Supplementary Information

Suppressing Electrolyte Decomposition at Cathode/Electrolyte Interface by Mg-Fe Binary Oxide Coating towards Room-Temperature Magnesium Rechargeable Battery Operation

Reona IIMURA, Hiroaki KOBAYASHI* and Itaru HONMA

Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi, 980-8577, Japan.
E-mail: h.kobayashi@tohoku.ac.jp

1. Experimental Section

1.1.Synthesis of $MgMn_2O_4$

MMO, core particle for cathode material, was synthesized via alcohol reduction (AR) process[1] with modification. *n*-Bu_4NMnO_4 (10 mmol) was added into dehydrated $MgCl_2$ solution with methanol and ethylene glycol dimethyl ether (0.05 M 200 mL, 1 to 1 volume ratio) under 1 h-vigorous stirring to get a brown colloidal solution. Then, deionized water (50 mL) was added to the solution with string for 10 min. The precipitate was collected, washed by five-times centrifugation with ethanol. The washed sample was dispersed into 150 mL *t*-butyl alcohol and freeze-dried.

1.2.Oxide coating to $MgMn_2O_4$

Coating processes of MFO@MMO were performed as described below: synthesized MMO was coated with two-step alkoxide method (Fig. 1). As for the first step, 2.5 mmol MMO was added into 0.5 mmol magnesium ethoxide solution in 100 mL ethanol, and stirred for 5 hours under reflux conditions. The precipitates were collected by centrifugation with ethanol and dispersed into deionized water to promote the hydrolysis reaction of Mg ethoxide on the MMO surface. Then, Mg ethoxide-reacted MMO (Mg@MMO) was freeze-dried in deionized water. Now for the second step, 0.8 mmol iron(III) isopropoxide was coated to 2.0 mmol Mg@MMO with the same process stated above. After the two-time alkoxide coating, the sample was calcinated at 300 °C for 2 hours to obtain MFO@MMO. In addition, $MgAl_2O_4$@MMO (MAO@MMO) was also

synthesized by 2 step alkoxide process as we stated above, where aluminum isopropoxide was used as an Al source. For the comparison, Mg-oxide@MMO and Fe-oxide@MMO were synthesized one-step alkoxide method. In brief, First step of alkoxide method was performed with magnesium ethoxide and iron(III) isopropoxide respectively. Then, each reacted MMO was calcined at 300 °C for 2 hours.

1.3.Material Characterization

Powder X-ray diffraction (XRD) measurements using Cu Kα radiation were performed using Burker D2 PHASER 2ndGen. The obtained XRD patterns were fitted with Rietveld refinements using RIETAN-FP program.[2] X-ray absorption spectroscopy (XAS) measurements were carried out using the transmission method at the BL11S2 beamline of the Aichi Synchrotron Radiation Center. X-ray absorption near edge structure (XANES) was analyzed by Athena program. [3] Transmission electron microscopy (TEM) images were obtained using (JEM-ARM200F). To obtain cross-sectional TEM image, sample was ion-sliced with EM09100IS.Energy dispersive X-ray analysis (EDS) using transmission electron microscopy (TEM) was performed. X-ray photoelectron spectroscopy (XPS) measurements were carried out with Ar^+ sputtering at the sputter rate of 0.4 nm for SiO_2. Brunauer–Emmett–Teller (BET) surface areas of the sample were measured by N_2 adsorption at 77 K (BELSORP MAX G).

1.4.Electrochemical Measurements

The cathode material: MMO, MFO@MMO, Mg-oxide@MMO or Fe-oxide@MMO was mixed with acetylene black (AB; Denka Black, FX-35, Denka Co., Ltd.) and polytetrafluoroethylene (PTFE; Teflon, 6-J, DuPont-Mitsui Fluorochemicals Co., Ltd.) at a weight ratio of 60/30/10. These mixtures were hollowed out to a 7 mm-diameter disk of approximately 2.5 mg and pressed onto a 10 mm-diameter Al mesh. This prepared electrode was dried at 373 K under vacuum overnight and moved to an Ar-filled glove box. As for anode material, Mg ribbon was cut to 1 cm long and polished with metal file to remove Mg oxide films. Regarding electrolyte, 0.3 M $Mg[B(HFIP)_4]_2$ dissolved into triglyme (G3; Kanto Chemical Co., Inc.) was prepared. The cathode, the anode and the electrolyte (150 μL) were assembled in a 2032-type coin cell with two pieces of glass-fiber separator (15 cm, GA-55, Toyo Roshi Kaisha, Ltd.). Charge-discharge tests were performed at 25 °C in constant-current (CC) mode using a battery test system (HJ-1001SD8, Hokuto Denko Corp.). XPS measurements were carried out with MMO@MFO and MMO at pristine, discharge and charge state. Electrochemical impedance

spectroscopy (EIS) to measure the cathodic interface resistance was performed in a frequency range from 0.2 MHz to 0.1 Hz using active carbon as anode: mixed with maxsorb, AB and PTFE at a weight ratio of 80/10/10 in a 2032-type coin cell. Each cathodic interface resistance was showed with the equation below in order to ignore active carbon resistance.

$$Z = Z_{carbon-cathode} - \frac{1}{2} Z_{carbon-carbon}$$

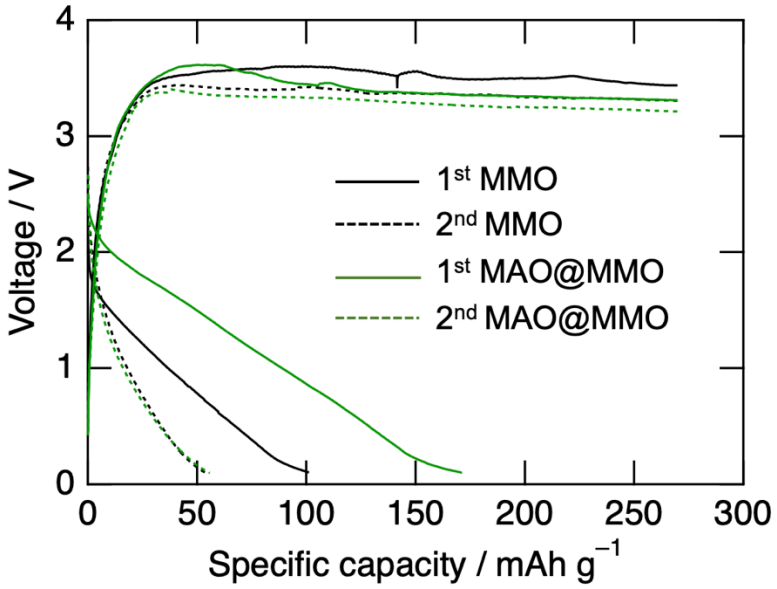

Fig. S1. Voltage curves of MAO@MMO

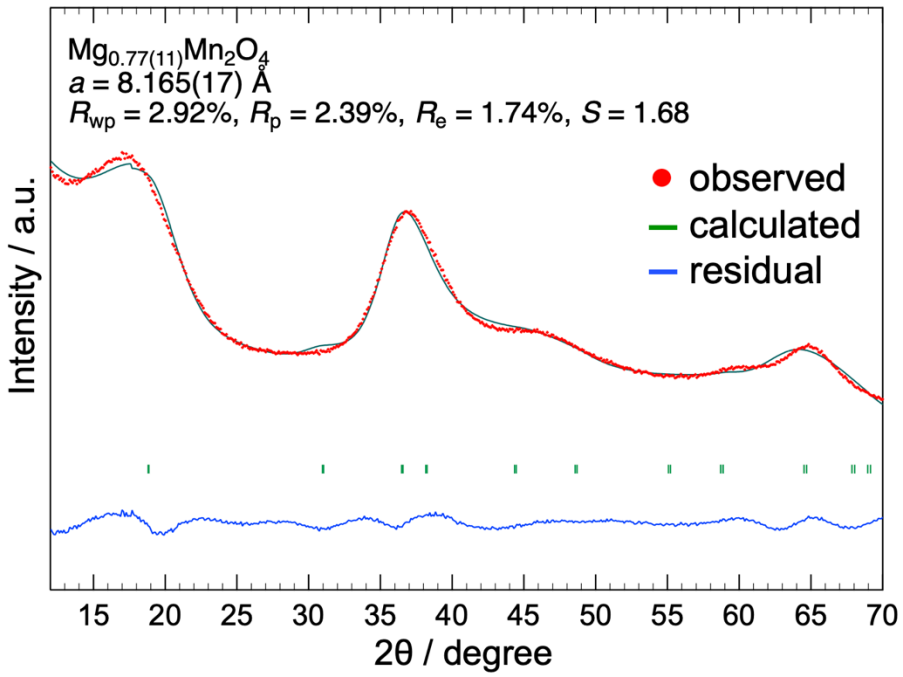

Fig. S2 XRD patterns of MMO with fitting curve by Rietveld refinement.

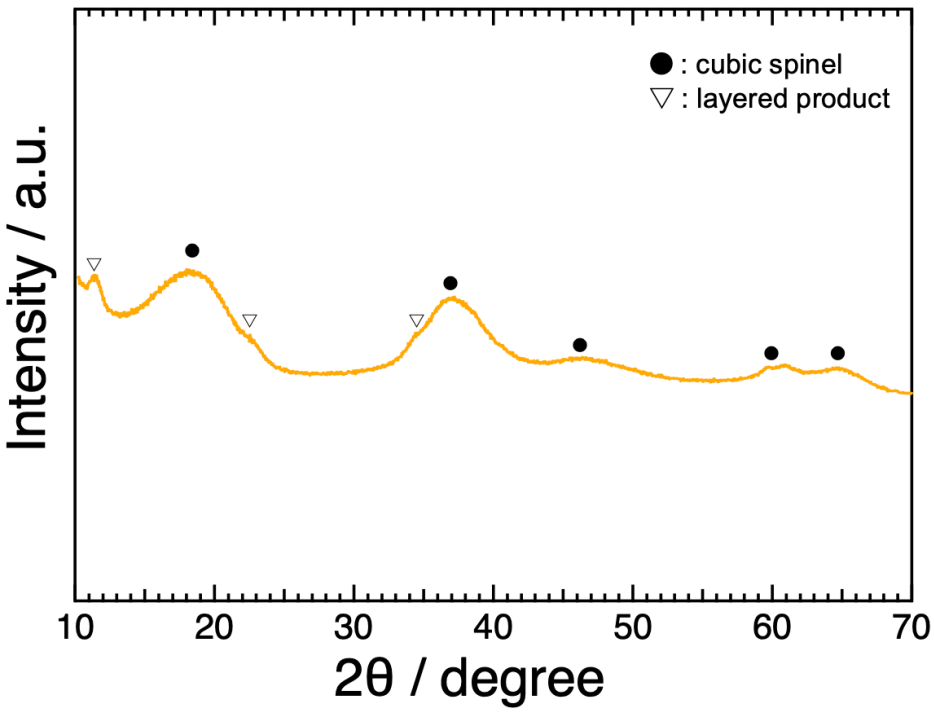

Fig. S3 XRD patterns of Mg@MMO.

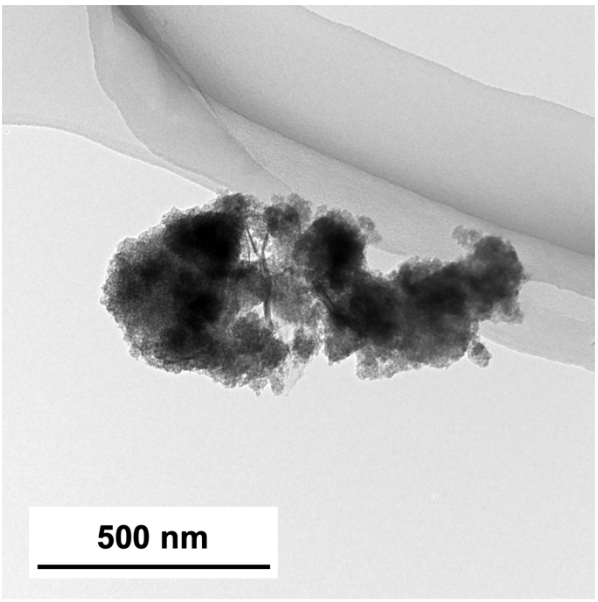

Fig. S4 TEM image of MFO@MMO aggregates.

Table S1 Crystalline size and BET specific surface area.

	Crystalline Size [nm]	Specific Surface Area [m^2 g^{-1}]
MMO	2.0	436
MFO@MMO	2.6	254

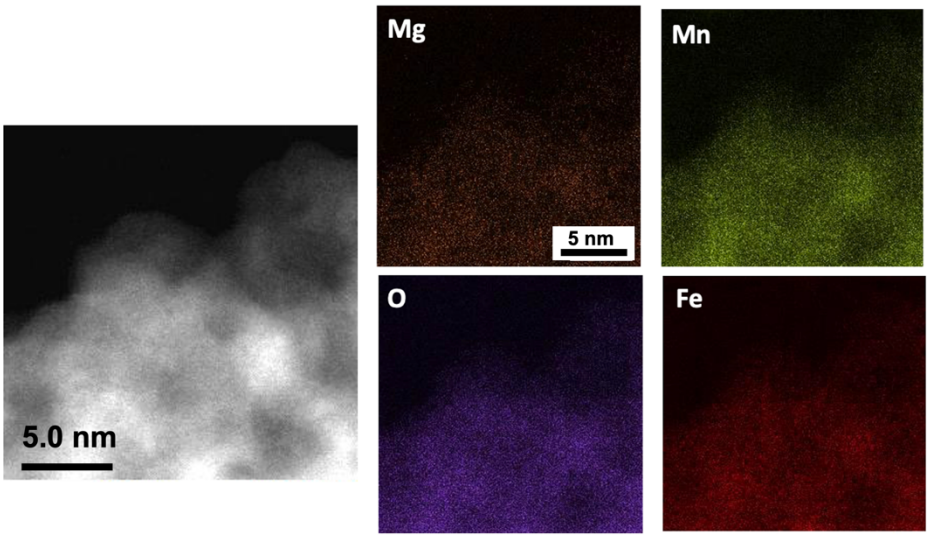

Fig. S5 TEM-EDS image of MFO@MMO.

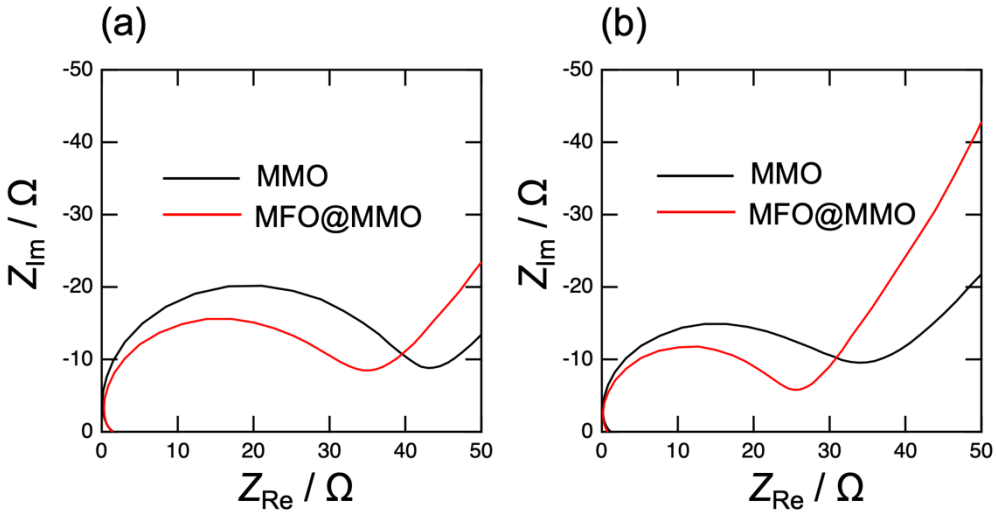

Fig. S6 Electrochemical impedance spectroscopy of MMO and MFO@MMO: (a)discharge state (b) charge state.

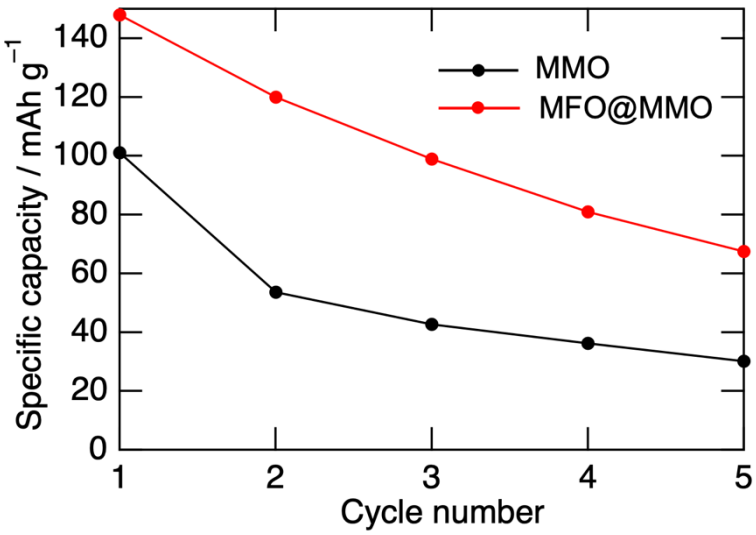

Fig. S7 Cyclabilities of MMO and MFO@MMO.

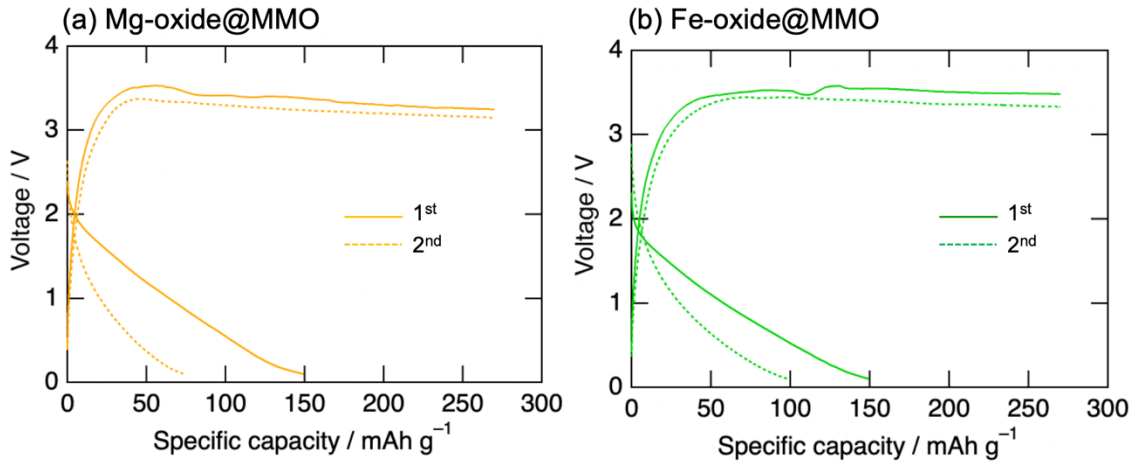

Fig. S8 Voltage curves of (a)Mg-oxide@MMO (b)Fe-oxide@MMO.

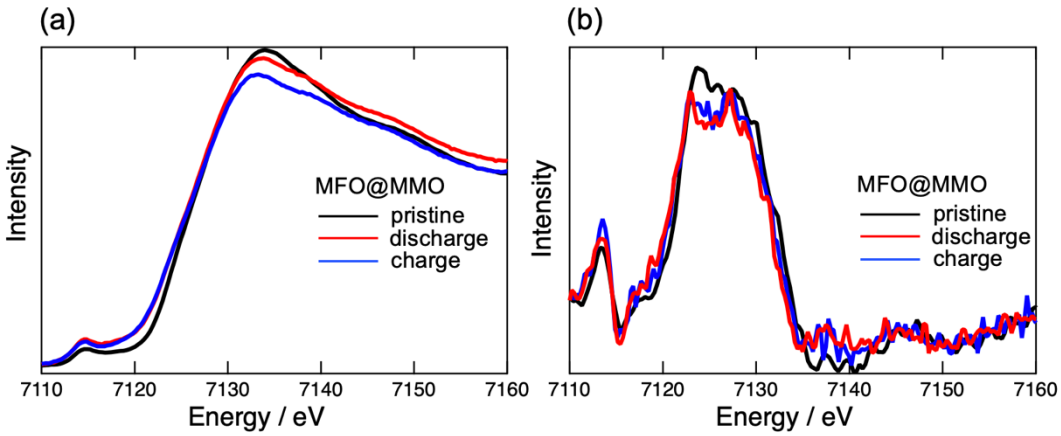

Fig. S9 (a) Fe K-edge XANES spectra of MFO@MMO and (b) derivative plot.

References

1. Y. Sugawara, H. Kobayashi, I. Honma and T. Yamaguchi, *ACS Omega*, **5**, 29388 (2020).
2. F. Izumi and K. Momma, *Solid State Phenom.*, **130**, 15 (2007).
3. B. Ravel and M. Newville, *J Synchrotron Radiat.*, **12**, 537 (2005).