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# Analysis of electrolyte of an automotive accumulator at different temperatures at start condition

# Análisis del electrolito del acumulador automotriz a diferentes temperaturas en condición de encendido

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## Abstract

An automotive battery of the acid lead type is an element that generates an electromotive force capable of supplying energy to the entire electrical system of the vehicle. In this investigation, the behavior of the specific density of the electrolyte during the start-up condition of a heat engine is analyzed; the operating temperature gradient at which the battery can be exposed is also considered as a variable. According to the results, the electrolyte temperature is inversely proportional to its density in the cells of the accumulator during the start-up condition. It is concluded that external conditions, such as the temperature, can directly affect the density and electrical conditions of an accumulator, and can identify the behavior of these during the operation in a vehicle.

***Palabras clave***: Starting, Battery, Leaf acid, Temperature.

## Resumen

Una batería automotriz del tipo plomo ácido es un elemento que genera una fuerza electromotriz capaz de abastecer de energía a todo el sistema eléctrico del vehículo. En el presente estudio se analiza el comportamiento de la densidad específica del electrolito durante la condición de arranque de un motor térmico; además, se considera como una variable, el gradiente de temperatura de funcionamiento que puede estar expuesto una batería automotriz. Obteniendo resultados de una variación inversamente proporcional del comportamiento de la temperatura del electrolito y su densidad en las Cells del acumulador durante la condición de arranque. Se concluye que las condiciones externas como la temperatura pueden afectar directamente a la densidad y las condiciones eléctricas de un acumulador, así como identificar el comportamiento de estas durante el funcionamiento en un vehículo.

***Keywords***: arranque, batería, electrolito, temperatura.

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## 1. Introduction

An automotive battery has been designed to work together with the starting motor, when an internal combustion engine needs to turn on. In particular, the battery should have the capacity of supplying energy to produce the initial turns of the engine. Therefore, during the start-up condition the battery should have its highest performance and correlation between the specific density of the electrolyte of the accumulator and the temperature [1]. Such specific density is related with the state of charge of a battery and the interaction with the active material, and the temperature is related with the voltage and the intensity of current it can supply [2]. The variation in the temperature gradient and the start-up condition give results that can be related with the obtained in the study of the electrolyte gasification of the accumulator during charging operation and the temperature of exposure [3], which gives additional data about the behavior in a rather common condition during the operation of an automotive. It is very important to study the effect of the temperature on the operation of the negative and positive plates, during the process of charge, discharge, behavior at start-up and external conditions such as temperature that affect its useful life and, besides, when being exposed to an electrolyte like sulfuric acid [1].

### 1.1. Automotive battery

Essential element in the electric system of the vehicle, designed to supply energy in some electrical conditions, being the most important to provide start-up capability to achieve the key objective of turning on the engine [4]. In an accumulator, the start-up capability is effective for a time period of 10 seconds, during which it should supply the maximum possible amperage that it can deliver based on the internal design, in the electrical condition that occurs when the initial turns of the engine are produced. This test, known as start-up condition, has been standardized at an ambient temperature of 25°C, while the test carried out at a temperature between 0°C and –18°C is known as cold start-up condition [5].

### 1.2. Specific density

In 1860, Gaston Plante combined Pb / $PbSO_4$ with an electrode of $PbO_2$ / $PbSO_4$ in a solution of sulfuric acid, and obtained a source of electrochemical energy with a significant electromotive force [4].

The temperature is an important factor that influences the electromotive force of an accumulator, thus the automotive batteries exposed to low temperatures have internal design problems them prevent them from working normally; this is the characteristic of the vehicles in cold regions [6]. On the other hand, the exposition of the accumulator to high temperatures accelerates the deterioration of the internal elements and the rusting of positive plates.

The electrical resistance, specifically the resistivity of the $H_2SO_4$ electrolyte, is one of the basic parameters that determine the internal resistance and the power of each of the cells in an acid lead battery [7]. When the internal resistance of the cell is high, a significant portion of the usable energy is consumed inside the own cell, i.e. the energy is dissipated as heat when the electrical current flows through the cell, depending on the concentration and temperature of the electrolyte [7].

### 1.3. Temperature

It is considered that the electrolyte ($H_2SO_4$ + $H_2O$) has a density of 1280 g/cm$^3$, i.e. 1280 times heavier than a similar volume of pure water, when both liquids are at the same temperature [8].

In automotive diagnosis, the most useful and effective tool to know the state of the specific density is known as hydrometer [5]. A density between 1290 g/cm$^3$ and 1270 g/cm$^3$ indicates that the accumulator is completely charged, while a density between 1240 g/cm$^3$ and 1200 g/cm$^3$ indicates that the charge has reduced. When the specific density obtained in the hydrometer is smaller than 1150 g/cm$^3$, it is considered that the battery is discharged. These values are established for a temperature of the electrolyte between 20°C and 25°C [5]. Therefore, a correction of 0.0035 units should be applied in the relative density, for every 5 degrees of variation in the temperature of the electrolyte above 25°C [5].

### 1.4. Start-up condition

During the start-up condition of a heat engine, the starting motor is the fundamental device since it is responsible of producing the initial turns of the engine thus it can become on [5]. A particular behavior of the voltage occurs in the electrical system when the motor initiates turning, as can be seen in Figure 1. The ISO 16750-2 standard establishes that during the start-up condition, the voltage oscillates for a standardized time between 3 and 10 seconds during which there is a high demand in start-up intensity. This causes that the battery discharges due to the work done, and this is reflected in the specific density of the electrolyte [9].

The voltage of the electric system decreases momentarily during engine start-up. The particular value of the voltage depends on the condition of the battery. The values may decrease at a level between 10.5 and 10.9 volts when the accumulator is in good condition [5].

The temperature is determining in the performance of the accumulator, which is better at high temperature as compared to the capability of cold start-up [9]. The specific electrical resistance (resistivity) of the $H_2SO_4$ electrolyte is one of the essential parameters that determine the internal resistance and the power an acid lead cell.

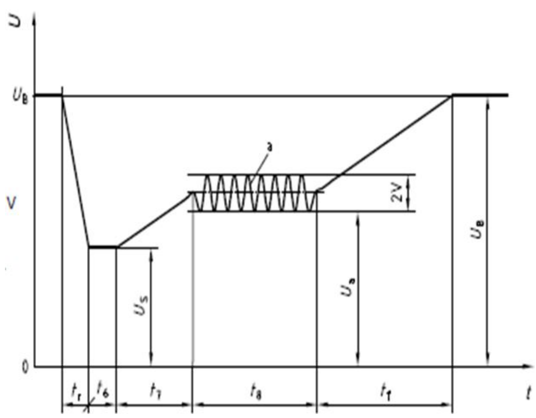


**Figure 1.** Behavior of the voltage of the electric circuit during start-up of the heat engine [4].

In an acid lead accumulator, the sulfate is a closed system that can be found in the plates or in the electrolyte, according to the state of charge or the operating condition. If the battery is completely charged, the sulfate is in the electrolyte; on the other hand, if the battery is discharged, the sulfate is in the plates. The final result of the specific density is a picture related to the voltage and, therefore, to the state of charge [9].

The objective of this analysis is to know the behavior of the specific density of the electrolyte of an automotive accumulator during the start-up condition, causing a variation of the ambient temperature to which the battery is exposed. In general, the analysis of the specific density of the electrolyte is carried out in order to know the state of the charge, but searching for an analysis of its effect when it is subject to a change in ambient temperature during the storage process, and confirm the structural change in the density and its relationship with the voltage and intensity offered by the battery [10].

This study searches to identify the behavior of the specific density of the battery during the start-up condition, to find sign that can direct this analysis toward initial research elements, and future improvements regarding the design of automotive batteries. There are no studies about the behavior of the specific density of acid lead batteries during start-up, thus it is desired to obtain values based on the variation of the temperature.

## 2. Materials and methods

The research is based on an experimental method, which comprises the analysis of the behavior of the specific density of an automotive battery during the start-up condition, for different values of ambient temperature. To achieve this purpose, the specific density has been measured in the six cells that constitute the automotive battery in optimal operating conditions, with a nominal voltage of 12 volts.

The process applied is for determining, in a practical manner, the status of a battery during the start-up of an engine. At the beginning of the study, the value of the specific density in each cell is determined at the initial rest condition. Then, the engine start-up process is initiated, but avoiding to completely turning it on. This test is repeated 6 times, and the specific density of the cells is measured at the end of each test. It is important to mention that the temperature of the electrolyte is also registered before and after the test, to further fit a model that gives the specific density as a function of transition temperature.

## 3. Results and discussion

### 3.1. High temperature condition

The external temperature of the battery is progressively increased, for which a thermal heater is used to simulate ambient temperature. Then, the value of specific density for each of the cells in the battery is registered. Table 1 shows the data obtained at 20°C, and the fitted values calculated as a function of temperature [5].

The fitted values of density are calculated based on the percentage of loss and expansion, but the obtained and fitted values in each test and measurement are analyzed during the process.

Figure 2 illustrates the behavior of the density for a temperature stable at 55°C, which indicates a significant change in the first block of cells, but a greater stability mostly on the central cells, and the greatest stability for the group of cells close to the negative terminal.

**Table 1.** Density and temperature before the start-up

| **Cell** | **Ambient temperature °C** | **Temperature of the battery box °C** | **Temperature of the electrolite °C** | **Specific density g/cm$^3$** | **Voltage of the battery (V)** | **Fifted specific density g/cm$^3$** |
|---|---|---|---|---|---|---|
| 1 | 55 | 44 | 21,7 | 1,2 | 11,62 | 1,198 |
| 2 | 55 | 44 | 19,3 | 1,19 | 11,67 | 1,186 |
| 3 | 55 | 44 | 19,3 | 1,2 | 11,57 | 1,196 |
| 4 | 55 | 44 | 19,3 | 1,2 | 11,57 | 1,196 |
| 5 | 55 | 44 | 19,4 | 1,175 | 11,6 | 1,171 |
| 6 | 55 | 44 | 20,5 | 1,2 | 11,57 | 1,197 |

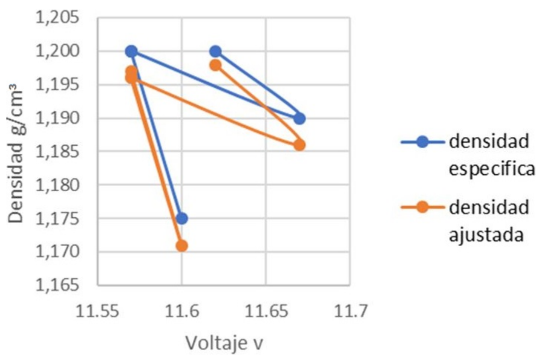


**Figure 2.** Plot of the behavior of the density before start-up at 55 °C.

Table 2 shows the results obtained after carrying out the continuous start-up process, to observe the stability condition of the accumulator and the fitted values calculated as a function of temperature [5].

**Table 2.** Density and temperature after the start-up

| Cell | Ambient temperature °C | Temperature of the battery box °C | Temperature of the electrolite °C | Specific density g/cm$^3$ | Voltage of the battery (V) | Fifted specific density g/cm$^3$ |
|---|---|---|---|---|---|---|
| 1 | 55 | 44 | 20 | 1,190 | 11,62 | 1,187 |
| 2 | 55 | 44 | 18,9 | 1,180 | 11,67 | 1,176 |
| 3 | 55 | 44 | 19 | 1,205 | 11,57 | 1,201 |
| 4 | 55 | 44 | 18,6 | 1,210 | 11,57 | 1,206 |
| 5 | 55 | 44 | 19,9 | 1,180 | 11,6 | 1,176 |
| 6 | 55 | 44 | 22,1 | 1,175 | 11,57 | 1,173 |

Figure 3 shows the behavior of the density for a temperature stable at 55°C, keeping also stable the voltage of the battery when the start-up process is generated. This results in a notable change in the first block of cells, stability in the central cells, and also an important change for the group of cells close to the negative terminal.

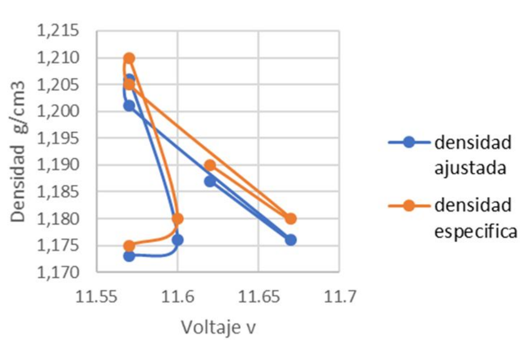


**Figure 3.** Plot of the behavior of the density after start-up at 55 C.

### 3.2. CLow temperature condition

The low temperature condition is achieved by enclosing the battery in a capsule with dry ice until the indicated value of temperature is reached. In order to register the data for this condition, the cells are subject to a temperature variation smaller than in the previous test, being stabilized at a temperature of 1 °C. Table 3 includes the obtained and fitted values calculated as a function of the temperature [5].

**Table 3.** Density and temperature after the start-up

| Cell | Ambient temperature °C | Temperature of the battery box °C | Temperature of the electrolite °C | Specific density g/cm$^3$ | Voltage of the battery (V) | Fifted specific density g/cm$^3$ |
|---|---|---|---|---|---|---|
| 1 | -2 | 1,4 | 6,4 | 1,250 | 11,17 | 1,231 |
| 2 | -2 | 1,4 | 7,7 | 1,245 | 11,24 | 1,226 |
| 3 | -2 | 1,4 | 8,3 | 1,250 | 11,24 | 1,231 |
| 4 | -2 | 1,4 | 8,9 | 1,250 | 11,11 | 1,231 |
| 5 | -2 | 1,4 | 9 | 1,245 | 11,2 | 1,226 |
| 6 | -2 | 1,4 | 9,3 | 1,225 | 11,23 | 1,206 |

Figure 4 shows the behavior of the density for a temperature stable at -2 °C: the behavior of the electrolyte at low temperatures is more stable than for high temperatures.

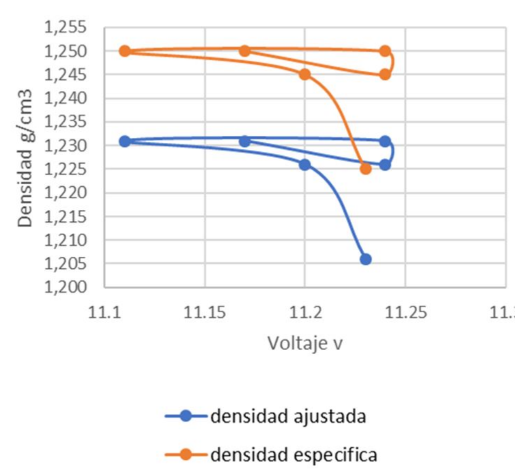


**Figure 4.** Plot of the behavior of the density before start-up at -2 °C.

Table 4 shows the results obtained after carrying out the continuous start-up process, to observe the stability condition of the accumulator and the fitted values calculated as a function of temperature [5].

**Table 4.** Density and temperature after the start-up

| Cell | Ambient temperature °C | Temperature of the battery box °C | Temperature of the electrolite °C | Specific density $g/cm^3$ | Voltage of the battery (V) | Fifted specific density $g/cm^3$ |
|---|---|---|---|---|---|---|
| 1 | -2 | 1,4 | 6,4 | 1,230 | 12,46 | 1,211 |
| 2 | -2 | 1,4 | 7,7 | 1,215 | 12,28 | 1,196 |
| 3 | -2 | 1,4 | 8,3 | 1,250 | 11,43 | 1,231 |
| 4 | -2 | 1,4 | 8,9 | 1,275 | 11,27 | 1,256 |
| 5 | -2 | 1,4 | 9 | 1,250 | 11,31 | 1,231 |
| 6 | -2 | 1,4 | 9,3 | 1,265 | 11,3 | 1,246 |

**Table 5.** Density and temperature after the start-up

| Cell | Ambient temperature °C | Temperature of the battery box °C | Temperature of the electrolite °C | Specific density $g/cm^3$ | Voltage of the battery (V) | Fifted specific density $g/cm^3$ |
|---|---|---|---|---|---|---|
| 1 | 20 | 27,2 | 14,06 | 1,200 | 11,17 | 1,197 |
| 2 | 20 | 27,2 | 14,11 | 1,190 | 11,24 | 1,187 |
| 3 | 20 | 27,2 | 14.49 | 1,200 | 11,24 | 1,197 |
| 4 | 20 | 27,2 | 14,73 | 1,200 | 11,11 | 1,197 |
| 5 | 20 | 27,2 | 15,15 | 1,175 | 11,2 | 1,172 |
| 6 | 20 | 27,2 | 16,15 | 1,200 | 11,23 | 1,197 |

Figure 5 shows the behavior of the density for a temperature stable at -2°C, after the start-up process; there was a considerable drop on the values of electrolytic density and voltage, even more for the group of cells in the positive terminal. This indicates a minor reaction and an effort in the discharge process of the battery during this phase of the test.

### 3.3. Ambient temperature condition

The data for an ambient temperature of 27°C are obtained by means of the process established in previous cases. Table 5 shows the obtained values of specific density and temperature [5].

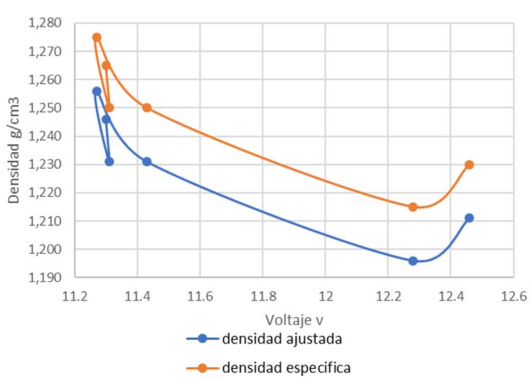


**Figure 5.** Plot of the behavior of the density after start-up at -2 °C

Figure 6 shows the behavior of the density for a temperature stable at 20°C, indicating stability of the voltage and of the density of the battery.

In addition, it can be observed that there is cyclic flow behavior of the electrolyte density, for more than one stable value of the voltage of the battery, which remains stable regardless of the start-up condition.

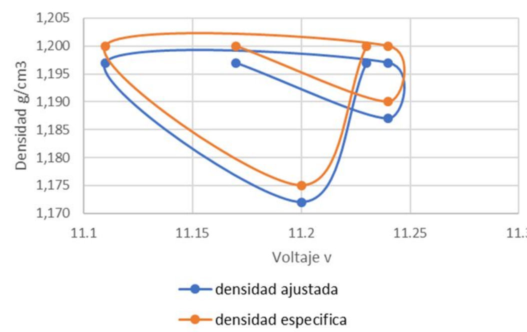


**Figure 6.** Plot of the behavior of the density after start-up at 20 °C.

The results are compared in the start-up test, to analyze the behavior of the voltage and density of the battery under extreme conditions, which results in a percentage of change of the ambient temperature of 0.39 % and of 3,1375 % with respect to the high and low temperature conditions, respectively. This indicates that the density of the electrolyte is more affected by low conditions, as opposed to the estimated time of start-up and voltage stability that are more affected by high temperature conditions, as can be seen in Figure 7.

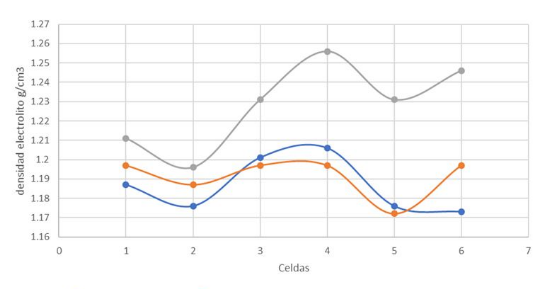


**Figure 7.** Comparison plot of the density at different temperatures

## 4. Conclusions

The figures show the change in density and voltage due to change in the temperature and stabilization. In addition, each point in the plots represents a cell, and shows the behavior of its electrolyte.

Figure 2 indicates the value of battery voltage before the consumption due to the start-up process. The stability of the accumulator during operation can be verified in both voltage and density.

Figure 3 indicates that the change in the battery voltage is not very significant due to the consumption at the moment of start-up, but the density of the electrolyte is altered, especially in the central cells.

An average of the operation of the cells indicates that the nominal tension keeps is maintained stable.

Figure 4 shows the value of the battery voltage before the consumption due to the start-up process. A stability can be observed in the density of the accumulator, but not in its voltage.

Figure 5 shows that the change in the battery voltage is very significant due to the consumption at the moment of start-up, but the change in the density of the electrolyte is small with respect to previous tests, especially in the final cells. This indicates that the stability drop in the operating conditions of the accumulator is more affected when the start-up process is carried out at low temperatures.

Figure 6 shows that the change in battery voltage is not very significant due to the consumption at the moment of start-up, but the density of the electrolyte is minimally altered in all cells. The stability drop in the operating conditions of the accumulator is more affected when the start-up process is carried out at ambient temperature.

Figure 7 presents the results corresponding to the behavior of the density at different temperatures. At low temperatures the density is more stable, but some strength is lost in the start-up condition. On the other hand, there is more start-up strength when hot, but the voltage drop is much greater.

The electrolyte density is directly proportional to the temperature change. When the temperature of the engine cabin increases to the higher values registered, the stability is maintained.

The stability condition of the density of the battery is altered, especially in the central and final cells, when the temperature drops significantly due to the displacement of electrons between them. This produces an abrupt drop in the voltage, but the recovery is much faster because the density of the electrolyte stabilizes.

The voltage remains constant as the temperature increases, but an extreme variation in the density occurs during start-up. This affects the operation and the durability of the battery, since its useful life is significantly reduced due to the variability in the density.

When the temperature of the electrolyte drops to its minimum values in real operation, there is an extreme change in the battery voltage, which produces a greater effort in the main consumers during the start-up process; this causes damage in the components of the vehicle.

When the electrolyte temperature decreases, the intensity drops due to the difficulty in the displacement of the electrons, placing a greater effort on the functionality of electric and electronic consumers. This would generate an improvement in the design of the structure of the batteries.

Based on the obtained results, it is concluded that the electrolyte temperature for different ambient conditions produces changes in the functionality. It is recommended to use new materials and designs, to improve the behavior of the battery during the start-up condition.

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