In-situ X-ray Absorption Spectroscopic Study of $LiMn_{1.5}Ni_{0.4}Fe_{0.1}O_4$ Spinel Cathode for Rechargeable Li-ion Batteries

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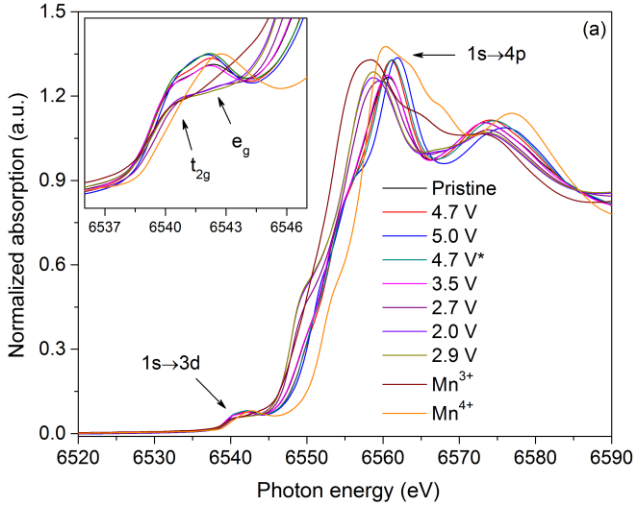
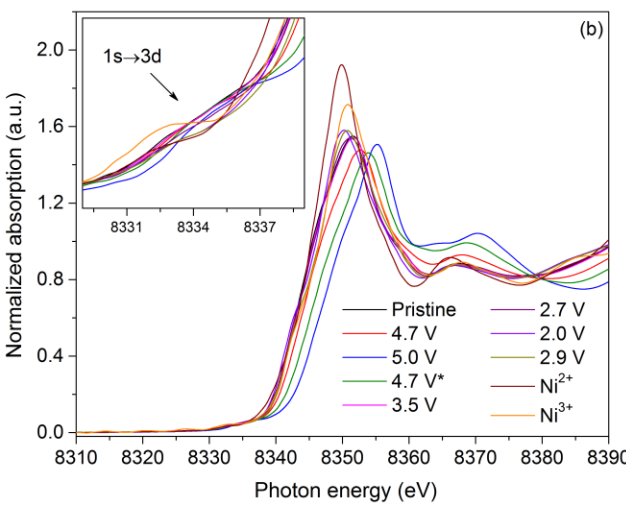
XANES

Mn K-edge



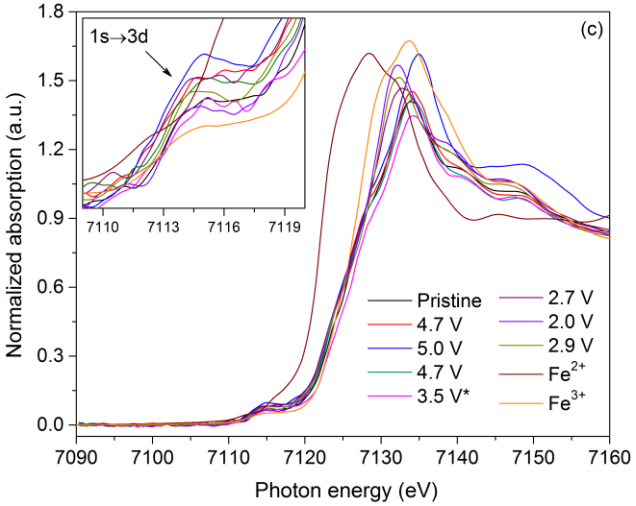
- Shift in 1s→4p peak
- But Mn^{4+} cannot oxidize
- Chemical shifts complex
- Higher intensity of t_g peak suggests high-spin configuration

Ni K-edge



- Between 3.5 V – 5.0 V, Ni^{2+}/Ni^{4+} redox reaction

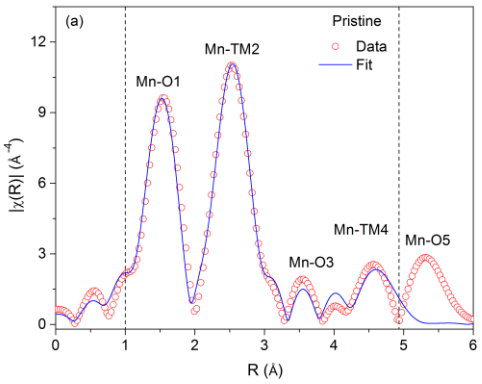
Fe K-edge

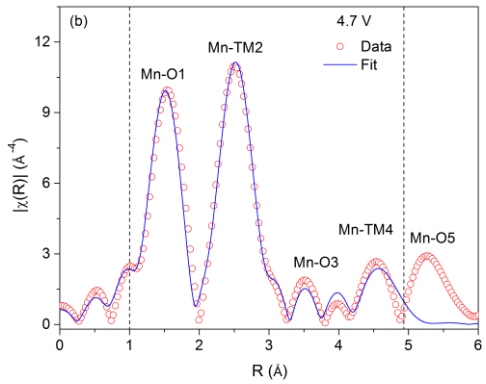


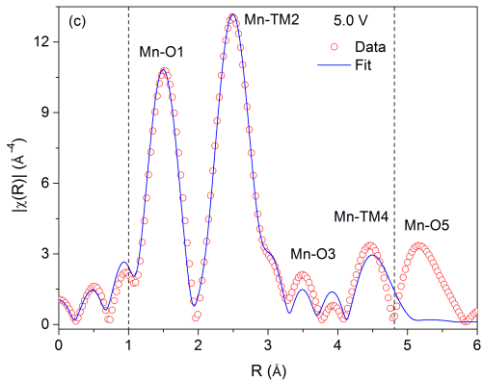
- Between 3.5 V – 5.0 V, Fe^{3+}/Fe^{4+} redox reaction
- Below 3.5 V, Fe^{2+}/Fe^{3+} redox reaction

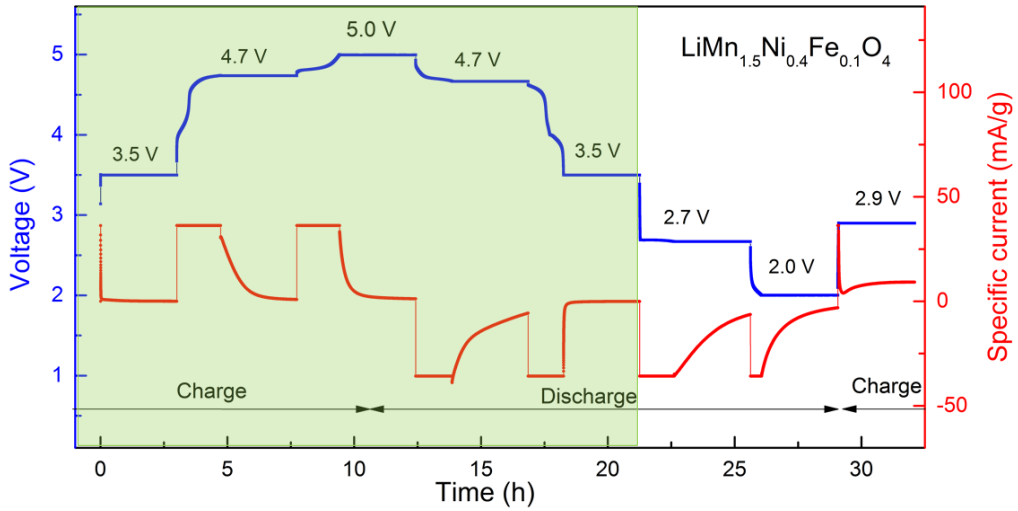
- Chemical shifts : ambiguous, multiple dependencies
- Need other means (i.e. bond lengths) to confirm the valence state of absorbing atoms

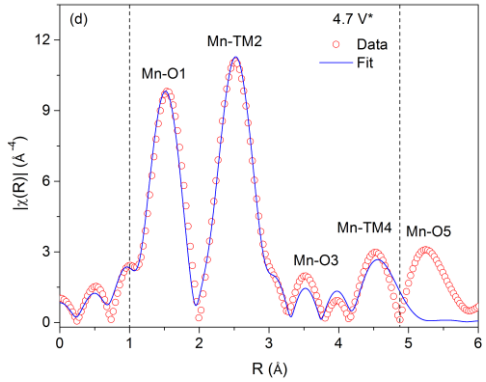
EXAFS fits at the Mn K-edge

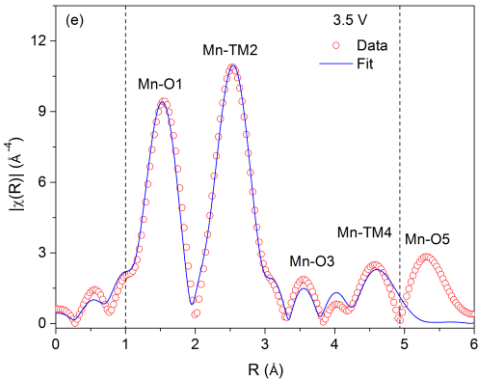






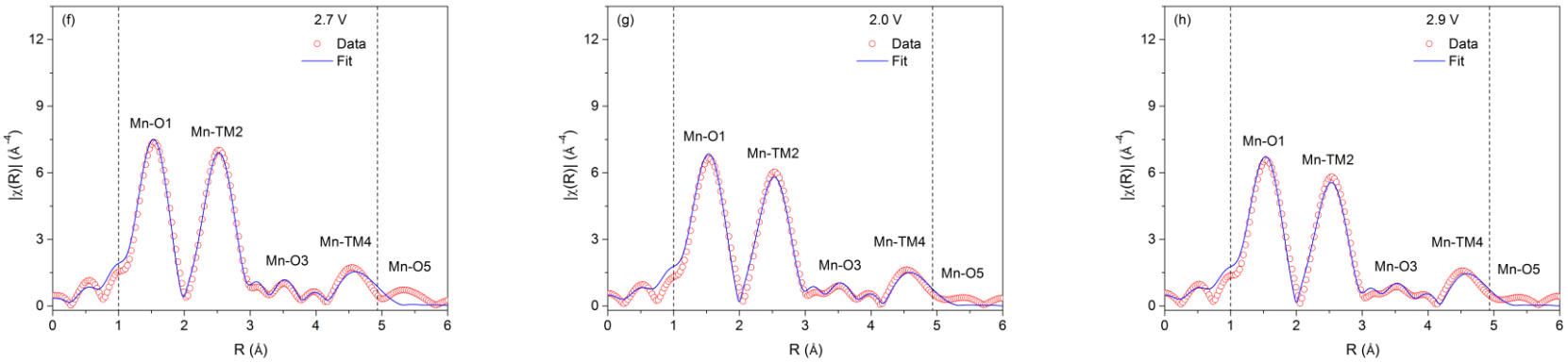


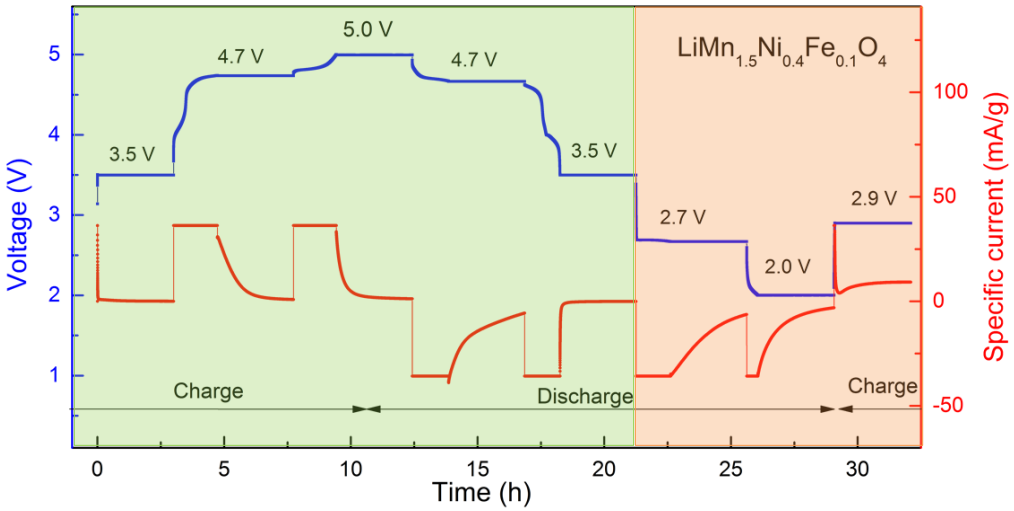




Structural changes are reversible between 3.5 V – 5.0 V

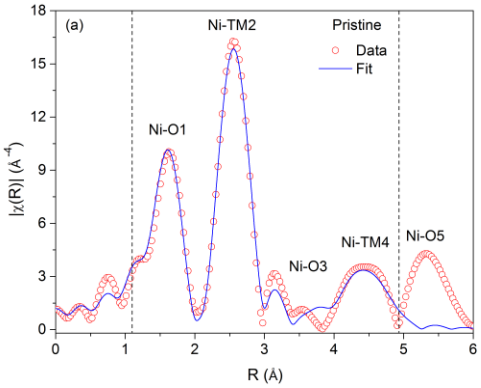
EXAFS fits at the Mn K-edge

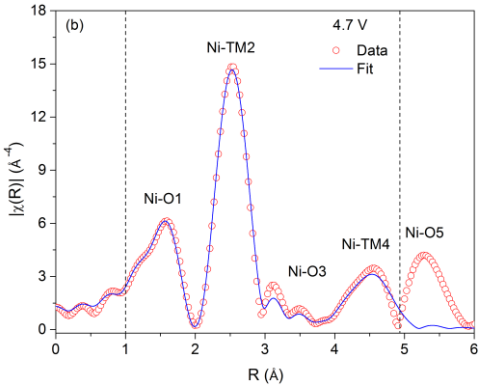


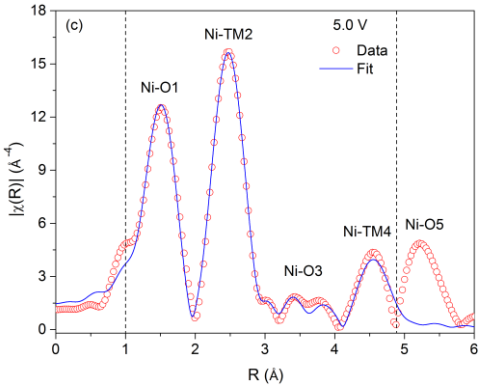


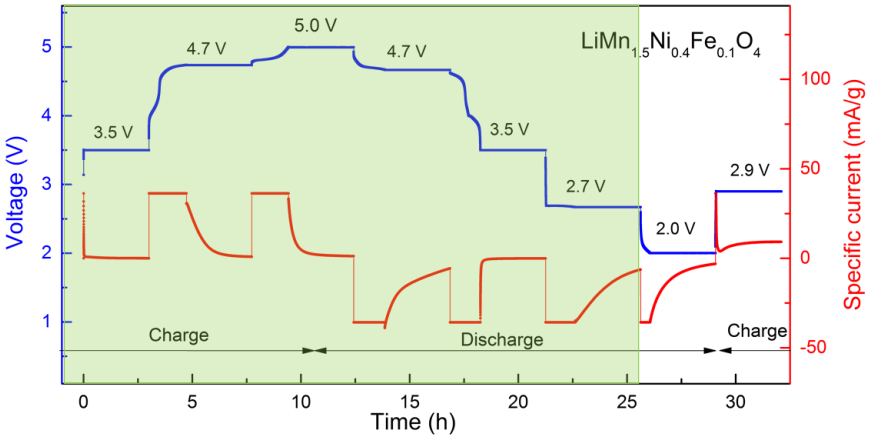
- Deep discharge below 3.5 V gives rise to the formation of tetragonal phase $Li_2M_2O_4$
- Tetragonal phase irreversible upon subsequent charge to 2.9 V

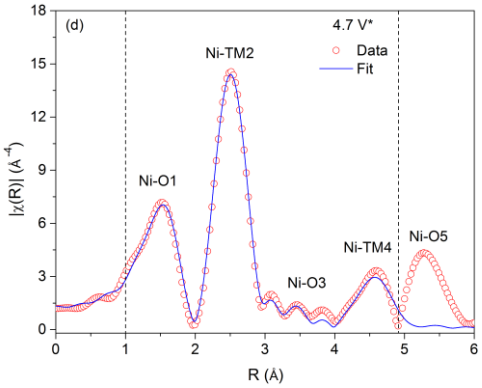
EXAFS fits at the Ni K-edge

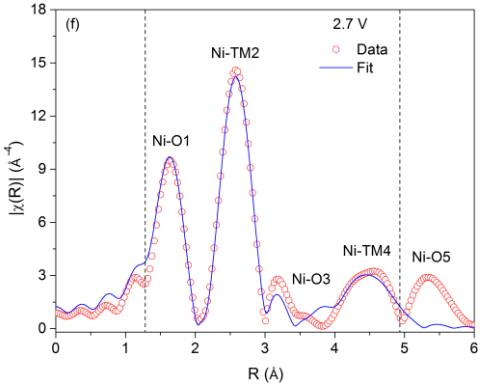


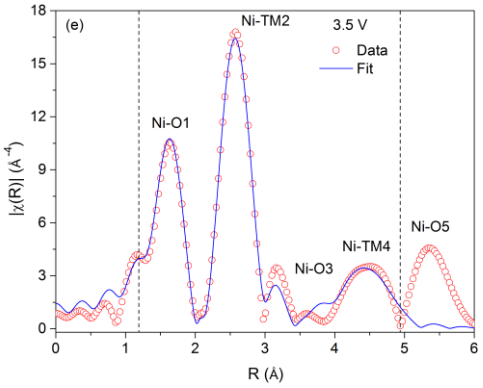








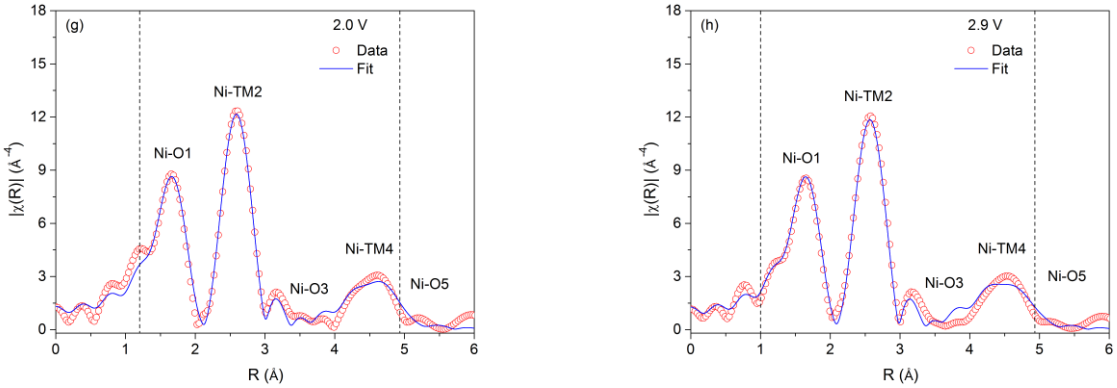


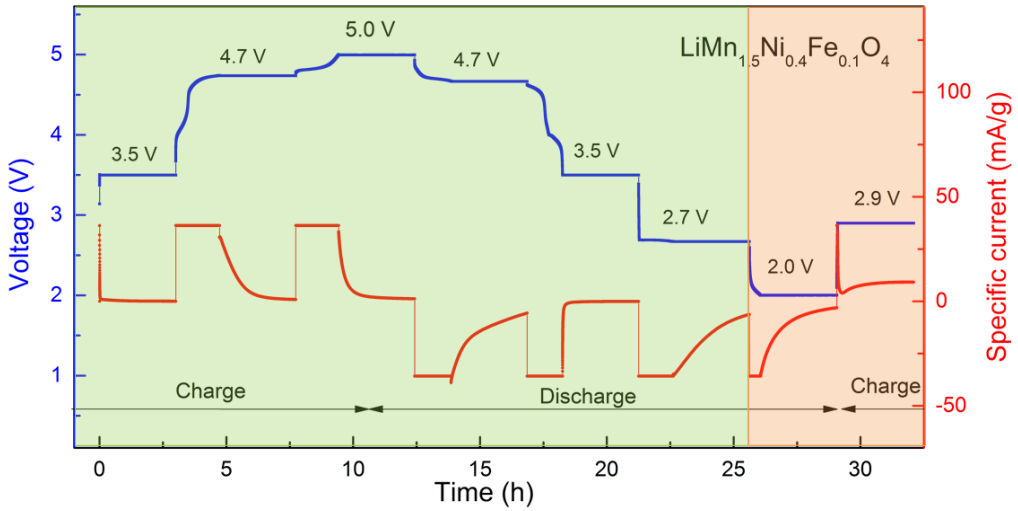


Structural changes are reversible

up to 2.7 V

EXAFS fits at the Ni K-edge

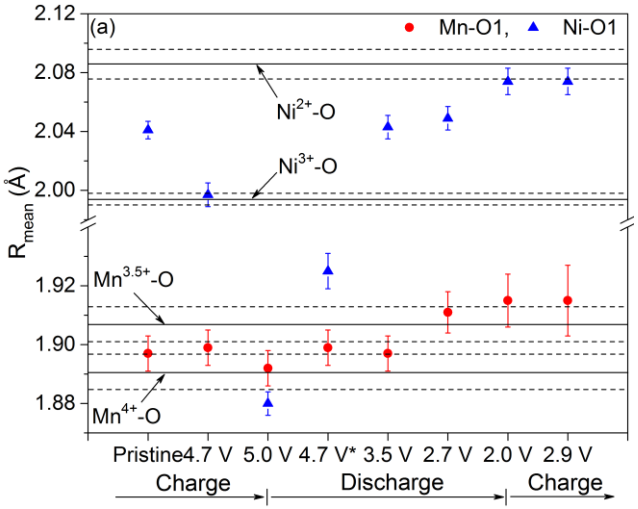




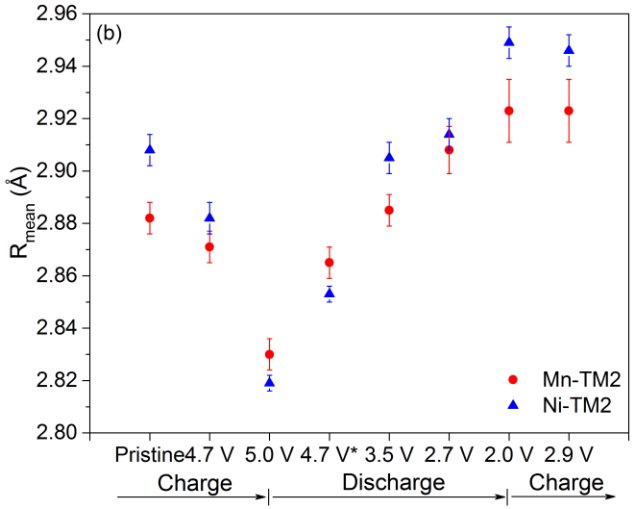
- Tetragonal phase observed at 2.0 V
- Tetragonal transition irreversible upon subsequent charge to 2.9 V

Variation in the bond length

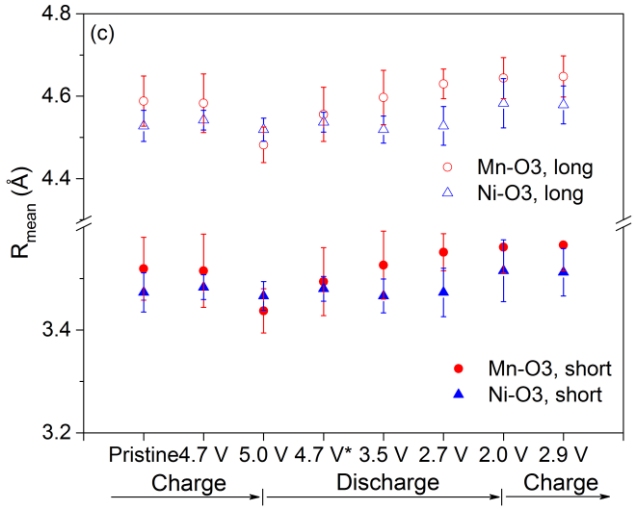
1st shell

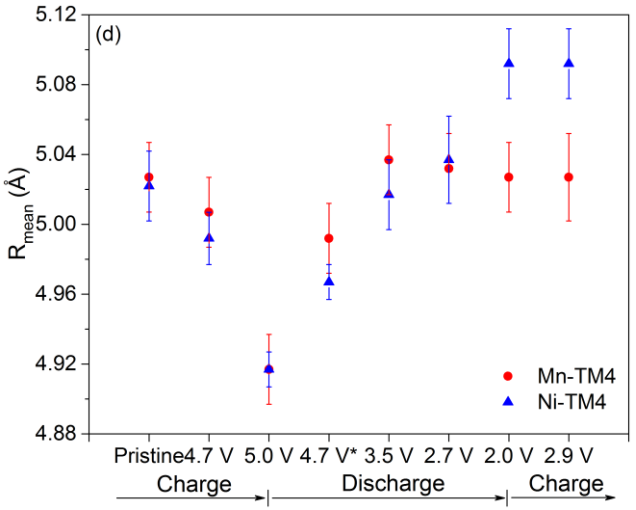


2nd shell



3rd shell



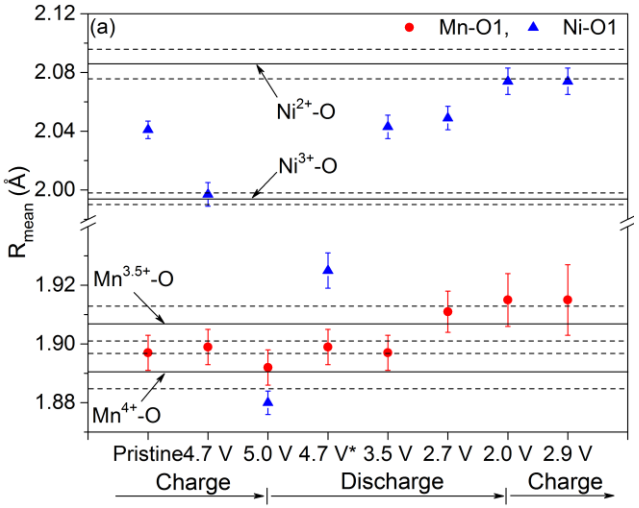


4th shell

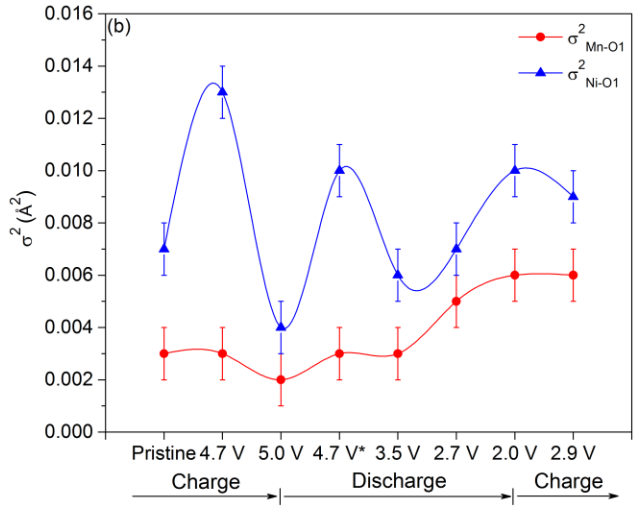
- For all shells, bond length,
  - Decreases during charge : Oxidation of TM ions
  - Increases during discharge : Reduction of TM ions
- Changes in the bond length around Ni atoms are larger than around Mn atoms
- Differences in the bond length disappear for higher shells

Metal-ligand bond length

Variation in the Metal-ligand bond length



Distribution of the Metal-ligand bond length



- Presence of Ni^{2+} and Ni^{3+} in the pristine state
  - Oxidation of $Ni^{2+} \rightarrow Ni^{3+} \rightarrow Ni^{4+}$ during charge
  - Reduction of $Ni^{4+} \rightarrow Ni^{3+} \rightarrow Ni^{2+}$ during discharge
  - Two-step Ni^{2+}/Ni^{4+} redox reaction
- Presence of Mn^{3+} in the pristine state and a small activity from Mn^{3+}/Mn^{4+} redox couple
- Deep discharge below 3.5 V involves the reduction of $Mn^{4+} \rightarrow Mn^{3+}$

Summary

- Electrochemical activity between 3.5 V – 5.0 V attributed to,
  - Two-step Ni^{2+}/Ni^{4+} and Fe^{3+}/Fe^{4+} redox reactions
  - Small contribution from Mn^{3+}/Mn^{4+} redox couple

- Structural changes are reversible between 3.5 V – 5.0 V

- Deep discharge below 3.5 V results in,
  - Irreversible transition to tetragonal phase of type $Li_2M_2O_4$ (~30 %)
  - Involves the reduction of $Mn^{4+} \rightarrow Mn^{3+}$ and that of $Fe^{3+} \rightarrow Fe^{2+}$

- Tetragonal distortion begins around Mn atoms and spreads throughout the material

Acknowledgements

Financial support from Europäischer Fonds für Regionale Entwicklung (EFRE) is greatfully acknowledged under Project BATMAT

Thank you !