Electronic Supplementary Information (ESI)

Urea-assisted hydrothermal synthesis of hollow hierarchical $LiNi_{0.5}Mn_{1.5}O_4$ cathode material with tunable morphology characteristics

Xing Qin, Mushang Zhou, Bo Zong, Jianling Guo, Jiajia Gong, Li Wang *[a,b,c] and Guangchuan Liang [a,b,c]

Institute of Power Source and Ecomaterials Science, Hebei University of Technology, Tianjin 300130, China
Key Laboratory of Special Functional Materials for Ecological Environment and Information (Hebei University of Technology), Ministry of Education, Tianjin 300130, China
Key Laboratory for New Type of Functional Materials in Hebei Province, Hebei University of Technology, Tianjin 300130, China

Experimental

(1) The measurement of Ni and Mn contents in $LiNi_{0.5}Mn_{1.5}O_4$ sample

A chemical titration method was adopted to measure the content of Ni and Mn in $LiNi_{0.5}Mn_{1.5}O_4$ sample. First, the total amount of Ni and Mn was determined by using EDTA titration. Second, the Mn content was titrated through ferrous ammonium sulfate titration. Finally, the Ni content can be dealt with the subtraction method. The specific procedures are as follows.

(i) Determination of Ni and Mn content: About 0.5 g of $LiNi_{0.5}Mn_{1.5}O_4$ powder was weighed accurately and dissolved in 20 ml concentrated hydrochloric acid under heating condition. The solution was fixed in 200 ml volumetric flask, and 20 ml solution was removed with pipette to 250 ml beater, and 3 ml ascorbic acid solution and 10 ml NH_3-NH_4Cl buffer solution (pH=10) were added to the beater. Add water to 150 ml, shake well, heat to ~ 40 °C and add 0.05~0.1 g ammonium purpurate as indicator. The thus-obtained solution was titrated with EDTA standard solution with color changing from yellow to pale purple, which is the end point of titration.

(ii) Determination of Mn content: Another 20 ml solution was removed with pipette from the above 200 ml volumetric flask to 250 ml conical flask. 5 ml phosphoric acid was added and then heated to ~ 50 °C. 5 ml perchlorate was added to the solution, which was heated up to take a lot of smoke and then removed to cool a little bit (to make all Mn^{2+} ions be oxidized to Mn^{3+} ions). Add 60 ml dilute sulphuric acid solution (H_2SO_4:H_2O=1:19, v:v), shake well, and then cool to room temperature. With ammonium ferrous sulfate standard solution titration to reddish color, 2 drops of N-phenylanthranilic acid was added as indicator, and ammonium ferrous sulfate standard solution was continued for titration with color changing from cherry red to light yellow, which is the end point of titration.

(2) The measurement of residual Ni^{2+} content in the filtrate of carbonate precursor

A standard nickel sulfate solution with the concentration of 20 mg/L was prepared. Take 1, 2, 3, 4, 5 mL of the standard solution into 50 mL volumetric flask, then add 5 mL of 30% $(NH_4)_2S_2O_8$ aqueous solution, adjust the pH value to about 10 by 5% NaOH aqueous solution and add 8 mL 0.5% dimethylglyoxime ($C_4H_8N_2O_2$) ethanol solution. Finally, the mixed solution was diluted to scale, shook well and placed in silence for 15 min for the measurement. The absorbance was measured at 470 nm, and an imitative straight-line equation was obtained. The filtrate obtained at different reactant concentrations was tested by repeating the above procedures, and the residual Ni^{2+} content was calculated based on the imitative straight-line equation.

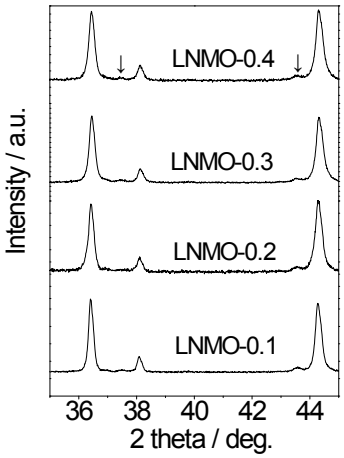

Fig. S1 Local enlarged image of XRD pattern between 35° and 45°

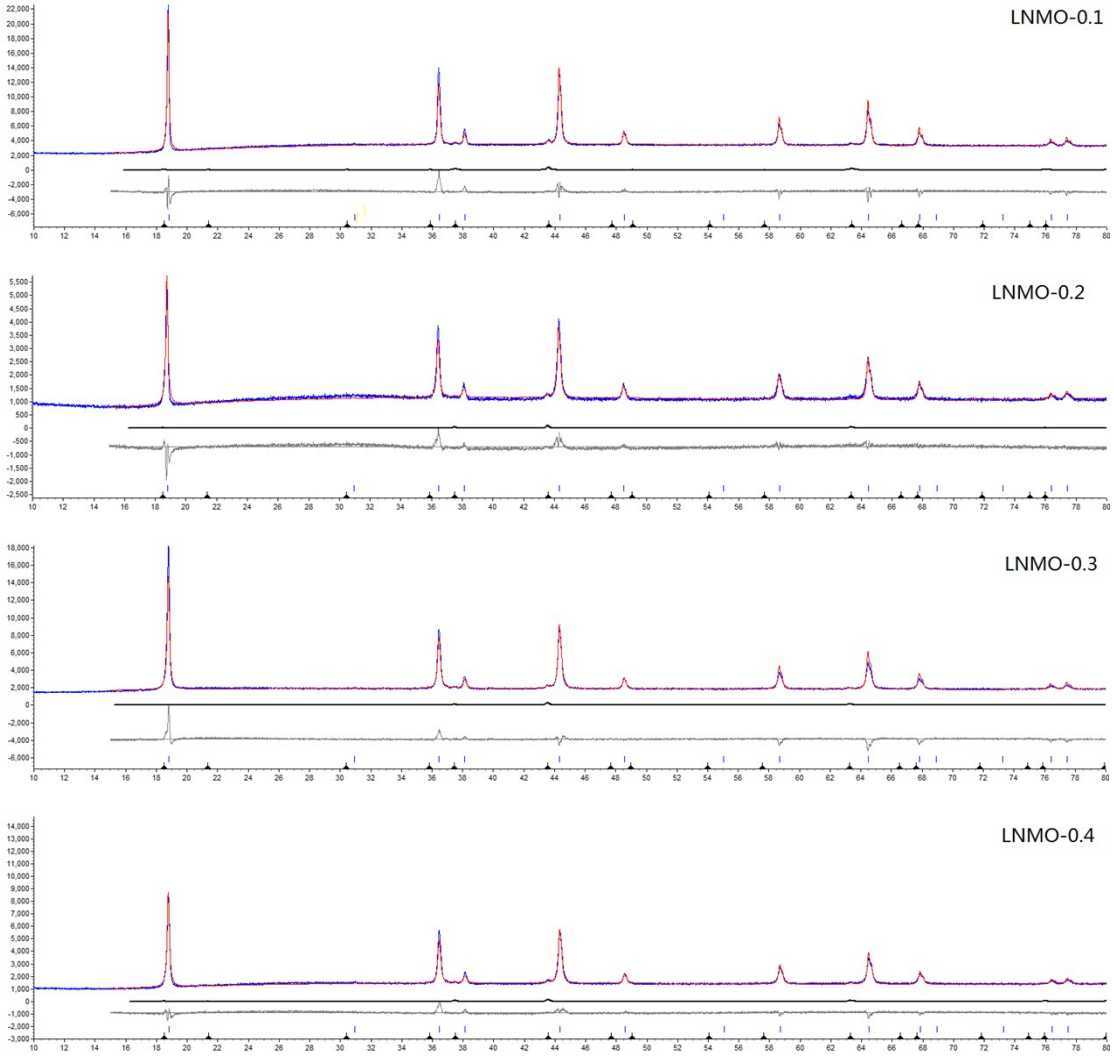

Fig. S2 XRD Rietveld refinement results for $LiNi_{0.5}Mn_{1.5}O_4$ samples

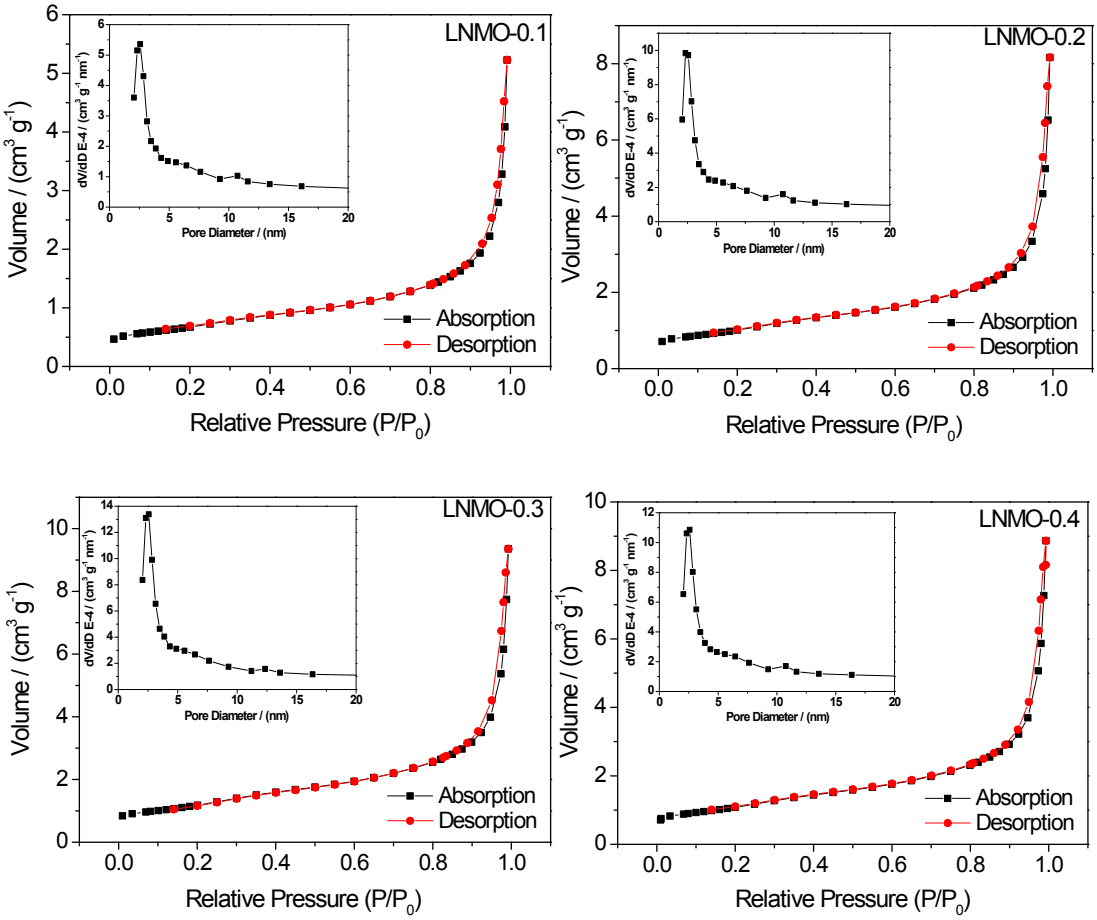

Fig. S3 Nitrogen adsorption-desorption isotherms and pore size distribution for $LiNi_{0.5}Mn_{1.5}O_4$ samples

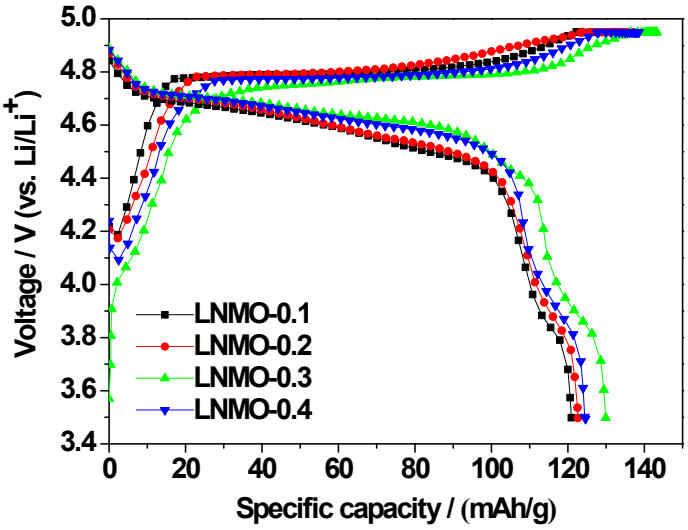

Fig. S4 Initial charge/discharge curves for $LiNi_{0.5}Mn_{1.5}O_4$ samples at 1 C rate

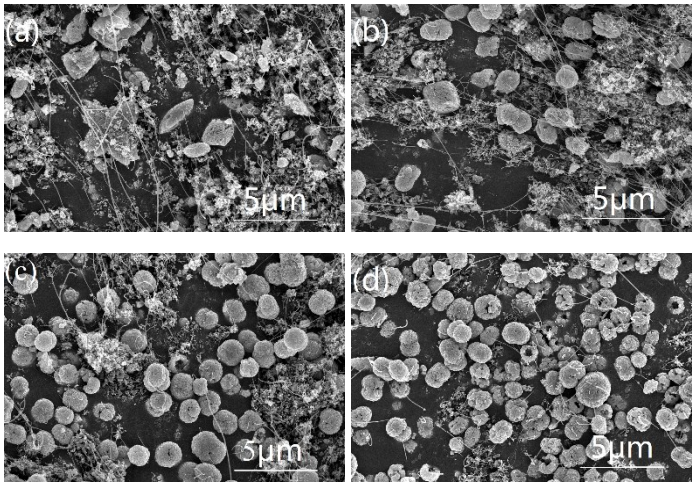

Fig. S5 SEM images of the electrodes after cycling 100 times at 1C rate

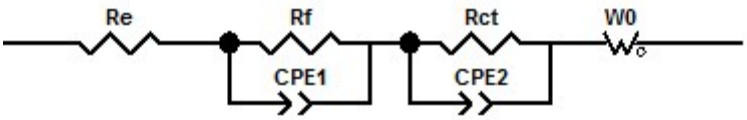

Fig. S6 Equivalent circuit for EIS spectra

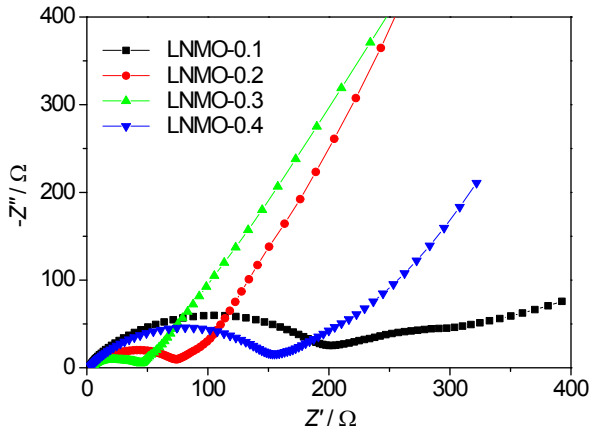

Fig. S7 EIS spectra of $LiNi_{0.5}Mn_{1.5}O_4$ samples after 100 cycles at 1C rate

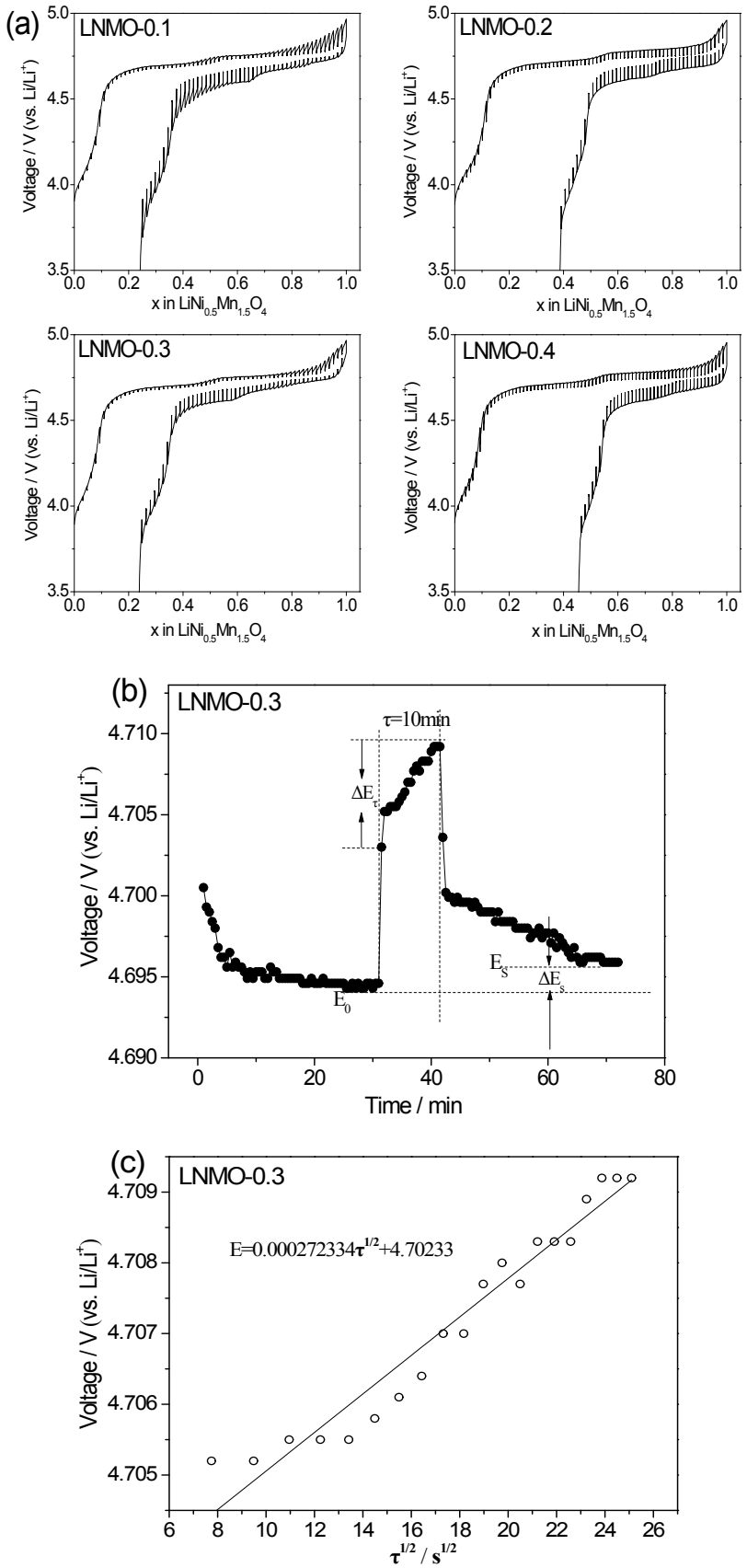

Fig. S8 (a) GITT curves for $LiNi_{0.5}Mn_{1.5}O_4$ samples, (b) *E vs. t* profile of LNMO-0.3 for a selected single GITT titration, (c) linear behavior of *E vs.* $\tau^{1/2}$

Table S1 Refinement factors for $LiNi_{0.5}Mn_{1.5}O_4$ samples

Sample	R_{exp} (%)	R_{wp} (%)	R_p (%)	GOF (=R_{wp}/R_{exp})
LNMO-0.1	2.68	4.40	3.06	1.64
LNMO-0.2	2.94	5.02	3.67	1.71
LNMO-0.3	2.79	5.26	3.55	1.88
LNMO-0.4	2.57	4.76	3.75	1.85

Table S2 Values of the CV peaks for all samples

Sample	Redox couple	ϕ_a / V	ϕ_c / V	$\Delta\phi$ / mV
LNMO-0.1	Ni^{2+}/Ni^{3+}	4.764	4.623	141
	Ni^{3+}/Ni^{4+}	4.813	4.666	147
LNMO-0.2	Ni^{2+}/Ni^{3+}	4.759	4.633	126
	Ni^{3+}/Ni^{4+}	4.811	4.676	135
LNMO-0.3	Ni^{2+}/Ni^{3+}	4.758	4.640	118
	Ni^{3+}/Ni^{4+}	4.805	4.687	118
LNMO-0.4	Ni^{2+}/Ni^{3+}	4.758	4.634	124
	Ni^{3+}/Ni^{4+}	4.806	4.686	120

Table S3 Impedance parameters for $LiNi_{0.5}Mn_{1.5}O_4$ electrodes after 3 cycles and 100 cycles at 1 C rate

Sample	after 3 cycles			after 100 cycles		
	R_e (Ω)	R_f (Ω)	R_{ct} (Ω)	R_e (Ω)	R_f (Ω)	R_{ct} (Ω)
LNMO-0.1	2.47	9.87	193.40	2.84	13.32	203.50
LNMO-0.2	1.79	6.99	63.47	4.67	13.64	77.41
LNMO-0.3	1.87	4.51	38.50	4.99	10.41	48.36
LNMO-0.4	2.92	8.50	143.90	3.14	11.58	158.00