The influence of temperature on the operation of batteries and other electrochemical energy storage systems

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1.Introduction

Like all chemical reactions, also electrochemical reactions are much influenced by temperature. The most important law describing the influence of temperature on a chemical reaction is the Arrhenius Law:

$$k = Ae^{-\frac{E_a}{RT}} \qquad (1)$$

k	reaction rate
A	rate constant
E_a	Activation Energy
R	molar gas constant
T	Temperature

The importance of this influence becomes obvious looking on the production of oxygen on a battery plate:

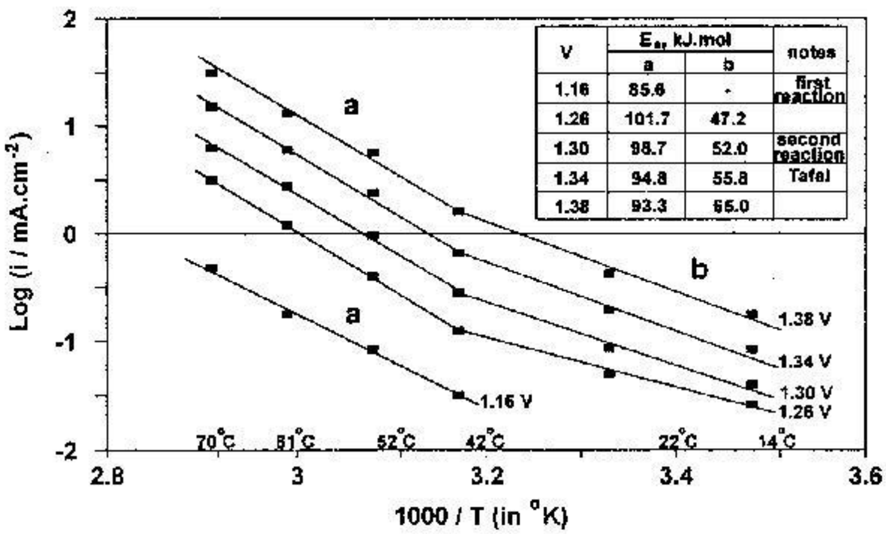

Figure 1: Arrheniusplot of O_2-Production on PbO_2 ([1])

Comparing the numbers between 42°C and 61°C, you can see a factor of 10 in reaction speed for a difference in temperature of just 19°C! So, temperature is a parameter which must not be neglected when working with batteries. An example for the significance of these effects on real batteries is shown in table 1 (out of an actual data sheet of a VRLA battery):

TEMPERATURE EFFECTS ON LIFE

Maximum Annual Average Battery Temperature	Maximum Battery Temperature	Percent Reduction In Battery Life
25°C (77°F)	50°C (122°F)	0%
30°C (86°F)	50°C (122°F)	30%
35°C (95°F)	50°C (122°F)	50%
40°C (104°F)	50°C (122°F)	66%
45°C (113°F)	50°C (122°F)	75%
50°C (122°F)	50°C (122°F)	83%

Table 1: Effect of temperature on lifetime of an actual lead acid battery (**Fehler! Unbekanntes Schalterargument.**)

As you can see, the old law for lead-acid batteries "increase temperature by 10 °C and get half of the lifetime" is still true (although there are neither oxygen evolution than corrosion effects which affect this reduction in lifetime).

In this paper, the influence of temperature on the operation of lithium-ion, nickel and lead-acid battery systems shall be described and some example measurements shown.

2. How does temperature influence operation of a battery?

Operation of a battery is both influenced by low and high temperatures. Usually, batteries are designed for operation at room temperature (which is 20 to 25°C), and both higher or lower temperatures do have effects.

When looking on these effects, we have to divide between

1. Influence on battery **power**
2. Influence on available **energy** (capacity)
3. Influence on **life time**

Of course, there are also correlations between them. For example, if battery capacity is reduced by temperature, the relative death of discharge (DoD) increases when taking out the same amount of energy and so lifetime is reduced.

The next important thing is what happens with the battery at this different temperature. It is a big difference whether a battery is just stored or also charged or discharged at high or low temperatures. Looking on storage, the state of charge (SOC) of the battery is also important to know when predicting performance of a battery on a certain temperature level. As self discharge is enhanced by elevated temperature, recharging on stock or stand by may be necessary more frequently than at room temperature.

2.1. Reaction rate

As temperature effects the reaction rates of the various chemical reactions taking place when operation a battery, the balance between these reactions will be destroyed.

At high temperatures, mainly the side reactions like gassing get increased. This results in higher self discharge, but also in reduced life time (by increased corrosion, increased detoriation of battery components, …)

At high temperatures, mainly charging becomes difficult:

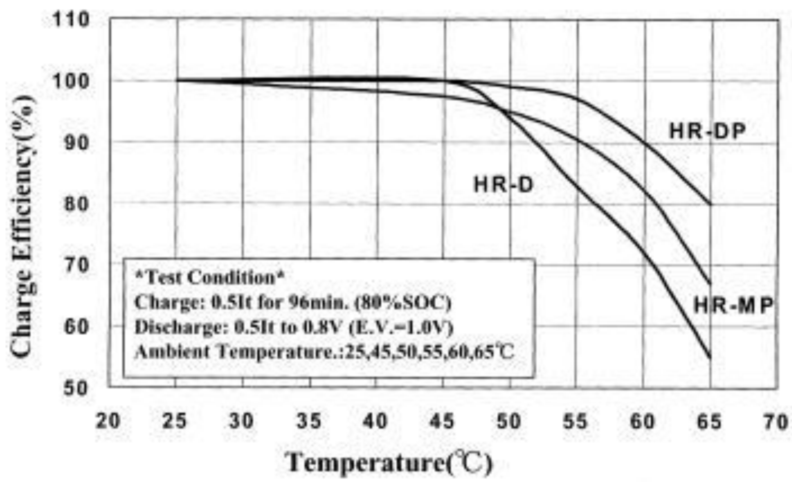

Figure 1: Charge Efficiency of different NiMeH-Cells as a function of temperature [3]

Reason for this is that the reduced gassing voltage reaches the voltage necessary to charge the battery at certain SOC, so above this point more and more charge goes into gassing instead of charging (hereby increasing temperature if oxygen is reduced, which can lead to a thermal runaway). So, the SOC which may be achieved is limited by high temperatures. Similar effects we have at lithium-ion and lead-acid batteries.

As side reactions are much influenced by additives, there can be big differences between batteries of the same chemistry, but a different manufacturer or type or manufacturing date. See Figure 1 as an example of evolution.

For Li-Ion battery systems, all side reactions directly reduce the life time of the battery, so the latter is much reduced by charging at high temperatures:

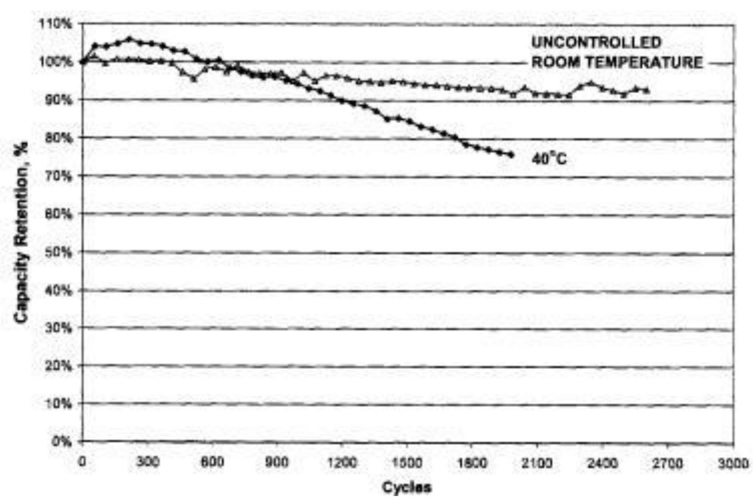

Figure 2: Capacity retention during cycling a Li-Ion battery at different temperatures [4]

In Figure 3, it seems as there would be no degradation at high temperatures. It is important to note that these measurements were made at only 50% SOC. At higher SOC, temperature effect is assumed to be stronger.

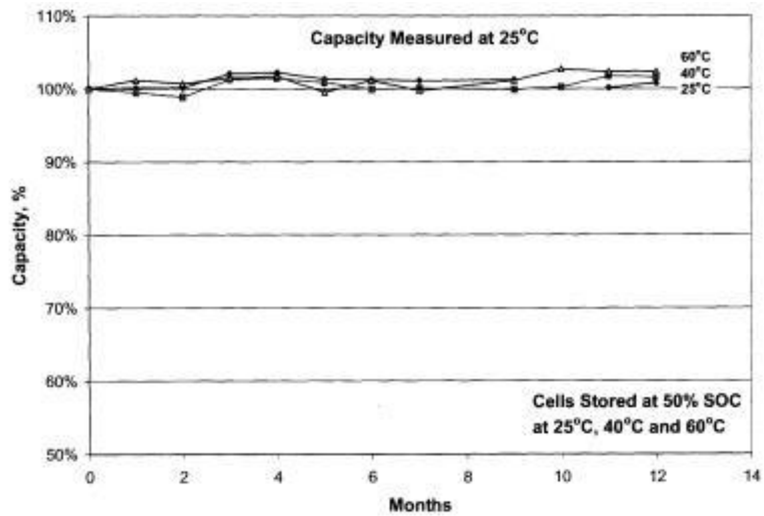

Figure 3: Capacity retention during storage of a Li-Ion battery at different temperatures [4]

For low temperatures, reduced oxygen recombination rate during charge of a NiMeH may cause water losses or corrosion effects and therefore reduce lifetime.

2.2. Conductivity and Diffusion

Low temperature much decreases conductivity of ionic conductors used in electrolytes, separators or electrodes, which reduces performance of a battery. Additionaly, low temperatures also much decrease diffusion. As diffusion is not voltage driven, there is a maximum current which can't be topped by setting higher potentials.

In electrochemistry, many reactions are limited by diffusion or may be limited by diffusion at low temperatures. Diffusion may be even impossible below a certain temperature, one reason for the high operating temperatures of high temperature batteries (like the ZEBRA) or fuel cells (solid oxide type). Unfortunately, also in our popular battery systems there are rate limiting diffusion processes: Li diffusion through the intercalation materials in Li-Ion batteries, proton diffusion through the metal-hydride of a NiMeH battery, Pb^{++} diffusion through the electrolyte of a lead/acid battery, and many more. Practically, there is a rate limiting diffusion process which prohibits operation below a certain temperature for almost all battery systems.

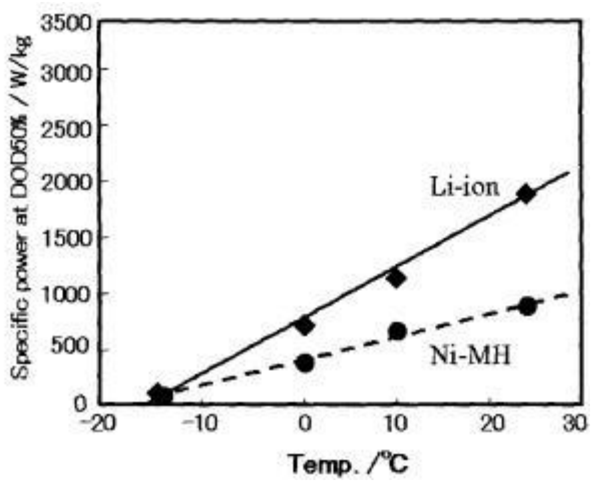

Figure 4: Battery power vs. temperature [5]

Therefore, while the pure ohmic resistance keeps almost constant, the total resistance of a battery may be much higher at low temperatures, as you can see in Figure 5 for the Lithium battery:

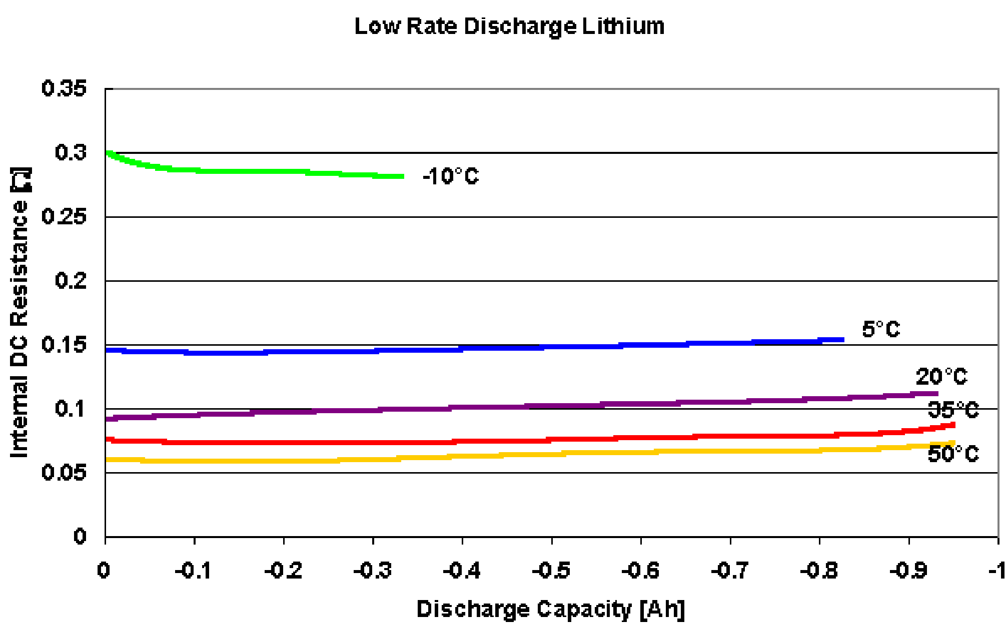

Figure 5: Internal DC resistance of a lithium battery during discharge

Here, the DC resistance is defined as the resistance calculated after a load of 3s duration.

2.3. Phase changes

Temperature may cause phase changes of components used in a battery (e. g. freezing of the electrolyte) which may disrupt operation of the battery. As the freezing point may be a function of the state of charge of the battery (for lead acid, the freezing point of the electrolyte is increased by low acid density because of low SOC), it may be necessary to know the SOC during storage.

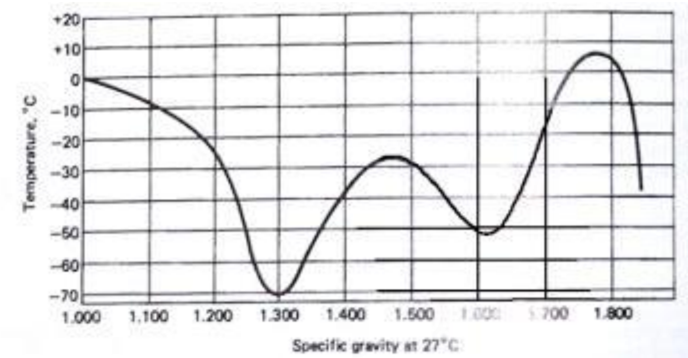

Figure 6: Freezing point of sulfuric acid vs. acid density in batteries, 1.05 to 1.3 is used [6]

Phase changes may also cause separation of the interiors of a battery, e. g. dissolution. As operation of the battery is usually impossible at these low temperatures, such effects are mainly important for storage.

2.4. Mechanical destroyment

If the volume of a component changes because of phase changes or thermal expansion, parts of the batteries (like the case) may be destroyed.

3. **Measurements**

To see some of the effects of temperature in practice, some measurements with commercially available batteries were made:

1. a 1 Ah prismatic Lithium-Ion battery out of a spare battery pack for a mobile phone
2. a AA size nickel-cadmium battery with a rated capacity of 700 mAh
3. a AA size NiMeH battery with a rated capacity of 1.5 Ah
4. a 6V VRLA battery with a rated capacity of 1.3 Ah

All batteries were new and cycled for 5 cycles at room temperature before carrying out the measurements. Discharge was carried out both at low rate (app. 5h rate related to rated capacity) and high rate (app. 1h rate related to rated capacity). Recharging was always at 20°C, after every change in temperature the cells were given 8h to get the temperature.

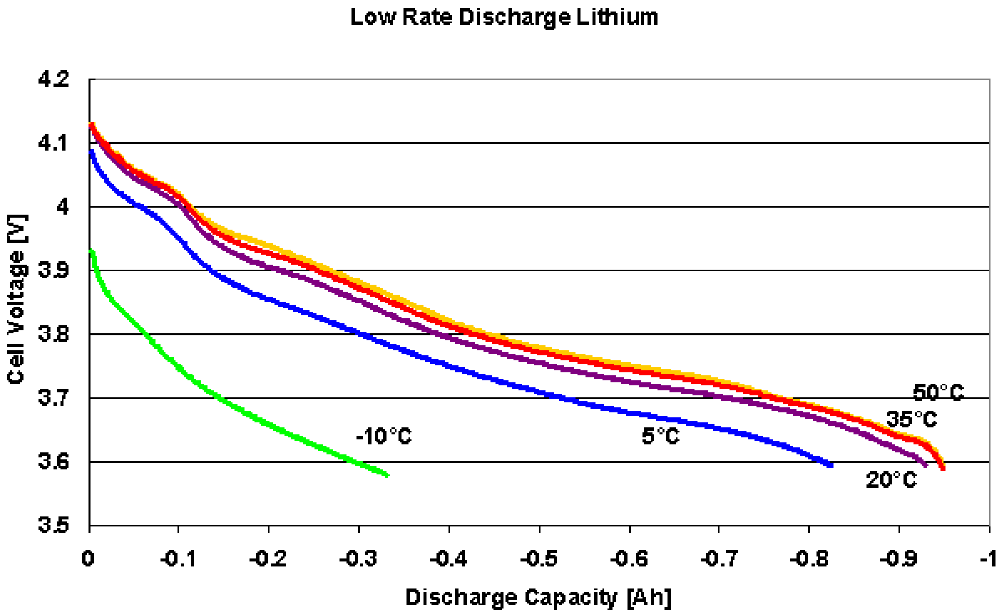

Figure 7: low rate discharge of the lithium-ion cell

For the lithium cell, even at the low rate capacity at –10°C was very low (see Figure 7 and

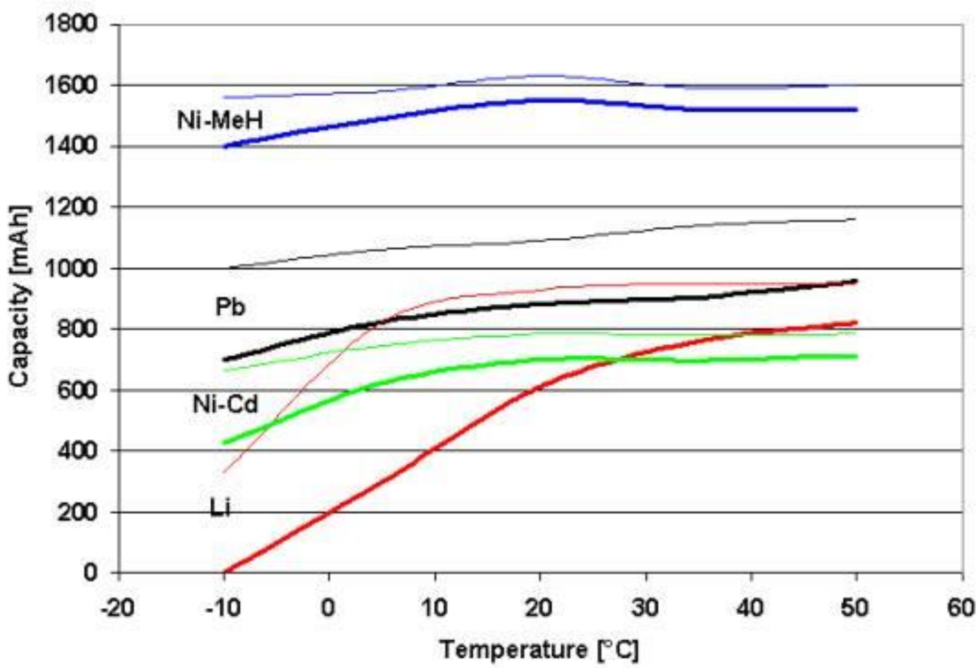

Figure 11). If the end of discharge voltage would have been chosen not as high as here, it would have been possible to get out some more, but still much less than at room temperature.

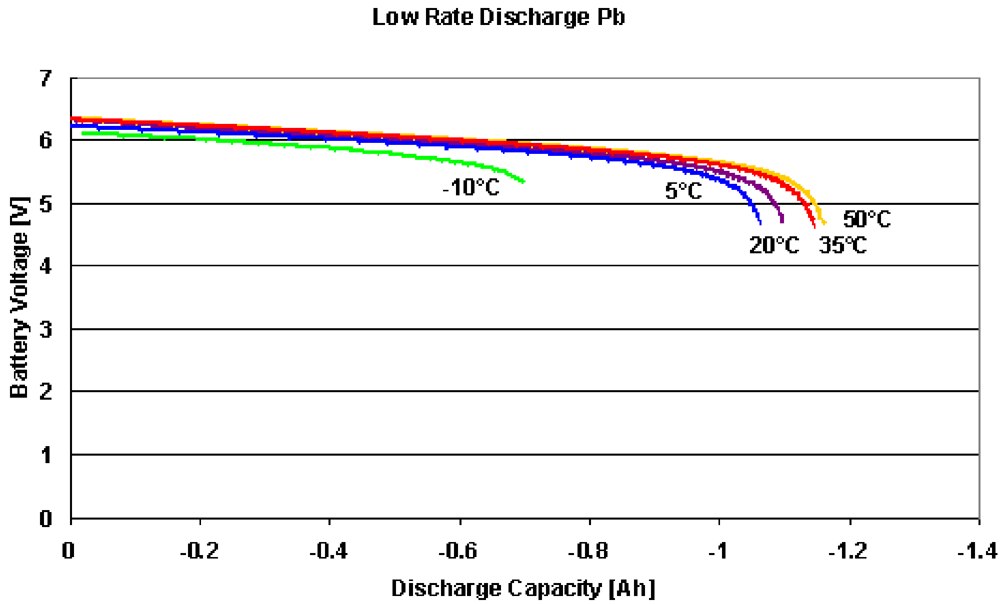

Figure 8: Low rate discharge of the lead-acid battery

This dramatically reduced capacity is mainly influenced by the high internal resistance of the cell (see Figure 5), mainly caused by the decreased diffusion rate of the lithium ions within the electrodes. So, at the surface there will be a lack (neg. electrode) and an excess of lithium.

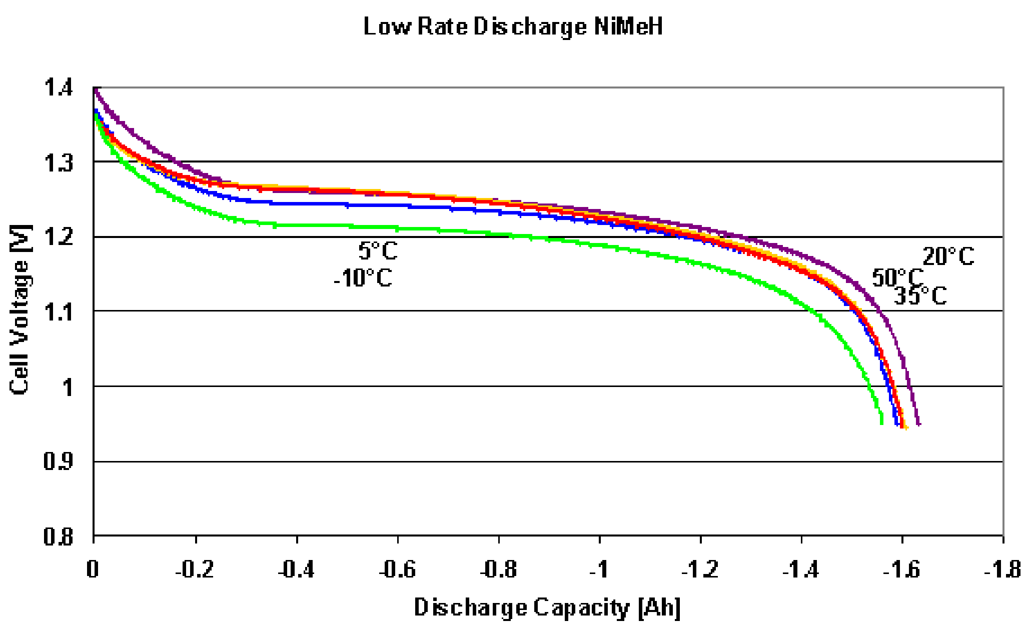

Figure 9: Low rate discharge of the Ni-MeH cell

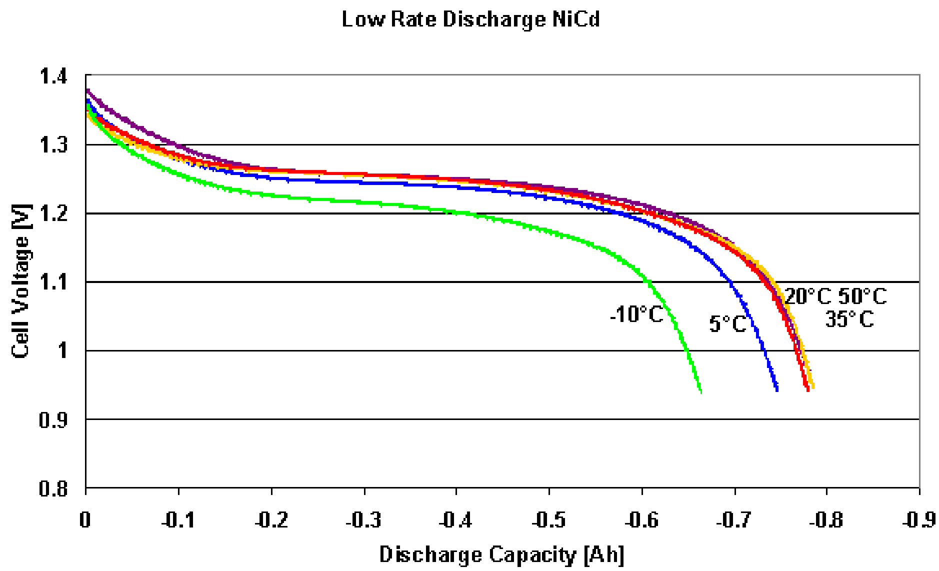

Figure 10: Low rate discharge of the Ni-Cd cell

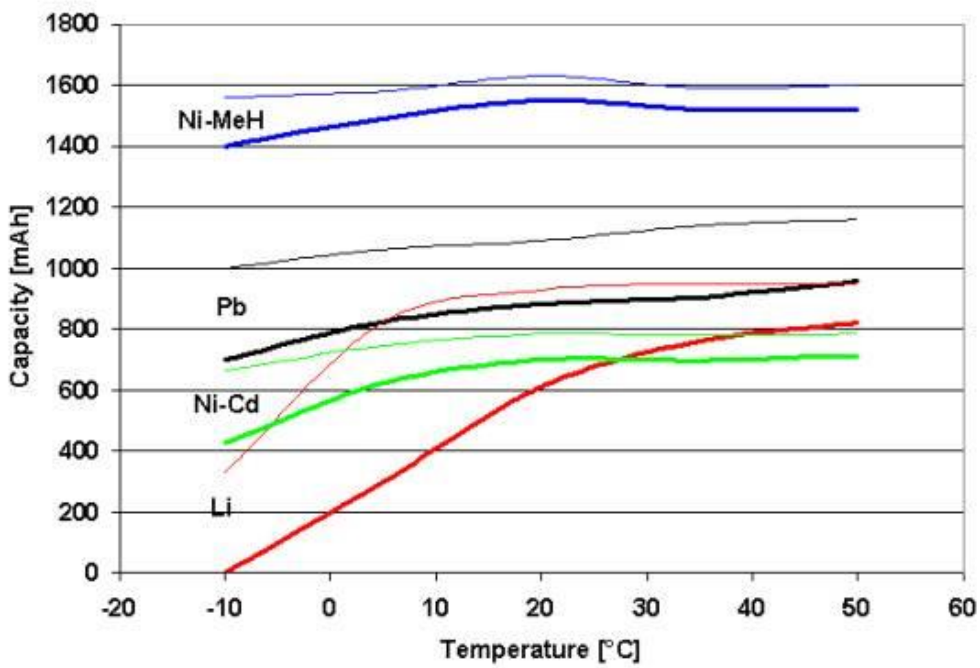

Figure 11: Capacity vs. temperature for low rate (thin) and high rate (thick) discharge

This increase in internal resistance is so high that at –10°C it is even impossible to discharge this battery with a one hour rate, as the battery voltage will immediately drop below the end of discharge voltage. It is no good idea to decrease the end of discharge voltage to overcome this, as it is mainly a question of diffusion which can't be influenced by voltage.

The Ni-MeH battery is the only battery where the discharge capacity is not the highest at 50°C. We assume that this is caused by some self-discharge which occurs at the high temperature level.

4. Conclusions

It is obvious that all of the batteries do have a lack of capacity at low temperatures. Therefore it is important to carefully choose the battery for an application, keeping in mind that there is a lack of performance at temperatures different to room temperature.

In this work some examples for the temperature behavior of some batteries were shown. This shall show the reader some of the problems. What we did not show is the influence on life time and at other discharge regimes than the two we named low rate and high rate.

For the application, it is important that none of the demands to the battery system will be missed. As price, size and weight are usually also an issue, this no easy thing to do. Not only to choose the right battery system, it is also hard to find out the right manufacturer and type of battery, as there are many different types of batteries, also of the same chemistry, where the design is focused on many different things: power density, energy density, low temperature behavior, high temperature behavior, life time, cost, size, … . Next, especially lithium-ion and Ni-MeH are quite new systems, where every year of development gives great improvements (see Figure 1 as an example). So, the battery requested last year may be available this year.

It is very difficult to get all performance data and pack it into a data sheet, because “performance” (which could be power or energy density, life time, high and low temperature behaviour, …) contains almost infinite relationships between the items included. Therefore it may be necessary to test the batteries under worst operating conditions including temperature whether they will meet the requirements before selling them with a product.

As a conclusion, life time of all the battery systems mentioned is much reduced by elevated temperatures, where lithium-ion batteries are still more sensitive. Charging increases this effect.

At low temperatures, especially power density but also charge acceptance is an item. Therefore it is no good choice to operate lithium-ion batteries below 0°C, where lead-acid and especially nickel batteries are still working at moderate power with slightly reduced capacity. For lead-acid, care has to be taken for the electrolyte not to freeze at low temperatures.

5.Literature

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