2180
doi:10.1017/S1431927619011632
Microsc. Microanal. 25 (Suppl 2), 2019

Investigating Surface Structure, Chemistry, and Thickness of NMC Cathodes Blended with LFO using EELS

Cesar J. Villa[1], Xiaobing Hu[1,2], Wesley M. Dose[3], Christopher S. Johnson[3], Vinayak P. Dravid[1,2]

[1.] Department of Materials Science and Engineering, Northwestern University, Evanston, IL, USA
[2.] NUANCE Center, Northwestern University, Evanston, IL, USA
[3.] Division of Chemical Sciences and Engineering, Argonne National Laboratory, Argonne, IL, USA

Rechargeable lithium-ion (Li-ion) batteries have been the battery of choice since the 1990s for portable electronics and, more recently, in hybrid/electric vehicles. In order to meet the rising energy demands, lithium ion batteries require higher power density, gravimetric, and volumetric capacity. The main system that became a commercial success was $LiCoO_2$, developed by Goodenough [1]. $LiCoO_2$ is a layered structure with Li and Co sitting in alternating octahedral sites forming a hexagonal symmetry. In order to improve cyclic stability, reduce toxicity, and cost, research became focused on adding dopants such as Ni and Mn, replacing Co sites. These efforts led to the realization of $LiNi_xMn_yCo_zO_2$ (NMC). [1]

Currently, NMC is the predominant system in the battery market due to its lower cost and similar operating potential as $LiCoO_2$. It has been found that there is a reconstruction of the surface in NMC particles from layered to spinel and eventually rock salt that is accompanied with oxygen release when it is cycled. This rock salt structure formation increases the impedance of the system because it makes it difficult for lithium ions to intercalate between the layers of NMC and results in capacity fade. [2,3] Electron energy loss spectroscopy (EELS) has been shown to be an important tool in determining the oxidation states of transition metals and measuring surface structure thickness. [4]

This work presents analysis on changes of oxidation state in Mn via tracking of energy shift in Mn L_3 and L_2 edges using EELS. $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ with 3.7% Li_5FeO_4 (LFO), as an additive, was cycled 100 times and imaged using HAADF-STEM, shown in Figure 1A. Integrated spectrum areas 1, 2, 3, and 4 showed obvious edges of O-*K*, Ni-, Mn-, and Co-*L* with energy shifts in the Mn *L*-edge being difficult to see, shown in Figure 1B. It is easier to visualize the shifting in edges by plotting energies of the edges against the positions along the spectrum map as shown in Figure 1C. The tracking of the edge shifting was done by extracting spectrums from a vertical region of interest with dimensions of 1×10 (W×H) pixels and each step was measured to be around 0.9 nm. A Matlab script was used to fit all the extracted spectrums with a gaussian curve and edge energies were collected using a peak finder function. The Mn L_3 edge has an energy shift from 640.5 eV to 642.5 eV and Mn L_2 shifts from 651.5 eV to 653.5 eV, indicating a change in the oxidation state of Mn. The thickness of the rock salt structure was determined to be approximately 21.5nm. It should be noted that the particle analyzed did not show any signal for Fe but the use of EDS, shown in Figure 1D, with an SEM on the bulk powder revealed that iron was present but not in direct contact with all NMC particles.

The use of EELS provides insight on the chemistry occurring at the surface of NMC particles. Interfacial chemistry behavior in battery materials is quite important and can control the power and energy capability of the system, thus one can better understand how additives affect their thickness to improve capacity retention by reducing impedance. [5]

References:

[1] N. Naoki *et al.*, Materials Today 5 **18** (2015),
[2] L. Feng *et al.*, Nature Comms. **5** (2014), p. 3529
[3] J. Roland *et al.* , Journal of The Electrochemical Society, **164** (2017), p. A1361-A1377
[4] X. Hu *et al.*, Chemistry of Materials, **30** (2018), p. 6124-6133
[5] J. Gilbert *et al.*, Journal of The Electrochemical Society, **164** (2017), p. A6054
[6] This work made use of the EPIC facility of Northwestern University's NU*ANCE* Center, which has received support from the Soft and Hybrid Nanotechnology Experimental (SHyNE) Resource (NSF ECCS-1542205); the MRSEC program (NSF DMR-1720139) at the Materials Research Center; the International Institute for Nanotechnology (IIN); the Keck Foundation; and the State of Illinois, through the IIN. This work was supported as part of the Center for Electrochemical Energy Science (CEES), an Energy Frontier Research Center funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences.

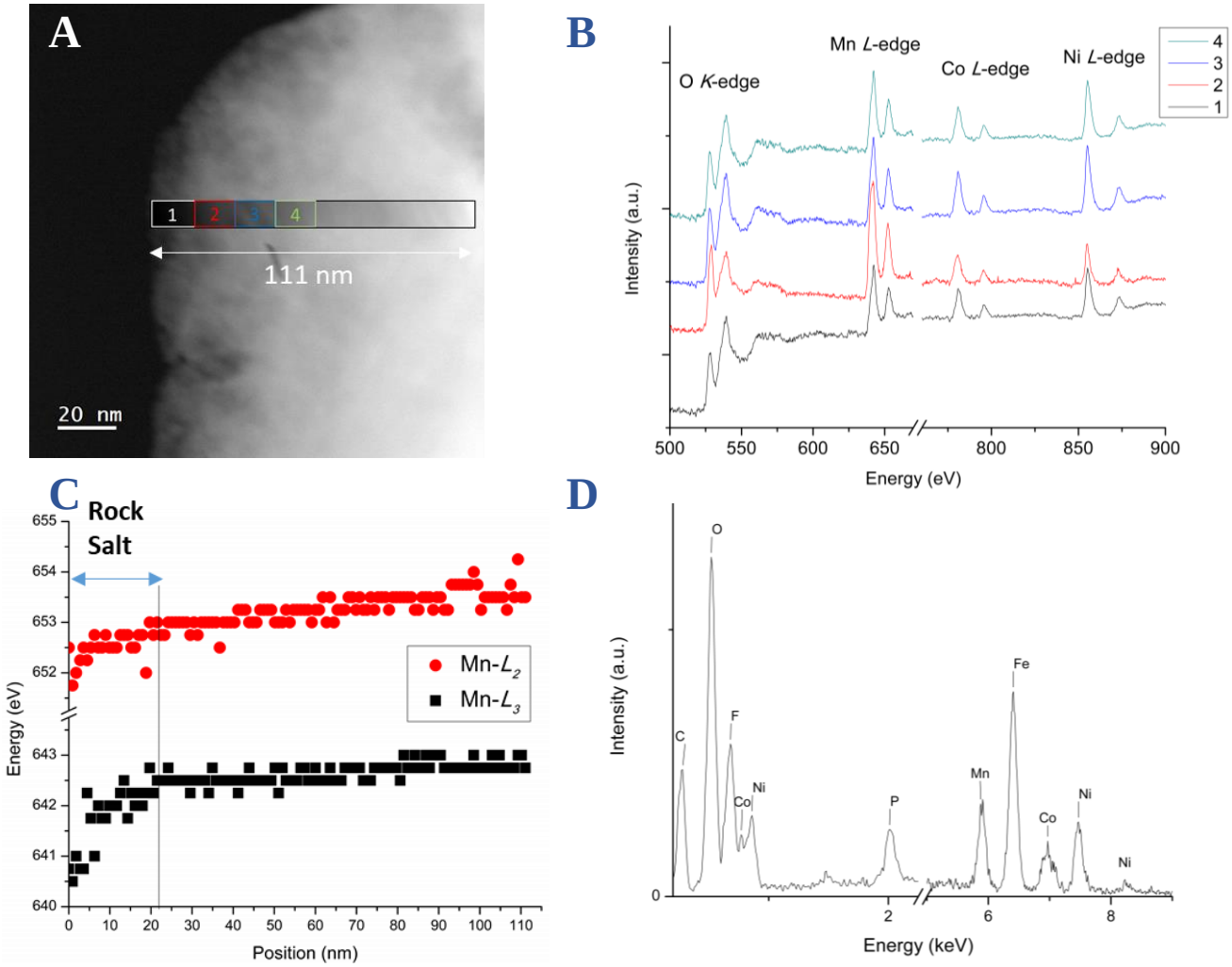

Figure 1. A) HAADF-STEM image of NMC particle cycled 100 times with EELS spectrum map taken from edge (0 nm) to inner (111 nm). (B) EELS spectra of integrated areas 1,2,3 and 4 C) Mn L_3 and L_2 edge energy shift plotted against position of spectrum map of (A) D) EDS scan taken of bulk powder on SEM confirming presence of Fe.

https://doi.org/10.1017/S1431927619011632 Published online by Cambridge University Press