

Electronic Supplementary Information (ESI)

Enhanced electrochemical performance of $\text{Li}_{2.72}\text{Na}_{0.31}\text{MnPO}_4\text{CO}_3$ as a cathode material in “water-in-salt” electrolytes

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Experimental

$\text{Na}_3\text{MnPO}_4\text{CO}_3$ was synthesized by the hydrothermal method. First, a solution A was made by dissolving 0.002 mol $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries) into DI (deionized water). Second, a solution B was made by dissolving 2 g Na_2CO_3 (Kishida Chemical) and 0.002 mol $(\text{NH}_4)_2\text{HPO}_4$ (Wako Pure Chemical Industries) into DI. After magnetic stirring, the mixture of solution A and solution B was transferred to an autoclave and heated at 120°C for 36 h. After cooling to room temperature, $\text{Na}_3\text{MnPO}_4\text{CO}_3$ (denoted as NMPC) was washed by DI and methanol before drying at 40 °C for 12 h.

$\text{Li}_3\text{MnPO}_4\text{CO}_3$ (denoted as LMPC) was synthesized by the ion exchange method with a starting material of NMPC using a sealed vessel in N_2 atmosphere. First, NMPC was transferred into a solution of 2 M LiBr (Wako Pure Chemical Industries) in 1-hexanol (Wako Pure Chemical Industries), and the obtained mixture was heated at 140 °C for 4 days with magnetic stirring. After cooling to room temperature, the samples were washed by DI and methanol several times.

$\text{LiTi}_2(\text{PO}_4)_3$ (denoted as LTP) was synthesized by the solid-state method. Stoichiometric amounts of TiO_2 (Sigma Aldrich), Li_2CO_3 (Kishida Chemical), and $\text{NH}_4\text{H}_2\text{PO}_4$ (Wako Pure Chemical Industries) were ball milled at a rotation speed of 400 rpm for 1 h using 3 mm diameter ZrO_2 balls. Before sintering at 900°C for 12 h with a heating speed of 200 °C/h in air, this mixture was dried and ground, then pressed into pellets.

Electrochemical testing

The electrochemical test in an organic electrolyte was carried out as follows. As-synthesized LMPC was ball milled with 50 wt% acetylene black (denoted as AB, Denka Co., Ltd.) at 200 rpm for 0.5 h in an Ar atmosphere. Cathode electrodes were fabricated by mixing 90 wt% LMPC/C with 10 wt% binder (polytetrafluoroethylene (PTFE), Daikin Industries Ltd.). After pellets with a diameter of 10 mm and a loading weight of 30 mg/cm² were fabricated, they were heated at 100 °C for 12 h in a vacuum oven. The pellets were then coupled with Li metal (Honjo Metal), an organic electrolyte of 1 M $\text{LiPF}_6/\text{EC}:\text{DMC}$ (1:1 volume ratio, Tomiyama Pure Chemical Industries), and a polypropylene separator (3501, Celgard). All of the operation involved in the assembly of coin cells (CR 2032) occurred in an Ar-filled glove box. The electrochemical test in an aqueous electrolyte was carried out as follows. Cathode pellets mixed with 90 wt% LMPC/C and 10 wt% PTFE were pressed into a diameter of 3 mm with a loading weight of 30 mg/cm². LTP as an anode was ball milled with AB with a weight percentage of 70:25 at 200 rpm for 0.5 h, and then LTP/C was heated at 400 °C for 4 h in N_2 . Anode pellets were mixed with 95 wt% LTP/C and 5 wt% PTFE. Aqueous battery testing in the three-electrode system was performed using a Ti metal mesh as a current collector, 10/15/21 m (mole of solute/weight of solvent)

LiTFSI as electrolytes, and Ag-AgCl/saturated KCl (RE-6, BAS Inc.) as a reference electrode. Aqueous battery testing of a full cell of a CR 2032 were performed using LTP as an anode and 15 m LiTFSI as an electrolyte.

Material characterization

Morphology and particle size were confirmed by scanning electron microscopy (SEM). The thermal stability analysis of LMPC was performed with a heating speed of 5 °C/min and Al₂O₃ as a reference material under N₂-flow using a Thermo Plus TG-DSC 8230 L system (Rigaku Corp.). Samples were characterized by X-ray diffractometry (XRD) measurements (50 kV and 300 mA, Cu-K α radiation, Rigaku Corp.). Chemical analysis of LMPC was accomplished by inductively coupled plasma analyses (ICP, Optima8300, PerkinElmerInc.).

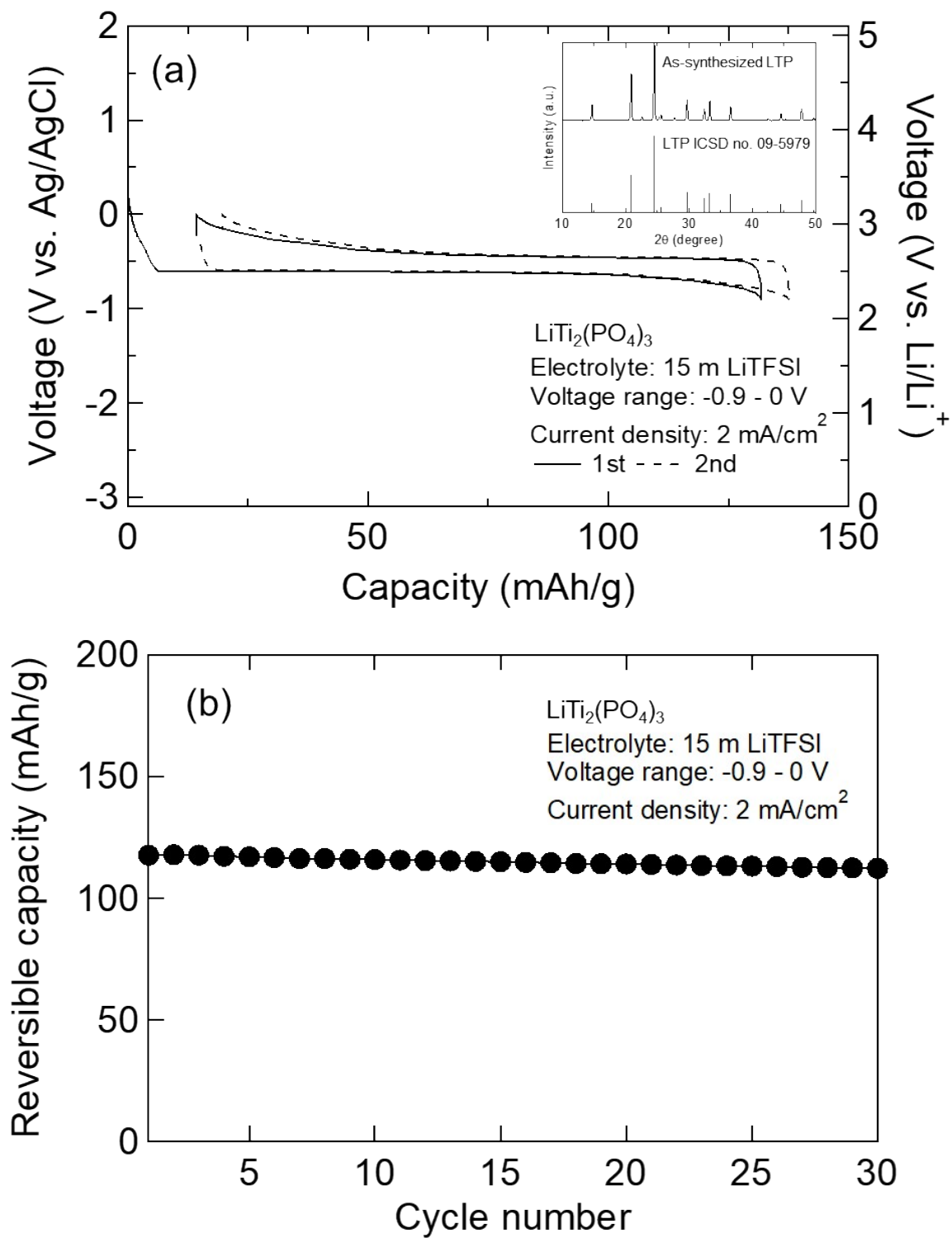


Fig. S1. XRD patterns (insets) and initial charge and discharge curves of LTP at a current density of 2 mA/cm² from -0.9 – 0 V (vs. Ag/AgCl) in 15 m LiTFSI (a); cyclability of LTP (b).

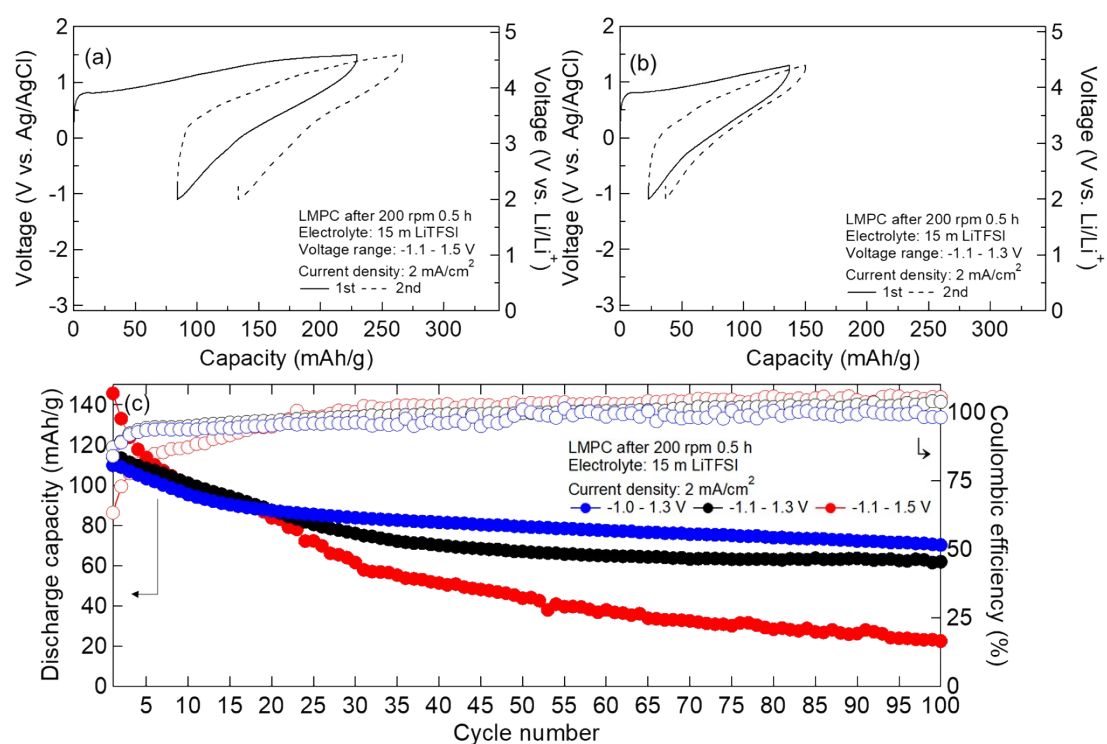


Fig. S2. Initial charge and discharge curves of LMPC//LTP at a current density of 2 mA/cm² in an aqueous electrolyte of 15 m LiTFSI from -1.1 – 1.3 V (a), -1.1 – 1.5 V (b); cyclability of various cutoff voltages after 100 cycles (c).

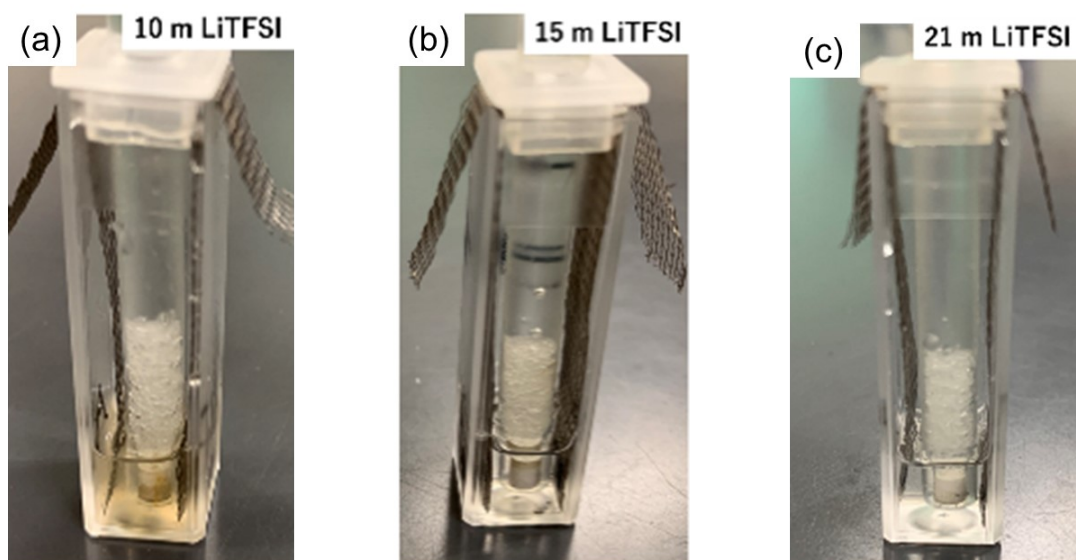


Fig. S3. The photo images of half cells of LMPC in 10 m (a), 15 m (b), and 21 m LiTFSI aq. after 100 cycles, respectively.

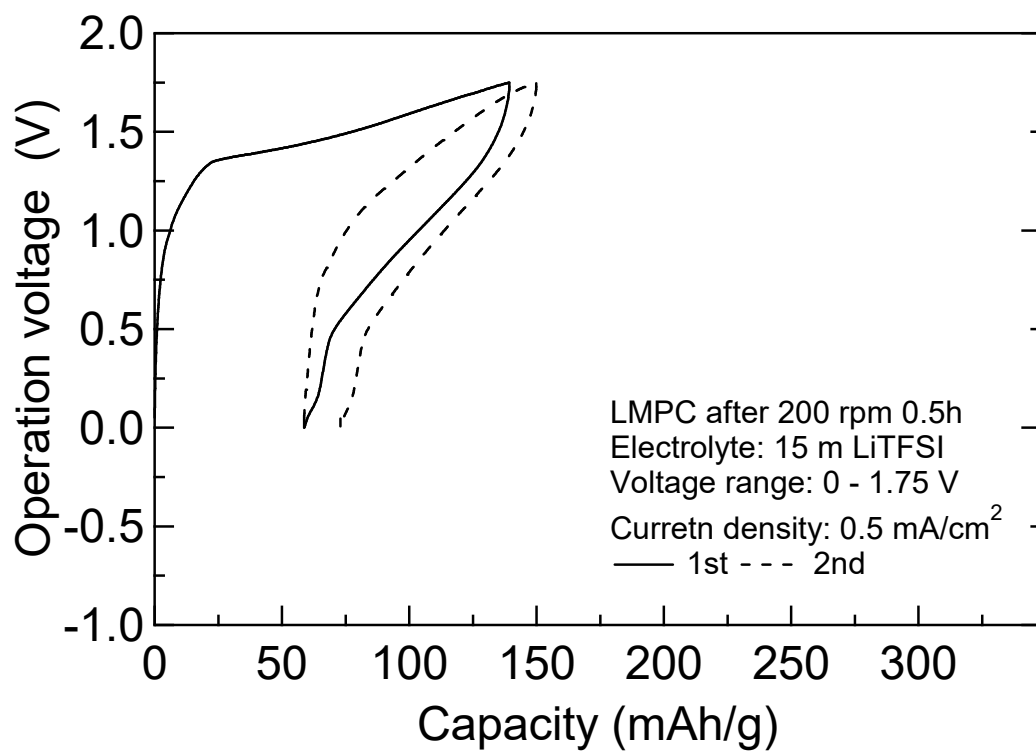


Fig. S4. Initial charge and discharge curves of LMPC//LTP in a coin cell at a current density of 0.5 mA/cm² from 0 - 1.75 V in 15 m LiTFSI.