Supplementary Information for

Single-Particle Measurements of Electrochemical Kinetics in NMC and NCA Cathodes for Li-Ion Batteries

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Supplementary Information

Single-particle electrode

Tungsten probe was fully coated with amorphous fluoropolymer CYTOP to prevent the side-reaction from tungsten oxidation **(Fig. S1)**. To prepare a single-particle microelectrode, the coating on the probe tip was etched by silicon source in FIB to gain electrical connection. An individual NMC secondary particle was then attached to the CYTOP-coated tungsten probe using manipulator in FIB. The electrical contact between the NMC and probe is made by depositing Pt metal in FIB and the Pt metal area is smaller than 1% to the NMC particle surface area. The reference and counter electrodes are both Li foils with an area of ~0.1 cm^2 and ~1 cm^2, respectively. Prior to cell assembly, the microelectrode was dried at 100 ˚C for ~8h under vacuum.

Exchange current density

Exchange current density (j_0) in the Butler–Volmer equation is the intrinsic materials parameter to describe interfacial kinetics at the electrode-electrolyte interface. We use the Butler-Volmer equation to quantitatively describe the interfacial performance of a single NMC particle with 1-electron transfer:

$$j = j_0\left(e^{\frac{-\alpha F}{RT}\eta} - e^{\frac{(1-\alpha)F}{RT}\eta}\right) \tag{1}$$

where j is the current density ($mAcm^{-2}$), j_0 is the exchange current density ($mAcm^{-2}$) η is the interfacial overpotential (V), α is the transfer coefficient (typically assumed to be 0.5), R is the universal gas constant (8.314 $Jmol^{-1}K^{-1}$), F is Faraday's constant (96485 $Cmol^{-1}$) and T is temperature (K). As an intrinsic property of the materials, j_0 is the rates of oxidation and reduction at equilibrium, which can be used to characterize the interfacial kinetics. In practice, we can estimate $j_0 = \frac{RT}{FAR_{ct}}$ at low overpotential (eqn (2)), where, A is the interfacial area of the single particle, which can be calculated from the observed particle diameter in SEM and R_{ct} is the charge-transfer resistance at the electrode-electrolyte interface, which can be calculated from electrochemical impedance spectroscopy (EIS).

Bulk diffusivity

Bulk diffusivity of Li ion (D_{Li}) is intrinsic materials parameter to describe Li bulk transport in the particle. Li diffusion in a single NMC particle is taken to follow the Fick's Second Law:

$$\frac{\partial C}{\partial t} = D_{Li}\frac{\partial^2 C}{\partial r^2} + \frac{2\partial C}{r\partial r} \tag{3}$$

where C (mol/cm^3) is the Li concentration, D_{Li} is the chemical diffusion coefficient (cm^2/s), t is time (t), and r is the radius of the electrode particle.

Electrochemical Biot number

The electrochemical Biot number B can be viewed as the relative rate of that of the overall charge-transfer process to the lithium bulk diffusion resistance. Note that electrochemical Biot number *B* is derived from the modified PITT analysis denoting the ratio of resistance from diffusion to that of the surface reaction, while *B'* represents the experimental fitted results from PITT current versus time curves. Consider the flux at interface driven by a small overpotential obeying BV equation, and the boundary condition can be written as:

$$\frac{\partial C}{\partial r} + B\frac{(C_f - C_i)}{r} = 0 \tag{4}$$

The first item $\frac{\partial C}{\partial r}$ is ascribed to the diffusion flux $N = -D\frac{\partial C}{\partial r}$, while the latter one $\frac{(C_f - C_i)}{r}$ from interfacial reaction. The definition of electrochemical Biot number *B* is given as $B = -\frac{ri0\frac{\partial U}{\partial C}}{DRT}$, where r is the radius of the electrode particle, j_0 is the exchange current density at the electrode surface, $\frac{\partial U}{\partial C}$ is the slope of the equilibrium potential (U) vs lithium concentration (C) curve at the given SOC, D is the diffusion coefficient, R is the gas constant, and T is the bsolute temperature.

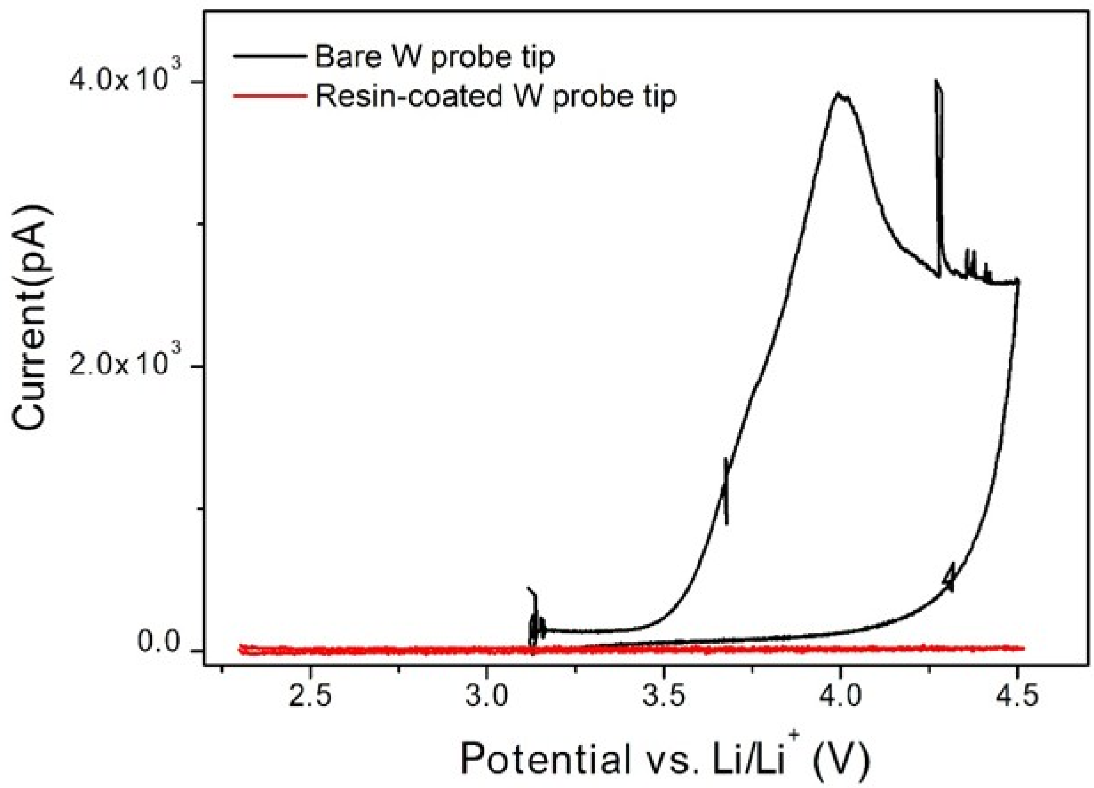

Fig. S1. Cyclic voltammagram for tungsten probe with and without coating by amorphous fluoropolymer (CYTOP), showing suppression of tungsten oxidation side-reaction for the coated probe.

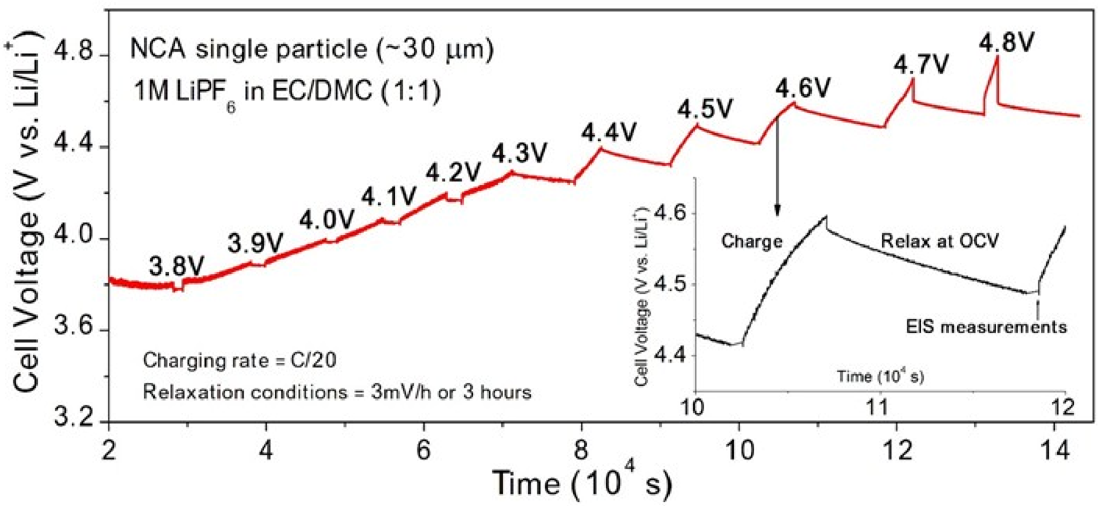

Fig. S2. Voltage vs. time during galvanostatic step-charging at C/20 rate of a single NCA ($Li_{1-x}Ni_{0.8}Co_{0.15}Al_{0.05}O_2$) particle. Each galvanostatic step is followed by voltage relaxation under open circuit conditions.

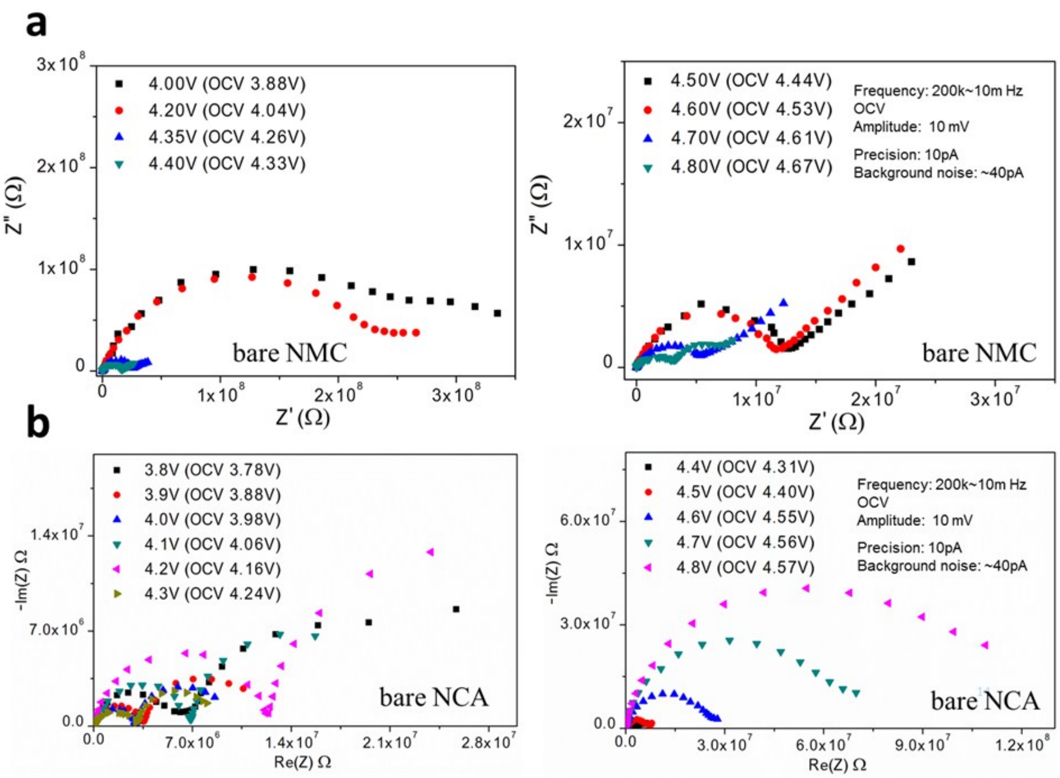

Fig. S3. The EIS spectra of (a) bare NMC and (b) bare NCA vary with specific charge voltage from 3.8V to 4.8V

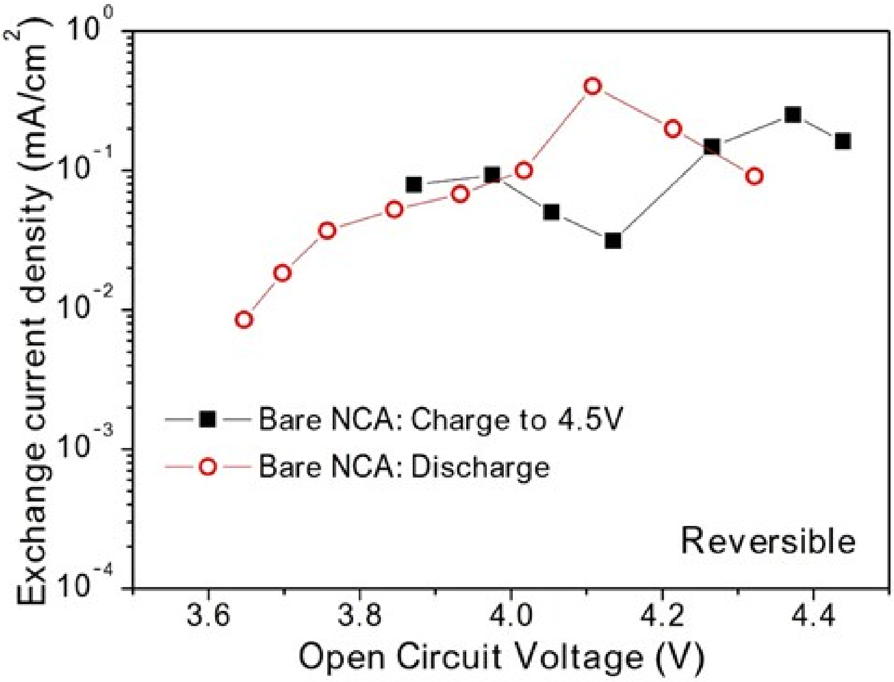

Fig. S4. Reversibility is observed in j_0 between charge and discharge for bare NCA charged to the lower voltage (4.5V).

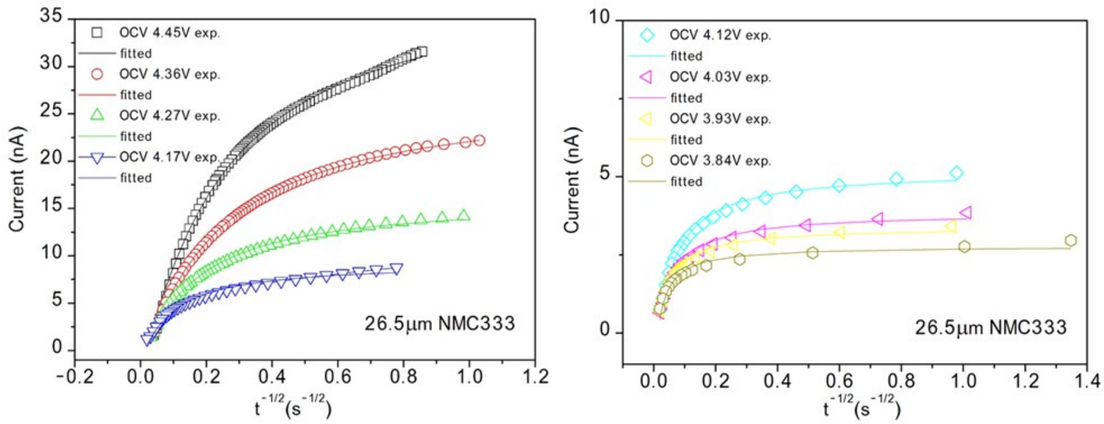

Fig. S5. PITT current vs time data, and corresponding least-squares fit from which kinetic parameters are obtained, for an NMC333 particle of 26.5 μm diameter, measured for a +15 mV voltage step from various relaxed OCV.

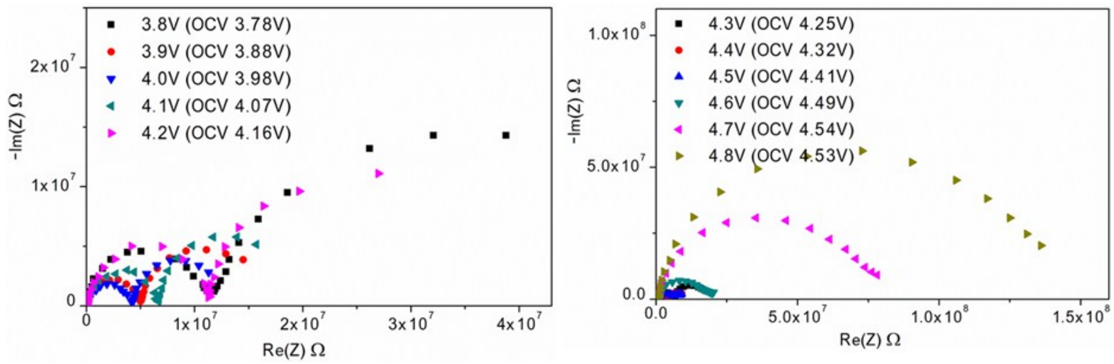

Fig. S6. The EIS spectra of a PVdF-coated NCA particle vary with specific charge voltage from 3.8V to 4.8V.

Table S1. The relaxed OCV, R_{ct}, and j_0 for three bare NMC333 particles during galvanosatic step-charging to 4.8V.

Particle A (diameter = 26.5µm)			Particle B (diameter = 23.0µm)			Particle C (diameter = 26.5µm)		
Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})	Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})	Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})
3.93	268	0.00437	3.88	534	0.003	3.99	469	0.002
4.07	243	0.00482	4.04	401	0.004	4.04	616	0.002
4.14	126	0.0093	4.26	28.7	0.054	4.19	342	0.003
4.27	26.2	0.0447	4.33	10.9	0.143	4.38	36.4	0.032
4.32	15.9	0.0737	4.44	5.58	0.279	4.52	6.68	0.175
4.41	12.2	0.0961	4.53	5.73	0.272	4.62	3.65	0.321
4.54	5.99	0.196	4.61	4.69	0.332	4.67	3.48	0.337
4.59	4.18	0.28						

Table S2 The relaxed OCV, R_{ct}, and j_0 for three bare NCA particles galvanostatically step-charged to voltages shown.

Step Voltage (V)	Particle A (diameter = 30.5µm)			Particle B (diameter = 32.0µm)			Particle C (diameter = 27.5µm)		
	Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})	Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})	Charge OCV	R_{ct} (x10^{6}Ω)	j_0 (mAcm^{-2})
3.8	3.781	6.52	0.1441						
3.9	3.887	3.57	0.2528	3.872	10.2	0.0791			
4.0	3.987	3.02	0.2993	3.975	8.68	0.0926			
4.1	4.067	6.74	0.1339	4.054	16.1	0.0499			
4.2	4.164	1.25	0.0725	4.135	25.8	0.0312			
4.3	4.246	3.59	0.2517	4.266	5.42	0.1483			
4.4	4.311	3.41	0.2645	4.373	3.21	0.2508			
4.5	4.408	5.87	0.1537	4.439	4.96	0.1619	4.432	10.5	0.104
4.6	4.552	28.2	0.032				4.502	58.5	0.0186
4.7	4.565	66.3	0.0136				4.519	96.7	0.0113
4.8	4.569	114.0	0.0079				4.521	196.0	0.0056

Table S3. The relaxed OCV, R_{ct}, and j_0 at a set of selected specific charge voltages for bare NMC333 particle galvanostaticallly step-charged to, and discharged from, 4.8V.

Particle A (diameter = 26.5μm)					
Charge OCV	R_{ct} ($\times10^6\Omega$)	j_0 ($mAcm^{-2}$)	Discharge OCV	R_{ct} ($\times10^6\Omega$)	j_0 ($mAcm^{-2}$)
3.93	268	0.00437	3.95	56.5	0.0207
4.07	243	0.00482	3.98	50.5	0.0232
4.14	126	0.0093	4.06	33.3	0.0352
4.27	26.2	0.0447	4.15	20.6	0.0569
4.32	15.9	0.0737	4.24	12.4	0.0945
4.41	12.2	0.0961	4.33	7.70	0.152
4.54	5.99	0.196	4.42	5.27	0.222
4.59	4.18	0.28	4.57	3.58	0.327

Table S4. The relaxed OCV, R_{ct}, and j_0 for bare NCA particles galvanostatically step-charged to 4.5V and 4.8V, respectively. , and then discharged.

Step Voltage (V)	Charge to 4.8V				Charge to 4.5V			
	OCV (charging)	j_0 ($mAcm^{-2}$)	OCV (discharging)	j_0 ($mAcm^{-2}$)	OCV (charging)	j_0 ($mAcm^{-2}$)	OCV (discharging)	j_0 ($mAcm^{-2}$)
3.8	3.781	0.1441	4.027	9E-4			3.647	0.0085
3.9	3.887	0.2528	4.096	1E-3	3.872	0.0791	3.698	0.0183
4.0	3.987	0.2993	4.163	1E-3	3.975	0.0926	3.757	0.0371
4.1	4.067	0.1339	4.226	0.0011	4.054	0.0499	3.846	0.0526
4.2	4.164	0.0725	4.269	0.0014	4.135	0.0312	3.933	0.0678
4.3	4.246	0.2517	4.367	0.0046	4.266	0.1483	4.017	0.1
4.4	4.311	0.2645			4.373	0.2508	4.108	0.4038
4.5	4.408	0.1537			4.439	0.1619	4.214	0.1991
4.6	4.552	0.032					4.322	0.0912
4.7	4.565	0.0136						
4.8	4.569	0.0079						

Table S5. The relaxed OCV, R_{ct}, and j_0 for PVdF-coated NCA galvanostatically step-charged to 4.8V and then discharged.

Step Voltage (V)	*Charge*			*Discharge*		
	OCV	R_{ct} (Ω)	j_0 (mAcm^{-2})	OCV	R_{ct} (Ω)	j_0 (mAcm^{-2})
3.8	3.781	11.9	0.082	3.541	218.0	0.0037
3.9	3.881	5.16	0.1895	3.565	102.0	0.0079
4.0	3.982	4.30	0.2275	3.628	35.1	0.0229
4.1	4.07	6.67	0.1467	3.714	9.83	0.0818
4.2	4.168	11.4	0.0857	3.808	4.4	0.1829
4.3	4.252	6.67	0.1467	3.907	2.62	0.3064
4.4	4.324	4.16	0.2352	4.005	1.37	0.5876
4.5	4.414	6.02	0.1626	4.104	0.98	0.8186
4.6	4.489	17.1	0.0571	4.206	1.68	0.4781
4.7	4.541	79.0	0.0124	4.316	8.04	0.1
4.8	4.535	145.0	0.0068			

Table S6. Analysis of fracture surface area from TXM results for a pristine NCA particle, and NCA particles charged to 3.9V, 4.1V, and 4.5V. The surface and volume of the particle is defined by a voxel count for each particle. Note that the voxel size is $(25.3 nm)^3$.

Status	Diameter (µm)	Surface (μm^2)*	Volume (μm^3)	Surface/volume ratio (μm^{-1})	Ratio of fracture surface area to initial particle surface area
pristine	11	360	690	0.53	0
3.9 V	10	460	550	0.83	0.58
4.1 V	11	500	620	0.80	0.52
4.5 V	11	920	770	1.2	1.28

*There is approximately a 5% error in the surface area due to vibrational instability in one of the X-ray microscopy beamlines that creates misaligned projection images resulting in some reconstruction artifacts.

Table S7. Fitting to PITT data yields j_0, D_{Li}, and B as a function of relaxed OCV for a bare NMC333 particle during discharged from 4.8V.

Particle D (diameter = 26.5µm)			
Discharge OCV	j_0 (mAcm^{-2})	D_{Li} (cm^2/s)	Biot number B (26.5 µm NMC333)
3.84	0.032	1.31E-10	3.43
3.93	0.039	1.26E-10	4.36
4.03	0.047	1.12E-10	5.89
4.12	0.053	1.06E-10	6.98
4.17	0.065	6.16E-11	14.76
4.27	0.103	6.79E-11	22.29
4.36	0.150	8.28E-11	29.06
4.45	0.196	1.37E-10	23.89