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Supporting Information

Alluaudite $LiMnPO_4$: New Mn-based positive electrode for Li rechargeable batteries

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S1. Experimental

S1. 1. The synthesis of $Na_{0.67}MnPO_4$

$NaNO_3$ (Sigma Aldrich, 98%), Mn_2O_3 (Sigma Aldrich, 98%), MnO (Sigma Aldrich, 98%), and $NH_4H_2PO_4$ (Fluka, 98%) with molar ratios of 0.67 : 0.33 : 0.67 : 1 were used as precursors. They were thoroughly mixed and grounded by high energy ball-milling. The mixed precursors were then fired at 350°C under O_2 conditions for 5 hours. The mixture was then re-ground and manually pelletized using a disk-shaped mold. After pre-heating, we calcined the pellet at 685°C under O_2 conditions for 10 hours.

S1. 2. The ion-exchange process of $Li_{0.67}MnPO_4$

The powder was mixed with 5 times excess amount of the eutectic composition of $LiNO_3$ (99%, Sigma Aldrich) and LiCl (99%, Sigma Aldrich). The mixture was heated at 280°C for 15 minute in air. After ion exchange, the mixture was rinsed/filtered with distilled water and ethanol several times. Finally, Li-containing powder was dried in air for a day in an oven.

S1. 3. Materials characterization

The stoichiometry of the delithiated compound was determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Powder XRD of all materials was carried out on a Bruker D8-Advantage powder diffractometer using Cu Kα radiation (= 1.54178 Å) from 2θ =10 to 60 ° at 1s per step of 0.01°. The *ex-situ* XRD of fully lithiated alluaudite-$LiFePO_4$ was determined by XRD (Bruker D8 ADVANCE) with Cu Kα radiation (= 1.54178 Å). Data were recorded over a 2θ range of 10° to 60 °, with a step size of 0.01°.

ND data were collected over a 2θ range between 0^{o} and 180^{o} with a step size of 0.05^{o}, and λ = 1.388141 Å in *a*-$Na_{0.67}MnPO_4$ and λ = 1.8348 Å in *a*-$Li_{0.67}MnPO_4$ analysis were supplied by a Ge (331) single-crystal monochromator on a high-resolution powder diffractometer (HRPD) at the HANARO facility at the Korea Atomic Energy Research Institute. Structural refinements were done by the Rietveld method with Fullprof software. Mn K-edge X-ray absorption spectra (XAS) were taken on the 8C beamline at the Pohang Accelerlator Laboratory (PAL). Mn K-edge energy calibration was performed using Mn metal foil as reference. A reference spectrum was simultaneously recorded for *in-situ* spectrum using Mn metal foil.

S1. 4. Electrochemistry

Electrochemical tests were performed in a CR2016-type coin cell assembled in an Ar-filled glove-box. The slurry of 70 wt% $Na_{0.67}MnPO_4$ or $Li_{0.67}MnPO_4$, 20 wt% carbon black (Super-P), and 10 wt% polyvinylidene fluoride dispersed in N-methy1-2-pyrrolidone (NMP) was prepared and cast on aluminum foil. NMP was evaporated at 120°C for 2 hours. Electrochemical cells were assembled in a CR2016 type coin cell with a Li counter electrode, separator (Celgard 2400), and 1 M $LiPF_6$ electrolyte in a mixture of 1:1 ethyl carbonate/dimethyl carbonate in an Ar-filled glove box. The charge/discharge test was performed using a galvanostat (WonA Tech).

S1.5. Electrical Conductivity (ac) Measurements

The powder was pressed into pellets with 15 mm diameters and ~2 mm thicknesses using a uniaxial press (400 kg cm^{-2}). It was further compacted at 200 MPa for 5 min by cold isostatic

press and sintered at 300 ^{o}C during 12 hour. The 50 nm-thick platinum layers were deposited on both sides of the pellet by sputtering. The bulk conductivities of the pellet was measured using two-probe ac impedance spectroscopy (models 1260 and 1296; Solatron, UK) and the ZView electrochemical impedance software (Scribner Associates, U.S.). EIS data were recorded from 10 MHz to 1 Hz. Bulk conductivities (ac) were calculated from both the geometries of the pellets and the bulk resistance values, which were obtained by one-circle fitting of the high-frequency region in the EIS spectra. Finally, activation energies (ac) were obtained using linear interpolation of the conductivity values at various temperatures by the Arrhenius equation: $\sigma T = \sigma_0 \exp(-E_a/k_B T)$, where σ is conductivity, T is temperature, E_a is activation energy, and k_B is the Boltzmann constant.

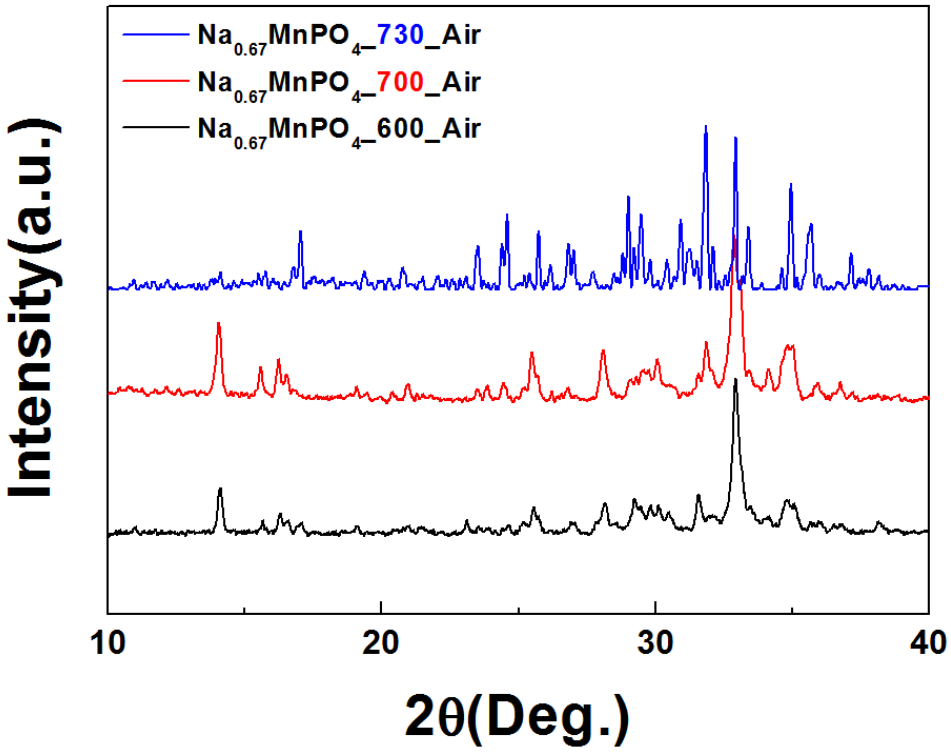


Figure S1. The XRD patterns of alluaudite $Na_{0.67}MnPO_4$ at various calcination temperature (600°C, 700°C, and 750°C) in air condition

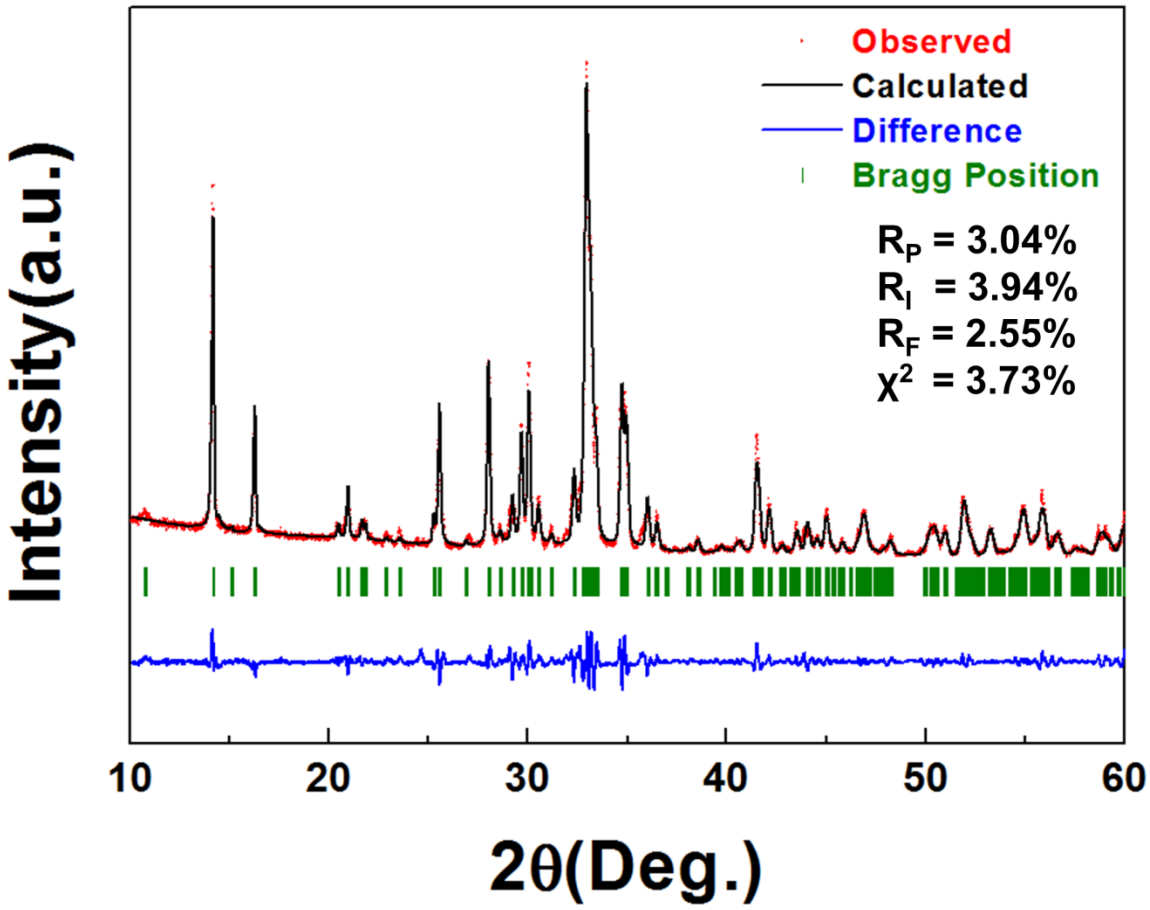


Figure S2. The XRD pattern of alluaudite $Na_{0.67}MnPO_4$

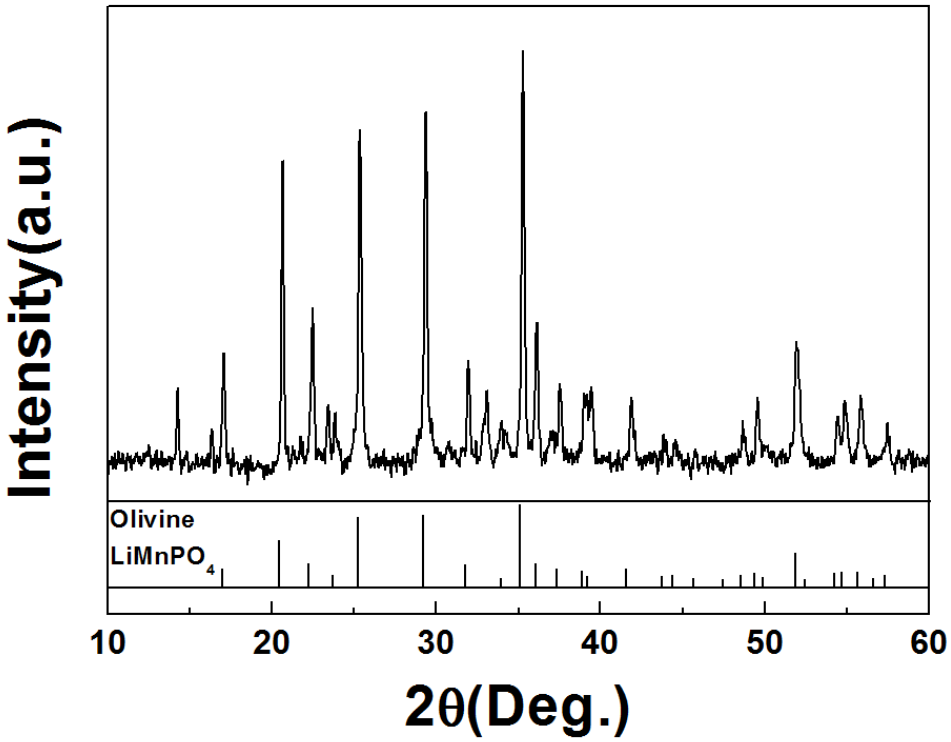


Figure S3. The XRD pattern of ion-exchanged alluaudite $Li_{0.67}MnPO_4$ at harsh condition (The powder was mixed with 10 times excess amount of the eutectic composition of $LiNO_3$ and LiCl for 1 hours at 280°C)

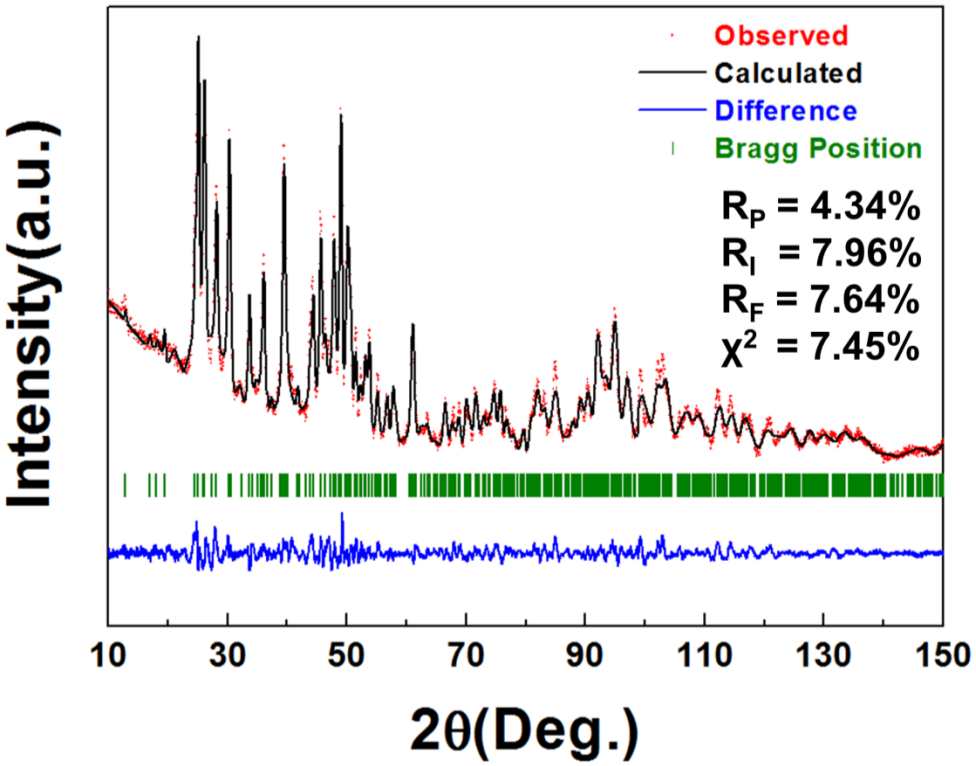
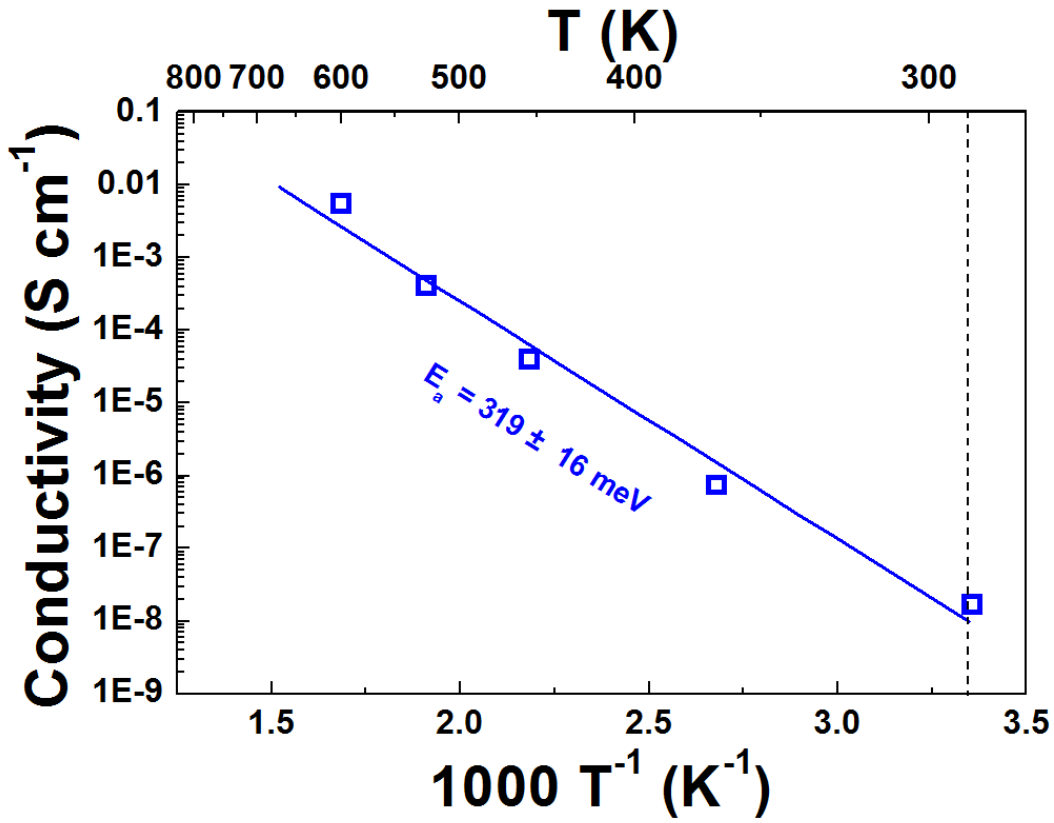
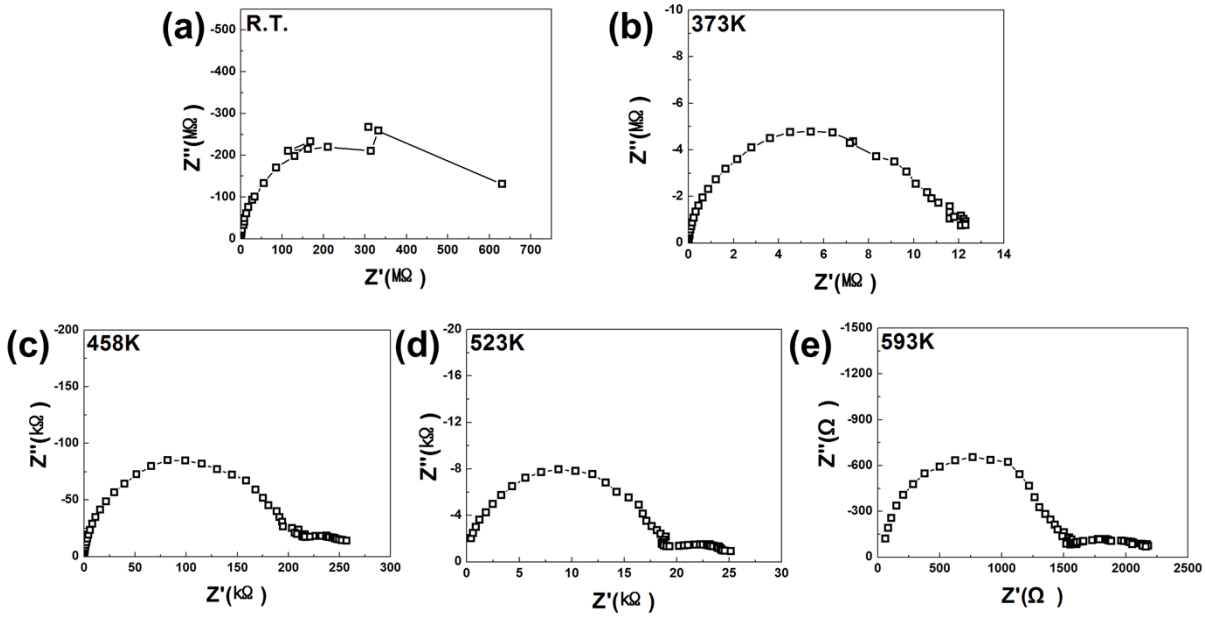


Figure S4. The refined ND pattern of alluaudite $Li_{0.67}MnPO_4$



Supporting Figure S5. Arrhenius plot of electrical conductivity of *a*-$Li_{0.67}MnPO_4$ pellet at various temperatures. Activation energies (*E*a) were calculated from the slopes of the fitted lines. *E*a for the former and the latter were 319 ± 16, respectively



Supporting Figure S6. Electrochemical impedance spectroscopy (EIS) spectra of *a*-$Li_{0.67}MnPO_4$ at (a) room temperature, (b) 373K, (c) 458K, (d) 523K, and (e) 593K.

		Lattice parameter
$Na_{0.67}MnPO_4$	***a***	12.0724(4) Å
	b	12.4615(5) Å
	c	6.6770(2) Å
	β	115.775(6) Å

Table S1. Lattice parameters of alluaudite $Na_{0.67}MnPO_4$