

Unlocking Inert Material to Durable Cathode for Magnesium Storage Inspired via Synergistic Spin-Orbital Reconfiguration and Adaptive Crystal Transformation

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1. Experimental section

1.1 Preparation of cathode material

Pure Cu_3VS_4 , prepared by hydrothermal synthesis, basing on the experiments in the previously published literature.^[1] Specifically, 1.393 g of vanadyl acetylacetonate, 0.161 g of thioacetamide, and 0.301 g of copper nitrate were simultaneously dissolved in 35 ml of anhydrous methanol. After magnetically stirring at room temperature for 2 hours, the mixture was transferred into a 50 ml autoclave and maintained at 160 °C for 12 hours. Subsequently, the product was alternately washed with anhydrous ethanol and deionized water, and then dried in an oven at 60 °C for 12 hours.

Na-doped Cu_3VS_4 , was prepared as the above process and introduced different molar amounts of SDS.

1.2 Electrochemical measurements

In this study, electrode sheets were prepared by the rolling method, consisting of 70% active material (Cu_3VS_4 and Na-doped Cu_3VS_4), 20% conductive agent (acetylene black), and 10% binder (PTFE emulsion). The average mass loading of the active material was 3.5-4 mg cm⁻², with an average thickness of 104 μm.

The electrolyte used was a commercial all-phenyl complex electrolyte (APC) in the official website of the chemical reagent supplier (<https://www.dodochem.com/>). 0.4 M $(\text{MgPhCl})_2\text{-AlCl}_3$ in THF=100 Vol%. Then, A Whatman GF-D glass fiber separator was used, and the electrolyte volume was 85 μL. And, using magnesium metal as the anode, CR-2016 coin-type cells were assembled in a glove box with O_2 and H_2O below 0.01 ppm. The electrochemical cycling performance and ion diffusion rates were tested on a Land-Battery testing system, while cyclic voltammetry curves and in-situ electrochemical impedance spectra were obtained using an EC-Lab workstation.

Galvanostatic discharge–charge and galvano-static intermittent titration technique (GITT) tests were conducted using a Neware battery test system. A constant current pulse with a current density of 0.04 A g⁻¹ for 5 min was used and a relaxation step of 10 min was performed later. The diffusion coefficient was calculated based on the following formula:

$$D_{\text{Mg}^{2+}} = \frac{4}{\pi\tau} L^2 \left(\frac{\Delta E_s}{\Delta E_t} \right)^2$$

where τ is the relaxation time and L is the ion diffusion distance (equal to the thickness of the electrode). ΔE_s is potential change during one single-step experiment, and ΔE_t is the voltage change during a constant current pulse after excluding the i_R drop.

1.3 Materials characterizations

Bruker D8 Discover XRD with Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$) was applied to obtain crystallographic characterization of the cathode materials, including the ex-situ XRD testing. SEM images were collected by a JEOL-7100F microscope with an acceleration voltage of 20 kV. TEM, energy dispersive X-ray spectroscopy (EDX) element mapping. TEM was performed on an FEI Titan 60-300 Cs image-corrected microscope operated at 300 kV. Raman spectrum measurement was implemented by a Renishaw RM-1000 laser Raman microscopy system. X-ray photoelectron spectroscopy (XPS) measurement was employed to obtain the valence state of cathode materials and UPS by using the VG K-Alpha Probe spectrometer (ThermoFisher Scientific) with Al K α radiation as the excitation source.

2. Theoretical calculation and simulation methods

The density functional theory (DFT) calculations were performed using the Vienna Ab-initio Simulation Package (VASP) and the DS-PAW software of DeviceStudio2023.^[2] Crystal structure diagrams were drawn with Visualization for Electronical and Structural Analysis (VESTA).^[3]

The electron-ion interactions were described by the projector augmented wave (PAW) potential. The exchange-correlation interactions were determined using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).^[4] The plane-wave cutoff energy was set to 480 eV, with convergence criteria for forces and energy set to 0.02 eV $\text{\AA}^{-1}$ and 10^{-5} eV, respectively. A $2 \times 2 \times 2$ k-point mesh was used, and DFT-D3 dispersion correction was applied to account for weak interactions and improve computational accuracy.^[5] The HSE06 functional method was employed to calculate the DOS and electron spin. Climbing

Image-Nudged elastic band (CI-NEB) calculations were performed to determine the activation barrier of Mg^{2+} ion diffusion in the optimized structure.

VASP was employed to optimize the geometric structures of Cu_3VS_4 doped with different Na concentrations, and to calculate electronic properties such as the density of states and ELF, Mg^{2+} intercalation energy, and Mg^{2+} migration energy barriers.

DS-PAW software of DeviceStudio2023 was used to obtain charge density difference (Including Na-doped Cu_3VS_4 , the Mg^{2+} inserted Cu_3VS_4 and Na-doped Cu_3VS_4), assess the structural stability under different Na doping levels using AIMD (Ab Initio Molecular Dynamics) methods, and evaluate the Mg^{2+} diffusion coefficient in disordered structures.

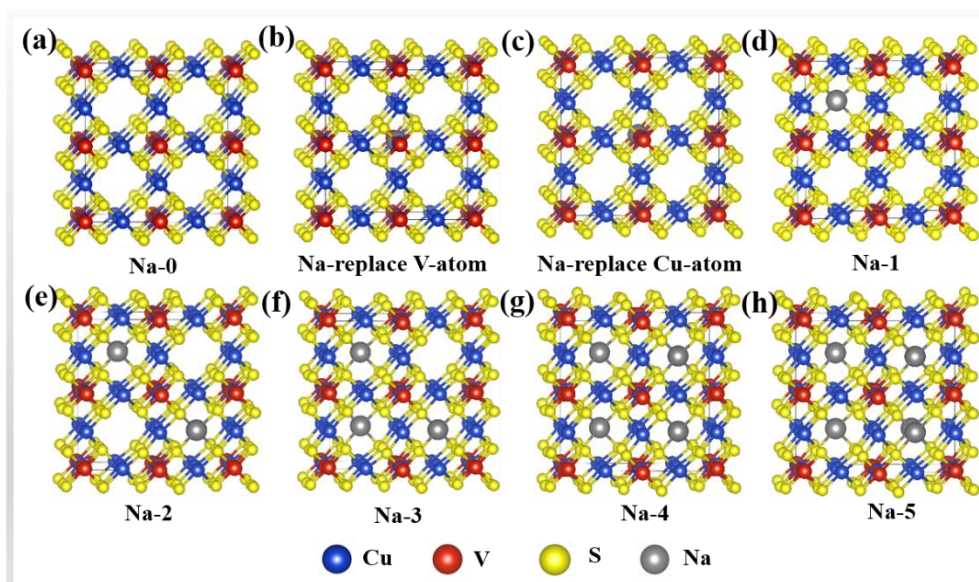


Figure S1. (a) Pure Cu_3VS_4 , (b-c) crystal structure diagrams of Na^+ substituting V and Cu atoms in Cu_3VS_4 , and (d-i) crystal structure diagrams of Cu_3VS_4 with Na^+ doped at interstitial sites with different concentrations.

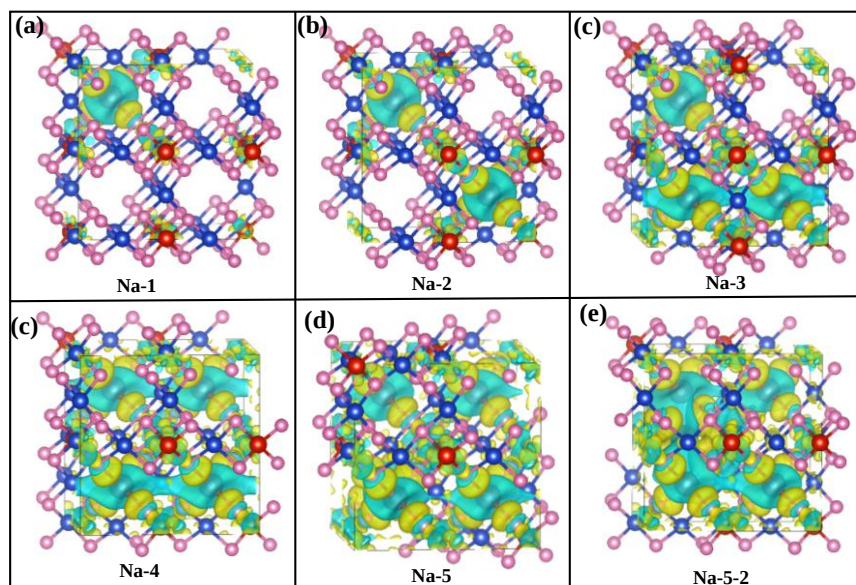


Figure S2. Charge density difference plots for Na-0, Na-1, Na-2, Na-3, Na-4, Na-5 and Na-5-2.

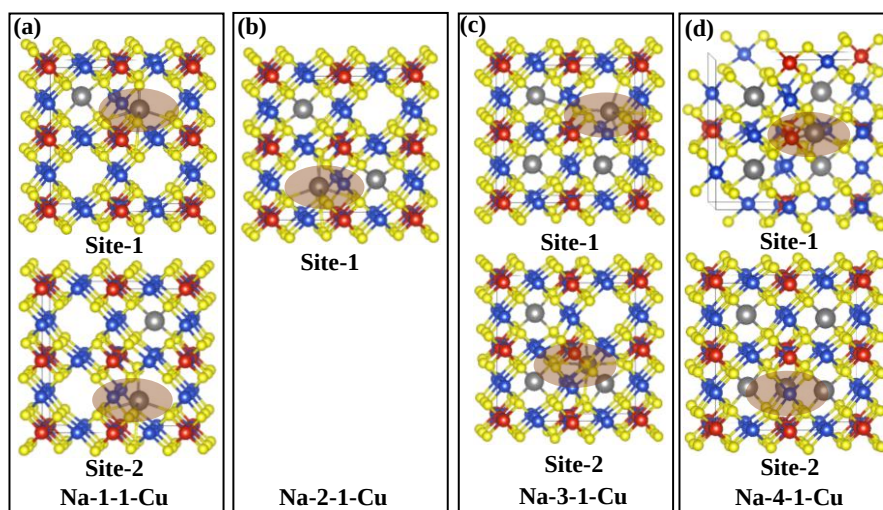


Figure S3. Crystal structure models of Na⁺ substituting Cu⁺ ions after interstitial doping with varying concentrations of Na⁺, followed by structural optimization.

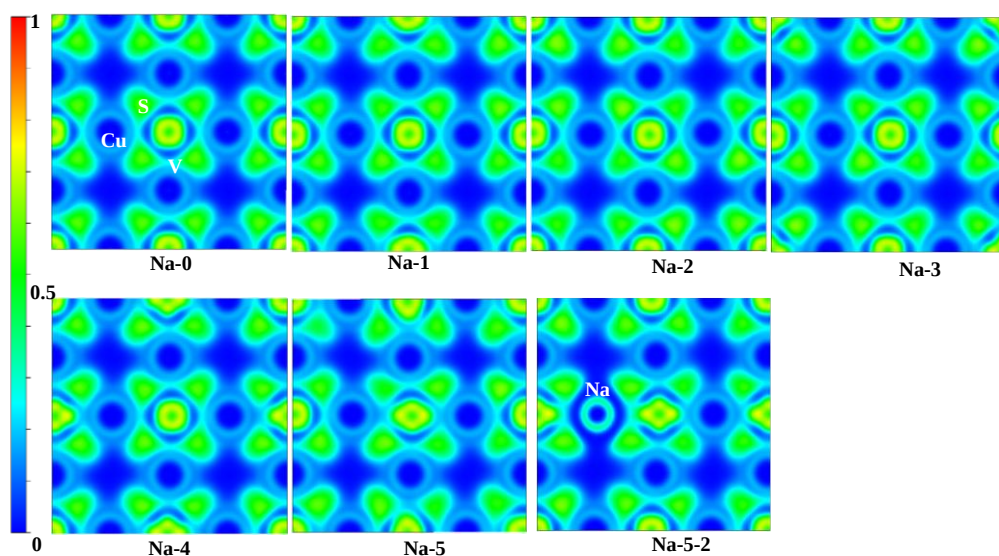


Figure S4. ELF result of (100) crystal plane for Na-0, Na-1, Na-2, Na-3, Na-4, Na-5 and Na-5-2.

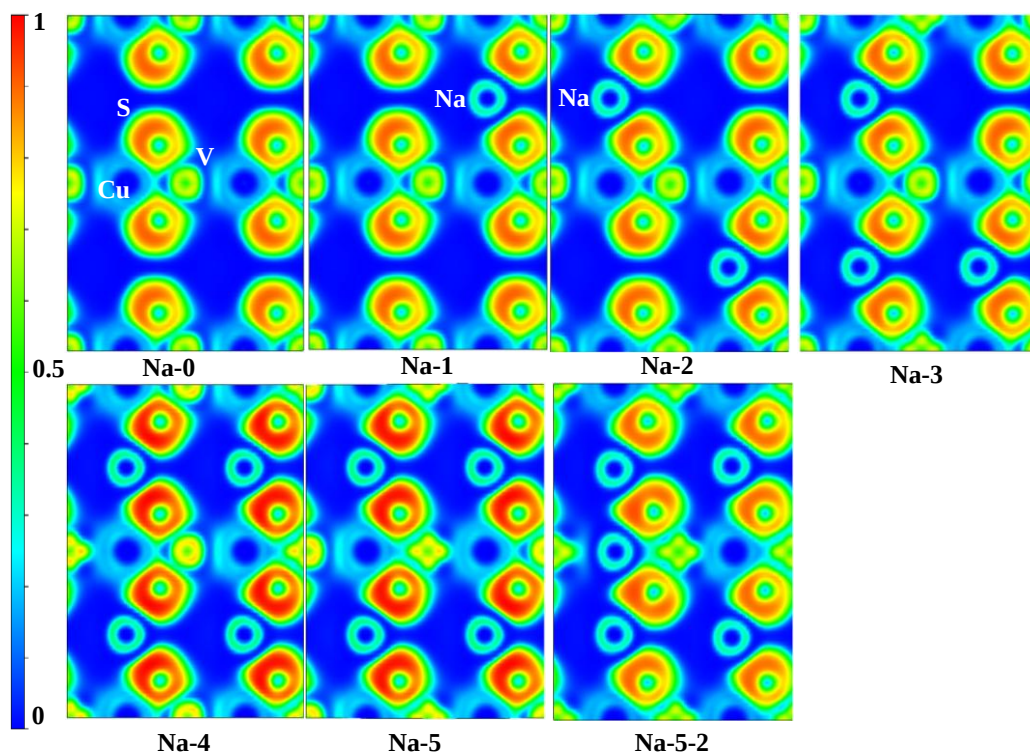


Figure S5. ELF result of (110) crystal plane for Na-0, Na-1, Na-2, Na-3, Na-4, Na-5 and Na-5-2.

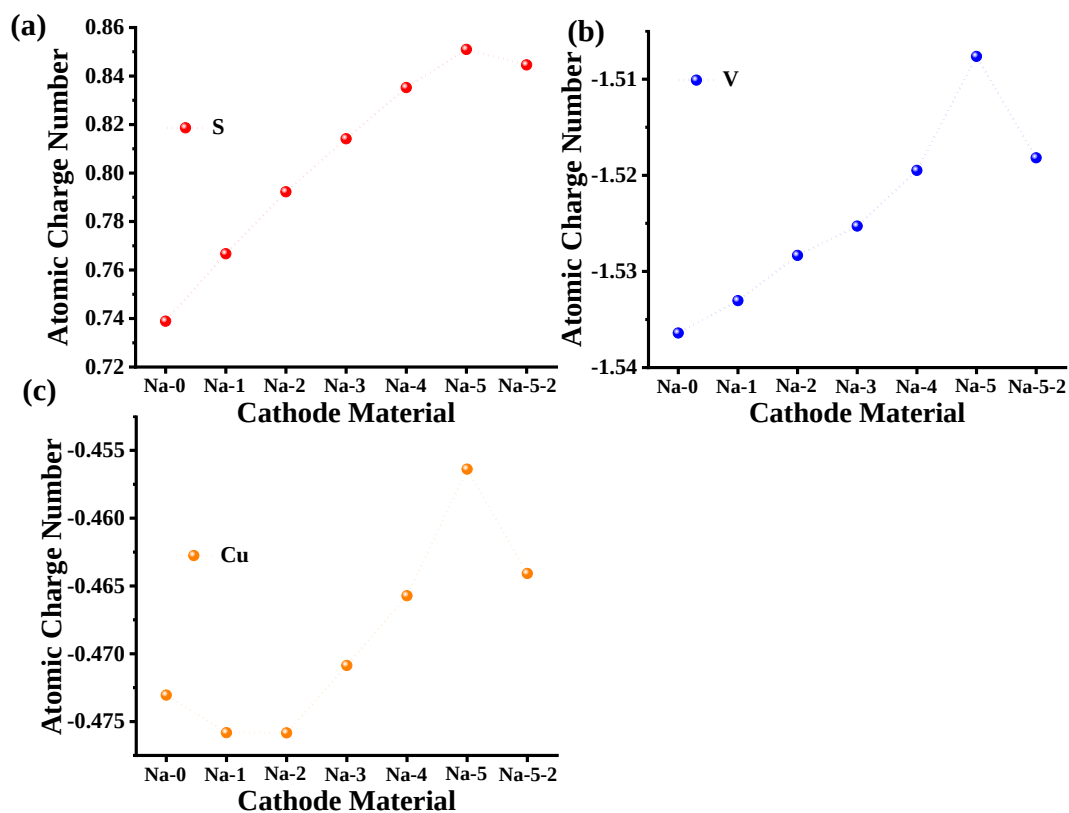


Figure S6. Barder charge of S, V and Cu for Na-0, Na-1, Na-2, Na-3, Na-4, Na-5 and Na-5-2.

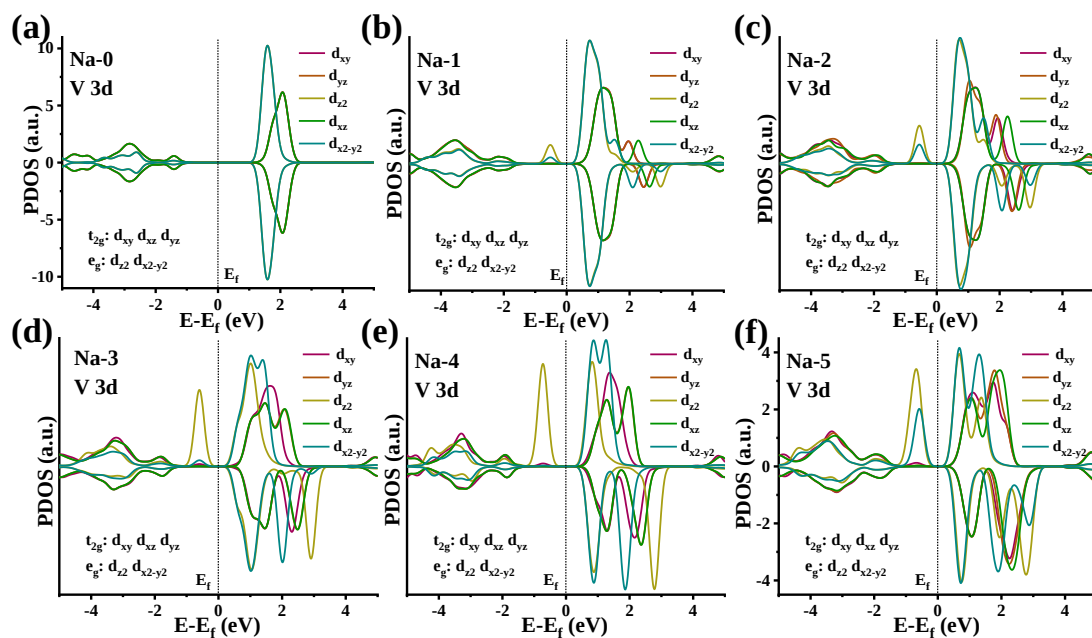


Figure S7. PDOS of V-3d for Na-0, Na-1, Na-2, Na-3, Na-4 and Na-5.

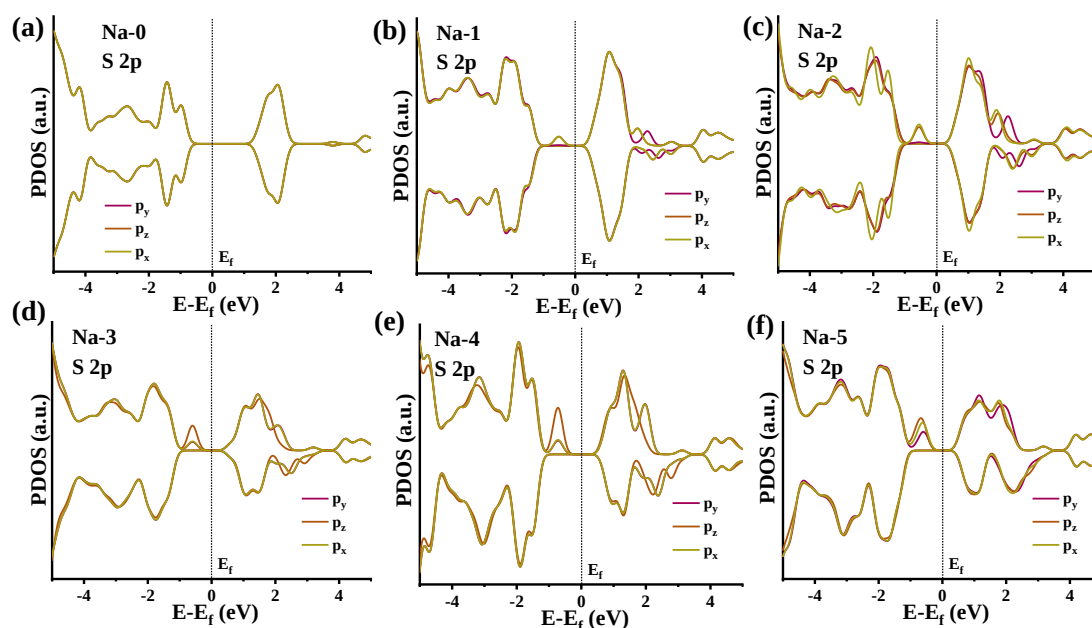


Figure S8. PDOS of S-p for Na-0, Na-1, Na-2, Na-3, Na-4 and Na-5.

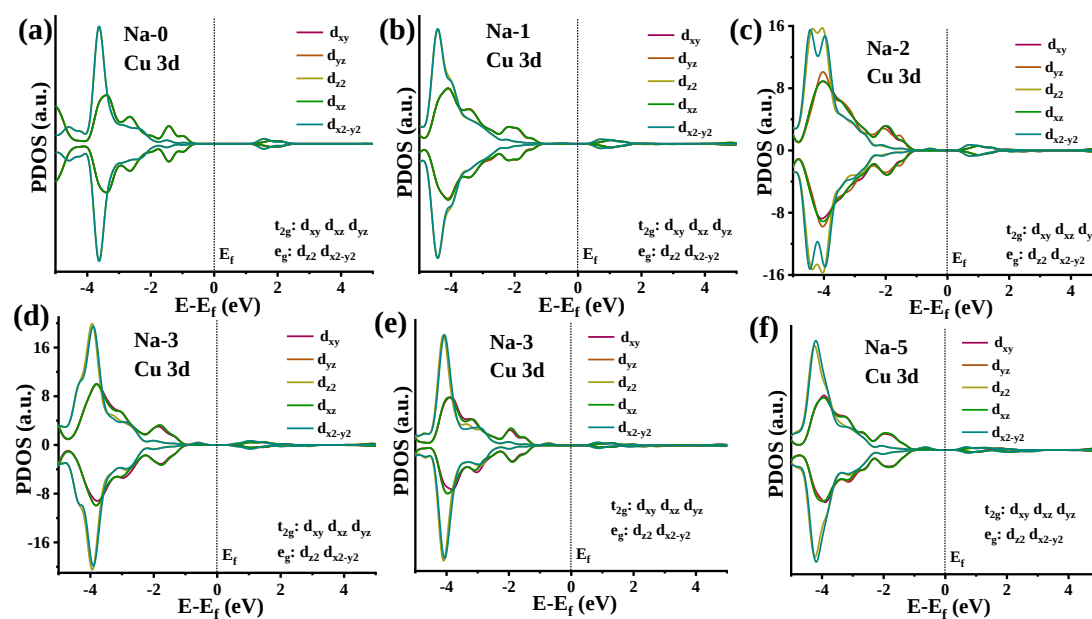


Figure S9. PDOS of Cu-3d for Na-0, Na-1, Na-2, Na-3, Na-4 and Na-5.

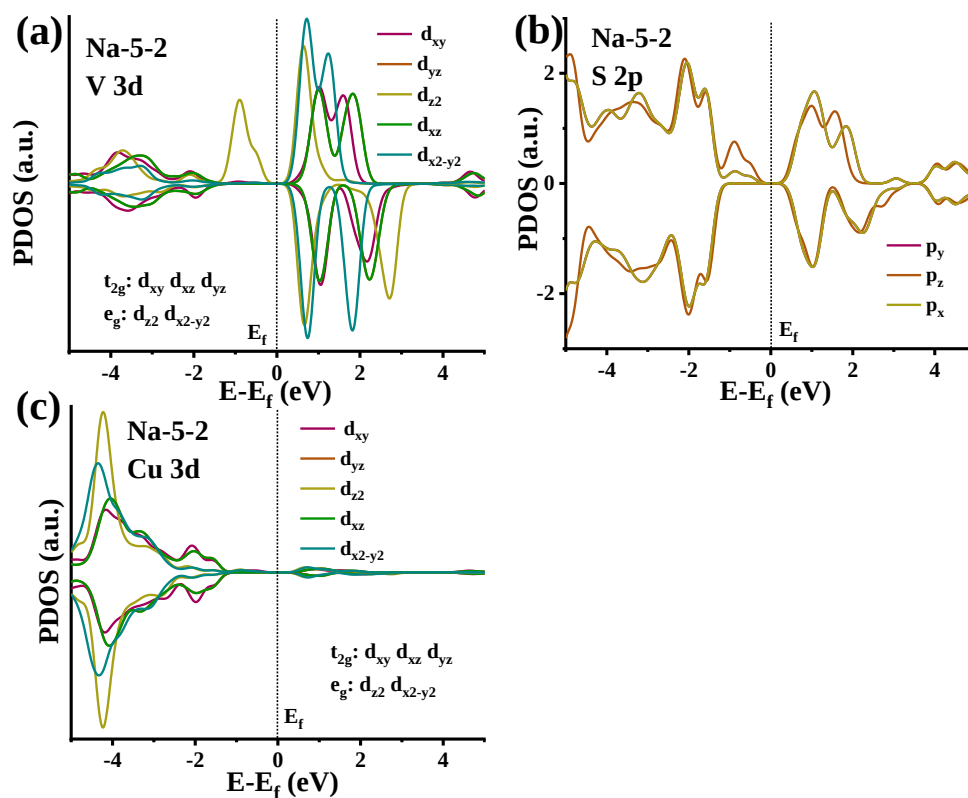


Figure S10. PDOS of V-3d, S-p and Cu-3d for Na-5-2.

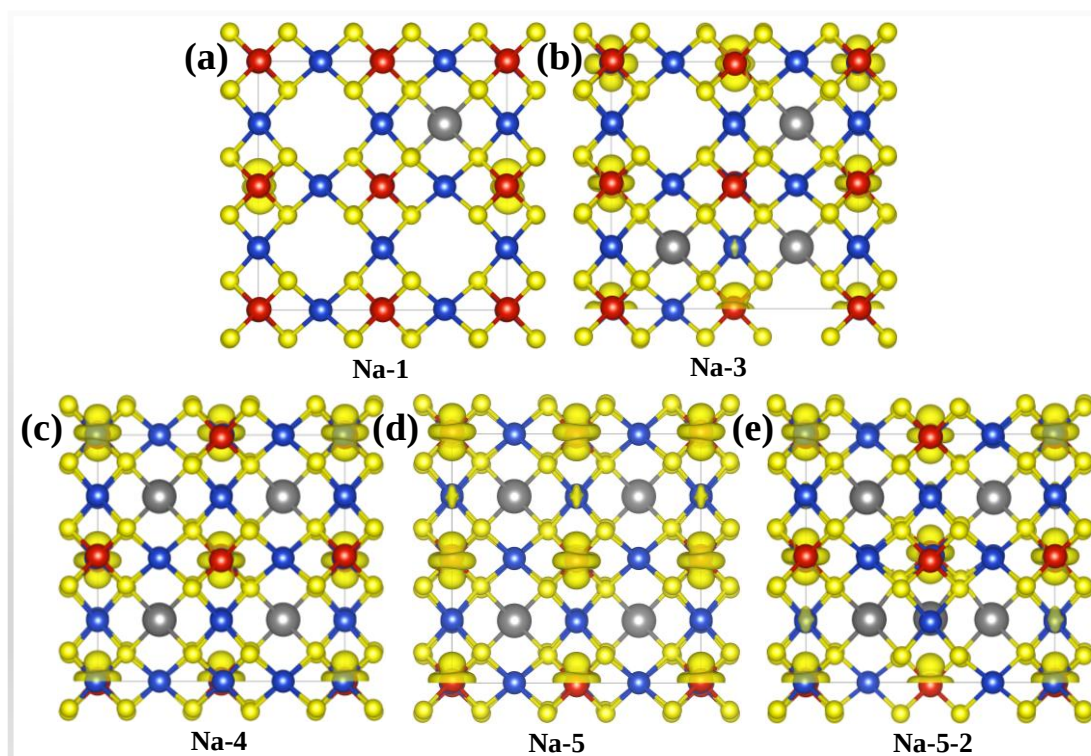


Figure S11. Electron spin density diagrams for Na-1, Na-3, Na-4, Na-5 and Na-5-2.

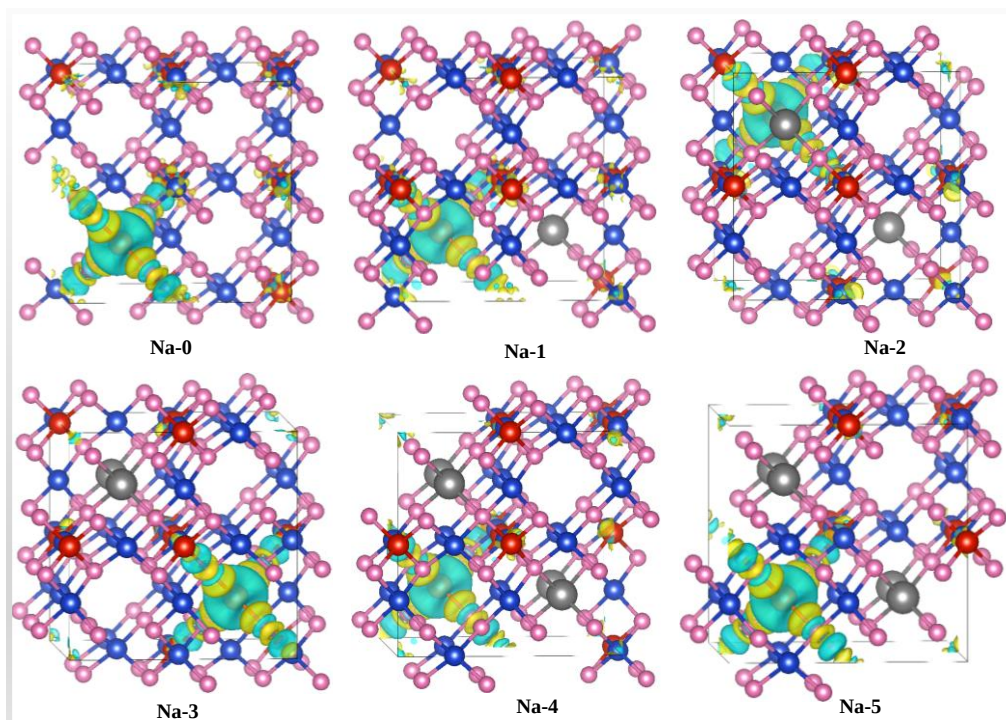
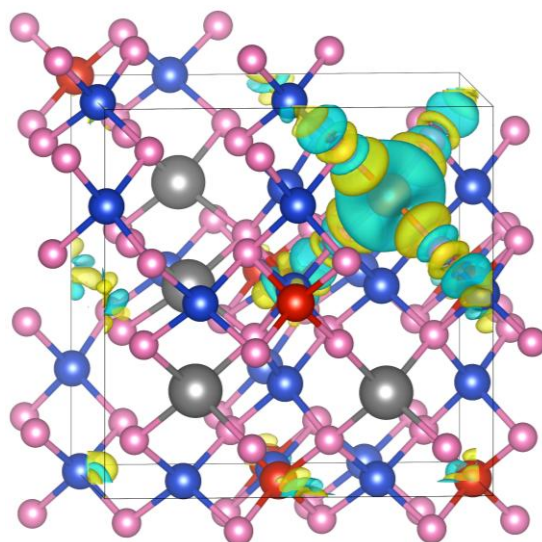


Figure S12. The Charge density difference between Mg^{2+} ion and host-material in Na-0, Na-1, Na-2, Na-3, Na-4, Na-5.



$$E_{\text{inser.}} = -0.56 \text{ eV}$$

Figure S13. The Mg^{2+} insertion energy and Charge density difference between Mg^{2+} ion and host-material in Na-5-2.

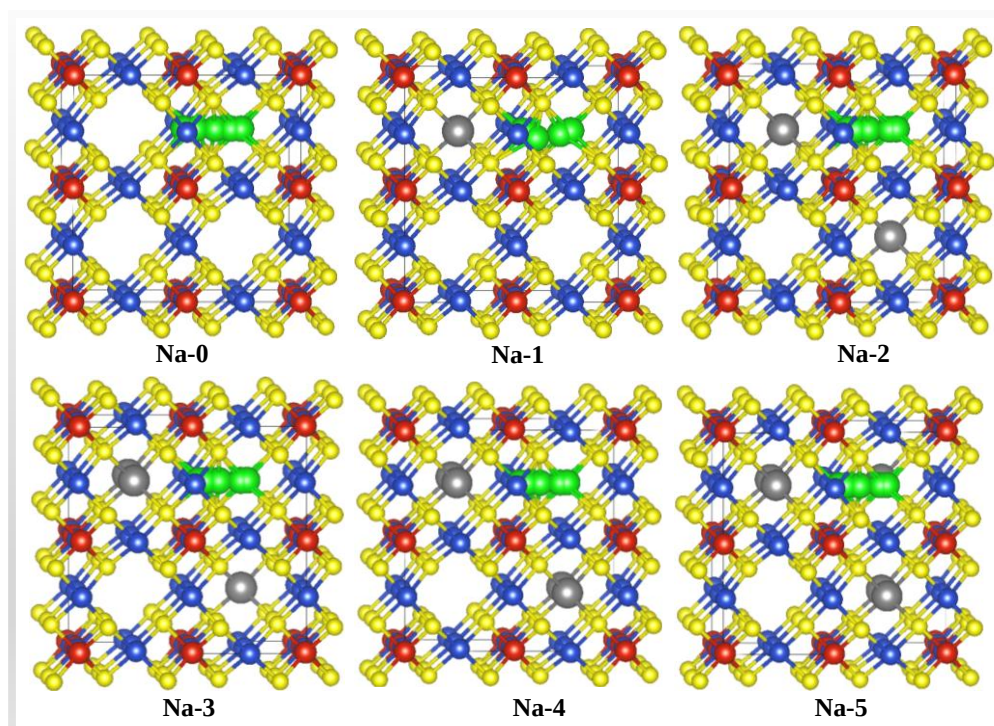


Figure S14. The Mg^{2+} ion diffusion path in Na-0, Na-1, Na-2, Na-3, Na-4, Na-5.

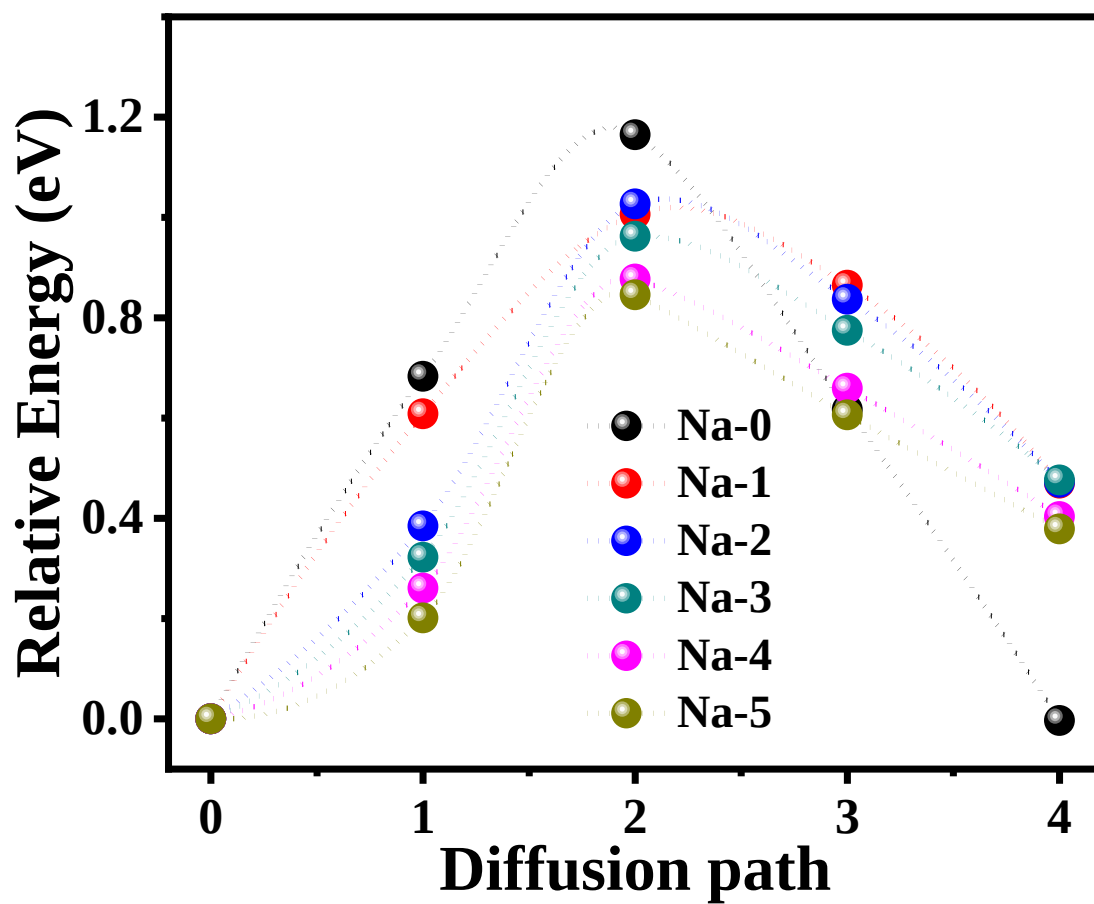
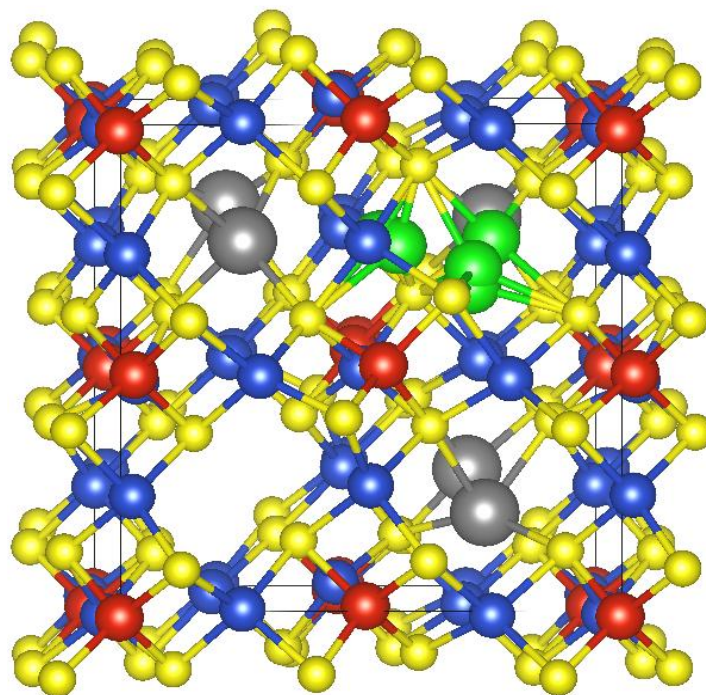
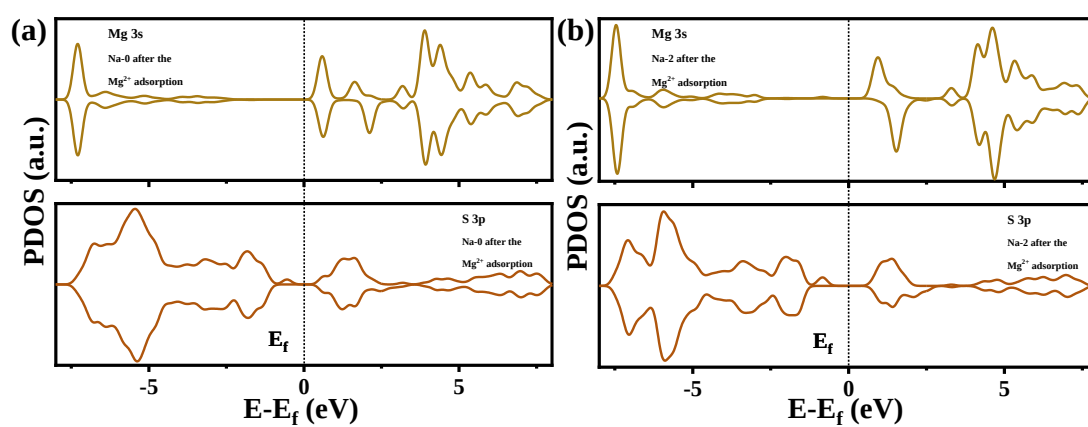


Figure S15. The Mg^{2+} ion diffusion energy barrier in Na-0, Na-1, Na-2, Na-3, Na-4, Na-5.

**Na-5-2****Figure S16.** The Mg^{2+} ion diffusion path in Na-5-2.**Figure S17.** (a-b) The projected density of states of Mg-s and S-p orbital in Na-0 and Na-2.

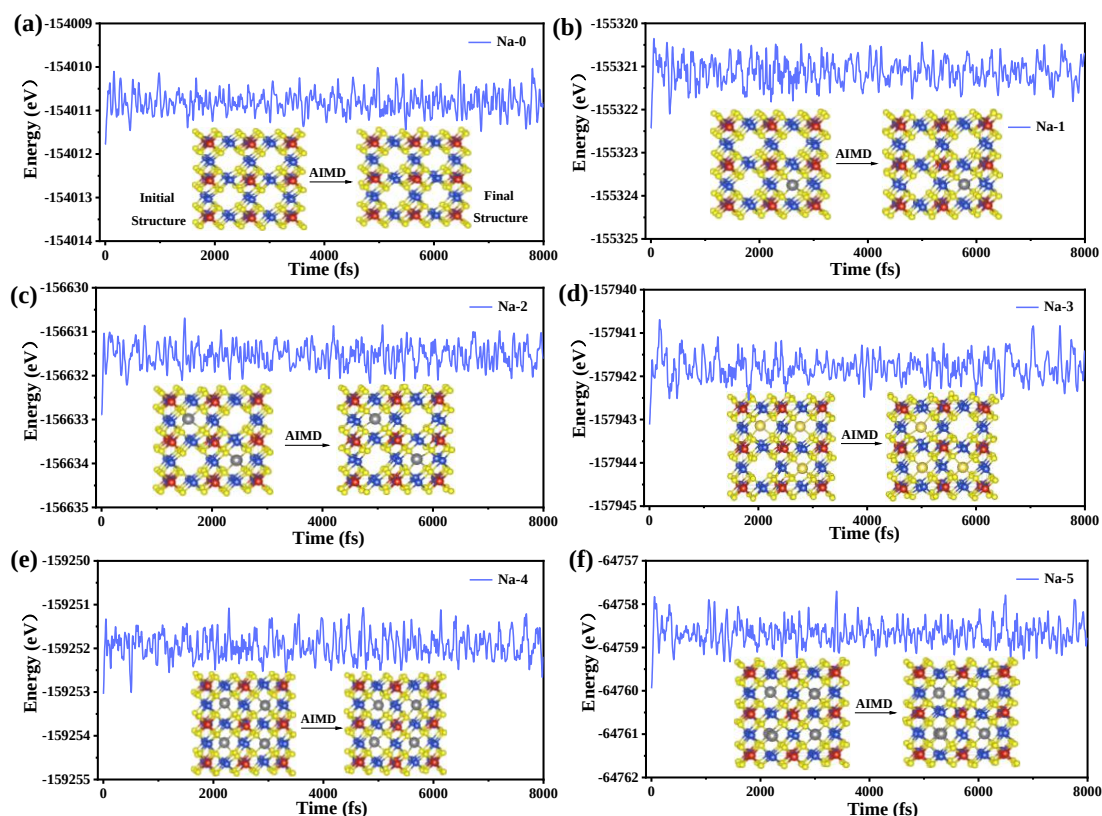


Figure S18. The Energy-Time curves during the AIMD simulation process in Na-0, Na-1, Na-2, Na-3, Na-4, Na-5.

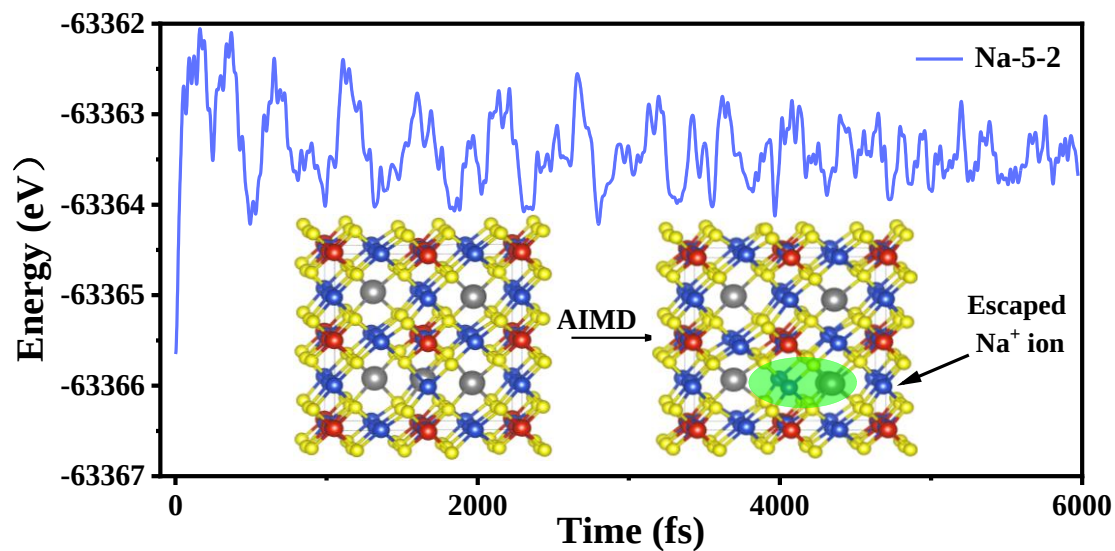


Figure S19. The Energy-Time curves during the AIMD simulation process in Na-5-2.

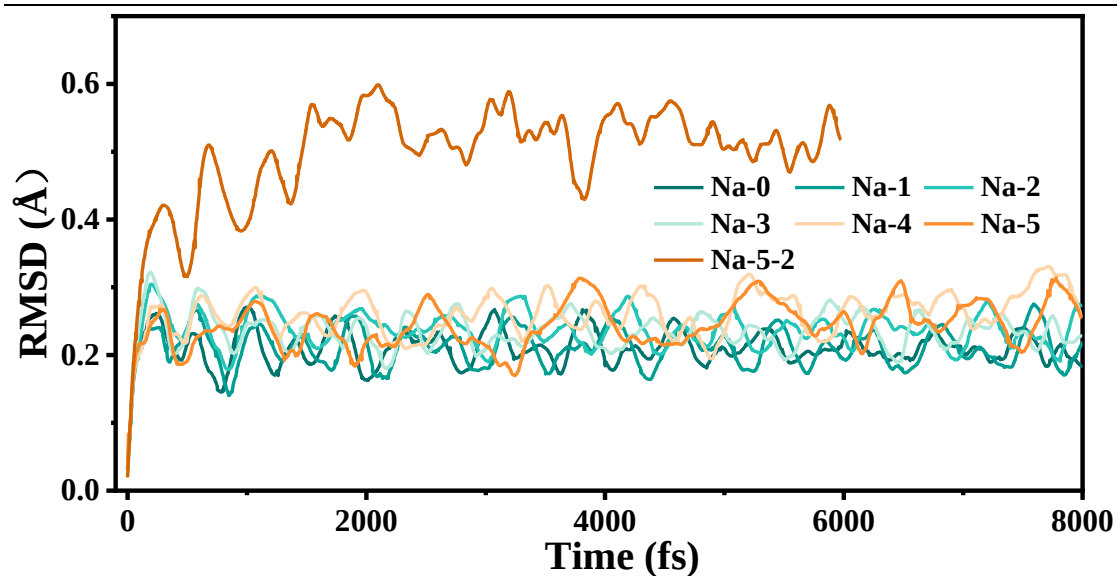


Figure S20. The RMSD curves during the AIMD simulation process in Na-0, Na-1, Na-2, Na-3, Na-4, Na-5 and Na-5-2.

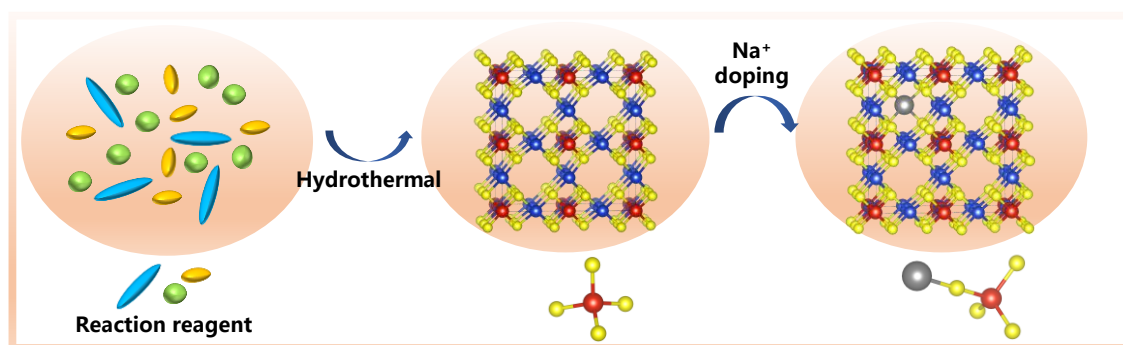


Figure S21. Schematic illustration of the synthesis for target cathode materials with different Na^+ concentration.

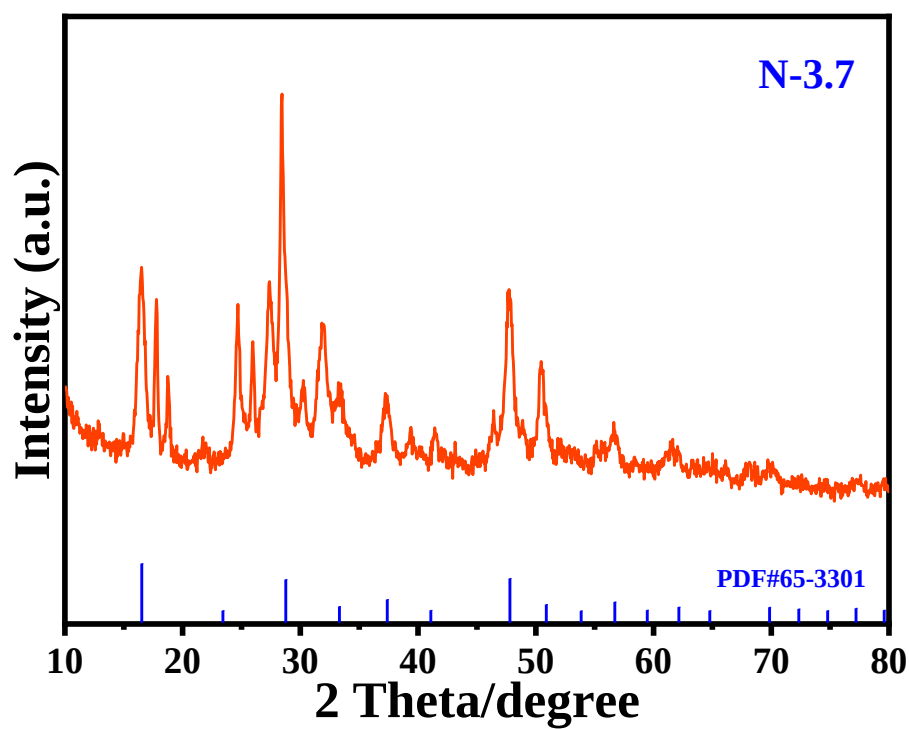


Figure S22. XRD patterns of sample with excessive Na^+ -ion doping.

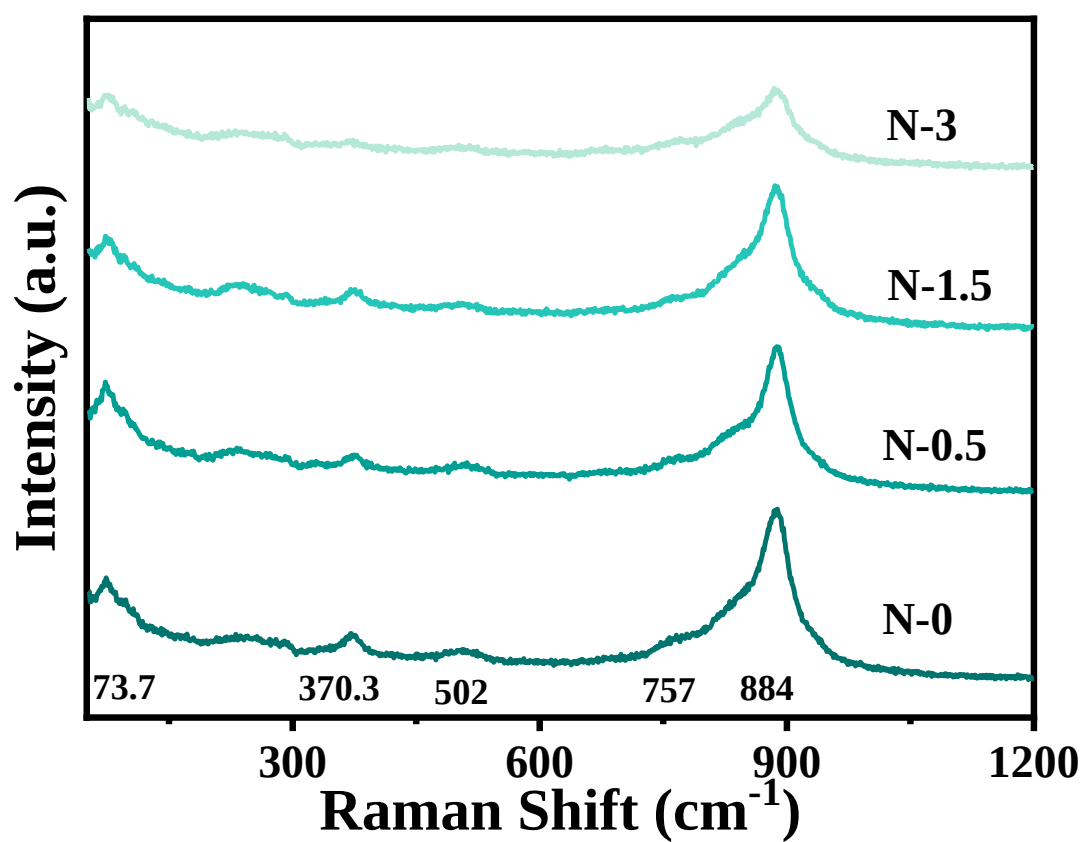


Figure S23. Raman of N-0, N-0.5, N-1.5 and N-3.

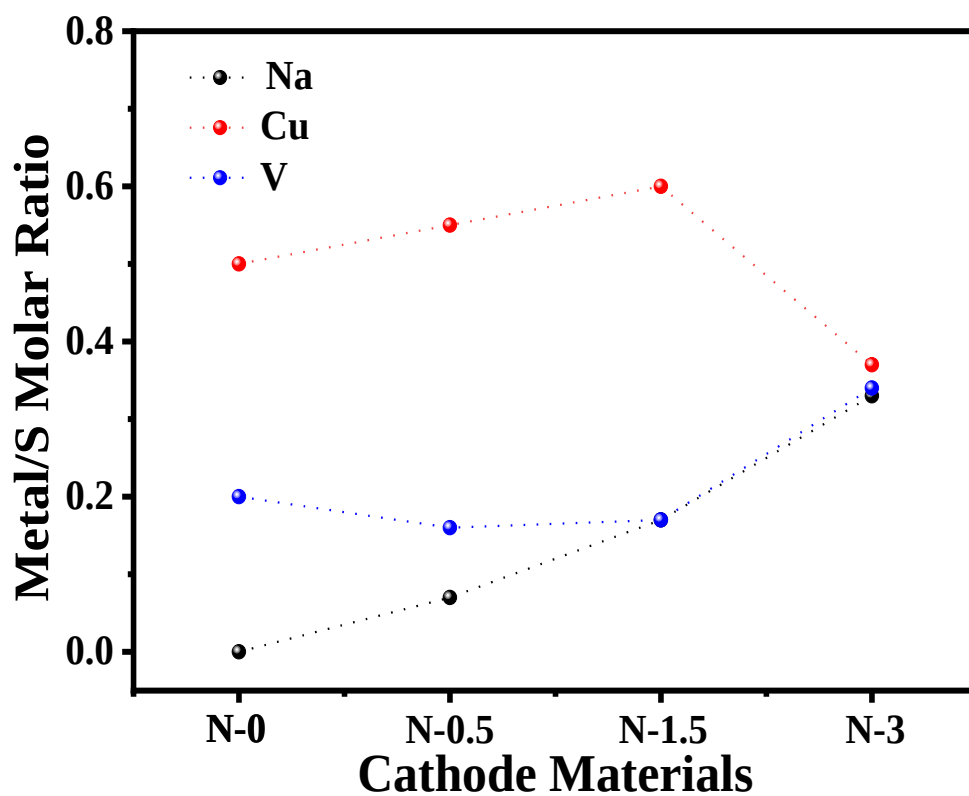


Figure S24. ICP testing result of prepared cathode materials with different Na^+ concentration.

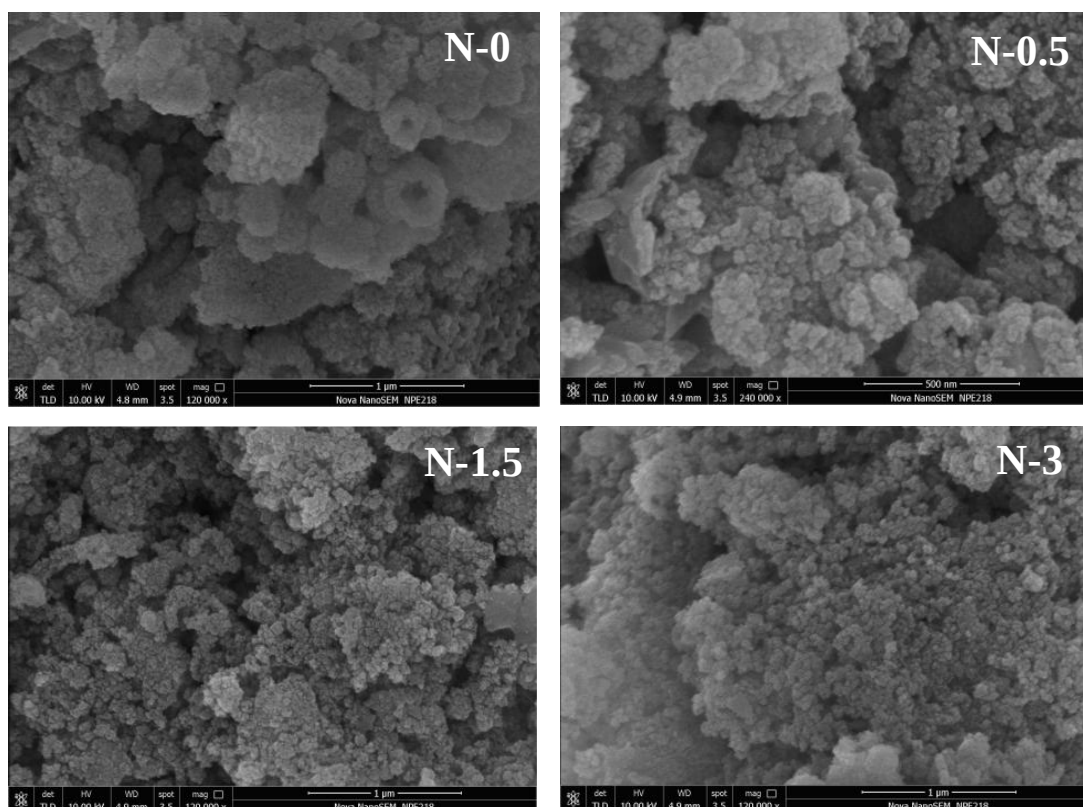


Figure S25. SEM of N-0, N-0.5, N-1.5 and N-3.

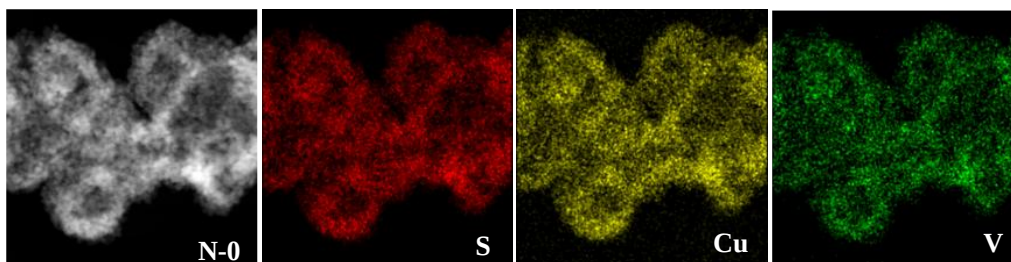


Figure S26. TEM-Mapping of N-0.

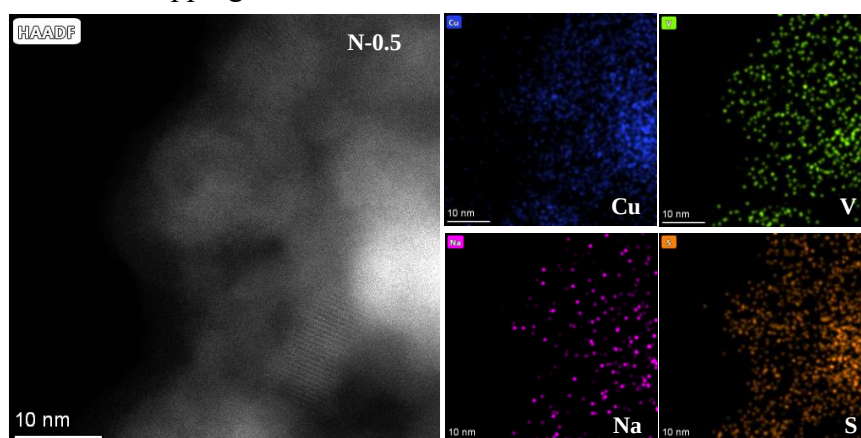


Figure S27 TEM-Mapping of N-0.5.

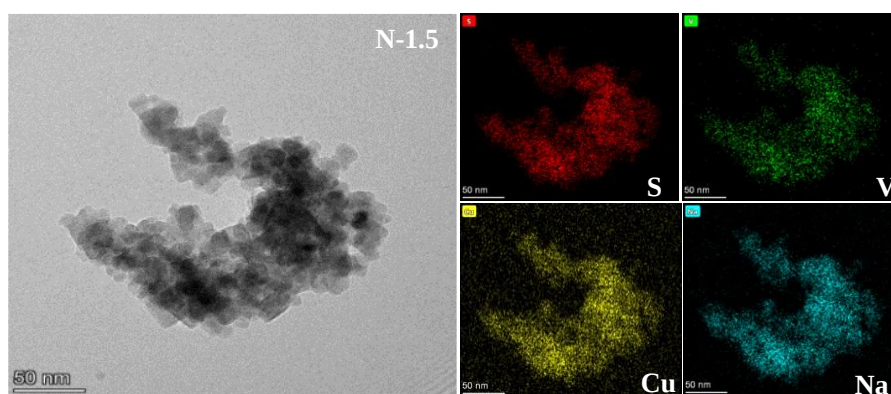


Figure S28. TEM-Mapping of N-1.5.

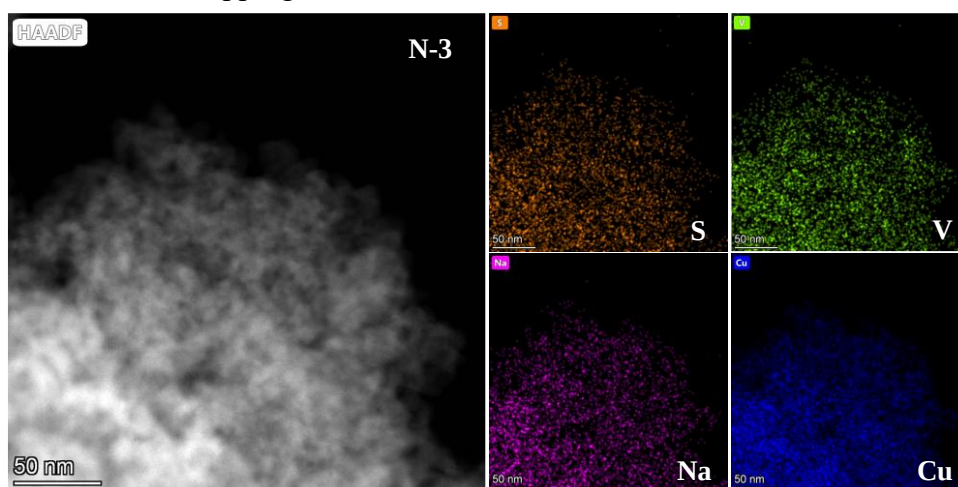


Figure S29. TEM-Mapping of N-3.

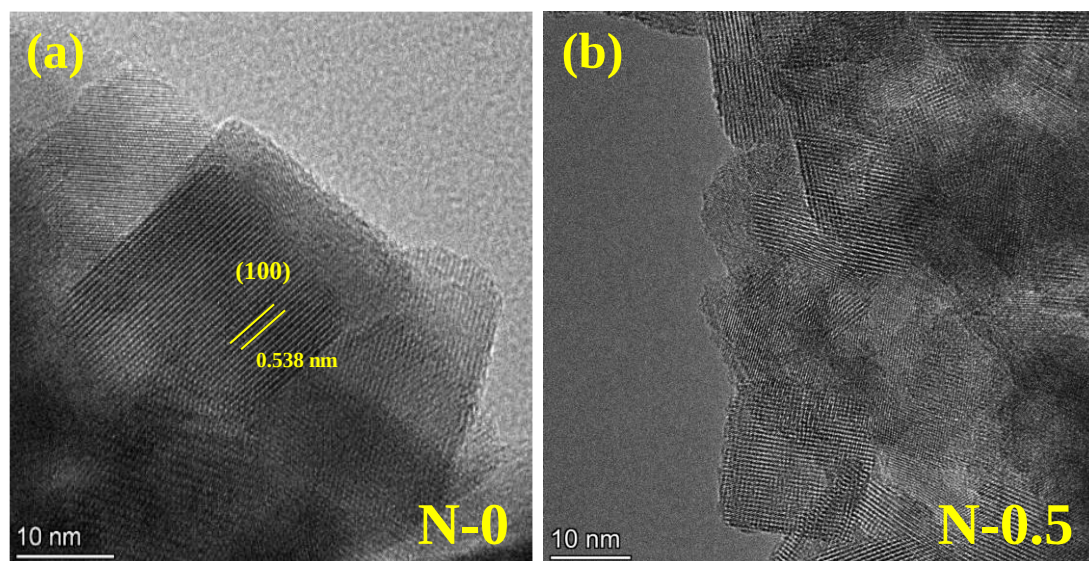


Figure S30. HRTEM of N-0 and N-0.5.

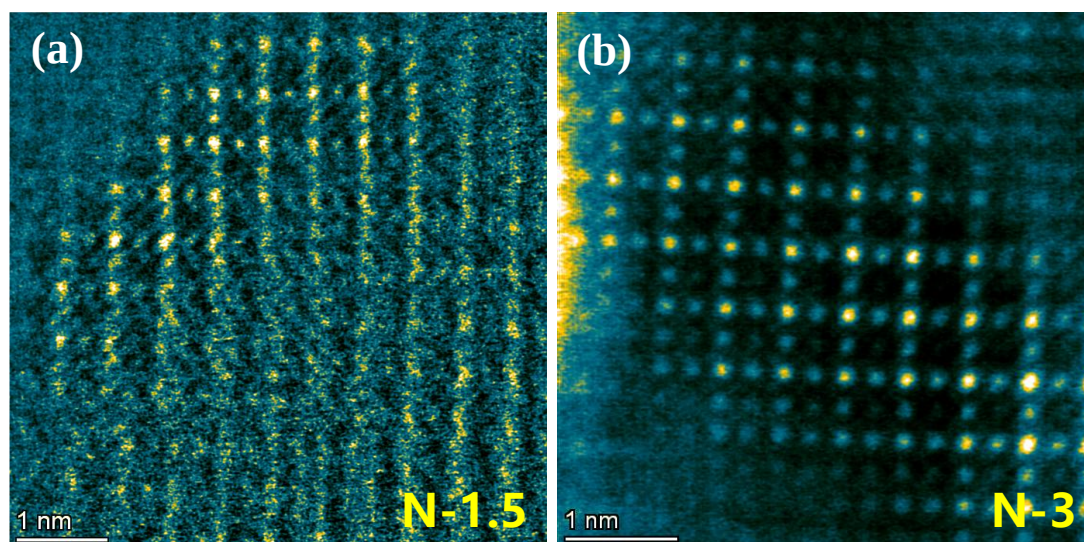


Figure S31. HAADF-STEM images N-1.5 and N-3.

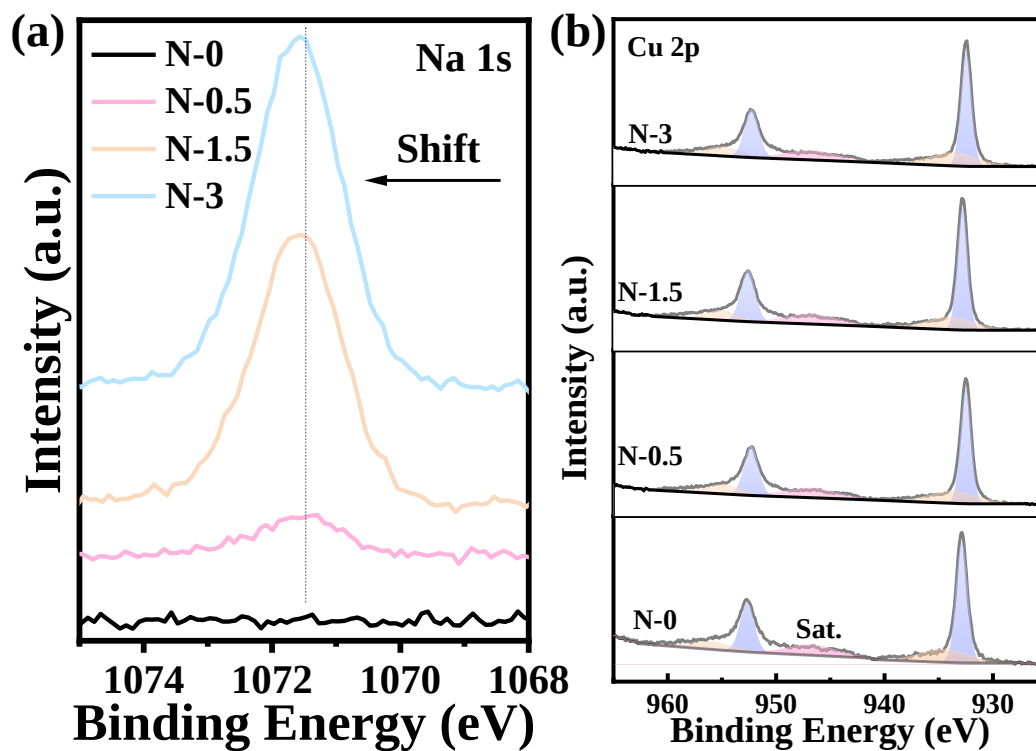


Figure S32. The high-resolution XPS spectra for Na 1s and Cu 2p in Na-0, Na-0.5, Na-1.5 and Na-3.

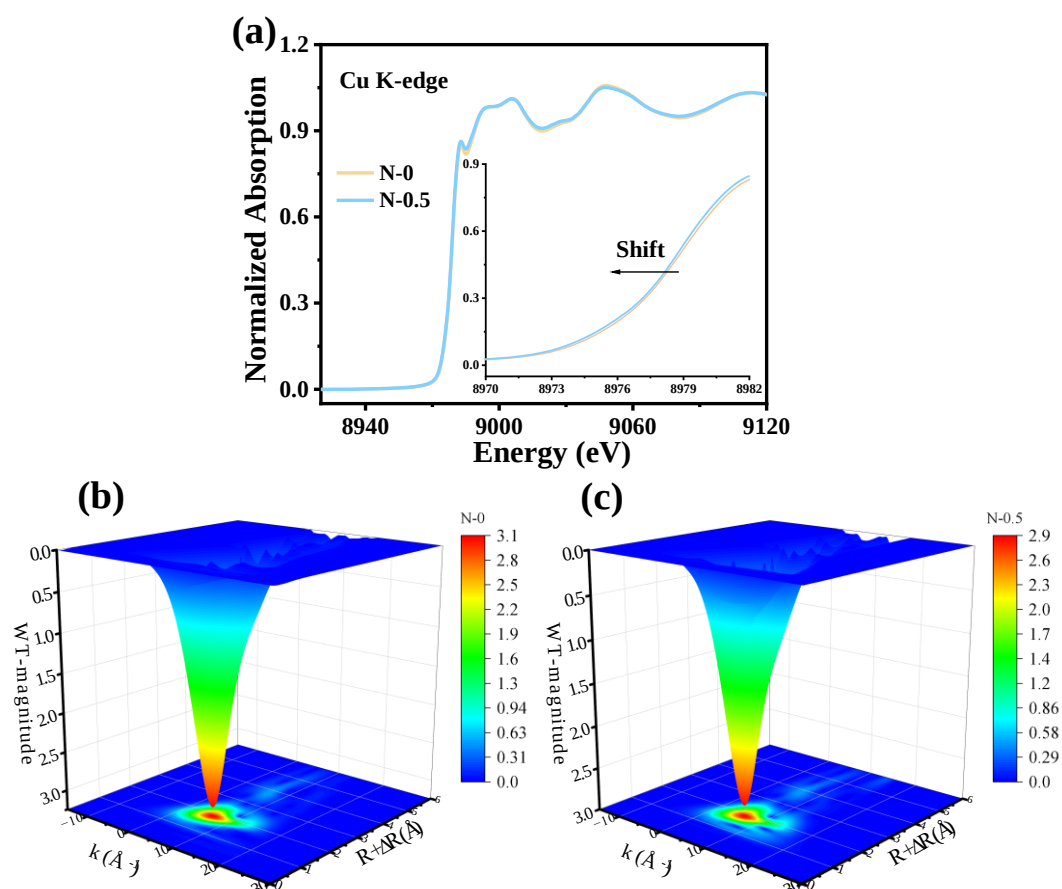


Figure S33. The K-edge XANES spectra of V and corresponding WT-EXAFS spectra

of Na-0.5.

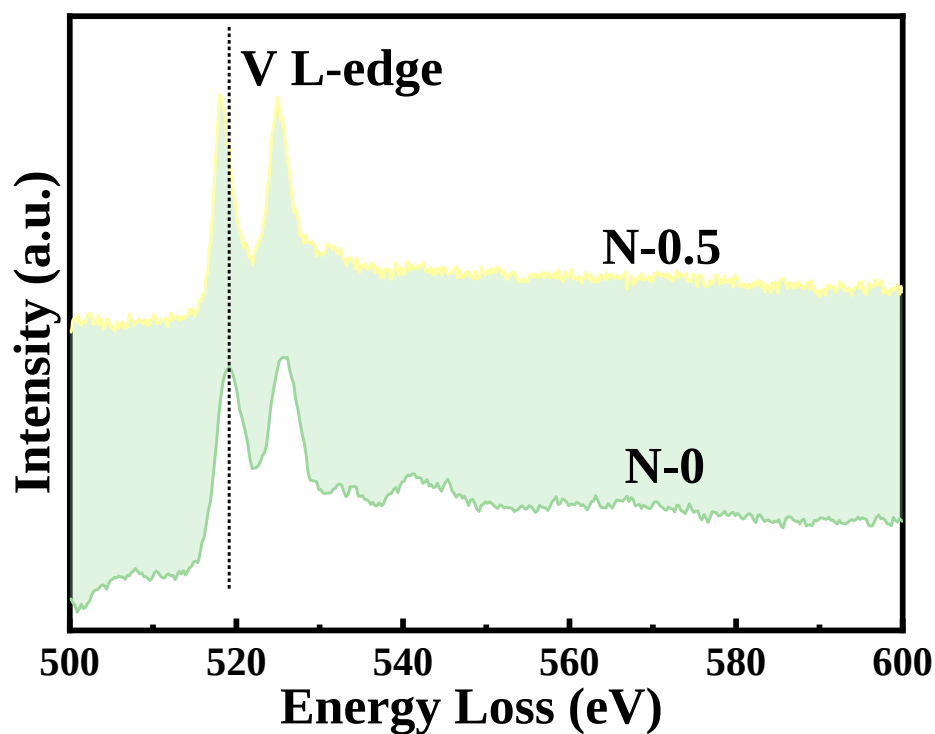


Figure S34. The Electron Energy Loss Spectroscopy of V L-edge in N-0 and N-0.5.

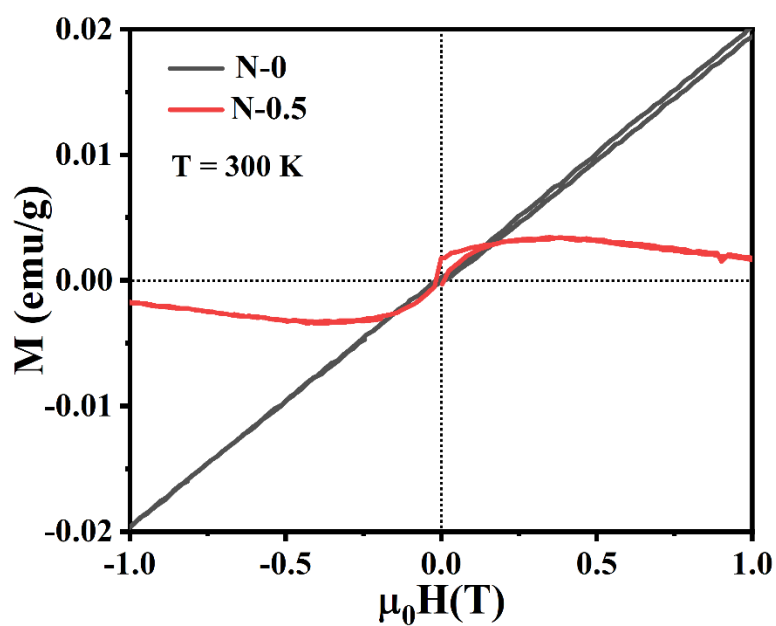


Figure S35 Field dependence of the magnetization of N-0 and N-0.5.

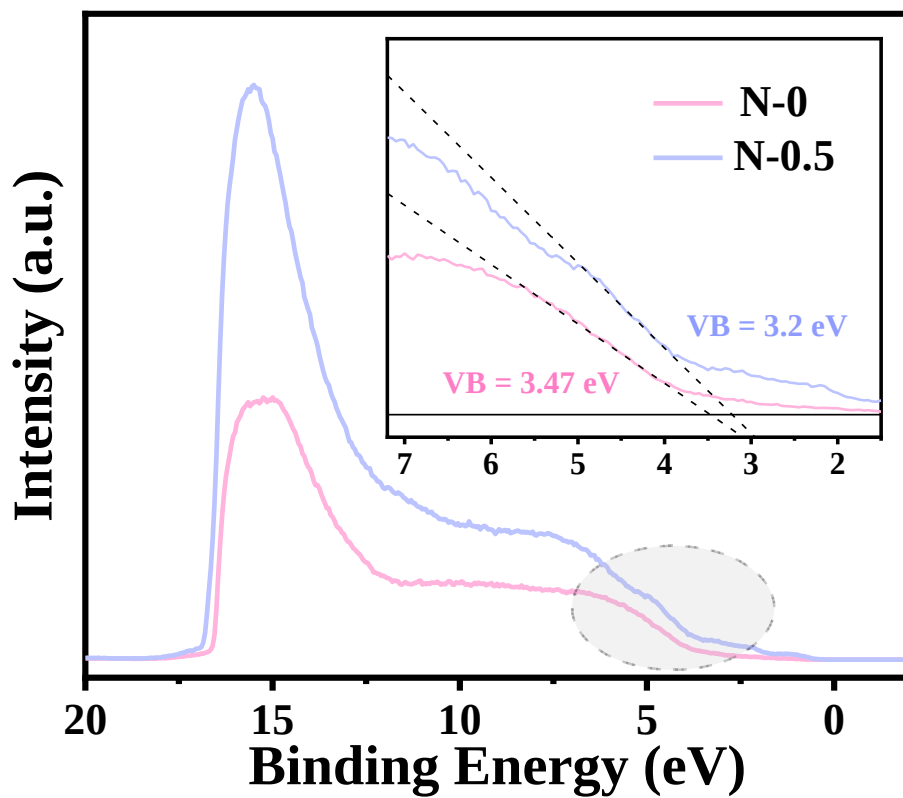


Figure S36. The UPS spectra of N-0 and N-0.5.

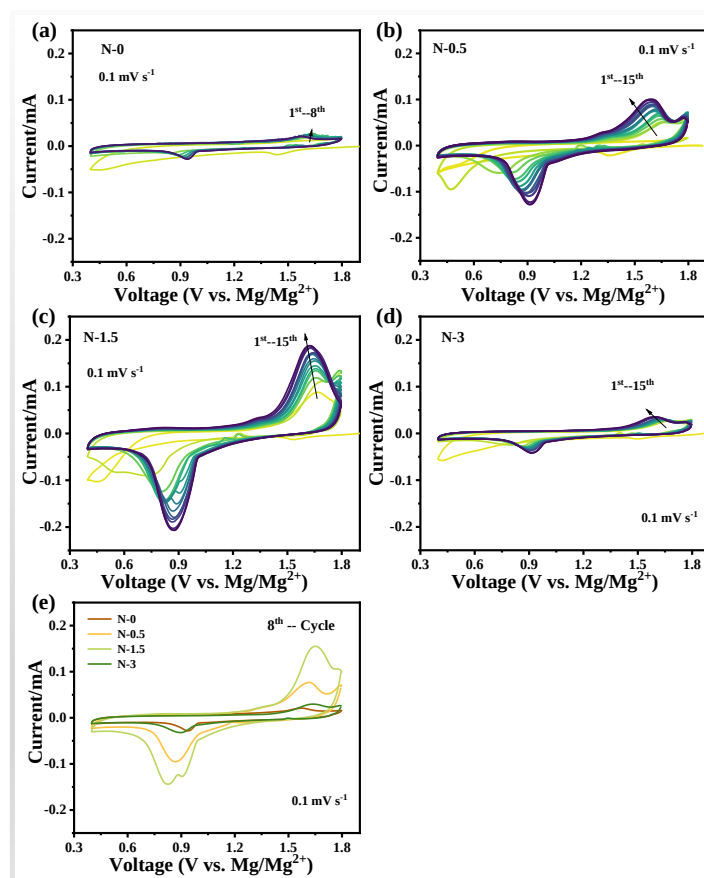


Figure S37. The CV curves of Na-0, Na-0.5, Na-1.5 and Na-3.

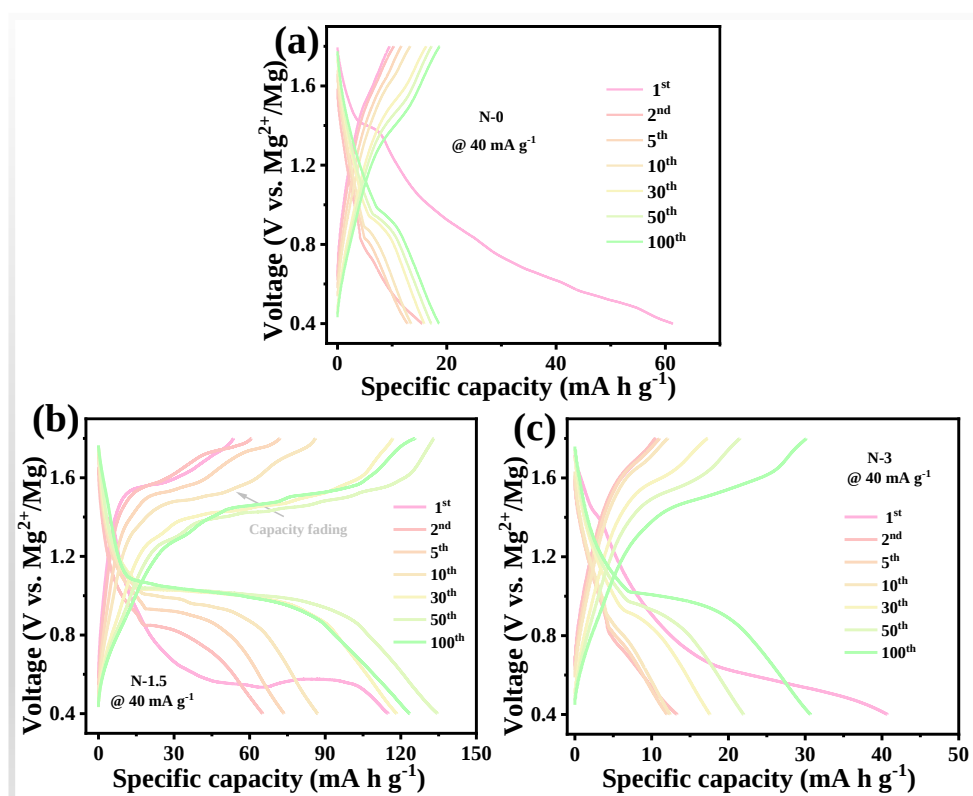


Figure S38. The GCD curves of Na-0, Na-1.5 and Na-3.

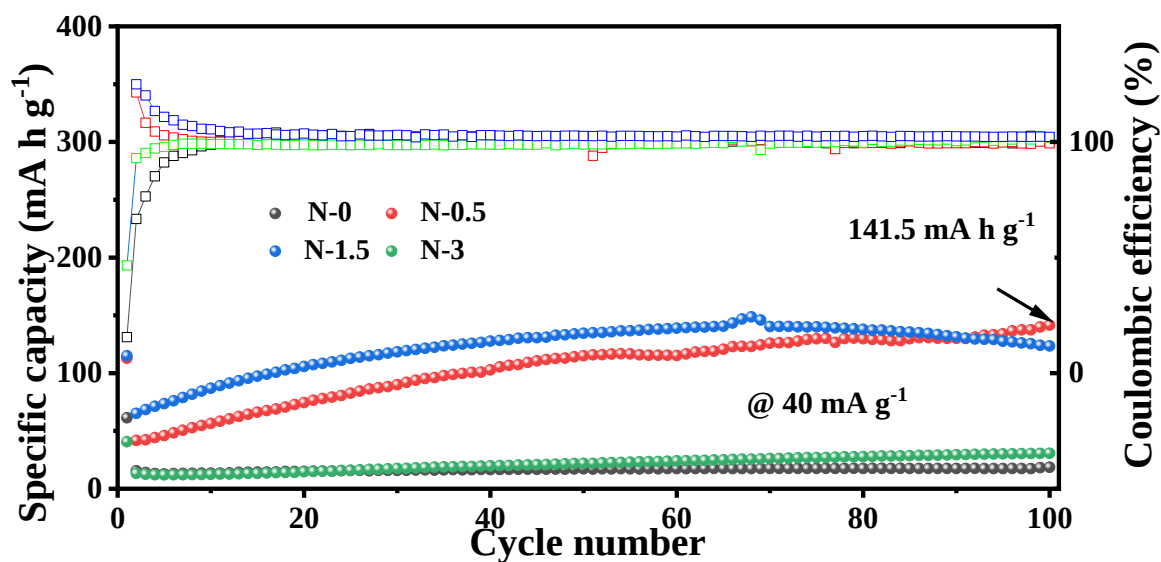


Figure S39 The cycling performance of N-0, N-0.5, N-1.5 and N-3 at 40 mA g^{-1} during the electrochemical reconstruction process within 100th cycles.

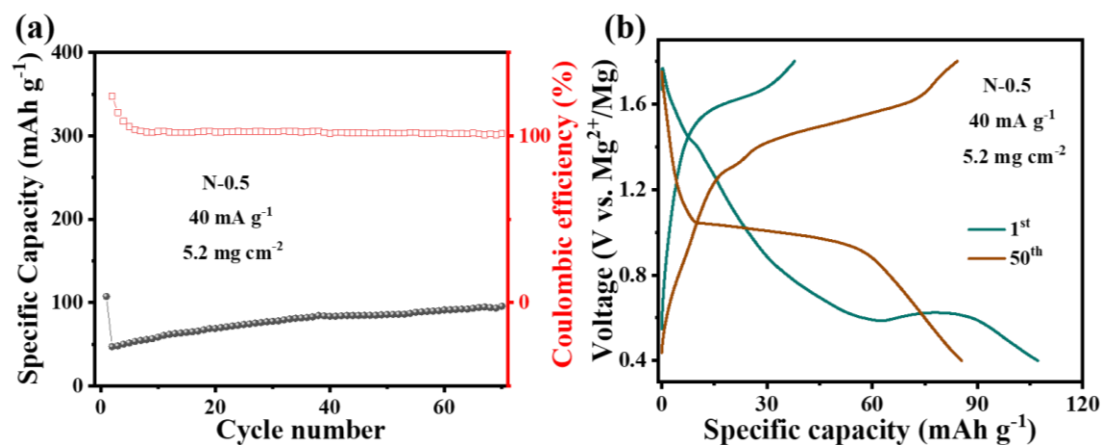


Figure S40 (a) The cycling performance and (b) GCD curves at 1st and 50th cycle.

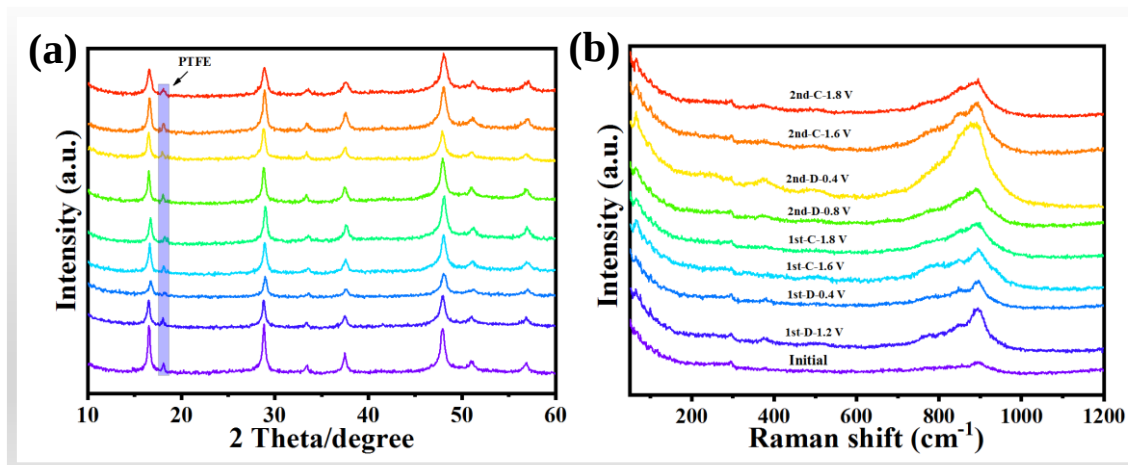


Figure S41. The ex-situ XRD and Raman of N-0 during 1st and 2nd cycles.

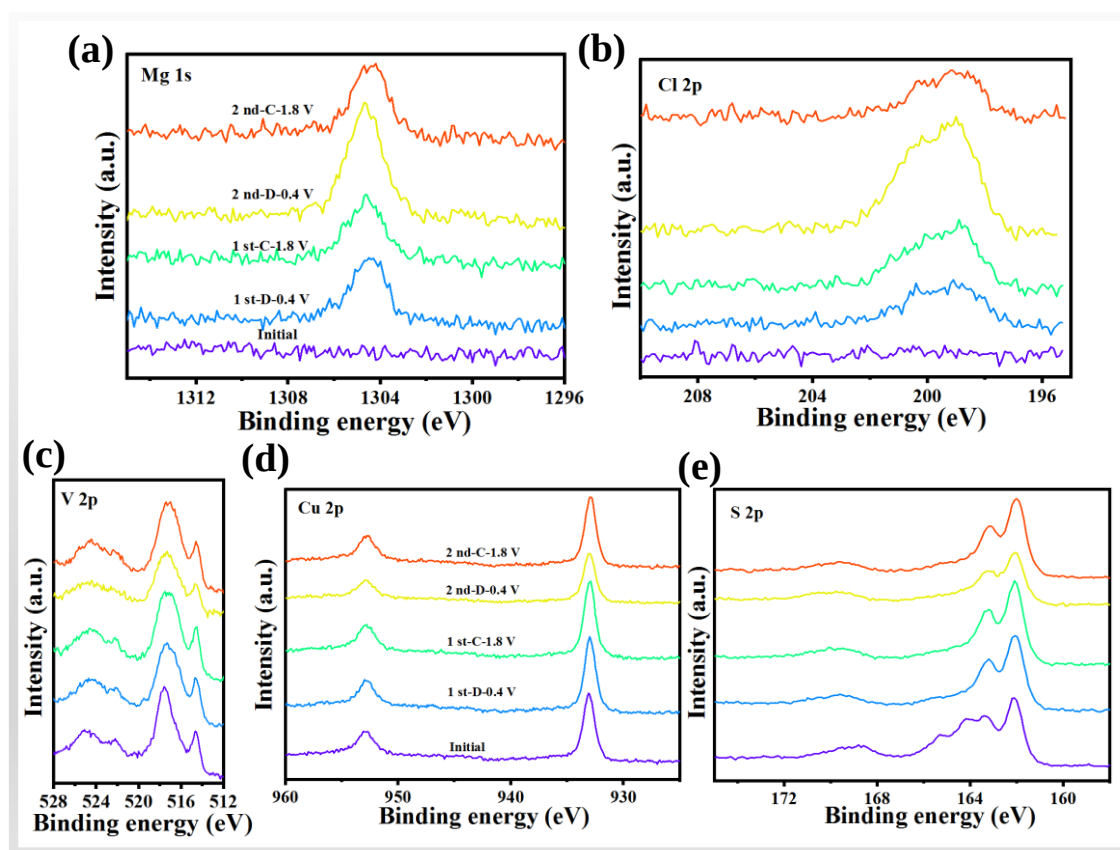


Figure S42. The ex-situ XPS of Mg 1s, Cl 2p, V 2p, Cu 2p and S 2p for Na-0 during 1st and 2nd cycles at fully discharged and charged state.

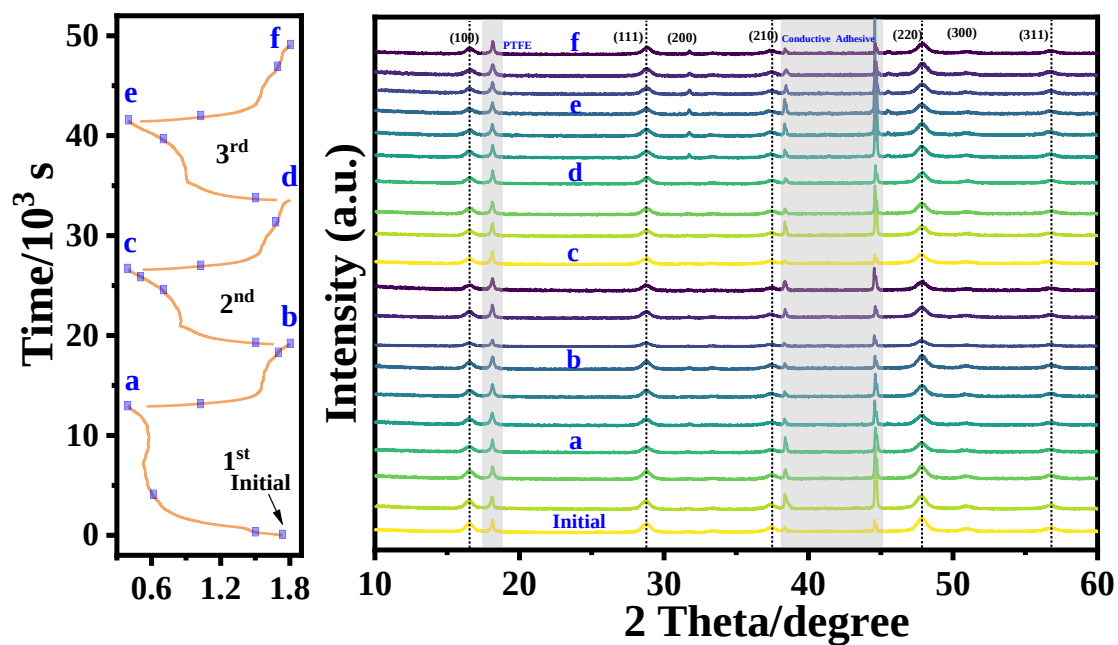


Figure S43. The ex-situ XRD of N-0.5 during the initial 3 cycles.

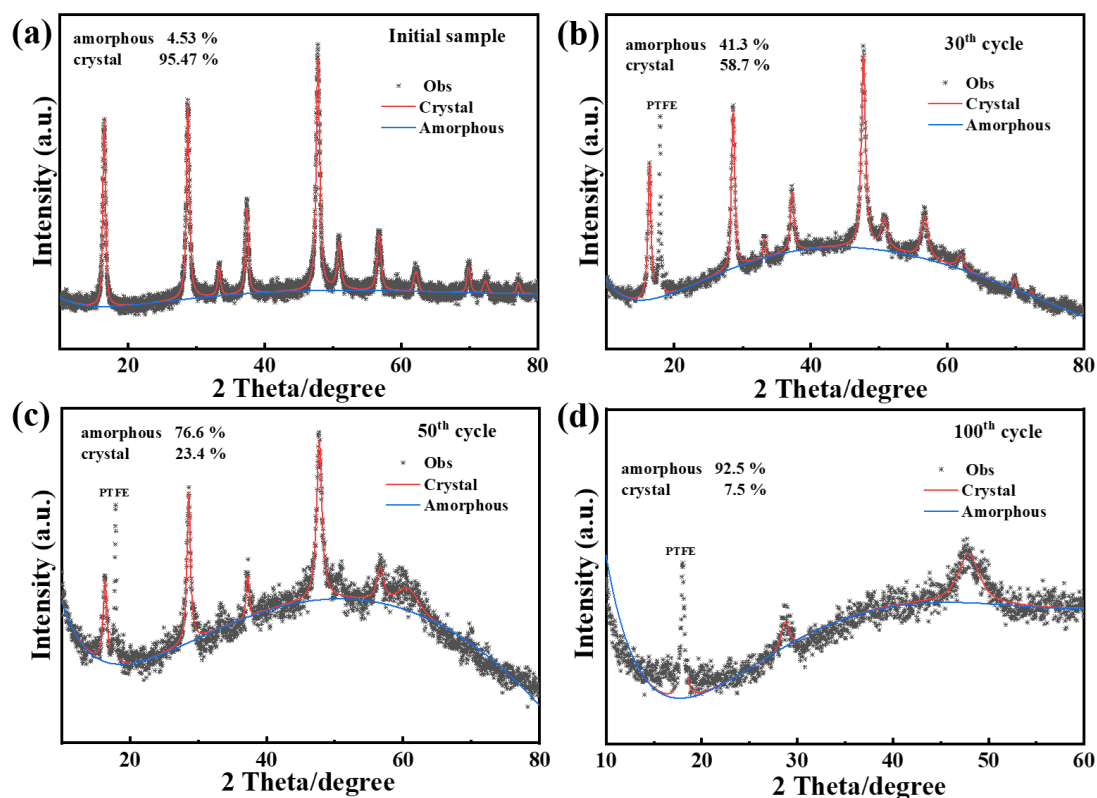


Figure S44 XRD refinement patterns of N-0.5 at (a) initial, (b) 30th, (c) 50th and (d) 100th cycle.

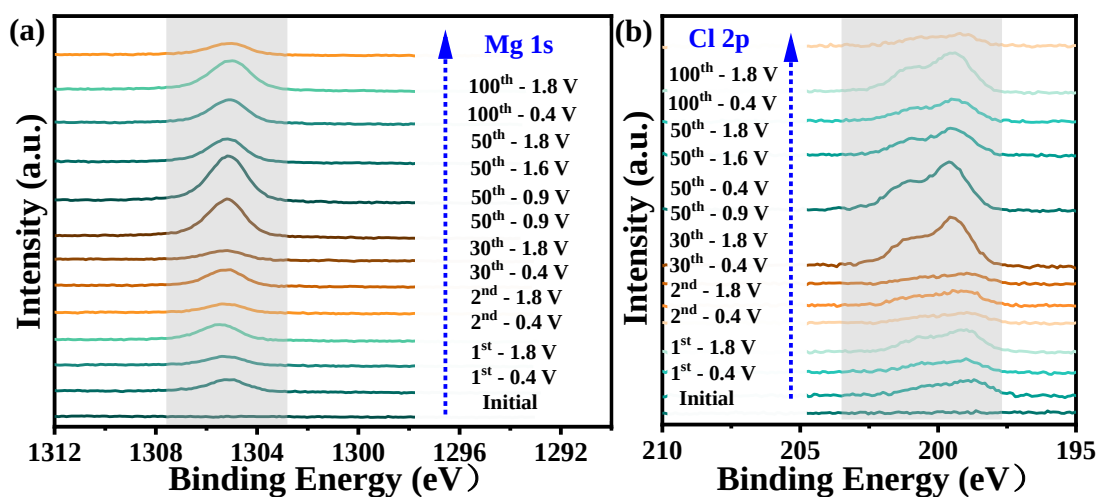


Figure S45. The ex-situ XPS of Mg 1s and Cl 2p for N-0.5 at fully discharged and charged state during the electrochemical reconstruction process.

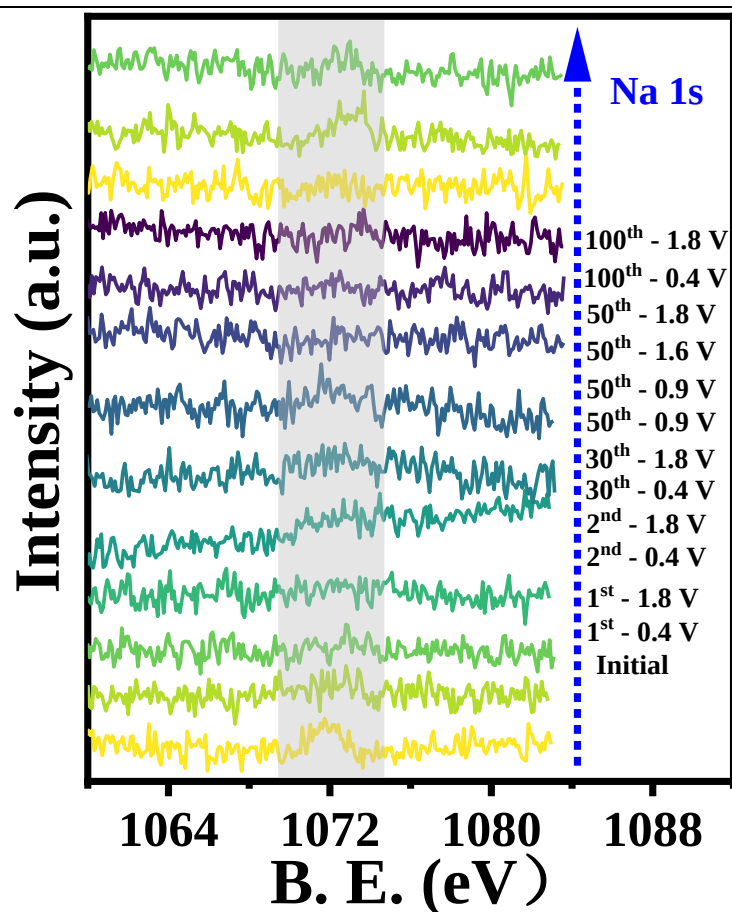


Figure S46. The ex-situ XPS of Na 1s for N-0.5 at fully discharged and charged state during the electrochemical reconstruction process.

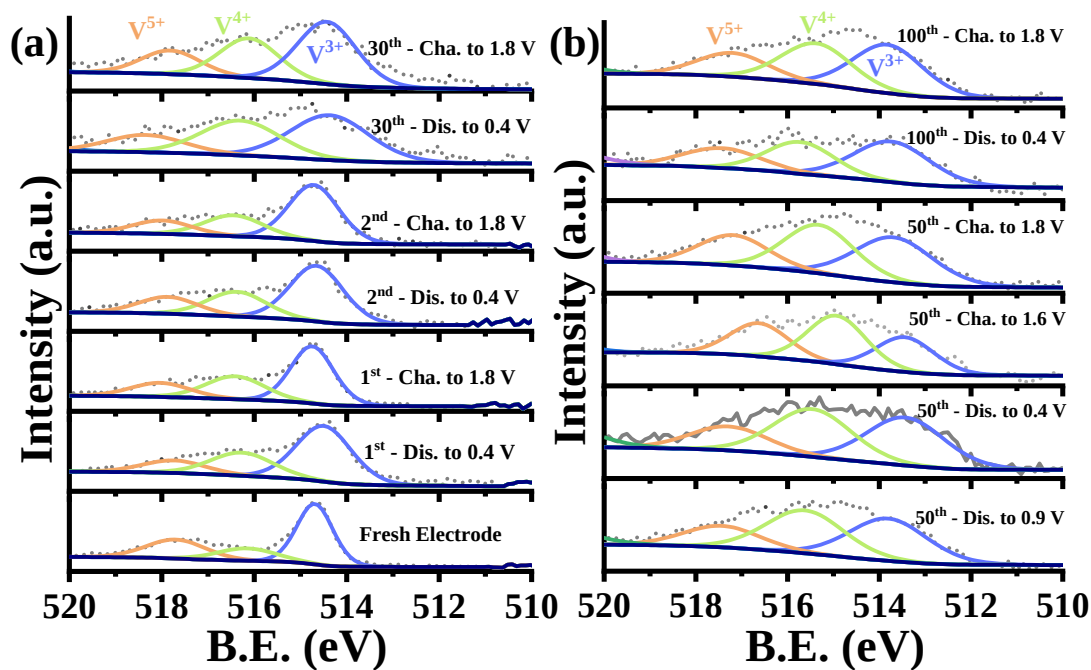


Figure S47. The ex-situ XPS of V 2p for N-0.5 during the initial 2 cycles at fully

discharged and charged state.

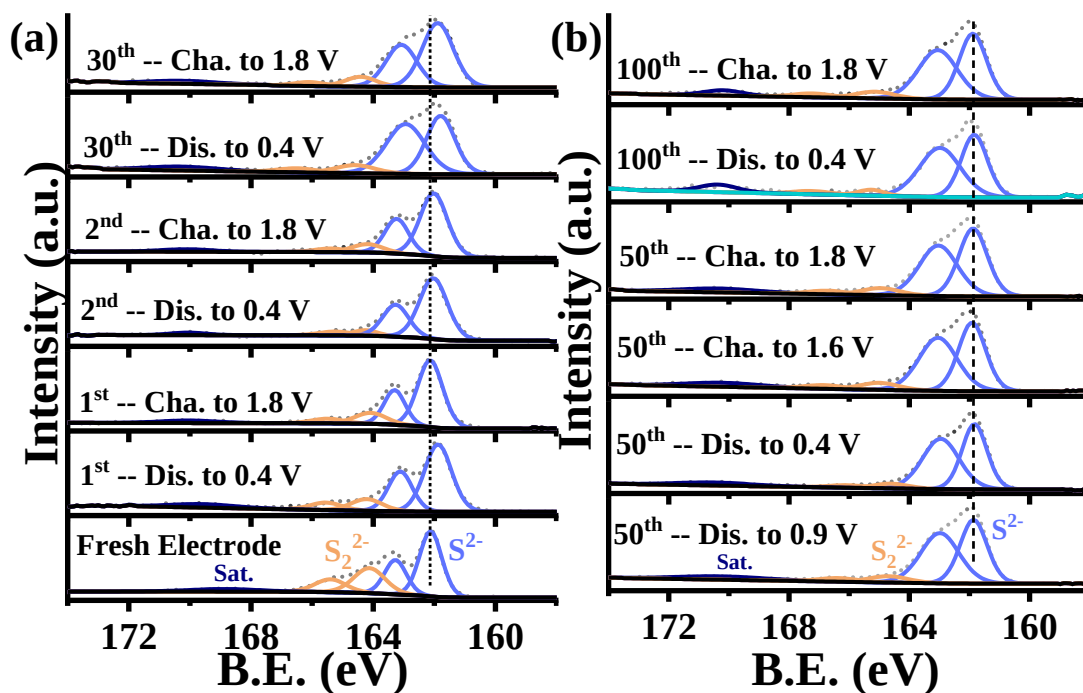


Figure S48. The ex-situ XPS of S 2p for N-0.5 at fully discharged and charged state during the electrochemical reconstruction process.

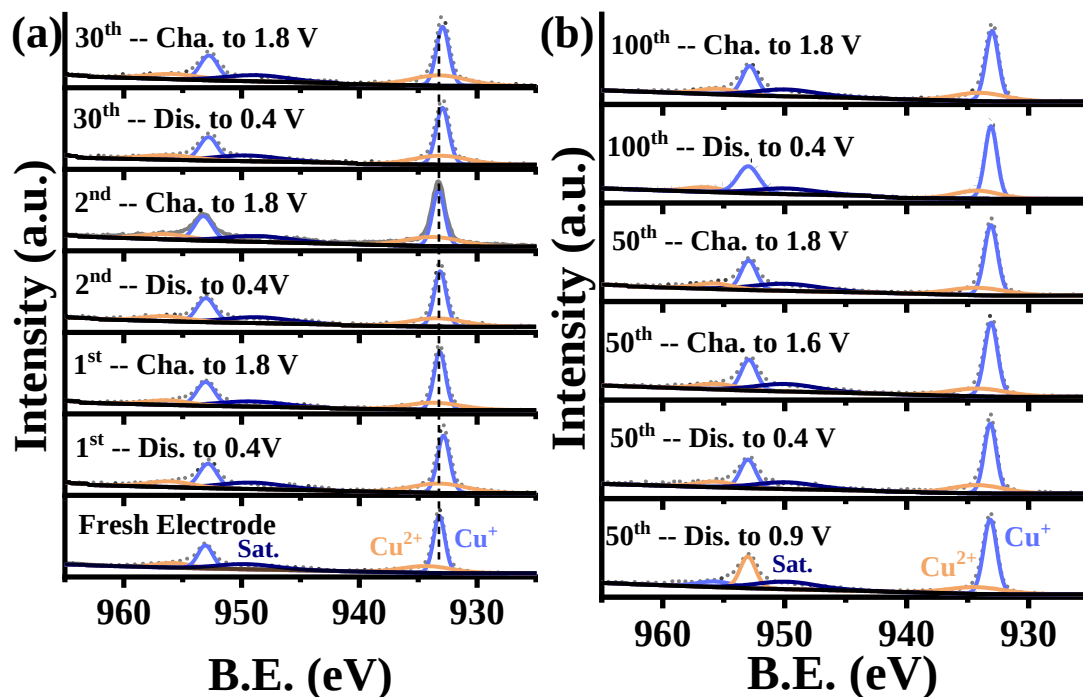


Figure S49. The ex-situ XPS of Cu 2p for N-0.5 at fully discharged and charged state during the electrochemical reconstruction process.

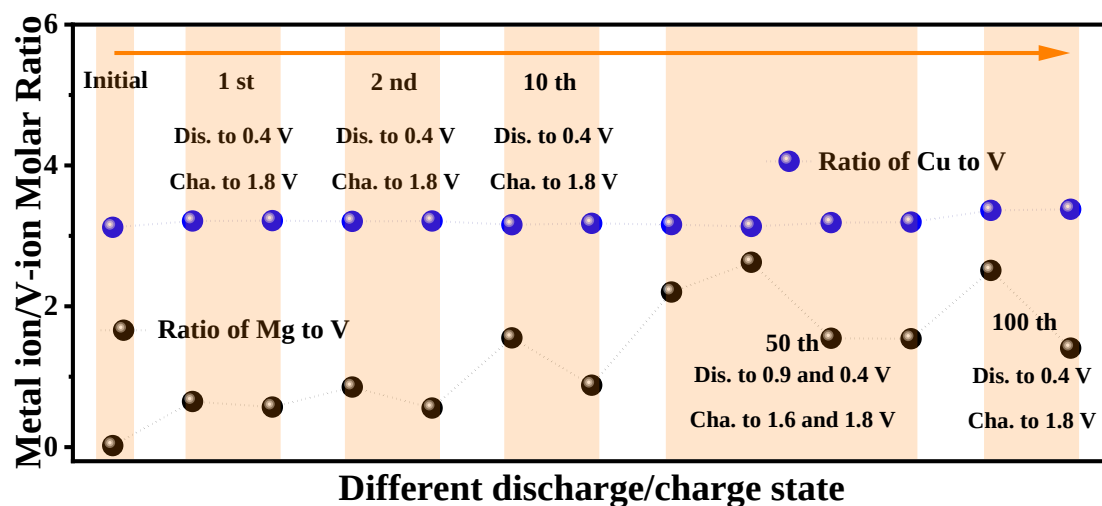


Figure S50. The ex-situ ICP of Na 1s for N-0.5 at fully discharged and charged state during the electrochemical reconstruction process.

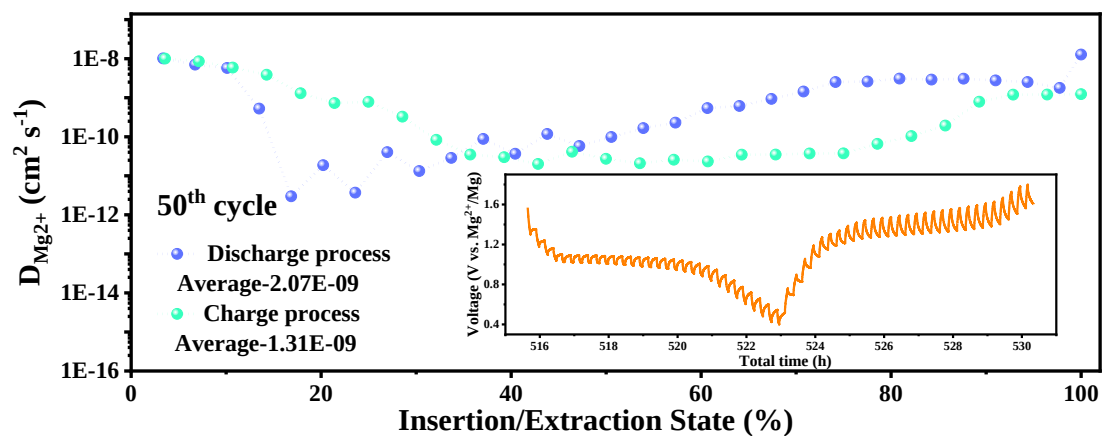


Figure S51. The GITT curves and Mg^{2+} diffusion efficient of N-0.5 at 50th cycles during the electrochemical reconstruction process.

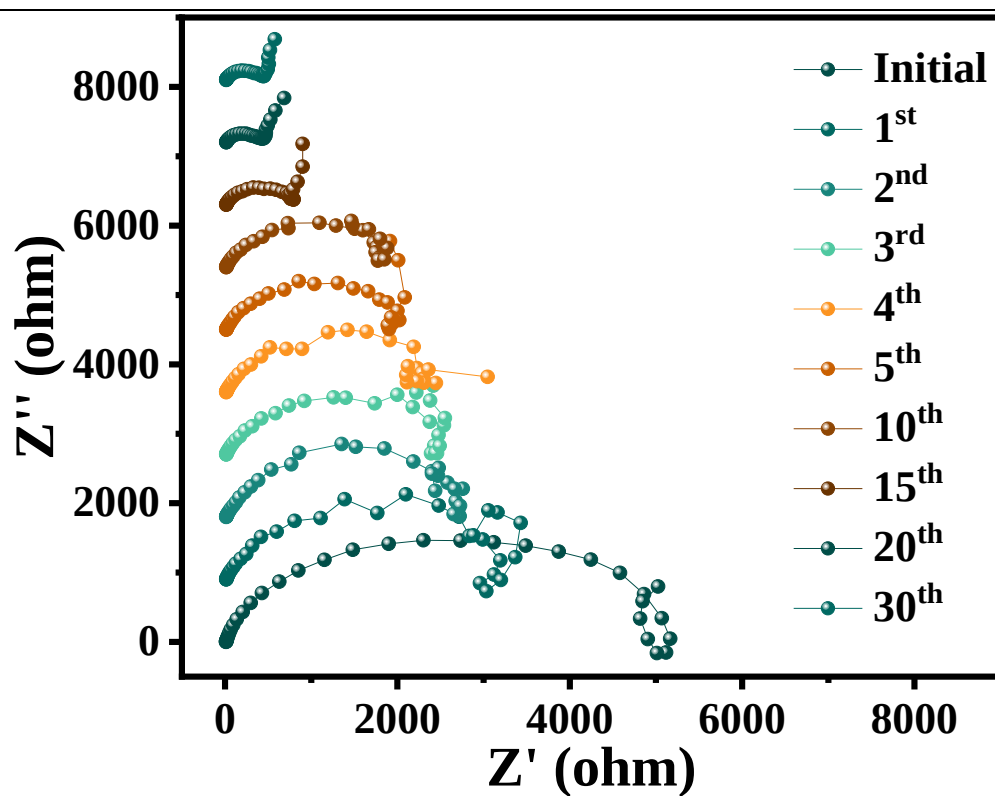


Figure S52. The in-situ EIS of N-0.5 at selected cycles during the electrochemical reconstruction process.

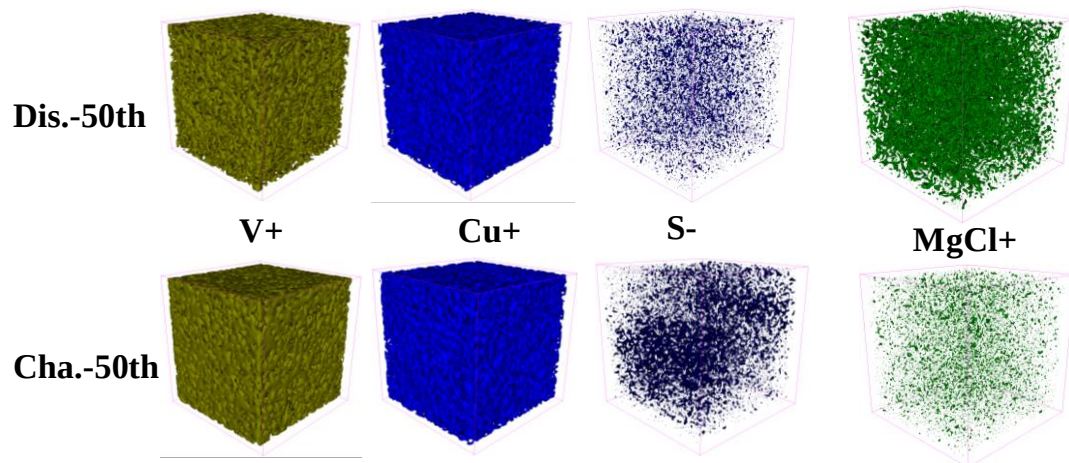


Figure S53. The 3D TOF-SIMS images of V^+ , Cu^+ , S^- and $MgCl^+$ for N-0.5 at fully discharged and charged state after 50th cycles.

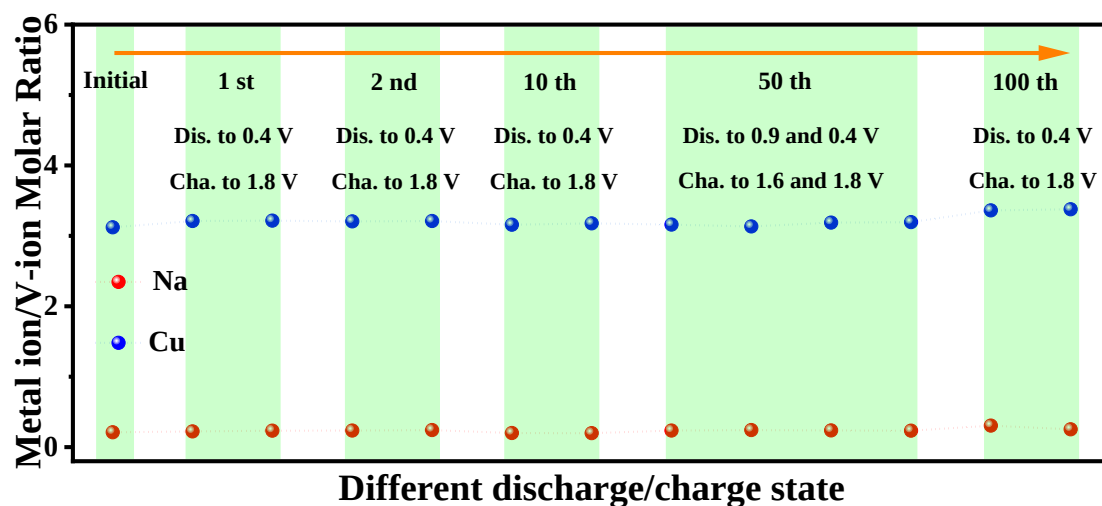


Figure S54 The molar ratio of Metal ion (Na, Mg and Cu) to V-ion based on ex-situ ICP testing within 100th cycles during the electrochemical reconstruction process.

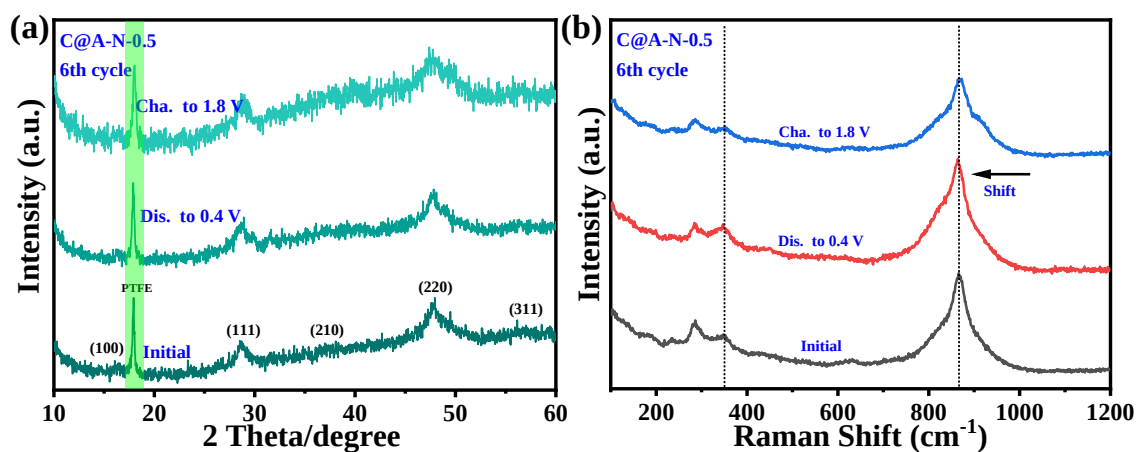


Figure S55. The ex-situ XRD and Raman of C@A-N-0.5 at the fully discharged and charged state after 6th cycle.

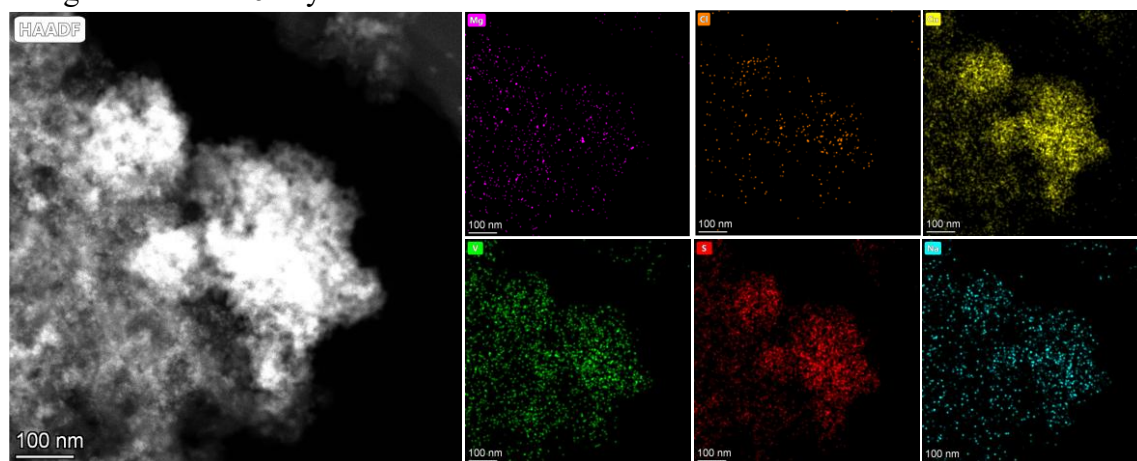


Figure S56. The TEM-Mapping of C@A-N-0.5 at the fully charged state after 6th cycle.

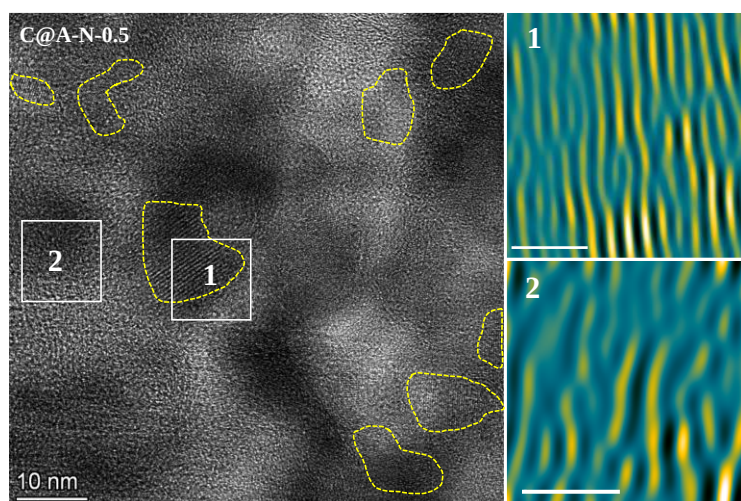


Figure S57. The HRTEM of C@A-N-0.5 at the fully charged state after 6th cycle.

Table S1 Comparison of Cycling performance and capacity retention at low current density

Cathode Material	Current density (A g ⁻¹)	Cycling performance @ capacity retention	Ref.
C@A-N-0.5	0.04	141 mAh g⁻¹ for 350 cycles (92%)	This work
CuS/CF-HP	0.05	164 mAh g ⁻¹ for 50 cycles (73.7 %)	[6]
CuS	0.1	124 mAh g ⁻¹ for 100 cycles (28.2 %)	[7]
CuS	0.1	212 mAh g ⁻¹ for 100 cycles (83.2 %)	[8]
V _{0.5} Cr _{0.5} S ₂	0.1	106 mAh g ⁻¹ for 50 cycles (87 %)	[9]
VS ₄ @rGO	0.05	268.3 mAh g ⁻¹ for 100 cycles (54.9 %)	[10]

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