

A Guide to Li-ion Battery Research and Development



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The commercialization of Li-ion batteries in 1991 was the culmination of in-depth R&D conducted by scientists and engineers around the globe over the preceding few decades. Further development of Li-ion batteries and alternative rechargeable batteries has continued until today. As the world is rapidly moving towards a new era defined by green technologies, more practical and accurate R&D is required in order to meet the increasing demands for energy storage systems, specifically from the automotive industry. This white paper presents the basics of the Li-ion battery technology and guides the reader through the relevant techniques and terminologies in Li-ion battery research.

Introduction to batteries

A battery is an electrochemical device that converts chemical energy into electrical energy. Generally speaking, batteries can be categorized into two main groups: primary and secondary. Primary batteries are not rechargeable because the electrochemical reaction corresponding to them is irreversible. In contrast, the electrochemical reaction is reversible in secondary batteries, and therefore recharging is possible. Secondary batteries can be reused many times, and this characteristic makes them more sustainable than primary batteries.

Lead-acid batteries, nickel-cadmium, and lithium ion batteries are rechargeable battery technologies from which the Li-ion batteries are the most interesting, as they offer more energy density. In fact, lithium is both the most electropositive and the lightest metal. These characteristics make it an ideal candidate for designing a high energy density storage system.



Li-ion batteries

Lithium ion batteries are composed of two insertion electrodes (anode and cathode) with an electrolyte in between. The electrolyte is an ionically conductive medium which allows lithium ions to shuttle between the anode and cathode. The anode and cathode are electronically separated by a non-conductive membrane, allowing transportation of lithium ions but not allowing any electrons to pass through, in order to avoid a short circuit. **Figure 1** shows the main components of a Li-ion battery.

The electrode materials are manufactured in a discharged state so that they remain inactive in air prior to the cell assembly. The negative electrode of a Li-ion battery is usually made of graphite, which follows the reaction below when lithium is inserted to the negative electrode.

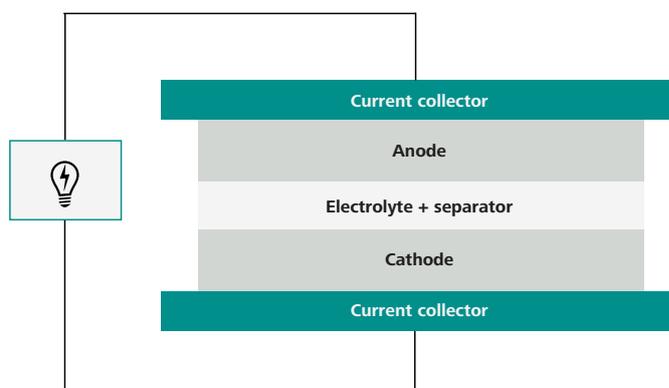
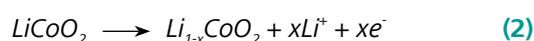


Figure 1. Schematic view of the Li-ion battery components.

A single lithium ion is inserted per aromatic ring of the graphite structure, corresponding to a theoretical capacity of 372 mAh/g. This value is equal to about 10% of the theoretical capacity of metallic lithium itself (3800 mAh/g). Metallic lithium tends to grow dendrites upon cycling, which increase the risk of a short circuit as they can potentially penetrate through the separator and create an electrical connection between the electrodes. Substituting lithium metal with graphite results in more safety, stability, as well as higher calendar and cycle life.

One way to make the execution/use of metallic lithium anodes a possibility is to develop and use solid electrolytes which are resistant to the growth of these lithium dendrites. The solid electrolyte needs to have a comparable ionic conductivity to the liquid electrolyte. To achieve that, the main challenge is to design a system with a low resistance at the interface of the solid electrode and solid electrolyte.

The positive electrode is usually made from a transition metal oxide in which Li-ions can reversibly insert themselves into the structure. The cathode is actually the sink for the lithium ions during the discharge when the thermodynamically favorable reaction occurs. Among the positive electrodes, Lithium Cobalt Oxide ($LiCoO_2$, known as LCO) is the first commercial, and most common, cathode technology that manufacturers utilize in their Li-ion batteries. It has a layered structure and practical capacity of about 150 mAh/g. The electrochemical reaction for LCO upon charge is shown in the following reaction:



The electrode (either anode or cathode) active mass is mixed with an additional conductive agent (usually carbon black which is highly conductive) and a binder that maintains the

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whole composite together and also provides the adhesion between the loaded material and the current collector. The usual anodic current collector is copper, and aluminum for the cathode, which stays inactive at low and high potential versus Li/Li^+ , respectively.

Typical electrolyte solutions for Li-ion batteries consist of LiPF_6 dissolved in alkyl carbonates, including ethylene carbonate (EC) and another solvent like ethyl methyl carbonate (EMC). The electrolyte is unstable at low potential, and the reduction of the electrolyte on the surface of graphite forms an insoluble film called the solid electrolyte interphase (SEI), introduced by Peled in 1979 (see resources and references). Fortunately the SEI layer is both electronically insulating and ionically conductive, therefore, the reaction rates slow down due to the electronically insulating property of the SEI layer. Stability of the SEI layer is crucial for the longer lifetime of lithium ion batteries. To make the SEI layer more stable, an electrolyte additive or a combination of electrolyte additives can be added to the electrolyte e.g. vinylene carbonate (VC) or fluoroethylene carbonate (FEC). Though the main role of electrolyte additives is to stabilize the SEI layer, they could have a role in decreasing the rate of electrolyte oxidation reactions on the cathode surface at higher potentials.

Lithium insertion mechanism: Intercalation

As discussed earlier, graphite is the common anode material for Li-ion batteries. The insertion mechanism of ions into the graphite structure is called intercalation, and defines the insertion of Li-ions between the graphite sheets. Graphite can intercalate up to one Li atom per six carbon atoms at room temperature, resulting in a theoretical capacity of 372 mAh/g. However, the practical capacity of graphite is less than its theoretical capacity; it reaches an optimum value after early charge discharge cycles of the battery when the loss of active lithium takes place as a result of irreversible consumption which forms the SEI layer.

Intercalation is the main insertion mechanism in Li-ion batteries, and most of the electrode materials (both positive and negative) follow the same mechanism (Figure 2). Several electrode compounds such as LiCoO_2 (LCO), $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO), LiMn_2O_4 (LMO), LiFePO_4 (LFP), and LiNiMnCoO_2 (NMC) are common examples which support this mechanism for Li-ion batteries. Out of these compounds, only LTO can be used as a negative electrode; the rest react with lithium ions at higher potentials, and therefore they are suitable as cathode materials.

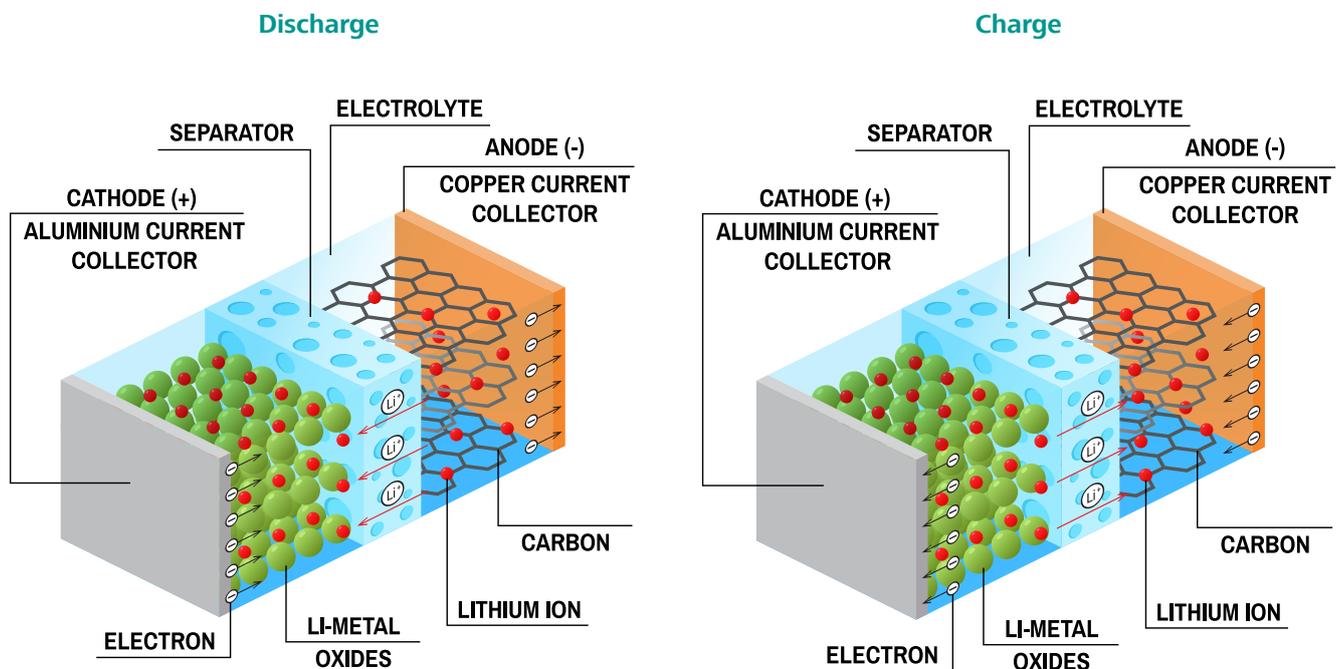


Figure 2. Schematic view of intercalation mechanism in Li-ion batteries during charge and discharge.

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Lithium insertion mechanism: Alloying

The mechanism of Li insertion can differ from the main mechanism of intercalation. It has been shown that Li-ions can electrochemically react with a number of metals at room temperature, including gold, tin, zinc, silicon etc. Upon the lithium insertion reaction, Li-ions form a Li-metal alloy and therefore this mechanism is known as alloying. De-alloying occurs upon the reverse electrochemical reaction. For example in case of silicon, the alloying process results in the formation of the compounds $\text{Li}_{12}\text{Si}_7$, $\text{Li}_{14}\text{Si}_6$, $\text{Li}_{13}\text{Si}_4$, and $\text{Li}_{22}\text{Si}_5$. Since silicon uptakes a high amount of lithium per atom, an expansion of up to 300% occurs on the silicon electrode. This expansion causes electrical isolation of the silicon particles as well as extra side reactions mostly on the reformation of the SEI layer which results in fading of the silicon anode upon cycling and eventually its failure. FEC is a well-known electrolyte additive, extensively reported as good solution to suppress the side reactions when a silicon anode is used. However, to date, the practical use of pure silicon anodes remains challenging and the use of silicon is limited to a small scale (about 10–15%) in the carbonaceous anodes.

Theoretical capacity of active materials

Generally speaking, the theoretical capacity of an active material (in mAh/g) can be calculated using the equation below:

$$\text{Theoretical capacity} = \frac{nF}{3.6 \times M_w} \quad (3)$$

Where n is the number of exchanged electrons, F is the Faraday constant (96485 C/mol), $1/3.6$ is the conversion factor from A·s to mAh, and M_w (g/mol) is the molecular weight of the active materials.

Using LCO as an example, the molecular weight of this positive electrode compound equals 97.868 g/mol, the number of exchanged electrons is 1, and therefore the theoretical capacity of LiCoO_2 is 273.85 mAh/g. This is of course a theoretical value, and therefore higher than its practical capacity value of approximately 150 mAh/g.

Active materials and electrode preparation

In order to study a potential material for suitability as an anode or cathode for Li-ion batteries, a mixture of active materials with a proper conductive agent and a binder is needed. The percentage of each component in the electrode composite affects the performance of the final electrode. This mixture, or so-called «slurry» is coated on an appropriate current collector. In academic research environments, the coating is usually applied either manually or by an automated doctor-blade film coater. To further increase the conductivity of the electrode and also to increase the electrode density, the electrodes need to go through the compressing step. Compressing the electrode decreases the surface area of the electrode, resulting in a lower amount of side reactions. The film then undergoes drying steps using vacuum ovens, as it is critical for battery materials to be water free. Cells containing H_2O , would suffer from extra gas generation (usually hydrogen and carbon dioxide) and swelling which leads to mechanical stress to the device that is being powered by the cell. It also might decrease the stack pressure (in the case of pouch cells) leading to an increase in the internal impedances and a decrease in energy density.

Cell preparation

Li-ion battery materials are usually air and water sensitive. Even though the electrode materials are synthesized in a discharged state (inactive in the atmosphere), the materials in the final cell have to be water free. Therefore, access to a water free glovebox with a non-reactive atmosphere (e.g., argon) is important. Different types of cells can be used for Li-ion battery research e.g., three electrode cell setup, coin cells, Swagelok cells, pouch cells, advanced, and custom-made cells. The most popular cell is the two electrode coin cell which is widely used in battery research and development. For materials study purposes, usually a «half-cell» configuration is preferred where the metallic lithium acts as a negative electrode. A «full-cell» configuration is necessary when study of the complete battery is of interest, and therefore proper anode and proper cathode materials are used as the electrodes.

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For the half-cell configuration, it is important to keep in mind that the source of lithium ions is unlimited, while in a full-cell configuration the amount of active lithium is limited by the capacity of the cathode material. Therefore, the lithium ions lost to the side reactions will be recovered from the metallic lithium foil in the half-cell configuration, while in the full-cell configuration the lithium loss results in decreasing the lithium source of the cathode material, and a loss in capacity. This is very crucial when, for example, the performance of the silicon anode is under study.

See references 1 and 2 to learn more about production of half coin cells and full coin cells which are the R&D approaches when developing Li-ion batteries.

Experimental setup

All of the experiments shown in this white paper were executed using a Metrohm Autolab PGSTAT302N equipped with an Electrochemical Impedance Spectroscopy module (FRA32M) and Booster 10A (Figure 3). NOVA 2 software was used for data acquisition and data analysis. The batteries used in these experiments were 18650 cylindrical batteries with a nominal capacity of 2600 mAh, a nominal potential of 3.7 V, and operational voltage window of 3 V to 4.2 V. The 18650 cells reported here have been used for an unknown number of cycles prior to these experiments.

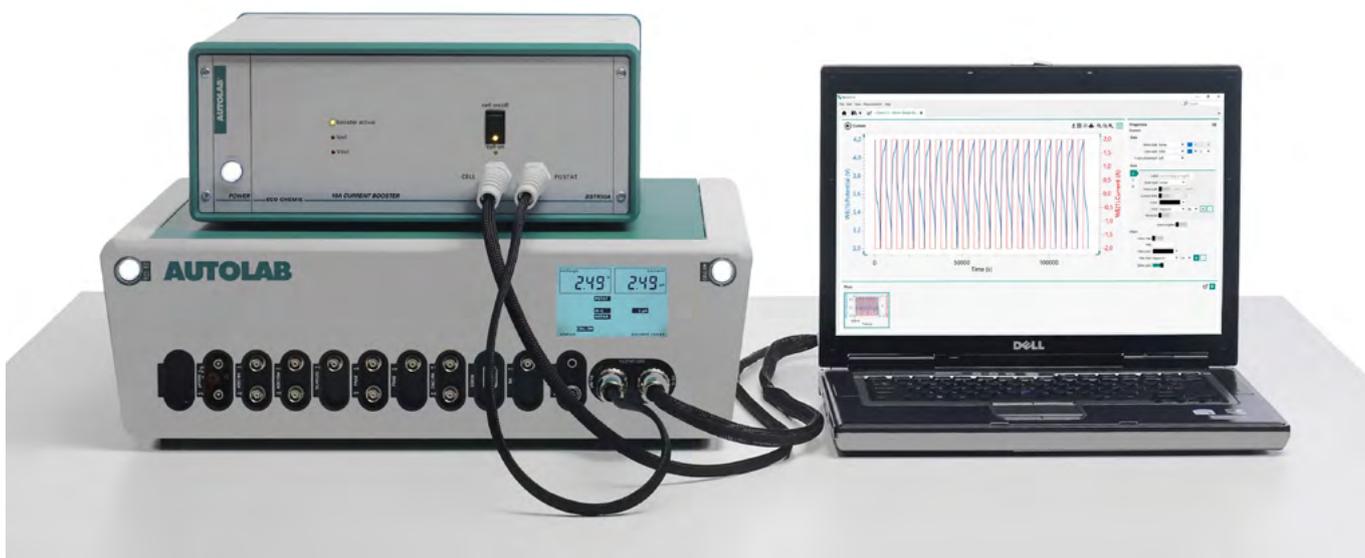


Figure 3. The Autolab PGSTAT302N equipped with the FRA32M module and the Booster10A.

Galvanostatic charge-discharge cycling

Li-ion batteries are sensitive to overcharge and unsafe potentials. The main technique to study Li-ion battery materials is galvanostatic (constant current) charge/discharge cycling. With this technique, the user can ensure that the battery stays within a safe operating potential. It consists of a series of charge and discharge cycles in galvanostatic mode within a specific potential window. The cycle life, voltage behavior, and coulombic efficiency of batteries or battery materials can be determined using this technique. A constant voltage step between each charge and discharge can be added to the procedure in order to ensure the fully charged or discharged state of the battery, specifically at higher C rates.

What is the «C-rate»?

The C-rate is an indication of the rate of cycling and describes how fast or slow the cycling is done. For example, 1C rate indicates that the provided current can charge or discharge the battery in 1 hour. 2C means that the applied current corresponds to a total time of 30 min for either a charge or discharge. Finally, C/2 represents a rate at which it takes 2 hours for the battery to be fully charged or discharged. For example: 1C rate for the 18650 cylindrical cell with a nominal capacity of 2600 mAh would be 2.6 A.

The combination of these two galvanostatic and potentiostatic techniques is called Constant Current Constant Voltage (CCCV), which is also the charging protocol for commercial chargers. The CV portion is maintained until the current drops below a certain threshold.

Figure 4 shows an example of galvanostatic charge discharge cycling of a 18650 cell with a nominal capacity of 2600 mAh within a potential window of 3 V to 4.2 V at 1C. The potential versus time plot provides an overview of the voltage characteristic of the battery upon cycling.

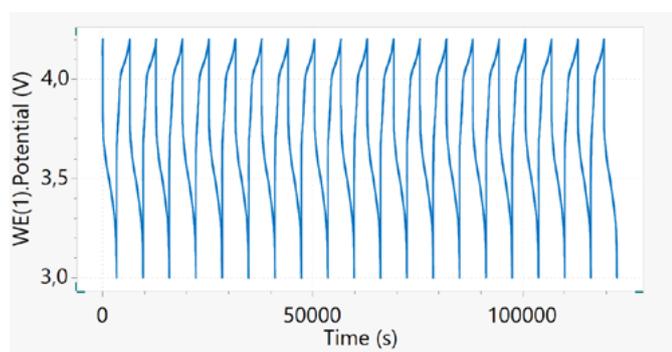


Figure 4. Potential versus time plot for the 18650 Li-ion cell cycled at 1C.

To gain a better overview of the changes in voltage profiles of the battery over cycling, the time of each cycle can be corrected, starting from zero seconds. **Figure 5** shows this approach in the potential versus time plot.

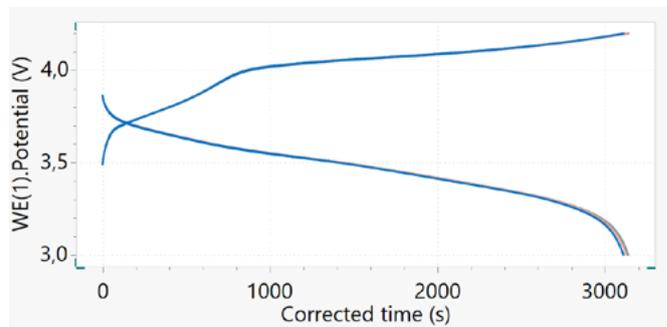


Figure 5. Potential versus corrected time for the 18650 Li-ion cell cycled at 1C.

One of the main characteristics of a battery or battery materials is the capacity. Capacity of the battery can be calculated using the following equation:

$$\text{Capacity (mAh)} = \text{Time (h)} \times \text{Current (mA)} \quad (4)$$

Therefore, the commonly used plot of capacity versus potential can be easily explored. **Figure 6** shows the capacity versus the potential plot of the 18650 cell, here shown only for cycle 1.

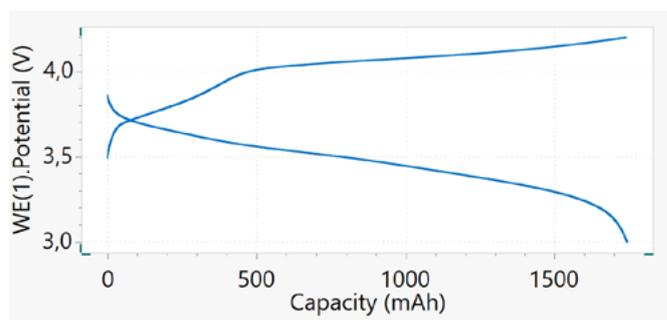


Figure 6. Capacity versus potential plot upon charge/discharge cycling of a Li-ion battery at 1C rate, cycle 1.

Further analysis can be performed on the data depending on the scope of the experiment (e.g. dQ/dV vs. V and dV/dQ vs. Q) which highlights the small features in the potential versus capacity plot.

Figure 7 shows the voltage profile of 18650 cell, cycled at $\sim C/15$, and its corresponding dQ/dV vs V plot for one cycle. The analysis of dQ/dV was executed by NOVA 2 software. The dQ/dV peaks are marked with their corresponding plateau in the voltage profile of the cell during the charge. Both peak position and peak height may experience changes during cycling of the battery. These data are useful to learn about the aging mechanisms of the batteries during their cycle and calendar life. For example, the shifting of charge peaks to higher voltages suggests a rise in internal resistance of the battery during its cycling. Shrinkage of these peaks during the cycling indicates a decrease in the capacity corresponding to the relevant plateau in voltage profile of the battery.

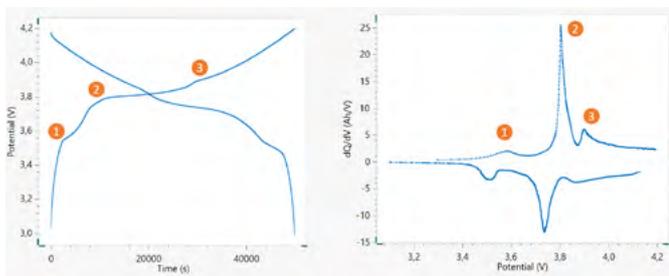


Figure 7. Voltage profile of the 18650 Li-ion battery, cycled at $\sim C/15$ (left), and its corresponding dQ/dV versus V plot (right). The corresponding peaks and plateaus are marked in the figures.

It is very important to explore the capacity fade of a battery over long-term cycling. This can be done by tracking the charge and discharge capacities versus the cycle number.

Figure 8 shows a typical capacity versus cycle number plot for the battery used in this experiment.

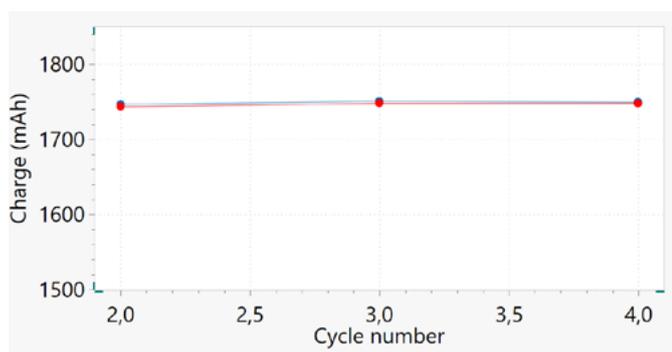


Figure 8. Capacity versus cycle number plot for cycles 2, 3 and 4. Blue and red dots correspond to charge and discharge capacity, respectively.

Here, only three cycles are shown. As mentioned in the previous section, this battery has a nominal capacity of 2600 mAh, whereas the capacity measured for these cycles is about

1750 mAh at 1C, showing an approximately 33% reduction compared to its nominal capacity.

The energy density

The energy density of a battery can be calculated using the following equation:

$$\text{Energy density (Wh/kg)} = \text{Capacity (Ah/kg)} \times \text{Voltage (V)} \quad (5)$$

Therefore, in order to increase the energy density of a battery, it is important to explore materials with higher capacity and/or cathode materials with higher operating potential. Of course this needs to be done relative to the specific volume or mass. For example, for a 18650 battery with a nominal capacity of 2600 mAh, a nominal potential of 3.7 V and the total mass of 46 g, the energy density is about 209 Wh/Kg.

The C-Rate

Applications vary in their energy release requirements—some require a quick release of energy whereas others require a constant release over a sustained period of time. Battery chemistry also varies in terms of rate performance. Therefore, it is important to use a battery chemistry which is suitable for the specific application, considering the required power.

As explained earlier, the C-rate is an indication of the rate of cycling and describes how fast or slow the cycling is done.

Figure 9 shows the cycling of an 18650 battery at different C-rates. It is obvious that at higher C-rates the cycling time is lower, but the capacity retained also decreases with increasing C-rate.

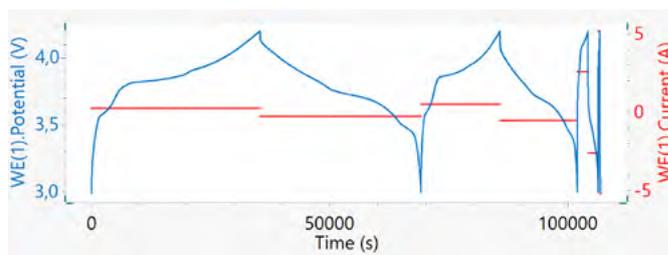


Figure 9. Potential vs. time (left axis) and current vs. time (right axis) of four consecutive cycles at $C/10$, $C/5$, C , and $2C$ rates.

Figure 10 shows the discharge potential profile versus the capacity at different C-rates. This plot gives a better overview of the capacity retention, and voltage profile at different C-rates. A decreasing trend is observed in the capacity when increasing the C-rate. This is more noticeable at a high rate of 2C where the battery can retain only about 12% (320 mAh) of its nominal capacity; while for a lower rate of $C/5$ the capacity retained is about 90% (2340 mAh) of its nominal capacity

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of 2600 mAh. It is obvious that this battery technology is not suitable for high power applications where the battery needs to be capable of delivering the energy in a shorter time period.

Looking at the voltage profile of the battery at higher rates, one can see the fading of plateaus that appeared in voltage profiles of the same battery cycled at lower C-rates.

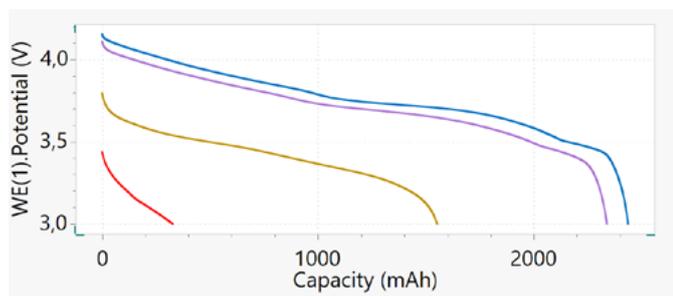


Figure 10. Plot of discharge potential vs. capacity at different C-rates: C/10 (blue), C/5 (purple), C (brown), and 2C (red).

When viewing the discharge voltage profile of the battery, one can see the existence of the voltage plateau at different depths of discharge. The plateau in voltage profile of the battery indicates the coexistence of two phases on the battery electrode. If discharging of the battery occurs upon formation of a non-stoichiometric compound on one of the electrodes, then discharging the battery further would go through a gradual change in potential instead of a plateau.

Coulombic efficiency (CE)

The coulombic efficiency of a cell can be simply defined as the ratio of the amount of charges delivered during the discharge to the amount of charges stored in the battery during the initial charge.

CE can be calculated using the following equation:

$$\text{Coulombic efficiency (\%)} = \frac{\text{Discharge capacity}}{\text{Charge capacity}} \times 100 \quad (6)$$

The commercial Li-ion batteries have a coulombic efficiency very close to, but never equal to, the ideal value of 100%.¹ When the coulombic efficiency equals 100%, a Li-ion battery would last forever. This is, of course, not the case and a fraction of charge is always lost at every cycle. This loss of charge at each cycle mainly comes from side reactions due to the formation or repair of the SEI layer. Of course other side reactions like electrolyte oxidation, dissolution of transition metals, loss of active materials from the current collector, and Li plating at the anode might be also responsible for the capacity loss at each cycle.

¹ In some cases of commercially made batteries, especially when the battery is subjected to storage at high state of charge (SOC), the coulombic efficiency might be more than 100% for early cycles. This is related to the safety engineering of the commercial cells where wider anode sheets are placed against the cathode sheets. Upon storage at high SOC, lithium ions diffuse in that region. As a consequence, the extra lithium coming from the overhang region of the anode during its cycling, causes the CE to be higher than 100% for early cycles.

Figure 11 shows the coulombic efficiency versus cycle number for a Li-ion cell cycled at $C/10$. When viewing the y-axis, one can see that the values nearly reach 100% and follow an increasing trend. For a brand new cell, the CE values are normally lower at the early cycles. Upon the battery aging, the coulombic efficiency increases as the amount of side reaction decreases over the time/cycle when the battery matures. Coulombic inefficiency (defined as « $1 - CE$ ») might be a more appropriate value to consider when observation of capacity loss at each cycle is of interest.

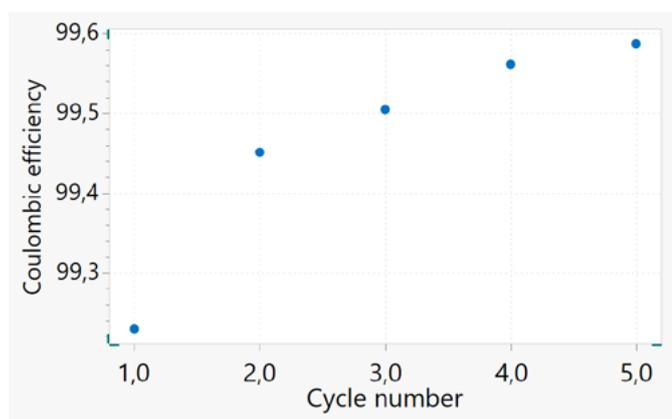


Figure 11. Coulombic efficiency plotted against the cycle number for the aged 18650 battery.

Therefore, the coulombic efficiency of a cell is a very useful parameter in order to understand the level of side reactions with different battery technologies. One of the main advantages of the coulombic efficiency as an evaluation

parameter is the possibility of assessing the performance of the battery in a short period of time. However, this needs to be measured accurately and supported by precise control of battery temperature.

Electrochemical impedance spectroscopy (EIS)

One of the objectives of battery research is minimizing the internal resistance. With EIS, it is possible to measure the internal resistance of the battery, as well as to model it with an electronic circuit to understand more about the root cause of the impedance within the battery components.

A potential electrode material and electrolyte also need to have a minimum impedance. To have an accurate impedance spectroscopy measurement, it is important to have the correct connection to the batteries. The 4-point Kelvin configuration, where the current leads are isolated from voltage leads, is a suitable cell connection for EIS measurement of batteries.

Figure 12 shows the Nyquist plot for the 18650 cylindrical cell at fully discharged state (3 V) at room temperature. The EIS measurement is done in potentiostatic mode. From the properties of the Nyquist plot one can simply identify the parameters required for the equivalent circuit fit. In this diagram, L represents the inductance given by the cables, R_s represents a series resistance corresponding to the battery terminals, cables and mostly electrolyte resistance, R_{CT} is the charge transfer (between electrode and electrolyte) resistance, C_{DL} is the double layer capacitance, which corresponds to the SEI layer, and W_{diff} is the diffusion impedance, modeled by a Warburg element (semi-infinite transmission line) at low frequencies.

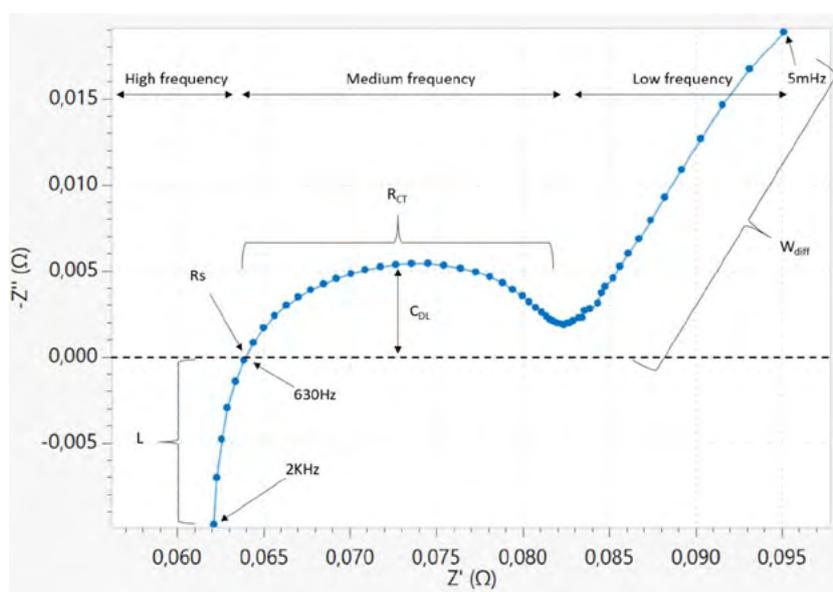


Figure 12. Nyquist plot: Negative imaginary part of impedance as a function of the real part of impedance for the 18650 cell.

Figure 13 shows the Bode plot corresponding to the same EIS measurement of the 18650 cell. Here, the real impedance and phase are plotted as a function of the logarithm of the frequency. Giving the possibility of impedance comparison at the same frequency, Bode plots are very useful to compare the impedance of negative and positive symmetric cells and full cells in post-mortem EIS analysis of the batteries. A symmetric cell of cathode/cathode and anode/anode could be made for EIS measurement and ideally the sum of these impedances divided by 2 should be equal to total impedance of full cell. This approach is useful to study the electrochemical processes at the cathode side and anode side of the battery separately.

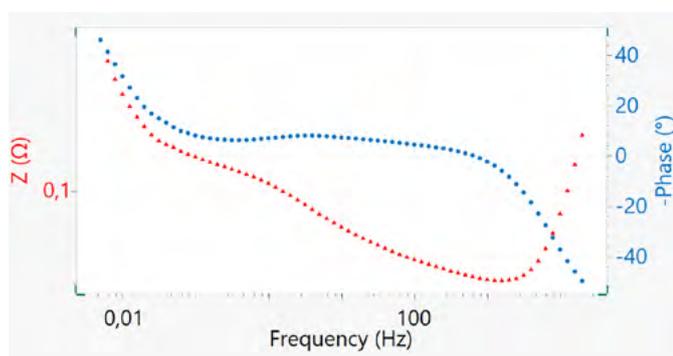


Figure 13. The bode plot of the 18650 Li-ion cell.

The EIS characterization can be done at different states of charge, corresponding to different cell potentials. If needed, e.g., during the charge or discharge of the battery, the EIS can also be performed in galvanostatic mode where a current perturbation is sent to the battery instead of a potential. **Figure 14** shows the EIS measurement at different states of charge. To change the state of charge, the battery was charged in galvanostatic mode up to a certain potential and then the battery was left at open circuit potential to relax for about 2 hours. A long relaxing time is needed in order for the battery to reach its equilibrium condition. Although the features in the Nyquist plot do not change dramatically, the overall impedance decreases when charging the battery to higher states of charges. The changes are mostly at medium and low frequencies where diffusion resistance and charge

transfer resistance are affected at different states of charge. It is also important to track the impedance of the battery upon the cycling. When characterizing the impedance over battery cycling e.g. after 50, 100, or 500 cycles, the impedance experiments need to be done at a fixed potential in order to be able to make a correct comparison.

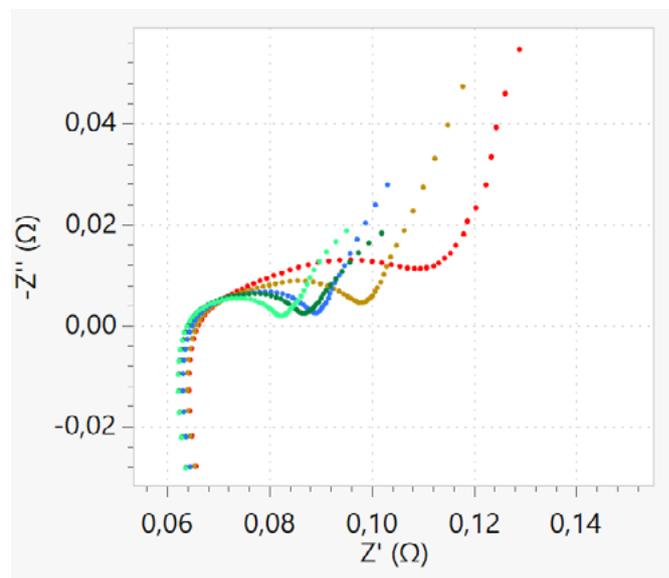


Figure 14. Nyquist plot corresponding to EIS measurement done at different potentials of 3 V (red), 3.4 V (brown), 3.7 V (blue), 3.9 V (green) and 4.15 V (light green).

Alternative technologies to Li-ion batteries

Other than Li-ion batteries which are currently the main rechargeable battery technology, research and development is being done on alternative battery chemistries, e.g. Li-Air, Li-Sulfur, Na-ion, and solid state batteries, to name a few. These other cell chemistries face different challenges which hamper their commercialization. Nevertheless, the interest in these alternative technologies has been growing as they promise different advantages with respect to Li-ion batteries.

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Summary

This study provides an overview of the main principles and techniques to study the performance of a battery and other battery materials. It is essential to have access to high quality instrumentation in order to assure accurate, high quality measurements.

Two main techniques to study the performance of batteries and battery materials are constant current cycling and electrochemical impedance spectroscopy. With constant current cycling, it is possible to calculate values like coulombic efficiency and capacity over cycling as well as understanding the potential characteristic of the battery and its rate capability. In addition, by conducting some additional analysis on the data (e.g. dV/dQ versus Q and dQ/dV versus V), one can understand more about the changes in the potential profile of the battery. This specifically is very interesting when studying the failure mechanism of the battery or the battery materials. With EIS, it is not only possible to measure the internal resistance of the battery but also possible to model the resistance using the equivalent circuit and understand the contribution of the battery components in the total impedance of the cell.

When preparing the battery electrode using the active material slurry, one should take good care regarding its mechanical stability when deposited on the current collector, as it potentially could be the source of a failure. When the constant current charge and discharge in a half-cell configuration is under study, it must be considered that the source of lithium is unlimited and a cumulative capacity loss approach needs to be taken into account to resemble the performance in a full-cell configuration. To evaluate the battery performance, a very interesting parameter to calculate is the coulombic efficiency. The coulombic efficiency calculation has to be precise and accurate in order to be able to compare technologies with very similar behaviors at early cycles. This requires highly precise instrumentation and accurate control of the test temperature.



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Metrohm has developed a number of application notes which can help your battery research activities:

- Determination of the MacMullin number
- Galvanostatic Intermittent Titration Technique (GITT)
- Galvanostatic charge-discharge of a Li-ion battery with Autolab
- High voltage measurements: Characterization of NiMH batteries with Autolab PGSTAT302N in combination with voltage multiplier
- Metrohm Autolab DuoCoin Cell Holder with EIS measurements on a commercial battery
- Potentiostatic Intermittent Titration Technique (PITT)
- Simple CV and EIS test measurements carried out with the electrochemical cells for air or moisture sensitive measurements

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