Supporting Information for

Shape-controlled synthesis of hierarchically layered lithium transition-metal oxide cathode materials by shear exfoliation in continuous stirred-tank reactors

Weibo Hua,^{a,b,c} Zhenguo Wu,^a Mingzhe Chen,^d Michael Knapp,^b Xiaodong Guo,^{a,*} Sylvio Indris,^{b,*} Joachim R. Binder,^{c,*} Natalia N. Bramnik,^b Benhe Zhong,^a Haipeng Guo,^d Shulei Chou,^{d,*} Yong-Mook Kang,^{e,*} and Helmut Ehrenberg^{b,*}

a. Sichuan University, No.24 South Section 1, Yihuan Road, Chengdu, 610065, China. *Email: xiaodong2009@scu.edu.cn

b. Institute for Applied Materials - Energy Storage Systems (IAM-ESS), Karlsruhe Institute of

Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen,

Germany. *E-mail: sylvio.indris@kit.edu; helmut.ehrenberg@kit.edu.

c. Institute for Applied Materials - Ceramic Materials and Technologies (IAM-KWT),

Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, D-76344

Eggenstein-Leopoldshafen, Germany. E-mail: joachim.binder@kit.edu.

d. Institute for Superconducting and Electronic Materials (ISEM), University of Wollongong,

Wollongong, NSW 2522, Australia. *E-mail: shulei@uow.edu.au.

e. Department of Energy and Materials Engineering, Dongguk University-Seoul, Seoul, 100-

715, Republic of Korea. *E-mail: dake1234@dongguk.edu.

Section 1: Crystallization Kinetic Calculations

Herein, a continuously operated mixed-suspension mixed-product removal (MSMPR) crystallizer is used to obtain the crystallization kinetics at steady state because this method can determine the growth and nucleation rates simultaneously ¹. Provided that crystal breakage and agglomeration effects are negligible, the population balance equation for a continuous MSMPR crystallizer at the stable phase can be described as follows:

$$\frac{d(Gn)}{dL} + \frac{n}{\tau} = 0 \tag{1}$$

where *G* is the overall crystal growth rate, *n* is the population density, *L* is the crystal size, and τ is the mean residence time. In stable state operation of a MSMPR crystallizer, all crystals are taken to be identical in size distribution and shape, and all nuclei are assumed to be prepared at zero size.

Because of the co-precipitated particles show a "size-dependent" growth, the crystal growth dynamics estimation was conducted by using the Abegg, Stevens, and Larson (ASL) growth rate equation ²:

$$G(L) = G^0 (1 + \gamma L)^b \tag{2}$$

where G^0 is the nuclei growth rate, γ is defined by $\gamma = 1/G^0 \tau$, *b* is the empirical parameters. Thus, the size-dependent liner growth rate, $G(L) = dL/d\tau$, can be reduced to the following equation:

$$\frac{d(nG(L))}{dL} = -\frac{n}{\tau} \tag{3}$$

Combine these equations, the population balance integrates as follows:

$$n = n^{0} (1 + \gamma L)^{-b} exp[\frac{1 - (1 + \gamma L)^{1 - b}}{1 - b}]$$
(4)

At a steady state of crystallization, the population density of the particles was calculated by the subsequent equation:

$$n_i = \frac{M_T \Delta V_i}{k_v \rho_c \Delta L_i L_i^3} \tag{5}$$

where is ${}^{M_{T}}$ the suspension density, ${}^{\Delta V_{i}}$ is the volume fraction of solids, ${}^{k_{v}}$ is the volume shape factor, ${}^{\rho_{c}}$ is the solid density, ${}^{\Delta L_{i}}$ is the length of the *i* channel (${}^{L_{i} = L_{i} - L_{i-1}}$), ${}^{L_{i}}$ is the mean particle size at the *i* channel (${}^{\bar{L}_{i} = (L_{i} + L_{i-1})/2}$).

Finally, values of G^0 in the two crystallizers can be calculated from the population density plots of the precursors, as shown in Figure 1(i). Consequently, the nucleation rate (B^0) can be also obtain by the following equation:

$$B^0 = n^0 G^0 \tag{6}$$

Section 2: Diffusion Kinetic Calculations

Electrochemical impedance spectroscopy (EIS) was firstly carried out to detect the differences in the kinetic parameters of the Li-ion intercalation and de-intercalation reaction. Figure S19 shows the Nyquist curves of the NCM-H and NCM-T cathodes. The simulated results in Table S5 show that the NCM-H and NCM-T electrodes have a similar ohmic resistance (R_s). However, the R_{ct} (35.77 Ω) of the former is much less than that (287.41 Ω) of the latter, suggesting that the NCM-H has a lower Li-ion transfer resistance on the surface than the NCM-H. This comparison of Li-ion conductivity can be also further checked by the calculation of the "apparent" chemical diffusion coefficient of Li-ion (D_{Li^*}) in eqn (7) and (8) below ^{3,4}.

$$D_{\rm Li^+} = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2}$$
(7)

$$Z' = R_{\rm s} + R_{\rm ct} + \sigma \omega^{-1/2} \tag{8}$$

where *R* is the gas constant, *T* is the absolute temperature, *A* is the surface area of electrode, *n* is the number of electrons transferred in reaction, *F* is the Faraday constant, *C* is the concentration of Li-ion, and σ is the Warburg factor. The Warburg factor (σ) can be calculated from the slope of the lines between *Z'* and $\omega^{-1/2}$ because it is relative to the real impedance (*Z'*) in eqn (8) ^{3, 4}. As shown in Table S7, the *D*_{Li⁺} of the NCM-H is much larger than that of the NCM-T. Hence, the NCM-H has a fast Li diffusion due to the hierarchical microstructure and the exposed active {010} facets.

Second, galvanostatic intermittent titration technique (GITT) method was utilized to investigate the variation of Li-ions diffusion coefficient at different charge-stages. Before test, the coin cells were galvanostatically charged/discharged in two cycles at 0.1 C in voltage range of between 2.7 and 4.3 V at room temperature. The GITT was employed at a constant current pulse of 0.1 C for 30 min, and then an open-circuit stands for 150 min to release the cell voltage

to reach a near equilibrium. According to the GITT measurements, lithium ion diffusion coefficient can be obtained by the following equation ⁵:

$$D_{\mathrm{Li}^{+}} = \frac{4}{\pi} \left(\frac{m_{B}V_{M}}{M_{B}S}\right)^{2} \left(\frac{\Delta E_{s}}{\tau (dE_{\tau}/d\sqrt{\tau})}\right)^{2} \qquad \qquad \tau \ll \frac{L^{2}}{D_{Li^{+}}} \tag{9}$$

where m_B is the mass of the as-synthesized material, V_M is the molar volume of the material, M_B is the molecular weight of the sample, S is active surface area of the positive electrode, and L is the thickness of the electrode. If E is linearly associated with $\sqrt{\tau}$ (as shown in Figure S20(b)), the eqn (9) can be deduced as follows ⁶:

$$D_{\mathrm{Li}^+} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S}\right)^2 \left(\frac{\Delta E_s}{\Delta E_\tau}\right)^2 \tag{10}$$

Generally, the D_{Li^+} is known as an intrinsic property for a given positive electrode and it only depends on the structure of active material in the charge-stage ⁷. It has been proven that with the hierarchical nanoplates and the exposed {010} surface area, the activation energy for the Li-ion transport can be effectively reduced. In this way, the good capacity retention in the discharge capacity of the NCM-H with increasing current density can be ascribed to its high Li-ion diffusion.

Section 3: Additional Results



Figure S1. Crystal structure of layered $LiNi_{1/3}Co_{1/3}Mn_{1/3}O_2$.



Figure S2. Schematic illustration for (a) the modified CSTR and (b) the traditional CSTR.



Figure S3. Experimental setup diagram for preparing NCM-H.



Figure S4. Schematic diagram showing electron migration through secondary particles composed of several irregular primary nanoparticles.



Figure S5. The morphology evolution of the co-precipitated particles as a function of reaction time.



Figure S6. Changes in FBRM total counts during co-precipitation process.



Figure S7. (a) Nitrogen absorption and desorption isotherms and (b) the pore size distribution of the precursors. The pore size distribution was calculated from the nitrogen isotherms using the Barret–Joyner–Halender (BJH) method.



Figure S8. XRD patterns of the precursors.



Figure S9. Structure refinement results, based on SXRD patterns for NCM-T.



Figure S10. (a) Nitrogen absorption and desorption isotherms and (b) the pore size distribution of NCM-H and NCM-T.



Figure S11. (a) SEM image and (b) elemental mapping (Ni, Co, Mn and O) of NCM-H;



Figure S12. EDS spectrum of NCM-H.



Figure S13. XPS spectra for Ni, Co, Mn, and O elements of NCM-H.



Figure S14. SEM image of NCM-T.



Figure S15. Particle size distributions of NCM-H and NCM-T.



Figure S16. (a) The pore size distribution plots and corresponding N₂ adsorption-desorption isotherms of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$; (b) particle size distributions and (c) EDS spectra of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$.

The morphology and microstructure of hierarchical structured $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ are displayed in Figure 3(b). Many primary nanoplates self-assemble into quasi-spheres with an average particle size of 3.65 µm (Figure S16(b)), forming a nanoporous structure (Figure S16(a)). The chemical composition of the prepared $\text{LiNi}_{0.6}\text{Co}_{0.2}\text{Mn}_{0.2}\text{O}_2$ was analysed by EDS, as shown in Figure S16(c), confirming that the atomic ratio of the Ni, Co, Mn matches with their ratio in the educts.



Figure S17. (a) The pore size distribution plots and corresponding N_2 adsorption-desorption isotherms of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$; (b) particle size distributions and (c) EDS spectra of $Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$.

The micro-morphology of the prepared $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ also exhibits a unique hierarchical architecture, as shown in Figure 3(d). The N₂ adsorption and desorption isotherm for the sample (see Figure S17(a)) shows a typical irreversible type IV adsorption and a H3 hysteresis loop. It was found that the specific surface area of the material is $1.72 \text{ m}^2 \text{ g}^{-1}$. The cumulative curve and histogram profile are shown in Figure S17(b). The maxima in the cumulative curve is observed at about 3 µm, corresponding to the secondary particles and in good agreement with the SEM images. The ratio of Ni:Mn measured by EDS is approximately 1:309 (Figure S17(c)), which is very close to the theoretical value.



Figure S18. Discharge curves of (a) NCM-H and (b) NCM-T at different current densities; charge-discharge profiles of (c) NCM-H and (d) NCM-T for selected cycles.



Figure S19. Electrochemical impedance spectra of two electrodes.



Figure S20. (a) Applied current pulse *vs.* voltage for a single titration at 3.3 V for NCM-T electrode with schematic representation of various parameters and (b) corresponding variation of the potential for titration plotted against $\sqrt{\tau}$ to show a linear fit; variation of ${}^{D}_{Li}^{+}$ as a function of cell potential for (c) NCM-T and (d) NCM-H determined by GITT.



Figure S21. Lithium diffusion coefficients of the cathodes determined by GITT method.



Figure S22. (a) Initial charge and discharge curves of the as-prepared $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ and (b) its corresponding dQ/dV plot.

The electrochemical performance of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ was tested on the coin cells under 0.1-20 C (1 C = 200 mA g⁻¹) between 2.7 and 4.3 V at room temperature. Figure S22(a) shows the initial charge and discharge plot of the LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ electrode at 0.1 C. The curve exhibits a smooth and monotonous charge-discharge trait, which well agree with the results reported in the reference ⁸⁻¹⁰. The first charge and discharge capacity of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ is measured to be 213.8 and 183.1 mAh g⁻¹, respectively. The corresponding differential capacity vs. voltage (dQ/dV) displays a couple of redox peaks at about 3.8 and 3.7 V, suggesting the Li-ions intercalation and de-intercalation of layered LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ structure. The rate capability of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂ is shown in Figure 4(e). Clearly, the specific discharge capacity of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ decreases as the increasing of C-rate due to the ohmic drop and the polarization effect. At 5, 10 and 20 C, the discharge capacities of the LiNi $_0 6$ Co $_0 2$ Mn $_0 2$ O $_2$ are 142.6, 132.7, and 115.4 mAh g⁻¹, respectively, which are superior to these results reported in the previous literature (see Table S10)^{8, 11-15}. Near 63.6 % of its capacity can be retained as the C-rate increases from 0.1 to 20 C. The good rate capability is also obviously confirmed the advantage of this special hierarchical structure.



Figure S23. (a) Initial charge and discharge curves of the as-prepared $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ and (b) its corresponding dQ/dV plot.

To explore the electrochemical properties of hierarchical structured $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ cathode material used in LIBs, different current densities from 0.1 C to 20 C between 2.0 and 4.8 V was tested at room temperature. Figure S23(a) shows the initial charge and discharge plot of the $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ electrode at 0.1 C, which is similar to the reported shape in the literature ^{16, 17}. A long plateau around at 4.5 V can be observed on the first charging (Figure S22(b)), due to the irreversible removal of Li₂O extraction from the Li₂MnO₃ structure ¹⁸⁻²⁰. The high rate performance of the $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ electrode is evidenced by Figure 4(f). As the increasing of the current densities, the clear IR drop is observed from the discharge plots in Figure 4(f). Amazingly, the prepared $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ yields high specific discharge capacities of 157.2, 126.6 and 96.3 mAh g⁻¹ at 5, 10, 20 C, respectively, demonstrating an excellent high rate capability. These results are comparable to those values reported in reference (Table S11) ^{19, 21-25}, illustrating this peculiar microstructure ensuring the high rate performance of the $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$.

Samples	M_t (kg cm ⁻³)	τ (s)	B^0 (number m ⁻³ s ⁻¹)	$G^{0}(m s^{-1})$	R^2
NCM-H	200	36000	2.69×10^{8}	4.35×10 ⁻¹¹	0.98
NCM-T	200	36000	3.03×10^{7}	4.62×10 ⁻¹¹	0.99

Table S1. Kinetics parameters of the samples obtained by ASL model.

Note: M_t is the suspension density, τ is the mean residence time, B^0 is nucleation rate, G^0 is the nuclei growth rate, the coefficient of determination (R^2) is the proportion of the variability in a data set that is accounted for by a statistical model.

Samples	Tap density (g cm ⁻³)	Packing density (g cm ⁻³)	Surface area (m ² g ⁻¹)
NCM-H	1.9	3.3	6.4
NCM-T	2.2	3.7	1.7
LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	1.9	<mark>3.3</mark>	6.0
$Li_{1.2}Ni_{0.2}Mn_{0.6}O_2$	1.8	<mark>3.1</mark>	6.2

Table S2. Tap densities and specific surface area of the samples.

Cell parameters Space group: R^3m , $a = b = 2.8642$ Å, $c = 14.2441$ Å, $V = 101.1963$ Å ³ , $c/a = 4.9731$						
Atomic p	ositions					
Name	site	x	У	Z	B_{iso}	Fract
01	6 <i>c</i>	0.000	0.000	0.241	0.440	1.000
Li1	3 <i>a</i>	0.000	0.000	0.000	0.732	0.967
Ni2	3 <i>a</i>	0.000	0.000	0.000	0.732	0.031
Co1	3 <i>b</i>	0.000	0.000	0.500	0.128	0.333
Mn1	3 <i>b</i>	0.000	0.000	0.500	0.128	0.333
Ni1	3 <i>b</i>	0.000	0.000	0.500	0.128	0.302
Li2	3 <i>b</i>	0.000	0.000	0.500	0.138	0.033
		Pa	finement nar	ameters		

Table S3. Lattice parameters of the NCM-T.

Refinement parameters

Constraints:

$$\begin{split} B_{iso}(Ni1) &= B_{iso} (Co1) = B_{iso} (Mn1) = B_{iso} (Li2); B_{iso} (Li1) = B_{iso} (Ni2); Fract(Ni1) + Fract(Ni2) = 0.333; Fract(Li1) + Fract(Li2) = 1.000 \\ R_{wp} &= 9.15 \%, R_p = 7.72 \% \\ Selected interatomic distance (Å) \\ Li1-O bond length: 2.110(6) Å \end{split}$$

Ni1-O bond length: 1.966(6) Å

Cell parameters P^2 $k = 2.0741$ $k = 14.0204$ $k = 1.01.00005$ $k^3 = (4.0542)$						
Space grou	p: R ⁵ m, a = b	b = 2.8/41 A,	c = 14.2394	A, $V = 101.8$	$3665 \text{ A}^3, c/a =$	= 4.9543
Atomic pos	sitions					
Name	site	x	У	Z	B _{iso}	Fract
01	6 <i>c</i>	0.000	0.000	0.242	0.786	1.000
Lil	3 <i>a</i>	0.000	0.000	0.000	0.590	0.969
Ni2	3 <i>a</i>	0.000	0.000	0.000	0.590	0.065
Col	3 <i>b</i>	0.000	0.000	0.500	0.129	0.200
Mn1	3 <i>b</i>	0.000	0.000	0.500	0.129	0.200
Ni1	3 <i>b</i>	0.000	0.000	0.500	0.129	0.535
Li2	3 <i>b</i>	0.000	0.000	0.500	0.129	0.031
	Refinement parameters					

Table S4. Structural parameters of LiNi_{0.6}Co_{0.2}Mn_{0.2}O₂.

Constraints:

 $\begin{array}{l} B_{iso}(Ni1) = B_{iso} \ (Co1) = B_{iso} \ (Mn1) = B_{iso} \ (Li2); \ B_{iso} \ (Li1) = B_{iso} \ (Ni2); \ Fract(Ni1) + \\ Fract(Ni2) = 0.600; \ Fract(Li1) + Fract(Li2) = 1.000 \\ R_{wp} = 10.30 \ \%, \ R_{p} = 8.25 \ \% \\ & Selected \ interatomic \ distance \ (Å) \\ Li1-O \ bond \ length: 2.044(8) \end{array}$

Ni1-O bond length: 1.945(6)

Cell parameters						
Space grou	p: $C2/m$, $a =$	4.9633 Å, b =	= 8.5754 Å, d	c = 5.0342 Å,	beta = 109.2	87°, V=
202.2398 Å	3					
Atomic pos	sitions					
Name	site	x	У	Z	B _{iso}	Fract
01	4 <i>i</i>	0.221	0.000	0.222	Overall:	1.000
O2	8j	0.254	0.333	0.227	0.0565	1.000
Li1	2c	0.000	0.000	0.500		1.000
Li2	4h	0.000	0.689	0.500		0.958
Ni1	4h	0.000	0.689	0.500		0.042
Li3	2b	0.000	0.500	0.000		0.685
Ni2	2b	0.000	0.500	0.000		0.515
Mn1	4g	0.000	0.173	0.000		0.900
		Refi	nement parar	neters		

Table S5. Lattice parameters of $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$.

Constraints:

Fract(Ni1) + Fract(Ni2) = 0.200; Fract(Li2) + Fract(Li3) = 0.867

R_{wp}= 11.90 %, R_p= 11.10 %

Tuble 50. Results of fer Theb undrysts of the samples.							
Samples	Li: Ni:Co:Mn expected	Li: Ni:Co:Mn obtained	Standard deviation				
NCM-H	1:0.333:0.333:0.333	1:0.337:0.341:0.322	0.79				
NCM-T	1:0.333:0.333:0.333	1:0.335:0.342:0.323	0.83				

Table S6. Results of ICP-AES analysis of the samples.

Samples	$R_{s}\left(\Omega ight)$	$R_{ct}\left(\Omega\right)$	$D_{\rm Li^+} ({\rm cm}^2{\rm s}^{-1})$
NCM-H	9.2	35.8	5.7×10 ⁻¹¹
NCM-T	8.1	287.4	6.0×10 ⁻¹²

Table S7. Fitting results of equivalent circuit from Nyquist curves for the samples.

Structure	Voltage	Discharge capacity	Consoity rotantian	Dof
Structure	range (V)	$(mAh g^{-1})$	Capacity retention	Kel.
	2742	130.0 (10 C)	98.2 %	This work
INCIM-II	2.7-4.3	120.88 (20 C)	(20 C 500 cycles)	THIS WOLK
NCM T	2742	79.0 (10 C)	43.3 %	This work
	2.7-4.3	50.8 (20 C)	(5 C; 200 cycles)	THIS WOLK
Hallow migrosphere	2540	114.2(5.C)	$\sim 60 \%$	26
fionow inicrosphere	2.5-4.6	114.2(3C)	(0.5 C; 200 cycles)	
One-dimensional	2012	126.9 (10 C)	93.7 %	27
hierarchical structure	2.8-4.3	104.9 (20 C)	(1 C; 160 cycles)	
Cube-shaped		144.5(10.C)	73.4 %	28
hierarchical structure	2.3-4.3	144.3(10 C)	(2 C; 100 cycles)	
Nanobricks	25-16	136.1 (10 C)	93.5 %	29
Inditoortexs	2.3-4.0	130.0 (15 C)	(15 C; 100 cycles)	
Microscopically			94 2 %	
porous, interconnected	2.8-4.4	142.3 (2 C)	$(0.1 \text{ C} \cdot 50 \text{ cycles})$	30
single crystal			(0.1 C, 50 cycles)	
Hollow nano-micro			961%	
hierarchical	2.5-4.5	135.9 (10 C)	$(0.1 C \cdot 40 \text{ cycles})$	31
microspheres			(0.1 C, 40 Cycles)	
Nanostructured	28-11	122.0(10.C)	94.2 %	32
microspheres	2.0-4.4	122.0(10 C)	(0.1 C; 50 cycles)	
Graphene	2 5-4 4	1280(5C)	92.8 %	33
modification	2.3-4.4	120.0(50)	(5 C; 50 cycles)	

Table S8. Comparison of the electrochemical performances of NCM-H with reported results.

Structure	Voltage range (V)	Discharge capacity (mAh g ⁻¹)	Ref.
Hierarchical LiNi _{0.6} Co _{0.2} Mn _{0.2} O ₂	2.7-4.3	132.7 (10 C) 115.4 (20 C)	This work
Nanoparticles	2.8-4.3	119.5 (5 C)	11
Nanobricks	2.8-4.3	87.9 (10 C)	12
Submicron quasi- sphere	2.8-4.3	125.4 (5 C)	13
Al_2O_3 coating	2.6-4.3	~ 85.0 (5 C)	14
Surface-treating	3.0-4.45	120.0 (7 C)	8
F-doping	2.8-4.3	106.9 (10 C)	15

Table S9. Comparison of the electrochemical performances of $LiNi_{0.6}Co_{0.2}Mn_{0.2}O_2$ with reported results.

Structure	Voltage range (V)	Discharge Capacity (mAh g ⁻¹)	Ref.
Hierarchical Li _{1.2} Ni _{0.2} Mn _{0.6} O ₂	2.0-4.8	157.2 (5 C) 126.6 (10 C) 96.3 (20 C)	This work
Monodisperse	2.0-4.8	125 (4 C)	19
Nanoarchitecture Multi-Structure	2.0-4.6	159 (5 C)	21
Surface modification	2.0-4.8	~ 100 (5 C)	22
Gradient surface Na ⁺ - doping	2.0-4.8	185 (2 C)	23
Al ₂ O ₃ +RuO ₂ coating	2.0-4.8	161 (5 C)	24
AlF ₃ coating	2.0-4.8	~ 150 (5 C)	25

Table S10. Comparison of the electrochemical performances of $Li_{1,2}Ni_{0,2}Mn_{0,6}O_2$ with reported results.

Reference

- 1. X. Sun, Y. Sun and J. Yu, J. Cryst. Growth, 2015, 419, 94-101.
- 2. G. J and J. S. J, Chem. Eng. Sci., 1978, 33, 1623-1630.
- 3. B. Li, C. Han, Y.-B. He, C. Yang, H. Du, Q.-H. Yang and F. Kang, *Energy Environ. Sci.*, 2012, **5**, 9595-9602.
- 4. L. Mai, S. Li, Y. Dong, Y. Zhao, Y. Luo and H. Xu, Nanoscale, 2013, 5, 4864-4869.
- C.-H. Shen, S.-Y. Shen, F. Fu, C.-G. Shi, H.-Y. Zhang, M. J. Pierre, H. Su, Q. Wang, B.-B. Xu, L. Huang, J.-T. Li and S.-G. Sun, *J. Mater. Chem. A*, 2015, **3**, 12220–12229.
- 6. S. N. Lim, J. Y. Seo, D. S. Jung, W. Ahn, H. S. Song, S.-H. Yeon and S. B. Park, *J. Alloys Compd*, 2015, **623**, 55-61.
- 7. K. M. Shaju, G. V. Subba Rao and B. V. R. Chowdari, *J. Electrochem. Soc.*, 2004, **151**, A1324-A1332.
- 8. H. Kim, M. G. Kim, H. Y. Jeong, H. Nam and J. Cho, Nano Lett., 2015, 15, 2111-2119.
- 9. Z. Zheng, X.-D. Guo, S.-L. Chou, W.-B. Hua, H.-K. Liu, S. X. Dou and X.-S. Yang, *Electrochim. Acta*, 2016, **191**, 401-410.
- 10. Y. Chen, Y. Zhang, B. Chen, Z. Wang and C. Lu, J. Power Sources, 2014, 256, 20-27.
- 11. X. Zheng, X. Li, Z. Huang, B. Zhang, Z. Wang, H. Guo and Z. Yang, *J. Alloy Compd*, 2015, **644**, 607-614.
- 12. P. Yue, Z. Wang, Q. Zhang, G. Yan, H. Guo and X. Li, *Ionics*, 2013, 19, 1329-1334.
- 13. P. Yue, Z. Wang, W. Peng, L. Li, H. Guo, X. Li, Q. Hu and Y. Zhang, *Scripta Mater.*, 2011, **65**, 1077-1080.
- 14. Y. S. Lee, W. K. Shin, A. G. Kannan, S. M. Koo and D. W. Kim, *ACS Appl. Mater. Interfaces*, 2015, **7**, 13944-13951.
- P. Yue, Z. Wang, X. Li, X. Xiong, J. Wang, X. Wu and H. Guo, *Electrochim. Acta*, 2013, 95, 112-118.
- 16. L. Zhang, N. Li, B. Wu, H. Xu, L. Wang, X. Q. Yang and F. Wu, *Nano Lett.*, 2015, **15**, 656-661.
- 17. S.-X. Liao, B.-H. Zhong, X. Guo, X.-X. Shi and W.-B. Hua, *Eur. J. Inorg. Chem.*, 2013, 2013, 5436-5442.
- 18. J. Yang, F. Cheng, X. Zhang, H. Gao, Z. Tao and J. Chen, *J. Mater. Chem. A*, 2014, **2**, 1636-1640.
- 19. F. Cheng, Y. Xin, J. Chen, L. Lu, X. Zhang and H. Zhou, *J. Mater. Chem. A*, 2013, 1, 5301-5308.
- 20. L. Zhang, B. Wu, N. Li, D. Mu, C. Zhang and F. Wu, *J. Power Sources*, 2013, **240**, 644-652.
- 21. D. Wang, I. Belharouak, G. Zhou and K. Amine, Adv. Funct. Mater., 2013, 23, 1070-1075.
- 22. I. T. Kim, J. C. Knight, H. Celio and A. Manthiram, *J. Mater. Chem. A*, 2014, **2**, 8696-8704.
- 23. R.-P. Qing, J.-L. Shi, D.-D. Xiao, X.-D. Zhang, Y.-X. Yin, Y.-B. Zhai, L. Gu and Y.-G. Guo, *Adv. Energy Mater.*, 2015.
- 24. J. Liu and A. Manthiram, J. Mater. Chem., 2010, 20, 3961-3967.
- 25. Y. K. Sun, M. J. Lee, C. S. Yoon, J. Hassoun, K. Amine and B. Scrosati, *Adv. Mater.*, 2012, **24**, 1192-1196.
- 26. J. Li, S. Xiong, Y. Liu, Z. Ju and Y. Qian, Nano Energy, 2013, 2, 1249-1260.
- 27. Z. Yang, J. Lu, D. Bian, W. Zhang, X. Yang, J. Xia, G. Chen, H. Gu and G. Ma, *J. Power Sources*, 2014, **272**, 144-151.
- 28. Y. Wu, C. Cao, Y. Zhu, J. Li and L. Wang, J. Mater. Chem. A, 2015, 3, 15523–15528.
- 29. F. Fu, G.-L. Xu, Q. Wang, Y.-P. Deng, X. Li, J.-T. Li, L. Huang and S.-G. Sun, *J. Mater. Chem. A*, 2013, **1**, 3860-3864.

- 30. Z.-D. Huang, X.-M. Liu, S.-W. Oh, B. Zhang, P.-C. Ma and J.-K. Kim, *J. Mater. Chem.*, 2011, **21**, 10777-10784.
- 31. J. Li, C. Cao, X. Xu, Y. Zhu and R. Yao, J. Mater. Chem. A, 2013, 1, 11848-11852.
- 32. S.-H. Park H.-S. Shin, S.-T. Myung, C. S. Yoon, K. Amine and Y.-K. Sun, *Chem. Mater.*, 2005, **17**, 6-8.
- 33. C. Venkateswara Rao, A. Leela Mohana Reddy, Y. Ishikawa and P. M. Ajayan, *ACS Appl. Mater. Interfaces*, 2011, **3**, 2966-2972.