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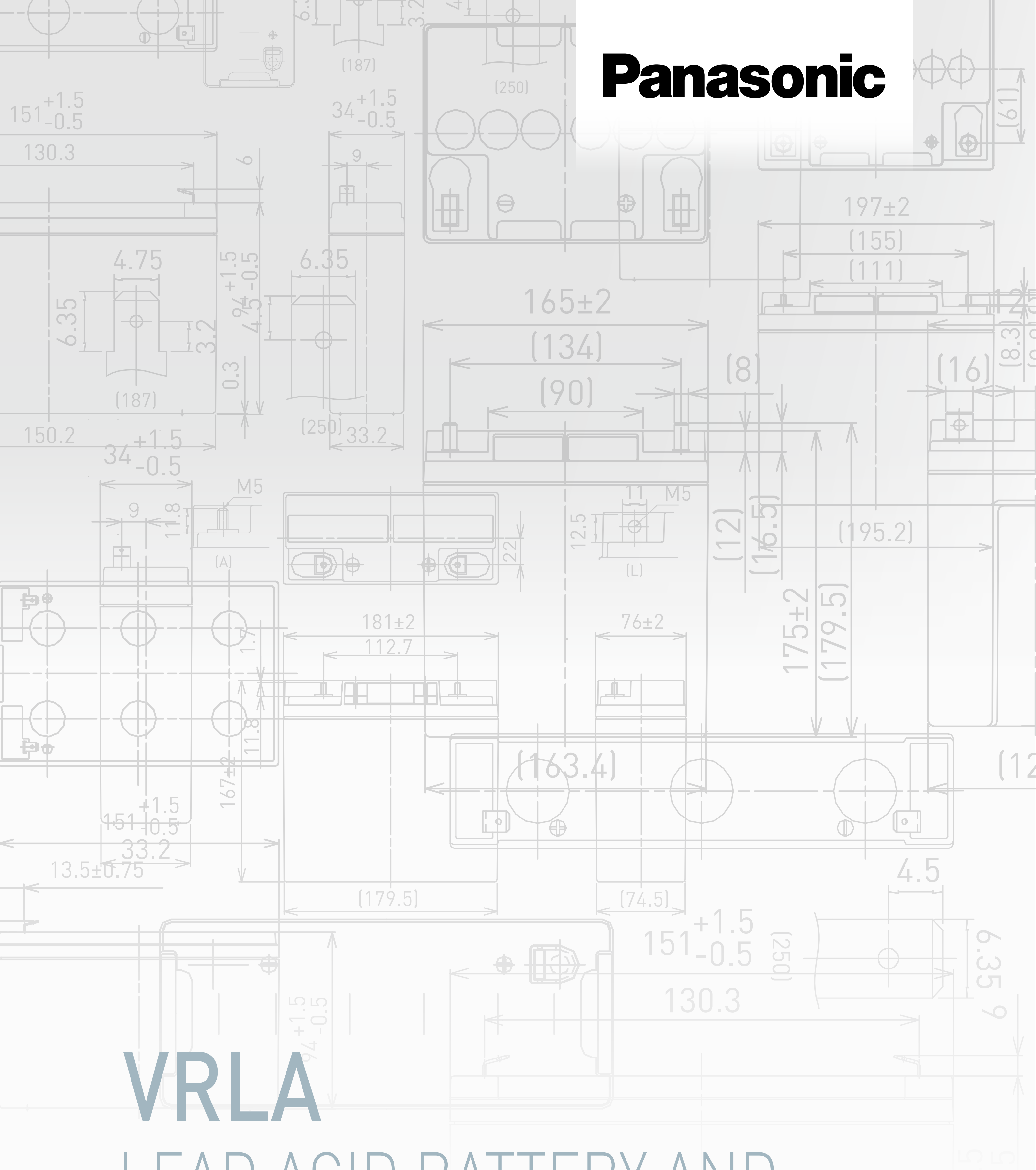

VRLA

LEAD ACID BATTERY AND ITS INTERNAL RESISTANCE

WHITE PAPER INDUSTRIAL BATTERIES FOR PROFESSIONALS

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Title: Lead acid battery and its internal resistance
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THEORY AND PRACTICABILITY

Background

Internal resistance or impedance measurements are a common method to assume the condition of a lead-acid battery. The readings could lead to predictions about the state-of-charge (SoC) and/or state-of-health (SoH) condition of a battery without the necessity of performing a full charge/discharge cycle. In practice, the readings will be compared with a pre-set value table and the differential value determines the SoC% or SoH% (if SoC is considered 100% the output value basically is the SoH%). The SoH determination may lead to battery replacements, quality and/or indemnity claims towards the manufacturer of the battery if published values are not kept. Therefore it is advisable to discuss the limitations of impedance diagnostics.

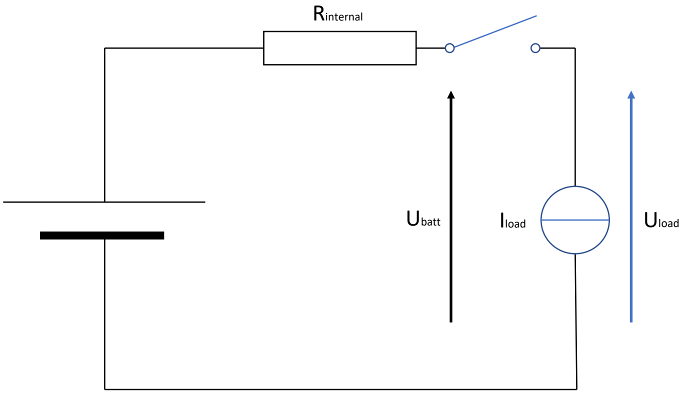
Impedance measurements are sometimes used to sort and select battery lots for subsequent serial connections or to compare between similar products of different manufacturers as an assessment for quality. It will be shown that it is – up to now – rather wishful thinking than hard evidence.

Scope

The theoretical fundamentals of the batteries' internal resistance will be described and the differences between DC resistance and AC impedance measurements are going to be explained. Some variables and tolerances influencing the measurements are being highlighted. Electrochemical impedance spectroscopy (EIS) and modelling will also be discussed. Some results from actual field tests of the scientific community are compared with the manufacturers measurements. The summary of the findings will discuss the practical aspects of impedance diagnostics for the determination of the battery SoH and suitability as a tool for quality assessment.

DC resistance measurement

In comparison to other methods, the DC resistance measurement comes closest to a full discharge capacity measurement result in terms of its means. This is mainly due to the fact that a substantial load is applied and the battery chemistry is forced to work and deliver real performance in terms of power. Although the duration of discharge is just a fraction of what is needed to determine a full capacity check. The theoretical model for this is the following:



$$R_{internal} = \frac{(U_{batt} - U_{load})}{I_{load}} = \frac{\Delta U}{\Delta I}$$

Fig. 1: DC internal resistance measurement model

The internal resistance ($R_{internal}$) of the battery is determined by voltage drop under load ($U_{batt} - U_{load}$). The equation could suggest that the voltage drop follows instantaneously after the load is applied. Reality though is different, as shown in this thesis*[1]:

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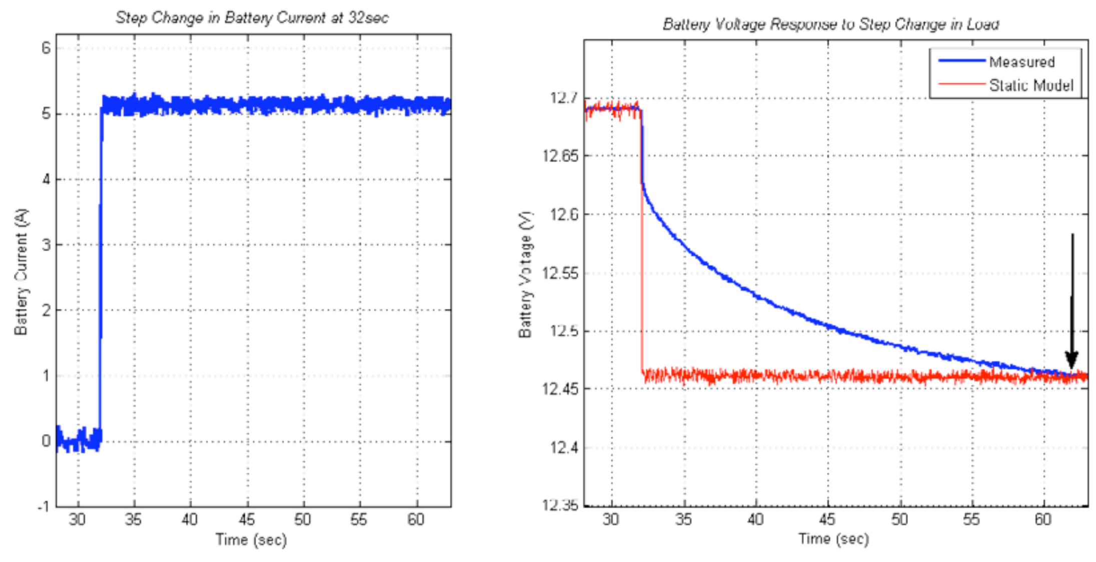
*[1] Christopher Suozzo, Lead-acid battery aging and state of health diagnosis, The Ohio State University, 2008, p. 27



(a) **(b)**

Fig. 2: Difference between model and battery voltage response [(a) load, (b) voltage]*[1]

In the subsequent text the post-graduate postulates a hold time of 30s for the battery to reach the theoretical threshold. This is due to various reasons which become more obvious when we continue with more complex models. At this stage we will focus on the time axis itself.

There is no direct reference in the master thesis to which particular battery was tested in the above voltage drop experiment, but it well could have been a 60Ah flooded type battery considering the resulting DC resistance of ~46mΩ. In an attempt to verify the test data from the thesis a Panasonic VRLA LC-R127R2PG1 battery was tested under 5A discharge conditions with the following results:

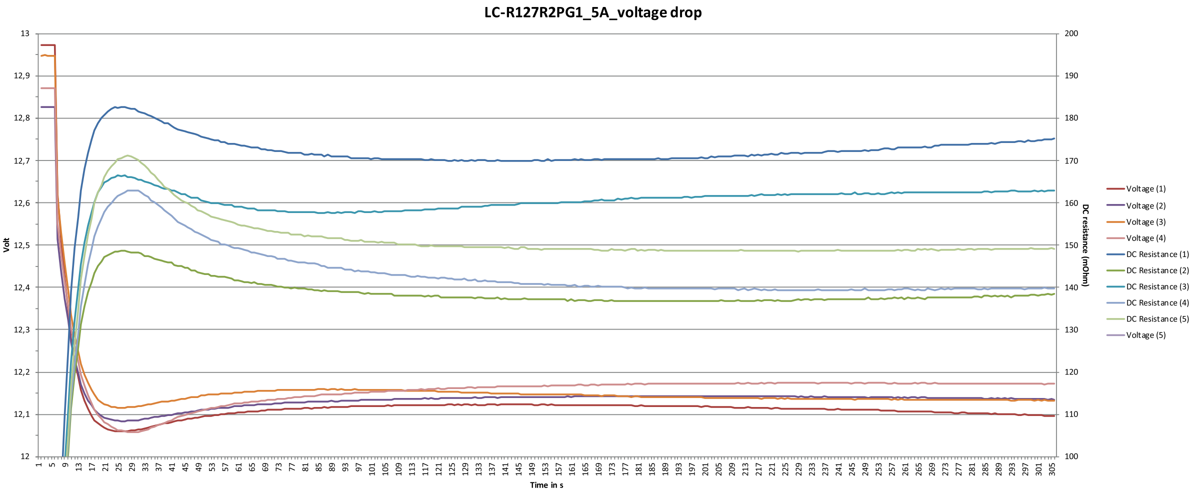


Fig. 3: Voltage drop and resulting DC resistance

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*[1] Christopher Suozzo, Lead-acid battery aging and state of health diagnosis, The Ohio State University, 2008, p. 27

The magnitude of voltage drop depends on the current load applied to the battery. Load versus voltage drop and resulting resistance is not linear-dependent.

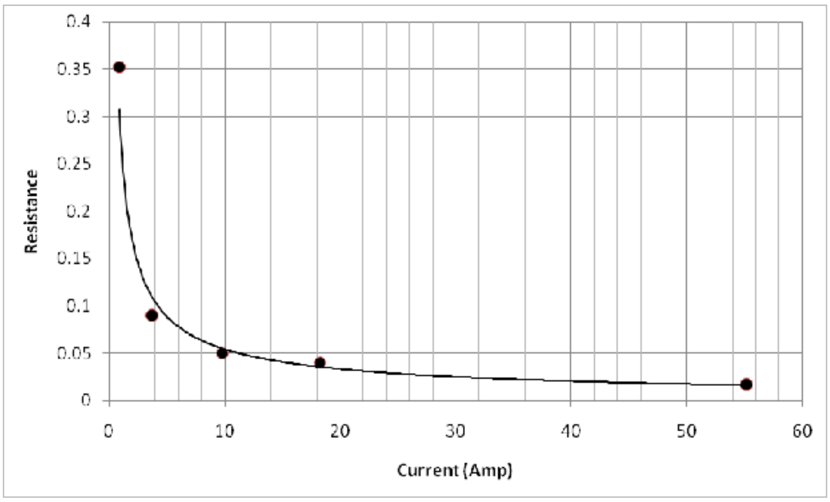


Fig. 4: Typical DC resistance at different loads*[2]

This exponential degressional curve flattens out at 0.62CA (assuming a 89Ah battery was tested) where the DC resistance value reference point should be somehow comparable to a 7.2Ah battery at 5A discharge rate (0.69CA).

The differences comparing figures 2 and 3 are the voltage drop curve itself and the settling time to stabilization. Figure 3 also shows that the DC resistance values differ between ~138 and ~175mΩ, depending greatly on the open circuit voltage before the load is applied.
The hold time for the open circuit voltage of the battery to become stable is about 3 times longer and a *coupe de fouet**[3] is visible. This initial voltage drop and recovery phase is commonly understood as related to hydrated PbO_2 zones on the surface of the positive active material (PAM)*[4]. Layers of gelled $PbO(OH)_2$ are causing an overpotential at the positive electrode after a full charge. The *coup de fouet* effect itself has been subject itself to various studies to relate it to the batteries' SoH with some success. For instance, Bose et al proved a widely linear correlation between SoH and the through voltage level, but not without certain exceptions nor backed by a general theory*[5].
The overpotential of the PAM does not only trigger the *coupe de fouet*, it is also affecting the open circuit voltage of the battery itself and thus the result of DC resistance calculation.

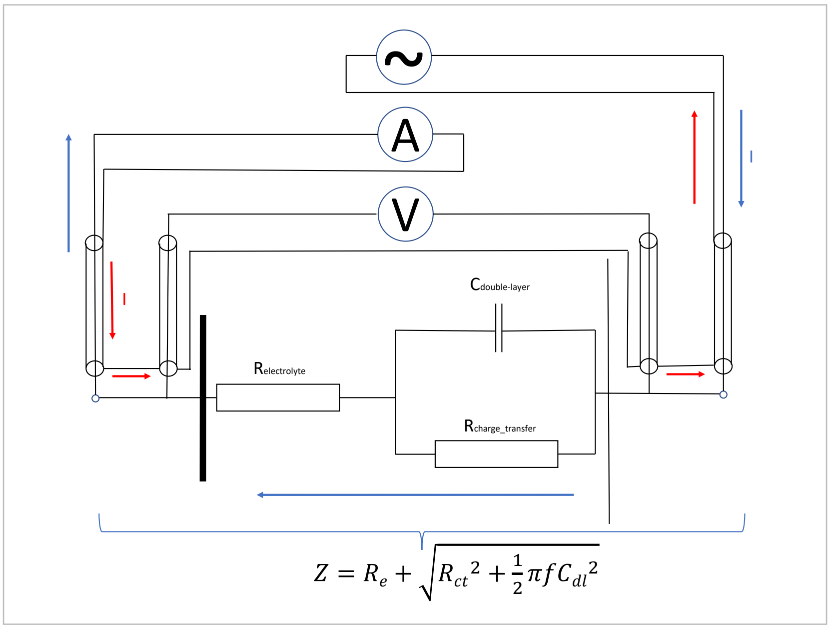
Although the same battery was fully charged 100% before each discharge the differences in OCV (Open Circuit Voltage) are up to 150mV as can be seen in Fig. 3. The resting periods between end of charge and discharge were 1h (1), 1 week (2), (3) and (5), 2 weeks (4). Again, there is a correlation between the relaxation period and the OCV development. However, at identical resting periods of (2) and (3) the variation is still 120mV. This experimental figure gets easily doubled when one considers the total tolerance over an extended production period.
Various scientists tried to narrow these variations as a correlation to SoC/SoH is proven, yet more research is needed in order to be successful in doing so*[6].
The hydrated PbO_2 zones could be tackled by a short discharge burst, but then the next problem arises, i.e. to determine the adequate relaxation time for the OCV to recover and stabilize.

*[2] W. Peng, Accurate Circuit Model for Predicting the Performance of Lead-Acid AGM Batteries, University of Nevada, Las Vegas, August 2011
*[3] D. Brendt and E. Voss, Batteries 2, Proc. of the 4th International symposium held at Brighton, U.K., Sept. 1964, First. Pergamon Press Ltd, 1965
*[4] D. Pavlov et al., Hydration and Amorphization of Active Mass PbO_2 Particles and Their Influence on the Electrical Properties of the Lead-Acid Battery Positive Plate, JES 136 (1989), 3189
*[5] http://www.academia.edu/29303629/Battery_State_of_Health_Estimation_Through_Coup_De_Fouet
*[6] G. Pilatowicz et al, RWTH Aachen, Comprehensive Study of Relaxation Behaviour of Lead-Acid Batteries for State-of-Charge estimation in Automotive Applications, proceedings at LABAT, 10-13 June 2014

On a practical note, DC resistance measurement proved its point in combination with the *coupe de fouet* when it was introduced to estimate SoH/SoC in back-up battery installations[*7]. Several minutes of discharge time and a relatively high load provided, the obtained results were promising.
Battery testers with only a few seconds but high load are used in stand-alone equipment and give a health assessment by measuring the voltage drop level. This does not provide an accurate SoH/SoC estimation, but it is good enough for a quick check on starter batteries for vehicles where thresholds on look-up tables are compared to the reading obtained.

The absolute value of the DC resistance therefore has little meaning due to the variance of the OCV, but the voltage drop under load as a result of the DC resistance is quite meaningful. Again, not in absolute figures but in relative terms and close observation of the surrounding parameters, e.g. temperature and age of battery.

Impedance diagnostics
The more common method these days to describe the internal resistance of a lead-acid battery is the AC impedance measurement. The battery will not be discharged under load like in the DC resistance measurement method, but a small AC current is imposed on the battery and the response signal for amplitude and voltage phase shift is measured. The difference between the input and output signal is determined by the Randles model as the underlying equivalent circuit:



$$Z = R_e + \sqrt{{R_{ct}}^2 + \frac{1}{2}\pi f {C_{dl}}^2}$$

Fig. 5: Randles model with 4-terminal sensing probe

The model can be extended by adding an inductive component, but the effect on the result is negligible. DC resistance (R) and AC impedance (Z) are both expressed by the same SI unit ohm (Ω), but this is where the similarities end.
As batteries physically cannot (or rather: should not) be part of an AC circuit, the frequency response (or imaginary) part of any equivalent circuit model is unrelated to the actual mode of operation. Battery engineers would look out for the real part of the equation which corresponds to the DC resistance of the battery parts (connectors, collectors, active masses, electrolyte and separators) the flow of electrons (current) is facing. While the resistance of connectors, collectors and separators is only affected by temperature changes, the resistance of the electrolyte and the active mass also changes with the depth-of-discharge (DoD).
But it should be pointed out that this real part of the AC resistance of a battery is not related to the DC resistance in any form.

[*7] P. E. Pascoe, H. Sirisena, and A. H. Anbuky, Coup de fouet based VRLA battery capacity estimation, The First IEEE International Workshop on Electronic Design, Test and Applications 2002, proceedings, pp. 149–153

This may sound funny for the seasoned electrical engineer, who knows that if the phase angle is zero, Ohm's and Kirchhoff's laws will prevail (R=Z).
If the first data point in Fig. 4 is at 0.16A on the x-axis (which is similar to the AC test current in an impedance meter), then the calculated DC resistance is ~350mΩ while the impedance measurement for this battery would be roughly 100 times less, i.e. ~3.5mΩ.
Measuring the same values for DC resistance and AC impedance will only occur if the battery is short-circuited (~3,400A in this example). The following (idealistic) graph will demonstrate this relationship:

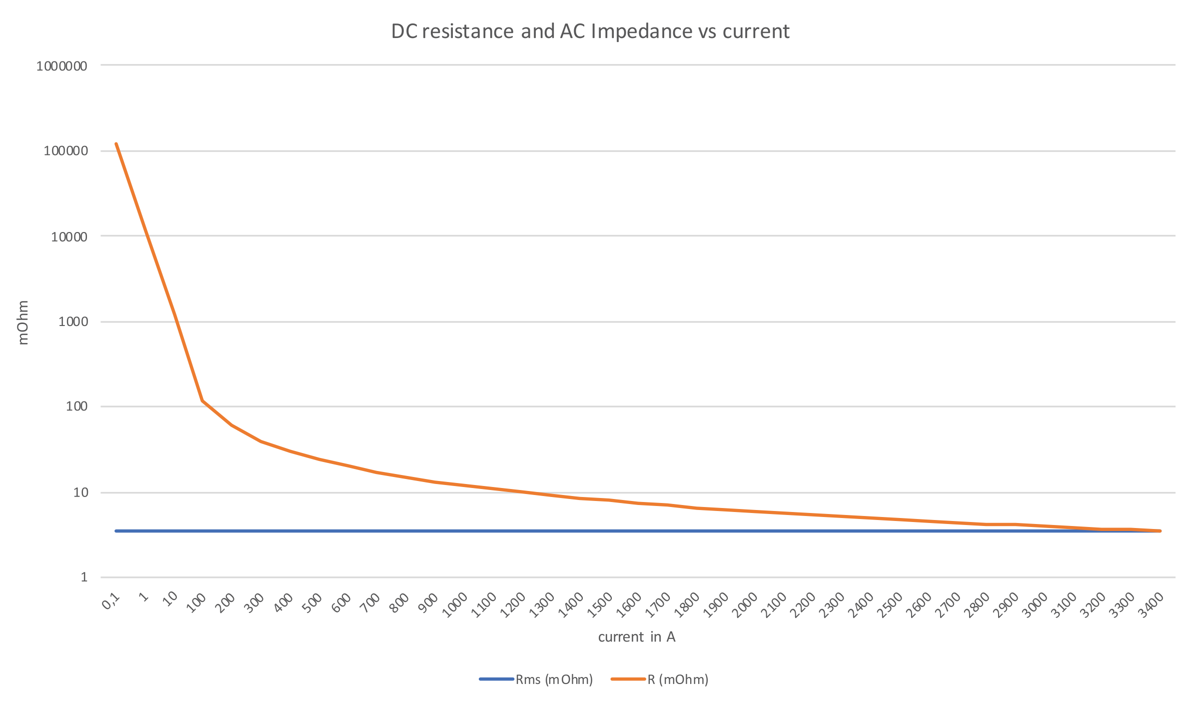


Fig. 6: DC resistance (=ΔU/ΔI) vs AC impedance

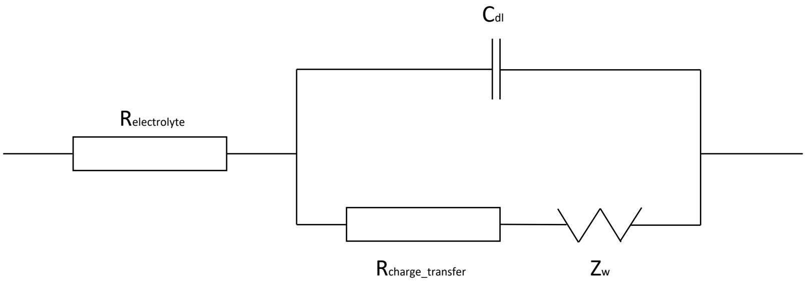
The frequency response (or imaginary) part of the impedance equation is supposed to cover for the charge transfer resistance, and the equivalent circuit model is a resistor in parallel to a double layer capacitor (Fig. 5).
The elctrochemical double layer capacitor (EDLC) working principle combines a Helmholtz double-layer and - as the abbreviation suggests – an electrochemical portion in form of a redox reaction.
However, this redox reaction is better described as electron transfer as there is no chemical reaction but "*...a physisorption of electrolyte ions onto nanopore surfaces of a carbon electrode.*"*[8]. Marcus theory describes it as an electron donor and acceptor pair*[9].

The lead-acid battery's charge transfer is characterized by an H_3O^+ "relay mechanism"*[10] where the molecule "*donates a proton (H+) to the closest water molecule transforming it into an* H_3O^+ *ion and so on. [...] This "relay" movement of protons proceeds at a higher rate than the rate of movement of a single* H^+ *ion through the solution.*"*[11]
A Helmholtz double layer can be found in the lead-acid battery primarily at the positive electrode, but no redox reaction without a chemical reaction.

The effect of the Helmholtz double-layer can be observed as part of the *coupe de fouet* in the DC resistance measurement method. The duration of this effect lasts for about 0.25 – 0.5 s when the battery is being discharged*[12].

*[8] Novel Carbon Adsorbents, p. 316, edited by Juan M. D. Tascón, Instituto Nacional del Carbón, INCAR-CSIC, Oviedo, Spain, published by Elsevier Ltd. ©2012, ISBN: 978-08-097744-7
*[9] https://en.wikipedia.org/wiki/Marcus_theory
*[10] I.N. Levine, "Physical Chemistry", p. 500, McGraw-Hill, New York, 2009
*[11] D. Pavlov, Elementary reactions during charge and discharge of the positive and negative electrodes in a lead-acid cell, p. 4, proceedings at LABAT 13-16 June 2017
*[12] K. S. Gandhi, Modeling of Effect of Double-Layer Capacitance and Failure of Lead-Acid Batteries in HRPSoC Application, p. 6, Journal of The Electrochemical Society, 164 (11) E3092-E3101 (2017), published April 14, 2017

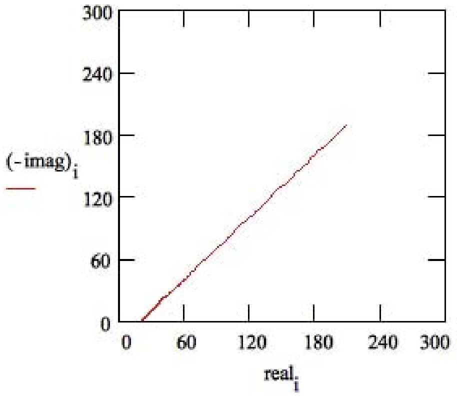
Electrochemical Impedance Spectroscopy (EIS)
EIS can be understood as an AC impedance measurement at various frequencies. As far as common methods are concerned, the impedance measurement based on the Randles model is usually done at a fixed frequency of 1kHz. For a frequency bandwidth measurement usually a Warburg impedance is added to account for the mass transfer which is part of the overall charge transfer process (during discharge: Pb, PbO -> $PbSO_4$).



$$Z = \mathrm{R}_e + \frac{1}{j\omega C_{dl} + \frac{1}{R_{ct} + \frac{(1-j)\sigma}{\sqrt{\omega}}}}$$

Fig. 7: Randles model with Warburg element

The equivalent circuit model in Fig. 6 includes electrolyte, capacitive and polarization resistances. The added Warburg element in the Fig. 7 circuit model should represent additional diffusional resistance in the mass transfer process. This occurs at lower frequencies according to the theory. A Warburg impedance is easily identified when the Nyquist plot's slope is linear at an angle of 45°:



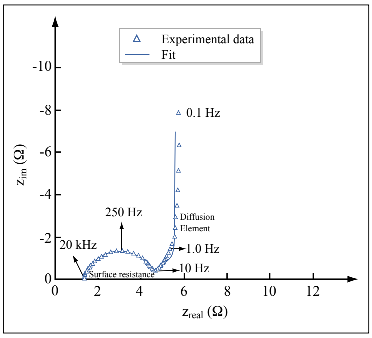


Image by MIT OpenCourseWare.

Figure: Impedance spectrum (Nyquist plot) for a silicon nanowire anode in a Li-ion battery, which is well described by a parallel RC element for the double layer (high frequency "surface resistance") in series with a finite-length Warburg element with capacitive cutoff (low frequency "diffusion element").

Fig. 8: Warburg impedance in a Nyquist plot*[13]

Fig. 9: Example of a Nyquist plot for an EIS spectrum*[14]

For each AC frequency applied Z(w) is calculated as per equation in Fig. 7 and displayed in a Nyquist or Bode plot.

If the electrochemical system real data does not fit the extended Randles model in Fig. 7, researchers fall back on extending the equivalent circuit modelling by letting software calculate the best fit.

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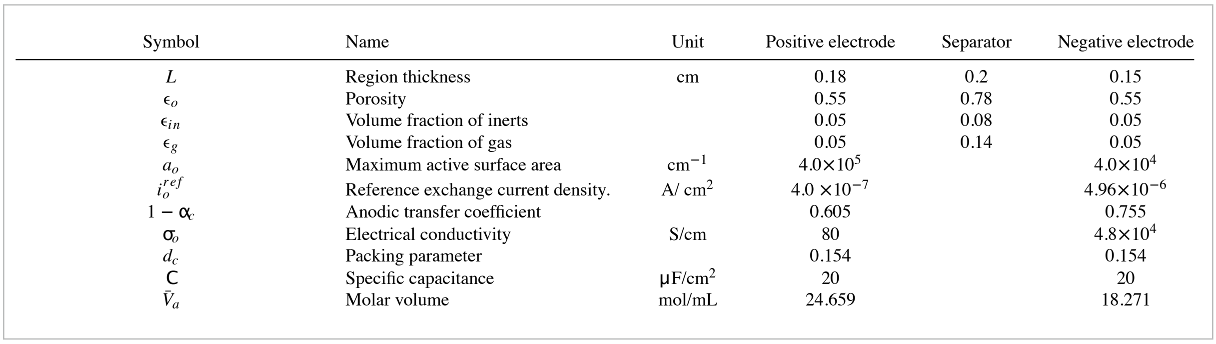
*[13] https://www.gamry.com/application-notes/EIS/basics-of-electrochemical-impedance-spectroscopy/, figure 17
*[14] https://ocw.mit.edu/courses/chemical-engineering/10-626-electrochemical-energy-systems-spring-2014/lecture-notes/MIT10_626S14_S11lec20.pdf, p. 6

Extended equivalent circuit models based on EIS

Although the Nernst, Warburg and many other equations are undisputed in their own domain, their adaption to commercial electrochemical products (especially lead-acid batteries) has been proven to be difficult so far.
Even the basic equations dating back to the 19th century are controversially discussed on how to interpret and adapt them to today's batteries[*15].
This does not come as a surprise when we look at the fundamental backgrounds. Take for instance the Warburg element which allegedly should account for the mass transfer process. Warburg's theory (strictly valid only for a single electrode or half-cell) was proven by Elsa Neumann[*16] using Hg electrode pairs; for the simultaneously tested Ag electrodes the obtained results were barely adequate due to capacity changes during the course of the experiments.
The techniques and theories in the electrochemical community became more and more refined throughout the coming years with the Nernst-Planck equation for the ion transfer process, Mosley and Rand[*17] regarding the double-layer capacitance, Butler-Volmer about the overpotential and many other scientists refining the lead-acid battery modelling concept as a whole.
These days the models are refined further with grain boundary diffusion aspects[*18] and spatial profiles[*19] taking into account the 2 dimensional aspects of actual battery design. More refinement is expected by mathematical and statistical models in regard to battery degradation prediction[*20].

But where do the simulations fail in detail? Impurities, amorphous structures, general tolerances - to name a few. To give a practical example let us have a look at the following parameter table from Gandhi's aforementioned paper[*19]:



Symbol	Name	Unit	Positive electrode	Separator	Negative electrode
L	Region thickness	cm	0.18	0.2	0.15
ϵ_o	Porosity		0.55	0.78	0.55
ϵ_{in}	Volume fraction of inerts		0.05	0.08	0.05
ϵ_g	Volume fraction of gas		0.05	0.14	0.05
a_o	Maximum active surface area	cm^{-1}	4.0×10^5		4.0×10^4
i_o^{ref}	Reference exchange current density.	$\mathrm{A/\ cm}^2$	4.0×10^{-7}		4.96×10^{-6}
$1-\alpha_c$	Anodic transfer coefficient		0.605		0.755
σ_o	Electrical conductivity	S/cm	80		4.8×10^4
d_c	Packing parameter		0.154		0.154
C	Specific capacitance	$\mu\mathrm{F/cm}^2$	20		20
$\bar{V}_a$	Molar volume	mol/mL	24.659		18.271

Fig. 10: Example of a parameter table[*19]

Almost all of the listed parameters are variables, supposed to change during battery life. Take for instance the thickness L of the electrodes: A fixed value and supposedly uniform one as the simulation is one-dimensional. But region thickness changes during charge, discharge and life of battery and in three dimensions. This is strictly not to be misunderstood as a critical note, but to make clear as one example of many that lead-acid battery modelling is customized and simplified to understand the basic concepts of specific observations (in this case of sulfation under HRPSoC operation). And that may work quite well.

In another paper, a simulation refers to itself as "precise" towards e.g. SoC estimation, but does that mean that this model is universal? Here, an equivalent circuit model is established to mimic the obtained EIS spectra from a real battery. After applying high discharge currents (100A/100s) the model will not respond to the real voltage:

[*15] G. Barbero, Theoretical interpretation of Warburg's impedance in electrolytic cells, 25 August 2017, https://arxiv.org/pdf/1708.07158.pdf

[*16] E. Neumann, Ueber die Polarisationscapacität umkehrbarer Elektroden, pp. 500, Annalen der Physik und Chemie, Neue Folge, Band 67, Leipzig 1899

[*17] P. T. Moseley and D. A. J. Rand, ECS Transactions, 3 (2012)

[*18] J.M. Deckwart, Impedanzspektroskopie bei schneller Korngrenzdiffusion am Beispiel des Silbertellurids, pp. 31-39, Wilhelms-Universität Münster, 2007

[*19] K. S. Gandhi, Modeling of Effect of Double-Layer Capacitance and Failure of Lead-Acid Batteries in HRPSoC Application, Journal of The Electrochemical Society, 164 (11) E3092-E3101 (2017), E3095

[*20] K. Goebel et al, Uncertainty Management for Diagnostics and Prognostics of Batteries using Bayesian Techniques, NASA Ames Research Center

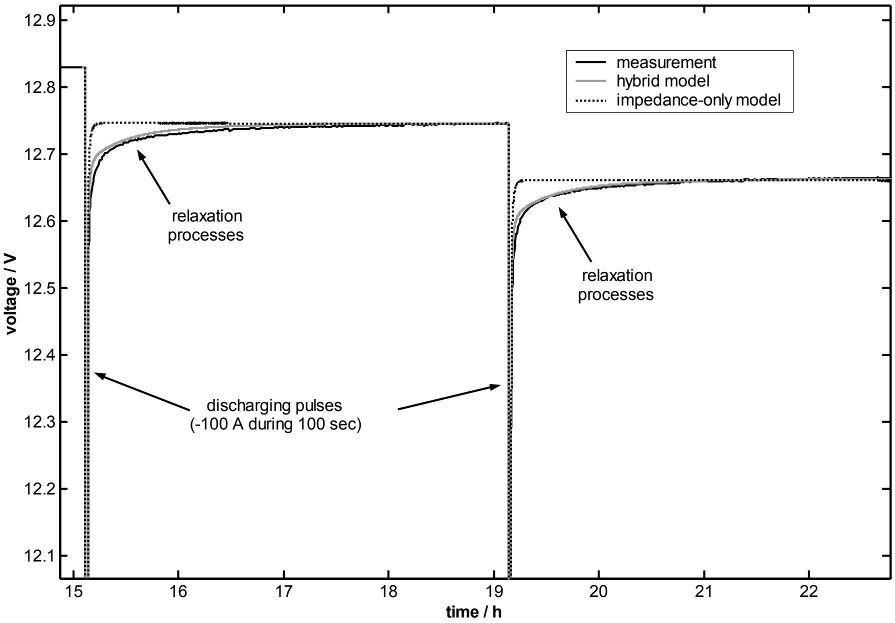


Fig. 11: Acquiring parameter values for a better fit*[21]

The obtained coefficient will be applied to make the electrolyte transport model of Nguyen et al.*[22] fit the measurements, and results are presented in this format:

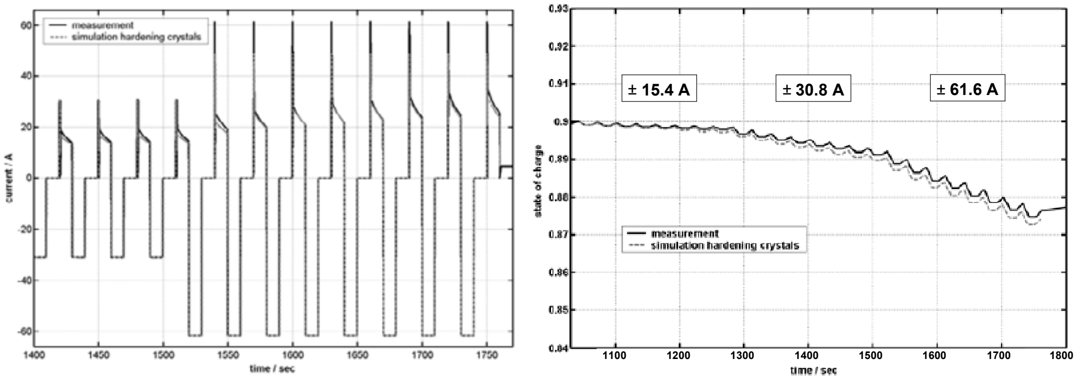


Fig. 12: SoC comparison simulation/real data after parameter fit*[23]

The SoC simulation is about 1% lower than the measurement at the end of the plot. The summary says: *"A precise SOC calculation has been accordingly enabled."* *[23].
The time scale is about 10 minutes, equivalent to 4ppm of total life or a slightly higher fraction of expected total energy throughput. Within the boundaries and constraints of the experimental setup the postulated precision of SoC calculation can be followed, but could it be extended to cover more than that?

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*[21] Thele, M., et.al. Impedance-based modeling considering the lead-acid battery as an example, p. 6, Technische Mitteilungen 99 (2006), Heft 1/3, S. 81-87, ISSN 0040-1439, 1. Symposium Impedanzspektroskopie, 16./17. Mai 2006, HdT Essen

*[22] T. V. Nguyen, R.E. White: A mathematical model of a hermetically sealed lead-acid cell, Electrochim. Acta, Vol. 38 (1993), No. 7, pp. 935-945

*[23] Thele, M., et al. Impedance-based modeling considering the lead-acid battery as an example, p. 9, Technische Mitteilungen 99 (2006), Heft 1/3, S. 81-87, ISSN 0040-1439, 1. Symposium Impedanzspektroskopie, 16./17. Mai 2006, HdT Essen

In one of the latest attempts to correlate EIS with SoH, researches have at least used part of a commercial battery as a test specimen to perform aging, cycling and partial state-of-charge operation*[24]. Altogether four cells were analyzed with an initial validation sequence over two weeks/each to obtain EIS spectra at SoC 80%, 40% and 0%. Additionally, the paper states that throughout the accelerated life tests real "*...capacity tests are indispensable...*" (p.19) and that the EIS spectra "[should]...*be recorded with small superimposed discharge currents in the range of* ~$1I_{20}$." (p.19). This should allow the question about the methods' practicability for the real world mixed with the curiosity on how the superimposition of DC discharge current differs from other proven DC discharge methods without implementing EIS measurements.

What actually happens when the closed-loop scenarios and tight boundaries of the laboratory experiments meet the open world is depicted in this paper:
Putting impedance and EIS measurements' joint forces into practice, the Institute of Non-Ferrous Metals, Division in Poznan, Central Laboratory of Batteries and Cells (IMN CLAiO) conducted a series of tests comparing batteries from the field (solar storage, UPS, telecom) with considerable age and low capacity to new batteries. Their results were summarized as follows:
"*Dependencies between values and/or changes in internal resistance and real battery capacity have not been found. The attempt to correlate impedance parameters with the real battery capacity has not been successful.*"*[25]

Summary

Today's commercially available products making use of the batteries' internal resistance rely deeply on DC resistance measurements in combination with parameter look-up tables. Their accuracy has not been subject to independent studies as far as the author is aware. It is also not known if an onboard diagnostic system or a stationary unit determined the end-of-life of the lead-acid batteries in the automotive field that were subject of the tests in a JCI paper*[26], but according to that paper 15% of more than 800 analyzed batteries were found to be still operational.
AC impedance/EIS measurements have helped to understand the batteries' electrochemical reactions to a greater extent. And the equivalent circuit models based on those measurements are a welcome support for future battery designs. It is also understood that EIS result modelling can be improved by applying DC currents during measurements*[27].
What has not been established yet is a battery simulation model which can be described by impedance/EIS spectra in order to determine SoC or SoH of a lead-acid battery. Therefore it is not a reliable tool to judge battery performance, degradation level or quality by this method alone.

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*[24] Monika Kwiecien et al., Determination of SoH of Lead-Acid Batteries by Electrochemical Impedance Spectroscopy, Applied Sciences 2018, 8, 873

*[25] M. Baraniak et al, Electrochemical impedance spectroscopy and internal resistance as methods of estimation of lead-acid battery condition, proceedings at LABAT 10-13 June 2014

*[26] J. Albers, Johnson Controls Power Solutions EMEA, Investigating AGM Batteries from Car Operation, p. 7, proceedings at ELBC 13-16 September 2016

*[27] Blanke, H., et. al., The art of impedance spectroscopy on batteries and fuel cells, Technische Mitteilungen 99 (2006), Heft 1/3, S. 184-188, ISSN 0040-1439, 1. Symposium Impedanzspektroskopie, 16./17. Mai 2006, HdT Essen

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