

Supplementary Material

Promoting Electrochemical Rates by Concurrent Ionic-Electronic Conductivity Enhancement in High Mass Loading Cathode Electrode

Ying Wang¹, Aleksandar S. Mijailovic², Tongtai Ji¹, Ercan Cakmak³, Xianhui Zhao³, Luyao
Huang¹, Brian W. Sheldon^{2,*}, Hongli Zhu^{1*}

¹ Department of Mechanical and Industrial Engineering, Northeastern University, Boston, MA
02115, USA

² School of Engineering, Brown University, Providence, RI 02912, USA

³ Manufacturing Science Division, Oak Ridge National Laboratory, Oak Ridge, TN, 37831, USA

*Corresponding author: Dr. Hongli Zhu, E-mail: h.zhu@neu.edu; Dr. Brian W. Sheldon, Email:
brian_sheldon@brown.edu



Figure S1. Digital image of freeze-dried CNC.

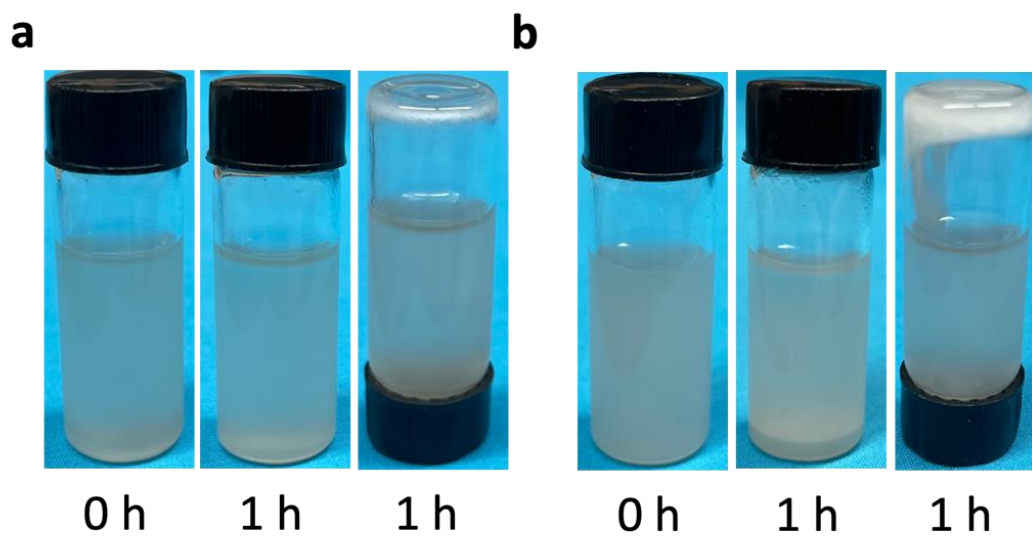


Figure S2. Digital images of 2.5% solid content (a) CNC:PVDF=1:2 and (b) pure CNC in NMP before and after storage for 1 hour.

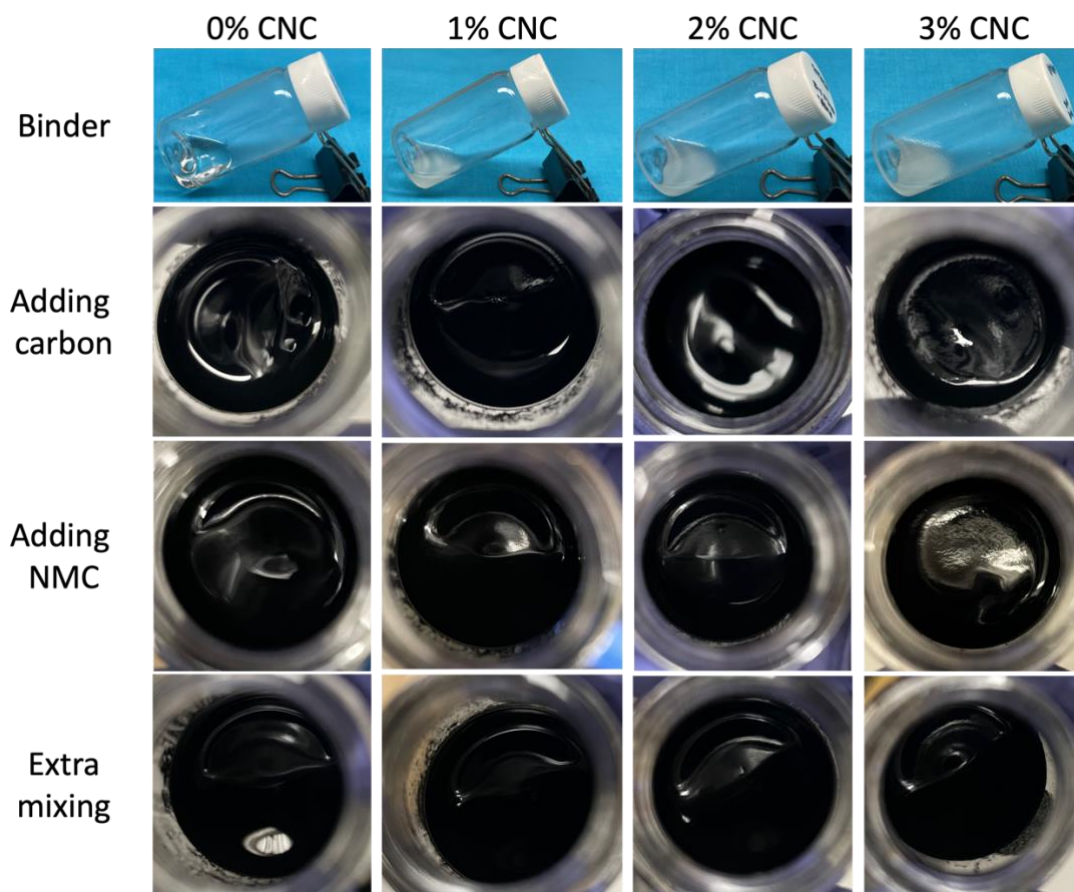


Figure S3. Digital images of electrode slurries during fabrication.

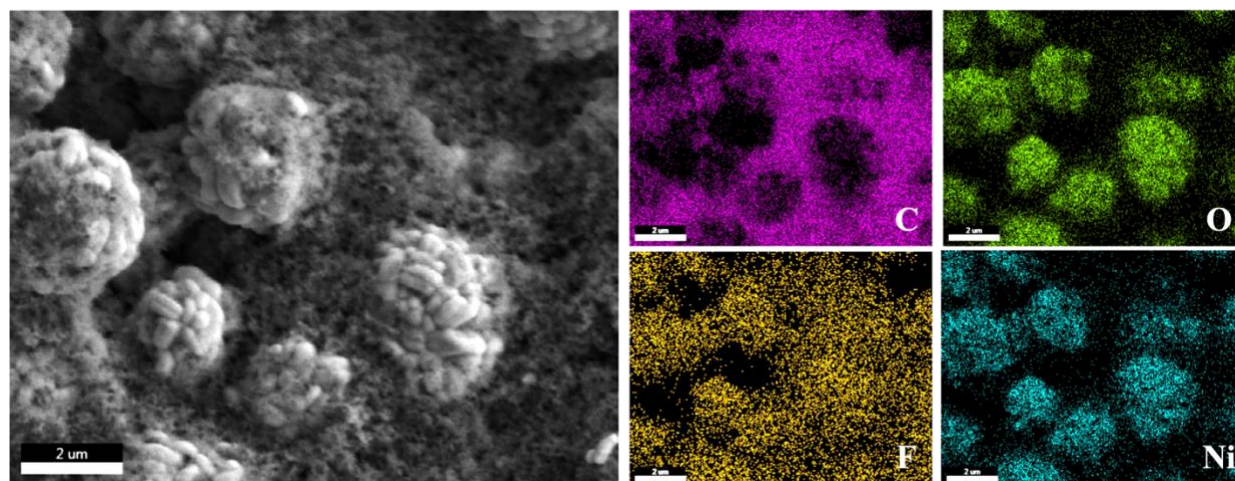


Figure S4. Elemental mapping of 1% CNC electrode to show the distribution of C in fuchsia, O in green, F in yellow, and Ni in cyan. The scale bar is 2 μm.

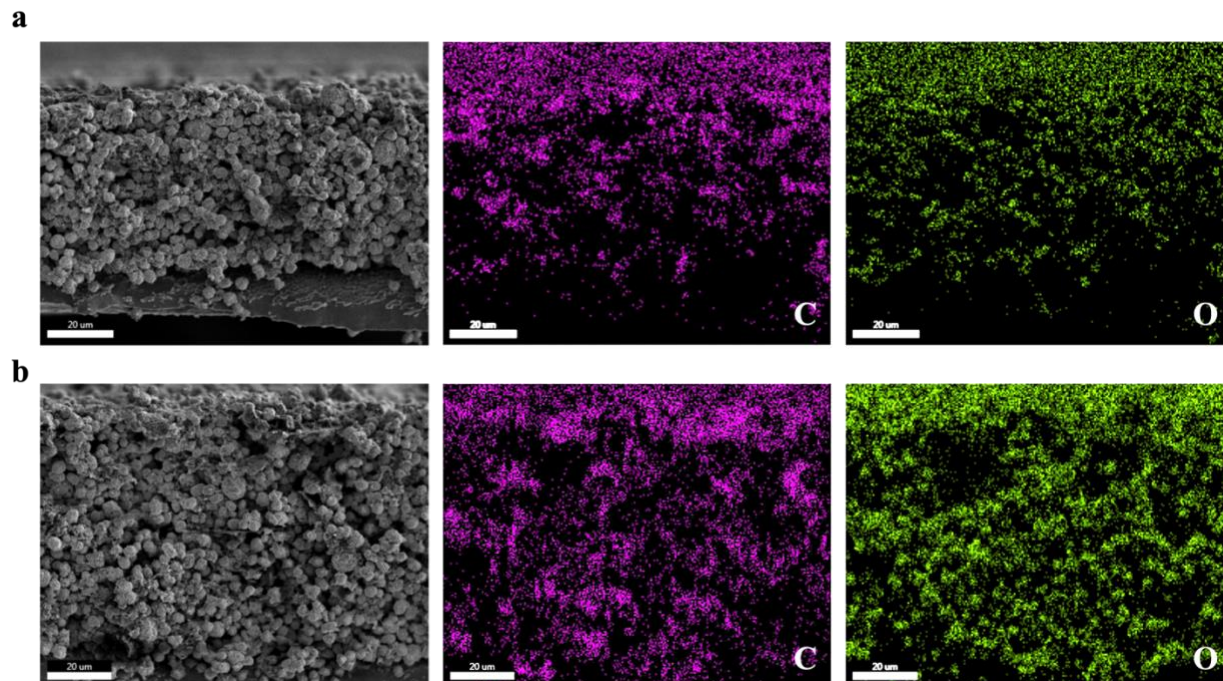


Figure S5. Cross-sectional elemental mapping images of (a) 0% CNC and (b) 1% CNC electrodes to show the distribution of C in fuchsia and O in green. The scale bar is 20 μm .

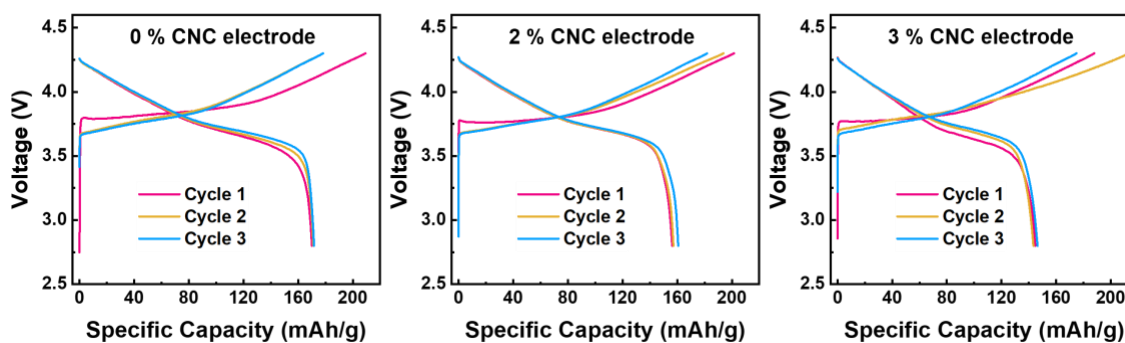


Figure S6. Galvanostatic charge and discharge curves of the initial three curves of 0%, 2%, and 3% CNC electrodes at 0.1 C. The mass loading is 17.0 mg/cm^2 .

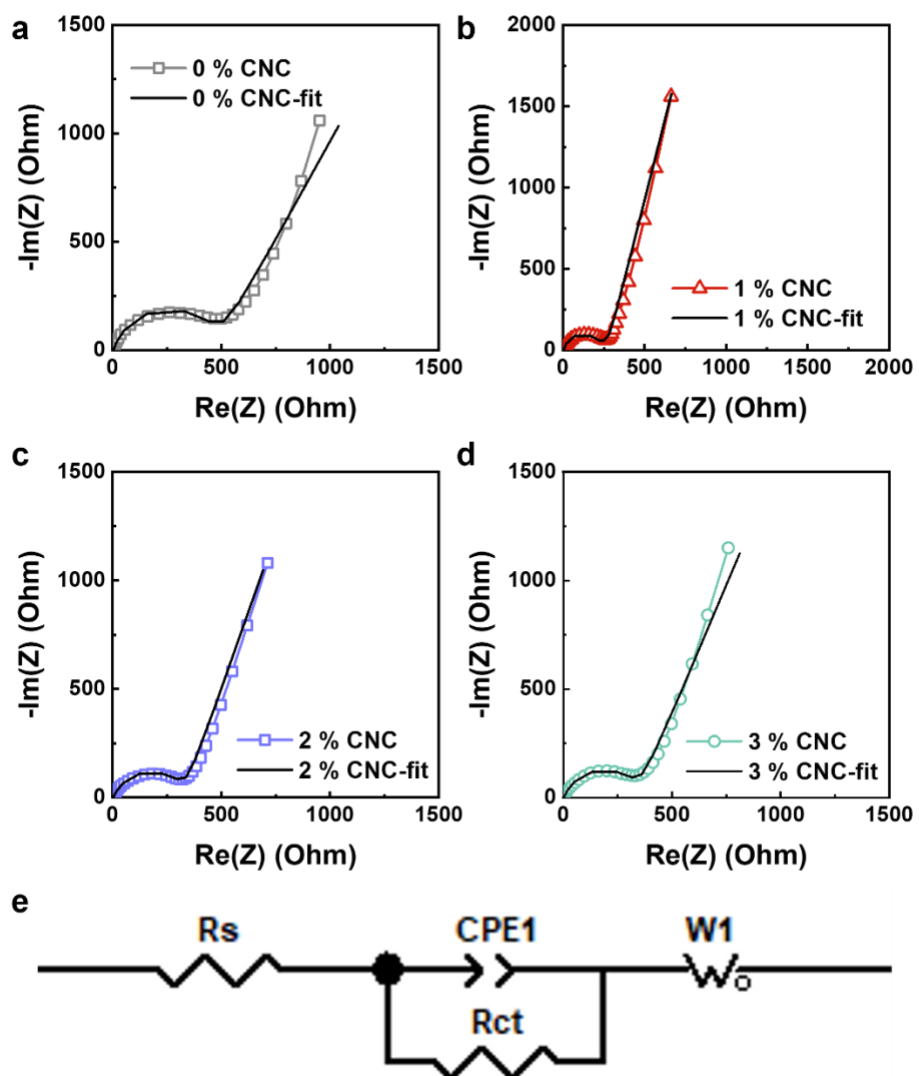


Figure S7. Nyquist plots and fit results of (a) 0, (b) 1, (c) 2, and (d) 3% CNC electrodes. (e) The equivalent circuit used for EIS. Zview software was applied for fitting. The bulk resistance, charge transfer resistance, Warburg coefficient, and diffusion coefficient of electrodes are listed and discussed below. The mass loading is 17.0 mg/cm².

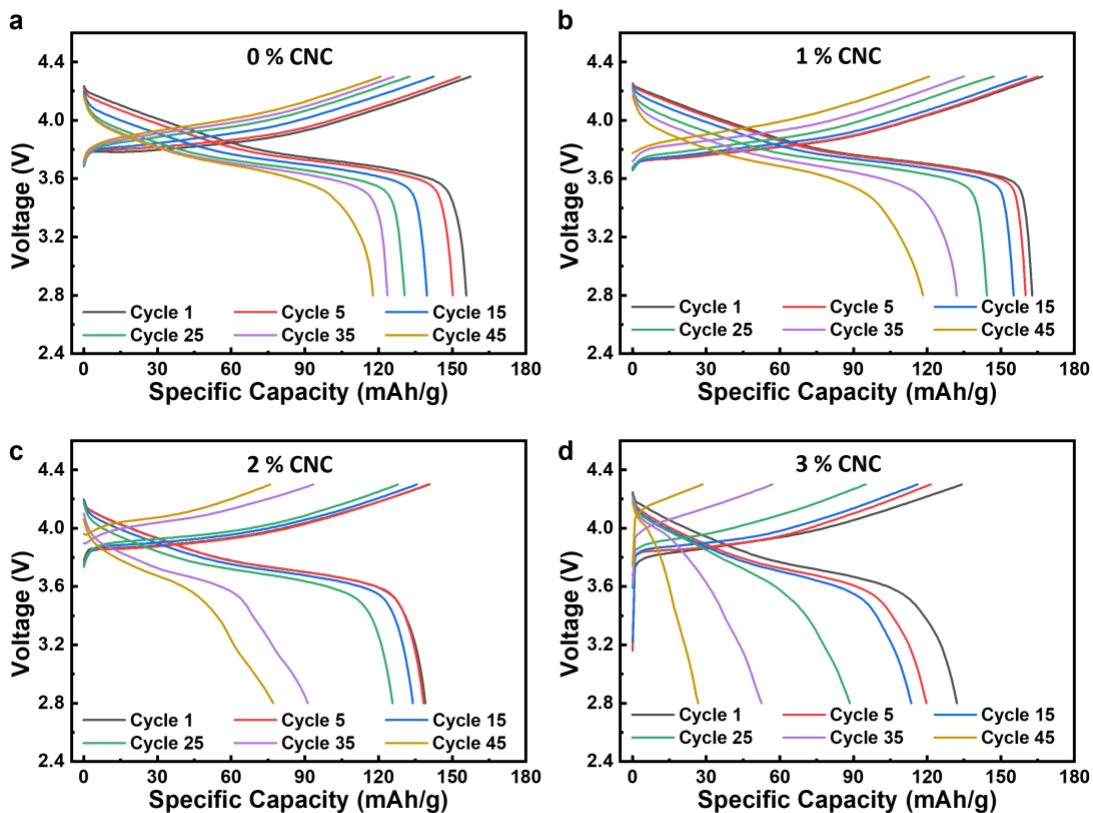


Figure S8. Galvanostatic charge and discharge curves of (a) 0%, (b) 1%, (c) 2%, and (d) 3% CNC electrodes at 1 C. The mass loading is 17.0 mg/cm².

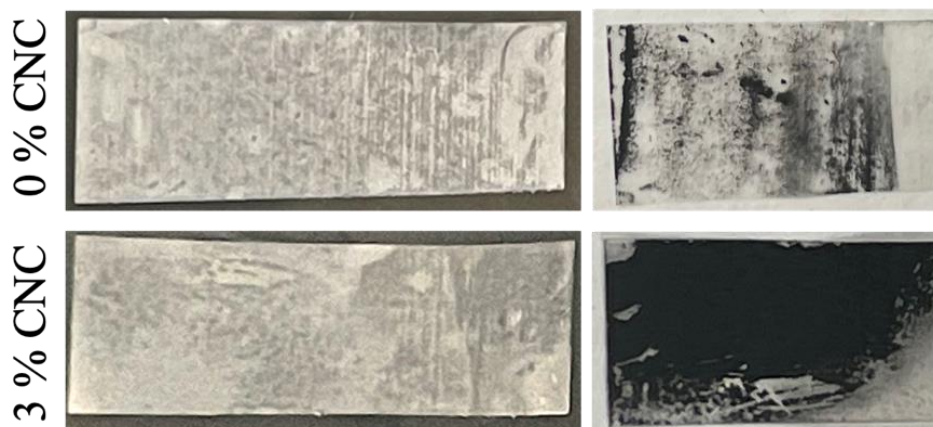


Figure S9. Tape peeling test of 0 and 3% CNC electrodes. The pictures on the left indicate the tape sticks on electrodes, and the pictures on the right indicate the particles remaining on the tape.

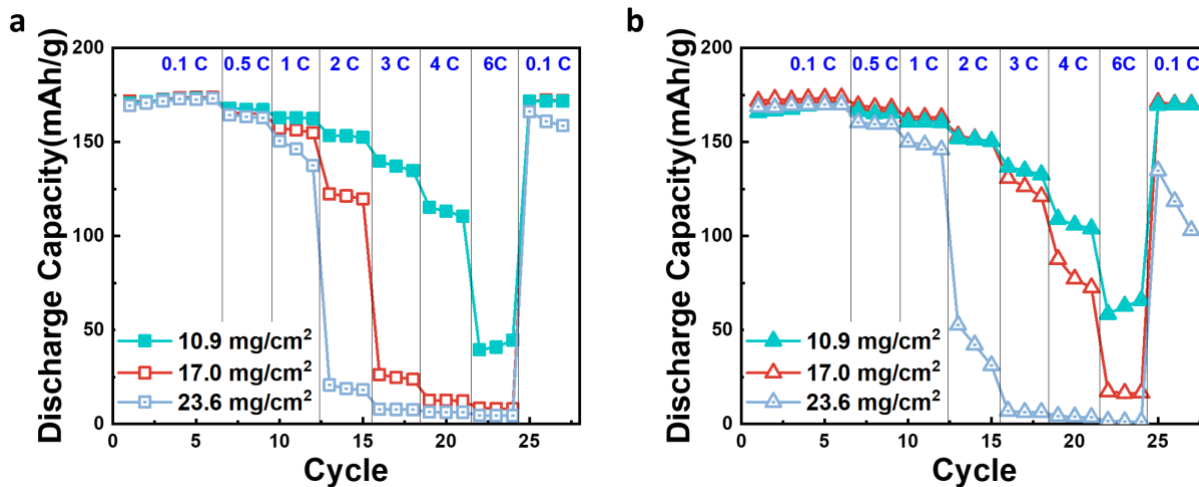


Figure S10. Rate performance of (a) 0% CNC electrodes and (b) 1% CNC electrodes with various mass loading.

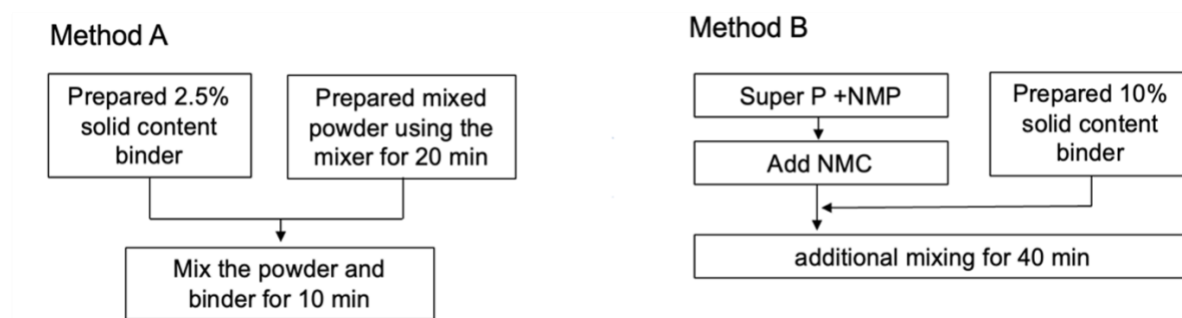


Figure S11. The specific fabrication procedures of other two electrode slurries (Method A and B).

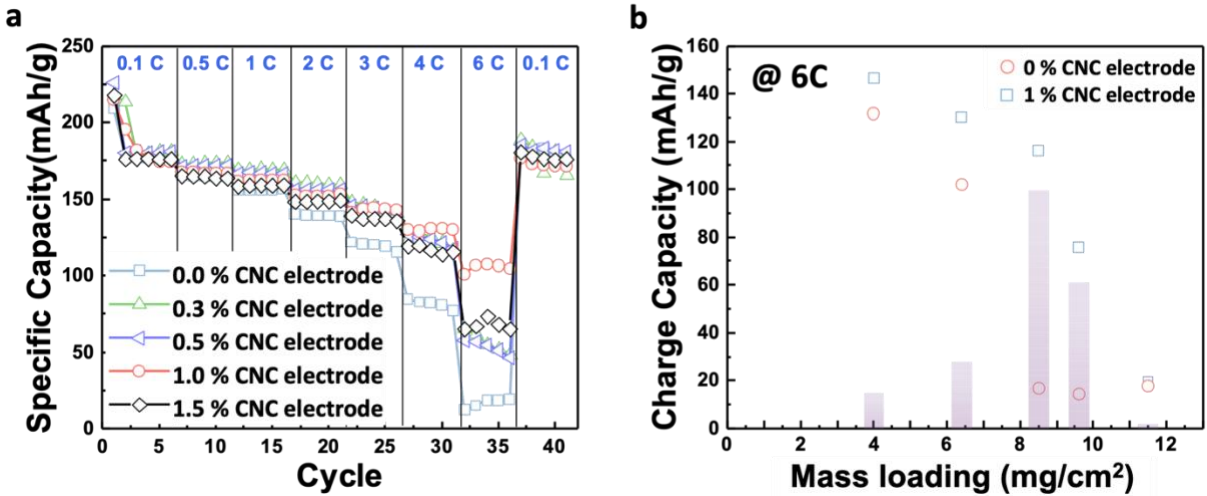


Figure S12. Rate performance of CNCs-added electrodes prepared using method A. (a) Electrodes with various amounts of CNC at mass loading of 9 mg/cm^2 . (b) Comparison of 0 and 1% CNC electrodes with different mass loadings at the current rate of 6 C. The purple column shows the capacity difference.

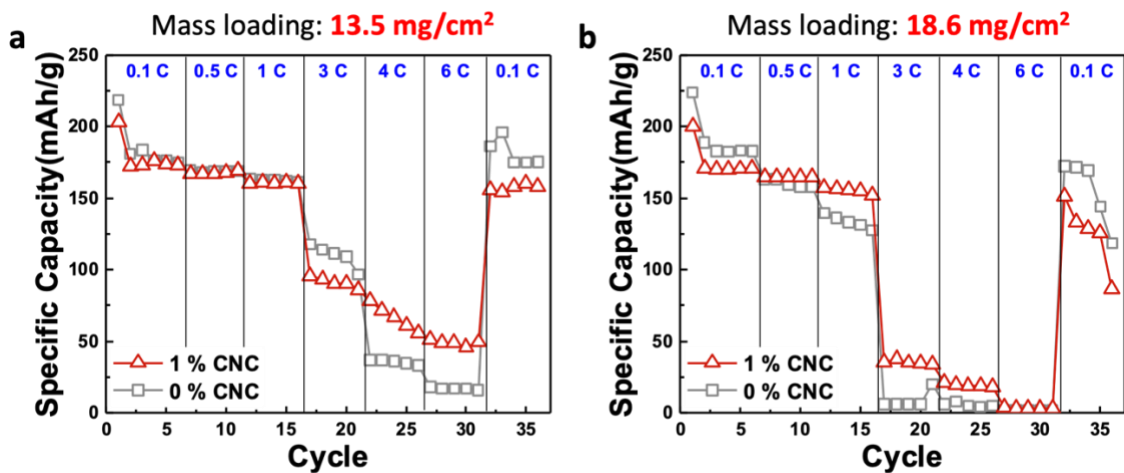


Figure S13. Rate performance of 0 and 1% CNC electrodes with different mass loadings of (a) 13.5 and (b) 18.6 mg/cm^2 . All cells were prepared using the method B.

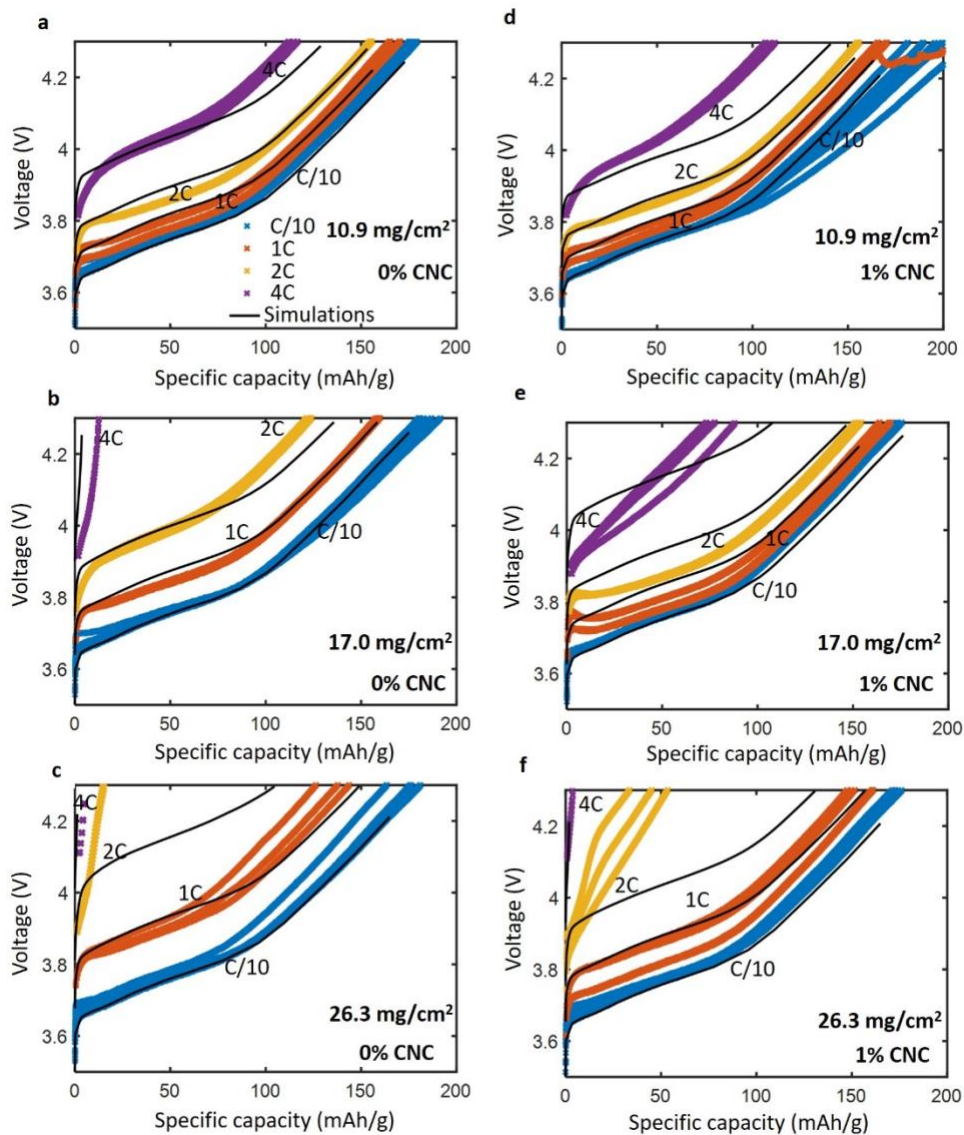


Figure S14. Experiment vs. simulated cell voltage vs specific capacity for (a) 0% CNC with 10.9 mg/cm² mass loading (b) 0% CNC with 17.0 mg/cm² mass loading (c) 0% CNC with 26.3 mg/cm² mass loading (d) 1% CNC with 10.9 mg/cm² mass loading (e) 1% CNC with 17.0 mg/cm² mass loading (f) 0% CNC with 26.3 mg/cm² mass loading. Experiments are represented by colored points and simulations by black lines. Different colors represent different C-rates, and C-rates for simulations are indicated in the figure.

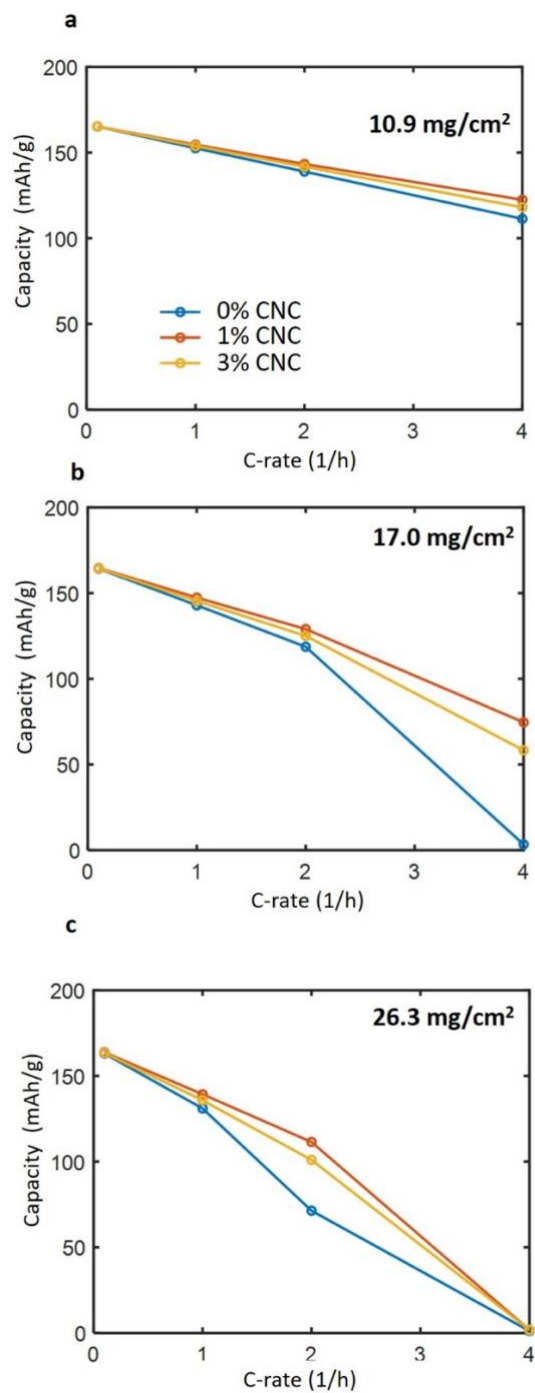


Figure S15. Simulated cell capacity at 4.2 V vs. C-rate for (a) 10.9, (b) 17.9, and (c) 26.3 mg/cm² mass loadings. Simulations show highest capacity for 1% CNC, lowest capacity for 0% CNC, and an intermediate capacity for 3% CNC. These relative improvements for 1% and 3% CNC compared with the 0% CNC group are both C-rate and mass loading dependent.

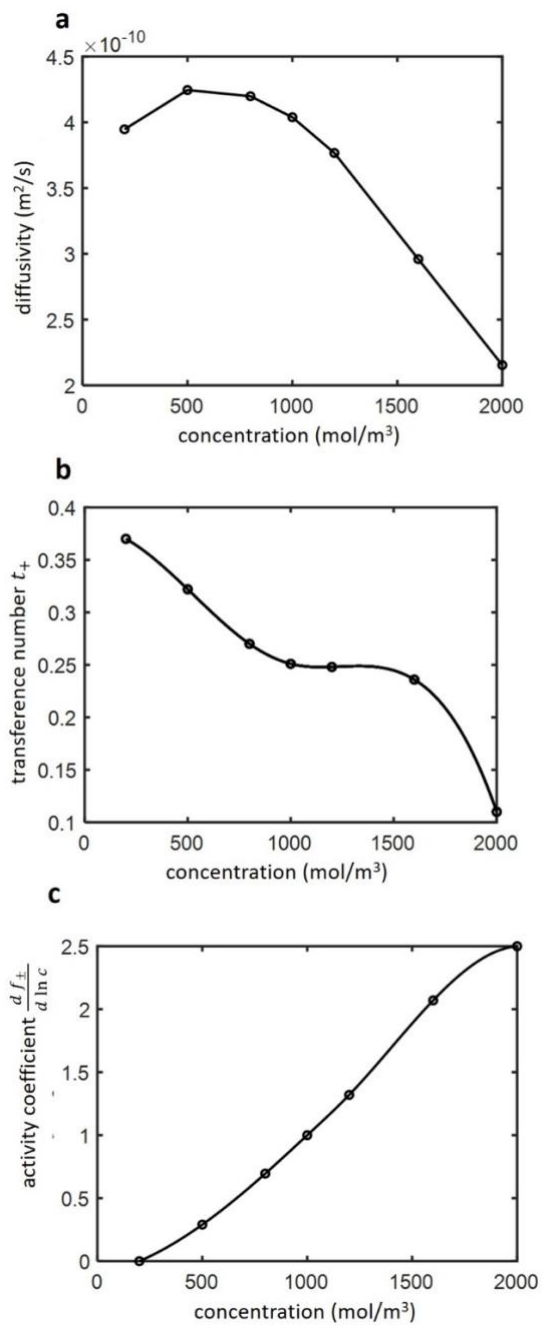


Fig. S16. (a) Li⁺ diffusivity, (b) transference number, and (c) activity coefficient as a function of Li⁺ ion concentration in the liquid electrolyte.

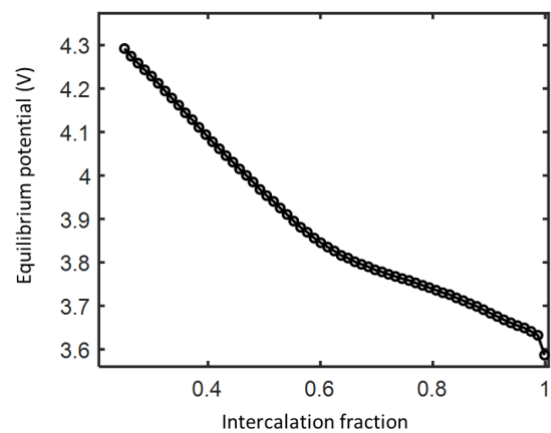


Figure S17. Computational input of the equilibrium potential for NMC622 as a function of intercalation fraction.

The diffusion coefficient (D) of various electrodes was measured by EIS and calculated following the eq. 1,[1-3]

$$D = \frac{R^2 T^2}{2A^2 n^4 F^4 C^2 \sigma^2} \quad (1)$$

in which the σ is the Warburg coefficient, R is the gas constant, T is the temperature, n is the number of electrons transferred in the half-cell reaction (here, $n= 1$), F is the Faraday constant, A is the electrode area, C is the concentration of Li^+ ions of NMC.

Table S1. Bulk resistance (R_s), charge transfer resistance (R_{ct}), Warburg coefficient (σ), and diffusion coefficient (D) of electrodes using various amounts of CNC additive.

	R_s (Ω)	R_{ct} (Ω)	σ ($\Omega \text{ cm}^2 \text{ s}^{-0.5}$)	D ($\text{cm}^2 \text{ s}^{-1}$)
0% CNC	3.411	468.6	389	8.58×10^{-16}
1% CNC	0.998	184.4	364	9.80×10^{-16}
2% CNC	2.512	325.1	352	10.48×10^{-16}
3% CNC	2.701	337.4	351	10.54×10^{-16}

All tortuosity was calculated based on our previous work.[4] Specifically, Tortuosity factor τ^2 was calculated following eq. 2,

$$\tau^2 = \frac{\sigma_{bulk}}{\sigma_{eff}} \epsilon \quad (2)$$

where the σ_{bulk} is the bulk conductivity; σ_{eff} is effective partial conductivity; and ϵ is the volume fraction.

Meanwhile, power-law form of eq. 3 is employed to calculate the tortuosity factor and volume fraction, in which the α_{NMC} was determined as 2.51 through simulation and fitting.

$$\tau^2 = \frac{1}{\varepsilon^a} \quad (3)$$

Considering the calculated porosity of our electrodes was around 50%, the above equations are reasonable to be applied in both electric and ionic tortuosity calculations. The calculated porosity was obtained using the areal mass loading (m_{areal}), thickness (L) of electrodes, as well as density (ρ_i) and mass fraction (ω_i) of components, in which i represents active material (AM), binder (B), and conductive agent (CA).[5]

$$\varepsilon = 1 - \frac{m_{areal}}{L} \left\{ \frac{\omega_{AM}}{\rho_{AM}} + \frac{\omega_B}{\rho_B} + \frac{\omega_{CA}}{\rho_{CA}} \right\} \quad (4)$$

We utilize the pressure cell to collect the electronic electric conductivity of as prepared electrode of $\sigma_{bulk} = 8.10$ S/m for electric tortuosity calculation. For ionic tortuosity calculation, σ_{bulk} is the ionic conductivity of liquid electrolyte of 0.92 S/m.

Tables S2-5 list the results of experimental measurements and calculations of electric conductivity, ionic conductivity, electric tortuosity, and ionic tortuosity, respectively.

Table S2. Electronic conductivity of electrodes using various amounts of CNC additive

	0% CNC	1% CNC	2% CNC	3% CNC	[S/m]
# 1	0.195	0.166	0.107	0.058	[S/m]
# 2	0.051	0.277	0.096	0.053	[S/m]
# 3	0.1123	0.078	0.108	0.148	[S/m]
# 4	0.049	0.191	0.065	0.177	[S/m]
# 5	0.151	0.095	0.107	0.059	
Average	0.11166	0.1614	0.0966	0.099	[S/m]
Standard Deviation	0.056744	0.071589	0.0164	0.052692	[S/m]

Table S3. Ionic conductivity of electrodes using various amounts of CNC additive

	0% CNC	1% CNC	2% CNC	3% CNC	
# 1	0.365	0.624	0.984	0.805	[S/m]
# 2	0.288	0.633	0.571	0.723	[S/m]
# 3	0.438	0.583	0.714	0.923	[S/m]
# 4	0.334	0.583	0.534	0.748	[S/m]
# 5	0.356	0.682	0.651	0.569	[S/m]
Average	0.3562	0.621	0.6908	0.7536	[S/m]
Standard Deviation	0.048811	0.036775	0.15939	0.115224	[S/m]

Table S4. Electronic tortuosity of electrodes using various amounts of CNC additive

	0% CNC	1% CNC	2% CNC	3% CNC	
# 1	3.790327	4.014939	4.69756	5.847427	[1]
# 2	6.122613	3.343259	4.883346	6.038981	[1]
# 3	4.617057	5.259689	4.681962	4.183131	[1]
# 4	6.210819	3.81852	5.613986	3.92388	[1]
# 5	4.153224	4.901663	4.69756	5.811796	[1]
Average	4.978808	4.267614	4.914883	5.161043	[1]
Standard Deviation	1.005095	0.707982	0.357337	0.911292	[1]

Table S5. Ionic tortuosity of electrodes using various amounts of CNC additive

	0% CNC	1% CNC	2% CNC	3% CNC	
# 1	1.514769	1.143037	1.18595	1.089977	[1]
# 2	1.391728	1.148905	0.97624	1.048902	[1]
# 3	1.303897	1.177165	1.09487	0.998837	[1]
# 4	1.436603	1.177165	1.2147	1.076809	[1]
# 5	1.404208	1.112968	1.13164	1.187441	[1]
Average	1.410241	1.151848	1.12068	1.080393	[1]
Standard Deviation	0.068278	0.024	0.08337	0.061979	[1]

Table S6. Cathode modeling parameters

Parameter	Value
Porosity (For 10.9/17.0/23.6 mAh/g, respectively)	0.48/0.47/0.50
Thickness (μm) (For 10.9/17.0/23.6 mAh/g, respectively)	108/153/205
Solid fraction	1-porosity
Particle diameter (μm)	4
Diffusivity in solid (m^2/s)	5×10^{13}
Maximum Li conc. in solid (mol/m^3)	50060
Anodic transfer coefficient	0.5
Cathodic transfer coefficient	0.5
Reaction rate constant ($\text{mol}/\text{m}^2\text{s}(\text{mol}/\text{m}^3)^{-1.5}$)	1×10^{-11}
Electronic conductivity (S/m)	See main text

Table S7. Electrode modeling parameters

Parameter	Value
Initial salt concentration (mol/m^3)	1200
Ionic conductivity κ (S/m)	See main text
Li^+ diffusivity D (m^2/s)	Figure S11A
Activity coefficient	Figure S11C
Transference number	Figure S11B

Table S8. Separator modeling parameters

Thickness (μm)	25
Porosity	0.4
Tortuosity	1.6

Reference

- [1]. Huang, B., et al., *Nitrogen-Doped Carbon-Coating Disproportionated SiO Materials as Long Cycling Stable Anode for Lithium Ion Batteries*. *Molecules*, 2021. **26**(6): p. 1536.
- [2]. Zhang, N., Y. Li, and Y. Qiao, *Boosting the electrochemical performance of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ through a trace amount of Mg-B co-doping*. *Journal of Materials Science & Technology*, 2021. **89**: p. 167-178.
- [3]. Mao, Z., et al., *Multi-particle model for a commercial blended lithium-ion electrode*. *J. Electrochem. Soc.*, 2015. **163**(3): p. A458.
- [4]. Stavola, A.M., et al., *Lithiation Gradients and Tortuosity Factors in Thick NMC111-Argyrodite Solid-State Cathodes*. *ACS Energy Lett.*, 2023. **8**(2): p. 1273-1280.
- [5]. Parikh, D., T. Christensen, and J. Li, *Correlating the influence of porosity, tortuosity, and mass loading on the energy density of LiNi_{0.6}Mn_{0.2}Co_{0.2}O₂ cathodes under extreme fast charging (XFC) conditions*. *J. Power Sources*, 2020. **474**: p. 228601.