Supplementary Data

Experimental

***Synthesis*:** The organic-inorganic hybrid polymers with the composition of 40 wt% SiO_2 (COMPOCERAN P501) and 70wt% SiO_2 (COMPOCERAN HBP70) in their hardening resins were kindly supplied by Arakawa Chemical Industries Ltd. An aqueous solution of $LiOH{\cdot}H_2O$ was dropwise added under magnetic stirring to a mixed ethanol solution containing the hybrid polymer and $Mn(CH_3COO)_2{\cdot}4H_2O$ with the stoichiometric molar ratio (Li/Mn/Si=2/1/1). The solution was stirred for 12 h at room temperature and then dried at 100 °C to evaporate ethanol and water. The residue was ball-milled at 300 rpm for 2 h and then was pre-calcined at 500 °C for 2 h in an Ar atmosphere, followed by the ball-milling for 36 h in ethanol and the calcination at 650 °C for 20 h. A nanocomposite of Li_2MnSiO_4 and carbon nanotubes (CNTs) was also synthesized by the similar manner. Single-walled CNTs (ASP-100F, Hanwha Nanotech Corp.) were dispersed in an ethanol by an ultrasound sonication (40 W, 42 kHz) for 1 h, and then COMPOCERAN HBP70, $Mn(CH_3COO)_2{\cdot}4H_2O$ and an aqueous LiOH were added to this solution in order under the sonication for 1 h to form a gel. The mixing ratio of CNTs/HBP70 was 1/14 by weight. The obtained gel was subjected to dryness, ball-milling and calcination treatments at the same conditions as mentioned above. The samples obtained by using COMPOCERAN P501 and HBP70 are abbreviated as LMS-P501 and LMS-HBP70, respectively. The LMS-HBP70 including CNTs is denoted as LMS-HBP70-CNT. A Li_2MnSiO_4 sample without CNTs, denoted as Bulk-LMS, was synthesized as a reference by using $Si(CH_3COO)_4$ instead of the hybrid polymer at the same synthetic conditions except for the final calcination condition of 700 °C for 24 h to yield a single crystalline phase.

***Instrumental Analysis*:** X-ray diffraction (XRD) patterns of samples were obtained on a Rigaku RINT-2200 diffractometer using Cu Kα radiation. The morphology of samples was investigated by scanning electron microscopy (SEM, JEOL JCM-5100), transmission electron microscopy (TEM, JEOL JEM-2010UHR) and N_2 adsorption/desorption isotherms (BEL Japan BELSORP-mini). The composition of Li, Mn and Si in samples was analyzed by induced coupled plasma atomic emission spectroscopy (Horiba, ULTIMA2). The amount of carbon remained in the samples was determined by elemental analysis (Parkin-Elmer 2400II analyzer). Raman spectra of samples were taken by using JASCO RMP-210 with 532 nm laser (100 mW). Electrochemical charge-discharge curves were measured on an electrochemical analyzer (Hokuto Denko, HJ1001SD8) using a beaker-type three-electrode cell with metallic Li as a counter and reference electrode at room temperature. The electrolyte used was a 1.0 mol dm^{-3} solution of $LiPF_6$ in ethylene carbonate/dimethyl carbonate (1/1 by volume). The composite samples mixed with poly(tetrafluoroethylene) (PTFE) and additionally acetylene black (AB) were pressed on Al mesh, and then were used as working electrodes; the weight ratio of sample/AB/PTFE was 62.5/25/12.5 for Bulk-LMS, 85/10/5 for LMS-HBP70, and 90/0/10 for LMS-P501 and LMS-HBP70-CNT. To minimize the effect of IR drop associated with the electrolyte resistance, the tip of a capillary in connection to the reference electrode was placed as close as possible to the working electrode. The electrode was charged by a constant current–constant voltage (CC–CV) mode and subsequent discharged by the CC mode. The CC mode measurement was carried out at the current density of 16.6 mA g^{-1} (C/20, 1C = 333 mA g^{-1}) based on LMS weight. The cut-off current of CV mode was set at 1.66 mA g^{-1}. The discharge process was carried out by the CC mode to the cut-off potential of 1.5 V vs. Li^+/Li. The charge-discharge property of CNTs was also measured by the same manner using a working electrode of a mixture of CNTs and PTFE (CNTs/PTFE = 90/10 by weight) pressed onto Al mesh.

Table S1 Atomic ratio of Li, Si and Mn in the samples

Sample	Li	Mn	Si
Bulk-LMS	2.10	1.00	1.33
LMS-P501	2.08	1.00	1.22
LMS-HBP70	1.92	1.00	1.29
LMS-HBP70-CNT	2.08	1.00	1.37

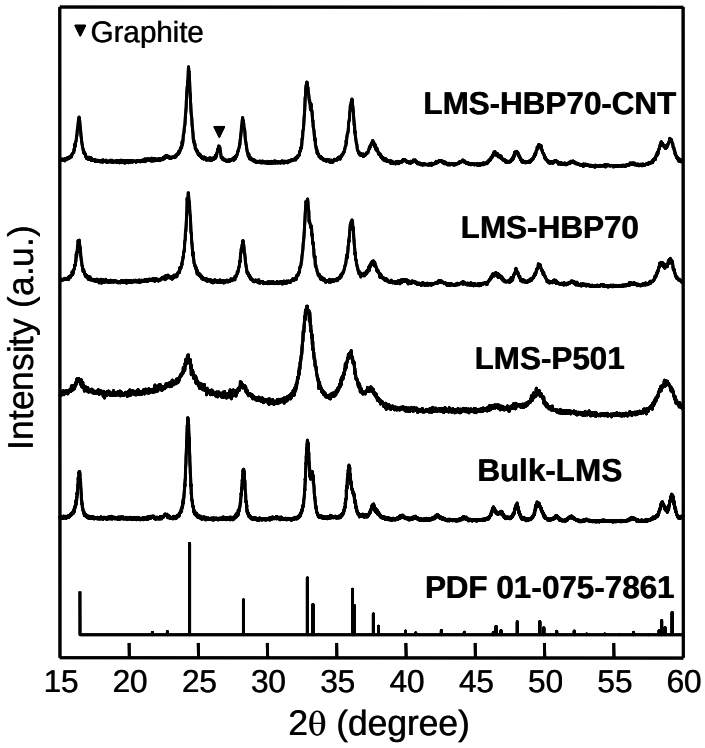

Fig. S1 XRD patterns of the samples.

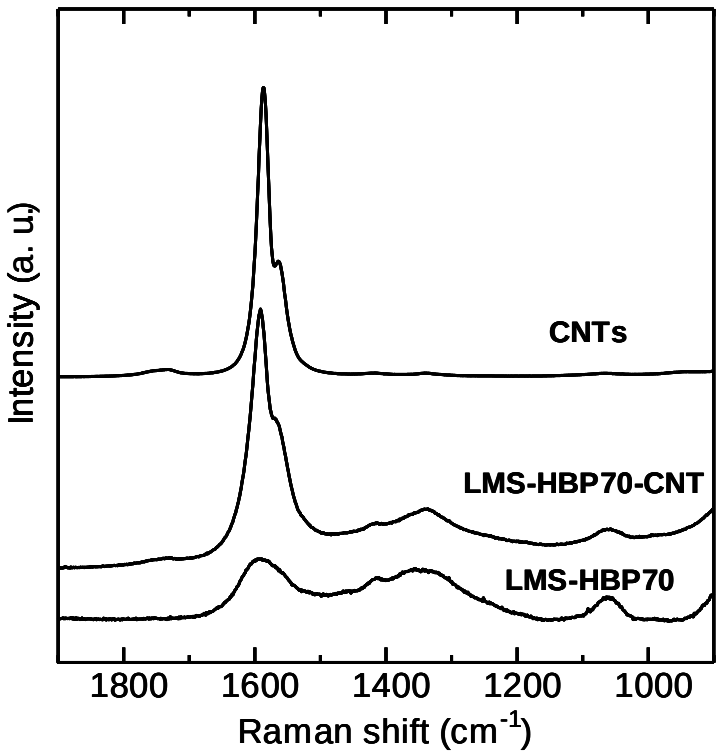

Fig. S2 Raman spectra of CNTs, LMS-HBP70-CNT and LMS-HBP70.

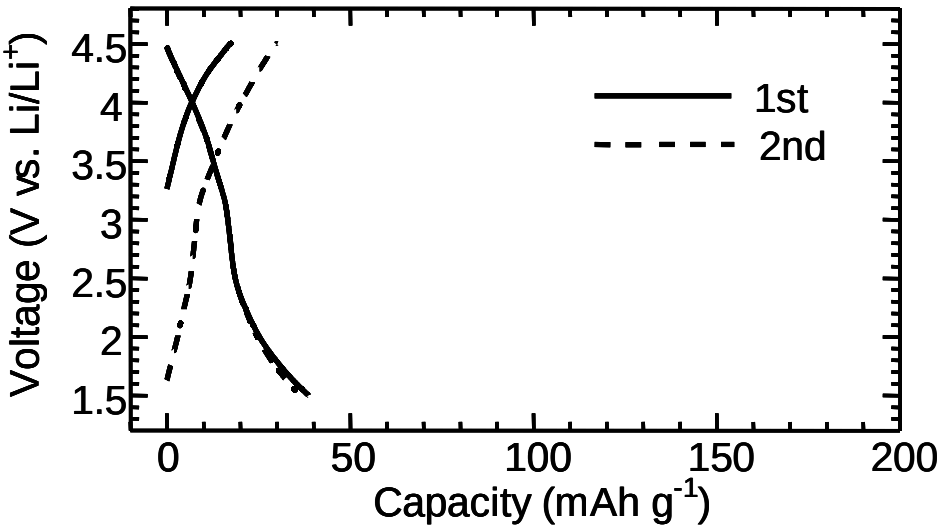

Fig. S3 1st and 2nd charge-discharge curves of CNTs.