Supporting Information

Ultra-thin Nanosheets of Li_2MSiO_4 (M=Fe, Mn) as High-Capacity Li-Ion Battery Electrode

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Experimental Section

Synthesis

Commonplace and inexpensive solvents water and ethanol were used as supercritical fluid (SCF) medium. All chemicals were purchased from Wako Chemicals. Firstly, a precursor solution was prepared by dissolving $FeCl_2 \cdot 4H_2O$ (0.1 mmol) and tetraethylorthosilicate in 15 ml ethanol at a constant temperature of 50 ºC. Solutions of $LiOH \cdot H_2O$ (0.4 mmol) and ascorbic acid (0.1mmol) were prepared by dissolving each compound separately in 5 ml water. These solutions were slowly added to the precursor solution with constant stirring over a period of 1h. In a typical synthesis, about 5 ml of precursor solution was charged into a 10 cc^3 volume stainless steel reactor and heated up to 350–420 ºC at a pressure of 38 MPa for 4–10 min. The reaction was then terminated by quenching the reactor in a cold water bath. The resultant Li_2MSiO_4 nanosheets were collected by repeated washing and centrifugation with ethanol, followed by drying in a vacuum oven at 120 ºC for 12 h. The resulting products showed a highly crystalline nanosheet structure. The conductivity of the samples were improved by ball milling the dried samples with the conductive polymer (PEDOT 10 wt-%) and multiwall carbon nanotubes (5 wt-%) at 300 rpm for 12 h followed by mild heat treatment at 300 ºC for 4h in Ar atmosphere.

Material characterization

The crystal structures were examined by X-ray diffraction (XRD) analysis using a Bruker AXS D8 Advance instrument with Cu Kα radiation. Crystal morphology was observed using high-resolution transmission electron microscopy (HRTEM; JEOL JEM-2010F). Atomic Force Microscopy (AFM) measurements were carried out using an S-image, Multi-Function unit. Sample suspensions were applied directly onto the substrate, which comprised a thin layer of native oxide on Si (100), by means of a spin coating method. After drying the substrate in a clean environment at room temperature, the measurements were performed in air at

ambient temperature and pressure. The X-ray photoelectron spectra were recorded using a PHI5600, ESCA System with monochromated Al X-rays. Electrochemical measurements were carried out using a Solartron Instrument Model 1287 system controlled by a computer.

Electrochemical characterization

The electrochemical properties of Li_2MSiO_4 nanosheets were studied using a beaker–type three–electrode cell assembly. The samples were vacuum dried overnight at 100 ºC before assembling the cell. The dried Li_2MSiO_4 nanosheet samples were mixed and ground with acetylene black and Teflon (poly(tetrafluoroethylene)) binder in a weight ratio of 85:10:5. The prepared paste was uniformly spread on a 0.1 cm^2 stainless steel SUS sheet (100 mesh). The cathode loading was 4–5 mg/cm^2. Li metal on stainless steel SUS mesh was used as counter and reference electrodes. The electrolyte consisted of a solution of 1 M $LiClO_4$ in ethylene carbonate (EC)/diethyl carbonate (DEC) (1/1 by volume). Cell assembly was carried out in a glove box filled with high–purity argon gas. The charge-discharge tests were performed with a Solartron Instrument Model 1287 controlled by a computer, in the potential range of 1.5–4.8 V versus Li under different current densities.

Supporting Information Figures

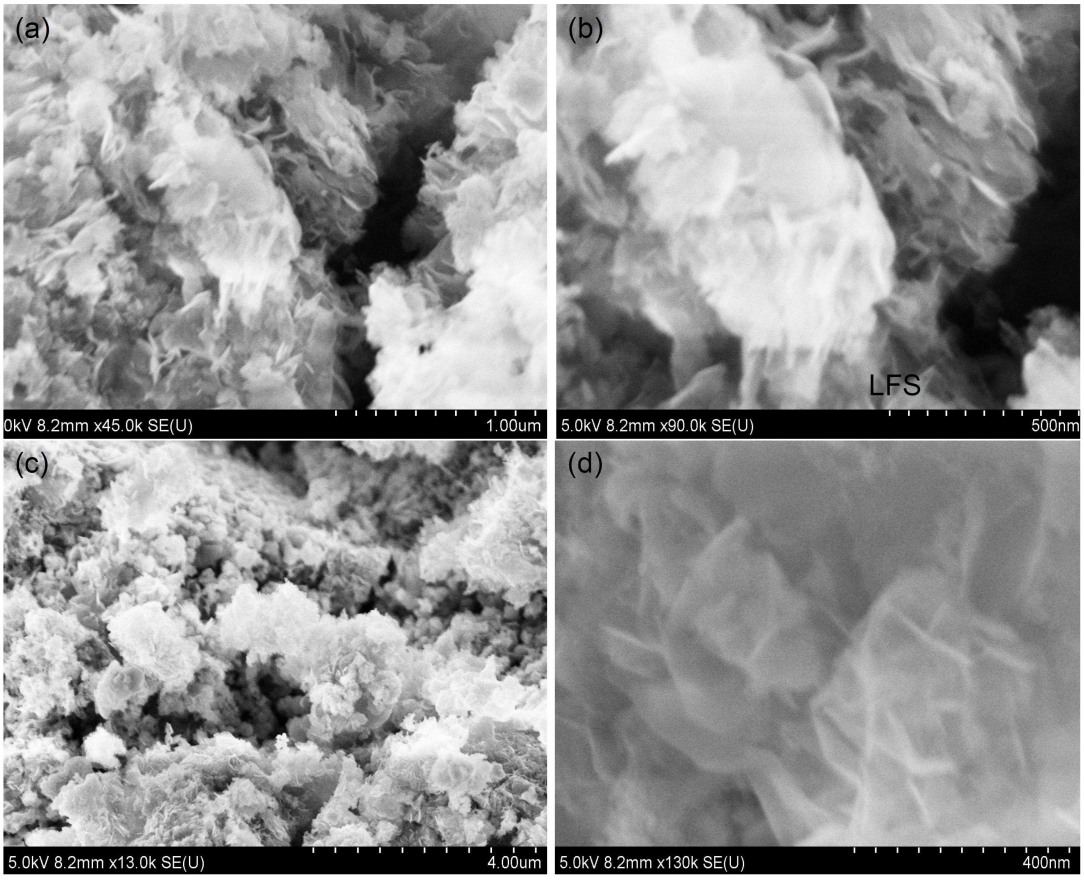

Figure S1. FE–SEM images of nanosheets samples: (a) – (b) Li_2FeSiO_4, and (c) – (d) Li_2MnSiO_4 samples synthesized by supercritical fluid process at 400ºC temperature for 10 min reaction time.

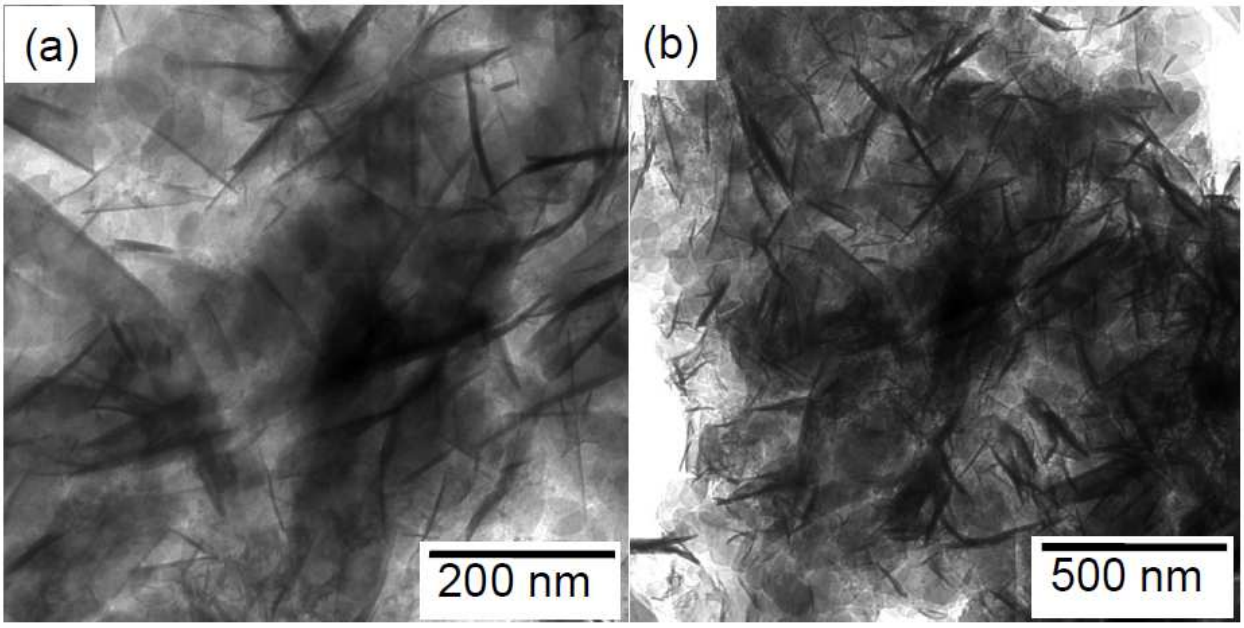

Figure S2. TEM image of lithium metal silicate samples containing mixture of nanosheets and nanoplates: (a) Li_2FeSiO_4, (b) Li_2MnSiO_4 synthesized at 400 ºC.

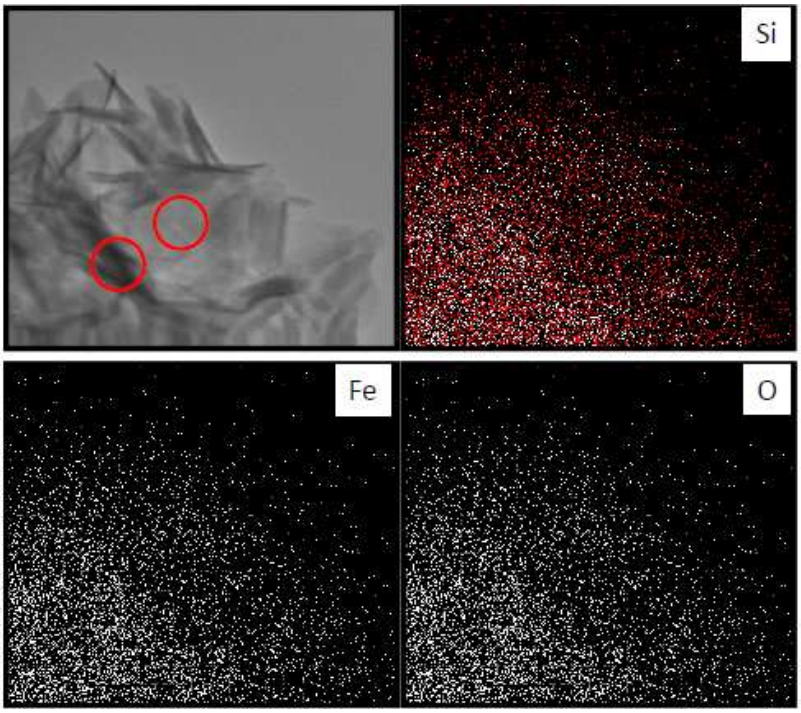

Figure S3. Elemental mapping of Li_2FeSiO_4 nanosheets. Uniform distribution of Fe, Si, and O atoms throughout the sheets can be seen, which indicates that sheet morphology comprises of Li_2FeSiO_4.

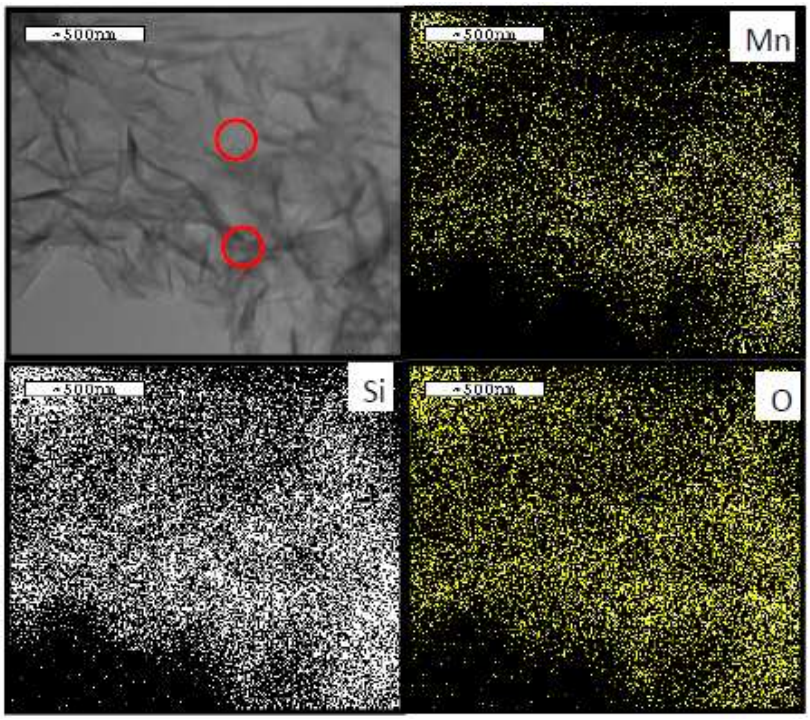

Figure S4. Elemental mapping of Li_2MnSiO_4 nanosheets. Uniform distribution of Mn, Si, and O atoms throughout the sheets can be seen, which indicates that sheet morphology comprises Li_2MnSiO_4.

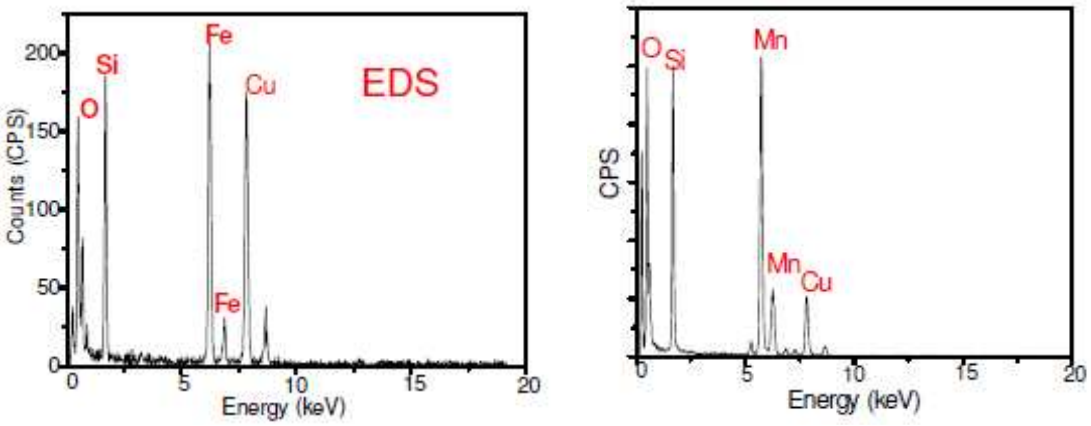

Figure S5. Energy dispersive spectra of Li_2FeSiO_4 and Li_2MnSiO_4 samples obtained by supercritical fluid process, at 400 ºC temperature and 10 min reaction time.

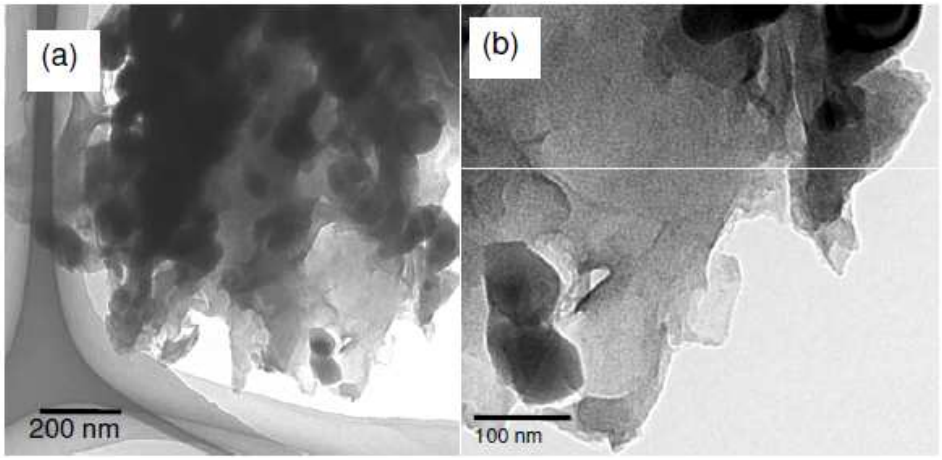

Figure S6. TEM images of Li_2MnSiO_4 after ball milling at 300rpm followed by mild heat treatment at 300 °C for 4h, under Ar + H_2 (5%) atmosphere.

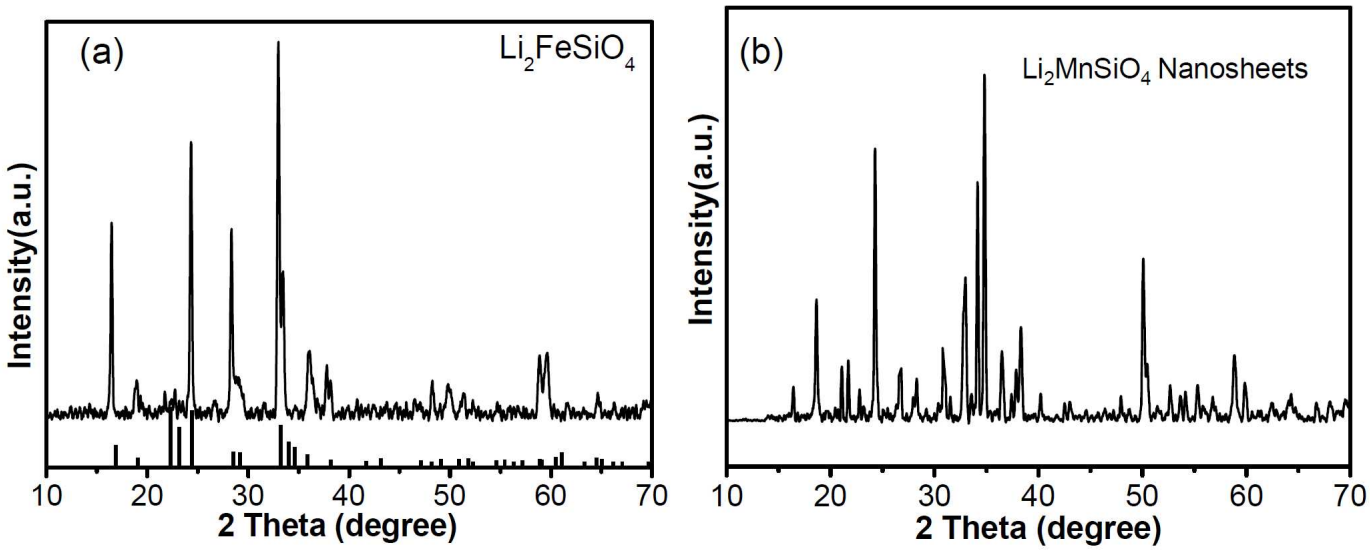

Figure S7. XRD patterns of (a) Li_2FeSiO_4, (b) Li_2MnSiO_4 samples synthesized by supercritical fluid process at 400°C temperature for 10 min reaction time.

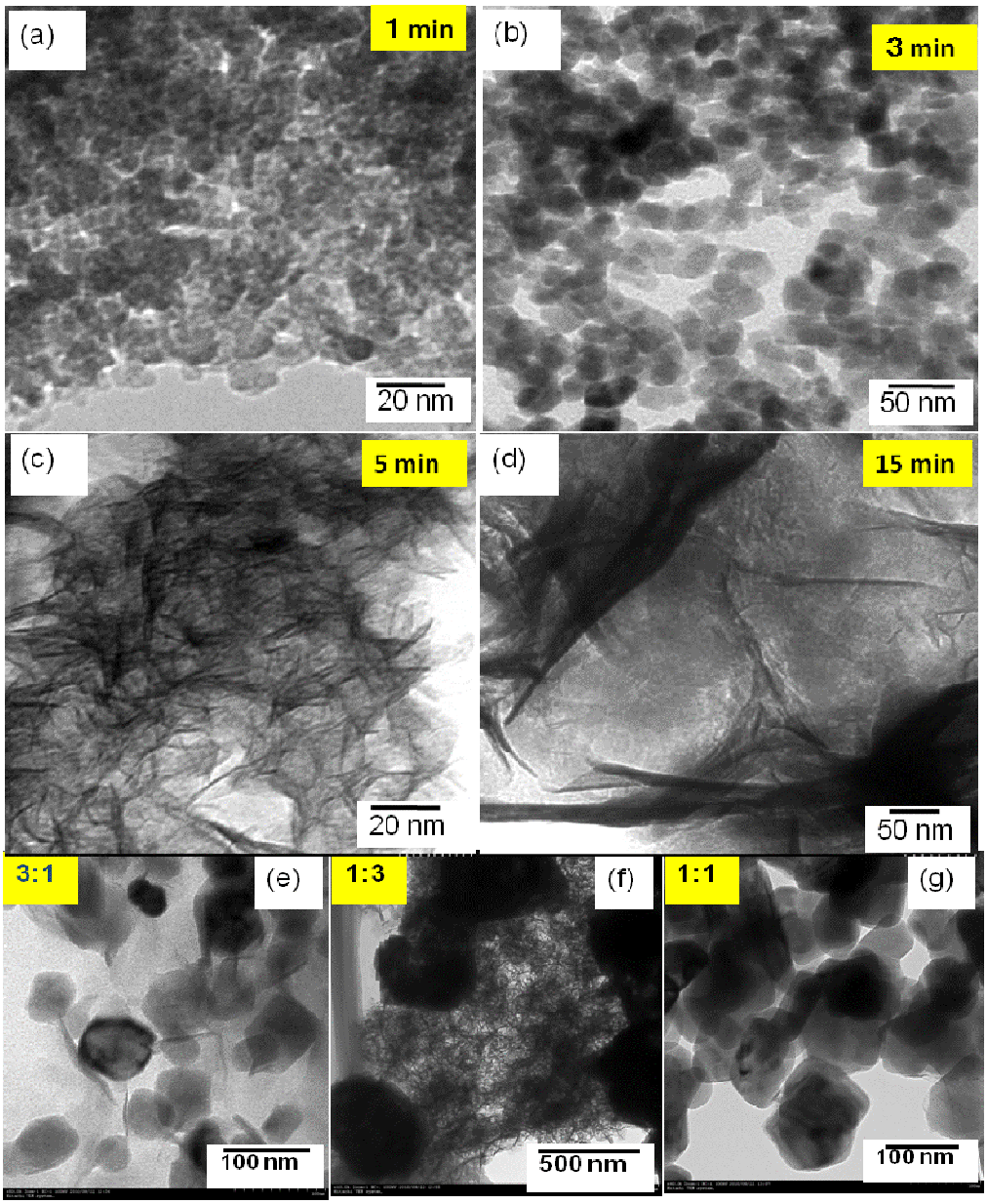

Figure S8. TEM images of Li_2MnSiO_4 samples synthesized at various reaction times: (a) 1 min; (b) 3 minutes, (c) 5 min, (d) 15 min. Images (e)–(g) show the Li_2MnSiO_4 samples synthesized using different solvent (water : ethanol) ratios at 400 °C.

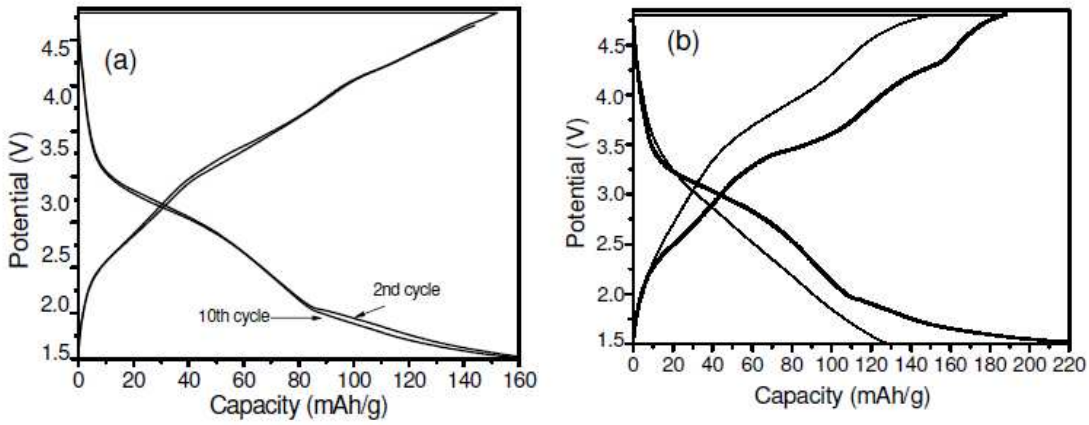

Figure S9. Charge-discharge profile of: (a) Li_2FeSiO_4, (b) Li_2MnSiO_4 samples measured at room temperature. The current rate for charge-discharge measurement was 0.02C.

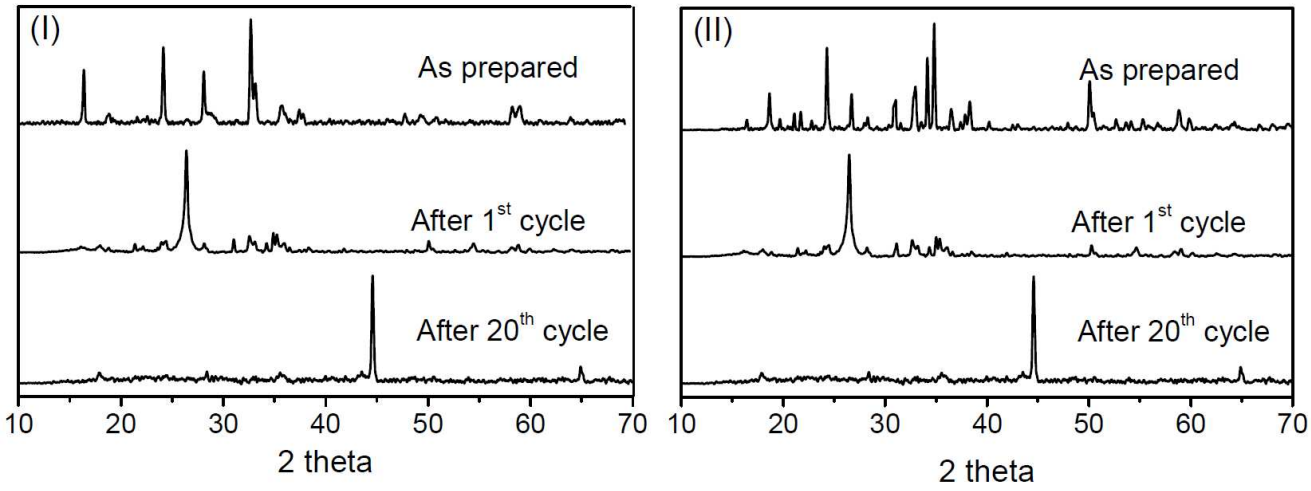

Figure S10. XRD patterns of lithium metal silicate samples before and after charge-discharge measurements: (I) Li_2FeSiO_4 and (II) Li_2MnSiO_4 electrode measured at 45 ºC. The current rate for charge-discharge measurement was 0.02 C.

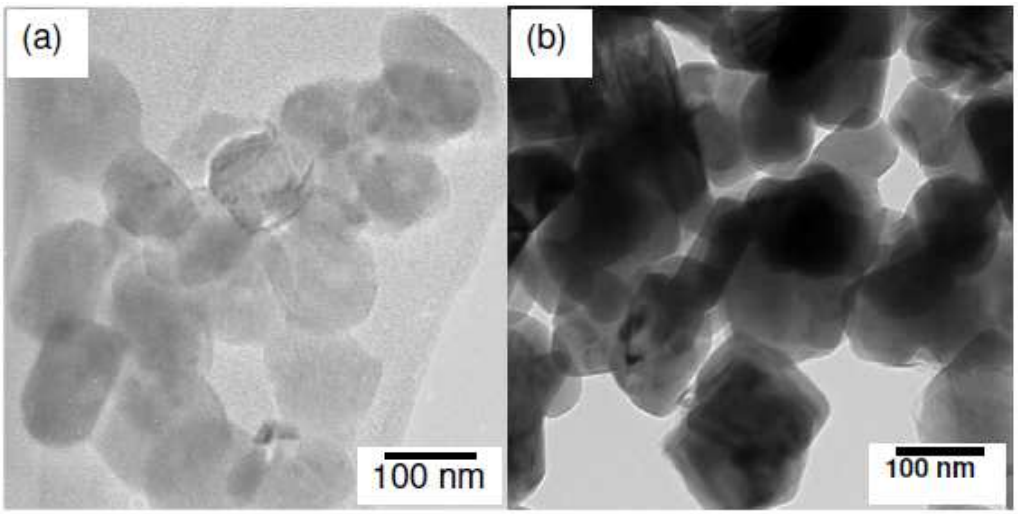

Figure S11. TEM image of lithium metal silicate nanocrystals: (a) Li_2FeSiO_4, (b) Li_2MnSiO_4 synthesized at 400 ºC.

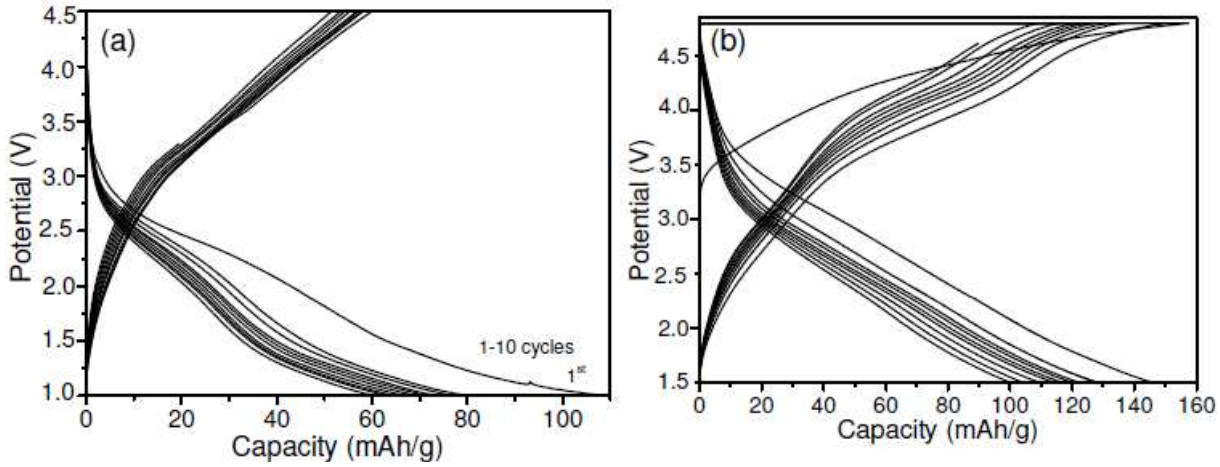

Figure S12. Charge-discharge profile of lithium metal silicate nanocrystals: (a) Li_2FeSiO_4 and (b) Li_2MnSiO_4 electrode measured at 45 ºC. The current rate for charge-discharge measurement was 0.02 C.

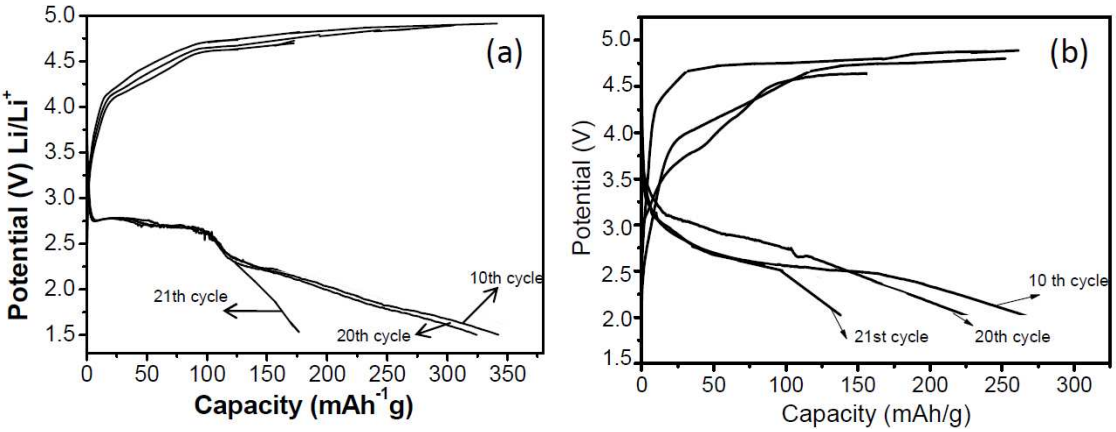

Figure S13. Charge-discharge profile of 10^{th} and 20^{th} cycles of: (a) Li_2MnSiO_4 and (b) Li_2FeSiO_4 electrode measured at 45 ºC. The current rate for charge-discharge measurement was 0.02 C.