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Structural Probing of Charging Mechanism in LiNiO2 at High Voltage using Microscopy and Spectroscopy

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Background

The demand of high-energy lithium-ion batteries boosts the interest in increasing Ni content in cathodes and raising charge cutoff voltage. LiNiO2 is a critical archetypal material for high energy density Li-ion batteries, forming the basis of Ni-rich cathodes in use today. Unfortunately, LiNiO2 suffers from a number of problems at high states of charge which have been linked with oxygen redox. Substantial efforts have been made to understand the structural transitions that take place when Li is extracted from LiNiO2, but there remains considerable debate over its structural mechanisms, in particular the extend of Ni oxidation and oxygen participation when charging at high cutoff voltage. [1,2]

Methods

We use polycrystalline LiNiO2 powder to make composite electrodes into Li coin cells. After charging and discharging to specific states of charge, we disassemble the cell for following characterizations. We use the annular dark-field scanning transmission electron microscopy (ADF-STEM) to directly examine structural changes at the atomic level. We employ combined neutron and synchrotron X-ray powder diffraction analysis that takes account of the stacking faults, and quantified the Ni vacancies formed when the material is charged across the voltage plateau. High resolution resonant inelastic X-ray scattering (RIXS) at the O K-edge is used to detect the molecular O2 that could be formed associated with O-redox. Ni L-edge and O K-edge X-ray absorption spectra are collected to probe the chemical state changing in LiNiO2. Chemical analysis by inductively coupled plasma-optical emission spectroscopy (ICP-OES) is used to check if there is Ni dissolution into the electrolyte after cycling.

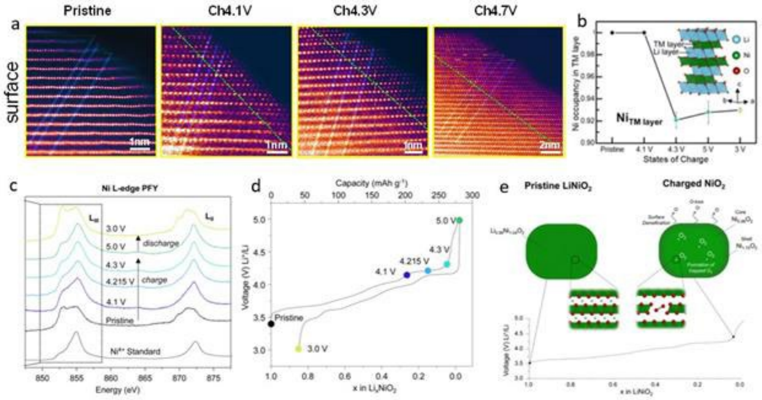
Results

The atomic-resolution showed the surface densification and cation mixing evolution near surface region of LiNiO2 over charging to high cut-off voltage (Fig. 1a). When charging acrossing the 4.2V plateatu vs. Li+/Li, the particles form core–shell nature, with a Ni-rich, Ni1.75O2 rocksalt-like shell approximately of 5 nm thickness at the top of charge. The refinement of neutron and synchrotron X-ray powder diffraction demonstrates 8% Ni vacancies form in the originally fully dense transition metal layer at 4.2 V (Fig. 1b). Chemical analysis by ICP shows that the Ni absent from the bulk does not leave the particles. While in principle there is sufficient Ni3+/4+ oxidation capacity to account for all the Li+ removed on charge without O2- oxidation, high resolution RIXS at the O K-edge confirms the presence of trapped molecular O2, on charging across the plateau, which is accommodated Ni vacancy clusters. Ni L-edge XAS measurements in fluorescence yield mode implies the average oxidation state of Ni of less than +4, coexisting with the presence of O-redox at the top of charge (Fig. 1c,d).

Conclusion

Our results reveal that the structural instability in LiNiO2 is more extensive than previously thought. As illustrated in Fig. 1e, beyond the 4.2 V vs. Li+/Li plateau, Ni accumulates at and near the surface of the particles, forming a Ni-rich shell approximately 5 nm thick; enhanced by loss of O2 from the surface. This shell has composition of Ni1.75O2 shell a Ni oxidation state of +2.3. The oxidation of O2− across the 4.2 V plateau forms O2 trapped in the particles and is accompanied by the formation of 8% Ni vacancies on the transition metal sites of previously fully dense transition metal layers. The overall Ni oxidation state of the particles measured by XAS in fluorescence yield mode after charging across the plateau to 4.3 V vs. Li+/Li is approximately +3.8; however, taking account of the shell thickness and the shell Ni oxidation state of +2.3, this indicates a Ni oxidation state in the core closer to +4 for compositions beyond the plateau.

Graphic:



Keywords:

LiNiO2, charging mechanism, electron microscopy

Reference:

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