

Cation Mixing in Li Rich Mn-Ni-Fe Oxide Cathodes and Its Impact on Voltage Fade

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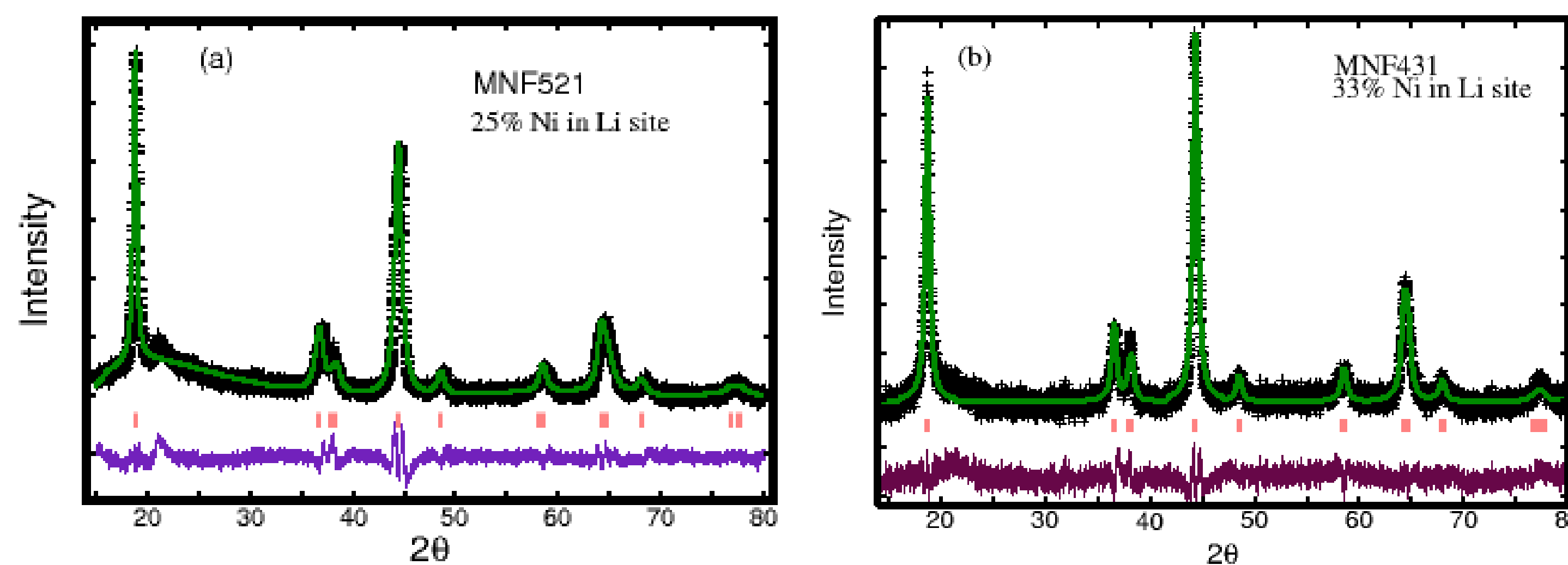


Motivation

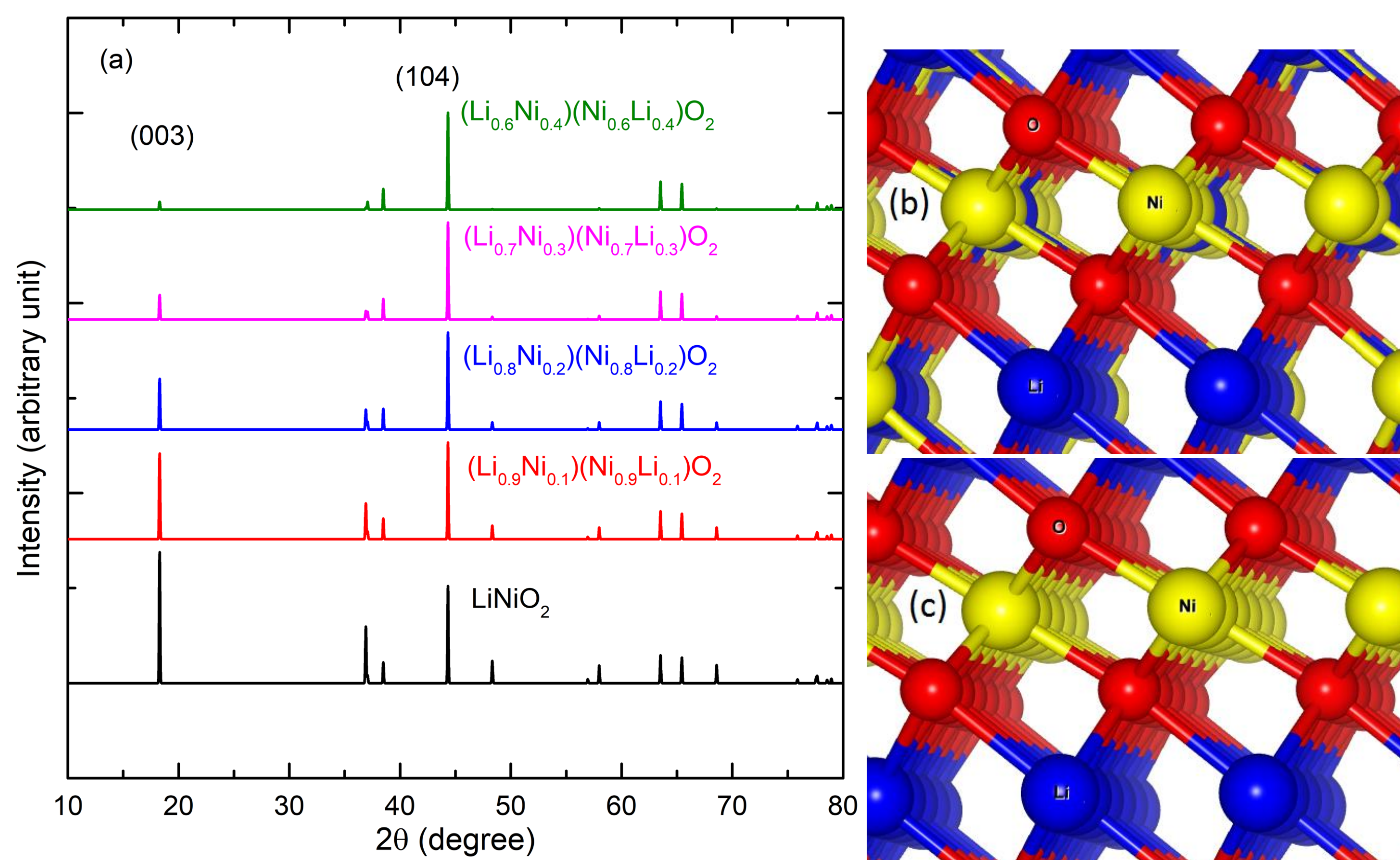
Li-rich oxides $\text{Li}(\text{Li}_{0.2}\text{Mn}_a\text{Ni}_b\text{Fe}_c)\text{O}_2$ ($a+b+c=0.8$) are promising high capacity, high voltage cathodes for Li-ion batteries. Voltage fading (decrease in discharge voltage with cycling) is a known problem for these materials and in this work we investigate correlation between the voltage fade and cation mixing.

The hypothesis is that as the ionic radii of Li^+ ion and Ni^{2+} ion are close, during synthesis some Ni ions occupy the Li sites and vice versa. Ni ions are critical for the formation of reversible layered structure and superior material capacity, however it is suggested that reduction of Ni content in the material will decrease the cation disorder and hence will stabilize the discharge voltage.

X-ray diffraction

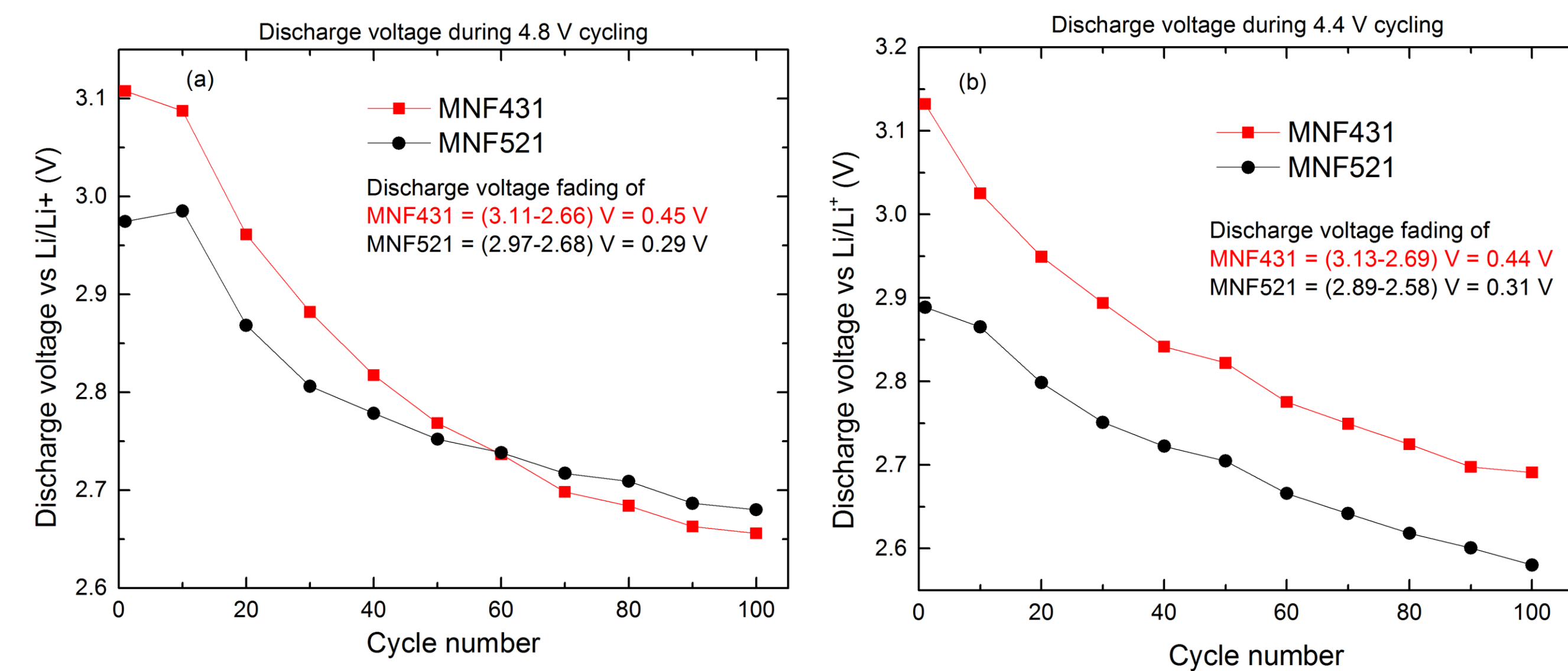


GSAS fitting showed more cation mixing in Ni rich material with 33% of Ni in Li sites in MNF 431 (b) and 25% in MNF521 (a) in agreement with the intensity ratio from modelling the cation disorder in Li layered oxide LiNiO_2 (CrystalMaker software). The ratio of $I(003)/I(104)$ decreases with increasing the cation mixing.



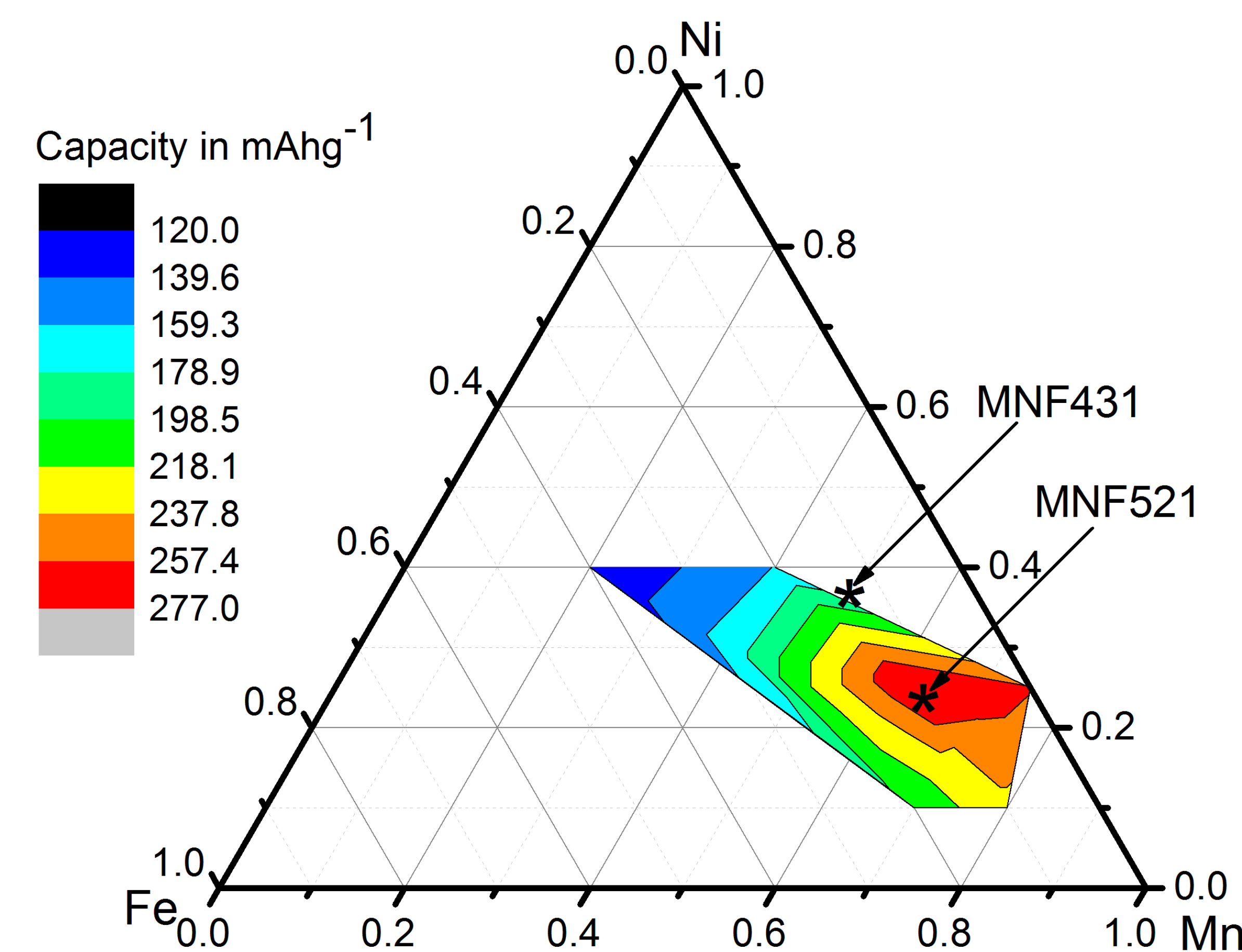
XRD modeling (CrystalMaker software) of Li and Ni mixing (a), structural visualization of cation mixing (b), ideal crystal structural of layered LiNiO_2 (c)

Investigation of voltage fade

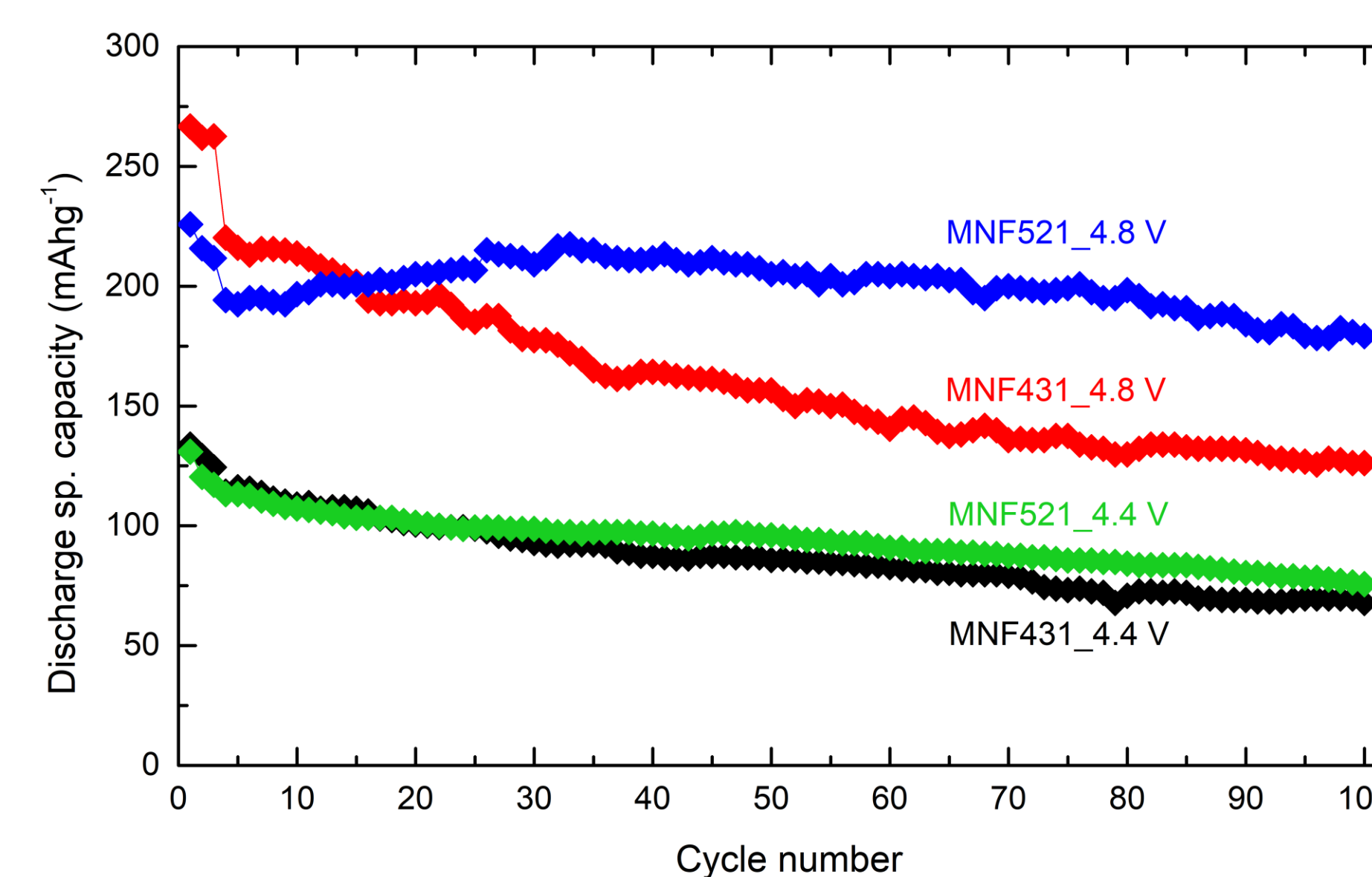


Comparison of equilibrium discharge voltage vs cycle number of MNF521 and MNF431 cathodes at 4.8 V (a) and 4.4 V (b) cut off voltage.

Why $\text{Li}_{1.2}\text{Mn}_{0.5}\text{Ni}_{0.2}\text{Fe}_{0.1}\text{O}_2$ (MNF521) and $\text{Li}_{1.2}\text{Mn}_{0.4}\text{Ni}_{0.3}\text{Fe}_{0.1}\text{O}_2$ (MNF431) cathodes?



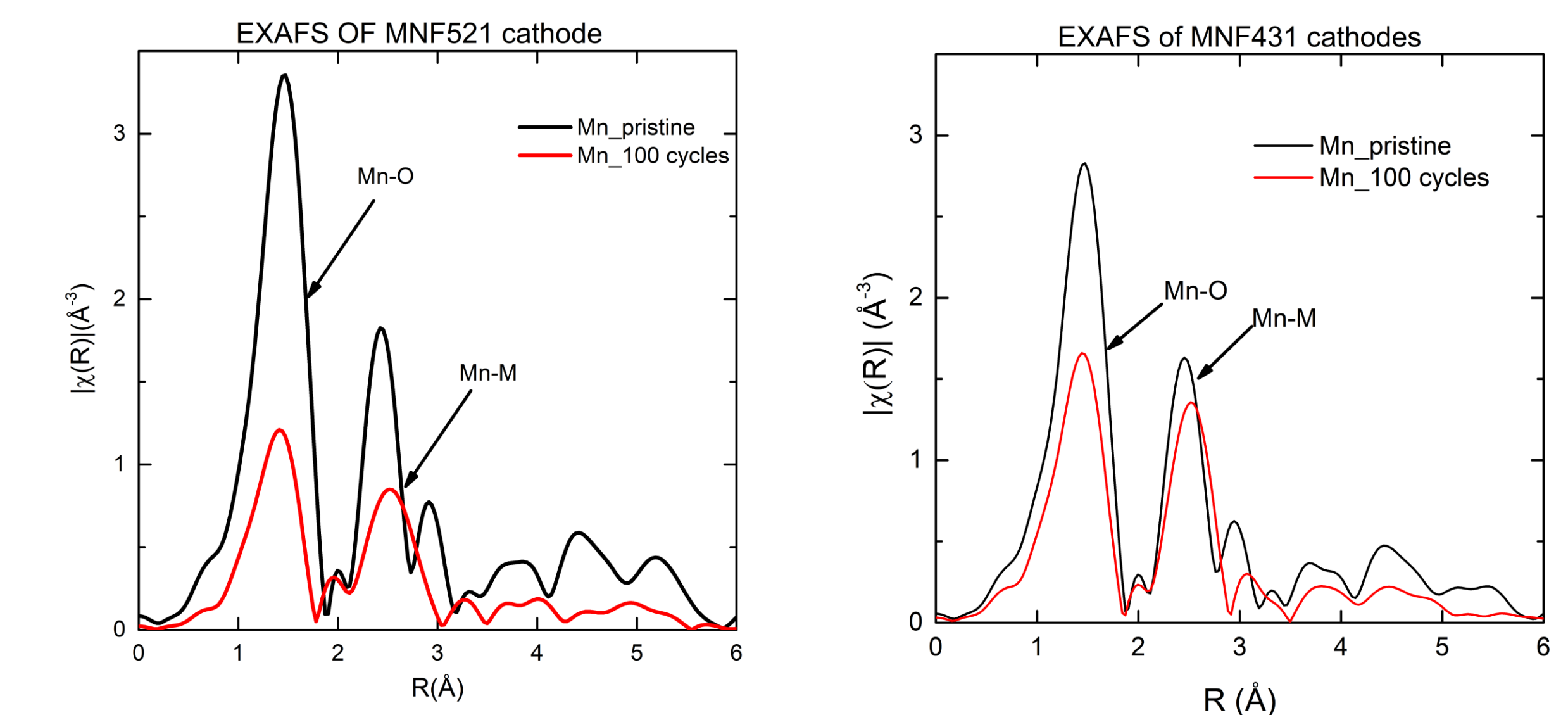
Cyclability results



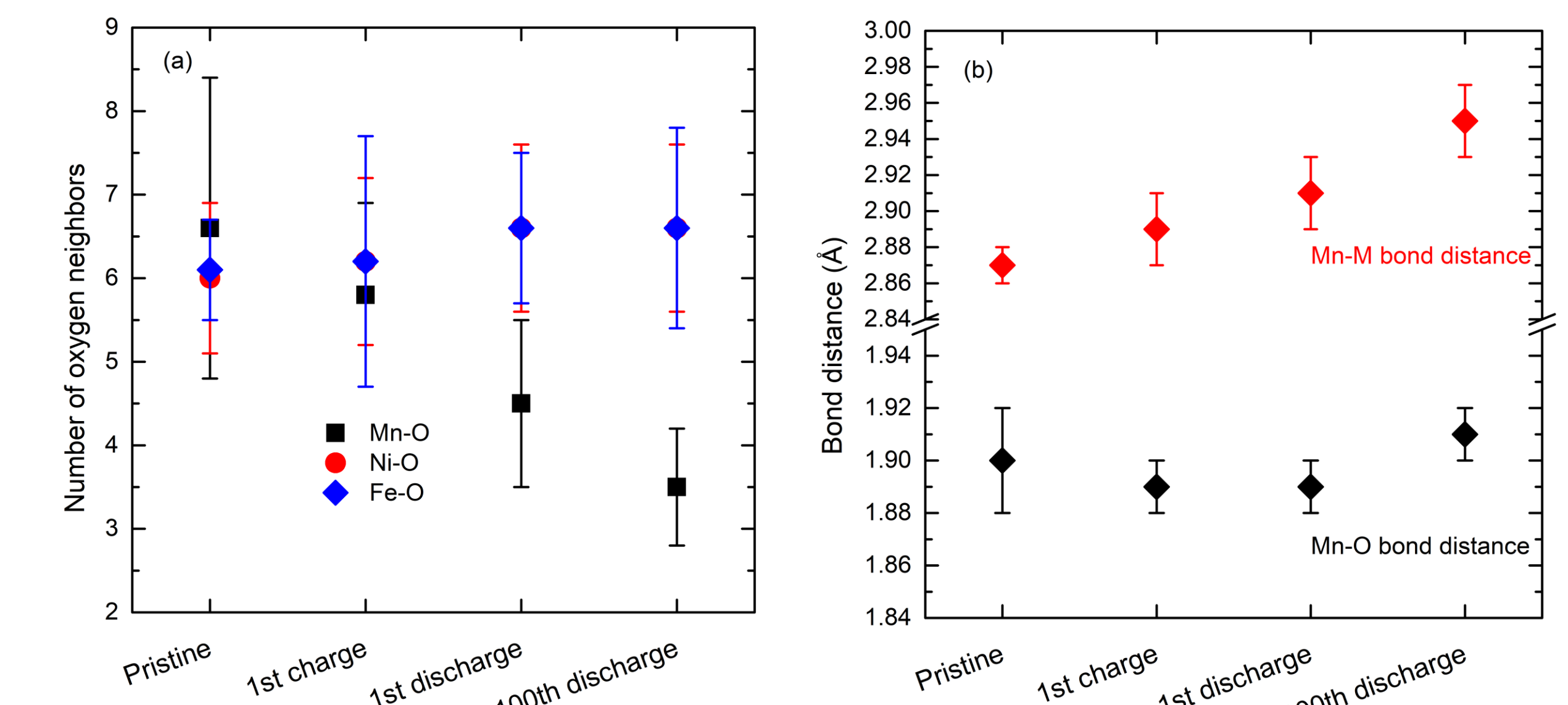
Cycling of MNF521 and MNF431 at different cut off voltages. First 3 cycles at 0.1C and all other cycles at 0.3C, C = 250 mAhg^{-1} .

X-ray absorption spectroscopy study

The noticeable decrease of Mn-O peak in case of both cathodes on cycling is the indication of oxygen loss in the form of $\text{Li}_2\text{O}/\text{Li}_2\text{O}_2$ during Li_2MnO_3 activation. The shift of Mn-M peak towards higher R value indicates the increase of metal-metal distance during cycling. Higher Mn content and hence higher disorder and oxygen loss is observed in MNF521 electrode although Mn-M shift is comparable in both samples per EXAFS fitting.



EXAFS fit results of MNF521



The fitting of Mn K-edge EXAFS spectra of MNF521 cathode showed decrease in oxygen number from 6.6 ± 1.8 to 3.5 ± 0.7 and increase in Mn-M distance from 2.87 ± 0.01 Å to 2.95 ± 0.02 Å after 100 cycles.

Summary

The XRD modeling of LiNiO_2 phase showed the different content of Li and Ni mixing in two compositions as per $I(003)/I(104)$ peak ratio. Higher Ni content in MNF431 compared to MNF521 induces ~10% more of Ni ions mixing in Li sites during crystallization. Detailed electrochemical study revealed that higher degree of cation mixing in MNF431 provides higher discharge voltage compared to MNF521, which also fades more rapidly. Capacity is also more stable in MNF521, even though the first discharge capacity values are higher in MNF431. Mn K-edge EXAFS provided important local structural information.

Acknowledgement

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