Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A. This journal is © The Royal Society of Chemistry 2024

Supporting information

Improved lithium-ion battery cathode rate performance via carbon black

functionalization

Donghyuck Park,^a Peter C. Sherrell,^{a, b} Fangxi Xie,^{a, c} and Amanda V. Ellis^{a*}

^a Department of Chemical Engineering, The University of Melbourne, Grattan Street, Parkville,

Victoria 3010, Australia

^b School of Science, RMIT University, Melbourne, Victoria 3001, Australia

^c School of Chemical Engineering and Technology, Sun Yat-Sen University, Zhuhai 519082, P.

R. China

*E-mail: amanda.ellis@unimelb.edu.au

Experimental section

Chemical treatment for carbon black: Hydrogen peroxide (H₂O₂) treated-, and nitric acid (HNO_3) treated-carbon blacks were prepared by functionalization of pristine carbon black (CB) (SuperP, Gelon, China) with $30\% v/v H_2O_2$ (ChemSupply, Australia) and $70\% v/v HNO_3$ (Thermo Fisher Scientific, Australia). Oxidation of pristine CB by H₂O₂ was carried out following previous methods.^{1, 2} Pristine CB (100 mg) was sonicated in 15 mL of H₂O₂ for 15 min. Subsequently, the mixture was placed onto a hot plate at 70 $^{\circ C}$ for 24, 48 or 72 h with continuous magnetic stirring. To maintain a sufficient concentration of H_2O_2 , 5 mL of H_2O_2 was added every 24 h to account for the loss of peroxide radicals. In the case of HNO_3 treatment, the HNO₃ concentration was adjusted to either 20% v/v or 70% v/v with deionized water. The pristine CB (100 mg) was added to 15 mL of adjusted HNO₃ and ultrasonicated (S30H, Techspan, Australia) for 15 min. Then, each mixture was refluxed at 140 °C for 1.5 h. After chemical treatment, the H₂O₂ or HNO₃ modified CBs were rinsed with deionized water and subjected to centrifugal filtration (Rotofix 32 A, Hettich, Germany). This rinsing process was repeated several times to remove residual peroxide or acid until the pH was approximately that of deionized water. Finally, the modified CBs were dried overnight at 60 °C.

Preparation of cathode electrodes and half-cell assembly: Active cathode materials, Ni_{0.6}Mn_{0.2}Co_{0.2}O₂ (NMC622), Ni_{0.8}Mn_{0.1}Co_{0.1}O₂ (NMC811), LiMn₂O₄ (LMO), and Ni_{0.8}Co_{0.15}Al_{0.05}O₂ (NCA) powders were purchased from Gelon, China. Cathode electrodes were fabricated by a conventional slurry-casting method (Scheme S1). The 90 wt% active material was mixed with 5 wt% CB (SuperP, Gelon, China), 5 wt% binder (polyvinylidene difluoride, PVDF, Gelon, China) and *N*-methyl-2-pyrrolidone solvent (NMP, Sigma-Aldrich, Australia) using a Thinky Mixer (AR-100, Thinky Inc., USA) at 2000 rpm for 20 min. The viscosity of slurry was controlled by amount of NMP. Afterwards, the slurry was cast onto aluminium foil using a doctor blade coater (K101 control Coater, RK Print Coat Instruments Ltd., U.K.). The coated cathode slurry was dried overnight at room temperature in a fume hood, and the remaining solvent was fully evaporated in a vacuum oven (AccuTemp-09, Across Int., Australia). Half-cells (2032-type coin cell) were assembled by pairing the punched working electrode (\emptyset = 12 mm; coating thickness = ~140 µm; active material mass loading = ~20.9 mg cm⁻²; porosity = 41.4 %) with a lithium metal disc (\emptyset = 14 mm) as the counter/reference electrode in an argon-filled glovebox. Celgard 2320 and lithium hexafluorophosphate (1 M) in ethylene carbonate: ethyl methyl carbonate (1 M LiPF₆ in EC: EMC 1:1 v/v, Sigma Aldrich, Australia) were used as a separator and electrolyte, respectively. The assembled cells were rested for 24 h before electrochemical testing. The ~20 mg cm⁻² mass loading cells were chosen to reduce the fraction of passive components and highlight ion transport kinetic in the rate-limiting factors.

Electrochemical testing / Electrode characterisation: The rate capability was measured using a Neware CT-4008T-5V10 mA battery cycler (Neware, China) at 25 $^{\circ \text{C}}$. The cathodes were cycled at 0.10 C to 0.75 C-rate (1 C-rate = 277.4, 200, 148, 279 mAh g⁻¹ for NMC622, NMC811, LMO, and NCA, respectively) in the voltage window of 3.0 – 4.3 V vs. Li⁺/Li at 25 $^{\circ}C$ in a temperature chamber (MHW-25, Neware, China) via the galvanostatic charge-discharge (GCD) method. Room temperature cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were conducted using a multifunctional potentiostat (VMP3, Bio-Logic, France). Before CV and EIS measurements, the solid electrolyte interphase formation process was conducted at 0.10 C-rate in a voltage window of 3.0 – 4.3 V vs. Li⁺/Li for three cycles using the GCD method. The CV curves were measured in a voltage range of 3.0 - 4.3 V vs. Li⁺/Li at a scan rate 0.1 - 1.5 mV s⁻¹. The cathodes were measured using EIS after maintaining a constant voltage for 2 h after reaching a specific voltage by GCD at 0.10 C-rate. The EIS spectra were obtained by averaging 3 measurements per frequency in the frequency range of 100 kHz – 10 mHz with a 10 mV voltage perturbation. Out-of-plane electrical conductivity measurements for the cathode electrodes were carried out using a digital multimeter (Fluke 8845A, USA) using a two-probe method. The resistance of the samples was measured using circular stainless-steel plates (\emptyset = 15 mm), then electrical conductivity was calculated based on resistance using the samples geometric information (Note S1, Supporting information).

Material characterisation: X-ray photoelectron spectroscopy (XPS) measurements for the CBs were performed on a Thermo Scientific K-alpha XPS using Al K α radiation (1486.7 eV). XPS spectra were collected at a step size of 1 eV in the range of 0 – 1300 eV (binding energy) for

overall survey and high-resolution scanning (step size 0.1 eV) for C, O, N regimes at approximately 1×10^{-9} mbar. The obtained peaks of O 1s core-level were fitted with C-O and C=O using CasaXPS software (see Fig. S1-4 and Table S1). Raman spectra of the chemically modified CBs were obtained using a Renishaw inVia Raman Microscope with a 532 nm laser and 1800 l mm⁻¹ grating (see Fig. S5 and Table S2). The surface morphologies of the cathode powders and electrodes were characterised by scanning electron microscopy (FlexSEM, Hitachi, Japan) in high-vacuum mode with 15 keV acceleration voltage (see Fig. S6). The structural properties of the cathode powders were observed using a powder X-ray diffractometer (XRD, Bruker D8 Advances, USA) with Cu K α radiation source ($\lambda = 1.5406$ Å). XRD patterns were collected at a step size of 2 $\theta = 0.02^{\circ}$ in the range of 5 < 2 θ < 85° (Fig. S13).



Scheme S1 Schematic diagram of chemical treatment for CB, and half-cell cathode fabrication.



Fig. S1 XPS survey scans for chemically modified CB.



Fig. S2 Normalized C 1s core-level XPS spectra for modified CBs. The C 1s core-levels were taken at three different locations (black, red, blue) for each samples. The C 1s core-level were normalized with relative to asymmetry sp² carbon peak.



Fig. S3 Normalized O 1s core-level XPS spectra for modified CBs. O 1s core-levels were taken at three different locations (black, red, blue) for each samples. The O 1s core-levels were normalized with relative to each C 1s peak, and the intensities of the deconvoluted peaks (C-O and C=O; Gaussian/Lorentzian = 50/50 weighting) were emphasised by orange line.

The high sp² carbon peaks of C 1s are observed because carbon blacks were chemically treated mildly to avoid defect generation (oxygen atomic concentration: 0.8 - 1.8 at. %). The dominant influence of the asymmetry sp² carbon peak makes deconvolution of C1s be ambiguous.³ In this case, many researchers have agreed on the need for O 1s analysis to avoid misleading results that may arise when analysing the low peak intensity of the oxygen group in C1s.⁴⁻⁶ In this study, oxygen atomic concentrations are evaluated by O 1s core-level.



Fig. S4 N 1s core-level XPS spectra for modified CBs.



Fig. S5 Raman spectra of modified CBs.

The vibrational energy modes of carbon black (CB) could be interpreted by the graphite phase (G-band, in-plain vibration of sp² bonding) and disordered phase (D-band, out-of-plain vibration attributed to the defects).⁷ Since there is a large amount of amorphous carbon in CBs, the intensity of vibration is lower than that of other carbon materials, and

superposition of bands reduce accuracy.^{8, 9} Therefore, the defect level of modified CB were evaluated by the intensity ratio of the D- and G-band, after deconvolution: D^{*} (~1183 cm⁻², small grain or disorder in carbon lattice), D (~1350 cm⁻², defects and disorders in carbon lattice), D" (~1504 cm⁻², amorphous phase), G (~1582 cm⁻², ordered carbon), and D' (~1615



cm⁻², resonance with the G-band but split due to impurities).⁷⁻¹¹

Fig. S6 Top-view scanning electron microscopy (SEM) images for CB, CB-OH (24 h), CB=O (72 h) and CB-COOH (20%).



Fig. S7 Cyclic voltammograms (CVs) at 0.1 mV s⁻¹ – 1.5 mV s⁻¹ scan rates for (a) CB, (b) CB-OH (24 h), (c) CB-OH (48 h), (d) CB=O (72 h) and (e) CB-COOH (20%).

Increasing the scan rate from 0.1 to 1.5 mV s⁻¹ broadens both the cathodic and anodic peaks and shifts them to either end of the cut-off voltage, due to polarization. Intercalation and deintercalation of Li⁺ ions are quasi-reversible processes showing a limitation in the

charge transfer kinetics. Therefore, as the scan rate is increased, the overpotential also increases.¹²



Fig. S8 Peak separation potential between cathodic and anodic peaks in the cyclic voltammogram (CV) as the scan rate is increased from 0.1 mV s⁻¹ to 1.5 mV s⁻¹.

The voltage (potential) separation between anodic and cathodic peaks is inversely proportional to the electron transfer rate, and a smaller peak potential separation corresponds to a more efficient electrochemical reaction by the Nernst equation:

$$E_{separation} = E_{separation} - \frac{RT}{zF} \ln Q_r$$
 (Equation S1)

Where $E_{separation}$ is the cell potential at a specific temperature, $E_{separation}^{\theta}$ is the standard cell potential, R is the universal gas constant, T is the temperature, z is the number of electrons transferred, and Q_r is the reaction quotient.

A well-known mechanism of LiB cathode degradation is transition metal dissolution, originating from electrolyte decomposition. The decomposed electrolyte (e.g., ethylene carbonate) generates water molecules, and subsequently, hydrofluoric acid (HF) can be generated by a chemical reaction between the lithium salt and the water (LiPF₆ + H₂O \rightarrow 2LiF

+ 2HF + POF₃).^{13, 14} Furthermore, transition metals can be dissolved by acidic attack.¹⁵ When evaluating electrochemical stability the oxidation potentials of electrolytes have been studied using cyclic voltammetry,^{16, 17} for example with 1 M LiPF₆ in ethylene carbonate at 0.1 mV s⁻¹ with a Pt electrode¹⁴ or 1.2 M LiPF₆ in ethyl methyl carbonate at 10 mVs⁻¹ with a glassy carbon electrode.¹⁹ In Figure S7(a-d), modified CB/PVDF cathodes with 1 M LiPF₆ ethylene carbonate/ethyl methyl carbonate were tested in the range of 0 – 5 V vs. Li⁺/Li at 0.1, 1.0 mV s⁻¹. The peaks at 0 and 280 mV vs. Li⁺/Li relate to lithium plating and stripping, respectively. Importantly, in the range of cathode operation (3 – 4.3 V vs. Li⁺/Li) no current peaks were observed, implying that there are no distinguishable redox reactions of the electrolyte and oxygen groups (i.e., no chemical decomposition).



Fig. S9 Electrochemical stability test for modified CB/PVDF (50:50 wt%) composite without any active material.



Fig. S10 (a) Real and (c) imaginary impedance plot of averaged CB and CB=O (72 h) at 3.7 V vs. Li⁺/Li discharging. The residuals of measured data and fitted curves of (b) real impedance and (d) imaginary impedance corresponding to (a) and (c).

It is worth noting that the impedances are normalised by active material mass loadings. Under the assumption that the morphological distribution of active particles is constant, mass-normalisation allows comparison of the electrochemical reaction for a constant surface area.²⁰

The DRT technique has been studied to show discrete electrochemical impedance data into continuous time domain. The DRT function $\gamma(\tau)$ were calculated using Matlab describing as follows.^{21, 22}

$$Z(f) = Z_{\infty} + \int \frac{\gamma(\tau)}{1 + i2\pi f\tau} d\tau$$
 (Equation
S2)

Where Z is the impedance, Z_{∞} is the offset resistance at $f \rightarrow \infty$, γ is the DRT function, τ is the relaxation time, and the f is the frequency ($f = 1/2\pi\tau$).



Fig. S11 Contact angle measurements for (a) CB and (b) CB=O (72 h). The 1 M LiPF₆ EC: EMC (20 μ L) is placed on a polytetrafluoroethylene film (PTFE; as a reference), CB and CB=O (72 h). Contact angle measurements were conducted in an argon-filled glovebox. Photos were taken by a Galaxy S10 5G SM-G977U camera.



Fig. S12 Rate performance of the (a-i) NMC811, (b-i) LMO, (c-i) NCA cathodes with CB or CB=O (72 h) at 0.1, 0.25, 0.5, and 0.75 C-rates. GCD curves on 0.10 – 0.75 C-rates of the (a-ii) NMC811, (b-ii) LMO, (c-ii) NCA cathodes. The plateaus of NMC811 GCD curve corresponding

to phase transition H2 \rightarrow H1 (~3.7 V vs. Li⁺/Li) and H3 \rightarrow H2 (~4.2 V vs. Li⁺/Li) are indicated by arrows. The plateau on the NCA CB=O (72 h) GCD curve corresponding to H2 \rightarrow H1 (~3.7 V vs. Li⁺/Li) is highlighted an arrow and IR drop of NCA CB at 0.10 C-rate is demonstrated. Error bars are representing standard deviation.

A CB/NMC811 cathode demonstrated a discharge capacity of 181, 152, 111, and 65 mAh g⁻¹ at C-rates of 0.10, 0.25, 0.50, and 0.75 C, respectively (Fig. S10a). The CB=O (72 h)/NMC811 cathode exhibited an enhanced rate capability, delivering discharge capacities of 194, 181, 160, and 136 mAh g⁻¹ at the same C-rate. A similar trend was observed for CB/LMO and CB=O (72 h)/LMO cathodes (Fig. S10b) with discharge capacities of 92 vs. 98 mAh g⁻¹, respectively, at 0.75 C; and CB/NCA and CB=O (72 h)/NCA cathodes (Fig. S10c) with discharge capacities of 45 mAh g⁻¹ vs. 121 mAh g⁻¹, respectively, at 0.5 C. In Figure S10a-ii, b-ii, c-ii, depending on the crystal structure, the GCD curves show the phase transition that appeared during charging and discharging. The NMC811 CB and CB=O (72 h) cathodes illustrated two distinguishable plateaus at ~ 3.7 V vs. Li⁺/Li (H2 \rightarrow H1 phase transition) and ~ 4.2 V vs. Li⁺/Li (H3 \rightarrow H2 phase transition) at 0.10 C-rate,²³ however, only CB=O (72 h) showed two clear plateaus at 0.25 C signifying Li⁺ ion intercalation. In the case of LMO, the reduction of Mn⁴⁺ to Mn^{3.5+}, arising from Li⁺ insertion, leads to a phase transition from a spinel to a cubic structure at ~ 4.1 V vs. Li⁺/Li, and subsequently at x< 1 in $Li_xMn_2O_4$, the $Mn^{3.5+}$ is reduced to Mn^{3+} with an accompanying large voltage drop, shown in Figure S10b-ii.²² LMO CB and LMO CB=O (72 h) showed a slight potential difference, but there was no significant difference in phase transition. In Fig. S10c-ii, the NCA CB delivered a higher discharge capacity than NCA CB=O (72 h) at 0.10 C-rate (165.1 vs. 153.8 mAh g^{-1}). The NCA CB at 0.10 C showed an ambiguous plateau at ~3.7 V vs. Li⁺/Li compared to NCA CB=O (72 h) denoting slower a phase transition behaviour. When applied current is zero right before discharging, significant IR drop of NCA CB depicts highly developed overvoltage during charging including the relaxation of Li⁺ ion

concentration gradient. Despite of slower phase transition and significant IR drop, NCA CB showed higher capacity than NCA CB=O at 0.1 C-rate.²⁵ This implies that there is an additional capacity contribution other than Li⁺ ion redox for NCA CB at 0.10 C-rate. This may occur due to lattice oxygen redox reactions on the NCA CB which can offer additional capacity,²⁶ however, lattice oxygen redox reactions are unstable electrochemical reactions that lead to irreversible oxygen loss from the NCA and detrimental structural effects.²⁷ However, the CB=O (72 h)/NCA cathode shows dramatically improved capacity at all rates greater than 0.10

C-rate.



ed ~ 190 mAh g⁻¹. The capacity of NCA CB and NCA CB=O were evaluated using the same NCA cathode materials, therefore key trends were analysed based on the relative effects of CB and CB=O (72 h) impact on the cathode performance.

Fig. S13 X-ray diffraction (XRD) spectra of (a) NMC622, (b) NMC811, (c) NCA and (d) LMO. XRD spectra of NMC622, NMC811, NCA are indexed to the layered structure of α -NaFeO₂ and LMO is indexed to the spinel structure.^{28, 29} SEM images of (e) NMC622, (f) NMC811, (g) NCA and (h) LMO. Magnified SEM images are placed in the insets.

Table S1 Summary of XPS C 1s and O 1s (C-O, C=O) curve fitting data with peak positions (binding energy; eV), full width half maximum (FWHM; eV), and atomic concentrations (at%). The error represents the standard error calculated after XPS measurements at three different locations for each samples.

		СВ	CB-OH (24 h)	CB-OH (48 h)	CB=O (72 h)	CB-COOH (20%)	CB-COOH (70%)
	Position	284.26 ± 0.01	284.21 ± 0.00	284.16 ± 0.03	284.10 ± 0.03	284.18 ± 0.01	284.08 ± 0.01
C 1s	FWHM	1.01 ± 0.01	1.00 ± 0.01	1.02 ± 0.01	1.08 ± 0.02	1.02 ± 0.01	1.18 ± 0.01
	at%	99.18 ± 0.09	98.89 ± 0.01	98.75 ± 0.17	98.53 ± 0.14	98.17 ± 0.11	93.21 ± 0.10
	Position	533.47 ± 0.19	532.97 ± 0.15	532.8 ± 0.08	532.98 ± 0.08	532.88 ± 0.12	533.1 ± 0.02
0 1s C-O	FWHM	2.09 ± 0.08	2.28 ± 0.05	2.22 ± 0.09	2.27 ± 0.06	2.54 ± 0.11	2.29 ± 0.03
	at%	0.16 ± 0.06	0.42 ± 0.06	0.63 ± 0.09	0.37 ± 0.19	1.01 ± 0.11	3.15 ± 0.04

0 1s (=0	Position	531.76 ± 0.09	531.74 ± 0.08	531.5 ± 0.04	531.57 ± 0.19	531.32 ± 0.11	531.35 ± 0.01
	FWHM	2.09 ± 0.08	2.28 ± 0.05	2.22 ± 0.09	2.59 ± 0.32	2.55 ± 0.11	2.29 ± 0.03
	at%	0.62 ± 0.05	0.71 ± 0.04	0.62 ± 0.10	1.07 ± 0.30	0.81 ± 0.09	3.65 ± 0.14

Table S2 Summary of Raman spectra curve fitting data with peak positions (Raman shift; cm⁻¹) and full width half maximum (FWHM; Raman shift cm⁻¹). The error represents the standard error calculated from three samples.

		СВ	CB-OH (24 h)	CB-OH (48 h)	CB=O (72 h)	CB-COOH (20%)	CB-COOH (70%)
D*	Position	1177.59 ± 3.64	1189.31 ± 4.71	1182.39 ± 2.82	1183.54 ± 3.15	1182.32 ± 3.32	1182.67 ± 3.55
D	FWHM	167.94 ± 8.90	174.47 ± 10.97	153.43 ± 8.72	154.60 ± 6.17	160.19 ± 7.90	153.62 ± 0.56
D	Position	1350.60 ± 1.42	1351.44 ± 0.39	1352.94 ± 0.49	1352.35 ± 0.51	1351.21 ± 0.16	1351.96 ± 0.41
U	FWHM	121.30 ± 2.64	126.83 ± 1.89	126.87 ± 2.43	126.19 ± 1.42	127.77 ± 0.95	119.69 ± 4.16
יים	Position	1495.76 ± 2.62	1499.41 ± 0.44	1507.58 ± 2.41	1506.58 ± 0.55	1501.72 ± 4.55	1502.22 ± 5.03
D	FWHM	131.40 ± 4.43	133.32 ± 2.20	129.13 ± 4.96	126.86 ± 1.32	129.24 ± 3.36	128.55 ± 3.81
G	Position	1582.43 ± 0.49	1583.31 ± 0.65	1586.24 ± 0.94	1583.83 ± 0.69	1583.71 ± 3.80	1581.88 ± 3.13
6	FWHM	66.86 ± 1.19	67.01 ± 0.44	62.84 ± 1.50	63.51 ± 0.30	65.96 ± 0.99	65.81 ± 2.92
D'	Position	1614.51 ± 0.21	1614.64 ± 0.69	1617.24 ± 0.74	1614.53 ± 0.77	1614.89 ± 3.14	1612.70 ± 1.86
D'	FWHM	49.89 ± 1.14	51.45 ± 1.60	48.28 ± 0.80	50.63 ± 1.00	50.22 ± 2.78	50.31 ± 3.17

Table S3 Current density, relevant peak potential, halfway potential, and peak separation potential for CB, CB-OH (24 h), CB-OH (48 h), CB=O (72 h), and CB-COOH (20%) at a scan rate of 0.1 mV s⁻¹.

		СВ	CB-OH (24 h)	CB-OH (48 h)	CB=O (72 h)	CB-COOH (20%)
Current	Anodic	0.129	0.133	0.135	0.138	0.122
density (A g⁻¹)	Cathodic	-0.096	-0.102	-0.103	-0.104	-0.092
V_{Peak}	Anodic	3.977	3.985	3.973	3.961	4.029
(V vs. Li⁺/Li)	Cathodic	3.526	3.528	3.544	3.546	3.486
Halfway p (V vs. 1	ootential Li⁺/Li)	3.751	3.757	3.759	3.760	3.758
Peak potential separation (mV)		451	457	429	401	543

Table S4 Slopes fitted in the range of 0.1 - 0.4 mV s⁻¹ scan rate in the cyclic voltammetry curves.

	СВ	CB-OH (24 h)	CB-OH (48 h)	CB=O (72 h)	CB-COOH (20%)
Anodic (+)	0.49	0.52	0.53	0.57	0.42
Cathodic (-)	0.33	0.34	0.35	0.38	0.27

Table S5 Raw data of peak separation potential between cathodic and anodic peaks in the CV as the scan rate is increased from 0.1 mV s⁻¹ to 1.5 mV s⁻¹. The peak separation potential is gradually saturated to ~1300 mV, the same as the cut-off voltage.

 Scan rate (mV s ⁻¹)	СВ	CB-OH (24 h)	CB-OH (48 h)	CB=O (72 h)	СВ-СООН (20%)
0.1	450.77	456.84	428.99	400.78	542.92
0.2	742.84	718.28	677.06	640.40	860.49
0.3	952.31	922.24	862.53	808.28	1027.28
0.4	1027.24	1009.02	977.21	957.01	1073.25
0.5	1081.25	1053.22	1027.40	1001.05	1113.45
0.6	1111.21	1087.40	1059.47	1043.44	1143.50
0.8	1163.40	1135.16	1115.27	1097.22	1187.43
1	1300.05	1155.36	1139.30	1129.46	1207.36
1.2	1299.86	1169.30	1163.46	1147.22	1300.01
1.5	1299.79	1300.29	1299.94	1299.84	1299.97

Note S1 Electrical conductivity and percolation effect

Electrical conductivity is inversely proportional to the electrode's thickness and proportional to its cross-sectional area. Electrical conductivity of the cathode was calculated using measured electrical resistance as follows.

$$\sigma = t/RA$$
 (Equation S3)

Where σ is the electrical conductivity (S m⁻¹), t is the thickness of cathode (m), R is the measured electrical resistance (ohms), and A is the cross-sectional area of the cathode (m²).

The conductive fillers make electrical networks according to percolation theory which is typically a function of conductive filler content in an insulating medium³⁰. By increasing the fraction of conductive filler, the distance between separated filler particles is decreased until

Unit: mV

the fillers are in contact, subsequently connected networks are formed. The electrical conductivity of a filler/insulator composite exponentially increases over the percolation threshold caused by the formation of the electrical network.^{31, 32} Zhu et al.³⁰ verified the dimensional effect of conductive additives on a NMC cathode. They used single-walled carbon nanotubes, which have a high-aspect ratio and superior electrical conductivity, to form electrical networks at a low percentage-weight content compared to CB. The universal power law expression for percolation theory equation is³³:

$$\sigma = \sigma_0 (\phi - \phi_c)^t$$
 (Equation S4)

Where σ is the electrical conductivity of composite, σ_0 is the electrical conductivity of filler,

 ϕ is the weight fraction of filler, ϕ_c is the percolation threshold, and t is the percolation exponent.

References

- 1. K. A. Wepasnick, B. A. Smith, K. E. Schrote, H. K. Wilson, S. R. Diegelmann and D. H. Fairbrother, *Carbon*, 2011, **49**, 24-36
- 2. Y. Peng and H. Liu, Ind. Eng. Chem. Res., 2006, 45, 6483-6488.
- 3. S. Yumitori, J. Mater. Sci., 2000, 35, 139-146
- 4. G. Zhang, S. Sun, D. Yang, J.-P. Dodelet, and E. Sacher, *Carbon*, 2008, **46**, 196-205.
- 5. D. Rosenthal, M. Ruta, R. Schlögl, and L. Kiwi-Minsker, *Carbon*, 2010, 48, 1835-1843.
- 6. S. Reiche, R. Blume, X. C. Zhao, D. Su, E. Kunkes, M. Behrens, and R. Schlögl, *Carbon*, 2014, **77**, 175-183.
- 7. T. Jawhari, A. Roid, and J. Casado, *Carbon*, 1995, **33**, 1561-1565.
- A. Y. Lee, K. Yang, N. D. Anh, C. Park, S. M. Lee, T. G. Lee and M. S. Jeong, *Appl. Surf. Sci.*, 2021, 536, 147990.
- 9. A. A. King, B. R. Davies, N. Noorbehesht, P. Newman, T. L. Church, A. T. Harris, J. M. Razal and A. I. Minett, *Sci. Rep.*, 2016, **6**, 19491.
- 10. S. Claramunt, A. Varea, D. Lopez-Diaz, M. M. Velázquez, A. Cornet and A. Cirera, *J. Phys. Chem. C*, 2015, **119**, 10123-10129.
- 11. A. Manea and M. R. Leishman, *Oecologia*, 2011, **165**, 735-744.
- 12. T. Kim, W. Choi, H.-C. Shin, J.-Y. Choi, J. M. Kim, M.-S. Park and W.-S. Yoon, *J. Electrochem. Sci. Technol.*, 2020, **11**, 14-25.
- 13. Y. Tesfamhret, R. Younesi and E. J. Berg, J. Electrochem. Soc, 2022, 169, 010530.
- 14. Y. Tesfamhret, H. Liu, Z. Chai, E. Berg and R. Younesi, *Chem. Electro. Chem.*, 2021, **8**, 1516-1523.
- 15. K. Guo, S. Qi, H. Wang, J. Huang, M. Wu, Y. Yang, X. Li, Y. Ren and J. Ma, *Small Sci.*, 2022, **169**, 010530.

- 16. Q. Zhao, X. Liu, S. Stalin, K. Khan and L. A. Archer, *Nat. Energy*, 2019, **4**, 365-373.
- 17. Q. Zhao, X. Liu, S. Stalin and L. Archer, *Cell Rep. Phys. Sci.*, 2020, **1**, 100146.
- 18. K. Abe, Y. Ushigoe, H. Yoshitake and M. Yoshio, J. Power Sources, 2006, 153, 328-335.
- 19. O. Borodin, W. Behl and T. R. Jow, *J. Phys. Chem. C*, 2013, **117**, 8661-8682.
- 20. M. A. Kamenskii, S. N. Eliseeva, E. G. Tolstopjatova, A. I. Volkov, D. V. Zhuzhelskii and V. V. Kondratiev, *Electrochim. Acta*, 2019, **326**, 134969.
- 21. F. Ciucci and C. Chen, *Electrochim. Acta*, 2015, **167**, 439-454.
- 22. T. H. Wan, M. Saccoccio, C. Chen and F. Ciucci, *Electrochim. Acta*, 2015, **184**, 483-499.
- 23. J. Li, L. E. Downie, L. Ma, W. Qiu and J. Dahn, J. Electrochem. Soc., 2015, **162**, A1401.
- 24. M. Thackeray, J. Croy, E. Lee, A. Gutierrez, M. He, J. S. Park, B. Yonemoto, B. Long, J. Blauwkamp and C. Johnson, *Sustainable Energy Fuels*, 2018, **2**, 1375-1397.
- 25. B. Zahiri, A. Patra, C. Kiggins, A. X. B. Yong, E. Ertekin, J. B. Cook and P. V. Braun, *Nat. Mater.*, 2021, **20**, 1392-1400.
- X. Liu, G.-L. Xu, V. S. C. Kolluru, C. Zhao, Q. Li, X. Zhou, Y. Liu, L. Yin, Z. Zhuo, A. Daali, J.-J. Fan, W. Liu, Y. Ren, W. Xu, J. Deng, I. Hwang, D. Ren, X. Feng, C. Sun, L. Huang, T. Zhou, M. Du, Z. Chen, S.-G. Sun, M. K. Y. Chan, W. Yang, M. Ouyang and K. Amine, *Nat. Energy*, 2022, 7, 808-817.
- 27. G. Assat, D. Foix, C. Delacourt, A. Iadecola, R. Dedryvere and J. M. Tarascon, *Nat. Commun.*, 2017, **8**, 2219.
- 28. Q. Wang, C.-H. Shen, S.-Y. Shen, Y.-F. Xu, C.-G. Shi, L. Huang, J.-T. Li and S.-G. Sun, *ACS Appl. Mater. Interfaces*, 2017, **9**, 24731-24742.
- 29. T.-F. Yi, C.-L. Hao, C.-B. Yue, R.-S. Zhu and J. Shu, *Synth. Met.*, 2009, **159**, 1255-1260.
- 30. Z. Ju, X. Zhang, S. T. King, C. D. Quilty, Y. Zhu, K. J. Takeuchi, E. S. Takeuchi, D. C. Bock, L. Wang, A. C. Marschilok and G. Yu, *Appl. Phys. Rev.*, 2020, **7**, 041405.
- 31. A. J. Marsden, D. G. Papageorgiou, C. Vallés, A. Liscio, V. Palermo, M. A. Bissett, R. J. Young and I. A. Kinloch, *2D Mater.*, 2018, **5**, 032003.
- 32. H.-J. Choi, M. S. Kim, D. Ahn, S. Y. Yeo and S. Lee, *Sci. Rep.*, 2019, **9**, 6338.
- 33. E. Chang, A. Ameli, A. R. Alian, L. H. Mark, K. Yu, S. Wang and C. B. Park, *Compos. B. Eng.*, 2021, 207, 108552