

## Supplementary information

### **Layered $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.5-x}\text{Mn}_{0.5-x}\text{Co}_{2x}\text{O}_2$ microspheres with Mn-rich core as high performance cathode materials for lithium ion batteries**

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## 1. Experimental

### 1.1 Synthesis of $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$ spheres with uniform distribution Mn element.

Analytical grade  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{NH}_4\text{HCO}_3$ ,  $\text{LiOH} \cdot \text{H}_2\text{O}$ , and deionized water were used to prepare Li-rich  $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  spheres with uniform distribution Mn element in the particle. All chemicals were used without further purification. In a typical synthesis, 0.267 mmol  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 0.489 mmol  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  and 0.133 mmol  $\text{Co}(\text{NO}_3)_2$  were dissolved in 100 mL of distilled water at room temperature. Subsequently, a sufficient amount of  $\text{NH}_4\text{HCO}_3$  water solution was added to precipitate all the metal ions. After vigorously stirring for another 3 hours, the  $\text{MCO}_3$  (M=Mn, Ni, Co) precipitate was collected, washed and dried in a vacuum. The as-prepared  $\text{MCO}_3$  microspheres were mixed with  $\text{LiOH} \cdot \text{H}_2\text{O}$  with the molar ratio of 4 to 5.1. They were then dispersed into 2 mL ethanol, ground to form a fine mixture, dried at room temperature, and then calcined at 850 °C for 15 h at atmospheric condition. After that, Li-rich  $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  spheres with uniform distribution Mn element in the particle was obtained.

### 1.2 Characterization of the as-prepared sample.

The crystalline structure of the as-prepared sample was characterized by X-ray diffraction (XRD) technique using a Siemens X-ray diffractometer with Cu  $\text{K}\alpha$  radiation. The morphology was studied by a Scanning electron microscope (SEM, JEOL-820).

### 1.3 Electrochemical performance measurement.

The electrochemical properties of the product was analyzed by making CR2032 coin-type cells using as-prepared sample as the cathode and lithium metal as the anode. The cathode slurry was prepared by mixing the active material, acetylene black and polyvinylidene fluoride (PVDF) in the weight ratio of 80:10:10. The blended slurry was then cast onto an aluminum foil current collector and dried at 120 °C for 10 h in a vacuum oven. Circular (1.6 cm<sup>2</sup>) cathode discs were punched from the aluminum foil and were weighed to determine the amount of active materials (approximately 3 mg) before being loaded into coin-type cells. The cell was assembled in a glove box filled with high purity argon gas with low oxygen concentration and low humidity. The electrolyte composed of 1 M LiPF<sub>6</sub> dissolved in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1 in volume). Galvanostatic charge/discharge experiments were performed between 2.0 and 4.6 V at different current densities (1 C rate corresponds to the current density of 300 mA·g<sup>-1</sup>).

## 2. XRD spectrum of Li-rich Li<sub>2</sub>MnO<sub>3</sub>·3LiNi<sub>0.4</sub>Mn<sub>0.4</sub>Co<sub>0.2</sub>O<sub>2</sub> spheres with unifrom distribution Mn element in the particle.

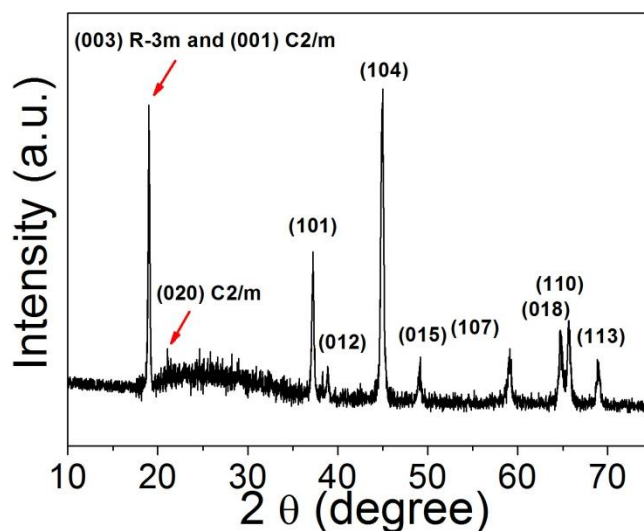


Fig. S1 The XRD spectrum of sample.

3. SEM image of Li-rich  $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  spheres with uniform distribution Mn element in the particle.

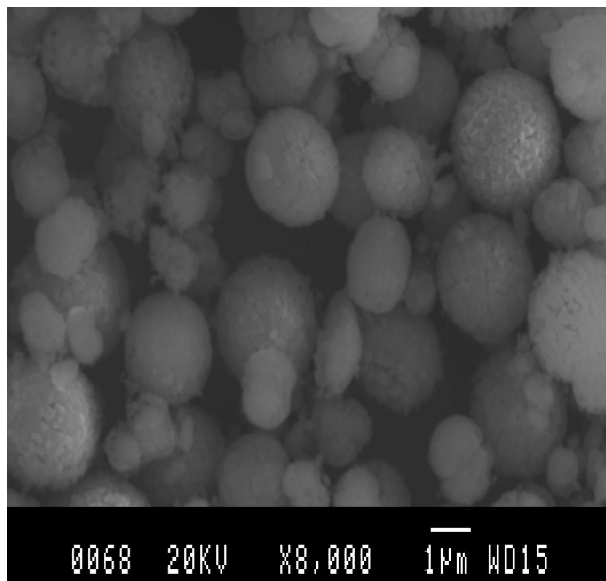


Fig. S2 The SEM image of sample.

4. Cycling performance of Li-rich  $\text{Li}_2\text{MnO}_3 \cdot 3\text{LiNi}_{0.4}\text{Mn}_{0.4}\text{Co}_{0.2}\text{O}_2$  spheres with uniform distribution Mn element in the particle.

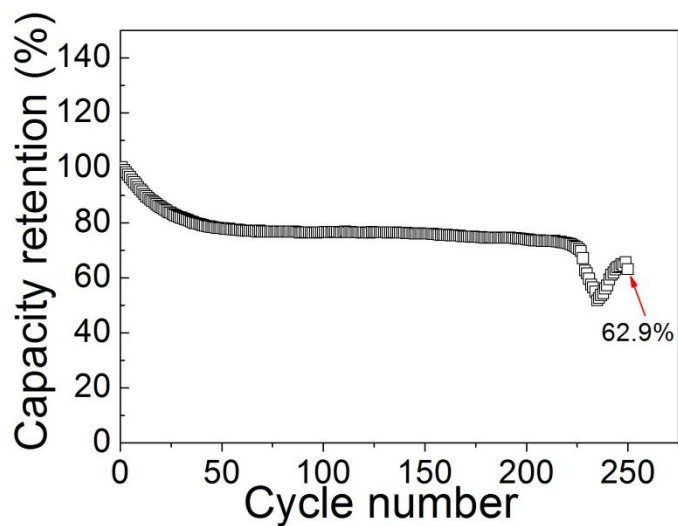


Fig. S3 The capacity retention of sample at 0.5 C rate.