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# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

## Study of Li-ion cell behavior during charging at low temperatures in general and comparison of different cell chemistries

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# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

## Summary of key findings

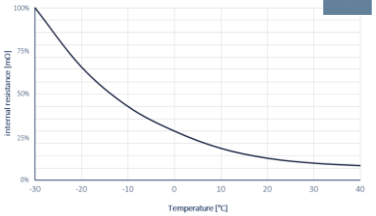
- The cell behavior at low temperatures is strongly dependent on multiple components, but mainly driven by **anode** and **electrolyte** especially during fast charging processes.
- Main low temperature effects are **higher internal resistances** (5 times higher at -20°C compared to RT)**, higher charge-transfer resistance, higher activation energy** which is needed as well as **lower Li-ion diffusion rates and conductivity** between the electrodes, SEI and the electrolyte.
- The low temperature effects lead to an overall impact of a **reduced power performance, loss of capacity** (up to 50%), but also to an enhanced cell **cycle life degradation** (~4 times higher compared to high temperatures at e.g., 60°C).
- Conducted tests show that **NCA cathode materials** show **better low temperature charging capabilities** compared to **LFP,** due to **longer constant current charging phases**, different material structure and electrode design**.**
- Automotive OEMs require **operating temperatures** between **-30 and 60°C** and have **additional thermal management solutions** implemented to avoid low temperature effects on cell level, which is why a **comparison** of low temperature behavior **on pack level** is crucial for final assessment.
- **Preconditioning and preheating** of the battery allows **higher initial charging power**, which influences the **entire charging process** and **enables faster charging**.

# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Low temperature effects:** Environmental effects of low temperatures have a strong influence on the performance of Li-ion batteries and can lead to power or capacity loss or even life degradation without proper preconditioning of the battery.

## LI-ION BATTERY ISSUES AT LOW TEMPERATURES

1

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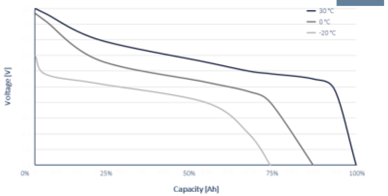


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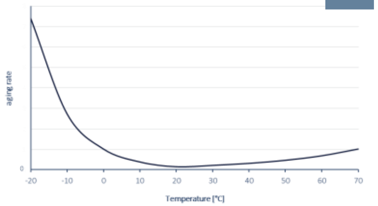



### POWER LOSS

- Decrease in power performance because of **increased impedance** due to higher internal resistance at electrodes, SEI and electrolyte at low temperatures.
- **Decreased ionic conductivity** of electrolytes at low temper-atures which typically freezes at temperatures below -30 °C.

### CAPACITY LOSS

- A low temperature affects the speed in which electrochemical reactions occur.
- Hence, it **decreases the speed of Li-ion diffusivity** in the electrodes leading to a reduction in range capability of the battery.

### CYCLE LIFE DEGRADATION

- With the application of high current rates at low temperatures, **Li-plating could occur** at the anode.
- This leads to an **increase of inactive Li-ions** during cycling and hence to cell life degradation and potentially to permanent damage when Li-dendrites will start to grow.

## KEY FINDINGS

- Li-ion batteries of an EV typically operate at an **ideal temperature range** between **15 and 35 °C**[1].
- However, they also need to perform in **countries with cold winters** as e.g., Canada or Norway. Thus, it is re-quired for EV applications to work from **-30 to +60°C**.
- Especially when driving an EV in winter, a significant **reduction in vehicle range** can be observed and when it comes to charging, **lower charge rates** can be realized mainly in order to avoid degradation reaction.
- Cold temperatures have the effect to **slow down internal chemical reactions & charge-transfer velocity** within a cell and directly affect the cell performance.
- Specifically, a **decrease in ionic conductivity** of electrolytes and **Li-ion diffusivity** within the electrodes occurs and leads to a **reduction of energy and power capability**, and sometimes even **performance failure**.
- **Efficient preheating** of the battery before driving or charging is of **high importance** to prevent from permanent damage and to improve vehicle range and charging performance even at cold temperatures.

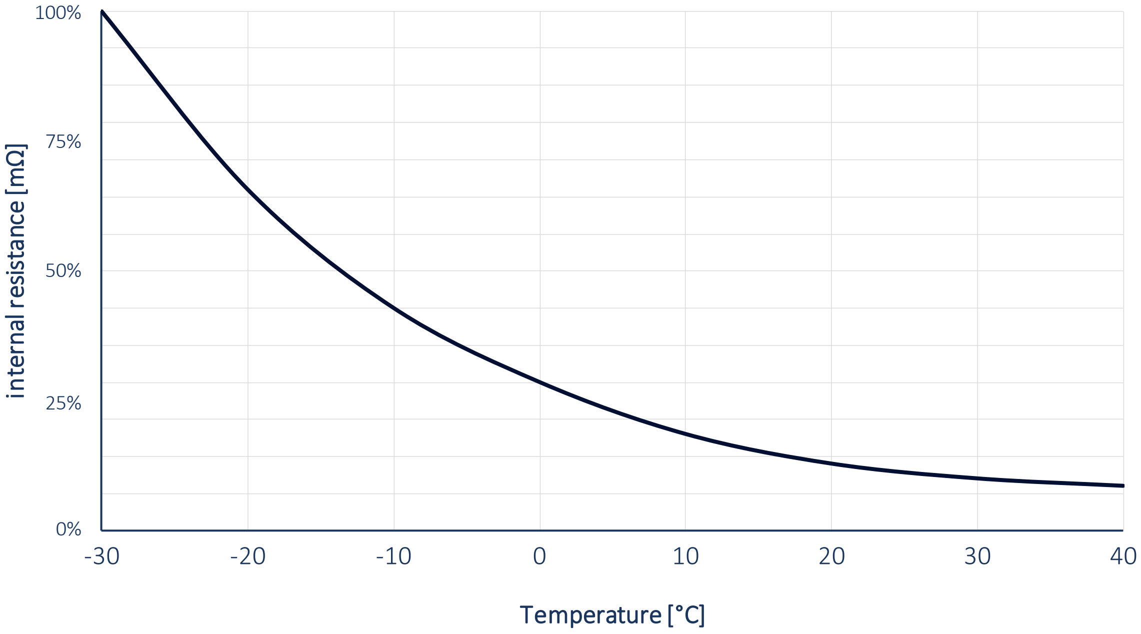
# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Decreased power performance:** The operation of Li-ion batteries at low temperatures leads to a significant reduction of diffusion rate and Li-ion conductivity in the electrodes, SEI & electrolyte leading to polarization of the cell and hence reduced power capabilities.

## POWER LOSS DUE TO INCREASED IMPEDANCE

1 2 3

– illustrative –




## KEY FINDINGS

- The rates of charge & discharge processes are largely dependent on **Li-ion transfer rate** at electrode/ electrolyte interfaces caused by kinetic electrochemical reaction.
- A high power performance can be achieved with **low diffusion time of Li-ions**, **low internal resistances** and **low activation energies** for electrochemical reactions.
- Operation at low temperatures leads to a **significant reduction of diffusion rate and Li-ion conductivity** in the electrodes, SEI & electrolyte but especially in graphite anode which leads to **polarization** of the cell.
- A high polarization leads to a **high diffusion time** between the electrodes and hence leads to **reduced power capabilities** within the cell.
- The effect of **low ionic conductivity** is reinforced by **increased viscosity of electrolyte** at low temperatures.
- This will additionally lead to a **reduced power at low temperatures**, because the majority of the power needs to be used to generate heat in order to reduce the resistances within the cell.

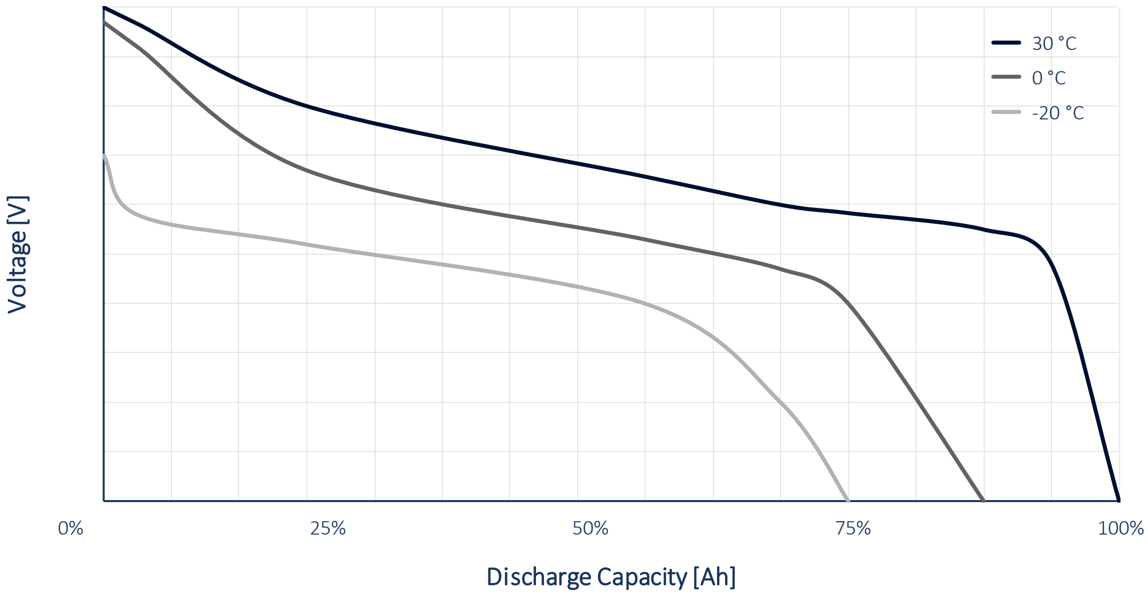
# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Capacity retention:** Cold temperatures can result in a reduction in driving range due to limited mobility of Li-ions between anode and cathode and remaining Li-ions in the material leading to a loss in total capacity of the cell of up to 30% or even larger.

## CAPACITY LOSS DUE TO DECREASED DIFFUSION RATE

1 2 3

– illustrative –




## KEY FINDINGS

- Previous studies indicated, that at low temperatures, the **internal resistances increase** and the **activity of Li-ions in the cathode is reduced** so that more **Li-ions remain in the material** and cannot be extracted anymore, reducing the available capacity.
- This was confirmed by comparing charge capacities of 190 mAh/g@25°C & 168mAh/g@0°C.[3]
- Additionally, the **increased resistance of electrolyte** and **decreased transfer rate of Li-ions** will further support the reduction of available energy.
- A **capacity loss of up to 30%** or larger could occur based on the temperature and (dis-)charge rate.
- Decreased nominal capacity can still be observed even at lower charging rates, because of **high electrode activation energies** and ratio between anode & cathode leading to **polarization effects** within electrodes.
- Another factor that affects the kinetic in LIBs is the **increase of charge-transfer resistance** at low temperatures. Studies report that the resistance of LFP cathodes at −20 °C is **three times higher** than at RT.[1]

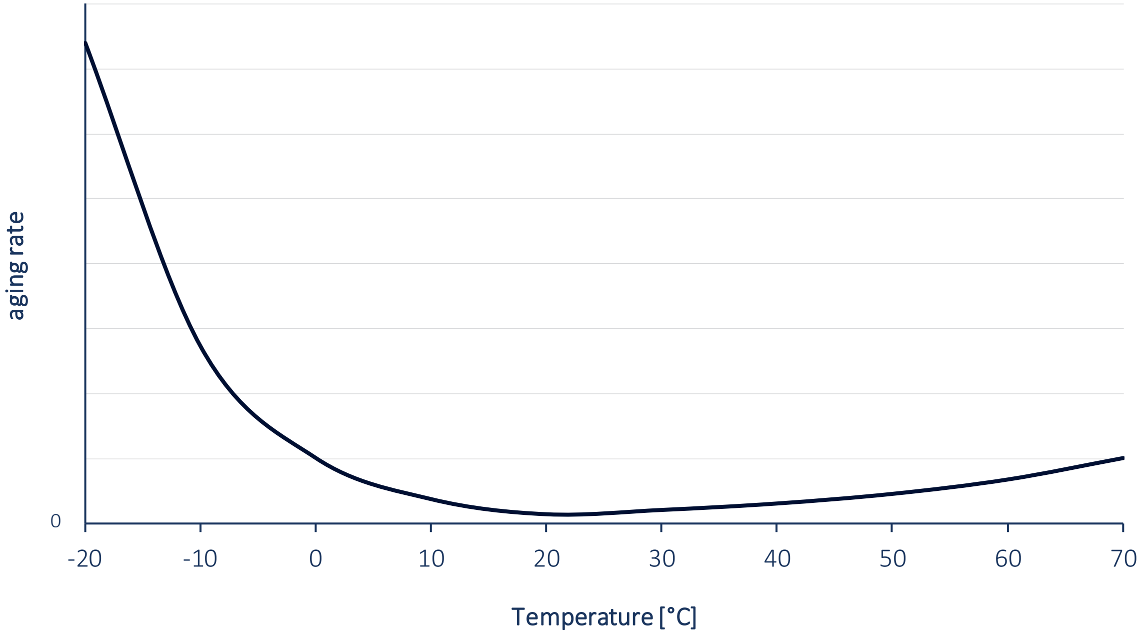
# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Cell cycle life degradation:** Cell aging is intensified, among other things, by operation at low temperatures, as this leads to increased SEI thickness, lower Li-ion diffusivity and intercalation rate, hence impacts power, capacity and cell life performances.

## CYCLE LIFE DEGRADATION DUE TO POTENTIAL LI-ION PLATING

1 2 3

– illustrative –



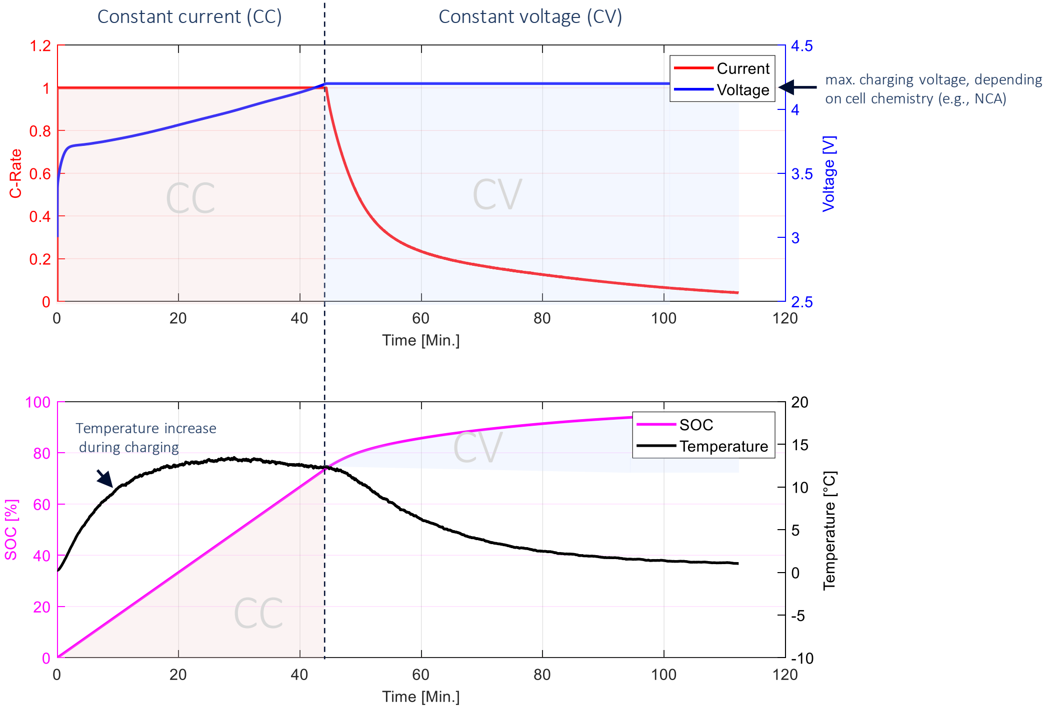

## KEY FINDINGS

- Along with battery aging, **performance of the EV fades** until EoL where 80% of capacity or 33% of internal resistance increase compared to BoL is reached.
- Operation or fast charging at low temperatures, **reduces the conductivity of electrolyte** but also **limits the diffusivity and intercalation rate of Li-ions** in graphite structure as the **thickness of SEI will increase**.
- Typically, at -20 °C or below, the **charge process is slower** than the discharge process in the electrode.
- The **effect of Li-plating** where Li-ions irreversibly deposit as metallic lithium on the graphite anode surface instead of intercalation within the layered structure of the material, has the impact of an **increased impedance, loss of active material and Li-ions for diffusion or even safety hazards** when dendrites would potentially grow.
- As a result, this would lead to a combined effect of **power degradation, capacity fade but also cell cycle life degradation**.

# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Charging tests[1] at low temperature:** The common charging process of a battery cell is divided into to phases - constant current & constant voltage (CCCV) phase. The plots below show a real charging procedure (CCCV) of one cell at 0°C starting temperature.

## CONSTANT CURRENT & CONSTANT VOLTAGE CHARGING PROCESS




## KEY FINDINGS

- The charging process is divided into two phases: **constant-current** and **constant voltage** phase.
- **Most of the charging amount** is being charged **during the constant-current phase.** The charging current is **limited to 1C** due to the low temperature (risk of Li-Plating).
- The **maximum charging voltage** per cell is **depending on the cell chemistry** and **cell specification.**
- The cell **temperature increases during the charging** process, which leads to **improved electrolyte conductivity** and favors the charging process.
- Operation or fast charging at low temperatures **reduces the conductivity of electrolyte** but also **limits the diffusivity and intercalation rate of Li-ions** in graphite structure as the **thickness of SEI will increase**.
- As a result, the charging behavior of a cell is highly depending on the **current consumption capacity** (CC-phase), **voltage limit** and **intrinsic heating** during the charging process.

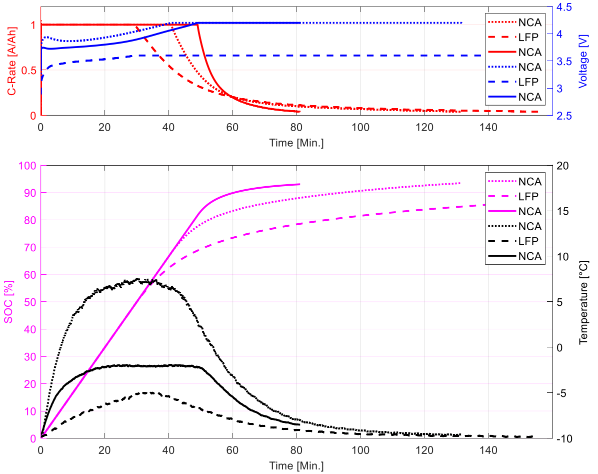

[1] conducted with Batterieingenieure GmbH

# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Comparison of different cell chemistries:** In a direct comparison of the charging behavior at 1C of three different cylindrical battery cells[1] at -10°C and 0°C starting temperature, NCA shows consistently good better charging performance compared to LFP.

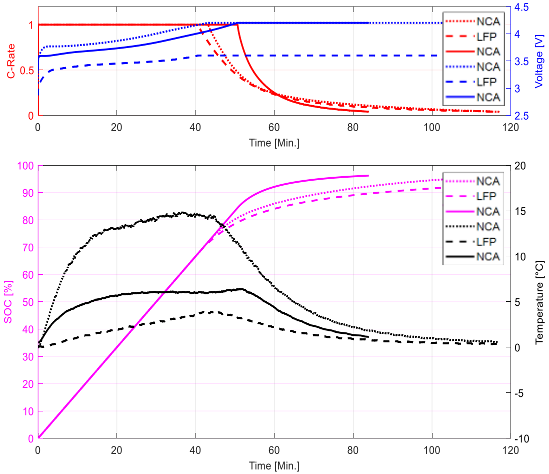
## TEMPERATURE EFFECT ON CHARGING FOR DIFFERENT CELL CHEMISTRIES

### Temperature: -10°C




| | NCA | LFP | NCA |
|---|---|---|---|
| Min. until 80% SOC | 53 | 90 | 48 |
| Min. until 90% SOC | 95 | > 140 | 60 |

### Temperature: 0°C




| | NCA | LFP | NCA |
|---|---|---|---|
| Min. until 80% SOC | 50 | 52 | 48 |
| Min. until 90% SOC | 73 | 87 | 56 |

+31 min.

## KEY FINDINGS

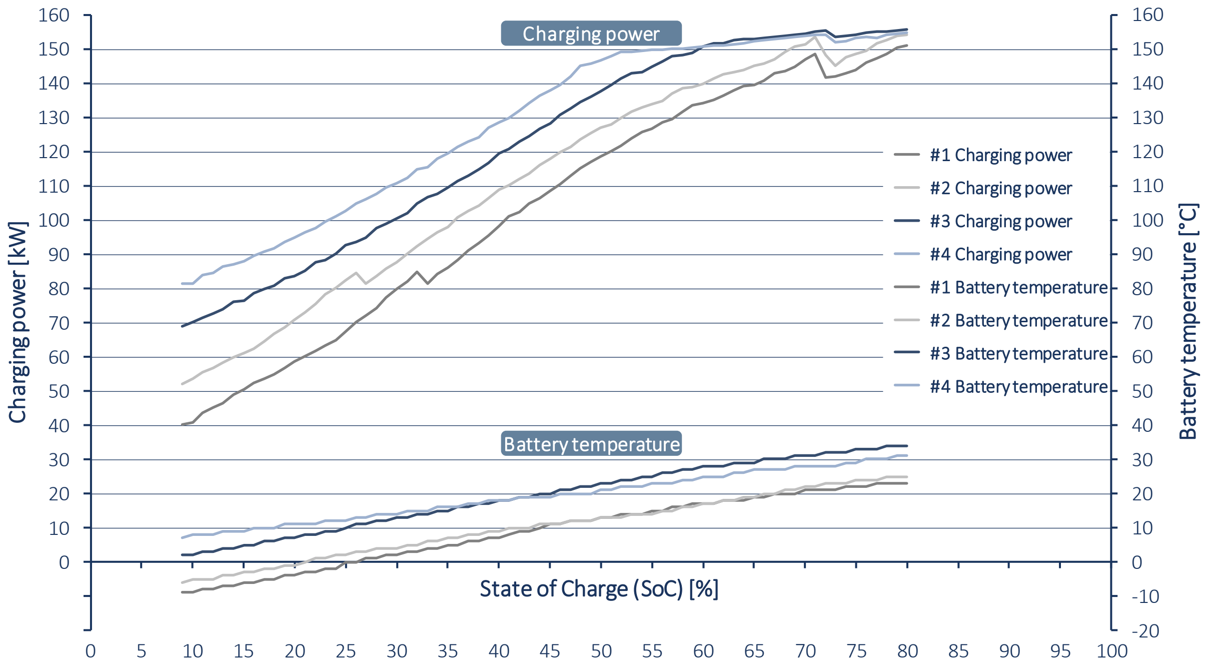
- In general, **NCA** chemistries show **better charging performance** due to longer CC-phase **until the maximum charging voltage is reached** (4.2V with NCA vs. 3.6V with LFP).
- The **LFP cell takes approx. 1.7 times longer** to reach **80% SOC** compared to the NCA cells at **-10°C starting temperature**.
- Cylindrical cell tests[1] show that different cell chemistries (LFP and NCA) have **similar charging performance at 0°C** from **0% - 80% SOC**, but **significant deviations** from **80% - 90% SOC**. **NCA** requires **31 min less** to reach 90% SOC compared to LFP.
- The **temperature increase** during charging leads to **improved electrolyte conductivity**, which favors the charging process. But intrinsic **heating** is **not the most dominant effect for fast charging capability.** NCA cell with medium heating shows best charging performance.
- **LFP** cell with **lowest heating** during charging process due to **lowest energy density** (Wh/kg), which results vice versa in the **highest thermal mass per energy charged**.

[1] Various manufacturers and conducted with Batterieingenieure GmbH

# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

**Charging at low temperatures:** Charging curves of EVs at different temperatures show a high impact on battery temperature and thermal management system on the charging performance, especially at the beginning of the charging process.

## CHARGING POWER PER SOC IN COMPARISON TO BATTERY TEMPERATURE




## KEY FINDINGS

- On vehicle level, especially at the **beginning of a charging process**, the **battery temperature has a high impact** on the **charging performance.**
- The **starting temperature** influences the **charging process** throughout the **entire charging procedure.** Therefore, different charging **curves** which have been measured at P3 charging tests **result from different start temperatures.**
- The **charging power** and the **battery temperature increases with running charging time** and **increasing SoC.**
- Accordingly, the **individual charging curves differ** over the **entire charging process based on the specific starting point for both.**
- At the **end of charging,** the **different charging powers** and thus also the **battery temperatures** have **moved closer together** or even **ended up at a similar level.**
- At **higher starting temperatures,** the battery pack can be **charged faster until 80% SOC**.

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# CELL BEHAVIOR AT LOW TEMPERATURES AND THE IMPORTANCE OF PRECONDITIONING

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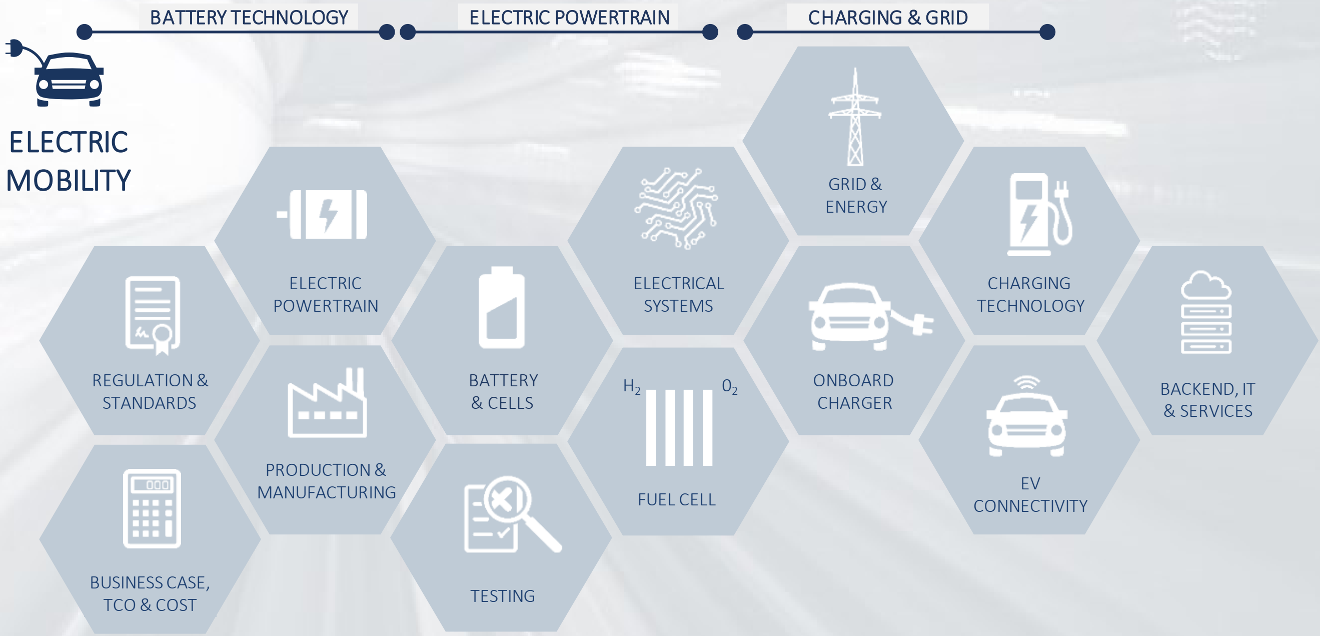

## Literature


[1] "Temperature effect and thermal impact in lithium-ion batteries: A review", Shuai Ma et al., Progress in Natural Science: Materials International, Volume 28, Issue 6, 2018.

[2] C. Vidal, O. Gross, R. Gu, P. Kollmeyer and A. Emadi, "xEV Li-Ion Battery Low-Temperature Effects—Review," in IEEE Transactions on Vehicular Technology, vol. 68, no. 5, pp. 4560-4572, May 2019.

[3] "Operando NMR of NMC811/Gr Li-Ion Batteries: Structure, Dynamics, & Li Metal Deposition" Katharina Märker, Chao Xu, and Clare P. Grey, Journal of the American Chemical Society 2020, 142 (41), 17447-17456.

[4] "An Experimental Study of a Li-Ion Cell Operation at Low Temperature Conditions." Asma Mohamad Aris, Bahman Shabani, Energy Procedia. 110, 2017.

[5] "Degradation of Commercial Lithium-Ion Cells as a Function of Chemistry and Cycling Conditions" Yuliya Preger et al 2020 J. Electrochem. Soc. 167 120532

[6] "Temperature dependent ageing mechanisms in Lithium-ion batteries – A Post-Mortem study", Waldmann et al., Journal of Power Sources. 262. 129–135, 2014.