Supporting informations

High stable post-spinel $NaMn_2O_4$ cathode of sodium ion battery

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Sample Preparation: The $CaFe_2O_4$-type $NaMn_2O_4$ sample was synthesized with a high-pressure high-temperature method using Na_2O_2 and Mn_2O_3 as starting materials.[26] The materials were mixed together in an agate mortar with a stoichiometric ratio and 5 at.% excess Na_2O_2 and pressed into a pellet. The pellet was sealed in an Au-capsule and heated at 1223 K under a pressure of 4.5 GPa for 1 h. The synthesized samples was washed by deionized water to eliminate water-soluble substances and post-heated at 623 K for 5 h in the air.

Structure Characterizations: Structure of the materials were analyzed by XRD of Bruker D8 using Cu Kα radiation at λ=1.54 Å. Morphologies were confirmed by a SEM of a LEO Gemini Supra 35 and TEM of JEOL 3100 F. Fourier transform infrated (FTIR) measurements were performed on a KBr pellet with sample by a JASCO instrument of FT/IR-6200 from 2000 to 400 cm^{-1}. Raman spectroscopy was conducted on a Micro Raman Spectrphotometer (Ventuno21, JASCO). All of the material characterizations were conducted on the as-synthesized samples. For the cycled sample characterizations, the cells were first subjected to certain cycles and disassembled in Ar-filled glove box, washed by blank EC:DEC and ethanol, finally collect the electrode materials for test.

Electrochemical Measurements: The electrochemical performance were conducted by coin cells (CR2032) consisting of a cathode, metallic sodium anode, separator and electrolyte. The $NaMn_2O_4$ cathode was prepared by mixing 60% $NaMn_2O_4$ powder, 30% acetylene black and 10% binder polytetra-fluoroethylene (PTFE) to form a film and pressed on a current collector of aluminum mesh. The electrodes were dried at 80 °C for 12 hours at vacuum. The microporous membrane Celgard 2400 was used as separator. The electrolyte was 1 M $NaPF_6$ dissolved in a

mixture of EC and DEC (1:1 by volume). The cells were assembled in an Ar-filled glovebox. The galvanostatic charge/discharge test was conducted in the voltage range of 2.0 to 4.0 V on a Hokuto Denko Battery Testing System. Cyclic Voltammetry (CV) was done with coin cells on a Solartron Instrument Model 1287 in the voltage range of 2.0-4.0 V at a varied scan rate from 0.1 to 0.5 mV/s.

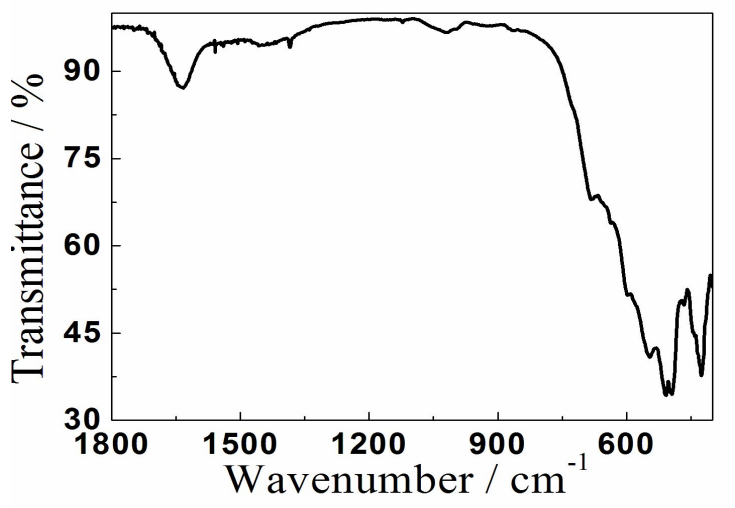

Figure S1. IR of as-prepared $NaMn_2O_4$

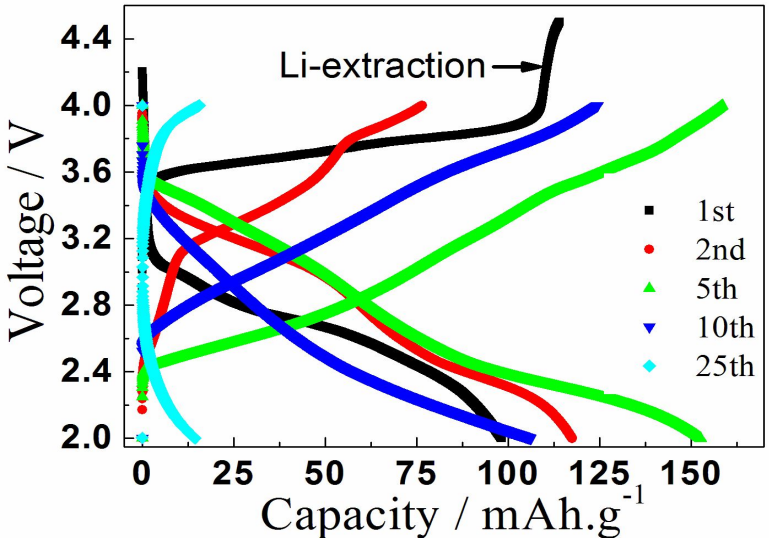

Figure S2. $LiMn_2O_4$/Na initial cycle at a current density of 5 mA/g in the voltage range of 2.0-4.5 V, the following 49 cycles at 20 mA/g in the voltage range of 2.0-4.0 V.