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A stable Li-deficient oxide as high-performance cathode for advanced lithium-ion batteries

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Experimental Section

The Preparation of precursors and Li-deficient oxides. To synthesize the precursor, stoichiometric $NiSO_4 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $MnSO_4 \cdot H_2O$ (cationic ratio of Ni:Co:Mn=2:1:7) were dissolved with a concentration of 2.0 mol L^{-1} as the starting materials. Then the aqueous solution were pumped into a continuously stirred tank reactor (CSTR, capacity of 170 L) under a nitrogen atmosphere and reacted with 10 mol L^{-1} NaOH solution (aq) as the pH control agent and 2 mol L^{-1} NH_4OH solution (aq) as the chelating agent in the reactor under 50 °C and constant pH (11.5) with 600 rpm stirring rate, leading to $[Ni_{0.2}Co_{0.1}Mn_{0.7}](OH)_2$ precursors.

Then, the as-prepared $[Ni_{0.2}Co_{0.1}Mn_{0.7}](OH)_2$ particles were filtered, washed, and dried 24 h in air. The obtained precursor particles were calcined with stoichiometric ratio LiOH (Li/M=0.35) powders at 800 °C in a furnace under air to form layered oxide powders.

After lithiation, the amount of the residual Li_2O and other alkaline compounds on the surface of particle, which is highly related to processability in a lithium battery system, can be measured by the following method. Firstly, 1.000 g oxides were added into 1000 mL redistilled water with continually stirring 0.5 h under a nitrogen atmosphere. Then, pH of solution was measured by Mettler PE20.

Materials Characterization. X-ray Diffractometry (XRD, Rigaku D/MAX-2500 Japan) was employed to characterize structure of the prepared materials. XRD datas were obtained at 2θ=10-80° with a step size of 0.02°, using Cu Kα radiation. The morphology of synthesized materials was observed by a Scanning Electron Microscope (SEM, S-4800, Japan). Surface solid-state chemistry of particles was characterized by X-ray photoelectron spectroscopy with a monochromatic Al Kα X-ray source (XPS, Thermo Scientific, USA) in fixed transmission mode with pass energy of 400 mV and the binding energy ranged from 0 to 1400 eV. High resolution transmission electron microscopy (HRTEM) characterization and single-crystal selected area electron diffraction (SAED) datas were conducted using a 200 kV JEOL-JEM 2100 transmission electron microscope.

For Differential Scanning Calorimetry (DSC) experiments, cells were finally charged to 4.8 V at a constant current density of 20 mA g^{-1} at 25 °C and opened carefully in the Ar-filled dry box. After opening the cells, the electrode materials were recovered from the current collector. The DSC datas were collected in a Differential Scanning Calorimeter (NETZSCH 204F1, Germany) using a scan rate of 5 °C min^{-1} in the range of 50-350 °C.

Electrochemical Measurements. For fabrication of cathode electrodes, the prepared materials were mixed with acetylene black and PVDF (80:10:10 in weight) in NMP. The obtained slurry was coated onto Al foil and dried at 80 °C for a day, followed by a roll-pressing. Prior to use, the electrodes were dried again at 120 °C for half a day in a vacuum oven. The electrodes were electrochemically characterized using a 2032 type of coin cell with lithium foil as the anode and 1 M $LiPF_6$ in ethylene carbonate diethyl carbonate (1:1 in volume) as the electrolyte. The cells were preliminarily charged and discharged in the voltage range of 2.0-4.9 V (versus Li/Li^+) at a constant current density of 10 mA g^{-1} for initial cycle and 20 mA g^{-1} for subsequent cycles and 3.0-5.0 V (versus Li/Li^+) at a constant current density of 10 mA g^{-1} and 25 °C.

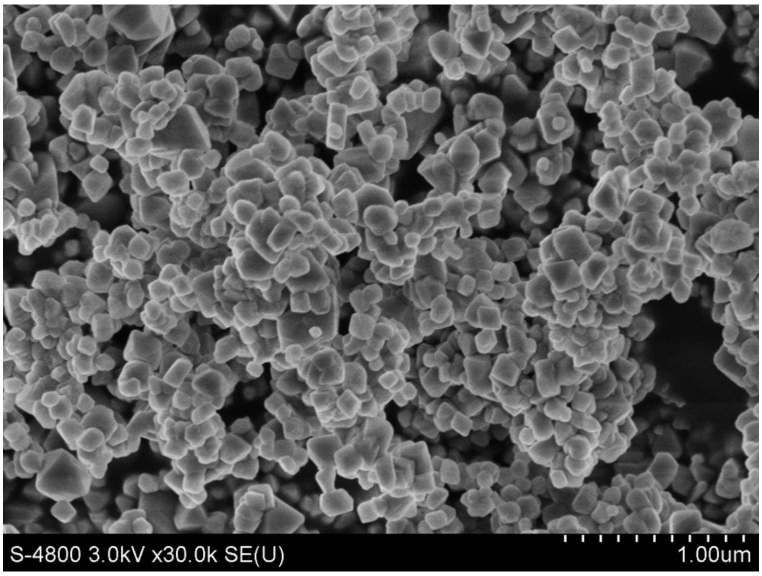

Fig. S1 SEM of as-prepared Li-rich layered oxides $Li_{1.5}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2.5}$ calcined at 800 °C in a furnace under air.

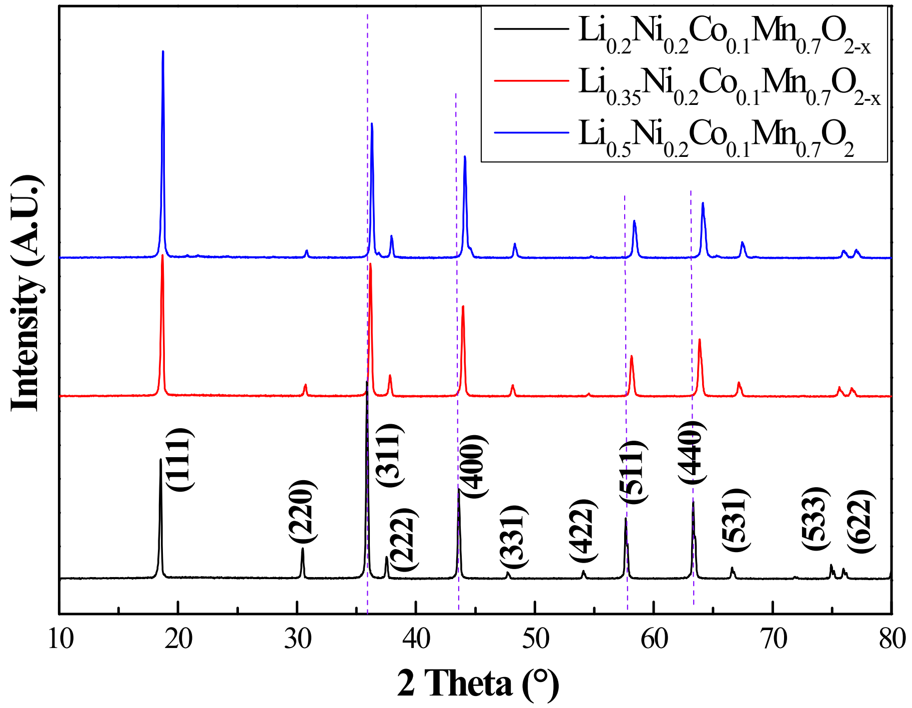

Fig. S2 XRD pattern of as-prepared Li-deficient spinel $Li_{0.2}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$, $Li_{0.35}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$ and spinel $Li_{0.5}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2}$.

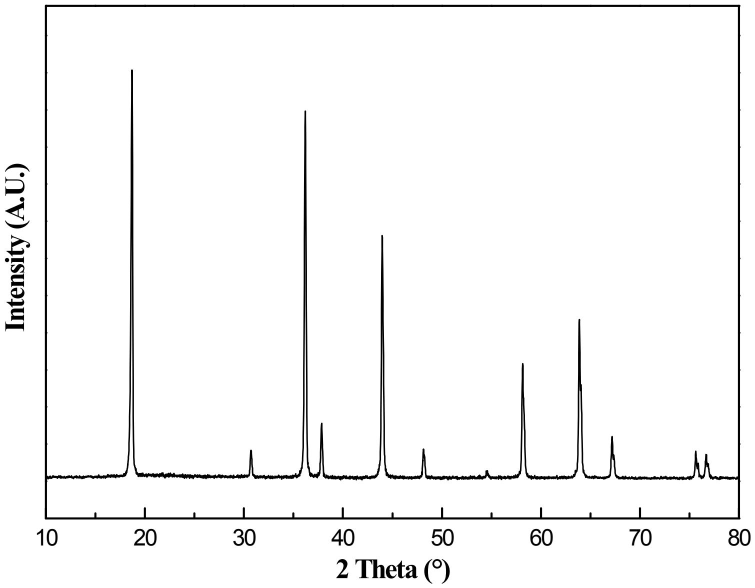

Fig. S3 XRD pattern of as-prepared Li-deficient spinel $Li_{0.35}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$ that store in air two months.

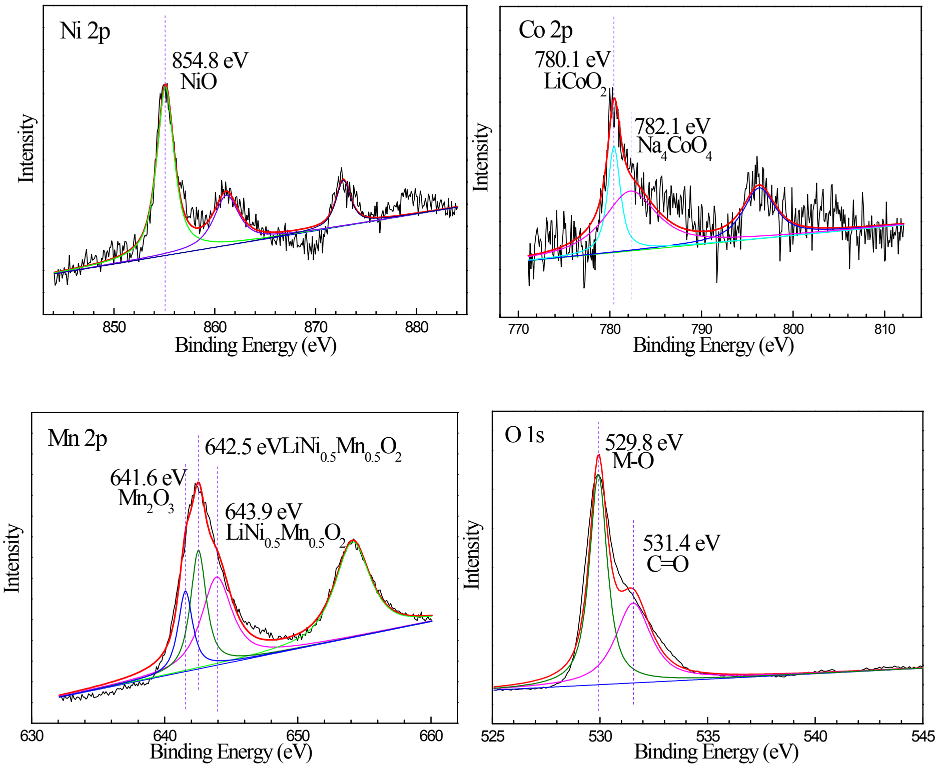

Fig. S4 XPS spectra of the as-prepared Li-deficient spinel $Li_{0.35}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$.

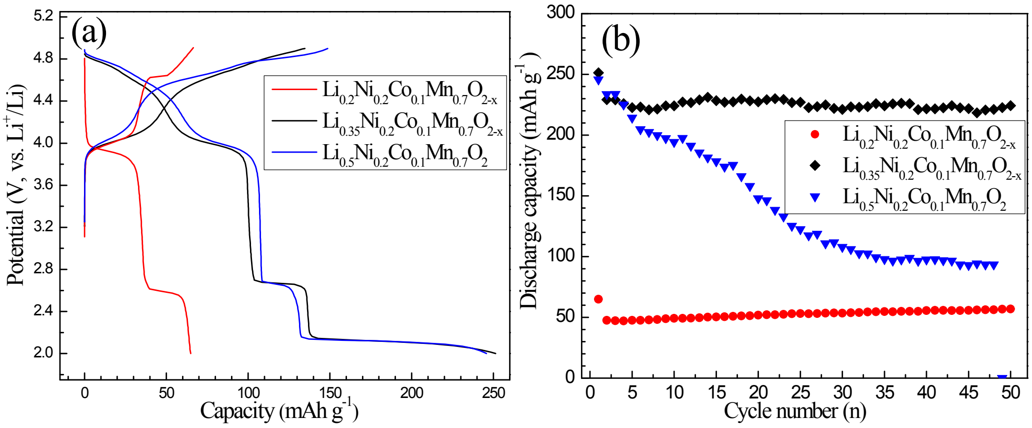

Fig. S5 Cycling performance of as-prepared Li-deficient spinel $Li_{0.2}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$, $Li_{0.35}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$ and spinel $Li_{0.5}Ni_{0.2}Co_{0.1}Mn_{0.7}O_2$.

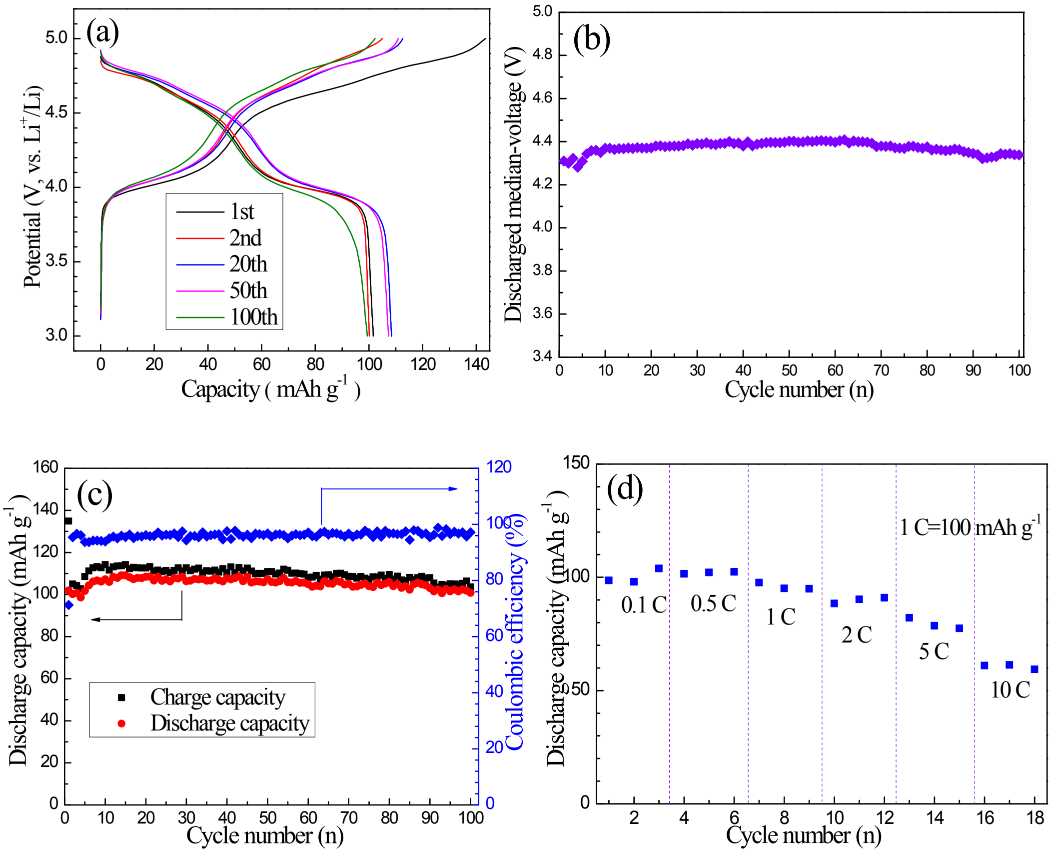

Fig. S6 (a) charge-discharge curves, (b) discharged median-voltage, (c) cycling performance and (d) rate property of Li-deficient spinel $Li_{0.35}Ni_{0.2}Co_{0.1}Mn_{0.7}O_{2-x}$ in the voltage of 3.0-5.0V.