

Supplementary data

Experimental

Synthesis: Li₂MnSiO₄nanoparticles were prepared from manganese chloride (II) tetrahydrate (Wako, Japan), tetra ethyl orthosilicate (TEOS: Wako, Japan) and Lithium hydroxide (Wako, Japan) were used as starting materials in 4:1:1 molar ratio. Ascorbic acid (Wako, Japan) was used as reducing agent. After dissolving appropriate amount manganese chloride (II) tetrahydrate in mixed solution of ethanol (15 ml) and water (5 ml) with constant stirring followed by addition of tetra ethyl orthosilicate and then lithium hydroxide. Finally, 0.1 mol of ascorbic acid was added and the solution mixture was stirred for 30 min. Later, the solution mixture (5 ml) was transferred to batch reactors (4 reactors, each 10 ml volume) followed by heating at 300 °C and at high pressure (38 MPa) for 5 min and then reactors were quenched in cold water. The products were recovered through repeated washings using ethanol and water.

Materials Characterization: The powder X-ray diffraction (XRD) analysis was carried out with a Bruker AXS D8 Advance instrument using Cu K α radiation. Transmission electron microscopy (JEOL TEM-2100F) high-resolution transmission electron microscopy (HR-TEM; JEOL JEM-2010F). X-ray photoelectron spectrophotometer of the product was carried out using ESCA SYSTEM (PHI 5600). Each spectrum was calibrated using the C1s binding energy at 284.6 eV. TG analysis was performed using TG-DTA 2000S to know the exact carbon content in Li₂MnSiO₄ nanoparticles. Electrochemical performances were recorded by assembling in a beaker type three electrode glass cell. Before measuring the charge-discharge, Li₂MnSiO₄ nanoparticles were carbon coated using PEDOT (20 wt%) by wet ball milling method. After ball milling the samples were dried at 300 °C under Ar/H₂ atmosphere and vacuum dried

overnight at 100 °C. The vacuum dried $\text{Li}_2\text{MnSiO}_4$ nanoparticles were ground well with 10 wt% acetylene black and 7 wt% PTFE (poly(tetrafluoroethylene)) binder was added to make the electrode paste. The weight ratio of PEDOT coated active material, AB and PTFE was 83:10:7. The prepared paste was spread uniformly on a 0.1 cm² Nickel sheet (100 mesh) using the doctor-blade method. The cathode loading was 6–8 mgcm⁻². Li metal on a Nickel mesh was used as a counter and reference electrodes. The electrolyte consist the solution of (18 to 20 ml) 1M LiClO_4 in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 by volume). The cell assembly was carried out in a glove box filled with high purity argon gas. The electrochemical performances of the prepared electrodes were characterized by galvanostatic charge-discharge (HOKUTO DENKO, Japan) in a potential range between 1.5 V to 4.5 V vs Li/Li⁺ and cyclic voltammetry (Solartron 1260, USA).

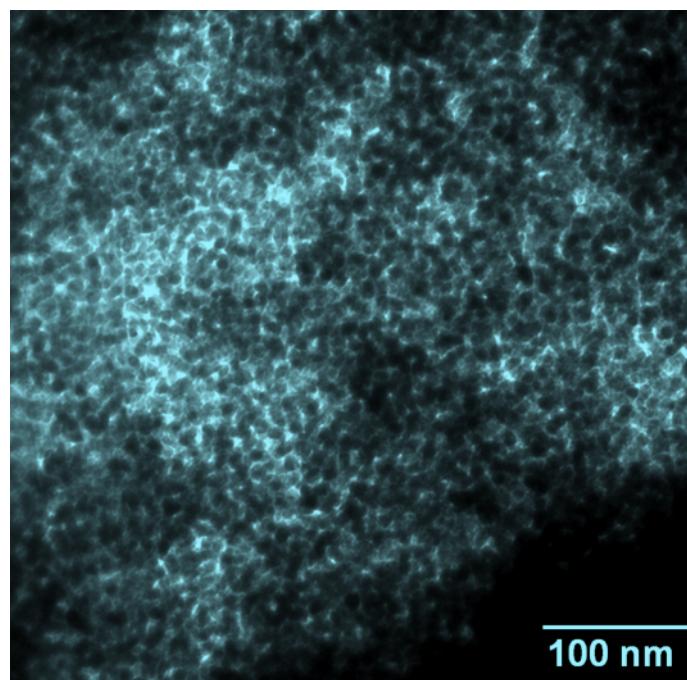


Fig. S1 TEM images of as –synthesized $\text{Li}_2\text{MnSiO}_4$ nanoparticles

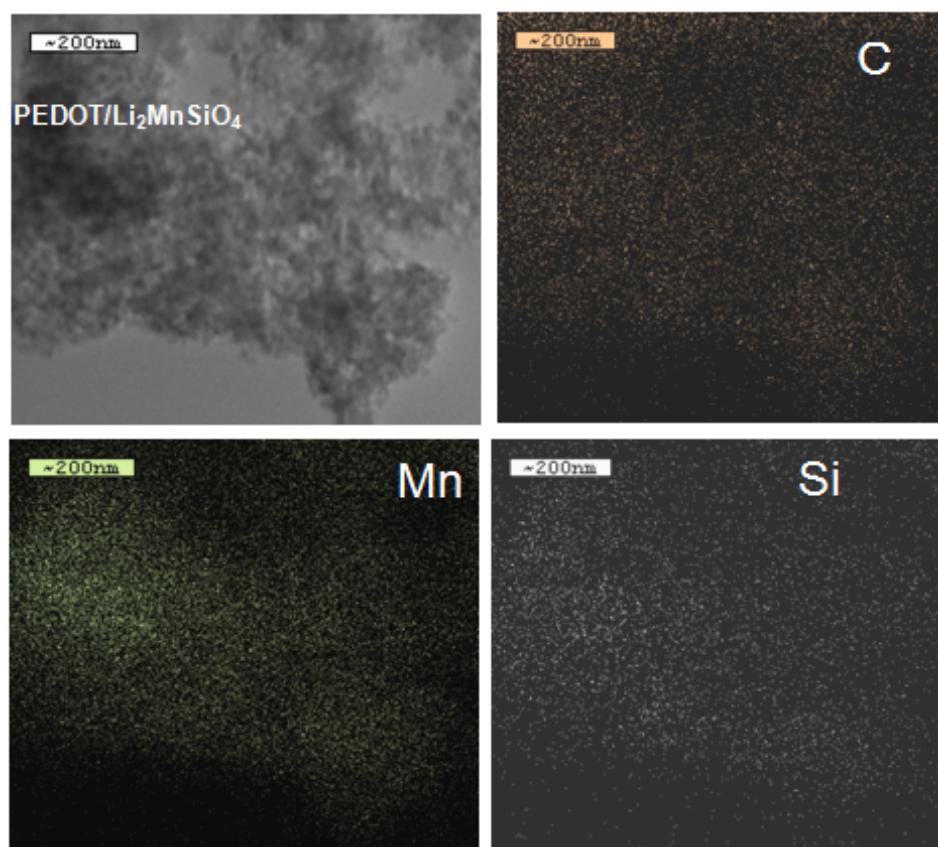


Fig. S2 STEM image of PEDOT coated Li₂MnSiO₄ nanoparticles showing the presence of carbon, Mn and Si.

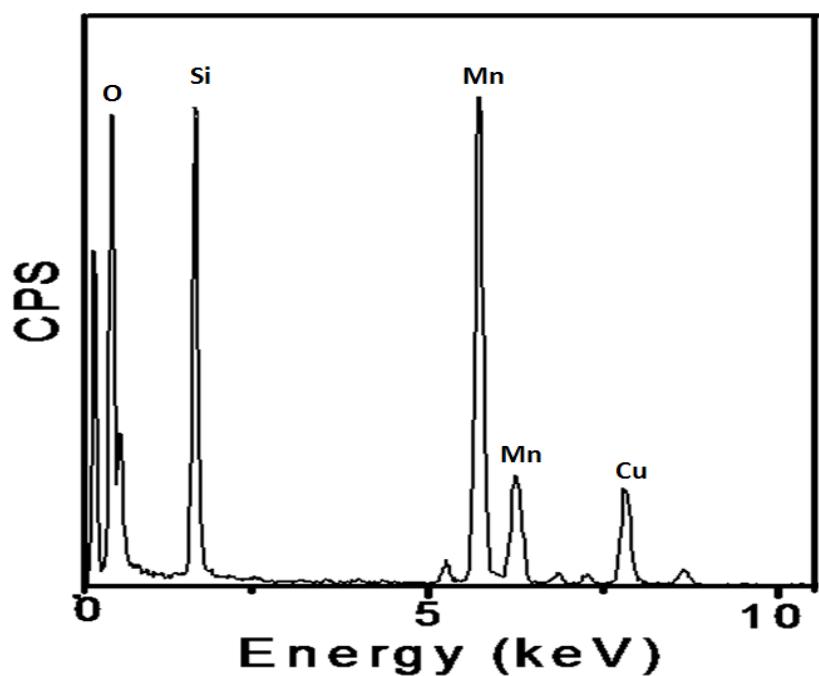


Fig. S3. EDS spectra of $\text{Li}_2\text{MnSiO}_4$ nanoparticles measured on Cu grid showing the presence of Mn, Si and O.

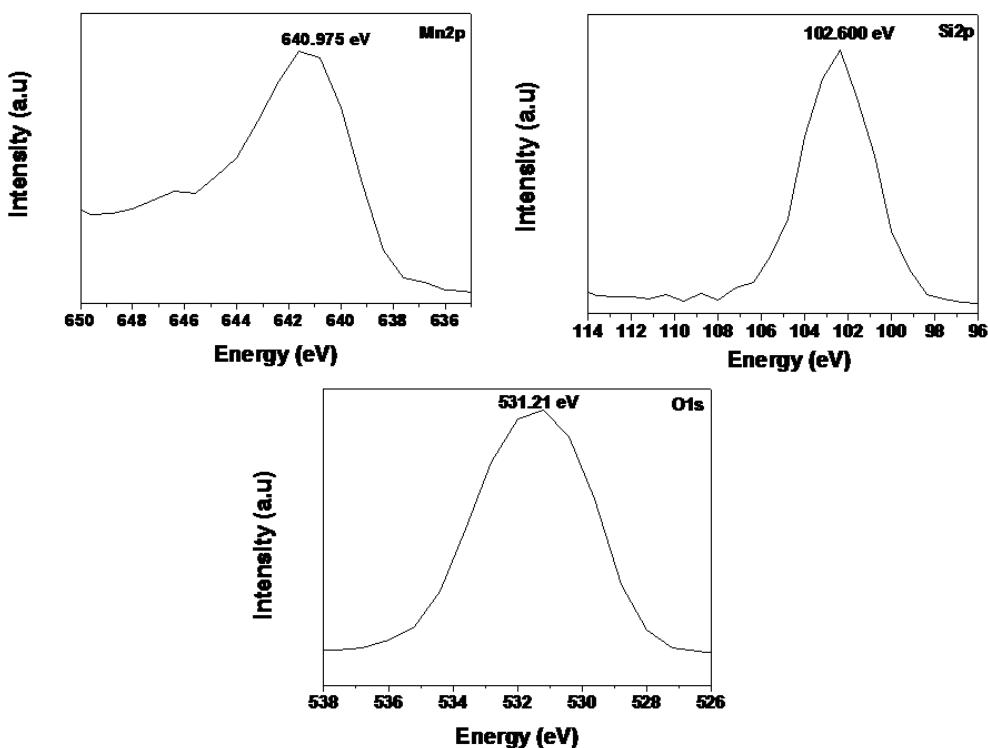


Fig. S4 XPS analysis of $\text{Li}_2\text{MnSiO}_4$ showing the presence of valance of Mn as Mn^{2+} , Si2p and O elements suggesting the purity of the sample.

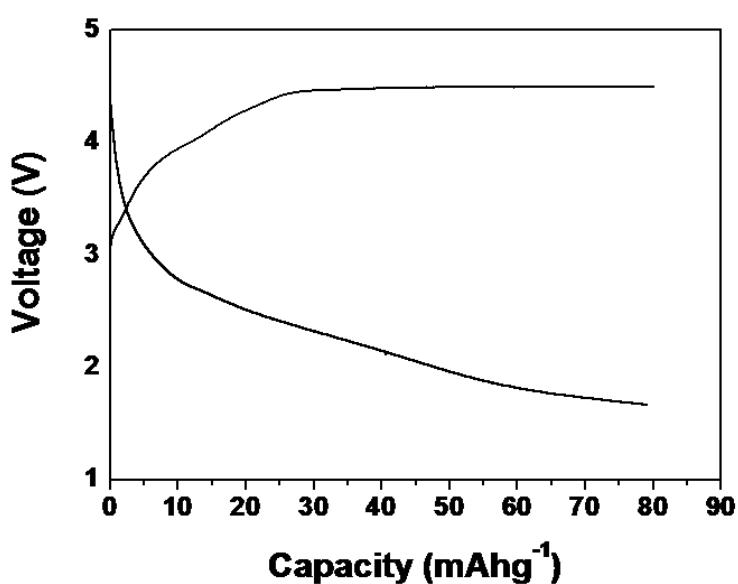


Fig. S5 Charge-discharge of pristine $\text{Li}_2\text{MnSiO}_4$ nanoparticles showing 80 mAh g^{-1} .

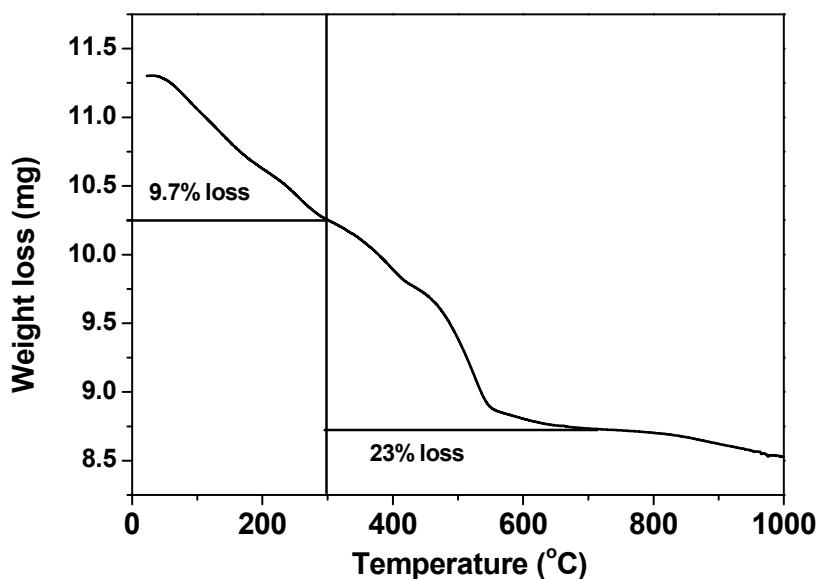


Fig. S6 TG analysis of PEDOT/Li₂MnSiO₄ nanoparticles showing 13.3% conductive carbon presence after 300 °C. Because sample was dried at 300 °C in Ar/H₂ atmosphere for 4h after wet ball milling.

To investigate the origin of potential plateaus, cyclic voltammetry (CV) was recorded for PEDOT/ Li₂MnSiO₄ nanoparticles. **Fig S7b** shows first two cycles in the potential window 1- 4.5 V at a scan rate of 0.1 mV/s at 40 °C. In the first and second cycles, two oxidation/reduction couples are observed at 3.2/2.8 and 4.23/3.15 V, respectively. For the two cycles, the positions of the oxidation/reduction couples remain the same. These values corresponds to the observed plateau regions in the charge-discharge profile of PEDOT/ Li₂MnSiO₄ measured at 40 °C and may originate from the Mn²⁺/Mn³⁺ and Mn³⁺/Mn⁴⁺ redox processes, respectively. The formation of two redox couples during electrochemical reaction may suggest the two stage Li-intercalation process in lithium metal silicate cathodes.

To know the presence of Mn³⁺ and Mn⁴⁺ in a charged PEDOT coated Li₂MnSiO₄ nanoparticles, XPS analysis was carried out. **Fig. S8a** shows the full scan spectra of PEDOT coated Li₂MnSiO₄ nanoparticles after charging to 4.5 V and which shows the X-ray signal of Mn, Si,O and PTFE (F1s signal from binder PTFE). **Fig. S8b** shows the Mn2p core level X-ray spectra, which consists of 2p1/2 and 2p3/2 of Mn³⁺ and Mn⁴⁺. The results showed the presence of Mn³⁺ and Mn⁴⁺ in the cathode after charging. The XPS and CV result confirms the two redox couples during charging and responsible for two lithium intercalation process.

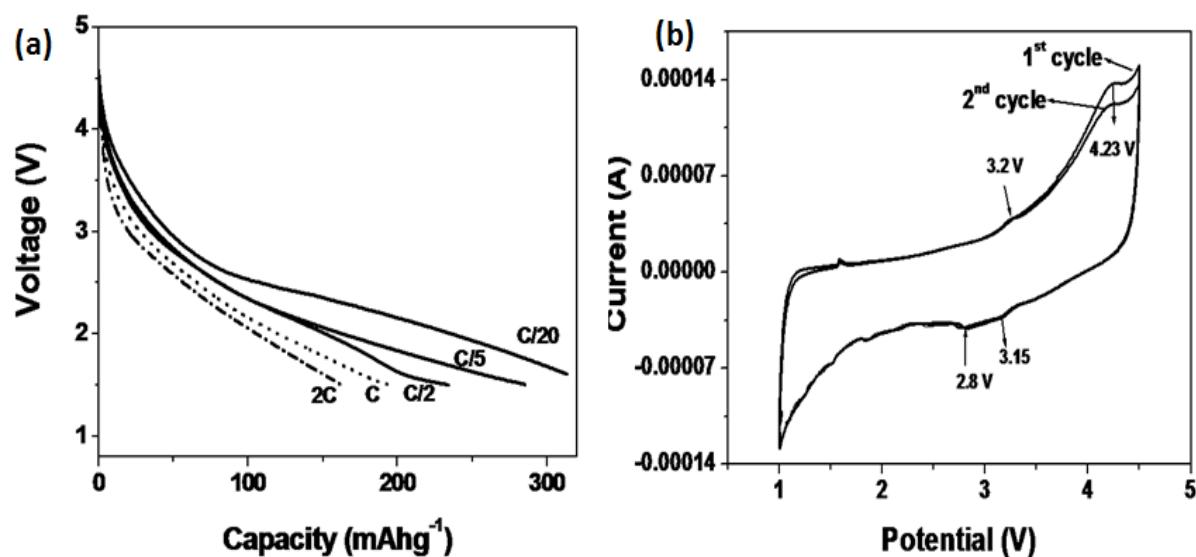


Fig. 7 (a) Discharge profiles recorded for PEDOT/Li₂MnSiO₄ nanoparticles at different C rates (at 40 °C) and (b) cyclic voltammetry of PEDOT/ Li₂MnSiO₄ nanoparticles recorded at C/20 in room temperature.

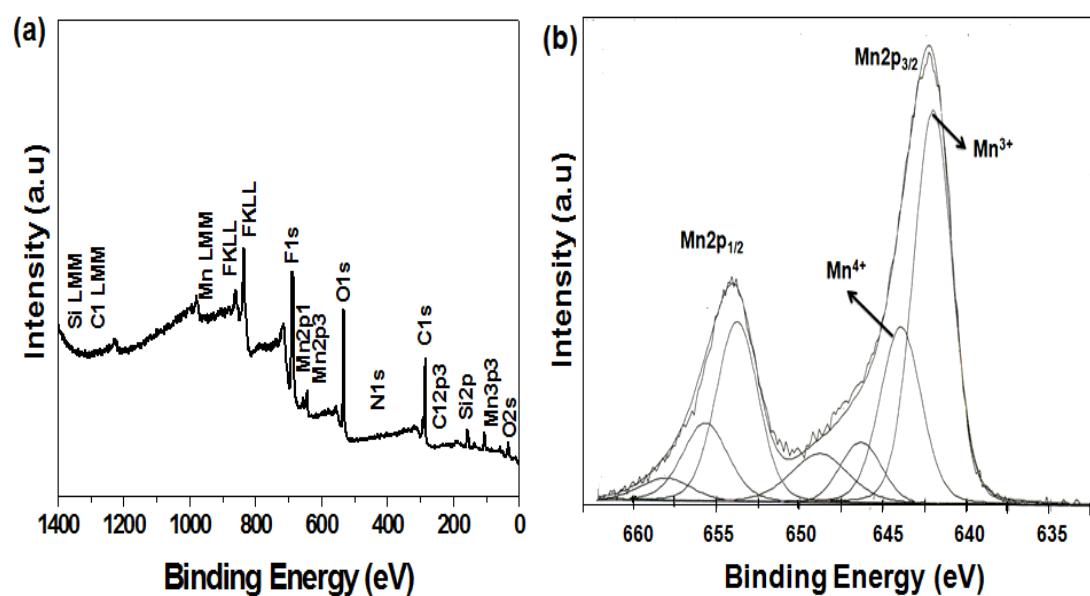


Fig. 8 XPS spectra of (a) full scan of PEDOT coated Li₂MnSiO₄ nanoparticles after the first charge, and (b) the Mn 2p core level X-ray Al-Kα spectra together with fitting lines.