Investigation of fatigue mechanisms in commercial lithium ion batteries containing blended cathode materials

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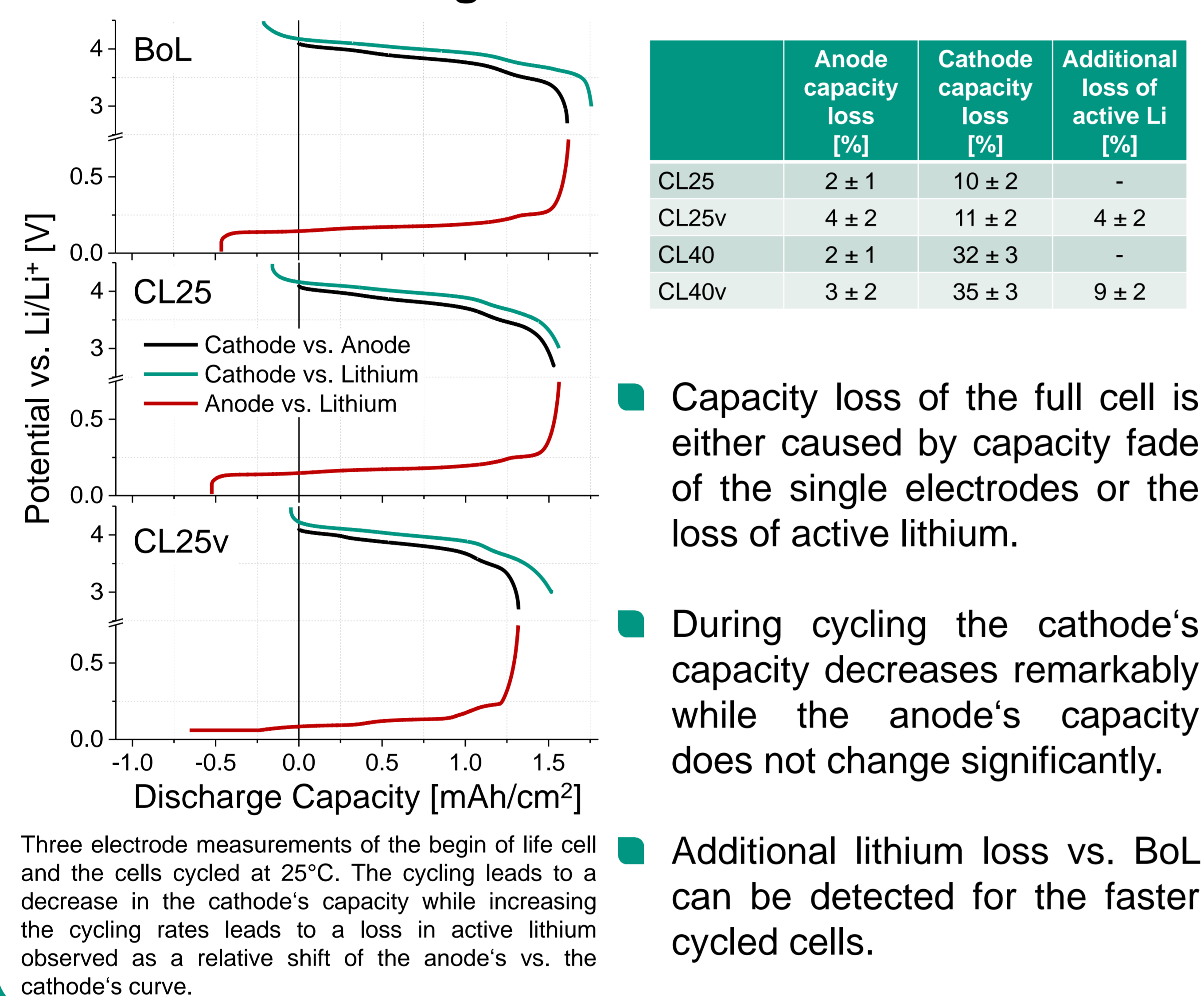[2]Bayerische Motoren Werke Aktiengesellschaft (BMW AG), Germany

Introduction

There are many applications using secondary batteries. In this case lithium ion batteries have been the most common battery type for the past two decades after their commercialization in 1991 and are still state of the art [1]. While for mobile applications such as smartphones the life time of the battery is not crucial due to short innovation cycles, going to long life applications such as electric vehicles or stationary energy storage systems generates the urge for long living battery solutions [2]. Hence long time cycling tests have been performed under different operation conditions studying corresponding fatigue mechanisms to understand and furthermore prevent battery degradation.

Experimental

Commercial lithium ion batteries were cycled 2000 times at a DoD of 100%. The operation temperature of two cells was set to 25°C while the other two cells were kept at 40°C. Within one temperature one cell was cycled at 1C charge and 2C discharge rate (CL25/CL40) while the other cell was cycled at 2C charge and 3C discharge rate (CL25v/CL40v). So the dependency of degradation mechanisms on temperature and rate could be investigated and compared to the fresh cell at the begin of life (BoL). The cells were opened under argon atmosphere and anode and cathode material were separated. The cathode consists of a blend of $Li(Ni,Co,Mn)O_2$ (NCM), $Li(Ni,Co,Al)O_2$ (NCA) and $LiMn_2O_4$ (LMO) while the anode is composed of graphite.

Identification of fatigue mechanisms

	Anode capacity loss [%]	Cathode capacity loss [%]	Additional loss of active Li [%]
CL25	2 ± 1	10 ± 2	-
CL25v	4 ± 2	11 ± 2	4 ± 2
CL40	2 ± 1	32 ± 3	-
CL40v	3 ± 2	35 ± 3	9 ± 2

- Capacity loss of the full cell is either caused by capacity fade of the single electrodes or the loss of active lithium.

- During cycling the cathode's capacity decreases remarkably while the anode's capacity does not change significantly.

- Additional lithium loss vs. BoL can be detected for the faster cycled cells.

Three electrode measurements of the begin of life cell and the cells cycled at 25°C. The cycling leads to a decrease in the cathode's capacity while increasing the cycling rates leads to a loss in active lithium observed as a relative shift of the anode's vs. the cathode's curve.

Capacity loss due to lithium loss

- During cycling active lithium is consumed in continuous growth and reformation of the SEI [3].

- Increasing the cycling rate leads to an increased growth of the SEI.

- Cell operation at elevated temperatures also leads to an increased thickening of the SEI.
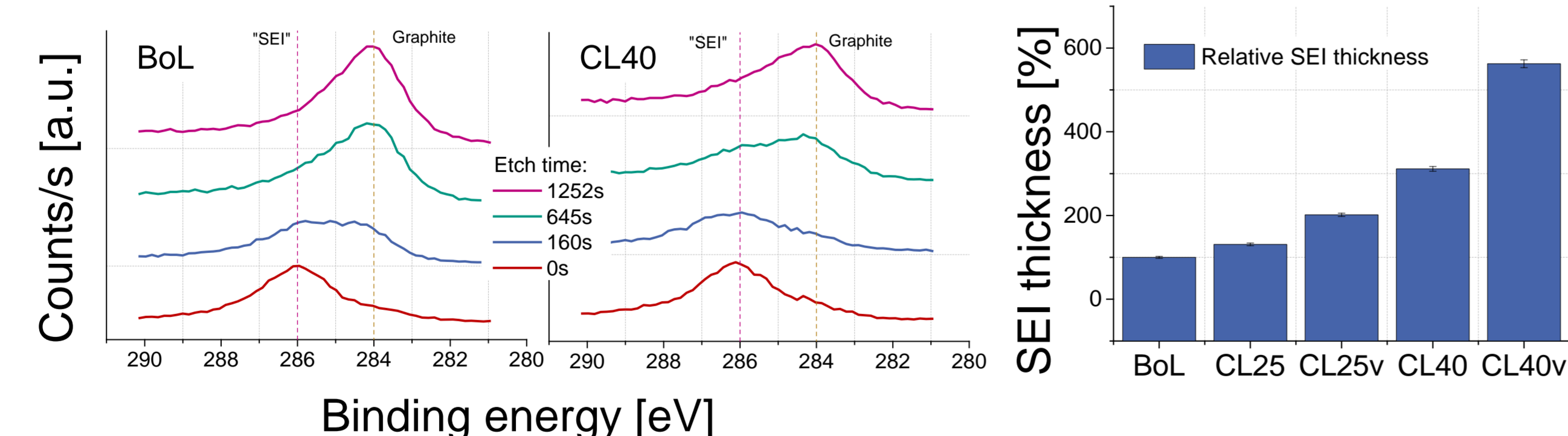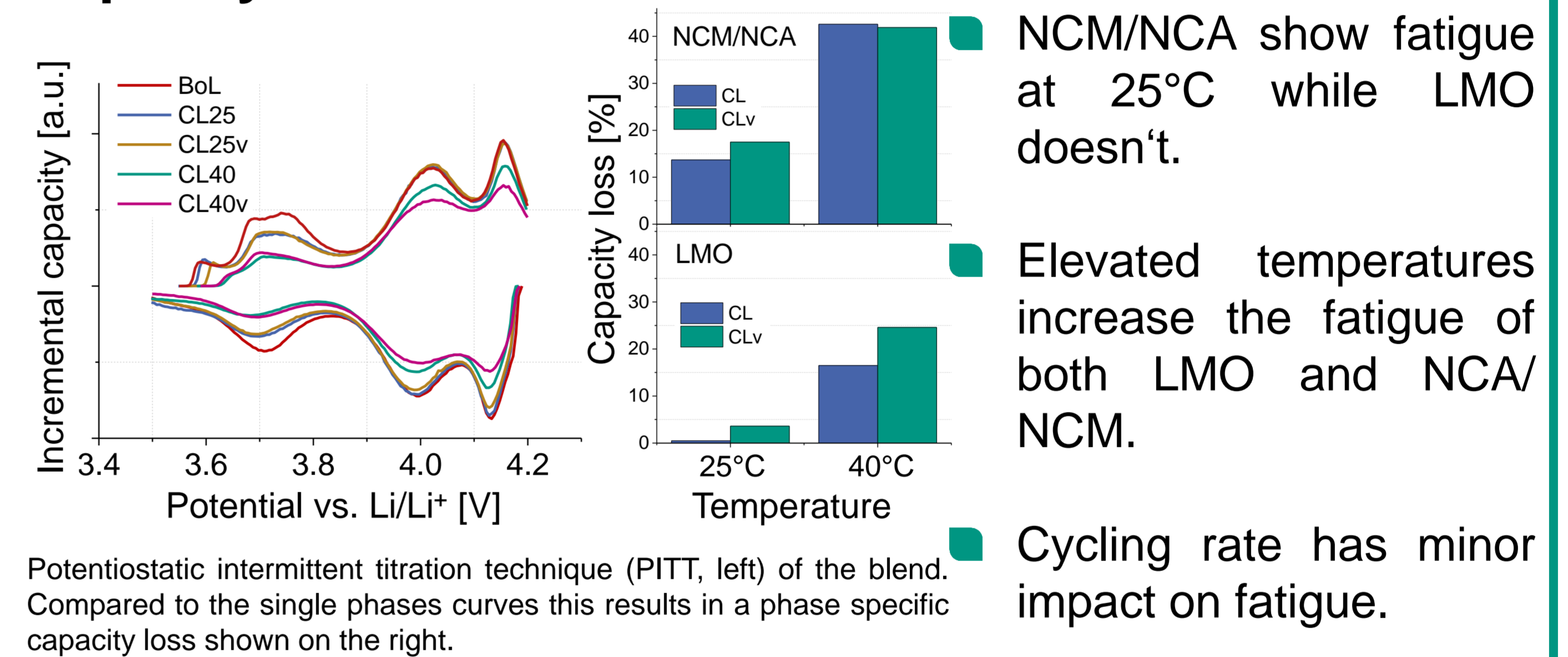

C1s spectra (left) obtained by X-ray photoemission spectroscopy (XPS). The peak at higher binding energies corresponds to C-O type bindings and therefore represents SEI components. The peak arising at lower binding energies corresponds to graphitic bindings and represents the bulk anode material. The spectra were obtain at different sputter depths. We assume the time by that the higher binding energy peak decreased to the half of the C1s area to be correlated to the SEI thickness (right). Due to the used method it is not possible to give a number for the thickness of the SEI but a relative value compared to the BoL state.
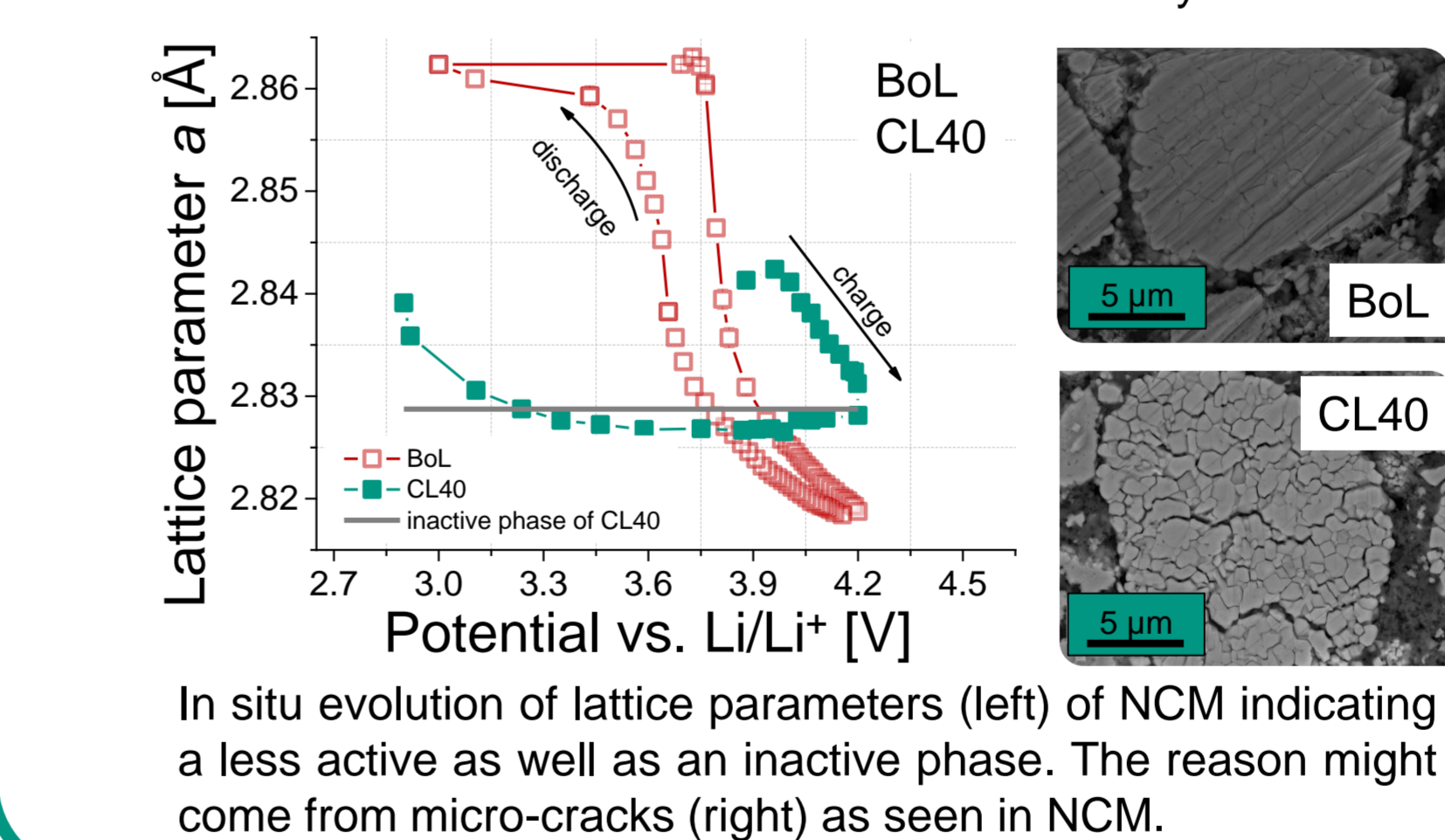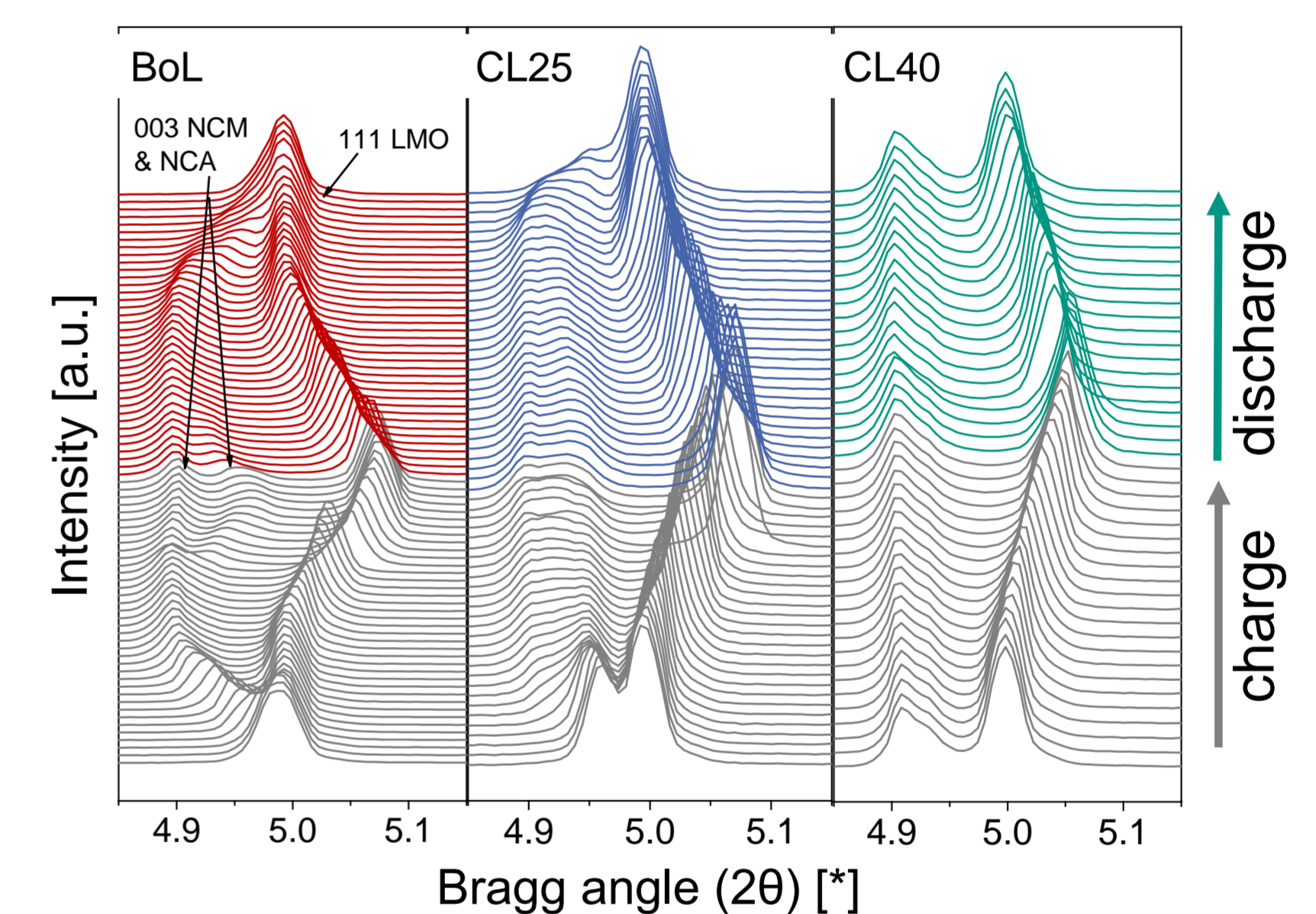
Capacity loss of cathode

Potentiostatic intermittent titration technique (PITT, left) of the blend. Compared to the single phases curves this results in a phase specific capacity loss shown on the right.

- NCM/NCA show less activity in all fatigued cells, the effect is increased by temperature but rarely affected by cycle rate.

- NCM shows inactive phases in all the cells at C/3.

- NCM/NCA show fatigue at 25°C while LMO doesn't.

- Elevated temperatures increase the fatigue of both LMO and NCA/NCM.

- Cycling rate has minor impact on fatigue.

In situ synchrotron diffraction data showing decreased activity of NCA/NCM for the fatigued cells.

In situ evolution of lattice parameters (left) of NCM indicating a less active as well as an inactive phase. The reason might come from micro-cracks (right) as seen in NCM.

- Micro-cracks were found to occur in NCM and NCA.

- Manganese loss was detected at 40°C and addressed to be lost in LMO.

Conclusion

- Two main fatigue mechanisms occur in the tested cells. Cathode capacity loss as well as loss of active lithium and therefore a relative shift of the electrodes curves lead to a capacity fade of the full cell.

- Loss of active lithium is increased at higher cycling rates and it is also influenced by elevated temperatures while only the elevated temperatures show a strongly impact on cathode capacity.

References

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