

Supplementary Information

A black zirconia cathode coating layer enabling facile charge diffusion and surface lattice stabilization for lithium-ion batteries

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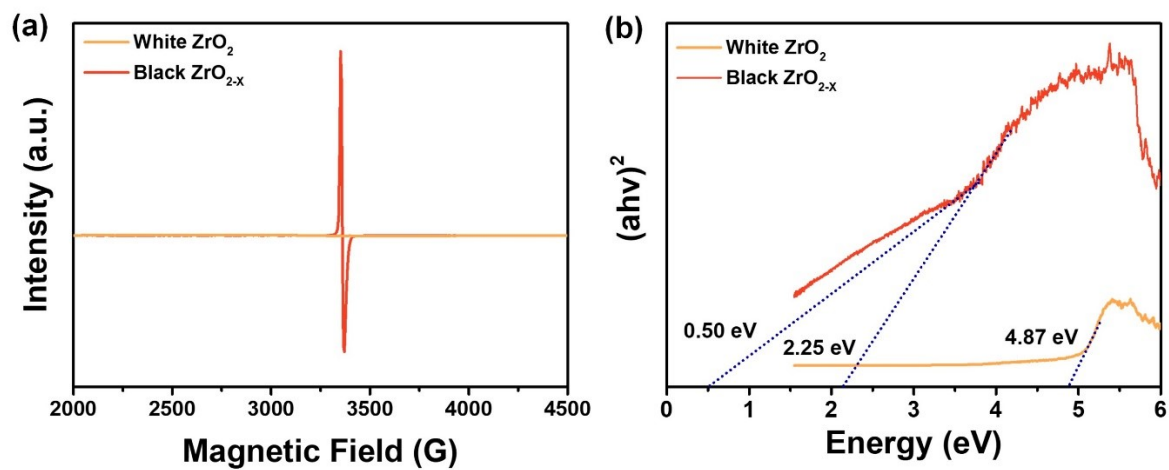


Fig. S1. (a) ESR spectra of white ZrO_2 and black ZrO_{2-x} . (b) Tauc plots of white ZrO_2 and black ZrO_{2-x} and the band-gap energies.

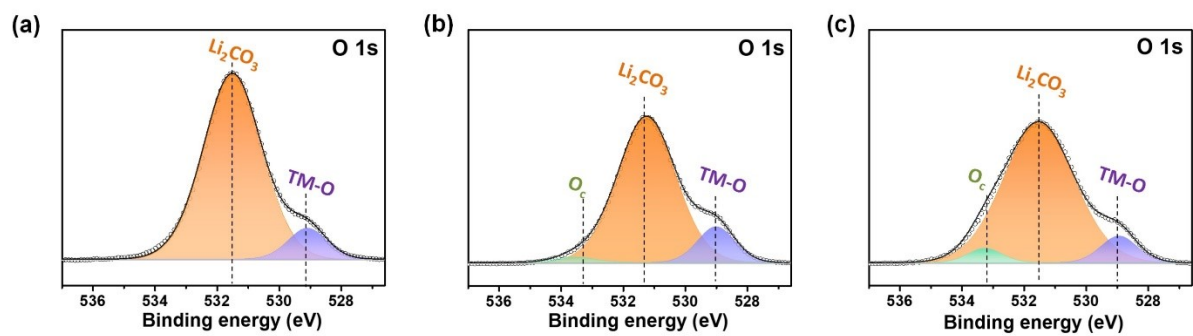


Fig. S2. O 1s XPS spectra of (a) NMC, (b) NMC@White ZrO_2 , and (c) NMC@Black ZrO_{2-x} .

4.5 V 20 cycles			NMC			NMC@White ZrO ₂			NMC@Black ZrO _{2-x}		
<i>a</i> (Å)			2.86792			2.86066			2.86652		
<i>c</i> (Å)			14.22399			14.17171			14.18529		
<i>Vol.</i> (Å ³)			101.31			100.43			100.94		
<i>R_p</i> (%)			14.3			9.04			8.96		
<i>R_{wp}</i> (%)			19.0			14.1			11.7		
			NMC			NMC@White ZrO ₂			NMC@Black ZrO _{2-x}		
Site	<i>x</i>	<i>y</i>	<i>z</i>	<i>B_{iso}</i>	Occ	<i>z</i>	<i>B_{iso}</i>	Occ	<i>z</i>	<i>B_{iso}</i>	Occ
Li1	0	0	0	1.4	0.81679	0	1.4	0.73439	0	1.4	0.81725
Ni2	0	0	0	1.4	0.03125	0	1.4	0.11361	0	1.4	0.03075
Ni1	0	0	0.5	0.3	0.76879	0.5	0.3	0.68639	0.5	0.3	0.76925
Co1	0	0	0.5	0.3	0.10000	0.5	0.3	0.10000	0.5	0.3	0.10000
Mn1	0	0	0.5	0.3	0.10000	0.5	0.3	0.10000	0.5	0.3	0.10000
Li2	0	0	0.5	0.3	0.01325	0.5	0.3	0.09561	0.5	0.3	0.01275
O1	0	0	0.25906	1.7	2.00000	0.25305	1.7	2.00000	0.24656	1.7	2.00000

Table. S1. Rietveld refinement result of NMC, NMC@White ZrO₂, and NMC@Black ZrO_{2-x}

after 20 cycles with charging until 4.5V.

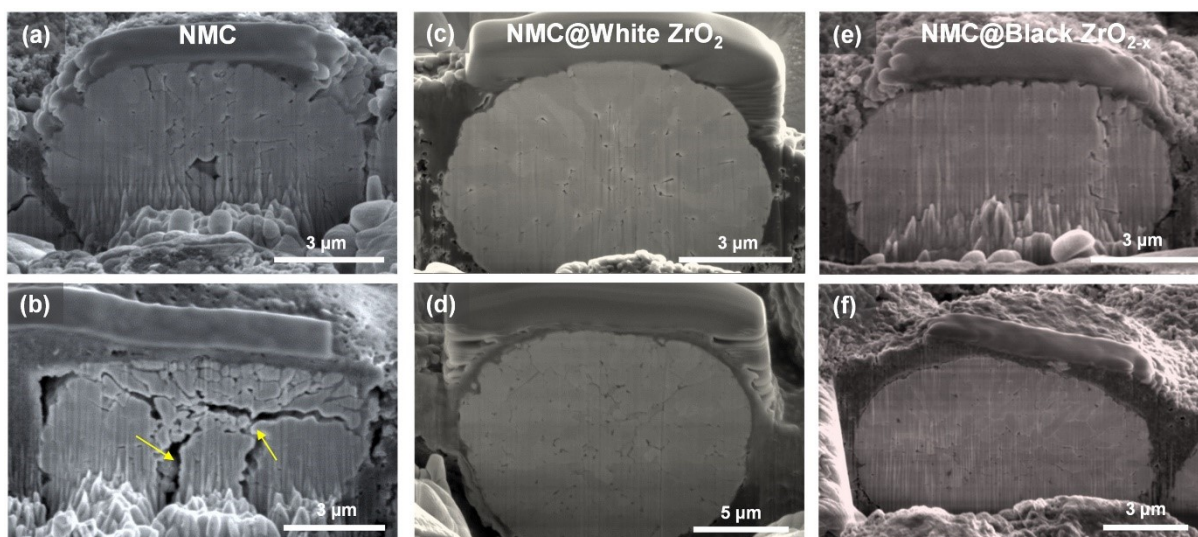


Fig. S3. (a, b) Pristine, (c, d) white ZrO_2 , and (e, f) black ZrO_{2-x} coated Ni-rich NMC cathode particle. Cross-sectional SEM images (a, c, e) before cycling and (b, d, f) after 20 cycles with FIB slicing.

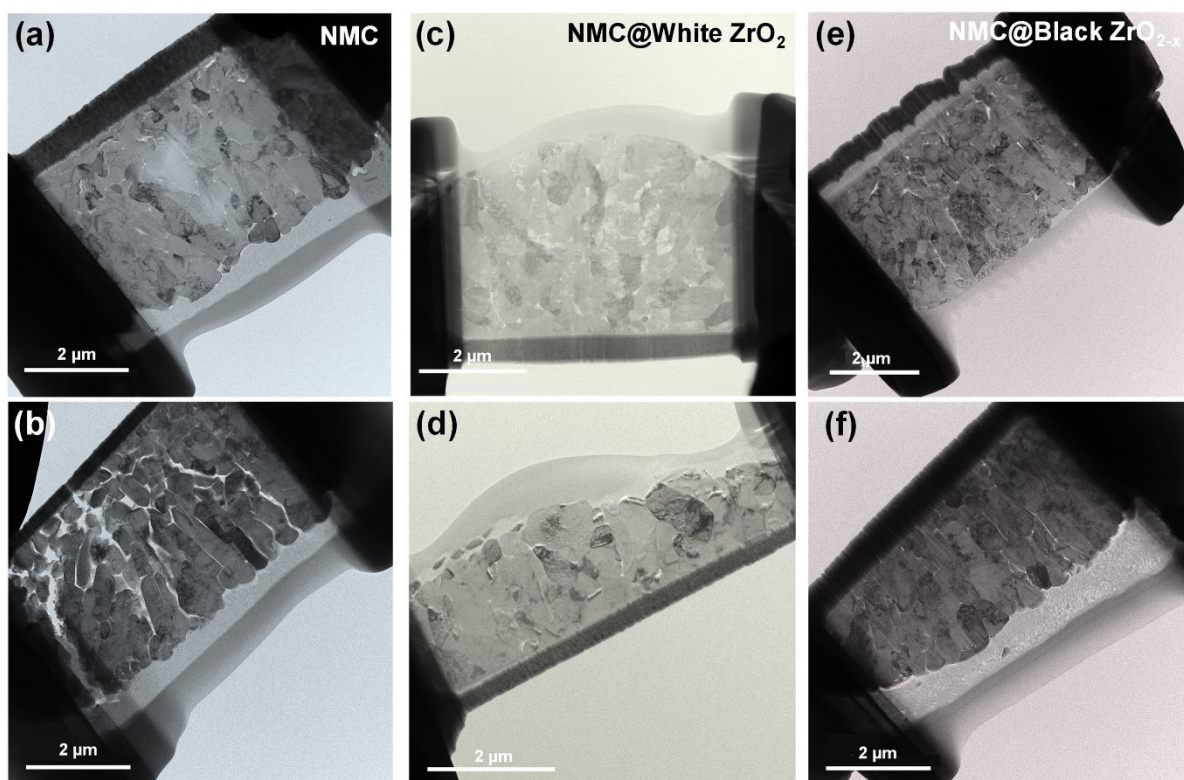


Fig. S4. (a, b) Pristine, (c, d) white ZrO₂, and (e, f) black ZrO_{2-x} coated Ni-rich NMC cathode particle. Cross-sectional HR-TEM images (a, c, e) before cycling and (b, d, f) after 20 cycles with FIB slicing.

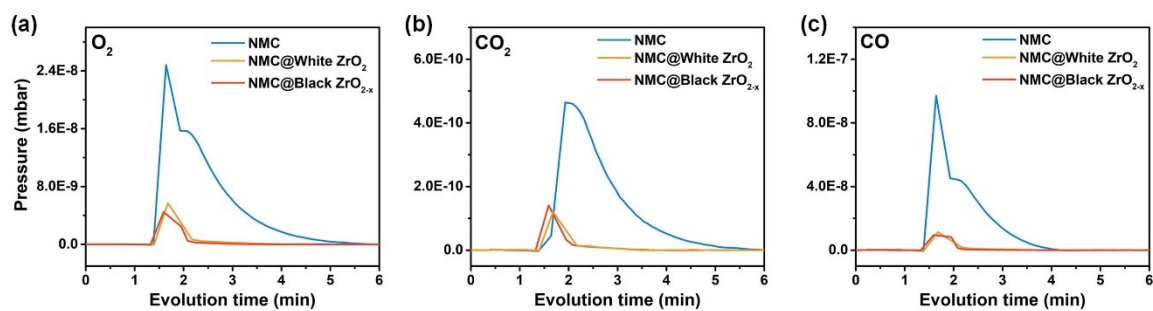


Fig. S5. *Ex-situ* DEMS measurements of (a) O₂, (b) CO₂, and (c) CO evolution from NMC, NMC@white ZrO₂, and NMC@black ZrO_{2-x} after the first charge.

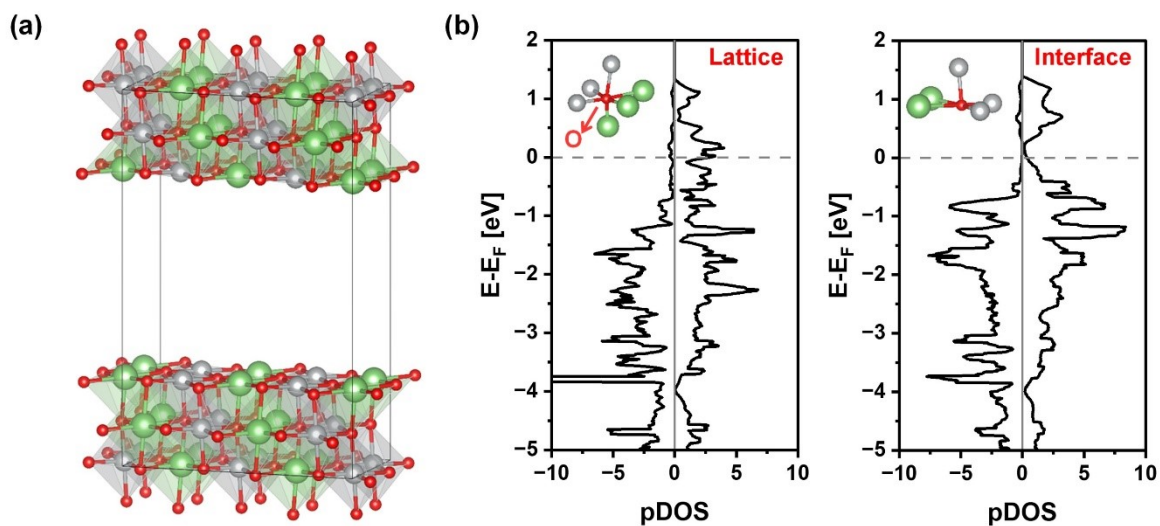


Fig. S6. (a) Structure of LiNiO_2 (104) after simulation. (b) The partial Density of states (pDOS) of Lattice O coordinated by 3 Ni and 3 Li and Interface O coordinated by 3 Ni and 2 Li with 2 Ni and 3 Li in bulk LiNiO_2 material.

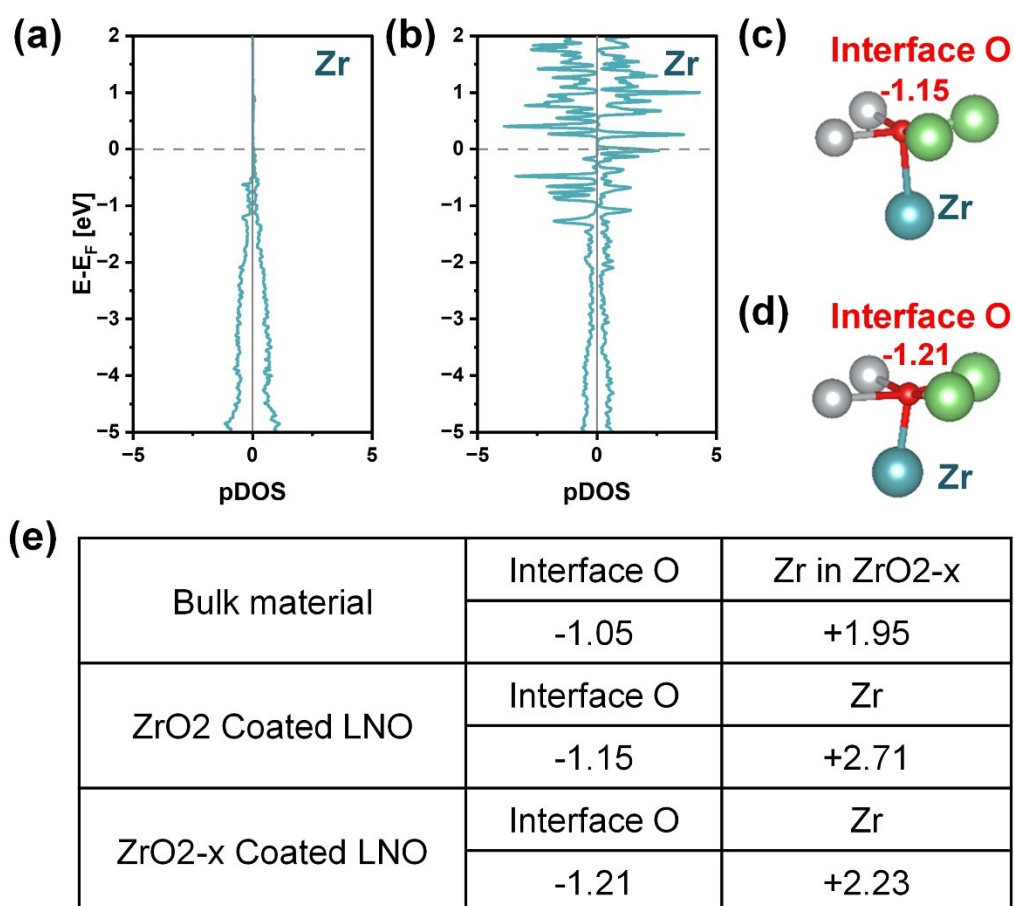


Fig. S7. (a, b) Density of states (DOS) of Zr in coating material. (c, d) Coating interface between LNO and coating material. The blue, red, green, and grey atoms represent Zr, interface oxygen, Li, and Ni, respectively. (e) Bader net charge analysis of interface oxygen and Zr in the coating material for quantitative analysis after coating.