Fundamentals of battery dynamics

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Abstract

Modern applications, such as wireless communication systems or hybrid electric vehicles operate at high power fluctuations. For some applications, where the power frequencies are high (above some 10 or 100 Hz) it is possible to filter the high frequencies using passive components; yet this results in additional costs. In other applications, where the dynamic time constants are in the range up to some seconds, filtering cannot be done. Batteries are hence operated with the dynamic loads. But what happens under these dynamic operation conditions?

This paper describes the fundamentals of the dynamic characteristics of batteries in a frequency range from some MHz down to the mHz range. As the dynamic behaviour depends on the actual state of charge (SOC) and the state of health (SOH), it is possible to gain information on the battery state by analysing the dynamic behaviour.

High dynamic loads can influence the battery temperature, the battery performance and the battery lifetime.
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1. Introduction

Most technical systems are dynamic systems. Such systems have an input and an output. If a time-dependent signal $u(t)$ is connected to the system, a time-dependent signal $y(t)$ can be measured at the system output. The input signal is the system stimulation and the output signal is the system response. Fig. 1 depicts the principle.

A dynamic system can be described by a set of differential equations:

$$\dot{y}(t) = f[y(t), u(t)] \tag{1}$$

The input and output signals $u(t)$ and $y(t)$ are generally vectors. In some cases, one or both values may be of scalar type.

If the system is of a non-linear type, the differential Eq. (1) are non-linear as well.

For batteries, the input and output signals can be defined in different ways, yet it is most common to define the current and the ambient temperature as input signals. The output signals are the battery voltage, the battery temperature, the state of charge (SOC) and the state of health (SOH). There may be other out-

put signals, such as the resistance or open circuit voltage, but from the dynamic viewpoint these additional output signals yield only small additional information and are therefore neglected here.

A simple example of the dynamic characteristic is shown in Fig. 2. The figure indicates the voltage of a NiMH battery at pulsed discharge. The discharge regime is in line with the GSM standard with a pulse duration of 577 μs and a period of 4.81 ms. The pulse current is 2 A and the current in the rest period is 0.2 A. The discharge voltage shows a voltage ripple of about 40–50 mV. Assuming that the voltage ripple is caused solely by an ohmic resistance, for simplification, the battery resistance can be calculated to 22–28 mΩ.

Comparing a battery that is operated with a pulse charge and/or discharge regime with a battery that is operated with constant current/voltage, the following questions arise for pulse operation:

- Voltage peaks/voltage drops?
- Additional heat generation?
- Battery performance?
- Longer or shorter battery lifetime?

The dynamic behaviour of batteries is influenced both by internal and by external parameters.
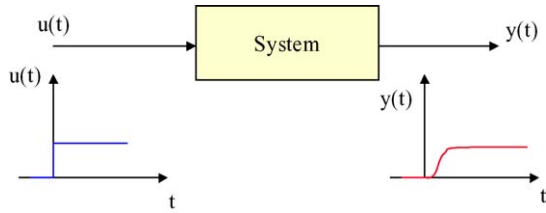
Fig. 1. A dynamic system with the system stimulation $u(t)$ and the system response $y(t)$.

Internal parameters:

- state of charge (SoC);
- state of health (SoH);
- dc and ac resistance;
- battery design parameters.

External parameters:

- temperature;
- dc current;
- short-term history;
- long-term history.

Conversely, the dynamic characteristic contains information on the above parameters. Quite a lot of work has hence been done in the past to analyse the dynamic characteristic for battery state determination. It is important to know the different frequency ranges and time domains of all the possible physical effects inside a battery to gain an interpretation of measured signals.

The time domain of the system response of a battery is in a wide range from some microseconds up to several years. This wide range is caused by different physical effects that can be divided into: electric and magnetic effects (very fast effects), operation principle effects, such as mass transport and double-layer effects and long-term effects caused by operation regimes. Fig. 3 depicts the time domains of the different effects. However, the figure can give only a rough overview, as the time domains of most effects strongly depend on the battery chemistry, the battery design, the temperature, the SOC and the SOH of the battery.

Temperature effects are not indicated in the figure. The dynamic of the battery temperature depends on the heat capacity, the heat dissipation and the heat generation of the battery. As the heat generation is contingent on the load profile, the time domain of the heating can be in a wide range from some 10 s up to some hours. In addition, the temperature influences most of the battery parameters [1], resulting in an interaction between
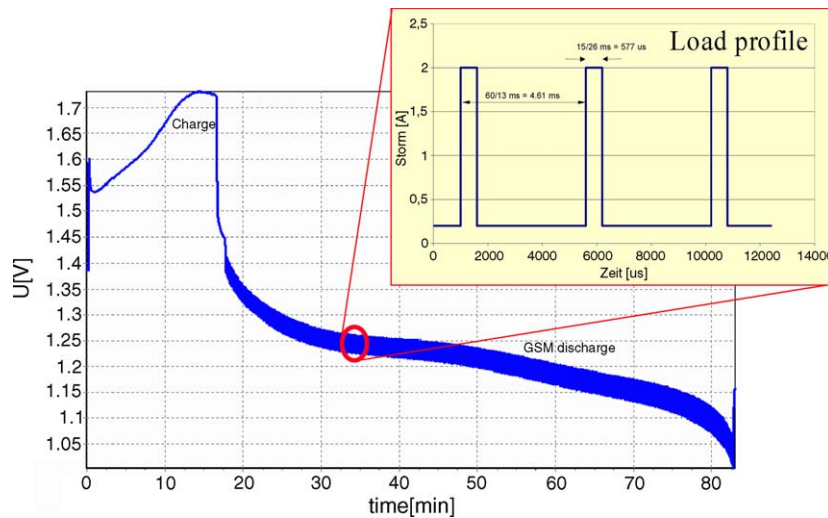

Fig. 2. Battery discharge with pulsed current, as is typical for a GSM cellular phone.
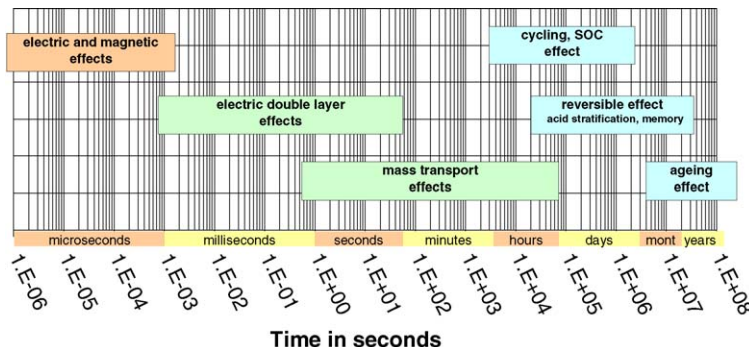

Fig. 3. Typical time ranges of different dynamic effects of batteries.

the temperature time domain with the time domains of the other effects.

The following chapters describe these effects in more detail.

2. Long-term effects

Long-term effects typically are related to the operation regime of the battery. Effects, such as battery ageing and change in state of charge belong to this category.

2.1. Ageing effects

Ageing influences the battery performance and hence the output parameters significantly. The time domain of battery ageing is typically in the range of months to years. For primary cells, ageing is understood as ageing due to storage only and not ageing through discharge.

2.2. Reversible effects

Some electrochemical storage systems show reversible effects. These effects occur during cyclic operation and the battery can be regenerated by a special charge or discharge regime. For example, vented lead-acid batteries show an acid stratification that can be removed by an extended charge. NiCd batteries can show the so called memory-effect: refreshing of the battery is possible by applying a full cycle. The time domain of such reversible effects lies between the values of the ageing effects and the cycling effects. Typical time constants are as short as some hours and as long as approximately 1 year.

2.3. Cycling and SOC effects

If a battery is discharged or charged, the state of charge is changed. This itself is a dynamic characteristic of each battery. Additionally, the voltage of the cell is influenced by the SOC. The time domain of SOC change or cycling depends on the operational conditions. Typically, the time domain is from some minutes up to several days.

During cycling, the battery can heat up, caused by the internal heat sources. The generated heat is influenced to a great degree by the discharge current and the current profile. Assuming an ohmic resistance as heat source, the heat is calculated by:

$$P_R = R I_{eff}^2 \tag{2}$$

In case of a GSM discharge profile, the effective current is 1.73 times that of the average current. This results in a three times higher heat generation in comparison to a constant current discharge with the same average current.

Fig. 4 shows the temperature increase for a AA-size NiMH cell for different discharge regimes, all with the same average current (1 C rate). Table 1 presents the different effective currents.

If the heat source were simply an ohmic resistance, the temperature increase for the different discharge regimes would have to be much higher. In other words, this means that the heat source
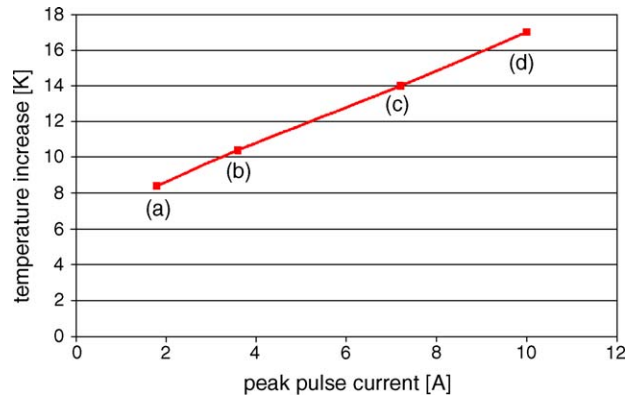

Fig. 4. Temperature increase of a AA-size NiMH battery at different pulse load profiles with the same average discharge current. (a) Constant current, $I = 1.8$ A; (b) 5 ms 0 A, 5 ms 3.6 A; (c) 7.5 ms 0 A, 2.5 ms 7.2 A; (d) 8.2 ms 0 A, 1.8 ms 10 A.

Table 1
Effective currents at different duty cycles

Pulse current (A)	Duty cycle (%)	I_{eff} (A)
1.8	100	1.8
3.6	50	2.55
7.2	25	3.67
10	18	4.2

is not simply an ohmic resistance but a more complex network with the ability to filter some of the alternating current.

3. Mass transport effects

Within batteries, the transport of ions is done by diffusion and by migration. Diffusion is caused by the gradient in concentration, whereas migration is caused by forces of the electric field. Both forces may have different directions. Migration is often hindered by solvated molecules that cover the ion. In most cases, the diffusion is largely responsible for the mass transport. Diffusion can be found at different locations inside the cell:

1. In the free electrolyte or the separator: as the ions are produced on the one electrode and are consumed on the other electrode, the ions have to move between the electrodes.
2. Within the porous electrode as the electrochemical reaction can take place anywhere (inner or outer part of the porous electrode) on the active mass surface: as the diffusion within the porous electrode is limited by geometry, it plays an important role in the dynamic behaviour of batteries.
3. The reaction products can move within the active mass to their final location by diffusion.
4. In case of lithium-ion batteries, there is a film, the solid electrolyte interface (SEI), on the surface of the anode. Diffusion of Li-ions through the SEI has a significant influence on the electric behaviour of Li-ion batteries. For aged cells in particular, the SEI is changed, resulting in an altered dynamic characteristic [2].
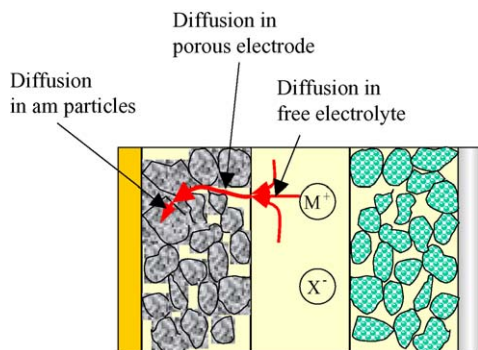
Fig. 5. Diffusion processes in a battery.

Fig. 6. Temperature and concentration dependence on the diffusion coefficient of diluted sulfuric acid.

Fig. 5 portrays the three locations where diffusion can take place. As the battery has two electrodes, the diffusion within the porous electrode and within the active mass (am) is in both electrodes.

Fick's first law describes the diffusion:

$$N_i = -D_i \frac{dc_i}{dz} \tag{3}$$

where N_i is the flux of component i [mol (s cm^2)$^{-1}$]; D_i is the diffusion coefficient [cm^2 s^{-1}]; c_i is the concentration of component i [mol cm^{-3}]; z is the direction of mass transfer [cm].

The diffusion coefficient is material specific. Typical values for the diffusion coefficients are set out below:

in gases: 10^{-1} cm^2 s^{-1};
in liquids: 10^{-5} cm^2 s^{-1};
in solids: 10^{-10} to 10^{-13} cm^2 s^{-1}.

The temperature is a key influencing factor in the diffusion coefficient. Fig. 6 shows the diffusion constant for diluted sulfuric acid as a function of the temperature and the concentration.

The limitations of the diffusion of the ions result in locally changed ion concentrations. From the electrical perspective, the diffusion results in an over-potential caused by reduced or increased ion concentration at the location of charge transfer. As a reservoir for ions exists in the free electrolyte and the porous structure of the electrodes, the diffusion shows a dynamic characteristic. Time constants representing the diffusion depend on electrode thickness and structure to a great degree. Typical response times are in the range of seconds to minutes.

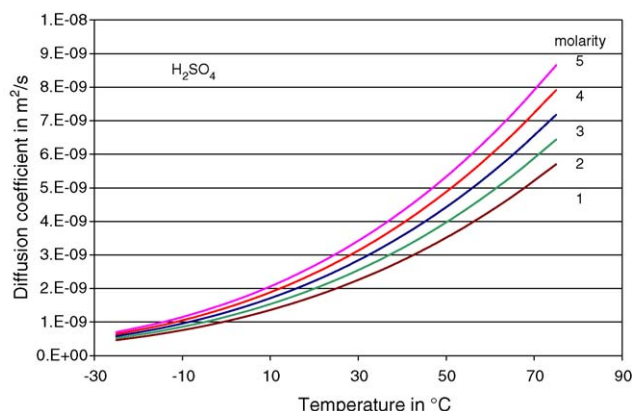Impedance spectroscopy can be employed for analysing the dynamic behaviour of batteries [3]. At low frequencies ($f < 1$ Hz), impedance measurements mainly show the mass transport effects. Fig. 7 sets out the Nyquist plot for three different types of diffusion layers (Fig. 8):

- *Left*: This is a semi-infinite diffusion layer. An example is a planar electrode in an infinite electrolyte reservoir. At this condition, the impedance plot has a constant phase of $-45°$ for the entire frequency range. An element describing this characteristic is the so-called Warburg element. The impedance is given by:

$$Z_W = \frac{\sigma}{\omega^{1/2}} - j\frac{\sigma}{\omega^{1/2}} \tag{4}$$

where σ is the Warburg coefficient, ω the angular frequency and Z_W is the impedance.
- *Middle*: This type of impedance curve is typical for a limited diffusion with an ideal reservoir at the boundary. An example is a rotating disc electrode. The thin layer on the electrode sees an ideal reservoir in the free electrolyte. At high frequencies, the characteristic is identical to the Warburg element, as the diffusion in the diffusion layer is not influenced by the limited diffusion layer.

  Such elements, also in a modified form (Gerischer circuit element), are often used for describing the porous electrodes of batteries.
- *Right*: This type of impedance curve is typical for layers that contain a limited amount of electroactive substance. At high frequencies, the curve is identical to the Warburg element, whereas at low frequencies the material limitation dominates the curve. At low frequencies, the electric equivalent circuit is a resistor and a capacitor in series.
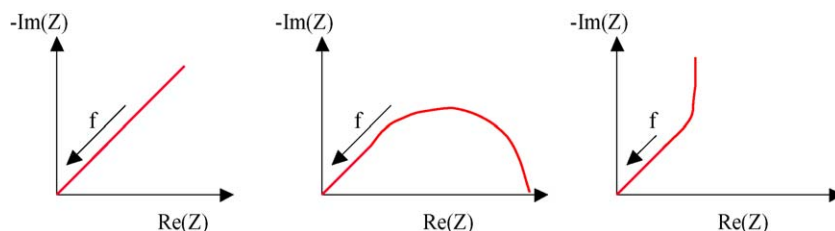

Fig. 7. Nyquist plots describing diffusion effects. Left: Semi-infinite diffusion layer. Middle: Limited diffusion layer with ideal reservoir at the boundary. Right: Limited diffusion layer with a fixed amount of electroactive substance.
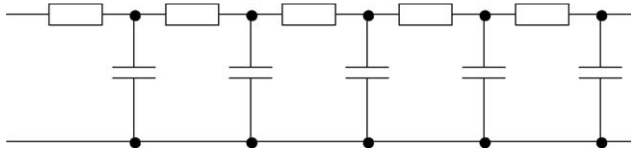
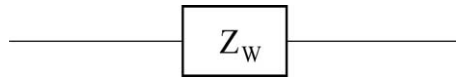Fig. 8. Electric equivalent circuit for diffusion effects.

Fig. 9. Electric equivalent circuit for diffusion effects.

Fig. 11. Simplified equivalent electric circuit.

Batteries and supercapacitors sometimes show this behaviour.

It is quite difficult to describe the electric characteristic of diffusion mechanisms by conventional (R, L, C) elements. However, this can be done using a chain of RC elements, as shown in Fig. 9. Examples in the literature can be found at [4,5].

Such electric circuits have complex equations, many parameters and a limited accuracy. Therefore, the elements describing mass transport effects are simply shown as impedance elements with the impedance Z_W. A detailed description of the mass transport impedance elements including their equations is given in ref. [6].

4. Double-layer effects

A charge zone is formed on the layer between the electrode and the electrolyte. Caused by the short distance and the large surface in porous electrodes, the charge amount cannot be neglected. The charge amount that is stored in this layer depends on the electrode voltage. As the behaviour resembles a capacitor, this effect is called electrochemical double layer or, more practical, double-layer capacitance. Different models that describe the electrochemical double layer have been introduced. The first model was the Helmholtz model (see Fig. 10, left), with simply a fixed single layer (Helmholtz layer). Other models that describe the characteristic in more detail followed. These models use a diffuse layer or a mixture of fixed and diffuse layers (see Fig. 10, right).

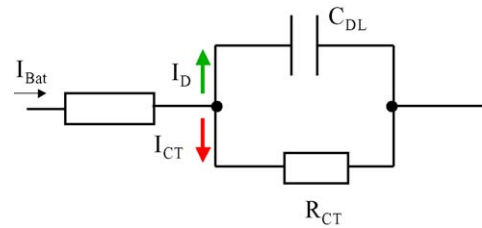As the double-layer capacitor is on the electrode surface, it occurs in parallel to the electrochemical charge transfer reaction. The electrochemical charge transfer reaction is typically described by the electrochemical potential and charge transfer over-potential as given by the Butler–Vollmer equation. From the electrical network point of view, the electrochemical potential is not of interest as it has a resistance of $0\,\Omega$. It is hence neglected in the equivalent electrical circuit (Fig. 11). The charge transfer over-potential is described by the charge transfer resistor R_{CT} and the double-layer capacitor by the capacitor C_{DL}. The serial ohmic resistor describes the ohmic resistance of the electrolyte, the current collector and the active mass. As this element is independent of the electrochemical double layer, it is discussed later.

It is important to know that C_{DL} and R_{CT} are not constant elements. They are impacted by the state of charge, the temperature, the battery age and the current.

The current that flows through the battery is divided at the phase boundary into a part that flows in the charge transfer reaction and a part that flows into the double-layer capacitor. As the capacitor can store only a limited charge amount, it is mainly charged in the first moment of a charge pulse. After a short time, the whole current flows through the charge transfer reaction. When the charge pulse is finished and the battery goes into a rest phase or phase with a smaller charge current, the double-layer capacitor is discharged and the charge amount flows into the charge transfer reaction. This means that the elements R_{CT}// C_{DL} form a low-pass filter for the charge transfer reaction. The double-layer capacitor can only carry alternative currents with a "high frequency", which results in filtering for the charge transfer reaction.

As the two electrodes of a battery are not equal, the dynamic characteristics of both electrodes are also different. For lead-acid batteries, the typical double-layer capacity of the positive electrode lies in the range of 7–$70\,F(Ah)^{-1}$, while the negative electrode has a typical double-layer capacity of 0.4–$1.0\,F(Ah)^{-1}$.
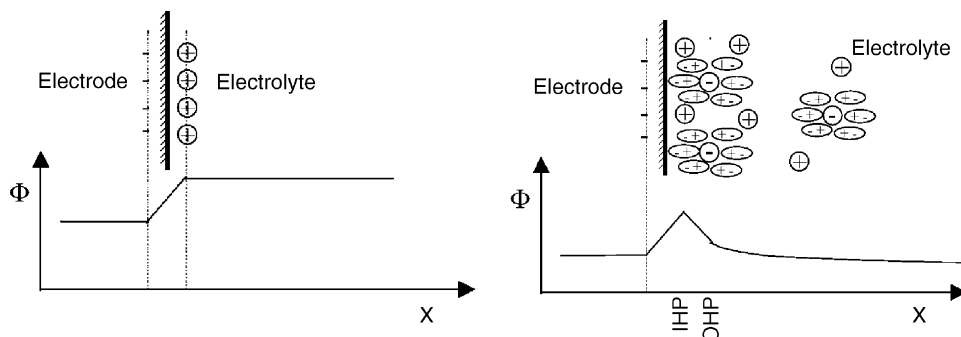

Fig. 10. Two models describing the double-layer capacity: on the left, the Helmholtz model and on the right, the Grahame model.
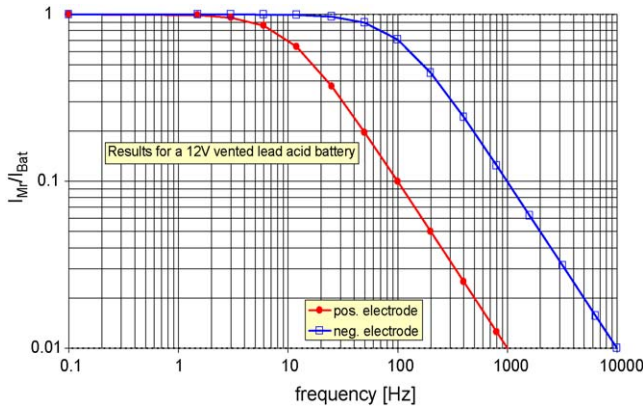
Fig. 12. Frequency response of the two electrodes of a lead-acid battery caused by the double-layer effect.

Taking the charge transfer resistance into account, the low-pass characteristic of both electrodes is given. Fig. 12 shows the characteristic for a typical automotive lead-acid battery. As the figure indicates, the cut-off frequency is approximately 10 Hz for the positive electrode and approximately 100 Hz for the negative electrode. This means that alternative currents with a frequency above 100 Hz do not flow through the charge transfer reaction. They are filtered by the double-layer capacitor. Also, pulse current profiles are filtered and the charge transfer reaction sees the average current. This effect is the main reason why the temperature increase for pulse current operation, as shown in Fig. 4, is not as high as initially expected.

The cut-off frequency f_g and the time constant τ_{RC} are given by the following equations:

$$f_g = \frac{1}{2\pi RC}, \qquad \tau_{RC} = RC \tag{5}$$

The impedance curve of the *RC* element (Fig. 13) is a simple semi-circle, where the diameter is given by the resistance and the angular point is the cut-off frequency. As the two electrodes may have different parameters, the impedance plot is given by superposition of both electrodes.

The time constants depend on the materials and the surface. For batteries, the time constant is in the range of milliseconds to some seconds.
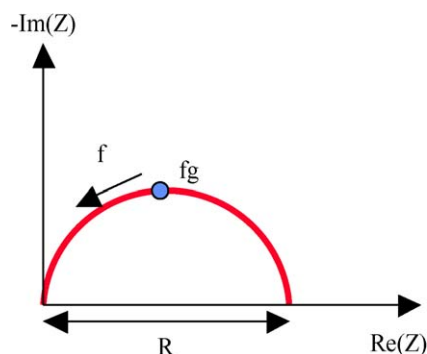
5. Effects caused by porous electrodes

Porous electrodes as used in batteries are complex components. Their behaviour is different from planar electrodes and they have a great influence on the dynamic characteristic. As mentioned above, the diffusion of ions through the porous structure is one of the limiting factors in batteries. Additionally, the porous structure changes during discharging, as the volume of the discharged active mass in most systems is much higher than the volume of the charged active mass. And this results in a reduction of the porosity during discharging. A lower porosity leads to a lower diffusion. In many systems, the conductivity of the discharged active mass differs from that of the charged active mass. This characteristic changes the ohmic resistance of the active mass during discharging. These effects result in an inhomogeneous discharge of the porous electrode, especially at high currents. Fig. 14 shows this relation: the higher the discharge current, the smaller the DOD to be reached, especially in the inner part of the electrode.

This characteristic can be described by a simple model as depicted in Fig. 15 . The resistors for electronic conductivity and the resistors for ion conductivity are then a function of the local state of charge. But this also means that the double-layer capacitor and the charge transfer resistance are distributed elements with different operation parameters. From dynamic viewpoint, this means that the time constant of the electrochemical double layer depends on the state of charge and the short-term history.

Looking at a complete porous electrode, the equivalent circuit can be expanded in the vertical direction. For the overall battery, both electrodes must be taken into account. The characteristic is described by a complex network. Fig. 16 shows the circuit for a whole battery. This circuit is able to describe a vertical non-homogeneous current distribution, which is typical for a lead-acid battery with acid stratification.

Summarising the effects of porous distributed electrodes, findings indicate that the dynamic characteristic is more blurred in comparison to the discussed effects.

6. Electric and magnetic effects

Next to the slow effects of mass transport and the electrochemical double layer, some much faster phenomena are found in a battery.
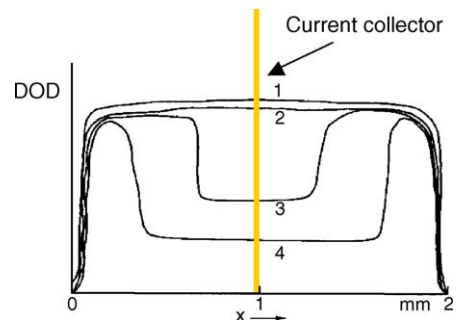

Fig. 13. Impedance curve of an *RC* element.

Fig. 14. Lead-acid, positive electrode at different discharge rates: 1: I_{20}, 2: I_5, 3: I_1, 4: $6I_1$ [7].
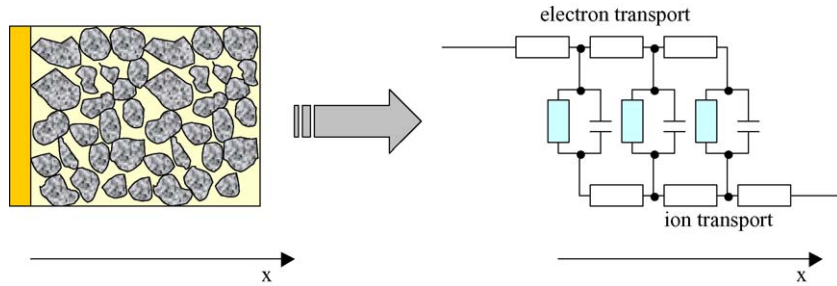
Fig. 15. Porous electrode (left) and equivalent circuit for a horizontal element (right).

The ohmic resistance R_B is the sum of the electrolyte resistance, the resistance of the current collector, the active mass and the transition resistance between the current collector and active mass. In theory, the voltage at the ohmic resistance immediately follows the battery current according to Ohm's law.

Caused by the geometry, each cell has a serial inductance. For a lead-acid battery, values between 10 and 100 nH/cell for 100 Ah cells are reported [4,9]. In case of batteries, the inductance of the serially connected cells must be added. Further, the inductance of the wiring must be considered. The inductance limits the maximum slew rate of the current. However, this effect is only of interest for large batteries (lead-acid) and for frequencies above 1 kHz. In case of small batteries, the inductance is much smaller and much higher frequencies (10–100 kHz) are necessary to show the conductance characteristic.

With increased frequency, the penetration depth of the ions in the porous structure decreases. The electrodes more and more resemble planar electrodes. At these high frequencies, the two electrodes form a simple plate capacitor C_P (interelectrode capacitance). A typical value for a lead-acid battery is some 10 nF/cell.

Fig. 17 sets out the equivalent electric circuit for the high-frequency characteristic.

Together, the capacitor and the conductance form a resonant circuit. Values of 30 nH and 30 nF result in a resonant frequency of approximately 5 MHz. Such resonant frequencies are sometimes reported by working groups developing pulse devices for desulfation of lead-acid batteries [10].

Another effect that cannot be neglected at high frequencies is the skin effect. Caused by electromagnetic field effects, the penetration depth of alternating current in conductive materials is limited. The current depth is contingent on the material properties and the frequency. For cylindrical materials, the current depth is calculated by:

$$d = \frac{1}{\sqrt{\kappa \mu \pi f}},\tag{6}$$

where κ is the conductivity and μ is the permeability of the material.

The current depth reduces the useable cross section area of the current collector, especially if the current depth is small in comparison to the radius of the current collector. In practice, this increases the ohmic resistance of the battery. It must be taken into account that the skin effect is only valid for the alternative current part of the flowing battery current. The resistance of the dc current part is not influenced by the skin effect at all, also if high-frequency alternative currents are superimposed.

Fig. 18 shows the current depth for different typical battery current collector materials as a function of the frequency.

As the figure indicates, lead has a very high current penetration depth. However, the grids in lead-acid batteries are thick in comparison to other battery technologies. Depending on the grid technology, the current collector has a thickness of 1–5 mm. Therefore, the skin effect shows an influence at frequencies of above some kHz.

Materials used in Li-ion batteries (Al, Cu) show a current depth of approximately only 1/3 of the depth of lead, however, the current collector's thickness for this battery technology is in the range of 0.1 mm. Only at frequencies above some 10 kHz –
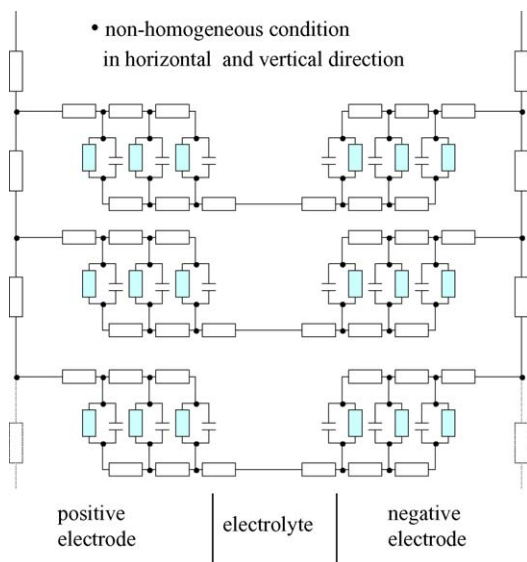

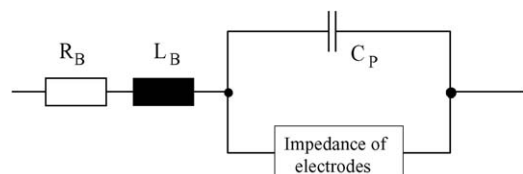Fig. 16. Electric equivalent circuit for a battery with porous electrodes.

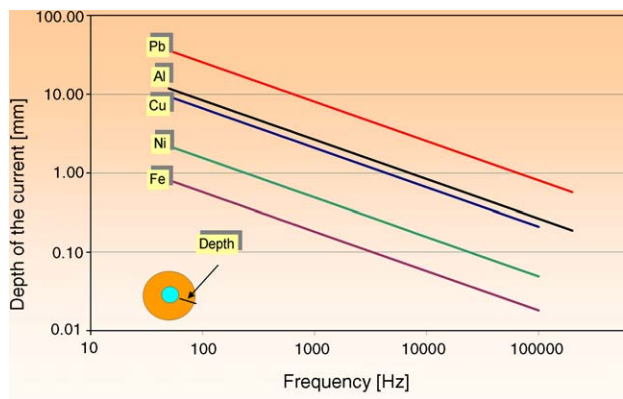Fig. 17. High frequency equivalent electric circuit for a battery.

Fig. 18. The skin effect for different materials as typically used for batteries. It is assumed that the material has a cylindrical shape.

Fig. 20. Impendance spectroscopy for a Li-ion battery for different states of charge.

or perhaps also above 100 kHz – does the skin effect influence the ohmic resistance.

Nickel and iron are used as current collector for NiCd and NiMH batteries. With pasted or sintered electrodes, the nickel substrate has a thickness of approximately 0.1 mm (AA-size cells). In foam electrodes, the current collector is much thinner. Therefore, the skin effect has an influence only at frequencies above 10 kHz in case of NiCd and NiMH batteries. With thicker electrodes in larger NiCd batteries, the skin effect becomes markedly stronger.

7. Analysis of the dynamic battery characteristic using electrochemical impedance spectroscopy (EIS)

EIS is an interesting technology for analysing the dynamic behaviour of batteries. Much work has been done in this field [3,6]. The idea behind the investigations was to find a SOC/SOH determination method.
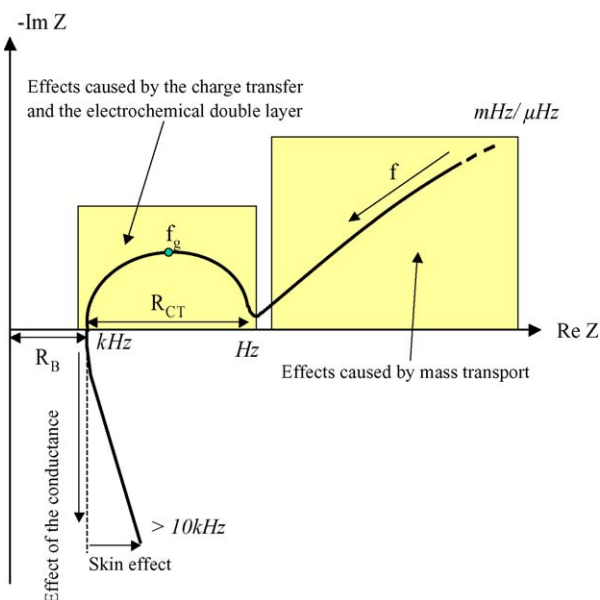
The Nyquist plot that shows the complex impedance in a single curve over the entire frequency range is in most cases used to show the impedance. As the characteristic of batteries is mainly capacitive, the sign of the imaginary axes is reversed to bring the curve into the upper part of the diagram.

Fig. 19 depicts a typical Nyquist plot for a lead-acid battery. The curve is simplified and assumes an identical characteristic of both electrodes. The diagram allows the effects caused by mass transport, the electrochemical double layer and the electrical effects to be separated. The resonant effect caused by the inter-electrode capacitance and the serial inductance are not shown in the diagram.

Fig. 20 sets out the Nyquist plot for a small Li-ion polymer cell at different SOCs. The half circle in this diagram is blurred due to the superposition of the two semi-circles of both electrodes. The figure shows that the change in the state of charge mainly influences the low frequency characteristic. This is largely caused by changes in the mass transport characteristic. If impedance measurements are used for state of charge determination, low frequency measurements are necessary, requiring a high measurement accuracy.

Fig. 21 shows a Nyquist plot for a new and an aged Li-ion polymer cell. The aged cell was operated at a simulated solar regime for 300 solar days (20% DoD) at a temperature of 40 °C.

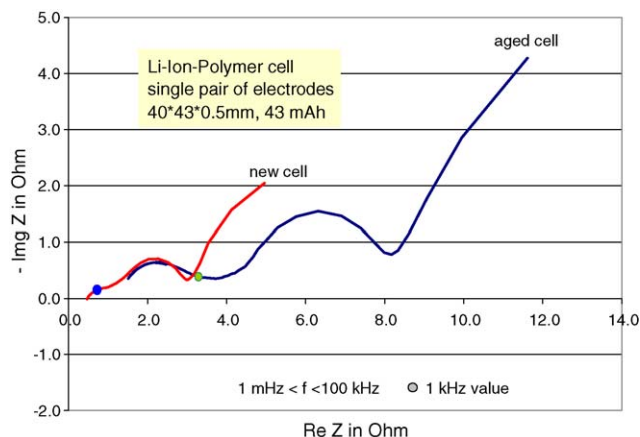Fig. 19. Typical Nyquist plot for a lead-acid battery.

Fig. 21. Impedance spectroscopy for a new and an aged Li-ion battery.

The final capacity of the aged cell was 35% of the initial capacity. The aged cell has a much higher impedance in comparison to the new cell. The change in impedance can be seen over the whole frequency range. In other investigations, where the battery ageing was limited to 80% of initial capacity, the change in the Nyquist plot was more significant at low frequencies and nearly unchanged at high frequencies.

Both diagrams show that the skin effect at frequency up to 100 kHz is immaterial for this type of batteries.

8. Conclusions

The dynamic response of batteries covers a wide frequency range, starting at frequencies of some μHz and ending at frequencies of some MHz. This wide range is caused by different physical effects, such as mass transport, the electrochemical double layer and simple electrical effects. Each effect has a typical frequency range of approximately three decades. However, the typical frequencies depend to a great degree on the battery technology and the battery design.

Some of the dynamic effects are influenced by the state of charge and the state of health, hence enabling measurements of SOC and SOH to be considered. A sound background knowledge is necessary for interpretation. Some fundamentals have been presented.

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