



## Carbonation

### Introduction

The term carbonation refers to the conversion of potassium hydroxide in the electrolyte to potassium carbonate. IEEE standards contain references to carbonation and at least one competitor, Hoppecke, treats the issue as a major problem for pocket plate cells. These technical notes put the carbonation issue into proper perspective regarding real applications. Information is provided on minimizing the extent of carbonation, and on taking corrective action, should this become necessary.

### Sources

There are two potential sources of carbonation:

- Oxidation of graphite contained in the positives of pocket plate cells. This process occurs during charging, and its rate is increased at high temperature and by repeated deep cycling.
- Absorption of carbon dioxide from the air. This can occur during operation of the battery, or, more likely, it may result from improper handling of electrolyte, particularly from storage in open containers. Cells that are filled in the factory are unlikely to suffer from this form of carbonation. Quality procedures ensure that carbonate in the bulk electrolyte remains at a very low level. Once the cells are filled, the mineral oil layer that floats on the electrolyte effectively prevents contact between the electrolyte and atmospheric carbon dioxide.

### Effects

Graphite is added to the positive active material in pocket plate cells to improve conductivity, and this material is the primary source of carbonation in these cells. Overcharging, repeated deep cycling and prolonged high temperature operation will all increase the rate of carbonation of the electrolyte.

The main effect of carbonation is to reduce the conductivity of the electrolyte, since there are fewer hydroxide ions to carry the ionic current. This will affect short duration discharges much more than those of long duration. It follows from this that a battery used in a low rate application can tolerate a much higher level of carbonation than one supplying high rate discharges.

In most applications, the buildup of carbonate is so slow that there is no effect on the life or operation of the battery. In high rate duties such as engine starting, it is quite normal for pocket plate batteries to provide trouble-free operation for 20 years or more. Even if carbonate starts to affect performance at that point, the economic benefits of Ni-Cd have already been realized.

In most cases, carbonation effects are limited to electrolyte conductivity issues. However, if potassium carbonate reaches a very high concentration in the electrolyte, to the extent that carbonate ions are forced to carry some of the ionic discharge current, there is the possibility of conversion of some of the negative active material to cadmium carbonate. This process is



effectively irreversible, and will therefore result in a permanent capacity loss. While moderate carbonation can be overcome by electrolyte renewal (see **Corrective action**), high carbonate levels mean that a large part of the graphite in the positive active material has been oxidized. This will result in a loss of conductivity and high performance capability, even if the electrolyte is renewed.

### **Preventive measures**

Repeated deep cycling and high operating temperature are application requirements and it is unlikely that anything can be done about them. Indeed, requirements such as these are among their main reasons for choosing Ni-Cd in the first place. The ability to withstand overcharging is one of the advantages of Ni-Cd, but it must be recognized that excessive overcharging of pocket plate cells will lead to a buildup in carbonate levels. Limiting such overcharging is the best way to reduce the rate of electrolyte carbonation in service.

If a battery has been shipped with the cells unfilled, or if electrolyte must be renewed onsite, the following measures must be taken to minimize carbonation:

- Do not leave unfilled cells open to the atmosphere for more than a few minutes.
- When mixing electrolyte with a powered stirrer, do not allow the mixing blades to cavitate, or draw air into the liquid.
- Use mixed electrolyte immediately, or transfer it to storage containers.
- Store electrolyte in containers with airtight closures. Do not store electrolyte with a large headspace of air in the container.

If heavy carbonation cannot be avoided with pocket plate cells, the use of sintered/PBE product should be considered, even for applications requiring lower discharge rates.

### **Testing**

Saft provides a test kit to allow carbonate levels to be determined. It is intended that such tests be carried out only as a troubleshooting measure, rather than as a routine. If the operation of a battery is satisfactory, carbonate testing is a waste of time and money. Moreover, since the procedures involve the handling of caustic electrolyte, this would represent needless exposure of technicians to hazardous materials.

In the past, the instructions have detailed a single pass/fail point, corresponding to approximately 57 grams of potassium carbonate per liter of electrolyte. While this level is appropriate for high rate applications, batteries providing lower discharge rates, such as in telecommunications and emergency lighting, may be safely operated with carbonate levels up to about 80 g/l. For railroad signaling and low rate photovoltaic applications in which the cells are filled with low temperature electrolyte, a limit of 120 g/l of carbonate may be used.



## SAFT

The existing test method calls for the use of 25 ml of barium chloride solution. To test for higher levels of carbonate, the test method should be modified to use the following solution volumes:

Carbonate test level (as $K_2CO_3$ )	Volume of barium chloride solution
57 g/l	25 ml
80 g/l	35 ml
120 g/l	53 ml

In each case, 10 ml of electrolyte would be used, as specified in the test procedure. After filtering the initial precipitate and adding extra barium chloride solution, the presence of a new precipitate indicates that the carbonate content is greater than the test level indicated in the table.

### **Corrective action**

Before considering corrective action, it should be determined whether electrolyte renewal can be economically justified. This involves the handling of hazardous materials and must be carried out by adequately trained personnel. Furthermore, the old electrolyte is a hazardous waste and must be disposed of in accordance with applicable regulations.

If a battery is nearing the end of its life expectancy and it is determined that the carbonate level is too high, electrolyte renewal is unlikely to be a cost-effective remedy. However, if battery replacement is not immediately possible, perhaps due to budgetary constraints, it may be possible to provide a temporary fix.

Topping up the cells with a solution of potassium hydroxide will provide a short-term improvement in the electrolyte conductivity and will thus offset the effects of carbonate. Of course, the carbonate will still be present and it will be only a matter of time before it again becomes a limiting factor. However, this fix may allow an additional year or so of battery operation, during which replacement can be planned. If this option is followed, care should be taken to ensure that the electrolyte specific gravity, measured at the maximum level, does not exceed 1.250.

For those situations where electrolyte renewal is economically viable, it is important to follow the procedures outlined in the published operating instructions. Observing the measures outlined above (see **Preventive measures**) will help to minimize additional carbonate formation during this process.

### **Note on sintered/PBE cells :**

The sintered/plastic bonded plates do not contain graphite and so carbonation cannot arise from oxidation due to this cause and so, with the sintered/plastic bonded product, the level of carbonate does not rise to a sufficiently high level to impair the functioning of the battery.