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Direct experimental probe of the Ni(II)/Ni(III)/Ni(IV) redox evolution in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes

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ABSTRACT

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel is an appealing cathode material for next generation rechargeable Li-ion batteries due to its high operating voltage of ~ 4.7 V (vs. Li/Li^+). Although it is widely believed that the full range electrochemical cycling involves the redox of Ni(II)/(IV) , it has not been experimentally clarified whether Ni(III) exists as the intermediate state, or a double-electron transfer takes place. Here, combined with theoretical calculations, we show unambiguous spectroscopic evidence of the Ni(III) state when the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode is half charged. This provides a direct verification of single-electron-transfer reactions in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ upon cycling, namely, from Ni(II) to Ni(III) , then to Ni(IV) . Additionally, by virtue of its surface sensitivity, soft x-ray absorption spectroscopy also reveals the electrochemically inactive Ni^{2+} and Mn^{2+} phases on the electrode surface. Our work provides the long-awaited clarification of the single-electron transfer mechanism in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. Furthermore, the experimental results serve as a benchmark for further spectroscopic characterizations of Ni-based battery electrodes.

Introduction

The rapid development of clean sustainable energy technologies over the past decades has stimulated the demand for high-performance electrical energy storage systems such as lithium-ion batteries (LIBs) ¹. Spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is an appealing cathode candidate of LIBs for applications in transportation and stationary storage. It is environmentally benign, low-cost, and provides high performance in terms of the energy and power densities ²⁻⁵. The high energy density of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ stems from the high operating voltage of 4.7V, which is defined by the $\text{Ni}^{2+/4+}$ redox reaction. The electron transfer process associated with this redox reaction is of critical importance for understanding its electrochemical properties. However, it remains elusive whether the $\text{Ni}^{2+/4+}$ reaction is a double or single electron transfer process. Although some electrochemical measurements suggest the formation of the intermediate Ni^{3+} state⁶⁻⁷, direct experimental evidence is missing.

Practically, the commercialization of high-voltage $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes encounters several technical challenges⁸⁻¹², especially electrolyte degradation at high voltage and transition-metal dissolution. The detailed mechanism of these technical issues has not been fully clarified, but it is believed that the surface activity of the electrode material plays a key role in such detrimental effects. Clarifying the surface reaction is non-trivial, and a multimodal approach is necessary. While the surface characteristics of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes could be studied by transmission electron microscopy (TEM) and x-ray photoelectron spectroscopy (XPS) ^{7, 13}, experimental approaches based on these techniques are still under scrutiny to understand degradation mechanisms associated with the electrode surface and/or interface .

In this work, we have performed high-resolution soft x-ray absorption spectroscopy (sXAS) to study a series of high-quality $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different electrochemical voltages. sXAS spectra are sensitive to the unoccupied electronic states in the vicinity of the Fermi energy E_F . They provide a powerful tool to study the oxidation states, chemical bonds, spin properties and orbital characteristics of the transition-metals involved in battery electrodes ¹⁴⁻¹⁵. Moreover, sXAS is a unique tool that can provide information about both the surface (probe depth of about 10 nm) and the bulk (probe depth of about 100 nm) through the total electron yield (TEY) and total fluorescence yield (TFY), respectively. Our high-resolution sXAS data show clear

transitions between $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ redox couples at half-charge, thus providing direct experimental evidence for the single-electron-transfer mechanism in $\text{Li}_x\text{Ni}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes. In addition, the data reveal that Ni^{2+} and Mn^{2+} phases are formed on the surfaces of the electrodes. The spectral evolution indicates that these di-valent transition-metal phases are electrochemically inactive.

Experimental Section

1. Material synthesis, structural and electrochemical characterization

$\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ was synthesized via solid-state reaction. Stoichiometric amounts of Li_2CO_3 , NiCO_3 , MnCO_3 were mixed using a ball-mill (SPEX 8000D) for 30 min. The mixed precursors were repeatedly ground, pelletized, and heated at the following different temperatures and times in air: 500°C for 12 h, 650°C for 12 h, 900°C for 6 h, and then 700°C for 2 h. Powder X-ray diffraction (XRD) measurements were carried out with a D8 diffractometer (Bruker) using $\text{Cu-K}\alpha 1$ radiation in Bragg-Brentano configuration. Scanning electron microscopy (SEM) images were obtained using Zeiss NVision.

The cathode consisted of 80:10:10 wt% of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel, super-P carbon, and polyvinylidene fluoride (PVDF, Kynar HSV900). Lithium foil was used as the anode (half cell). The cathode formulation was mixed with N-methylpyrrolidone (NMP) and coated onto Al foil via the doctor-blade method. A separator (Celgard, PP/PE/PP tri-layer), and 1 M LiPF_6 in ethylene carbonate (EC) / ethyl methyl carbonate (EMC) (1/1 vol. ratio) electrolyte were used for preparing coin cells (Hohsen, Al-cladding 2032 model). All coin cells were cycled using a Maccor 4000 battery testing system.

For sXAS experiments, $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes were electrochemically cycled in the argon glove box. Afterwards, the cells were disassembled and the cathodes were rinsed with DMC thoroughly to remove any electrolyte and salt residue, and to lock the state-of-charge of the cycled electrodes. The cathode samples were then loaded into the ultra-high vacuum sXAS characterization chamber through a sample transfer kit to avoid any air exposure.¹⁶

2. Soft x-ray absorption spectroscopy (sXAS) experiments and calculations

sXAS was performed at Beamline 8.0.1 of the Advanced Light Source (ALS) in Lawrence Berkeley National Lab (LBNL). The undulator and spherical grating monochromator supply a linearly polarized photon beam with resolving power up to 6000. The experimental energy resolution is about 0.15 eV. Experiments were performed at room temperature and with the linear polarization of the incident beam oriented at 45° to the sample surfaces. The sXAS spectra were collected using both total electron yield (TEY), with a probing depth around 10 nm, and total fluorescence yield (TFY) with a probing depth larger than 100 nm. All the spectra have been normalized to the beam flux measured by the upstream gold mesh.

Calculations were performed for a single impurity Anderson model (SIAM), coupling Ni with a 3 eV wide ligand band that can contain up to one hole. Implementation details for the model are discussed in Ref.¹⁷. Slater-Condon parameters were renormalized to 80%, 75% and 70% of Hartree-Fock values for nominal Ni²⁺, Ni³⁺ and Ni⁴⁺ calculations, respectively, and the simulation was thermally populated to 300K. The crystal field was set to 10Dq= 0.5, 2.0, and 2.5, in ascending order for higher valence, and metal-ligand hopping was assigned a similar trend with $V_{eg}=2, 2.5$ and 3 eV. The t_{2g} symmetry hopping parameter was assigned half the amplitude of e_g hopping ($V_{t2g}=-V_{eg}/2$). Configuration energies for states with a ligand hole were set to $E(d^{n+1})-E(d^n)=3.5, 0.5$, and -2 eV. Core hole configuration energies were set to $E(d^{n+1})-E(d^n)=3.1, -0.9$, and -4.4. These parameters result in a high spin state for Ni²⁺, and low spin states for Ni³⁺ and Ni⁴⁺, and are similar to parameter sets considered in Ref. ¹⁷⁻¹⁸.

Results and Discussion

Figure 1. (a) XRD pattern of LiNi_{0.5}Mn_{1.5}O₄ powder. Extra peaks marked with black dots belong to minor rock-salt (e.g., Li_{1-x}Ni_xO) secondary phases. (b) SEM image of LiNi_{0.5}Mn_{1.5}O₄ powder. (c) Voltage profiles of LiNi_{0.5}Mn_{1.5}O₄ cathode recorded during an initial charge/discharge cycling. The sXAS experiments were performed ex-situ at different states (marked with orange dots): pristine electrode (P), 50 % charge state (1/2Ch), 100 % charge state (1Ch), 50 % discharge state (1/2D), and 100 % discharge state (1D). (d) Capacity retention of LiNi_{0.5}Mn_{1.5}O₄/Li battery cell cycled with a C/10-rate at 30°C.

The LiNi_{0.5}Mn_{1.5}O₄ spinel powders used in this study have the typical structural and electrochemical characteristics of standard LNMO spectra reported in literature¹⁹. Figure 1(a) shows the XRD pattern of LiNi_{0.5}Mn_{1.5}O₄ powder sample which can be indexed based on cubic symmetry with a space group of *Fd-3m*. Minor amounts of secondary phases (~ 4.7 wt %), which

belong to rock-salt structures (e.g., $\text{Li}_{1-x}\text{Ni}_x\text{O}$), also exist in the powder sample²⁰. Formation of such rock-salt structures is inevitable during the high temperature (e.g., $> 800^\circ\text{C}$) synthesis process of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ because they are thermodynamically stable at temperatures higher than 700°C ²¹⁻²². However, these rock-salt phases have been known to be electrochemically inactive in Li-ion battery cells²³. In Figure 1(b), the SEM image shows that $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ sample consists of polyhedral particles with approximately 2 – 5 μm diameters.

The cathode prepared by using $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel powder displays voltage profiles of typical $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ battery cells¹⁹. Figure 1(c) shows that the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathode delivers the majority of its capacity through two distinct voltage plateaus at around 4.7 V, which are attributed to $\text{Ni}^{2+/4+}$ redox. A small shoulder appears around the 4.1 V region and is associated with $\text{Mn}^{3+/4+}$ redox. The formation of Ni-rich rock-salt phases and oxygen deficiencies are responsible for the presence of Mn^{3+} in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ ²⁰. In order to study the major electron transfer process associated with $\text{Ni}^{2+/4+}$ redox, comprehensive sXAS experiments were performed at different states (marked with orange dots). The results will be elaborated later. As shown in Fig. 1(d), the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4/\text{Li}$ cell exhibits initial discharge capacity of $\sim 130 \text{ mAh/g}$, and maintained a good capacity retention: $\sim 93\%$ at the 100th cycle (approximately after ~ 3 month testing period) by applying a constant current corresponding to $\sim \text{C}/10$ -rate.

Figure 2. Ni L_3 - (a) and L_2 -edge (b) TFY sXAS spectra. The experimental spectra were collected on a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes that were electrochemically cycled to different states as shown in figure 1(c). The calculated spectra of Ni^{2+} , Ni^{3+} and Ni^{4+} were done in an octahedral crystal field.

Soft x-ray absorption spectroscopy studies were carried out on a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes that were electrochemically cycled to different states of charge (SOC) as illustrated in figure 1(c). The evolution of the unoccupied valence electron states in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, namely, Ni, Mn $3d$ and O $2p$ states, can be directly probed by sXAS spectra through dipole allowed transition metal (TM) $2p$ - $3d$ and oxygen $1s$ - $2p$ transitions. Therefore, the Ni, Mn L - and O K -edge sXAS spectra provide abundant information on the electronic states of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$, and have specific sensitivity to chemical valences of the TM ions, spin and orbital properties, as well as charge transfer between TM ions and ligands. These factors fundamentally regulate the electrochemical properties of the material^{14, 16, 24-25}.

As shown in figure 2, the reversible evolution of the Ni electronic state in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes during electrochemical cycling is captured by the Ni L -edge TFY (bulk-sensitive) sXAS spectra. The TM L -edge sXAS spectra can be divided into two regions, the L_3 -edge at lower photon energy and the L_2 -edge at higher energy, due to $2p$ core hole spin-orbital splitting. Both the Ni L_3 - and the L_2 -edge sXAS clearly show that the spectral weight shifts towards higher energy during charge and goes back during discharge, which are indicative of increased (decreased) Ni oxidation states during delithiation (lithiation) processes²⁶. Moreover, the spectral profile especially on the L_3 -edge changes dramatically. In general, the L_2 -edge displays much broader absorption features than the L_3 -edge due to shorter lifetime of the $2p_{1/2}$ core hole as a consequence of Coster-Kronig Auger decay²⁷⁻²⁸. Therefore, below we will mainly focus on the analysis of the L_3 -edge absorption profile.

By virtue of the high-resolution bulk-sensitive TFY measurements, Ni absorption features in the electrodes at 50% SOC (1/2Ch and 1/2D) are well distinguished from those at 0% (P and 1D) and 100% SOC (1Ch). Note that the electrodes at 50% SOC have their predominant absorption features (b and c) located at different photon energies from these in 0% (peak a) and 100% SOC (peak d) ones. As a result, the experimental spectra of the 50% SOC electrode samples cannot be reproduced by the combination of the 0% and 100% SOC spectra. This provides direct evidence for the formation of a stable Ni intermediate state in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ at 50% SOC. To gain further insight on the evolution of the Ni electronic states, calculations were performed on Ni^{2+} , Ni^{3+} and Ni^{4+} in an octahedral crystal field based on a single impurity Anderson model, which improves correspondence relative to a more localized NiO_6 cluster. The calculations, which use similar parameter sets to those considered in reference¹⁷⁻¹⁸ result in a high spin state for Ni^{2+} , and low spin states for Ni^{3+} and Ni^{4+} . The resolved experimental sXAS features on electrodes of 0%, 50% and 100% SOC can be clearly assigned to Ni^{2+} , Ni^{3+} and Ni^{4+} ¹⁸, respectively. Therefore, the Ni L -edge sXAS spectra show unambiguously that Ni^{3+} is the stable intermediate state formed in the electrochemical reaction of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode. In other words, the electrochemical cycling of the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode consists of two single electron transfer processes, which involves two redox couples, $\text{Ni}^{2+}/\text{Ni}^{3+}$ and $\text{Ni}^{3+}/\text{Ni}^{4+}$ that take place at very close potential²⁹. Furthermore, the calculation shows a delocalization of significant hole density ($>\sim 0.5 e^+/\text{Ni}$) into nearby oxygen orbitals surrounding Ni^{3+} and Ni^{4+} , suggesting the existence of itinerant bands with mixed oxygen/nickel orbital symmetry. These simulated Ni^{3+} (d^7) and Ni^{4+} (d^6) states are

stable as a hole does not propagate away from nickel into the ligand bands, and the electron density borrowed from the ligands resides in the mostly vacant e_g orbitals. For example, having a roughly 60% hole density on the oxygens surrounding Ni^{4+} would mean that about 15% of an electron is hybridized into each of the otherwise vacant nickel e_g orbitals. Other than some finer details of core hole shake-up, this scenario may be well described on the great majority of Ni sites by treating e_g states as expanded molecular orbitals. The itinerant property of the electrons in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is associated with the good electronic conductivity of the electrode material.

We would like to point out that although some sXAS results of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ have been published previously, typically a broad hump was observed in partially charged $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ samples. The overall lineshape is consistent with the results here, however, Ni^{3+} cannot be clearly distinguished from Ni^{2+} and Ni^{4+} in these previous works^{6, 30}. The bulk-sensitive TFY measurements, combined with the spectra simulation and the high-quality electrode samples, enable us to clearly distinguish the Ni^{3+} phase and to clarify the Ni evolution. Moreover, the surface-sensitive TEY spectra reveal the phases on the surface, in comparison with the bulk phases probed by the TFY mode.

Figure 3. Surface-sensitive Ni L_{3-} (a) and L_{2-} edge (b) TEY sXAS spectra (solid lines) are compared with the bulk-sensitive TFY spectra (dash lines) that were also shown in figure 2.

Figure 3 compares the Ni L -edge TEY spectra (solid lines) with the TFY (dash lines) that have been discussed above. Compared with TFY, TEY is much more surface-sensitive due to the short escape depth of electrons. The probing depth of TEY is around 10 nm. In general, the TEY spectra of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ also evolve following the reversible electrochemical cycling in the same way TFY does. The same absorption features b and c are observed in the electrodes at 50% SOC (1/2Ch and 1/2D) and d at 100% SOC (1Ch), respectively, indicating the electrode surface goes through the same electrochemical reactions as the bulk, i.e., Ni^{2+} - Ni^{3+} - Ni^{4+} . However, unlike TFY, the absorption feature a shows the highest intensity among all TEY spectra that were collected at the different SOC, revealing that a significant amount of nickel on the electrode surface stays at Ni^{2+} in spite of the electrochemical status of the bulk electrode. In contrast, the TFY spectra of the 50% and 100% SOC electrodes contain only minor contributions of Ni^{2+} signal (peak a), which is mainly from the electrode surface (Fig. 3).

The observation of strong TEY signals of Ni^{2+} in all the samples with different SOC indicates the existence of a Ni^{2+} surface layer that is electrochemically inactive. Recently, surface rearrangement with inactive Ni^{2+} phase has been reported³¹⁻³². Moreover, reactions between the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes and electrolytes lead to the deposition of a decomposition product of the electrolyte and the reduction of transition metals in the active materials³⁰. Additionally, transition metal dissolution phenomena from the surfaces of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes result in the production of metal fluorides (e.g., NiF_2 , MnF_2 , and LiF) and $\text{Ni}^{2+}/\text{Mn}^{2+/3+}$ β -diketonate coordination complexes⁷, which will be responsible for the Ni^{2+} signal from the TEY spectra. Although it has been generally believed that these surface species cannot perfectly passivate the CEI, we recently demonstrated that there is a limited role from the surface species on cycled $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ cathodes to serve as a passivation layer^{13, 33}. However, it should be remembered that the stability and effectiveness of such surface species as a passivation layer is not satisfactory and is still questionable based on the continuous electrolyte degradation occurring in $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ /graphite full cells³³.

Figure 4. Mn *L*-edge sXAS spectra (TEY) of a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different SOC levels.

Similar to Ni, the Mn *L*-edge sXAS spectra are very sensitive to the Mn oxidation states. Manganese compounds with different Mn valences display dramatically different absorption profiles¹⁶. As shown in figure 3, the Mn *L*-edge sXAS spectra (TEY) collected on a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different SOC levels exhibit nearly the same shape. The spectra consist of Mn L_3 -edge (639 eV – 647 eV) and L_2 -edge (650 eV – 657 eV) absorption features. The peak positions and the overall lineshape resemble the Mn^{4+} system in a cubic ligand field^{16, 30}. The nearly unchanged Mn-*L* sXAS spectra confirm that Mn^{4+} is electrochemically inactive in the $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrode. Note the faint growth of leading edge absorption intensity around 640 eV, especially in sample 1D, which stems from the formation of manganese compounds with $\text{Mn}^{2+}/\text{Mn}^{3+}$ on the electrode surface. This is again related to the Mn^{2+} dissolution issue at the surface of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes, as discussed above⁹.

Figure 5. O *K*-edge sXAS spectra of a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different SOC. (a) and (c), bulk-sensitive TFY, (b) and (d) surface-sensitive TEY.

Figure 5 shows the O *K*-edge sXAS spectra collected on a series of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes at different SOC. The O *K*-edge sXAS spectra originate from an oxygen $1s$ - $2p$ dipole transition. The features of the spectra (Fig. 5a and 5b) are roughly divided into two regions, i.e., the pre-edge region (529 – 536 eV) with sharp peaks, which originate from the hybridization states between O- $2p$ and localized TM- $3d$ orbitals, and the broad peak region (above 536 eV), which is related to the itinerant O- $2p$ and TM- $4s,p$ hybridization³⁴. Both regions evolve systematically with the SOC of the electrodes. The pre-edge absorption region in O *K*-edge sXAS, which reflects the transition metal Ni and Mn $3d$ states, is focused in figure 5 (c) and (d). The $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ electrodes with 0% SOC (P and 1D) display two peaks related to Ni^{2+} ($3d^8$) and Mn^{4+} ($3d^3$). When the electrodes are charged and electrons are removed from the system through the delithiation process. Compared with the pristine Ni^{2+} ($3d^8$) state, the newly emptied Ni $3d$ states of the Ni^{3+} ($3d^7$) and Ni^{4+} ($3d^6$) (Fig. 2) manifest themselves in the O-*K* spectra through the hybridization feature at the lower energy at 530eV (Fig. 5c). The contrast between the O-*K* surface-sensitive TEY signal (Fig. 5b, d) and bulk-sensitive TFY signal (Fig. 5a, c) resembles

that of the Ni-*L* edges (Fig. 3). The spectral evolution of the TEY (Fig. 5d) data is much weaker than that of the TFY (Fig. 5c), which is consistent with the aforementioned electrochemically inactive Ni²⁺ phase on the electrode surface.

The sXAS features above 536eV become broader at the delithiation state (1Ch), and get sharpened when the material is lithiated (1D). The observed spectral broadening could stem from more itinerant electrons³⁵⁻³⁶ and/or structural distortion³⁷ of the electrode material under delithiated states. We note that a direct measurement of the electronic conductivity of a cycled Li_{1-x}Ni_{0.5}Mn_{1.5}O₄ material is non-trivial due to the existence of the conductive carbon. A recent work on Li_{1-x}Ni_{0.5}Mn_{1.5}O₄ thin films indicates the decrease of impedance of partially delithiated Li_{1-x}Ni_{0.5}Mn_{1.5}O₄ samples³⁸. In the meantime, the lattice of electrode materials often gets distorted and disordered during a delithiation process, which may also contribute to the spectral broadening.

Conclusions

In conclusion, we performed comprehensive soft x-ray absorption spectroscopy studies, including Ni, Mn *L*-edge and O *K*-edge on LiNi_{0.5}Mn_{1.5}O₄ electrodes at different electrochemical states. The Ni *L*-edge data show three distinct lineshapes at the discharged, half-charged, and charged states. The lineshapes correspond to dominant Ni²⁺, Ni³⁺ and Ni⁴⁺ phases at the different SOCs, as interpreted by the multiplet calculations. The combined spectroscopic and theoretical data provide direct evidence for single-electron-transfer reactions in the LiNi_{0.5}Mn_{1.5}O₄ electrode upon cycling, namely, Ni²⁺/Ni³⁺ and Ni³⁺/Ni⁴⁺. Moreover, an electrochemically inactive Ni²⁺ and Mn²⁺ phase is observed on the electrode surface, in contrast to the bulk phases that follow the redox reaction upon electrochemical cycling. With regard to the experimental technique, this work is another demonstration of the power of soft x-ray spectroscopy for clarifying the electronic and chemical state evolution of 3*d* transition-metal based battery electrodes.

AUTHOR INFORMATION

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