



Surface redox on $\text{Li}[\text{Ni}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}]\text{O}_2$ characterized by *in situ* X-ray photoelectron spectroscopy and *in situ* Auger electron spectroscopy

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ABSTRACT

This work applies *in situ* Auger electron spectroscopy and X-ray photoelectron spectroscopy to the study of surface redox on $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ during charging and overcharging. We observe that all three transition metals are surface redox active, and that oxygen oxidation occurs for voltages above ≈ 4.2 V O_2 loss above ≈ 4.7 V, mediated by carbon redox, leads to partial reduction of the transition metals at the surface during overcharging.

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1. Background

The limited energy density of cathodes generally constrains the overall energy density of Li-ion batteries [1–3]. Transition metal oxides, along with LiFePO_4 , have been the dominant commercially relevant cathode chemistries. LiCoO_2 (LCO) is in many ways the prototypical cathode, being simple to manufacture and having good cycle stability [4]. However, its capacity is limited and Co costs impede its application in large formats [5–8]. LiMn_2O_4 (LMO) provides a low cost alternative, with good safety, but limited cycle life [5,9–11]. LiNiO_2 (LNO) has good capacity, but is of limited commercial application due to irreversibility and safety issues [5,12,13]. Certain combinations of these three oxides exhibit properties superior to their pseudo-single component counterparts [14–16]. Amongst them $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ (NMC) is of considerable interest [17–21]. Its reversible capacity is as high as 200 mAh/g when cycling between 2.8 V and 4.6 V [22]. NMC exhibits better cycle stability, higher reversible capacity, and better thermal stability in the delithiated, i.e. charged, state. However, the origin of the high capacity and stability is not fully understood. Some have suggest that the average transition metal oxidation state increases monotonically with decreasing Li concentration until O_2 begins to

evolve [23]. Others have assumed that high capacity results from oxidation of Ni^{2+} to Ni^{4+} in addition to $\text{Co}^{3+/4+}$ redox, where Mn^{4+} is inactive and plays a role in stabilizing the crystal structure [24–26]. This was inferred from *in situ* X-ray absorption spectroscopy (XAS), which observed an ≈ 0.4 eV shift in the absorption edge of Mn that was considered too small to represent $\text{Mn}^{3+/4+}$ redox [26]. However, *in situ* XAS performed on pure LMO observes a similar ≈ 0.4 eV shift in the absorption edge associated with complete charging, i.e. Mn 3.5 + to $\approx 4+$ [27]. Several groups have reported XPS results for uncycled NMC powders and most, not all, observe mixed 3+/4 + oxidations states, but to different degrees [18,28–30]. Kumar et al. found that stoichiometric NMC had a mixed oxidation state close to 3.5, while Li-rich formulations were 4+ [28]. In prior work, it was found that exposure to organics alone could induce oxidation of surface Mn^{3+} to Mn^{4+} on LiMn_2O_4 . Therefore, one may observe different initial states of the material if they are comparing pristine raw powder to pristine electrodes processed in solvents such as NMP. While this is a surface phenomena, the XPS data has been in some cases extended to interpretation of the overall redox response of the system. Considering these points, the extent of Mn reaction and its role in NMC remains unclear. The exceptional capacity has also been attributed to partial oxidation of the oxygen sub-lattice upon Li removal, resulting in the formation of peroxo-like species (O_2^{n-} , $n = 1, 2$ or 3), which has been shown in a variety of high capacity layered-oxide cathode material [32–34]. Computational and experimental evidence support this

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hypothesis for NMC [19,26,35]. Charging above ≈ 4.6 V leads to complete oxidation of some O^{2-} in the near surface region and its loss as O_2 gas. The mechanism for O_2 loss is through CO and CO_2 gas evolution, resulting in an oxygen depleted near surface region [24]. This limits the practical voltage window for cycling along with the capacity; below the theoretical value of 275 mAh g^{-1} . The surface and near surface region may differ in chemistry from the bulk [36]. For example, it is well known in $LiMn_2O_4$ that the surface can be reduced relative to the bulk in the presence of electrolyte impurities, i.e. Mn^{3+} disproportionation in the presence of H^+ [37–39]. Since this near surface region largely controls the cycle life of the material, its chemistry and bonding are of considerable interest. In this work, we would like to understand how the surface oxidation states and compositions of the various NMC components change with potential.

Acquiring analytical surface chemistry from Li-ion electrodes is notoriously challenging. Li-ion electrodes are air and moisture sensitive and their surface oxidation states can change rapidly upon exposure to atmosphere. Samples can be cleaned in a glovebox after cycling and transferred directly to UHV analytical equipment. However, cathodes are sensitive to reactions with organics, often present in glovebox atmosphere, and they can undergo time dependent surface reactions on the order of minutes and hours [40]. For example, a comparative *in situ* versus *ex situ* Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS) investigation of $LiMn_2O_4$ found that Mn on the *ex situ* cycled sample was always oxidized relative to the material cycled *in situ* [40]. Analyzing traditional composite electrodes also introduces problems for techniques such as XPS that utilize large probes, since the binder and conductive phase contribute considerable signal to the spectra [41–43]. Some have utilized thin film electrodes to provide more meaningful data, but many multicomponent electrode systems, such as NMC, can not be prepared easily as high quality vapor deposited thin film electrodes. Surface analytical chemistry performed *in situ* circumvents many characterization challenges associated with environmental exposure. *In situ* XPS and AES have been applied to characterizing Li-ion cycling [40,44–46]. The technique has been applied to study thin film electrodes and particle based electrodes. The former has the benefit that information is only sampled from the electrode, but it can not be applied broadly to many commercial electrode materials of interest. Here we seek to characterize the surface chemistry of commercial NMC particles using *in situ* surface spectroscopies. We have previously demonstrated an electrochemical cell to perform such experiments [40,44,47,48]. The cell utilizes a standard counter electrode, vacuum stable ionic liquid electrolyte, and a working electrode consisting of electrode particles resting on a thin carbon film (see schematic in Fig. 1). The carbon film acts as a current collector and a Li permeable membrane, which isolates the particles from the liquid electrolyte. XPS probes both the particles and the underlying current collector material, i.e. carbon, which itself produces C, Li, and O signals. However, the Ni, Mn, and Co signals can be obtained unencumbered. In particular, this work emphasizes characterizing Mn redox during charging and overcharging, whose behavior is still the subject of some controversy. We combine *in situ* XPS with parallel *in situ* AES stimulated with an electron beam. AES is obtained from single particles and can be used to define the surface composition of the particles. While AES spectra are challenging to interpret due to the doubly ionized nature of the atom producing the signal, the spectra do contain all of the relevant bonding information. We therefore also utilize *in situ* AES fingerprinting techniques to provide qualitative insights into the evolution of oxygen bonding as a function of potential. This is done by comparison to reference spectra as well as the cycling behavior of constituent LCO, LNO, and LMO materials. The work primarily

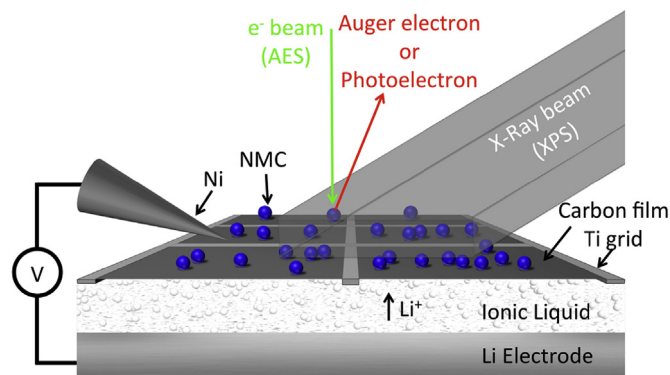


Fig. 1. Schematic of the electrochemical cell used for *in situ* X-ray photoelectron spectroscopy (XPS) and *in situ* Auger electron spectroscopy (AES). AES is performed with an electron beam source and XPS is performed with an X-ray source in a different instrument. However, the electrochemical cells share the same configuration. Images of the two sample stages are provided in [Supplementary Fig. S1](#).

focuses on the behavior of NMC while charging, and overcharging, to 5 V. This allows us to sample the response of the system in the reversible, as well as the irreversible, cycling regimes.

2. Experimental procedure

2.1. *In situ* XPS/AES cell preparation

NMC electrode powder from a commercial supplier was dispersed into ethanol at 1.0% by weight, drop cast onto a carbon ($\approx 30 \text{ nm}$) coated a 400 mesh titanium grid (Ted Pella, Inc.), and dried over a hot-plate in an Ar-filled glove box (LABstar, MBRAUN). This electrode rested on 10 wt% Lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in N-Methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)imide (P_{13} TFSI) soaked Whatman fiberglass separator, which was placed on a piece of lithium metal (1.5 mm in thickness) (Sigma-Aldrich). The lithium counter electrode was connected to the stainless steel current collector. A nickel-coated-bronze clip served as the contact to the working electrode. The cells were sealed in an air-tight jar prior to transfer to the XPS and AES chambers. For comparison, we also tested $LiNiO_2$ (Sigma Aldrich) and $LiCoO_2$ (Sigma Aldrich) prepared in the same manner, and compare to prior measurements of $LiMn_2O_4$ [40]. Samples were tested in the 2-electrode configuration shown schematically in Fig. 1. Images of both sample stages are provided in [Supplementary Fig. S1](#).

2.2. *In situ* AES acquisition and analysis

Auger electron spectroscopy (AES) data was acquired using a PHI 660 scanning Auger microprobe. The vacuum pressure of the chamber remained at 10^{-6} Pa . Acquisitions were performed with a 3 keV primary electron beam of spot size $\approx 350 \text{ nm}$. Each spectrum was averaged over 8 acquisition cycles between 20 and 1020 eV with measurements binned into 1 eV channels. Multiple particles were measured at each potential. Auger data was analyzed using PHI Multipak software. Auger peak energies are dependent on proper alignment of the electron beam elastic energy peak, which can lead to small, $<1 \text{ eV}$, variations between samples from different experiments. Compositions were determined by measuring the peak-to-peak heights for all of the components in the dE/dE plot and normalizing to the sensitivity factors for those peaks. The specific transitions highlighted in the text below were selected to avoid peak overlaps overlap between the transition metals. To

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