Supporting information for Tuning discharge voltage by Schottky electron barrier in P2-$Na_{2/3}Mg_{0.205}Ni_{0.1}Fe_{0.05}Mn_{0.645}O_2$

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Materials and Methods

Synthesis and battery test: P2-$Na_{2/3}Mg_{0.28}Mn_{0.72}O_2$ and P2-$Na_{2/3}Mg_{0.205}Ni_{0.1}Fe_{0.05}Mn_{0.645}O_2$ were synthesized by solid-state reactions. Sodium carbonate (Na_2CO_3, Alfa, 99.95%–100.05%), manganese oxide (Mn_2O_3, Aldrich, 99%), iron oxide (Alfa, 99.99%), nickel oxide (NiO, Aldrich, 99.8%), magnesium oxide (MgO, Alfa, 99+%) were mixed in appropriate ratios and ground by high-energy ball milling. The mixture was then pressed into pellets and calcined in a tube furnace in oxygen. The temperature was increased at 5 °C min^{-1} to 850 °C and kept constant for 10 h. The pellets were then quenched to room temperature with a Cu foil and transferred to an Ar-filled glovebox immediately to minimize the air contact. Positive electrodes consist of 80 wt% of active material, 15 wt% of carbon black, and 5 wt% of PTFE binder. Sodium metal was used as a negative electrode. 1 M $NaPF_6$ dissolved in a mixture of EC/DEC (1:1 v/v) and a glass fiber filter GF/D (Whatman) were used as an electrolyte and a separator, respectively. Swagelok type cells were assembled in an Ar-filled glove box and tested on an ArbinBT2000 workstation (Arbin Instruments, TX, USA).

X-ray diffraction (XRD): XRD data were obtained using a Rigaku Miniflex 6G. Powder samples are sealed with Kapton film in an argon-filled glovebox to prevent the air contamination. Rietveld refinement was performed on XRD patterns using TOPAS software.

High-resolution transmission electron microscopy (HRTEM): A Swagelok battery cell was dissembled after reaching designated potentials. Cathode films were sonicated in dimethyl carbonate (DMC). The DMC solutions were then dropped onto the TEM copper grids. The

TEM sample was sealed in an airtight bottle before loading into the microscope column. All the sampling processes were done in Ar-filled glove box. The HRTEM image was taken on the JOEL 2010F at an acceleration voltage of 200 kV.

X-ray absorption spectroscopy (XAS):

Transition metal K-edge X-ray absorption spectroscopy (XAS) were collected with a Si monochromator in transmission mode at beamline 7-BM (QAS) of National Synchrotron Light Sources II (NSLS-II). Oxygen K-edge soft XAS were performed at beamline 10-1 at Stanford Synchrotron Radiation Lightsource (SSRL). The XAS data were processed using Athena software packages.

Ab initio calculation: All DFT simulations were performed using the Vienna Ab initio Simulation Package (VASP) implementing the pseudopotential plane wave method[25,26]. The Perdew-Burke-Ernzerhof generalized-gradient approximation (PBE-GGA) was used for the exchange-correlation energy[27]. The spin-polarized GGA+U calculations were carried out to account for the correlated d orbitals of TM ions with the Dudarev implementation for the double-counting correction. The effective on-site correlations, $U_{eff} = U - J$ are 3.9 eV, 4.0 eV, 5.0 eV, and 4.0 eV for Mn, Fe and Ni respectively[28,29]. A 520 eV plane-wave energy cutoff was used for all calculations. The supercell size is 3*3*1 (2 Na layers) for all calculations. For TM ordering, $Na_xMg_{1/3}Mn_{2/3}O_2$ follows the Mg/Mn honeycomb ordering with AA stacking, and $Na_xMg_{2/9}Ni_{1/9}Mn_{2/3}O_2$ has Ni doped into the Mg sites in the the honeycomb ordering with AB stacking, both follows the previous reports[11-13].

Data availability

The datasets generated during the current study are included in this published article (and its supplementary information files) or are available from the corresponding author on reasonable request.

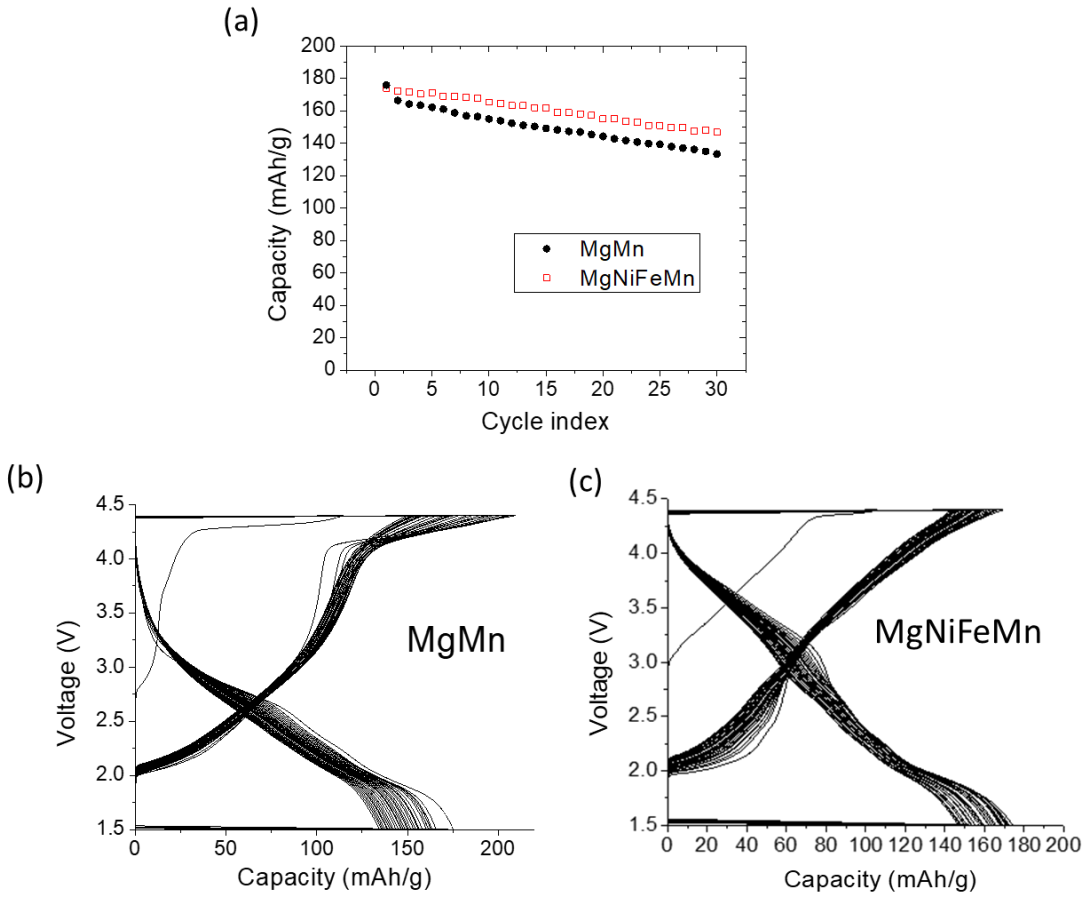

Figure S1. (a) Capacity retention over 30 cycles of MgMn and MgNiFeMn. 30-cycles charge-discharge curves at 0.1C-rate of (b)MgMn and (c) MgNiFeMn.

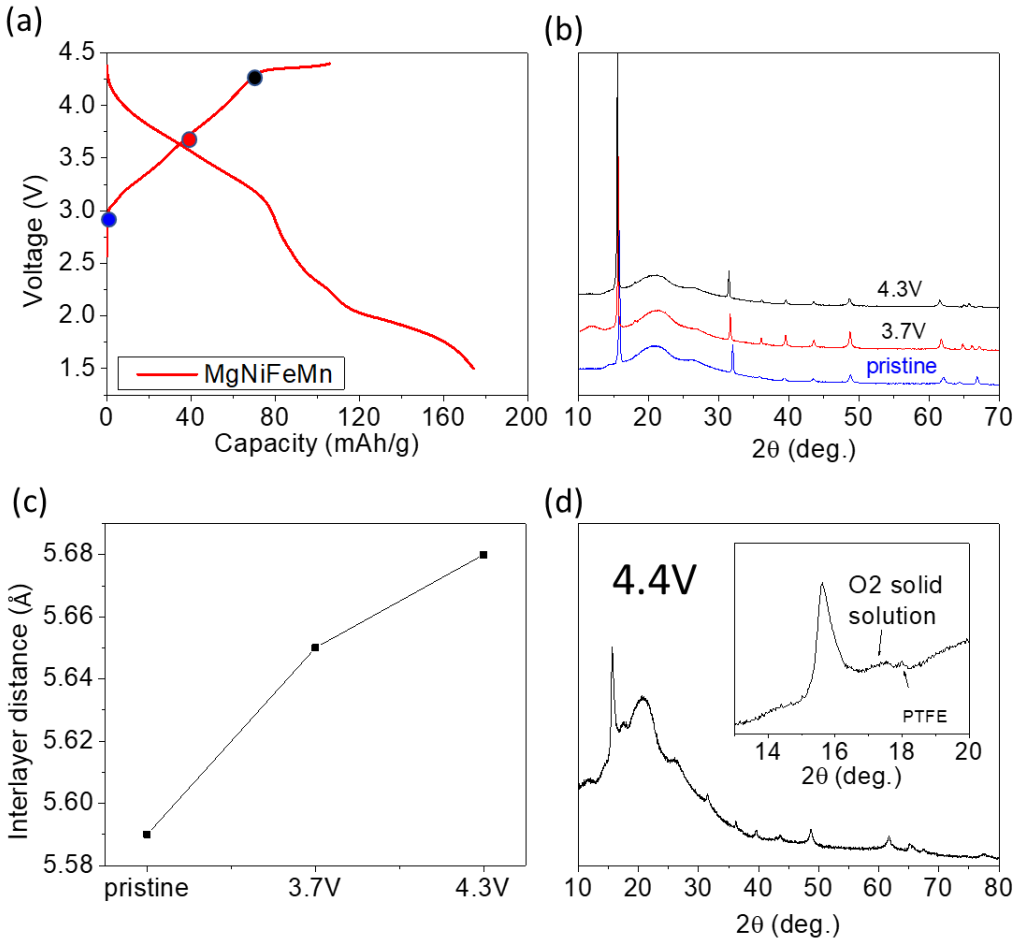

Figure S2. Additional XRD analysis for MgNiFeMn during slope region (3V, 3.7V, 4.3V) and at the end of high voltage plateau (4.4V). (a) Charge-discharge curve with dots indicating voltage states for XRD, (b) XRD patterns and (c) interlayer distances; (d) 4.4V XRD pattern with inset enlarging the 002 peak region showing a bump corresponding to the possible O2 solid solution.

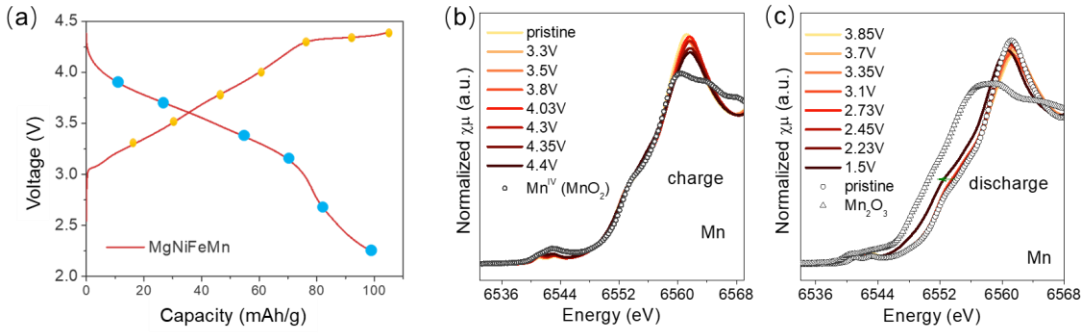

Figure S3: Ex situ XANES measurement of Mn in MgNiFeMn. (a) Charge-discharge curve with dots indicating the states at which the XAS patterns were collected; (b,c) XANES evolution of Mn during charge and discharge.

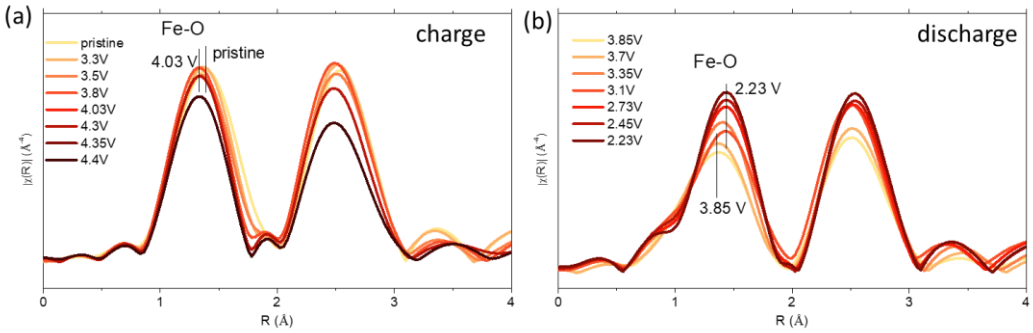

Figure S4 Extended X-ray absorption fine structure of Fe in MgNiFeMn during (a) charge and (b) discharge.

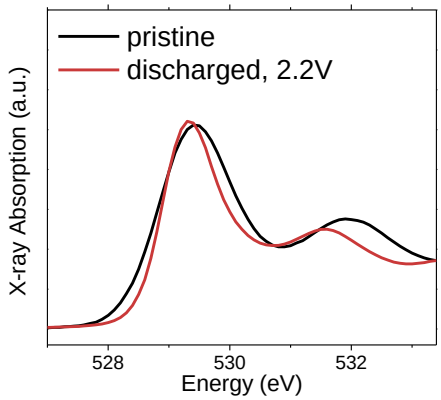

Figure S5. Oxygen K-edge XAS spectra of pristine film and the film after 1 cycle (2.2V).

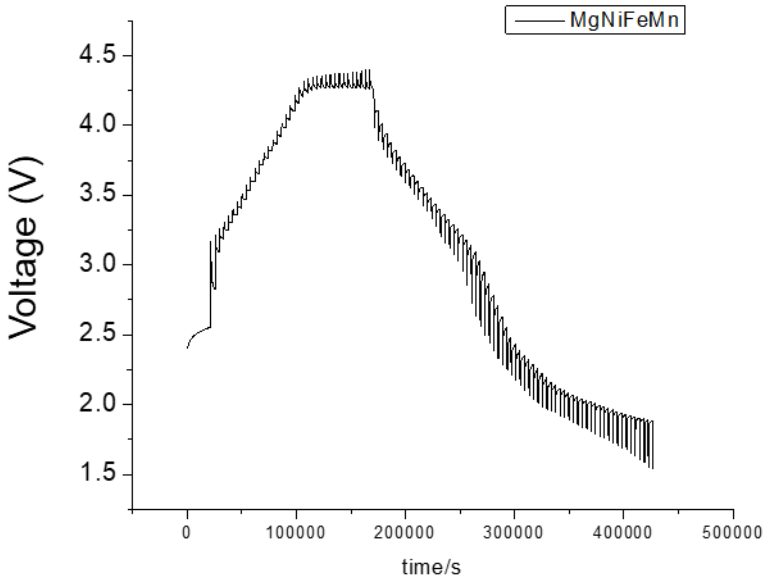

Figure S6. GITT of MgNiFeMn measured at 0.1 C charge step of 450 seconds each followed by OCV relaxation of 1 hour.