Electronic Supplementary Information

Introducing high-valence molybdenum to stimulate lattice oxygen in NiCo LDH cathode for chloride ion batteries

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Material Characterization

The crystal structure was analyzed by Cu Kα (λ=0.1518 nm) X-ray diffraction (XRD, Bruker D8) between 5 and 70° at a scanning rate of 10° min^{-1}. X-ray photoelectron spectroscopy (Thermo ESCALAB 250XI) technique was used to determine the chemical status of LDHs samples with monochromatic Al Kα X-ray source (hv = 1486.6 eV). The morphological characteristics of the materials were monitored via a Zeiss Supra 55 field emission scanning electron microscope (SEM) with an accelerating voltage of 20 kV. The transmission electron microscopy (TEM) investigations were recorded through a FEI TalosF200S microscope under an acceleration voltage of 200 kV, which is equipped with an energy dispersive X-ray detector. Fourier transform infrared (FTIR) spectra were collected using the Vector 22 (Bruker) spectrophotometer with a 2 cm^{-1} resolution. The proportion of different elements was determined by inductively coupled plasma emission spectrometry (Shimadzu ICPS7500). The thermogravimetric analyzer (TGA) was performed on a PCT-1A thermal analysis system in an air atmosphere with heating rates of 10 °C min^{-1} ranging from 30 °C to 800 °C.

Calculation details.

The theoretical calculations were performed by the density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP) package with the projector augmented wave (PAW) method. The generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) functional were used to describe the exchange-functional. The simulation was run with a cutoff energy of 450 eV throughout the computations and the force on each atom less than 0.02 eV/Å was set for convergence criterion of geometry relaxation. In the calculations, a 3×3×1 *k*-point sampling was used in the surface Brillouin zone and the self-consistent calculations apply a convergence energy threshold of 10^{-5} eV. 15 Å vacuum was added along the *z* direction in order to avoid the interaction between periodic structures. The intensity of the adsorption behaviour calculating with the following equation was used as the evaluation basis for the selection of Cl adsorption sites.

$$E_{ad} = \frac{E_{basal+atom} - E_{basal}}{n} - E_{atom}$$

where $E_{basal+atom}$ and E_{basal} are the energy of the Cl adsorbed on the surface and the energy of LDH models; n is the number of Cl atoms and E_{atom} is the chemical potential of an isolated Cl atom in vacuum.

Reagents and Materials. Cobalt nitrate hexahydrate ($Co(NO_3)_2 \cdot 6H_2O$, 99%), Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$, 99%), sodium molybdate (Na_2MoO_4, 96%) and urea were purchased from Shanghai Aladdin Industrial. 1-Butyl-1-methylpyrrolidinium chloride (Bpy14Cl, 99%, loLiTech) and propylene carbonate (PC) were purchased from Shanghai (China) Ailei Chemical Co. Ltd. Acetylene black conductor and polyvinylidene fluoride (PVDF) binder were obtained from Shenzhen (China) Kejing Co. Ltd. All reagents are analytical grade and used without further purification.

Synthesis of Mo_3NiCo_2-CO_3 LDH. $Mo_{0.3}NiCo_2$-CO_3 LDH sample was synthesized by one-step hydrothermal method as follows. 2 mmol of $Co(NO_3)_2 \cdot 6H_2O$, 1 mmol of $Ni(NO_3)_2 \cdot 6H_2O$ and 0.3 mmol of $Na_2MoO_4 \cdot 2H_2O$ were dissolved in a mixed solution, which was composed of 20 ml deionized water and 60 ml ethanol with 18 mmol of urea as ammonia releasing agent. Then, the above solution was placed in a 100 ml stainless-steel Teflon-lined autoclave for 10 hours at 100 ℃. The resulting LDHs slurry was cooled to room temperature and washed with deionized water and ethanol for several times. The $Mo_{0.3}NiCo_2$-CO_3 LDH powder was obtained after dried at 60 °C for overnight. Mo_xNiCo_2-Cl LDH samples with different molybdenum doping proportions (x = 0, 0.1, 0.2, 0.4, 0.5) were prepared by changing the mass of Na_2MoO_4 from 0 mmol to 0.5 mmol.

Synthesis of Mo_xNiCo_2-Cl LDH. The Mo_xNiCo_2-Cl LDH were obtained via the typical anion-exchange process. Firstly, 0.4g as-prepared $Mo_{0.3}NiCo_2$-CO_3 LDH powder was dissolved in 500 ml of decarbonized water consisted of 2 M NaCl and 5 mM HCl. Then, the flask filled with the mixed solution was constantly vigorous stirring for 24 hours under N_2 gas protection.The resulting Mo_xNiCo_2 LDH inserted with chloride ions were collected by a centrifuge process with boiled water followed by drying in a vacuum oven at 60 ℃ for overnight.

Electrochemical measurements

The Mo_xNiCo_2-Cl LDH cathodes were prepared by mixing 70 wt% active matreials, 20 wt% acetylene black and 10 wt% PVDF to form a homogeneous slurry in NMP. The obtained slurry was coated on 0.08 mm graphite paper current collector using a 100 μm blade and vacuum-dried at 100 ℃ for 12 h. All electrodes were cut into disks with diameter of 12 mm and the average mass loading of which was about 1.2 mg cm^{-2}. The LDHs-based chloride ion batteries (CIBs) were assembled with CR2032 coin cells using Li metal foil and glass fiber filter (GF/D, Whatman) separator. 0.5 M Bpy14Cl dissolved in

PC solvent was used as electrolyte. The galvanostatic charge/discharge measurements were carried out on LANHE CT3002AU battery testing devices. Cyclic voltammetry (CV) and electrochemical impedance spectra (EIS) results were tested on the CHI 660e electrochemical workstation.

Supplementary Figures and Tables

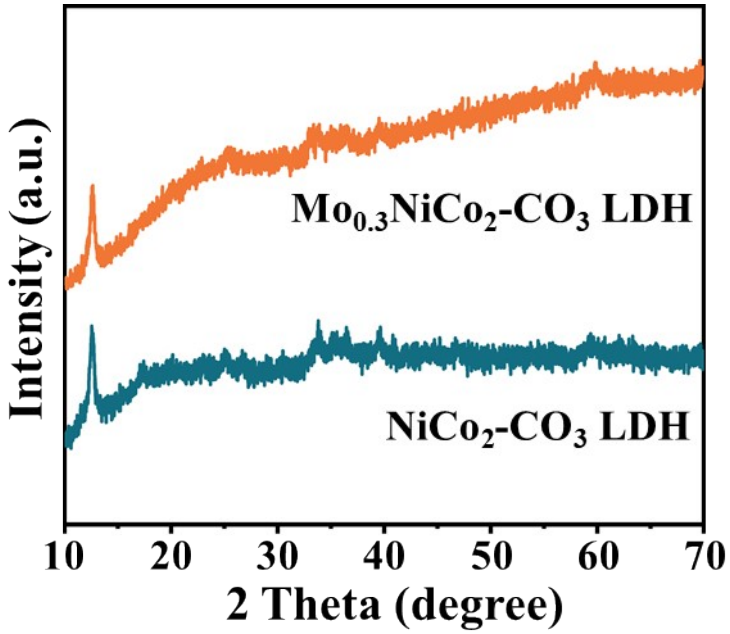

Fig. S1. Powder XRD patterns of $NiCo_2$-CO_3 LDH and $Mo_{0.3}NiCo_2$-CO_3 LDH samples.

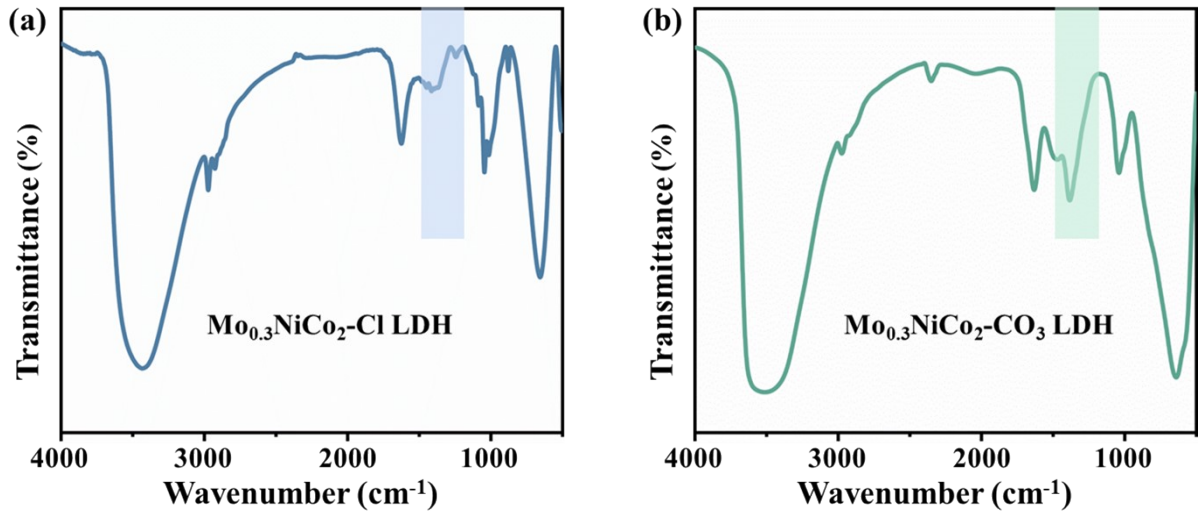

Fig. S2. IR spectra of (a) $Mo_{0.3}NiCo_2$-Cl LDH and (b) $Mo_{0.3}NiCo_2$-CO_3 LDH.

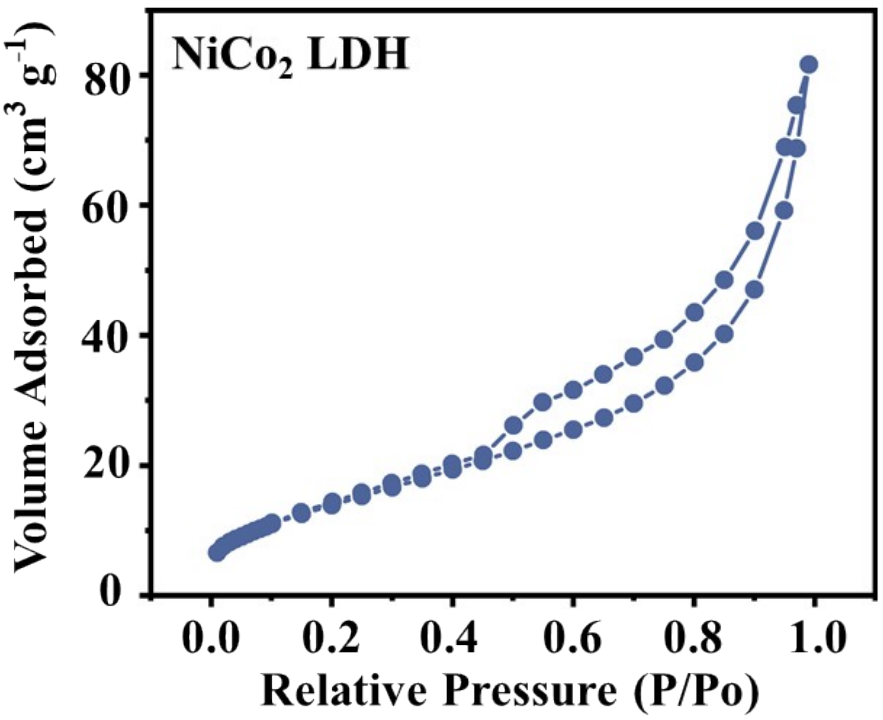

Fig. S3. N_2 sorption isotherm of $NiCo_2$-Cl LDH.

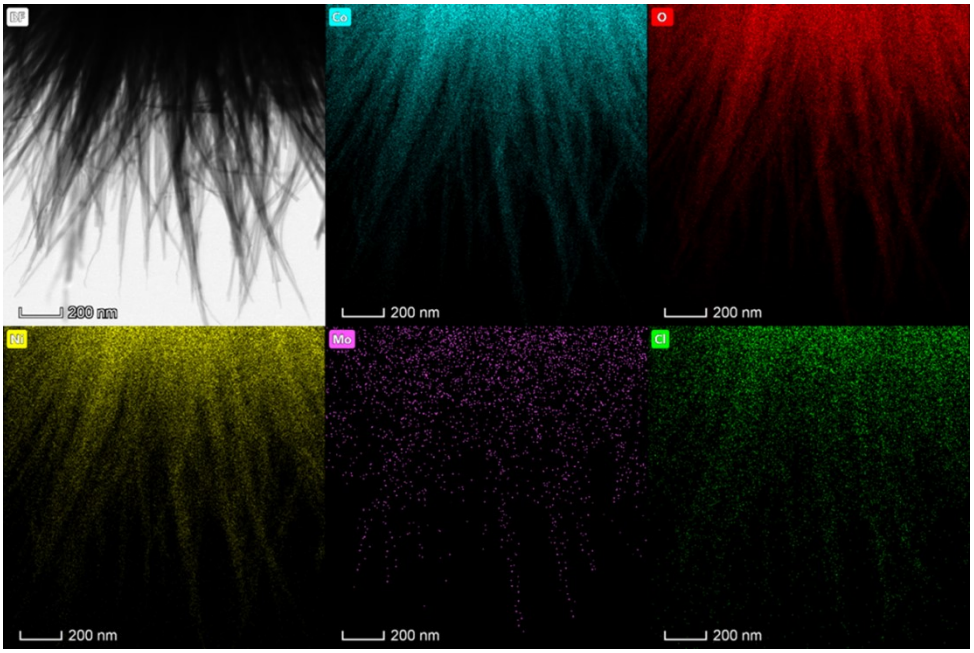

Fig. S4. The EDS mapping for enlarged sea urchin-like structure of $Mo_{0.3}NiCo_2$-Cl LDH.

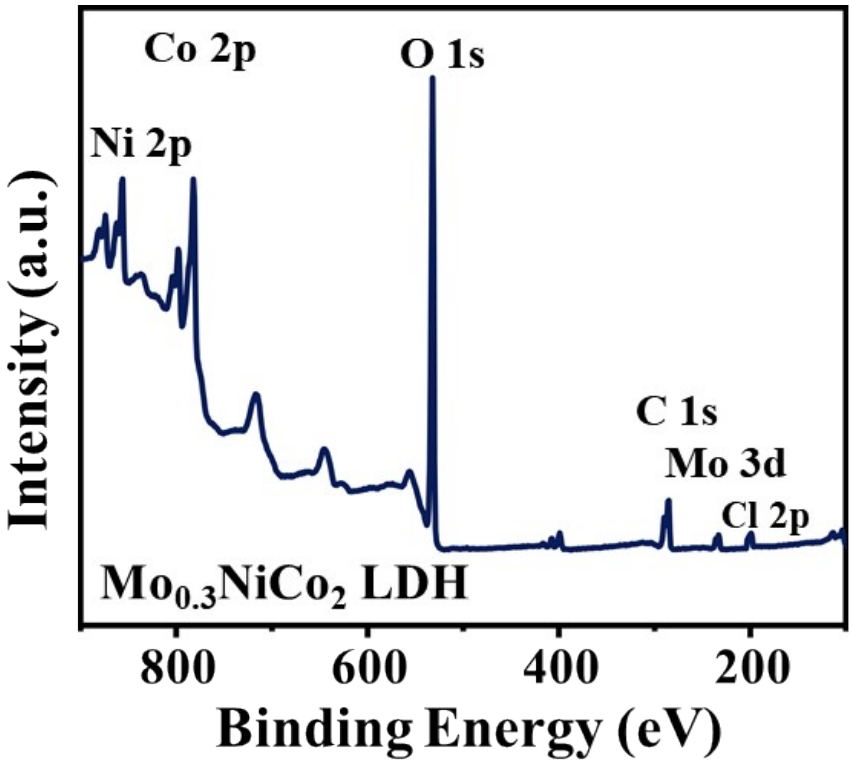

Fig. S5. XPS survey spectrum of $Mo_{0.3}NiCo_2$-Cl LDH.

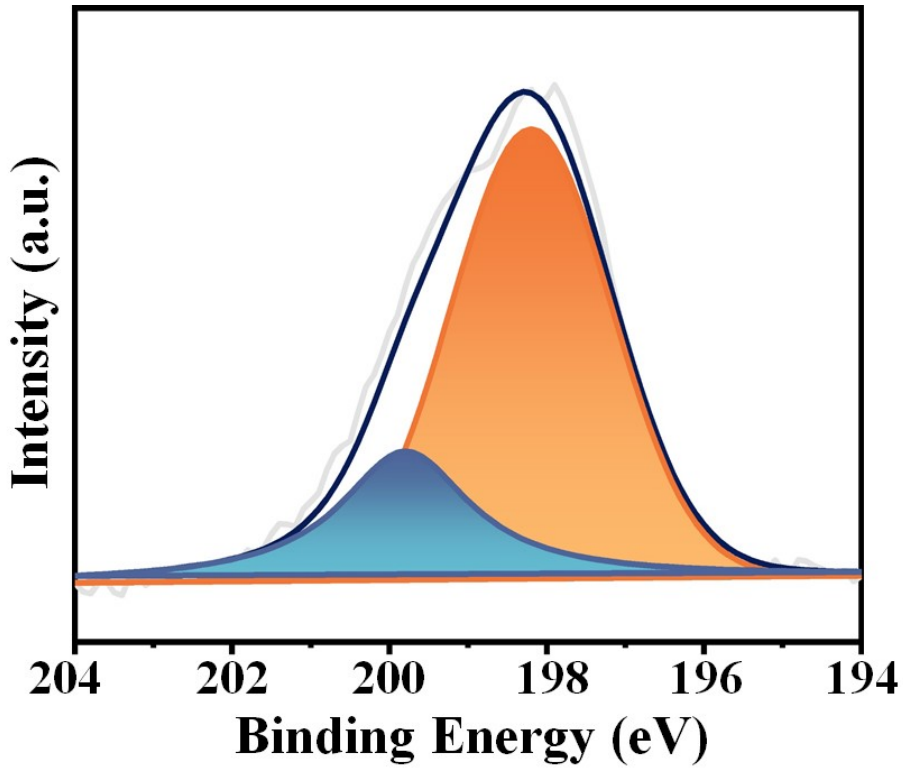

Fig. S6. Cl 2p spectrum of $Mo_{0.3}NiCo_2$-Cl LDH sample.

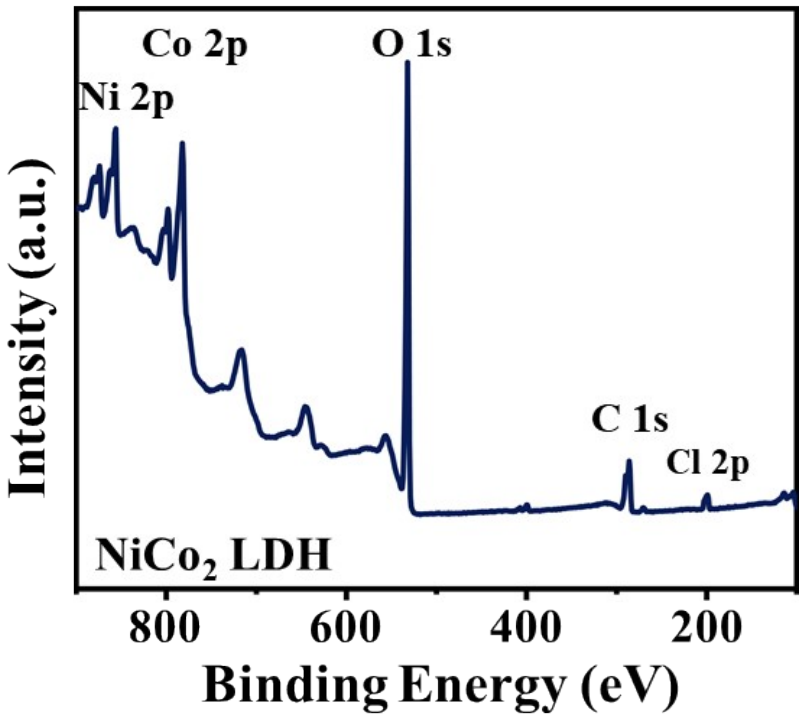

Fig. S7. XPS survey spectrum of $NiCo_2$-Cl LDH.

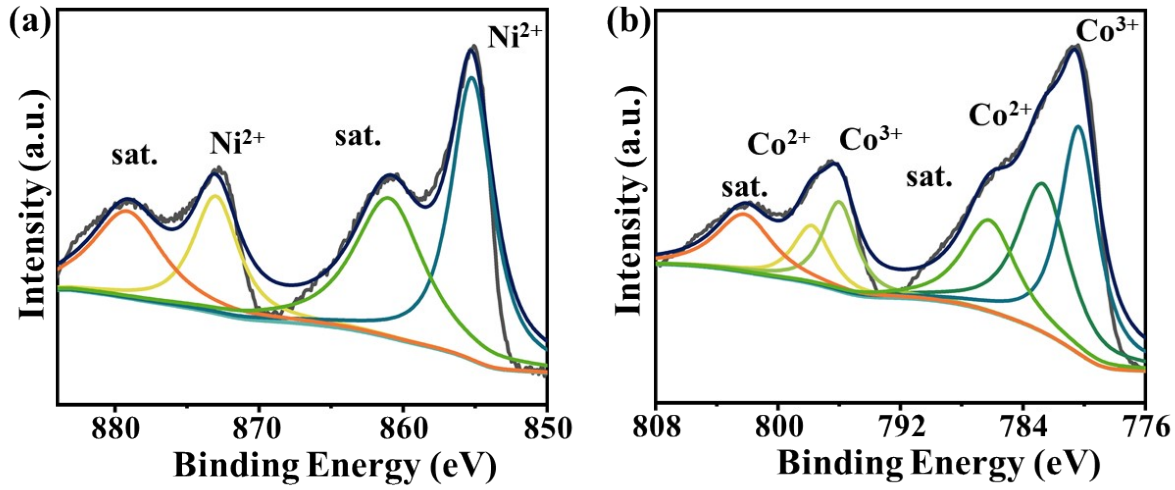

Fig. S8. High resolution XPS spectra of (a) Ni 2p and (b) Co 2p for $NiCo_2$-Cl LDH.

Table S1. Results of ICP test and the element proportion of $Mo_{0.3}NiCo_2$-Cl LDH.

Elements	Mo	Ni	Co
Mass concentration (ppm)	10.30	20.06	41.31
Molar concentration (mmol L^{-1})	1.07	3.45	7.01

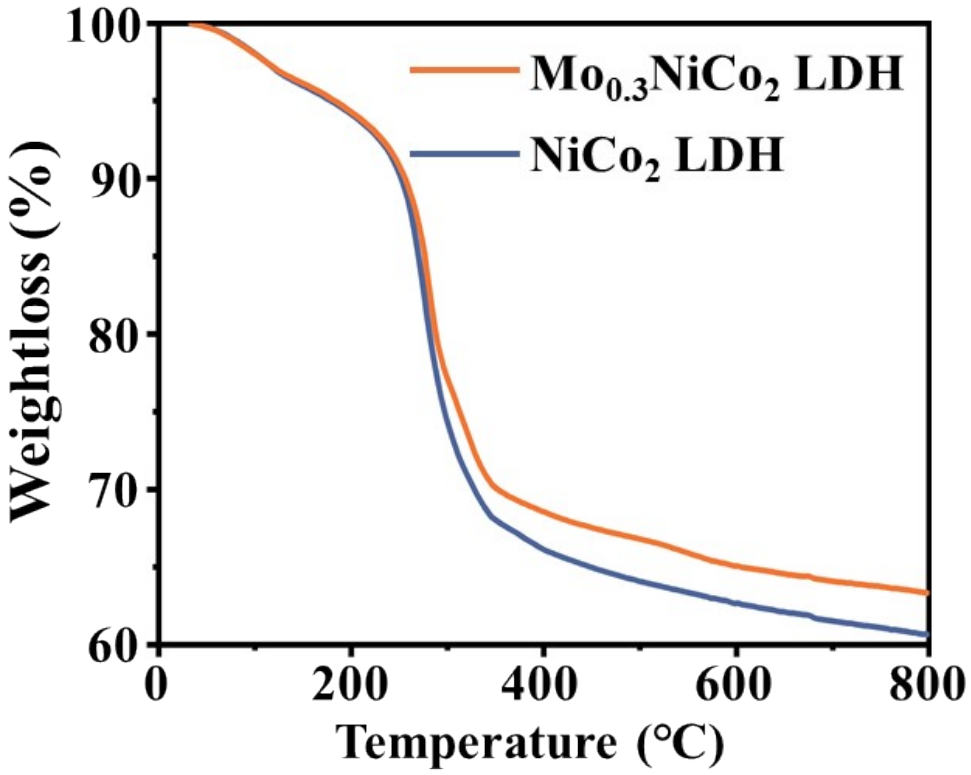

Fig. S9. Thermogravimetry analysis (TGA) of $Mo_{0.3}NiCo_2$-Cl LDH and $NiCo_2$-Cl LDH.

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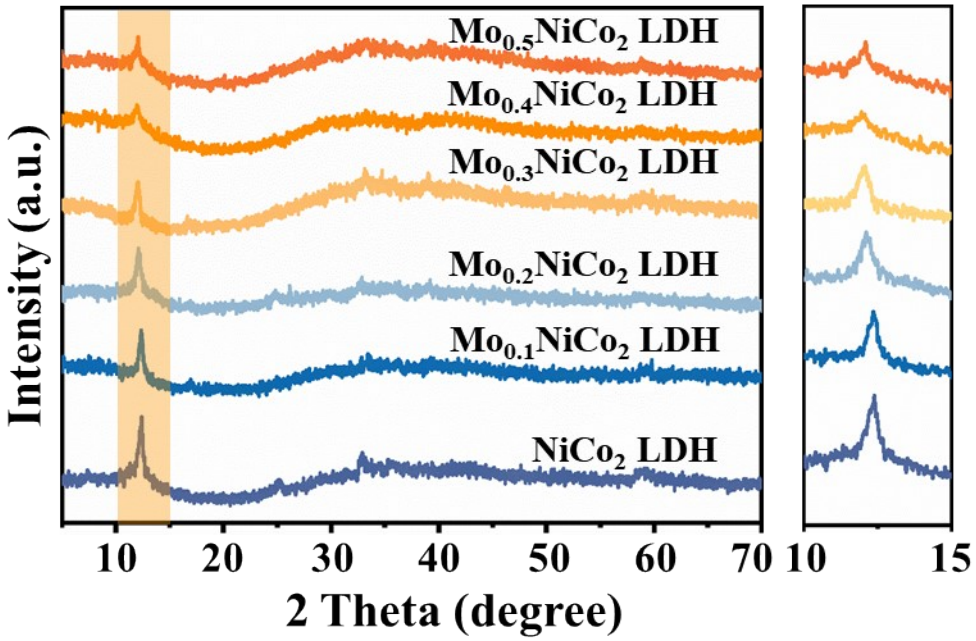

Fig. S10. XRD patterns of Mo_xNiCo_2-Cl LDH samples (x = 0, 0.1, 0.2, 0.3, 0.4 and 0.5).

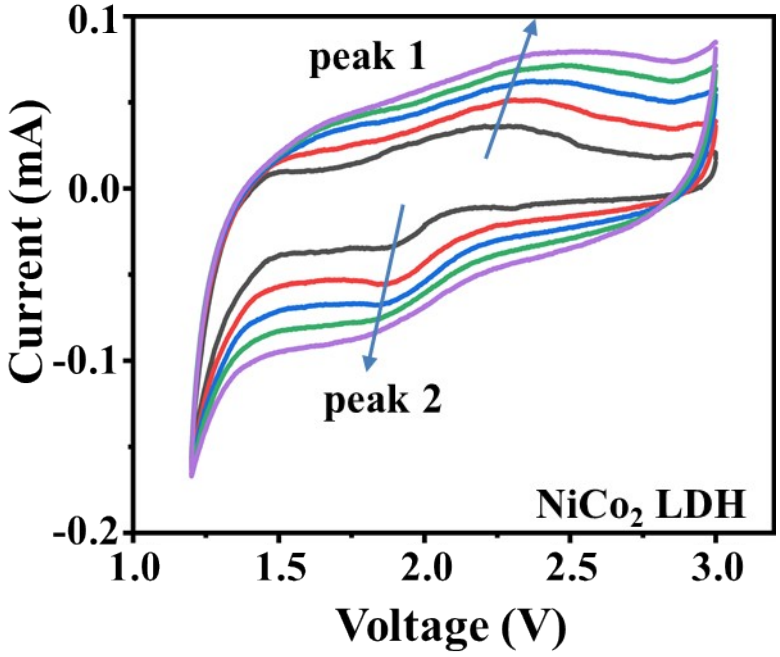

Fig. S11. CV curves of $NiCo_2$-Cl LDH at various scan rates ranging from 0.1 to 0.5 mV s^{-1}.

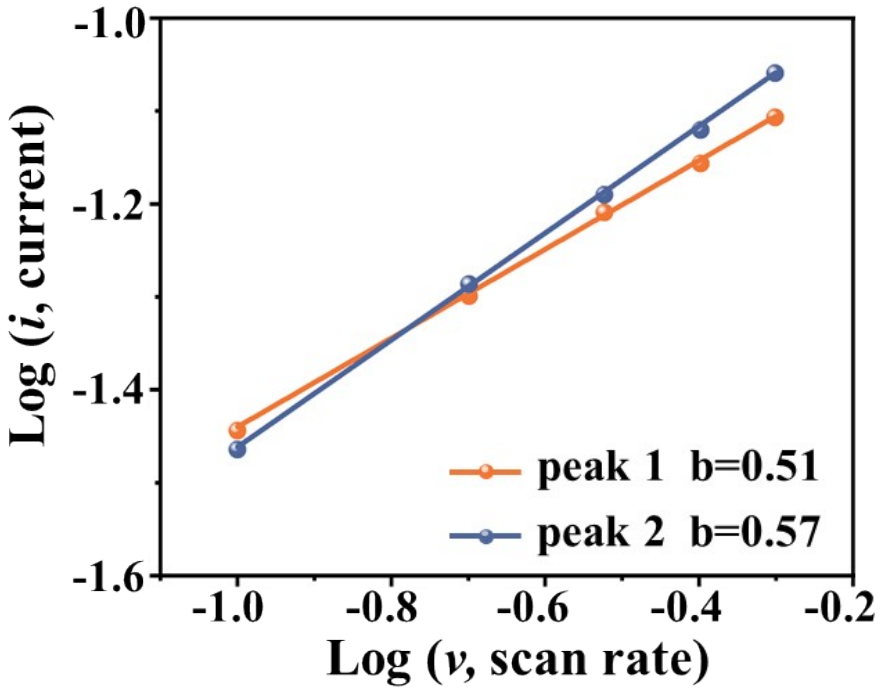

Fig. S12. The fitting plots between log(*i*) and log(*v*) of $NiCo_2$-Cl LDH.

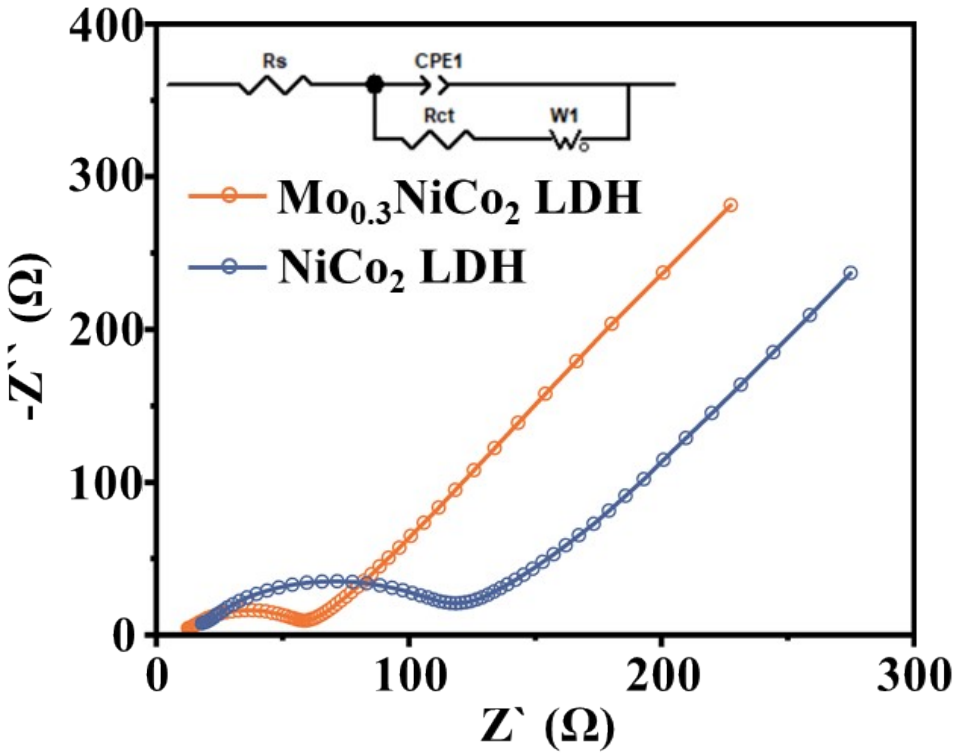

Fig. S13. Electrochemical impedance spectra (EIS) of $Mo_{0.3}NiCo_2$-Cl LDH and $NiCo_2$-Cl LDH electrodes.

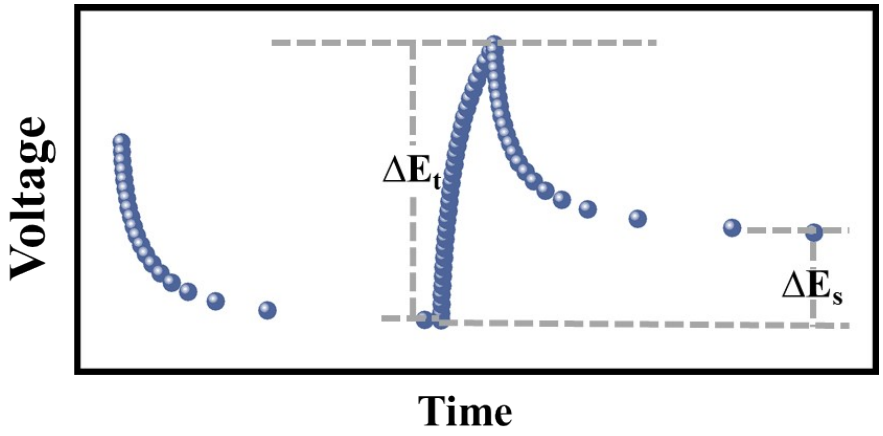

Fig. S14. Schematic illustration for a single step in GITT measurement to charge.

Galvanostatic intermittent titration technique (GITT) measurements were used to calculate the diffusion coefficient of bromide ions (D_{Cl^-}) in Mo_xNiCo_2-Cl LDH cathode by using the following equation:

$$D_{Cl^-} = \frac{4}{\pi\tau}\left(\frac{mV}{MA}\right)^2\left(\frac{\Delta Es}{\Delta Et}\right)^2 \qquad (1)$$

where m (g) and M (g mol^{-1}) are the loading mass and molecular weight of LDH materials; V (cm^3 mol^{-1}) represents the molar volume; τ (s) is constant current pulse time; A (cm^2) is the surface area of electrode; ΔE_s (V) and ΔE_t (V) denote the change of steady-state voltage and the total change of the voltage during a constant pulse t. In this work, A current flow of 30 mA g^{-1} is applied to the CIBs with τ = 10 min and then stood for 60 min without current impulse.

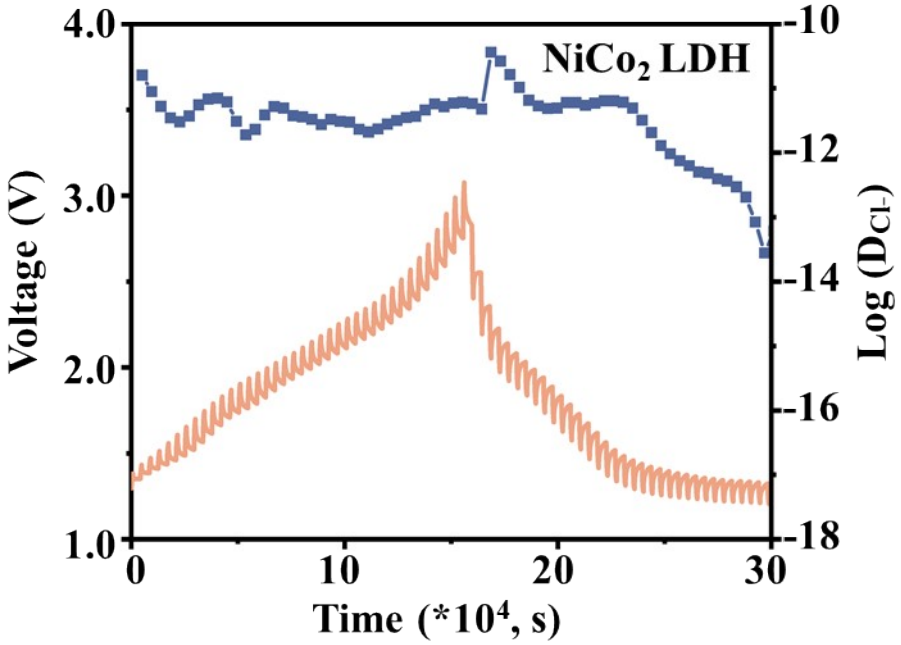

Fig. S15. GITT curves and the corresponding Cl^- ions diffusion coefficients of $NiCo_2$-Cl LDH.

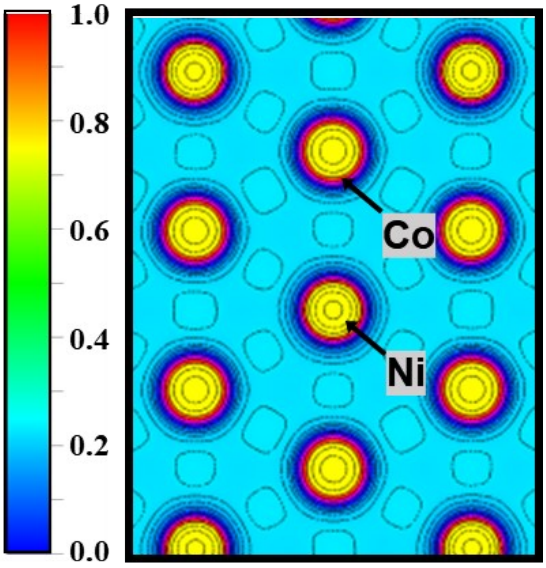

Fig. S16. Surface charge distribution of $NiCo_2$-Cl LDH.

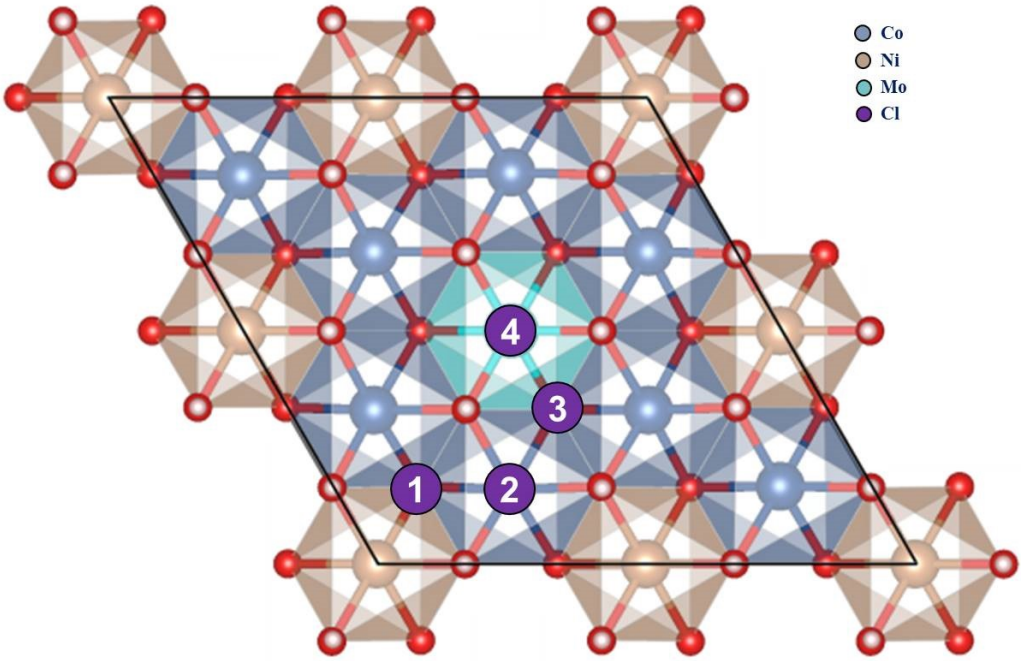

Fig. S17. Schematic diagram of adsorption sites of $Mo_{0.3}NiCo_2$-Cl LDH.

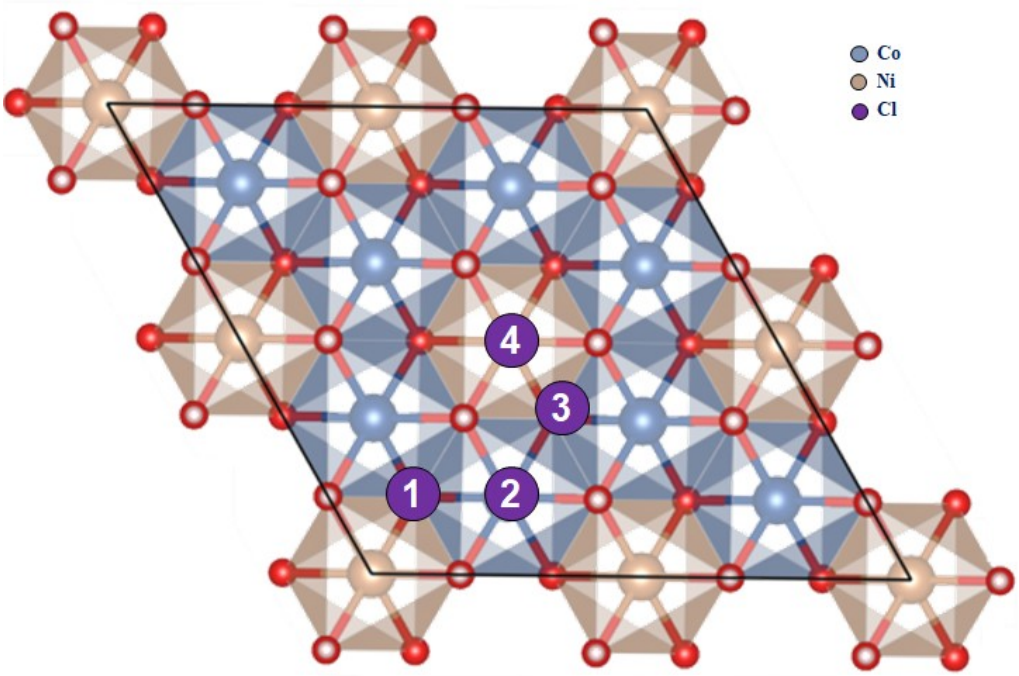

Fig. S18. Schematic diagram of adsorption sites of $NiCo_2$-Cl LDH.

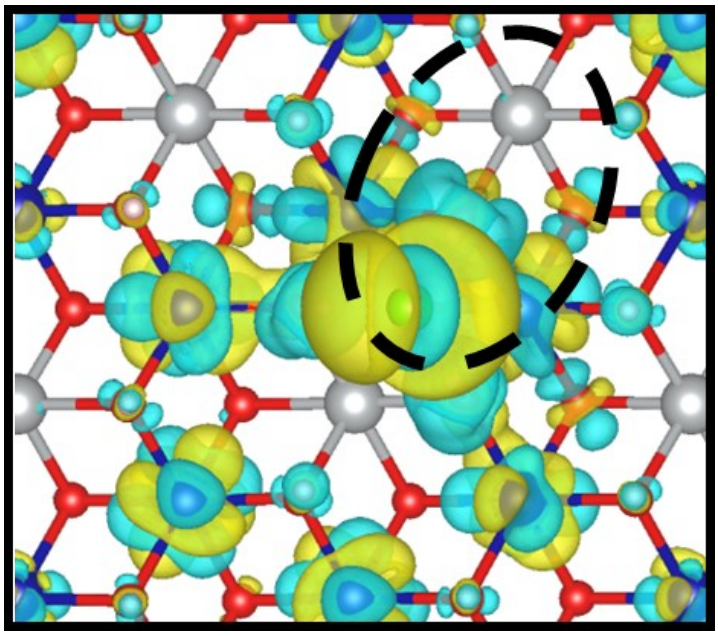

Fig. S19. Differential charge of adsorption process of $NiCo_2$-Cl LDH.