Understanding the Mn Dissolution Mechanism in Rock Salt-Type $Li_4Mn_2O_5$ Cathodes

Monica Theibault,[a] Dennis Nordlund,[b] Chaochao Dun,[c] Jeffrey Urban,[c] Wei Tong,*[a] and Marca Doeff*[a]

*corresponding authors

[a]Energy Storage and Distributed Resources Division, Lawrence Berkeley National Laboratory Berkeley, CA 94720, USA.

[b]Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, Menlo Park, CA 94025, USA

[c]The Molecular Foundry, Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA.

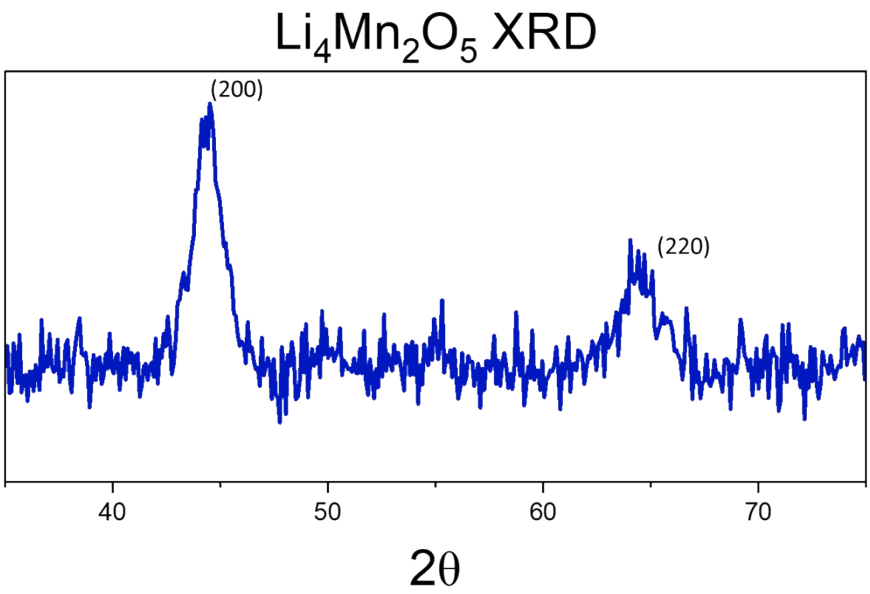

Figure S1. XRD pattern of as-synthesized LMO material. Miller indices were calculated using PowderCell software.

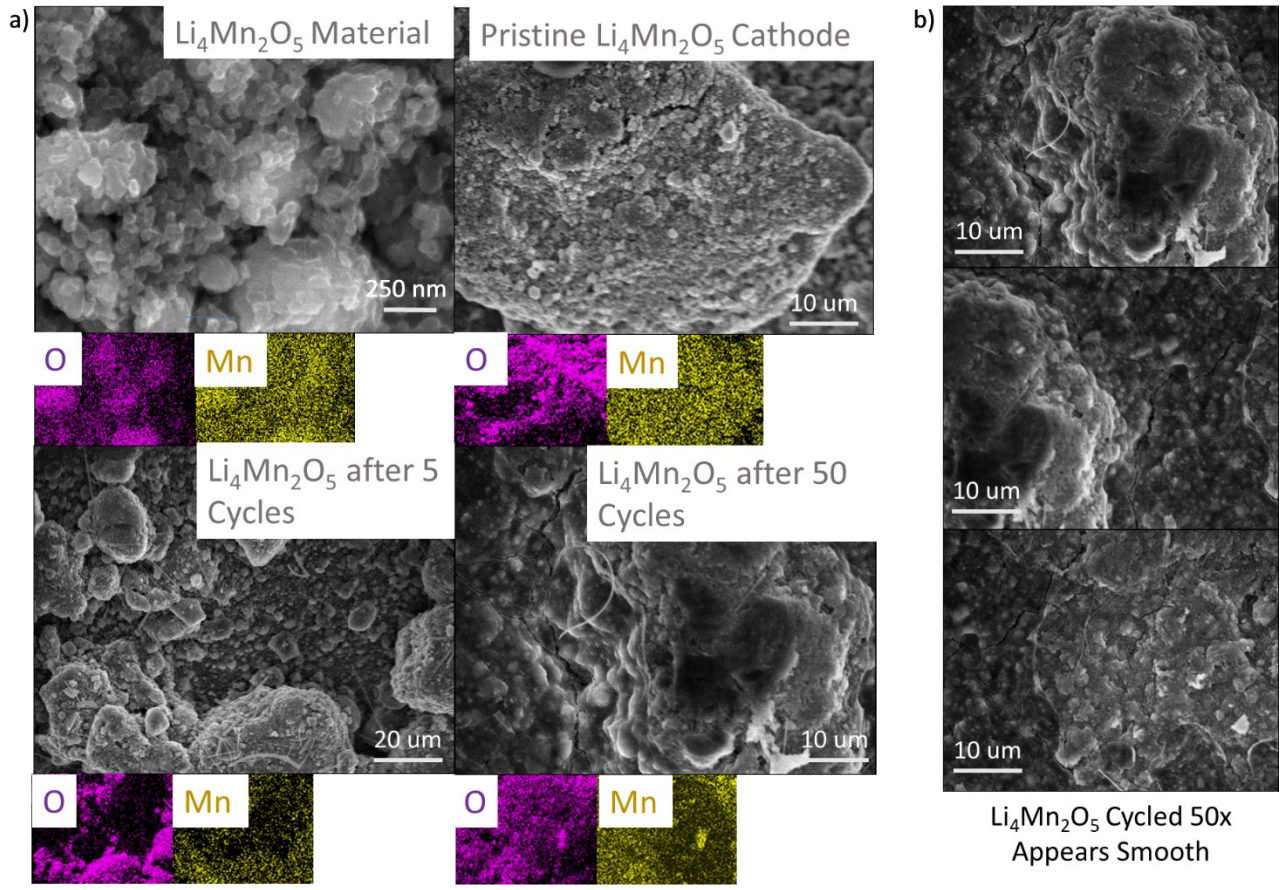

Figure S2. a) SEM and EDS elemental mapping of cathode after 50 cycles between 4.8 V and 2.0 V, after 5 cycles, before cycling, and of the pristine LMO material. b) Images of multiple spots on the cathode after 50 cycles.

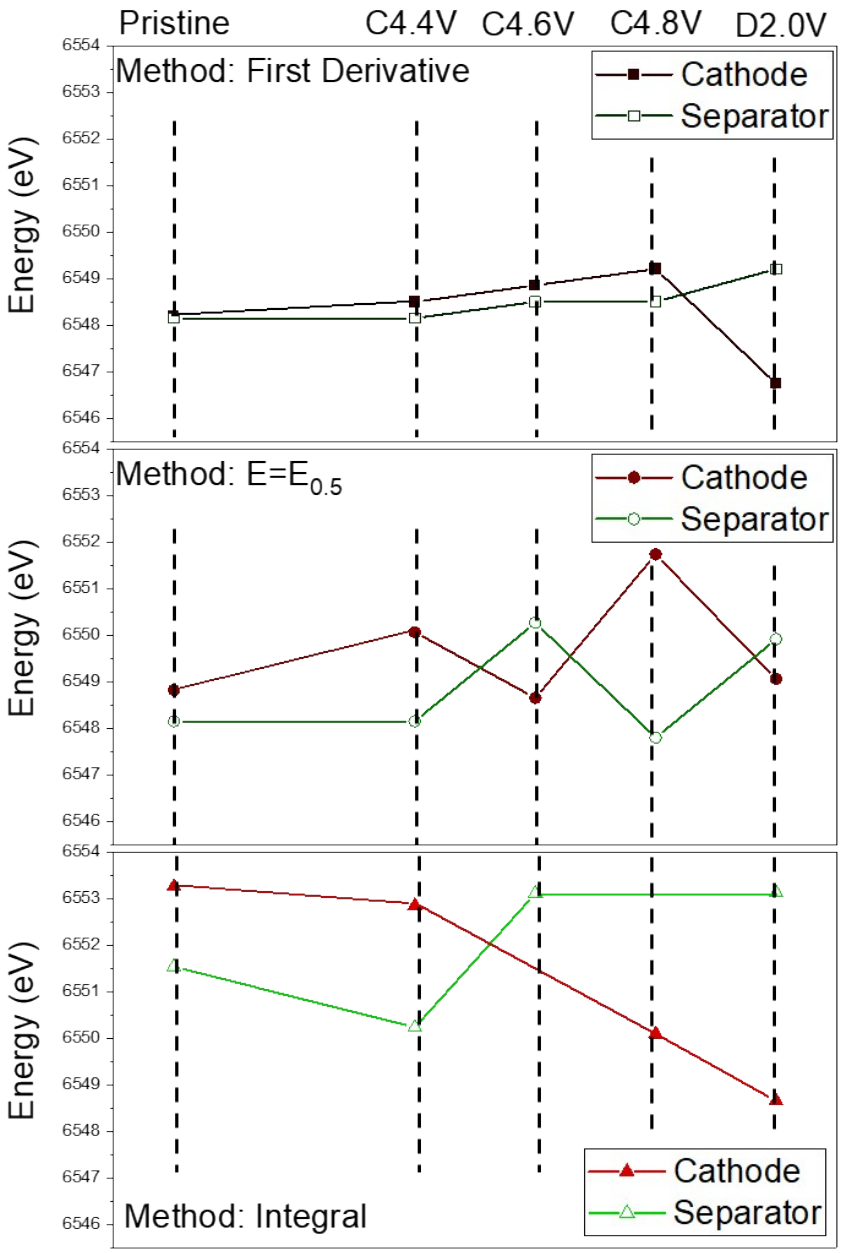

Figure S3. Comparison of three different methods of Mn K-Edge determination: first derivative, $E=E_{0.5}$, and integral. These methods did not yield significant differences. The analysis in the main text is based on the first derivative method. For a detailed explanation of the different methods, refer to the supporting information in Nam et al.[1]

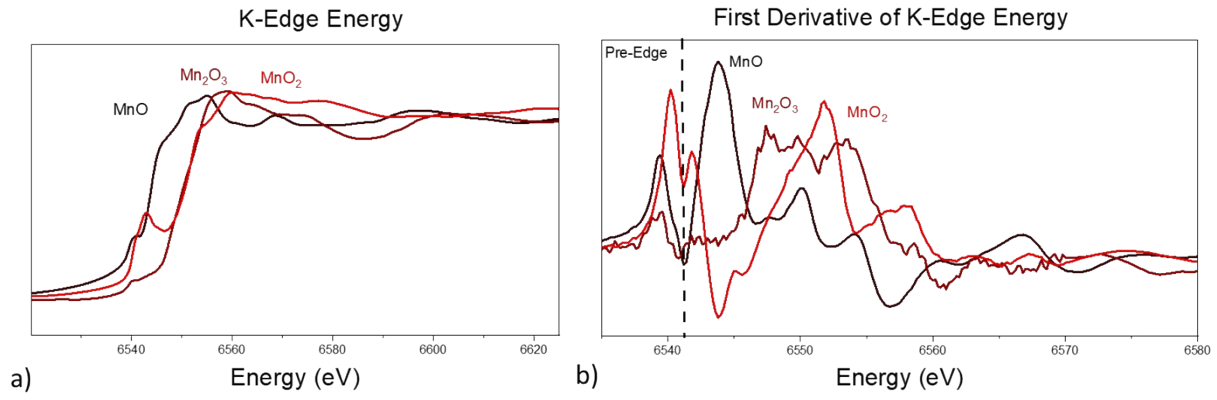

Figure S4. a) Hard XAS of Mn reference spectra for oxidation state determination, b) first derivative of Mn K-edge energy of Mn reference spectra.

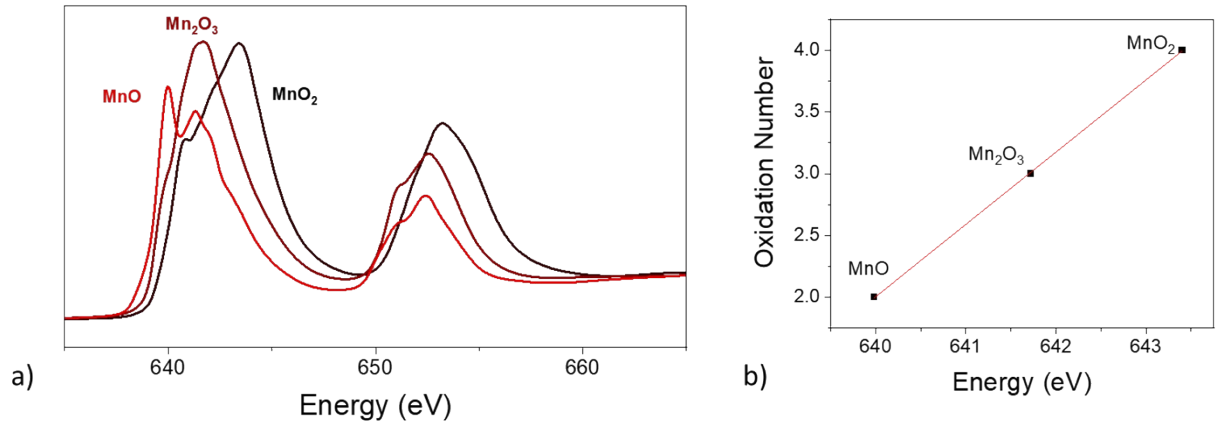

Figure S5. a) Soft XAS measurements of Mn reference spectra for oxidation state determination in TEY mode, b) plot of oxidation state versus Mn L-edge energy using linear combination analysis (LCA) fitting for the reference MnO, Mn_2O_3, and MnO_2 spectra.

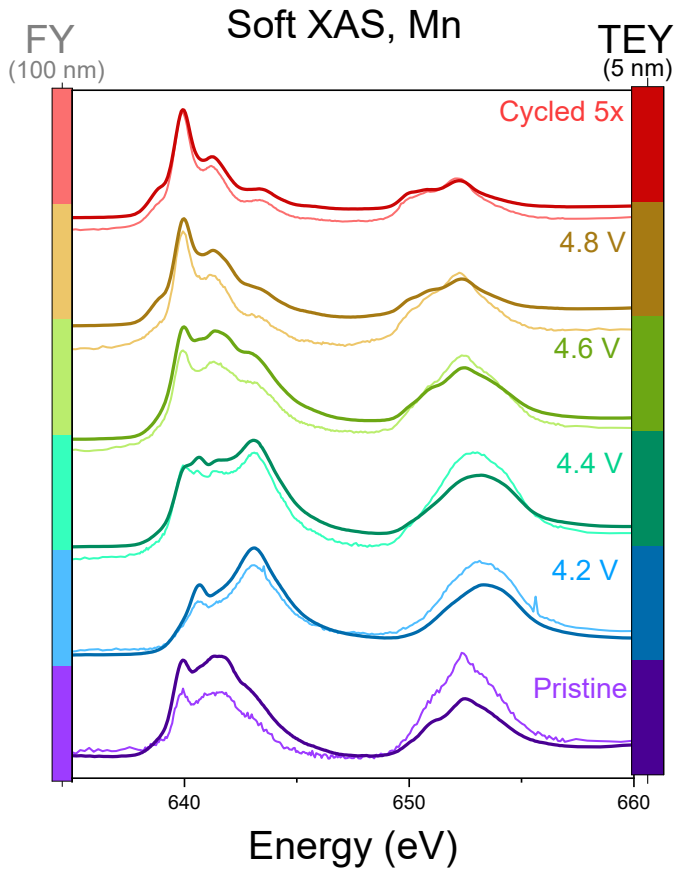

Figure S6. Soft XAS measurements of Mn at various states of charge and discharge in both TEY mode and FY mode.

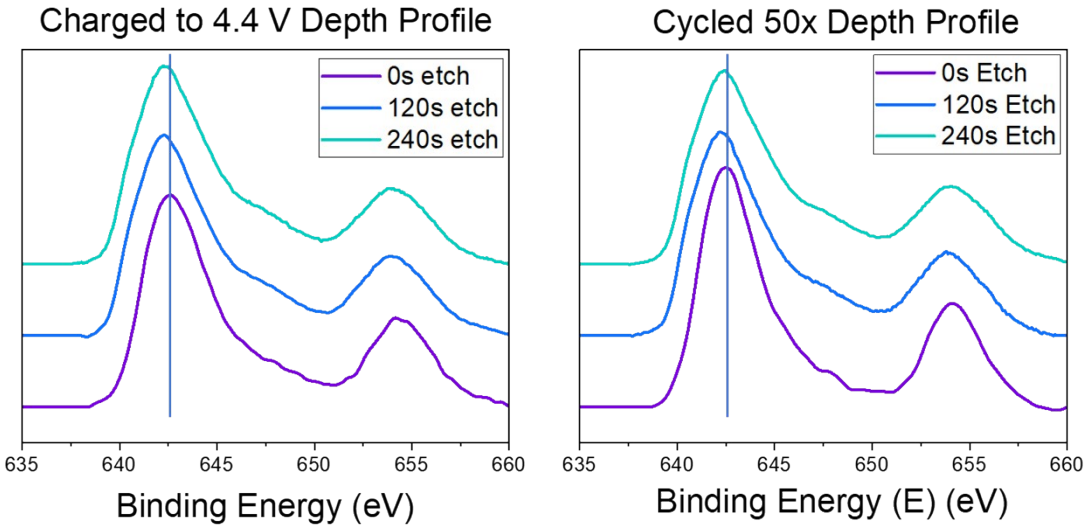

Figure S7. Mn XAS depth profiling measurements of the cell charged to 4.4 V and the cell cycled 50x. The vertical line, centered on the peak position of the measurement with no etching performed, serves as a guide for the eye.

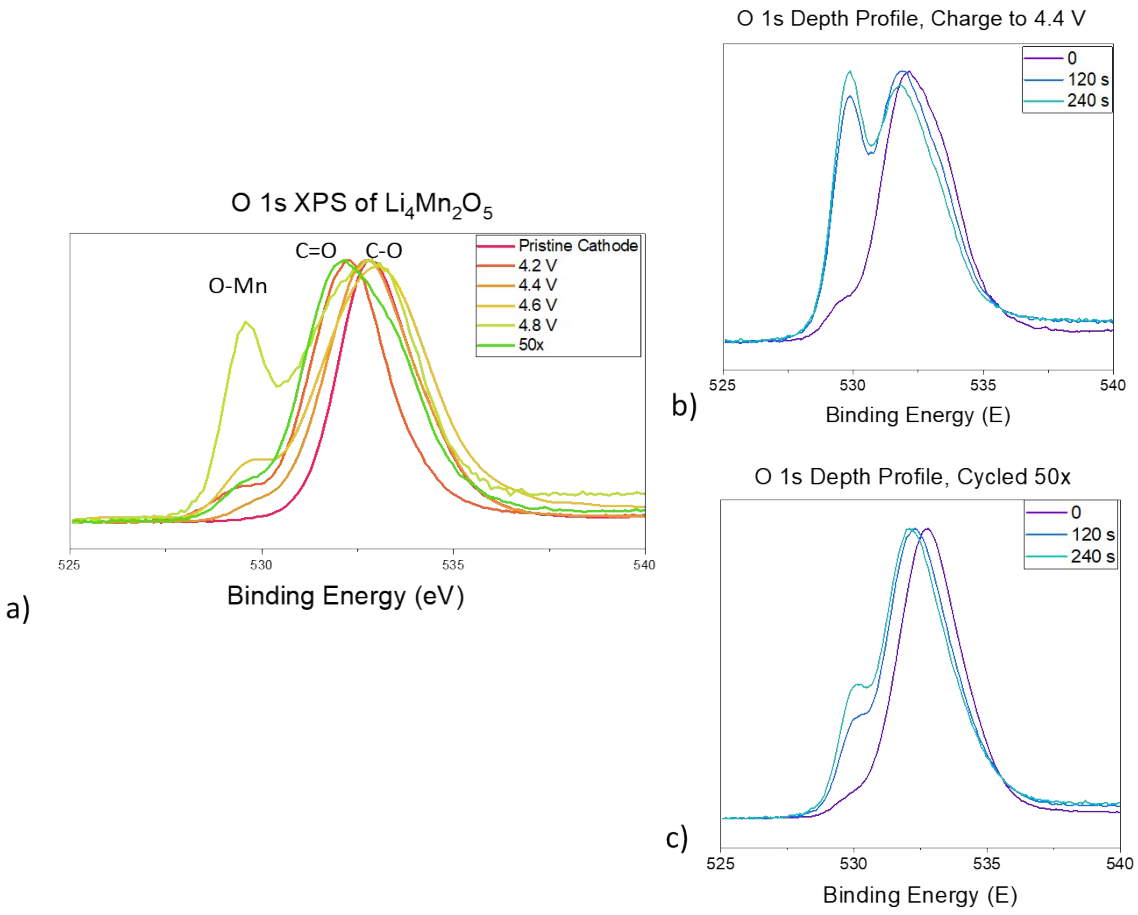

Figure S8. a) O1s XPS taken on $Li_4Mn_2O_5$ cathodes extracted from half-cells at indicated points in the charging and discharging process and O 1s depth profiling measurements taken of the cells charged to 4.4 V (b) and cycled 50x (c).

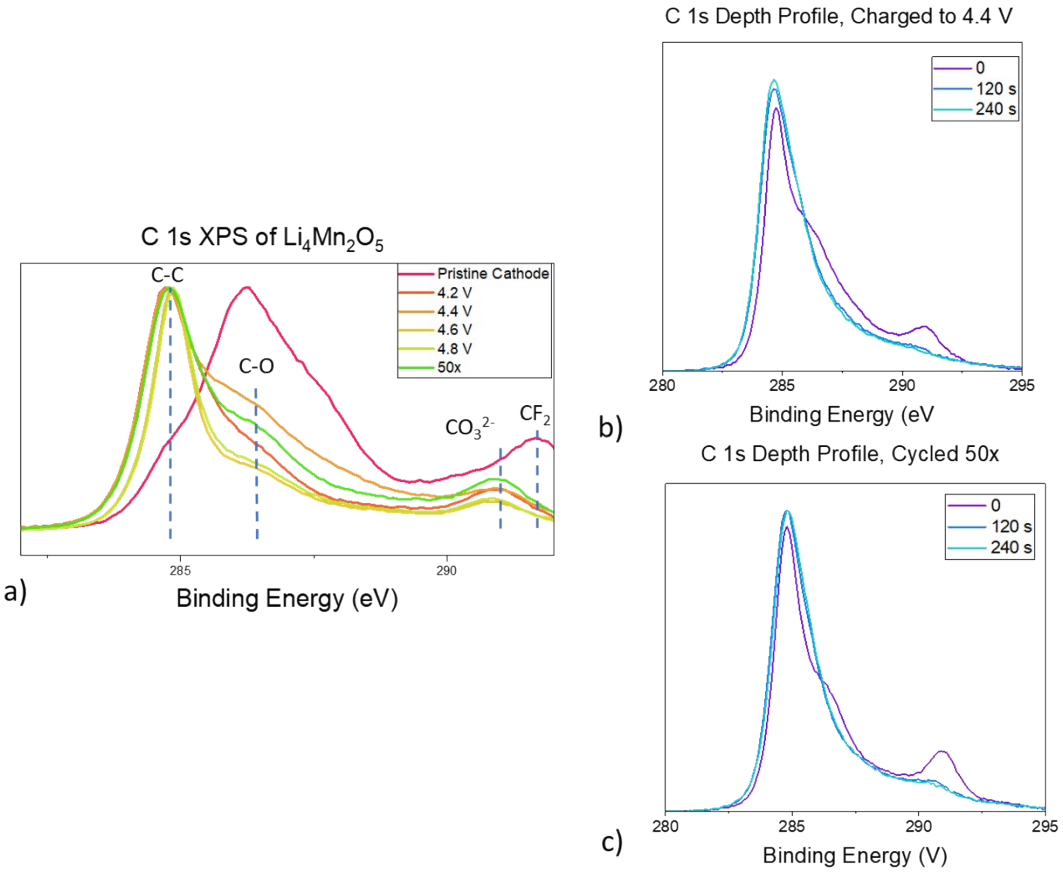

Figure S9. a) C 1s XPS taken on $Li_4Mn_2O_5$ cathodes extracted from half-cells at indicated points in the charging and discharging process and C 1s depth profiling measurements taken of the electrodes charged to 4.4 V (b) and cycled 50x (c).

1 K. H. Nam, Z. Wang, J. Luo, C. Huang, M. F. Millares, A. Pace, L. Wang, S. T. King, L. Ma, S. Ehrlich, J. Bai, E. S. Takeuchi, A. C. Marschilok, S. Yan, K. J. Takeuchi and M. M. Doeff, *Chemistry of Materials*, 2024, **36**, 4481–4494.