ba mv	bc mv
LiAsF <sub>6</sub>	3.2463	3.88 x 10 <sup>-7</sup>	91	137
LiPF <sub>6</sub>	2.5901	4.29 x 10 <sup>-6</sup>	102	94

**Table 5. Impedance analysis on Copper in EC : DMC (1:1) with LiAsF<sub>6</sub> and LiPF<sub>6</sub>**

Electrolyte	Potential at which measured (V)	R <sub>ct</sub>	R <sub>s</sub>
LiAsF <sub>6</sub>	3.2	9.44KΩ	0.06 KΩ
	3.4	3.69 KΩ	0.02 KΩ
LiPF <sub>6</sub>	3.3	20.41Ω	44.07Ω

EC:DMC (1:1) in LiAsF<sub>6</sub> and LiPF<sub>6</sub> are presented in Table 4. Impedance analyses on Cu in EC:DMC (1:1) with LiAsF<sub>6</sub> and LiPF<sub>6</sub> are given in Table 5.

From the results presented it may be concluded that electrolyte containing LiAsF<sub>6</sub> is less corrosive than LiPF<sub>6</sub>. The reason being the difference in the reaction of the salt at metal solution interface in the build up of surface films. The increased corrosion rate of copper in LiPF<sub>6</sub> may be due to the reaction of HF with Cu. HF may be produced by reaction of LiPF<sub>6</sub> with trace amounts of water.

Electrochemical impedance studies reveal a charge transfer resistance R<sub>ct</sub> of 20 ohms at copper dissolution voltage 3.3V (determined from the cyclic voltammetric experiments) for the electrolyte containing LiPF<sub>6</sub>. For electrolyte containing LiAsF<sub>6</sub> R<sub>ct</sub> of 9.24 and 3.693 kilo ohms at potentials 3.2 and 3.4V, respectively, were measured. The resistance value 9.24 kilo ohm may be attributed to protective film formation and 3.693 kilo ohm may be due to slight deformation of formed protective film by copper dissolution. This may be due to the nature of the protective film. The high solution resistance of electrolyte containing LiAsF<sub>6</sub> clearly confirms the instantaneous formation of a protective layer over copper.

It can be thus be concluded from the above observations that LiAsF<sub>6</sub> is more suitable to prevent corrosion of copper which is widely used as anode base material compared to LiPF<sub>6</sub> containing electrolyte because of the protective film formation in LiAsF<sub>6</sub>.<sup>14)</sup>

## 7. Conclusion

To surmise, therefore, corrosion in batteries can undermine their performance characteristics. So much so their utility for the purposes intended can suffer. Use of

constituent materials free from corrosion inducing impurities, corrosion-resistant inactive components, and incorporation of substances that arrest/minimize self-corrosion of active materials (as in alloy anodes of lead-acid battery) are cases in point. It must, however, be stressed that the juxtapositioning of highly active battery chemicals can only lead to thermodynamically unstable systems, where mere corrosion on the one extreme and explosive hazard on the other are expected characteristics. Such intrinsically reactive systems can be designed into practically useful packages only by restricting the kinetics of one or more of the parasitic processes. Kinetic stability of metallic lithium in contact with corrosive electrolytes is a classical example. Further beneficial characteristics of this interface may be realized by suitable additives to the electrolyte medium.

The extent to which corrosion can affect the useful life and performance characteristics of a battery is often complicated by several other factors such as the nature of welds, geometry of the electrodes, nature of the electrodes (sintered, pasted-type etc). Design considerations so as to reduce stress in batteries, choice of special sealing materials like tantalum and glasses in hermetically sealed systems, phase transitions at weld fusion zones (solidification of carbon steels with plated nickel into austenitic steels and subsequent transformation into martensitic steels), etc., are areas where intensive studies still need to be done. It is thus clear that each battery type -- in terms of battery chemistry, design and application -- must be considered individually for an assessment of corrosion damage. It goes without saying that alternative materials and designs must continually be evolved to mitigate corrosion problems. Like weeding out unnecessary vegetation from farmland, eliminating corrosion in all its manifestations should help in maximization of power output and performance benefits of battery systems.

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