

# Investigation of degradation behavior in Li-rich NCM cathode materials with spectroscopic methods



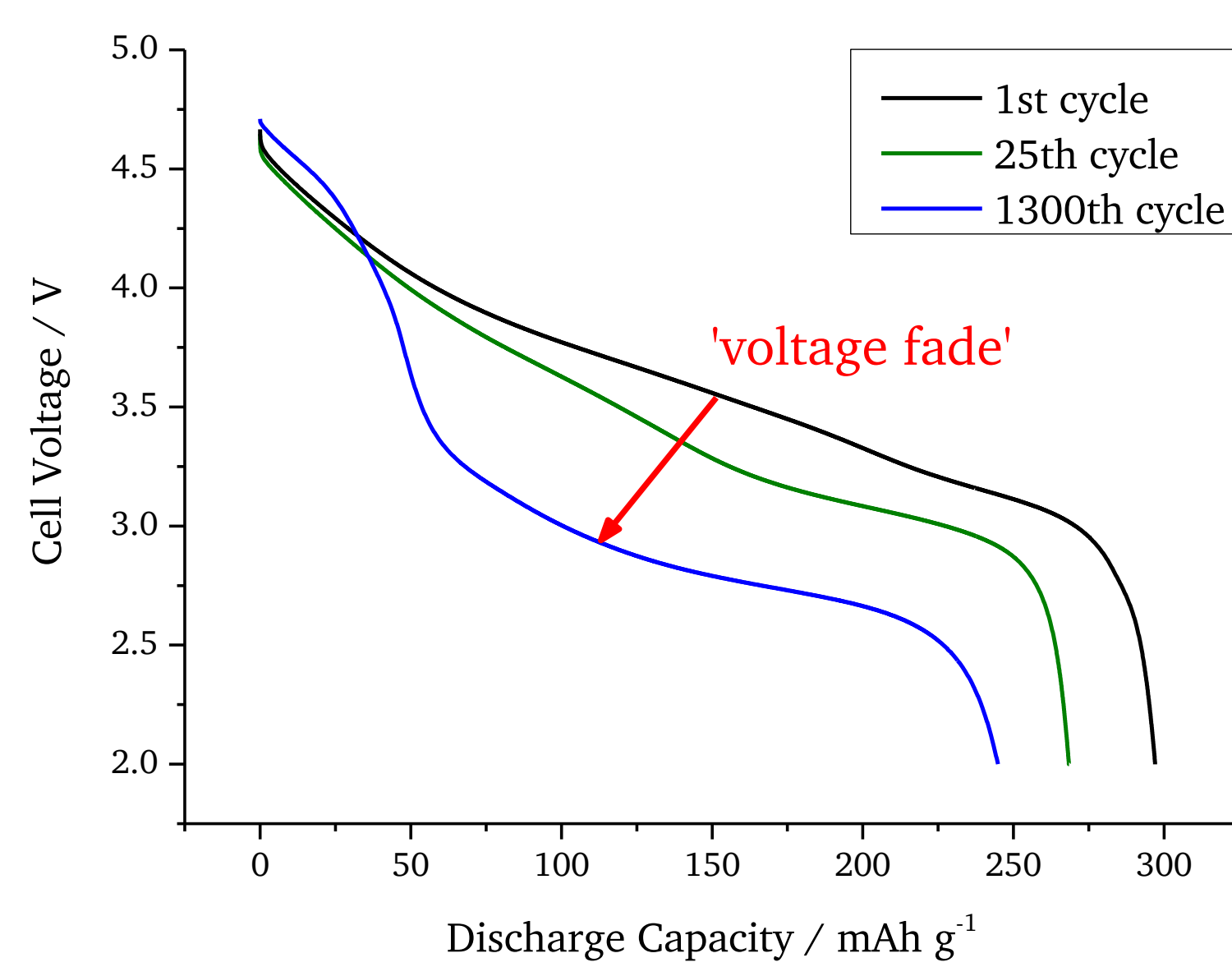
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## Transfer project T3

### Motivation

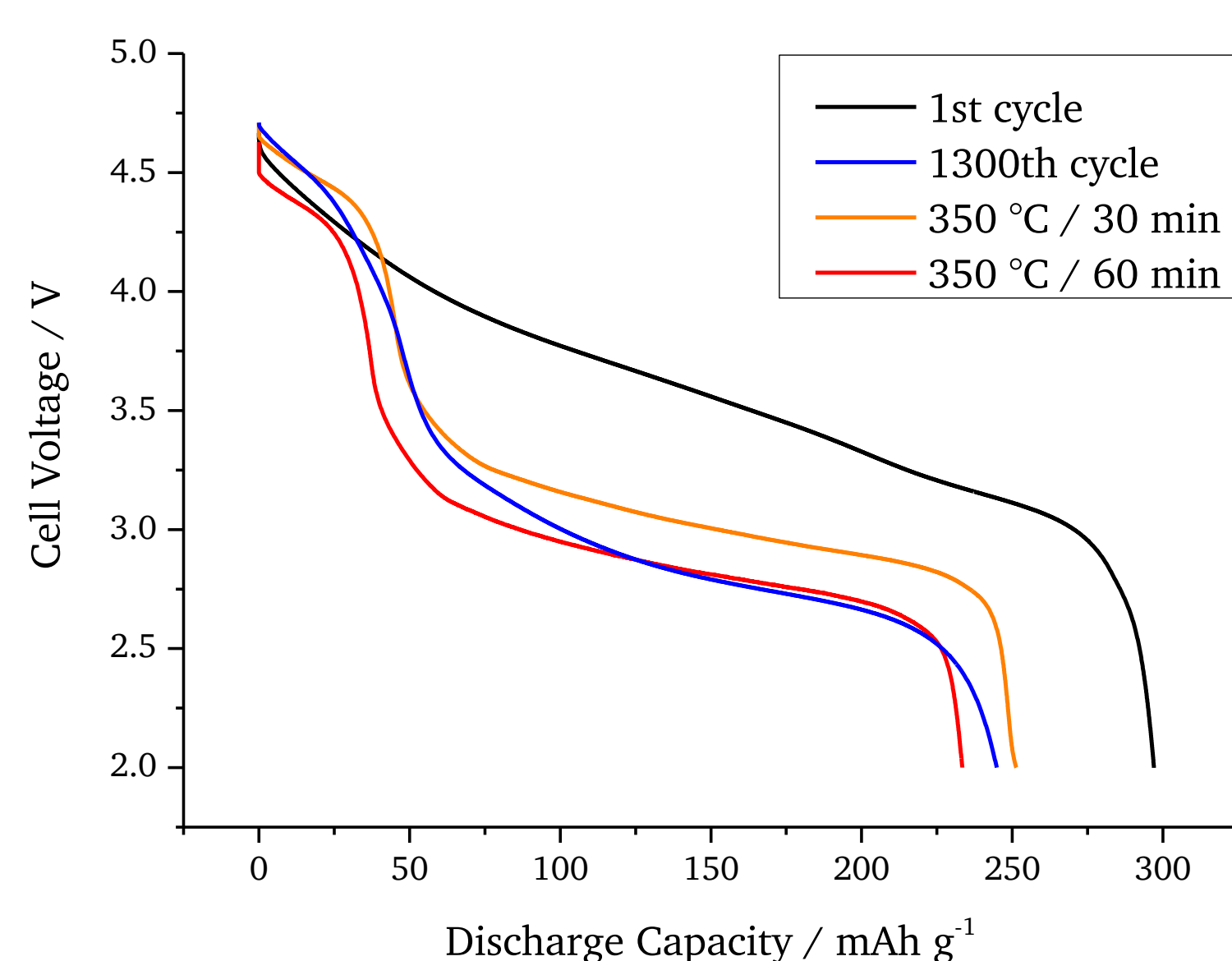
Layered transition metal oxides that are mainly based on either  $\text{LiCoO}_2$  or  $\text{LiNiO}_2$  are still used in portable electronic devices due to their high operating voltage and high specific capacity 140-160 mAh/g. Materials such as the 'Li-rich' layered oxides, formed as the composites between  $\text{Li}[\text{Li}_{1/3}\text{Mn}_{2/3}]\text{O}_2$  (LIR) and  $\text{LiMO}_2$  ( $M = \text{Ni, Co, Mn}$ ) (NCM) are promising candidates that offer even higher reversible capacities ( $> 250$  mAh/g) and higher safety together with reduced costs [1]. For an economic and efficient operation as cathode materials in electrified vehicles for example, knowledge about mechanisms of degradation in order to optimize these materials for longer life time is mandatory. So far, a gradual decrease of the energy density during electrochemical cycling called 'voltage fade' is a major drawback of this material class [2].



Synchrotron X-Ray diffraction and HRTEM investigations on Li-rich materials after long term cycling revealed the formation of  $\sim 5$  nm domains with spinel-like cation ordering within a layered oxide matrix and an overall still coherent ccp oxygen lattice. These micro/nano structural changes are supposed to cause the 'voltage fade' [3]. First results obtained by *ex situ* ESR and NMR spectroscopic methods on the structural changes related to the degradation processes in Li-rich NCM materials with high commercial potential are discussed with preliminary focus on the empirical correlation with electrochemical degradation. Furthermore, a fast and effective method for artificial aging of this cathode material by thermal treatment is shown.

### Thermal Aging

- The systematic study of degradation in Li-Ion battery materials often requires high numbers of electrochemical cycles to visualize the capacity and/or voltage fade of the battery. In order to reduce the duration for material development, we propose an alternative route via thermal aging.



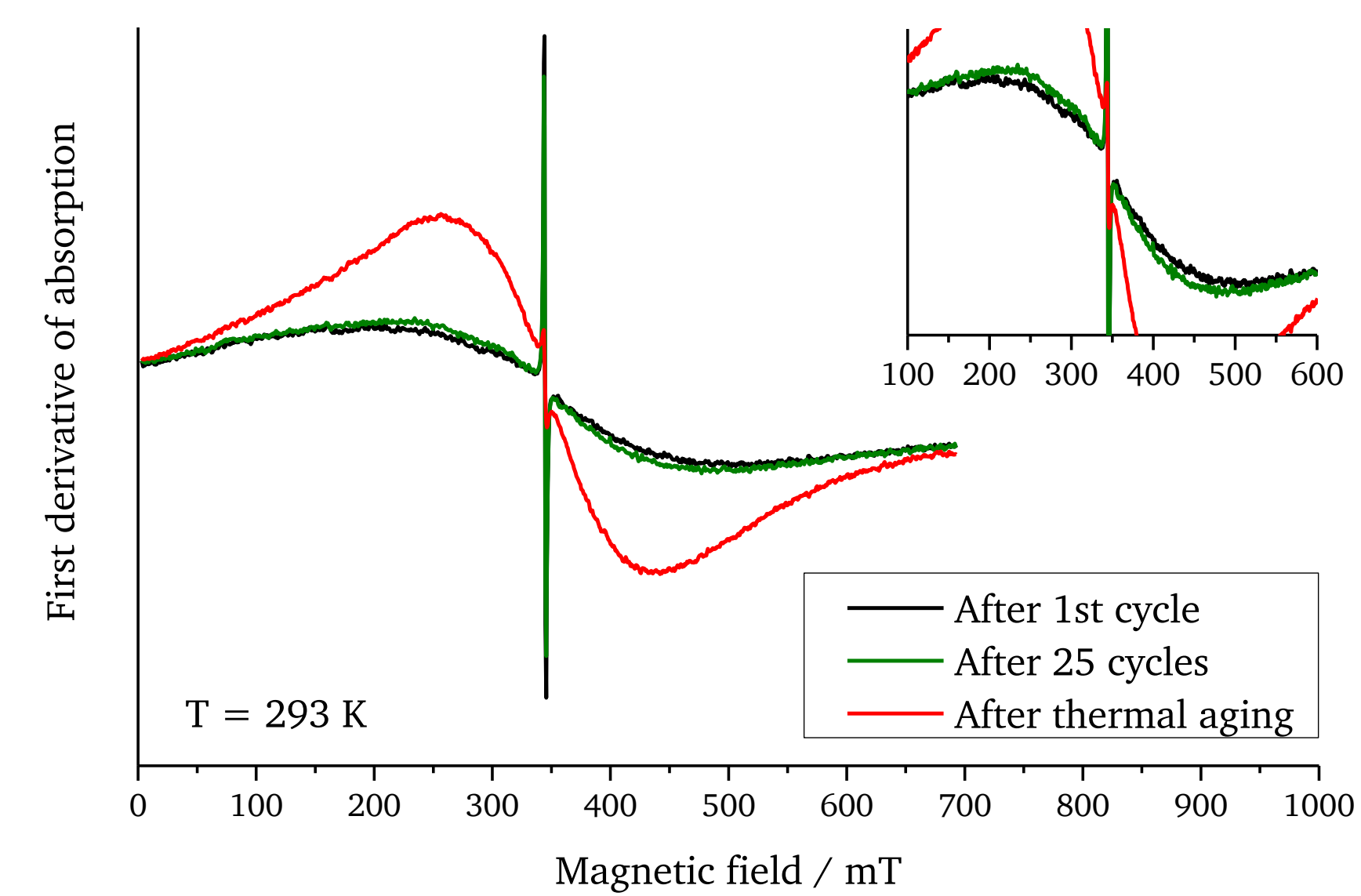
- The Li-rich NCM material was 'activated' with an initial charge/discharge cycle and annealed at 350 °C afterwards.
- The discharge curves show a similar degradation behavior in comparison to long-term cycled material.

### Literature

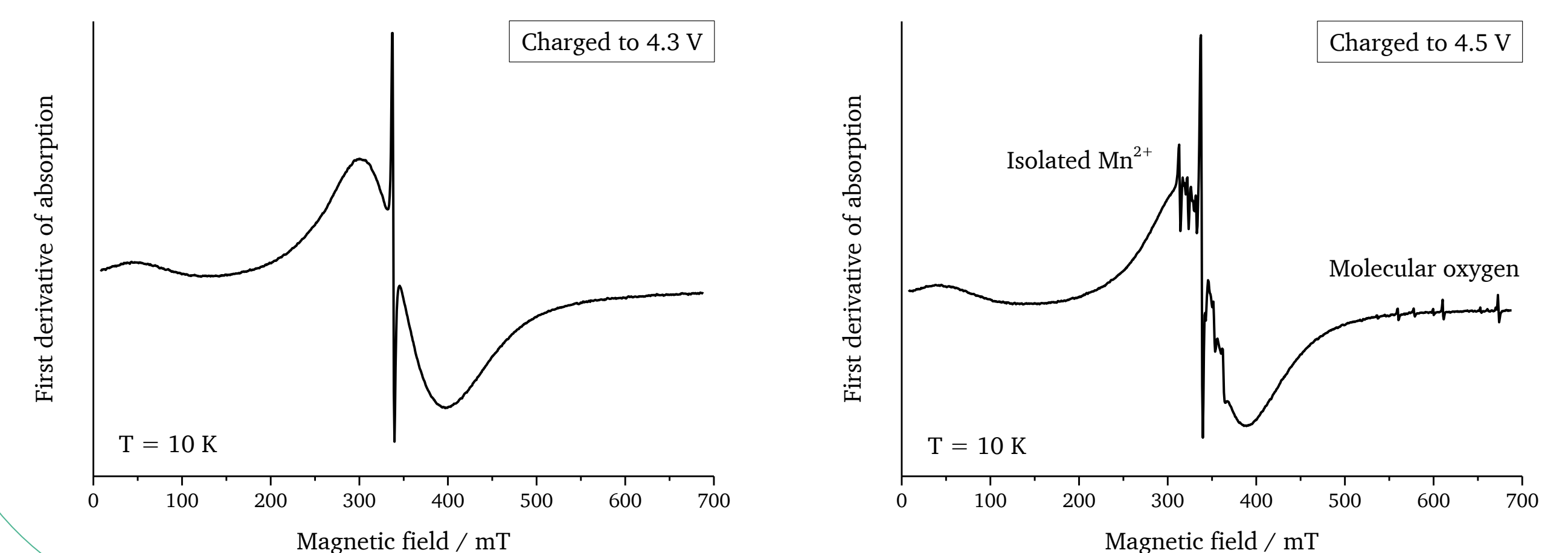
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- [3] M. Gu, I. Belharouak, J. Zheng, H. Wu, J. Xiao, A. Genc, K. Amine, S. Thevuthasan, D. R. Baer, J.-G. Zhang, N. D. Browning, J. Liu, and C. Wang, *ACS nano*, **2013**, 7, 760–767.

### Electron Spin Resonance (ESR) spectroscopy

- ESR spectra show a broad absorption peak attributed to unpaired electron spins in the transition metal ions (Ni, Co, Mn). With continuing aging of the cathode material the electromagnetic absorption increases.
- Free charge carriers on the conductive carbon surface result in a sharp absorption peak at around 340 mT.
- Amount of measured and theoretical available electron spins in the material are in the same order of magnitude, hence the measurement represents bulk information.

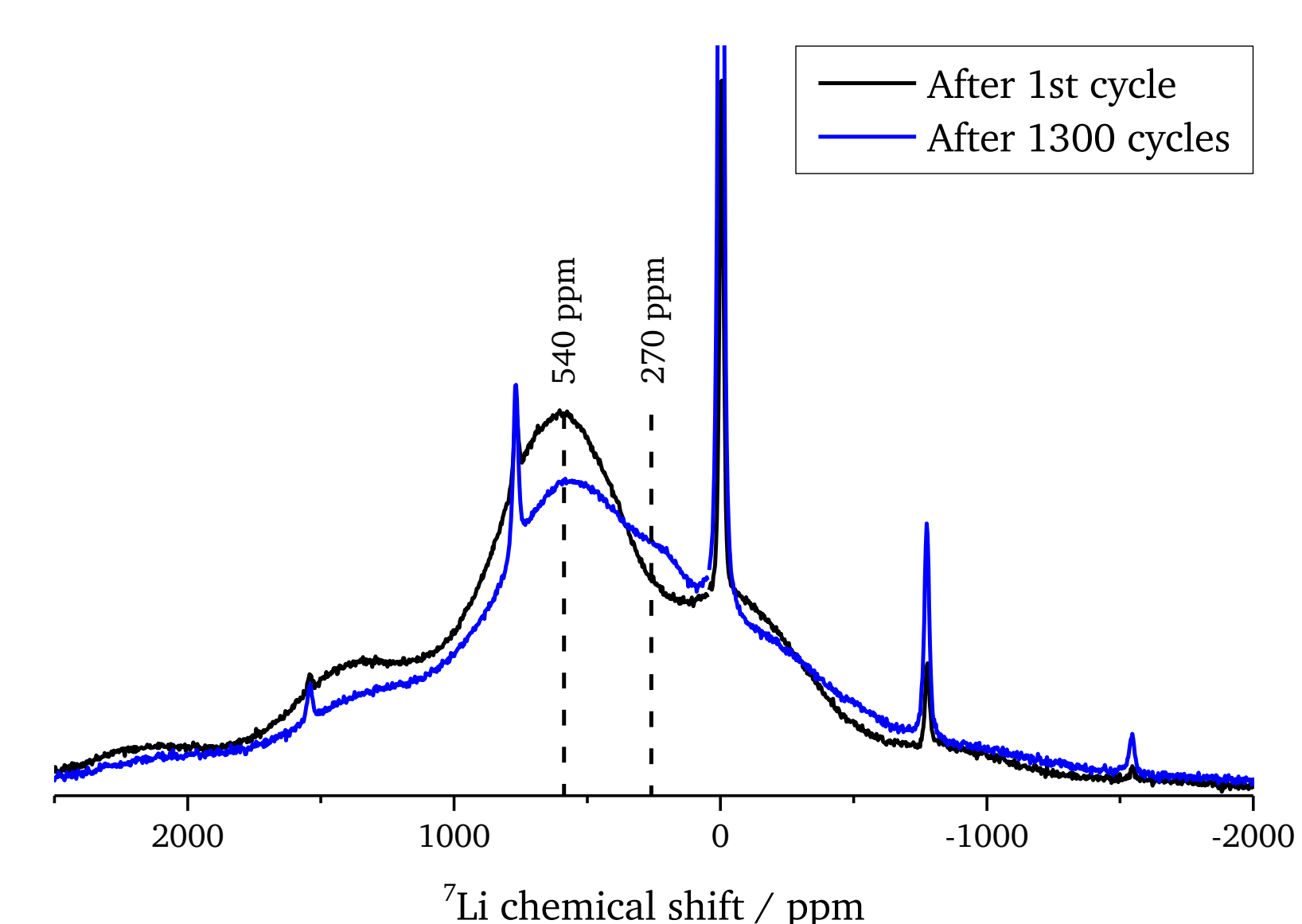


- ESR spectra reveal structural changes of bulk material during the initial 'activation' cycle of the material. Beyond a charging voltage of 4.5 V, absorption peaks of molecular oxygen and  $\text{Mn}^{2+}$  become visible.
- The sharp peaks indicate that  $\text{Mn}^{2+}$  as well as  $\text{O}_2$  have been dissolved from the bulk material into the electrolyte and the gas phase, respectively.



### Nuclear Magnetic Resonance (NMR) spectroscopy

- The Li local environment in samples after the initial activation cycle and 1300 cycles was monitored via  $^7\text{Li}$  Magic Angle Spinning (MAS)-NMR spectroscopy.
- The spectra show the evolution of a kind of modified Li coordination at around 270 ppm after 1300 charge and discharge cycles.



### Conclusion

- It has been shown that structural changes and accompanied electrochemical degradation in Li-rich NCM cathode materials during cycling can be monitored by ESR and NMR spectroscopy. Besides structural information from bulk material, ESR also provides sensitivity for released species like  $\text{O}_2$  and  $\text{Mn}^{2+}$  for instance.
- In our future research we intend to concentrate on *in operando* ESR measurements for a detailed study of structural changes during the initial 'activation' cycle and long-term cycling in order to contribute to a comprehensive model for the fatigue of Li-rich NCM cathode materials. Strategies for improved materials will be derived from such lifetime models and will be transferred into applications.