# Impact of Ni content on interface reactions at NCM electrodes

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## Motivation / Objectives

**Motivation:**
Layered nickel cobalt manganese oxides (NCM) have been and will likely increase to be of high commercial attractiveness as cathode materials for high-end Li-ion batteries [1]. The partial substitution of Co renders NCMs less costly than $LiCoO_2$ and, on top of this, the introduction of Ni has proven to result in higher reversible specific charge (~180 mAh $g^{-1}$ vs. ~150 mAh $g^{-1}$) [2]. Cell performance parameters such as capacity retention and thermal stability are being heavily investigated by various research groups, albeit typically with a strong focus on the bulk cathode material [3]. Even though these investigations are essential, a sufficiently complete picture of the complex performance-property relationships in electrode materials additionally requires the reactions at the respective cathode/electrolyte interfaces to be understood in more detail. Consequently, we are focusing our efforts on exploring interface reactions to provide valuable information for devising strategies to systematically improve batteries based on promising new cathode materials such as Ni-rich NCMs.

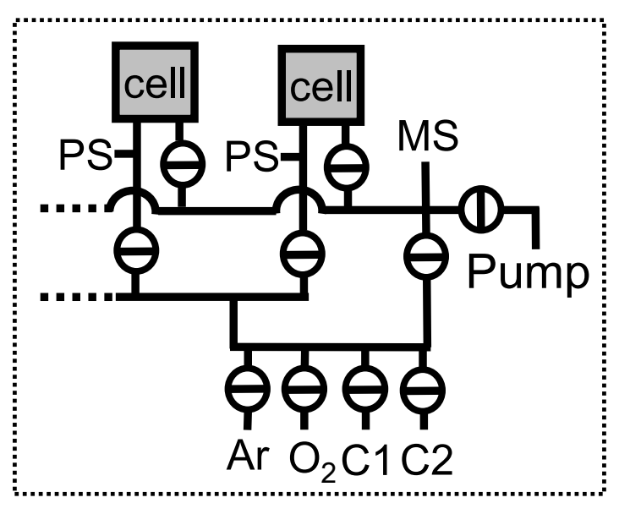
**Objectives:**

1. Is there a correlation between $CO_2$ evolution and Ni content of NCMs?
2. Is it possible to prevent or reduce the extent of $CO_2$ evolution?

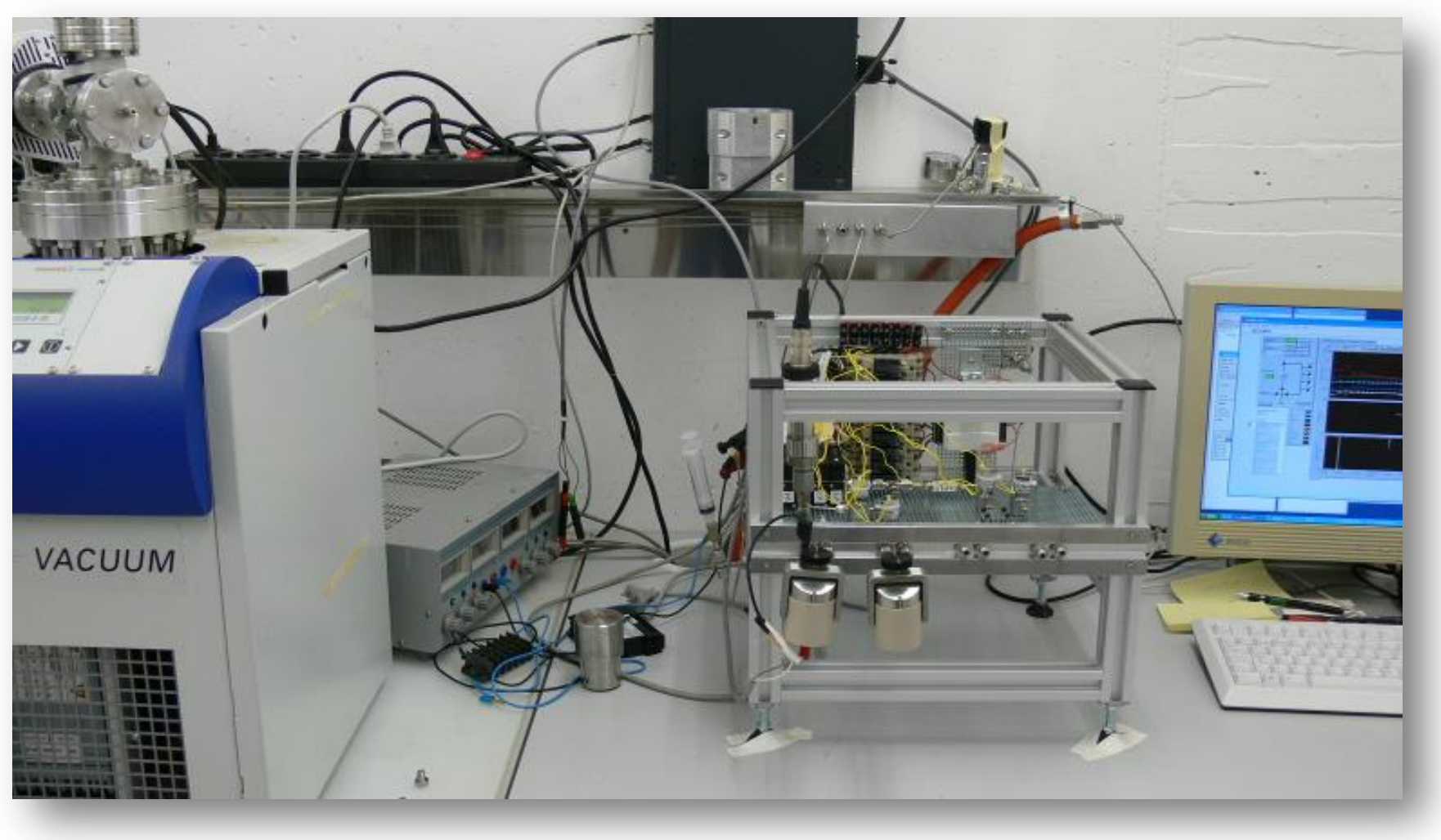
## Approach / Instrumentation

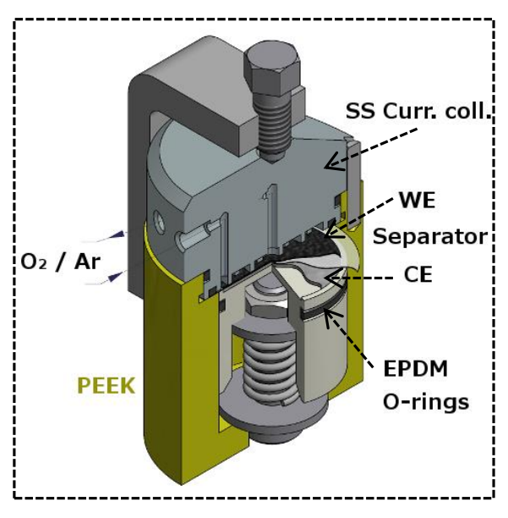
**Approach:**
Many interface reactions result in the evolution of gaseous species. Therefore, we try to get a better understanding of these reactions by using online electrochemical mass spectrometry (OEMS) to quantitatively analyze specific gaseous species evolving from cells during electrochemical cycling. The investigated cells contain cathodes based on a series of layered oxides of varying Ni content ($LiCoO_2$, NCM111, NCM622, NCM811), Celgard 2400 separator, Li metal foil anodes, and 1 M $LiPF_6$ in 3:7 (w/w) EC:DEC as electrolyte. Specific electrode surface areas and average potentials are also taken into account in our analysis.

**Instrumentation:**



**OEMS Setup**



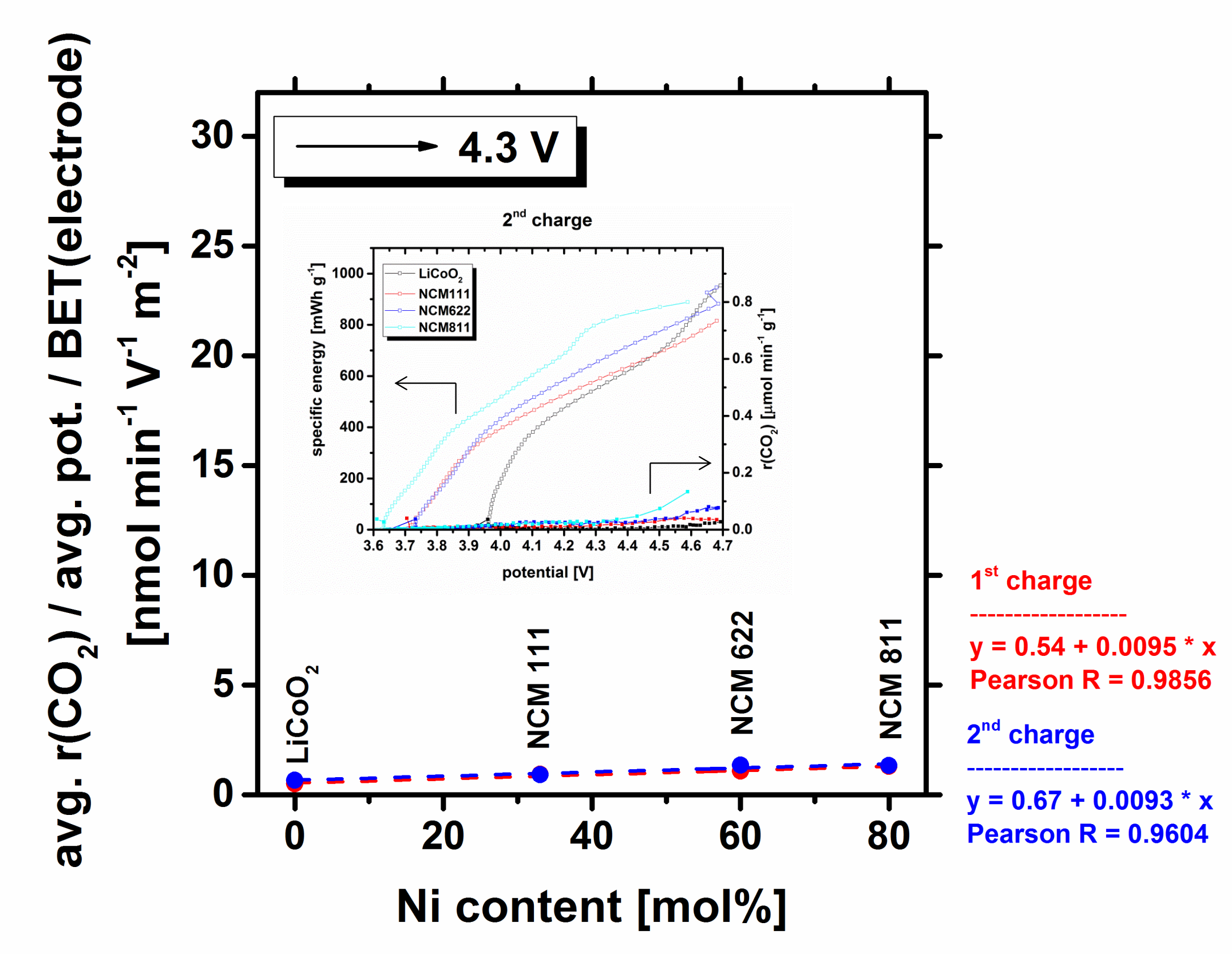


**Electrochemical cell**

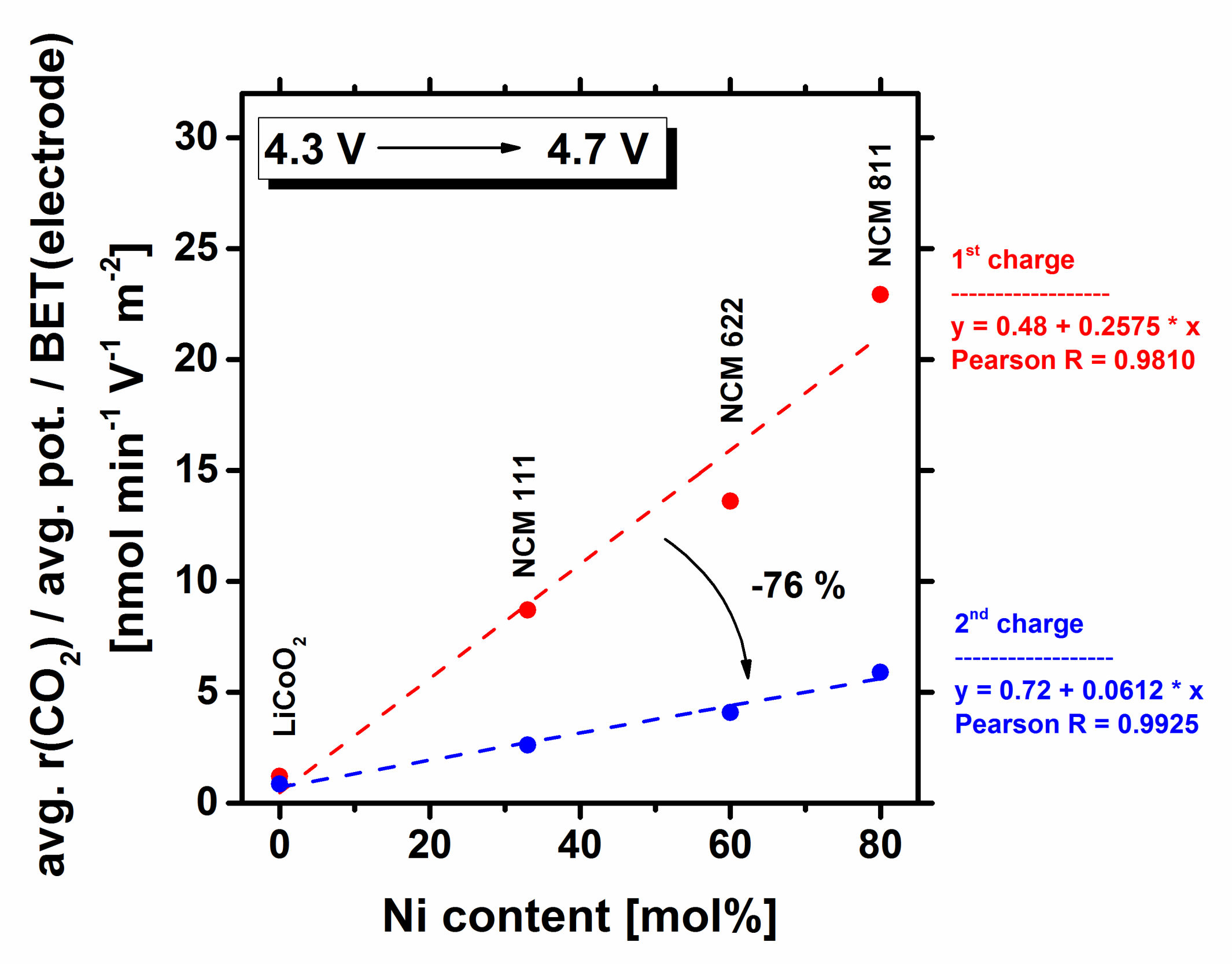
Ø18 mm working electrode (WE)
Ø22 mm separator
Ø20 mm Li counter electrode (CE)
120 µL Electrolyte

## OEMS results

### Correlation between $CO_2$ evolution and Ni content

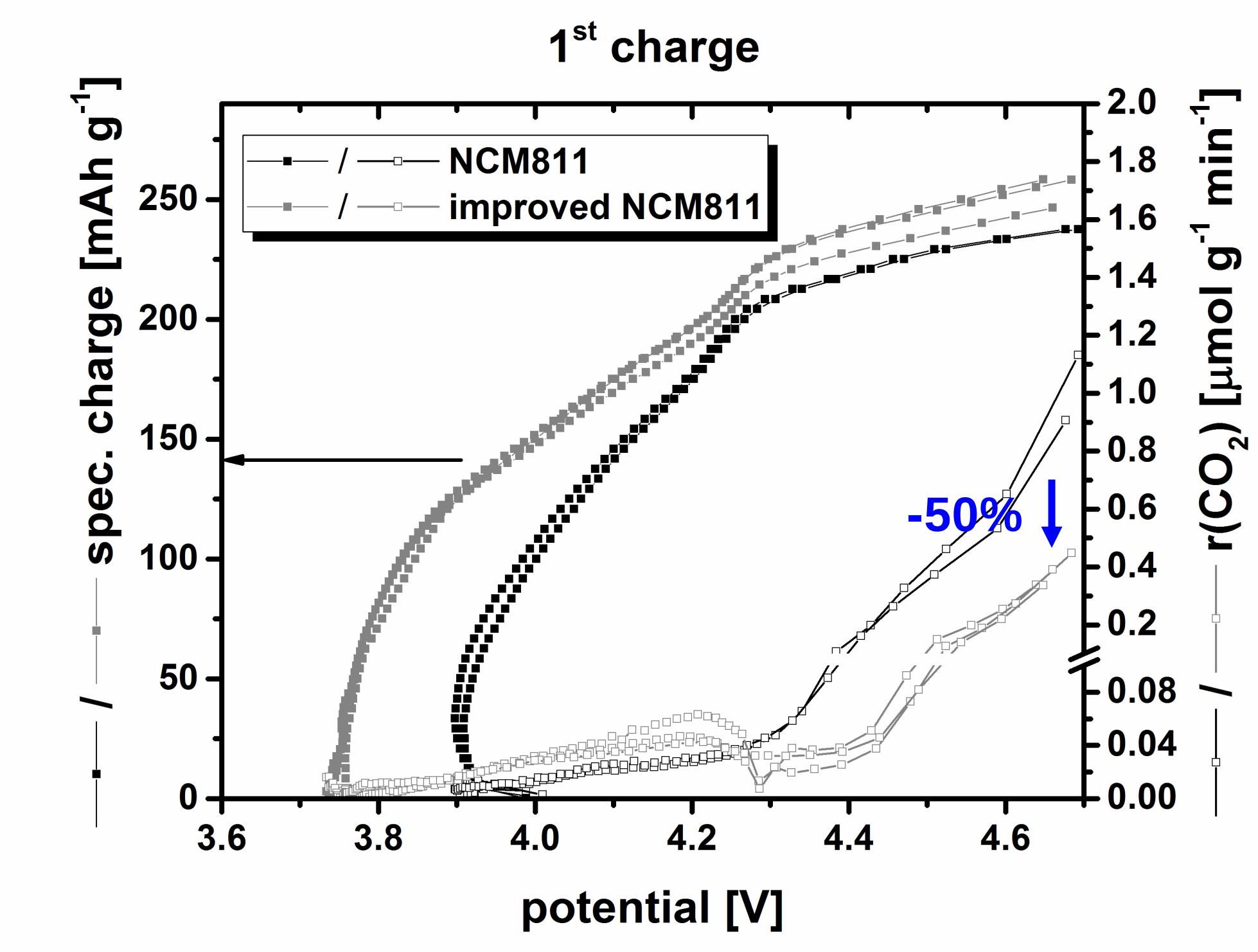


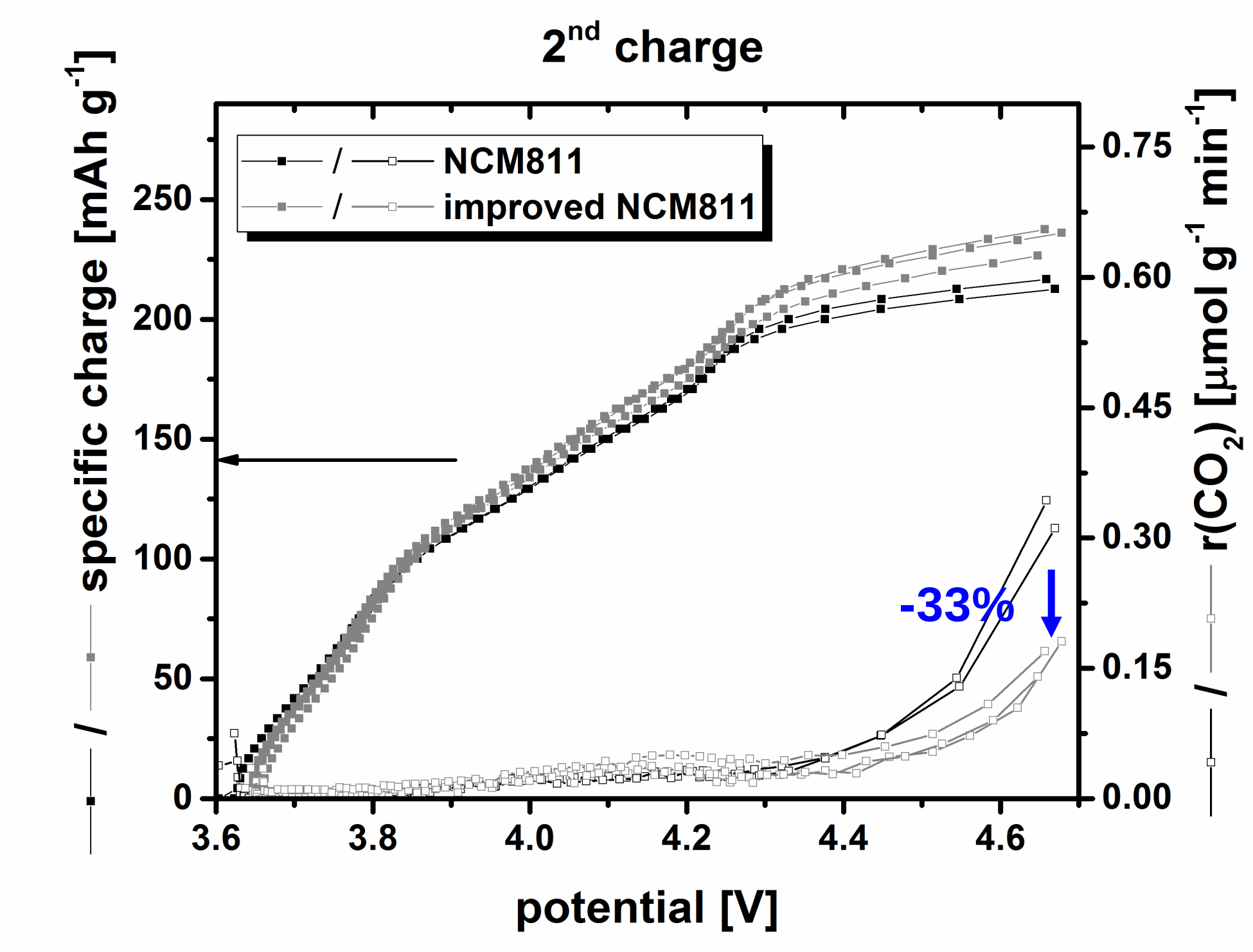
- Minor dependence on Ni content up to 4.3 V; no difference between 1st and 2nd charge.
- Inset: attractive gain in specific energy with Ni content; $CO_2$ evolution rate of NCM811 barely higher than $LiCoO_2$ up to 900 mWh $g^{-1}$!



- Strong dependence on Ni content between 4.3 and 4.7 V.
- Dramatic decrease in slope after 1st cycle.
- Decrease of similar magnitude after the 2nd cycle → slope(4.3 → 4.7 V) ≈ slope(→ 4.3 V)

### Prevention or reduction of $CO_2$ evolution





## Conclusions / Open issues

☞ **A strong correlation between $CO_2$ evolution and Ni content exists in the first cycle at voltages > 4.3 V.**

☞ **For state-of-the-art, commercially relevant cell voltages ≤ 4.3 V, the correlation is weak and cycle-independent suggesting that surface reactivity of the NCM materials is low.**

☞ **It needs to be further investigated whether the cycle-dependent loss of correlation at potentials > 4.3 V originates from interface reactivity changes or from bulk effects.**

☞ **NCM811 exhibits the highest specific energy of all tested NCM materials at $CO_2$ evolution rates barely higher than $LiCoO_2$.**

☞ **Low $CO_2$ evolution of Ni-rich NCM materials such as NCM811 can be further extended to even higher potential by tailoring the material.**

☞ **It remains unclear whether a reduction in early cycle $CO_2$ evolution would improve long term cell performance.**

☞ **The gassing observed in the first cycle could be irrelevant for a commercial cell where a degassing step after formation is standard.**

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## References

[1] Berg et al., *Journal of the Electrochemical Society*, **2015**, 162, A2468-A2475: «Rechargeable batteries: grasping for the limits of chemistry».
[2] Kim et al., *Chemistry of Materials*, **2015**, 27, 6450-6456: «Design of Ni-rich layered oxides using *d* electronic donor for redox reactions».
[3] Noh et al., *Journal of Power Sources*, **2013**, 233, 121-130: «Comparison of the structural and electrochemical properties of layered Li[$Ni_xCo_yMn_z$]$O_2$ ($x$ = 1/3, 0.5, 0.6, 0.7, 0.8, 0.85) cathode material for lithium-ion batteries».