

Properties of a Lithium-Ion Battery as a Partner of Power Electronics

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Acknowledgments

The authors marked with ^{*} contributed equally to this work.
This research received funding by:

Deutsche Forschungsgemeinschaft
(DFG, German Research Foundation)
Funding Code: GRK 1856 (mobilEM)



Federal Ministry of Education
and Research (BMBF)
Funding Code: 03X90330A (OSLiB)



Keywords

«Battery», «Battery impedance measurement», «Filtering», «Impedance analysis», «Impedance measurement», «Lithium-ion», «Lithium-ion battery», «Radio frequency (RF)»

Abstract

Lithium-ion batteries are nowadays offered in a large number of different cell designs and material combinations. This results in a wide range of performance parameters. However, in almost all cases, batteries are used together with power electronic converters, and a central question is the interaction between the converters and the batteries. This could, for example, be the influence of ripple currents or the implementation of impedance diagnostics. But this also leads to the question of the necessity of filters of the power electronics on the battery side.

Introduction

Lithium-ion battery technology is the dominating battery technology for mobile communication devices or electric vehicles. First, this paper gives an overview of the state-of-the-art battery characteristics. Then, after the principle design of lithium-ion batteries is described, the performance of nowadays battery systems is summarised. The chapter concludes with a resume of the ageing and cell design aspects

of battery applications.

Electrochemical impedance spectroscopy (EIS) is used to characterise and track the behaviour of batteries. The battery's impedance, which directly interacts with the power electronics, correlates with various internal and external conditions. Impedance data from one battery cell under different conditions is shown. Measurements at higher frequencies, up to 50 MHz, are also carried out. The impact of the temperature on the impedance is further analysed.

Lithium-ion batteries

Lithium-ion batteries are the key to far-reaching hybridisation and electrification of drives, cordless mobile devices, or stationary energy storage systems. Current forecasts predict an increase in battery cell production from a good 1000 GWh/year in 2025 to over 3000 GWh/year in 2030. By comparison, the storage capacity of all pumped storage power plants in Germany is currently around 40 GWh. While, according to the current state of knowledge, by 2030, a large number of batteries will probably be assigned to lithium-ion technology. There is now a high degree of differentiation of properties, so that a cell technology tailored to each application is available.

Principle design of lithium-ion batteries

"Lithium-ion" is a collective term for various material combinations that have in common that they contain about 3 %_{w/w} lithium and that this lithium takes over the actual charge storage and charge transport between the two electrodes. Various properties can be achieved by choosing different electrode materials, cell designs and manufacturing processes. Therefore, it is generally not correct to speak of the properties of "the" lithium-ion battery. Even for a given combination of materials, there are usually products with a wide range of properties. Therefore, statements such as "material X has a longer life than material Y" are rarely correct in absolute terms. Instead, it is necessary to look very closely at the characteristics of each product in terms of capacity, charge and discharge performance, calendar and cyclic life, safety, temperature operating ranges and costs.

A distinction is made between lithium-ion batteries, in which the lithium is never metallic in regular operation, and lithium-metal batteries. The latter deposits lithium metallically on the anode when charged. This technology plays almost no role in applications yet, but will gain importance in "solid-state batteries". Here we focus on lithium-ion batteries as the technology of choice for the coming years.

Lithium-ion batteries are pure intercalation batteries (Fig. 1). This means that the lithium diffuses into or out of the existing crystal structures of the positive electrode (called the cathode) and the negative electrode (anode). While lithium is present as a positive ion when it moves in the electrolyte, it is neutralised again by the external electron flow after it has been deposited on interstitial sites in the electrodes. The cathode material used in lithium-ion batteries today is predominantly a metal oxide in which nickel, cobalt, manganese and aluminium are used in various stoichiometric ratios. The stoichiometry essentially determines all technological properties and the costs. In particular, there is an effort to reduce the cobalt content as much as possible because it is the most expensive and scarcest of the materials. For example, cathode materials with eight parts nickel and one part cobalt and manganese are increasingly being used (NMC 811). In addition, lithium iron phosphate (LFP) plays a role as a cathode material with significantly lower energy densities. However, because iron is significantly cheaper than cobalt and nickel, lower costs per kWh can be achieved. In addition, LFP is a material with different electrochemical properties that make it an inherently safer material.

The anode in commercial lithium-ion batteries consists of various modifications of graphite, whereby some products with exceptionally high energy densities replace part of the graphite with silicon. This can increase the energy density because more lithium can be incorporated per silicon mass. However, while graphite has a volume increase of about 10 % when lithium is intercalated, this is up to 300 % for silicon, which causes enormous mechanical stress and thus problems with the cycle life. Therefore, only parts of the graphite have been replaced by silicon. Another anode material is lithium titanate (LTO). Cells with this material have a significantly lower cell voltage and thus also a considerably lower energy density. At the same time, with this material, which has virtually no change in volume during cyclisation

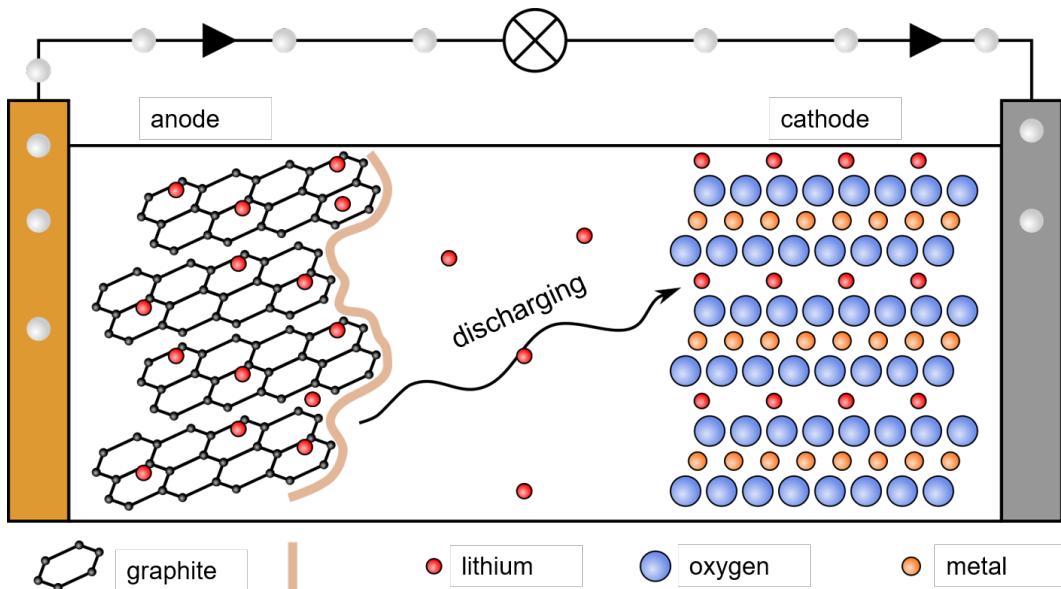


Fig. 1: Schematic of a lithium-ion battery

and top layer formation, lifetimes in the range of 100,000 cycles or very high charge rates of up to 100 C can be achieved. The C-rate expresses the current strength that can be achieved in relation to the capacity. The inverse of the numerical value indicates the duration in hours that is theoretically required for a complete charge or discharge. A typical current of 1 C thus corresponds to a duration of one hour, while 100 C corresponds to a duration of one-hundredth of an hour, i.e. 36 s.

Between the two electrodes there is a porous separator which acts as an insulator for the electronic current and reliably prevents a short circuit between the two electrodes. Today's commercial lithium-ion batteries contain an organic, water-free electrolyte ("solvent") with a conducting salt that provides sufficient lithium ions for good conductivity. The electrolyte fills not only the pore volume of the two electrodes by about 30 % so that ions can penetrate the deeper layers of the active material via the electrolyte without much resistance but also the pores of the separator and all other free spaces between the two electrolytes. If the moistening with electrolyte is incomplete due to inadequate filling or due to consumption of the solvent by ageing processes, this leads to an increase in internal resistance and a decrease in capacity. A large number of additives are usually added to the electrolyte, which has a very significant influence, for example, on the service life and safety of the battery cell. These additives' type, composition and quantity are among the best-kept secrets of battery cell manufacturers and can hardly be broken down using standard analysis methods.

Electrical performance

Today, lithium-ion batteries are offered in many modifications concerning the electrode materials, the design and the internal structure, which determines the performance. In addition, other factors such as electrolyte composition and additives play an essential role, e.g. for the maximum charging currents, low-temperature behaviour, safety or cycle and calendar life. Generalised statements about which material combinations are particularly good in terms of individual properties are often suggested in the literature and company publications. However, it can be seen in the market that there is extensive coverage of product properties for almost every material combination. Moreover, the manufacturer's specifications often only give an incomplete picture of the actual composition of the battery, as laboratory analyses show time and again. It is, therefore, worthwhile to systematically examine the products available on the market for their properties and not to automatically exclude products based on specific information from the manufacturer on the materials used.

Currently, there is an increasing differentiation of characteristics in the mobility sector. In the 2010s, vehicle manufacturers were keen to cover a wide range of different vehicle requirements with one cell to

achieve an economy-of-scale effect. In the meantime, the number of units planned for the coming years is so high that optimisation can take place with regard to costs, energy density or other properties for the respective product segment. In the process, much shorter cycle lives are now being accepted. Whereas in the 2010s, traditional vehicle manufacturers set requirements for cycle life in the range of 2000 to 4000 full cycles, today, 500 to 800 full cycles are usually sufficient. On the one hand, this is a consequence of the Wöhler effect, which leads to significantly higher energy turnover and thus a higher total mileage when the battery is partially cycled. On the other hand, batteries have become much larger and, today, typically have a range of between 300 and 500 km. 800 cycles at a range of 300 km are already 240,000 kilometres (without the Wöhler effect) and sufficient for almost all passenger cars. But battery cells with a service life of 3,000 cycles and more are needed for trucks or typical stationary applications since the battery capacity is ultimately used once or even twice a day in these applications.

The volumetric energy density related to the volume is around 2 to 2.5 times higher for lithium-ion batteries than the gravimetric energy density. Nevertheless, very high power densities can be achieved, which come into the range of supercaps. The highest power densities are achieved with LTO batteries. The highest energy densities among the commercially established technologies are achieved with NMC cathodes with high nickel contents in combination with graphite anodes with an admixture of about 5 to 15 % silicon. The highest power and energy densities cannot be achieved simultaneously for any battery technology. The internal resistance must be minimal for high performance, but this can only be achieved if the ionic resistance is as small as possible. For this, the electrodes must be very thin to allow short paths for the ions. With thin electrodes, however, the ratio between the weight and volume of the active masses needed for energy storage and the passive parts of the cell such as current conductors, housing and separators is significantly lower than with thick electrodes.

For hybrid vehicles, battery cells with very high power densities are primarily used, as high power must be retrieved from small batteries. Cells with high performance can be charged and discharged very quickly. Accordingly, high numbers of cycles per day can be achieved. Therefore, high-performance cells are usually batteries with high cycle life. Even at high current rates, a high proportion of the capacity available at low currents can be used in lithium-ion batteries. This makes lithium batteries very suitable for high current loads, such as those in power tools or uninterruptible power supplies in addition to hybrid vehicles. On the other hand, high amounts of energy are needed for all-electric vehicles for corresponding ranges; therefore, cells with high energy densities are used. The performance for the drive is achieved despite the lower energy densities because the batteries are large. With 60 kWh battery capacity, 180 kW of drive power can already be served with a 3 C discharge capacity, which virtually all automotive batteries achieve.

The efficiencies of lithium-ion batteries are 90 to 95 % and are thus very high compared to all other battery technologies. This is due to the low internal resistance and the high cell voltages of 3.3 to 3.7 V for LFP and NMC types, which are thus almost twice as high as lead-acid batteries with 2.0 V and around three times as high as NiCd and NiMH batteries with 1.2 V, for example. The high voltage level thus also reduces the wiring effort at a given system voltage and positively affects the internal resistance of the battery system. In operation, the efficiency can also be lower at low temperatures, leading to accelerated heating of the battery.

Ageing

Various processes on both electrodes and the boundary layers between electrolyte and electrode materials lead to the ageing of lithium-ion batteries. However, the most important effect in all NMC and LFP variants is the formation of a boundary layer between graphite and electrolyte on the negative electrode ("solid electrolyte interphase" (SEI)). At the negative electrode potential, the electrolyte is not stable and therefore reacts spontaneously with graphite and lithium. The process is only stopped because the reaction product itself forms a separating boundary layer. This boundary layer is very dense and reduces the reaction rates considerably. This makes it comparable to verdigris on copper, for example. Copper roofs can therefore become very old. The boundary layer also allows long lifetimes in lithium-ion batteries. At the same time, however, the boundary layer must remain permeable for the lithium

ions during charging and discharging. Therefore, in principle, it continues to grow depending on the voltage level, state of charge, temperature and cycle depth. Since the boundary layer contains lithium compounds that cannot be dissolved again, the growth of the boundary layer deprives the battery of free lithium necessary for charge storage. The available capacity decreases accordingly. At the same time, the internal resistance grows with increasing layer thickness. The growth of the boundary layer thus reduces the capacity and increases the internal resistance.

The performance decreases significantly towards lower temperatures. The exact temperature at which this becomes critical depends on the battery cell. Cell manufacturers can set lithium-ion batteries' "feel-good" temperature range in relatively wide ranges. Above all, it is important to prevent so-called lithium plating. This means a deposit of metallic lithium on the anode during charging. At any given temperature, there is a maximum charge current rate at which the ions have sufficient time to diffuse into the graphite structure. If it gets colder or the current is higher, a "jam" of ions forms, which are then reduced to metallic lithium on the surface. This metallic lithium then has no protective layer and is exposed to the direct reaction with the electrolyte. This produces insoluble reaction products, which on the one hand, hinder further ion transport, which leads to an increase in internal resistance, and on the other hand, active lithium is permanently bound and thus removed from charge storage. Therefore, lithium plating leads to greatly accelerated ageing. Modern charge management systems must pay particular attention to and prevent this effect, which is dependent on the respective state of charge and the ageing state. This is also a major reason why the real charging speed is often below the value possible due to the charging power of the charging station.

Cell designs

Three different cell designs are manufactured and used (Fig. 2). The electrodes and separators are wound from continuous rolls for round cells and placed in a cylindrical housing. These cells are traditionally used in consumer products and were initially used by Tesla in the 18650 size (18 mm diameter, 65 mm height) for their vehicles. Today, the 21700 format is increasingly used in vehicles, and a 46800 format has been announced for the next generation. Compared to the 18650 cell, this will have a volume around eight times larger and a correspondingly higher capacity.

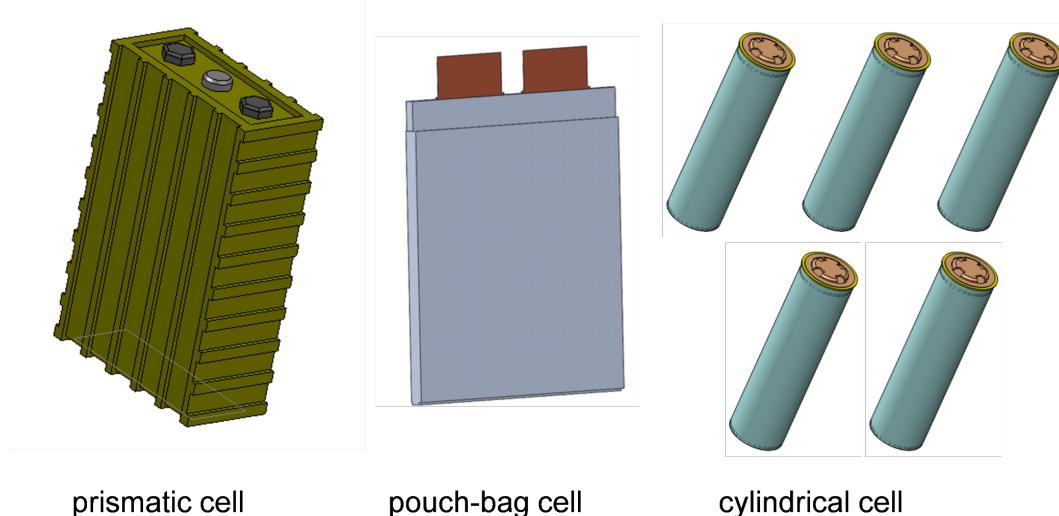


Fig. 2: Principal designs of lithium-ion batteries: prismatic, pouch-bag, and cylindrical

The electrodes are stacked and welded in a foil in flat or pouch-bag cells. Here, very different designs are known with regard to height, width and thickness and thus also capacities from less than one to well over one hundred Ah. The contacts can be attached to one side but also to opposite sides of the cell.

In prismatic cells, cubic housings are used, which are almost always made of metal for vehicles. The electrodes are either oval-wound cell stacks or layered designs like pouch-bag cells. There is currently

a trend toward layered stacks, which on the one hand, allow higher volumetric utilisation of the cell volume and, on the other hand, enable much more uniform pressure conditions and mechanical loads.

Extreme cell designs are sometimes used to house the batteries, with cells barely 10 cm high but up to a metre wide.

Due to the change in volume of the materials during charging and discharging and possible gas formation, prismatic and pouch-bag cells are usually braced in vehicles today. This makes it possible to achieve longer service lives. However, this is not necessary for cylindrical cells, as the housing builds up this pressure due to the geometry.

The cell designs have different properties with regard to cooling in the battery pack. In principle, however, almost all electrode materials can be used in all three cell designs. So far, it is unclear whether one of the three cell designs would prevail in the automotive sector to the detriment of the others or whether one of the three designs would be eliminated in the foreseeable future.

Impedance spectroscopy

As a lithium-ion battery is an electrochemical system, electrochemical impedance spectroscopy (EIS) can be used to characterise the electrical behaviour under different circumstances. The frequency range is often between 10 mHz and 10 kHz. For slide-state batteries, this might increase up to 10 MHz or even higher, as first tests on laboratory test cells suggest [1].

Non-solid-state batteries such as lithium-ion or lead-acid batteries are used in most battery-driven applications nowadays. The higher frequencies for characterisation are not interesting, as the chemical reactions have much lower time constants. However, if the system powered by the battery applies non-constant loads at high frequencies, the battery's response is of interest. The measurements have to be done first to model the overall behaviour at high frequencies. One example of such a load might be a DC/DC converter connected to a battery. Due to improper design or filtering, the DC/DC converter might have current ripples. This noise, considered from electromagnetic compatibility (EMC) perspective, must be reduced. Here also, the frequency response of the battery is a necessary parameter.

Tested batteries and used equipment

The cylindrical 18650 battery cell Samsung 35E, with lithium nickel cobalt aluminium oxides (NCA) on the cathode and silicon-carbon (Si/C) on the anode, is further investigated in the frequency range from 10 mHz to 50 MHz, thus covering corresponding time constants of 100 s down to 20 ns. The "Vector Network Analyzer - Bode 100" by the company "OMICRON electronics GmbH" is used in the frequency range of 5 Hz to 50 MHz, and the "Digatron EIS-Meter" by the company "Digatron Power Electronics GmbH" for the frequencies from 10 mHz to 6 kHz. The tests are performed in a temperature chamber "Binder MK56" by the company "BINDER GmbH".

In sum, four different batteries of the same type are used for the measurements. Two cells, "Samsung 35E Aged - Everlast 014" and "Samsung 35E Aged - Everlast 025", are aged cells. The description of the tests and the raw data of the cyclic tests is published in [2]. The cell's nominal capacity at begin of life (BOL) is 3.35 Ah. The end of life (EOL) is often defined as a state of health (SOH) concerning the normalised capacity (SOH_C) of 80 %. For this cell, this would be 2.68 Ah. The "Samsung 35E Aged - Everlast 014" shows after 417 Equivalent Full Cycles (EFC) a state of health (SOH_C) of 91.9 % as the capacity dropped to 3.08 Ah. As also shown in Fig. 3 the capacity of the Everlast 025 cell after 899 EFCs is 2.83 Ah resulting in an SOH_C of 84.5 %.

Electrochemical impedance spectroscopy

With the real-valued voltage and current signals, a battery's complex impedance is calculated. This data is available in the battery management system (BMS). First, the voltage (1) and the current (2) must be transformed to the frequency domain. If the measurement fulfills the linear time-invariant (LTI) criteria,

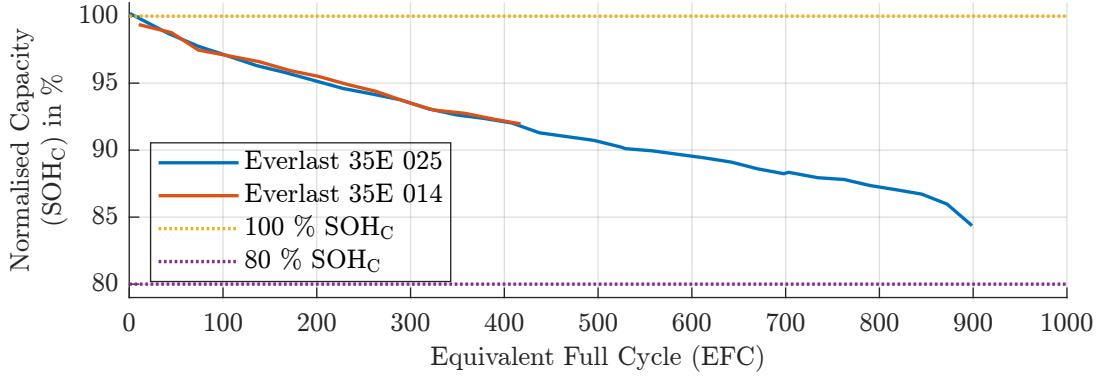


Fig. 3: Ageing of the Everlast 35E 014 and Everlast 35E 025 cell

the resulting real part of the impedance in the frequency domain possess point symmetry, and the imaginary part possesses mirror symmetry. Thus only positive frequencies are shown in the diagrams. Two representations are dominant in literature, the Bode diagram and the Nyquist diagram (3). The Bode diagrams x-axis, representing the frequency, is often scaled logarithmic, but the magnitude and the phase on the y-axis are scaled linearly. In the frequency domain of interest, often between 10 mHz and 10 kHz, the behaviour of a battery is conductive. In order to have most of the data in the I Quadrant, the y-axis is flipped.

$$v(t) \circ\bullet \underline{V}(f) \quad (1)$$

$$i(t) \circ\bullet \underline{I}(f) \quad (2)$$

$$\frac{\underline{V}(f)}{\underline{I}(f)} = \underline{Z}(f) = \underbrace{|\underline{Z}(f)| \cdot e^{j \cdot \angle \underline{Z}(f)}}_{\text{Bode Diagram}} = \underbrace{\text{Re}\{\underline{Z}(f)\} + j \cdot \text{Im}\{\underline{Z}(f)\}}_{\text{Nyquist Diagram}} \quad (3)$$

In Fig. 4 and Fig. 5, impedance data of Samsung 35E cells is shown. The impedance correlates with different states. The cell's ageing here is plotted with regard to the normalised capacity (SOH_C), the state of charge (SOC), represented by the open-circuit voltage after one hour of rest, and the temperature affects the impedance of a battery.

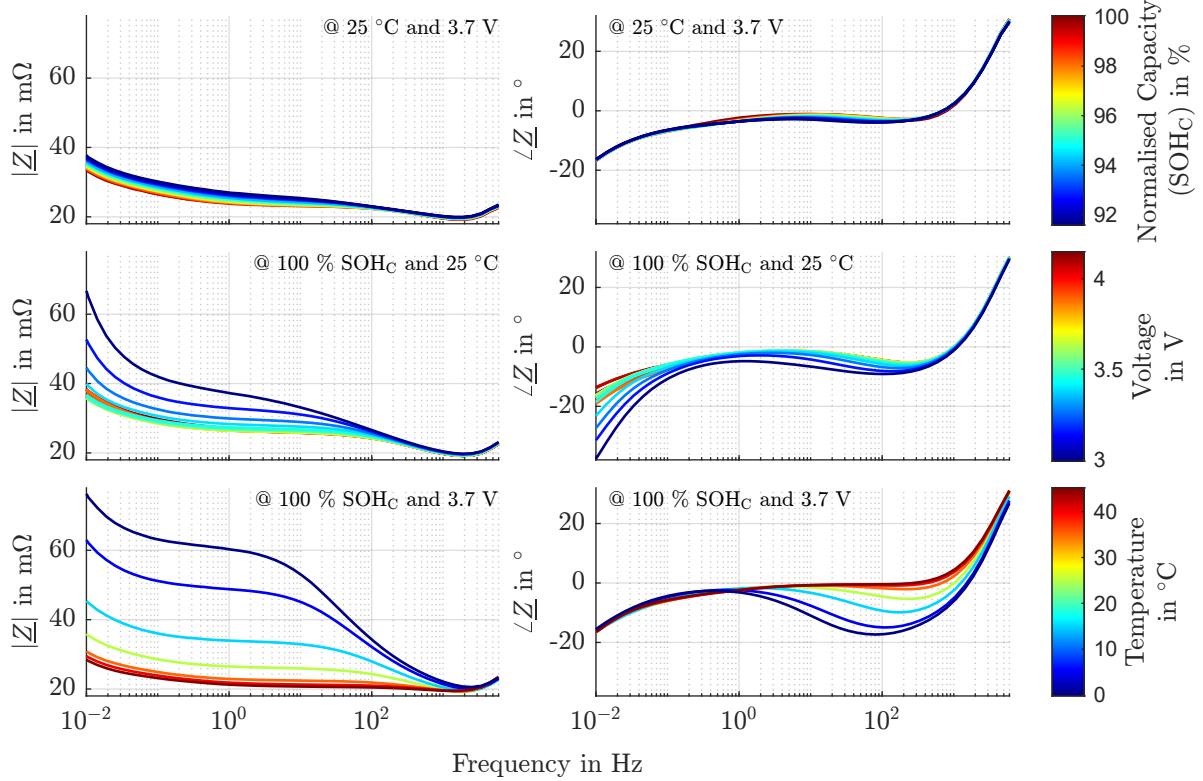


Fig. 4: EIS measurements in a Bode diagram

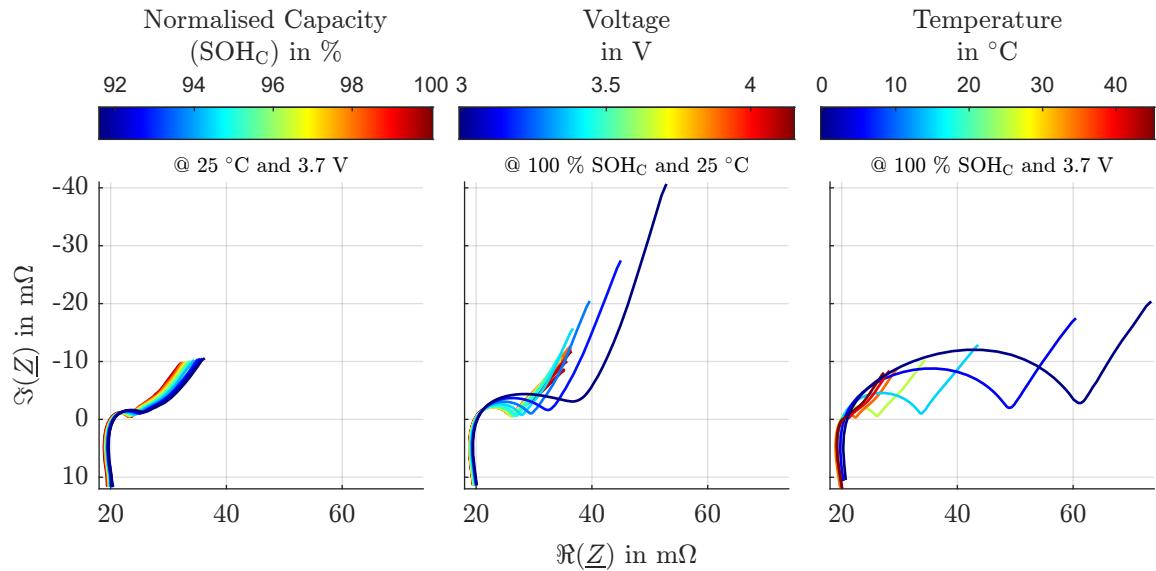


Fig. 5: EIS measurements in a Nyquist diagram

Radio frequency impedance analysis

As lately also analysed by Landinger et al. [3], the absolute value of the impedance in the radio frequencies is increasing and varies with the internal electrical connection, the state of charge and the temperature. In this work, we measure the impedance in the frequency range from 5 Hz to 50 MHz and investigate the influence of ageing, state of charge and temperature. Fig. 6 and Fig. 7 present the results. The noise in the range $|Z(f)| < 1 \Omega$ is relatively high, as the chosen measurement system and the connection are not designed for such low impedance. In contrast to the conventional representation in the Bode diagram for the battery sector, the y-axis is scaled logarithmic now.

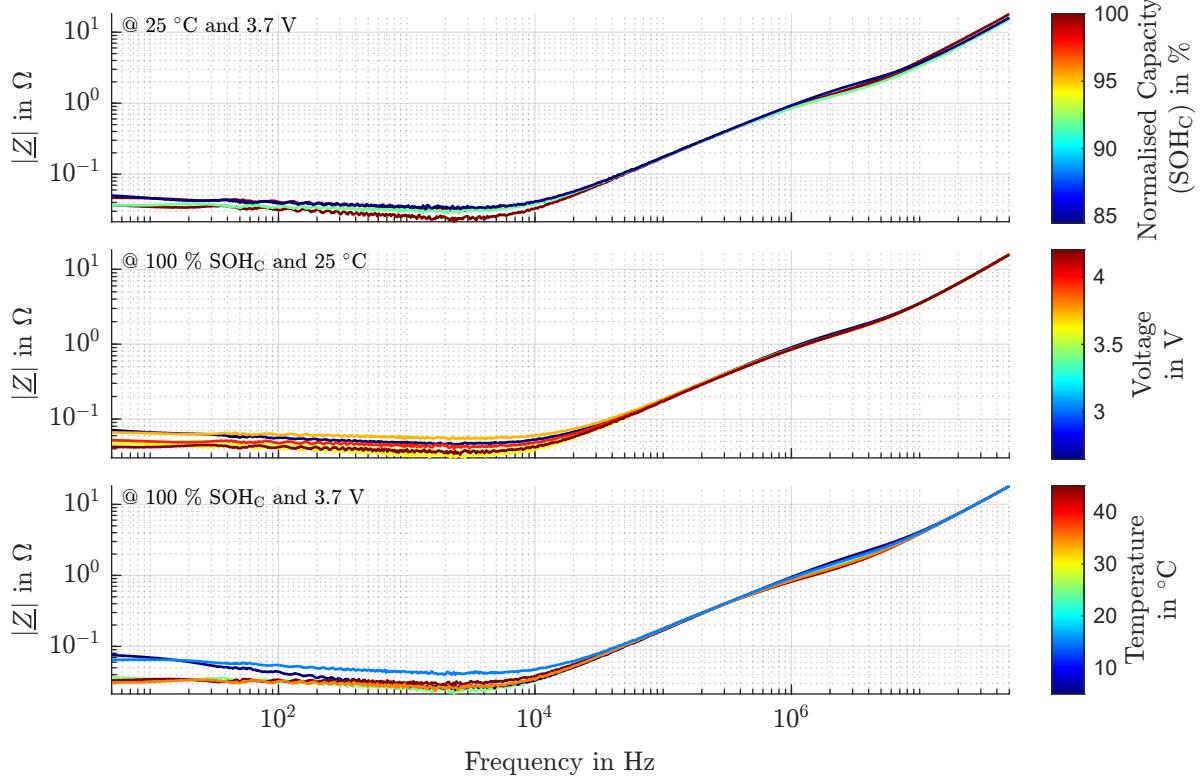


Fig. 6: Radio frequency impedance measurements in a Bode diagram

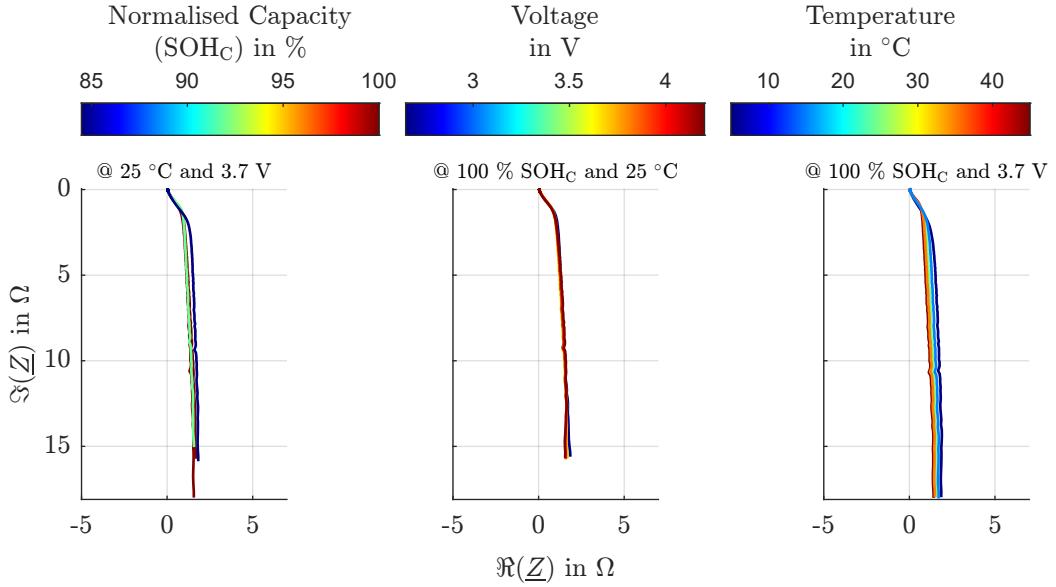


Fig. 7: Radio frequency impedance measurements in a Nyquist diagram

The measurements at different voltages and temperatures are performed with the same cell. For the measurements, at different capacities, four different cells are used. Two of them are new cells, and the other two are the aged cells from Fig. 3. For the state of charge (SOC), represented by the voltage, no significant change in the impedance curve is evident. The curves at the varying state of health (SOH_C) differ, but no correlation exists. This might be due to different batches of the four cells, as they were not bought together. Different characteristics of different batches of this specific cell were analysed in [4]. The temperature and the impedance show a correlation. In Fig. 8, the frequency range from 300 kHz to 13 MHz is shown with more detail. Furthermore, a 1 Ω Resistor was measured with the same setup and calibration to verify if the impact was due to the setup or the battery cell. Even though an offset

at the 15 °C measurement exists, no correlation with the temperature occurs for the 1 Ω Resistor. The Arrhenius diagram endorses this. With a coefficient of determination $R^2 = 0.99862$, the suggested fit between the temperature and the absolute value of the impedance indicates a correlation.

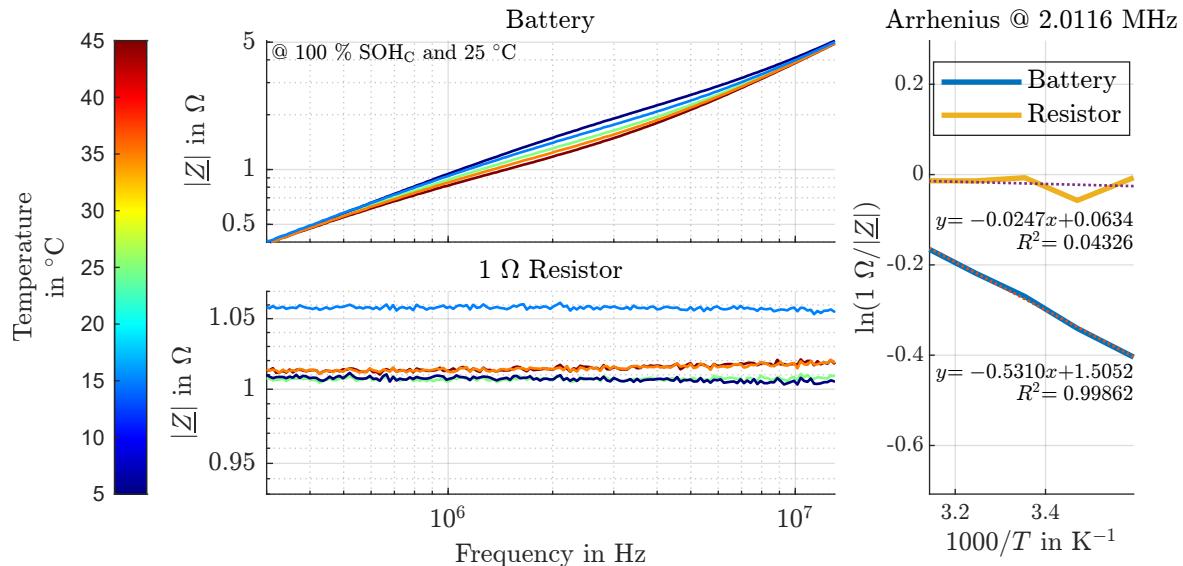


Fig. 8: Radio frequency impedance measurements at different temperatures and Arrhenius

Conclusion

As the number of battery cells on the market increases, so does the diversity. General statements about chemistries and cell formats are rarely universally applicable. The impedance of the battery characterises it, but is also an important parameter for the interconnection of the battery system and the power electronics. The absolute value of the impedance of the measured 18650 cell increases with the frequency and shows at least a correlation with the temperature. A correlation with ageing or the state of charge does not become apparent. All three conditions impact the impedance in the lower frequency range from 10 mHz to 6 kHz.

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