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A new high voltage alluaudite sodium battery insertion material

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ABSTRACT

Large-scale stationary storage forms a key sector that can be economically served by sodium-ion batteries. In realizing practical sodium-ion batteries, discovery and development of novel cathodes is essential. In this spirit, alluaudite-type $Na_2Fe_2(SO_4)_3$ was reported in 2014 to have the highest Fe^{3+}/Fe^{2+} redox potential (~3.8 V vs. Na). This finding led to reports on various PO_4^{3-} and SO_4^{2-} based alluaudite compounds exhibiting high energy densities. In 2017, MoO₄²⁻ based alluaudite, Na_{2.67}Mn_{1.67}(MoO₄)₃, was found as a 3.45 V cathode material. Exploring molybdenum chemistry further, this work reports alluaudite type Na_{3.36}Co_{1.32}(MoO₄)₃ (NCMo) as a novel versatile electroactive cathode for Li-ion and Naion batteries. It was synthesized by a wet solution-combustion route with a restricted annealing duration of 1 min at 600 °C. Calorimetric study revealed the formation enthalpy from component oxides $(\Delta H^{\circ}_{f,ox} = -575.49 \pm 7.75 \text{ kJ/mol})$ to be highly exothermic. Unlike the sulfate class of *alluaudites*, this material is highly stable in air and moisture ($\Delta H_{ds} = 537.42 \pm 0.78$ k]/mol). Having an ionic conductivity of 6.065×10^{-8} S/cm (at 50 °C), it offers a pseudo two-dimensional Na⁺ migration pathway. Without any material optimization, NCMo was found to work as a high-voltage insertion cathode (ca. 4.0 V vs. Na/Na⁺ and 4.1 V vs. Li/Li⁺) in sync with theoretically predicted potential of 3.98 V (vs. Na/Na⁺). Ex-situ X-ray diffraction and photoelectron spectroscopy studies revealed the occurrence of solid-solution redox mechanism solely involving Co^{3+}/Co^{2+} redox centre. It benchmarks $Na_{3,36}Co_{1,32}(MoO_4)_3$ as a novel electrochemically active Mo-based alluaudite-type polyanionic cathode insertion material.

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1. Introduction

Soon after their commercialization in 1991, rechargeable lithium-ion batteries (LIBs) have escalated the use of portable electronics and are increasingly playing a dominant role in (hybrid) electric vehicles in conjunction with stationary energy storage. However, these applications need massive production of LIBs to match up with the projected demands, which is expensive due to the low abundance of lithium on earth's crust [1]. At this juncture, sodium-ion batteries (SIBs) have emerged as pragmatic alternatives

* Corresponding author. E-mail address: prabeer@iisc.ac.in (P. Barpanda). to LIBs [2]. Considering battery development, it is necessary to focus on the cost, structural stability, energy density, safety, and sustainability of the cathode materials. Although layered oxide-based materials can give high discharge capacity, they mostly suffer from irreversible phase transitions and capacity fading over cycling with Na (de)intercalation. In contrast, polyanionic compounds consisting of 3D frameworks of anionic ($XO_4^{n-} = SO_4^{2-}$, PO_4^{3-} , MO_4^{2-} , WO_4^{2-} etc.) and transition metal (MO_6) polyhedra can provide structural stability upon long term cycling and prevent lattice oxygen release during (dis)charging [3,4]. Strongly covalent X–O bonds reduce the covalency of the M 3*d*-O 2*p* bonds, which in turn reduces the energy of the antibonding orbitals to upshift the redox potential [5]. Exploiting this inductive effect, several polyanionic families have been explored having sulfate (SO₄),



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fluorosulfate (SO_4F) , phosphate (PO_4/P_2O_7) , fluorophosphate (PO_4F) , borate (BO_3) , and silicate (SiO_4) moieties.

Alluaudites, a subclass of these polyanionic systems, are essentially alkali metal phosphate-based naturally occurring minerals having open frameworks and broad tunnels for facile alkali ion migration [6]. Their general formula is A(1)A(2)M(1) $M(2)_2(XO_4)_3$ where A sites are the alkali metal sites, M is the transition metal site and XO₄ is the polyanionic moiety. The structure has two tunnels along the *c*-direction offering feasible migration pathways for A sites (see Fig. 1). Till date, numerous alluaudite-type compounds have been unveiled for SIBs and LIBs, which mainly involve different phosphate and sulfate-based structures [7]. In 2010, the Delmas group reported the electrochemical activity of $NaMn_2Fe(PO_4)_3$ for sodium-ion batteries [8]. It opened various studies on several PO₄-based alluaudites for both LIBs and SIBs [7]. In 2014, the Yamada group reported an Fe-based sulfate alluaudite, Na₂Fe₂(SO₄)₃, acting as a 3.8 V SIB cathode material with excellent rate capability and energy density [9]. It ushered the discovery of various high-voltage sulfate alluaudites via optimizing different synthesis routes [10–12]. While they offer high-voltage performance, the presence of SO₄ species makes them susceptible to thermal decomposition and sensitive to moisture.

Recently, Gao et al. reported the first molybdate-based *alluau dite*, Na_{2.67}Mn_{1.67}(MoO₄)₃, working as a 3.45 V Mn-based insertion cathode for SIBs [13]. Extending the molybdate *alluaudite* chemistry, the cobalt-based analogue, Na_{3.36}Co_{1.32}(MoO₄)₃ (referred as NCMO), was synthesized by a rapid, energy saving solutioncombustion method (i.e., a wet chemistry synthesis protocol with restricted annealing duration, see Sec. 2). Synergizing both theoretical and experimental tools, the current work reports a suite of structural, physical, and ionic migration properties of NCMo *alluaudite*, which constitute critical components of electrochemical behavior. The feasibility of material synthesis and stability of resulting *alluaudite* product have been probed with thermochemical experiments and calculations. While the structure of NCMo is known [14], its electrochemical activity remains unexplored. This work reports, for the first time, the high voltage electrochemical (alkali-insertion) activity of this Co-based *alluaudite* for both Li- and Na-half-cells.

2. Experimental details

2.1. Synthesis procedure

The target alluaudite, Na_{3.36}Co_{1.32}(MoO₄)₃ (NCMo), was synthesized by employing the solution-combustion method. Stoichiometric amounts of NaNO₃ (SD Fine Chem., 99.5%), Co(NO₃)₂.6H₂O (SD Fine Chem., 99%) and (NH₄)₆Mo₇O₂₄.4H₂O (SD Fine Chem., 99%) were dissolved in distilled water. Pinch of glycine (C₂H₅O₂N, SD Fine Chem., 99.7%) was used to act as the fuel and carbon source. Upon heating the precursor solution, steady dehydration occurred over 100 °C. Then the precursor was transferred onto a hot plate and kept for combustion at 200 °C. The resulting intermediate powder was collected, ground well and was annealed at 600 °C for a soaking time of 1 min. Note that solution-based combustion synthesis involves high degree of atomic diffusion [15], thereby drastically reducing the annealing duration from 100 h as required for solid-state synthesis to only 1 min. The annealed material was directly quenched to room temperature to obtain the phase-pure target product. Prolonged annealing for 1 h (at 600 °C) led to higher degree of crystallinity, which was employed for all subsequent material characterizations. The net reaction can be formulated as:

$$\begin{split} NaNO_3 + Co(NO_3)_2.6H_2O + (NH_4)_6Mo_7O_{24}.4H_2O \\ + C_2H_5O_2N \rightarrow Na_{3.36}Co_{1.32}(MoO_4)_3 + NO_x + CO_x + H_2O \end{split}$$

2.2. Structural and physical characterization

The crystal structure was examined by acquiring powder diffraction patterns with a Panalytical Empyrean X-ray diffractometer equipped with a Cu K α source ($\lambda_1 = 1.5405$ Å,



Fig. 1. a) Rietveld refinement of powder X-ray diffraction (XRD) pattern of *alluaudite* Na₃₃₆Co_{1,32}(MoO₄)₃ collected at room temperature ($\lambda = 1.5405$ Å) assuming a monoclinic (space group: *C*₂/*c*) crystal structure, **b**) The *alluaudite* structure illustrated along *c* direction, **c**) Two slightly distorted CoO₆ octahedra connects to each other by edge-sharing to make a Co₂O₁₀ dimer forming infinite chains along a direction, **d**) The chains are corner-shared by MoO₄(1) tetrahedra to form a sheet parallel to *ac* plane, **e**) Presence of two different type of tunnels along *c* direction, **f**) Presence of a relatively narrow tunnel along *a* axis.

 λ_2 = 1.5443 Å) operating at 40 kV/30 mA. Rietveld analysis was performed using GSAS-I program with EXPGUI graphical interface [16-18] and the structure was visualized using VESTA software [19]. Thermal analysis (thermogravimetry coupled with differential scanning calorimetry or TG-DSC) of ~20 mg of the intermediate powder was conducted with an STA-8000 (PerkinElmer) unit in the temperature range of 25–700 °C (heating rate = 5 °C/min under steady N₂ flow). Particle morphology was inspected by a Carl Zeiss Ultra55 field emission scanning electron microscope (FESEM, W-source) operating at 0.1-30 kV. Elemental distribution was mapped using the energy dispersive spectrometry (EDS) analyzer of the SEM instrument. Further, transmission electron microscopy (TEM) was conducted with an FEI Tecnai T20 ST microscope operating at 200 kV. For TEM, the powder samples were dispersed and sonicated in isopropyl alcohol (C_3H_8O , Merck, $\geq 99.5\%$) and drop casted onto carbon film meshed copper grids (EMS).

Fourier transform infrared (FTIR) spectrum was collected with a PerkinElmer instrument in attenuated total reflectance (ATR) mode within the spectral range of 4,000–650 cm⁻¹. Raman spectra were recorded with a Horiba Jobin Yvon HR-Raman-123 MicroPL spectrometer with a green laser source ($\lambda = 519$ nm). UV–Vis–NIR spectra were acquired in diffused reflectance mode with a Shimadzu MPC3600 instrument covering a broad wavelength region (200–2,500 nm). The simplified Kubelka–Munk theory was followed to estimate the optical band gap. The obtained spectra were treated with the Kubelka-Munk function, $f(R) = \frac{(1-R)^2}{2R} = \frac{K}{s}$ (R = reflectance, K = absorption coefficient, s = scattering coefficient). The graph of $[f(R).hv]^n$ vs energy (hv) was plotted, where n was varied between 0.5 and 2 for the indirect and direct band gap, respectively [20,21].

2.3. Magnetic measurements

Magnetic susceptibility measurements were performed using a Quantum Design MPMS-XL EverCool SQUID magnetometer (between 2 and 420 K, dc applied field ranging from -5 T to +5 T). Both field-cooled (FC) and zero field cooled (ZFC) measurements were employed as a function of temperature in the range of 5-300 K at a steady external field of 1,000 Oe. Hysteresis measurements were performed at 5 K showing the variation in magnetization with the applied external field.

2.4. Alternating current (AC) impedance measurement

lonic conductivity of the pressed pellets was measured using AC impedance spectroscopy. The mixture of pristine powder and 1 wt% of polyvinyl alcohol binder was pelletized by applying uniaxial pressure of 200 MPa followed by sintering at 500 °C (heating rate = 3 °C/min) for 24 h (in air) for further compaction. The relative density was calculated to be ~77%. Both sides of the pellet were silver-coated to serve as electrical contacts while inhibiting ion exchange from the surface. AC impedance spectra were acquired using a BioLogic SP300 bipotentiostat with a voltage excitation of 500 mV (amplitude) (frequency range = 0.1 Hz to 1 MHz, temperature range = RT-400 °C). These spectra were analyzed using EC Lab software.

2.5. High-temperature oxide melt solution calorimetry

High-temperature oxide melt solution calorimetry was performed using a custom-built Tian–Calvet twin calorimeter as described by Navrotsky [22,23]. This calorimeter allows the direct determination of the enthalpy of formation $(\Delta H^{\circ}_{f,ox})$ of multicomponent compounds from their binary oxides. In a typical

experiment, ~5 mg of sample was pelletized and dropped from ambient temperature into the calorimeter at 800 °C containing the solvent molten sodium molybdate (3Na₂O·4MoO₃), in a platinum crucible. The measured enthalpy of drop solution (ΔH_{ds}) is a sum of the sample heat content from the ambient temperature to 800 °C and its heat of solution in the solvent at 800 °C. At least 8–10 experiments were done per sample and the results are reported as average values with error being two standard deviations of the mean. The calorimetry glassware was flushed by oxygen gas at a flow rate of 65 mL/min to maintain constant atmosphere and the solvent was bubbled with the same gas at 5 mL/min to remove liberated evolved gases, aid dissolution, provide oxidizing condition and prevent local saturation of the solvent. The calorimeter was calibrated using the heat content of 5 mg pellets of α -Al₂O₃. The details of the calorimeter and procedures have been described previously [22,23]. The NCMo sample was stored and pelletized in a glove box filled with nitrogen and transported to the calorimeter in glass vials, limiting contact with laboratory air to a few seconds.

2.6. Electrochemical study

The electrode in the form of a sheet was made from a mixture of 70% active material, 20% carbon black (Super-P) and 10% C-TAB (i.e., Teflonized Acetylene Black) binder. The sheet was further cut into 12 mm discs to work as cathode in both LIB and SIB configurations. Corresponding metal foils were used as anodes in the cells. CR2032 type coin cells were assembled inside an Ar-filled glove box (MBraun LabStar GmbH, O_2 and $H_2O < 0.5$ ppm) to avoid any moisture contamination. The working electrode and lithium/sodium metal foil (as counter electrode) were separated by a sheet of Whatman GF/C glass fiber separator soaked with freshly prepared 1 M NaClO₄ in propylene carbonate (PC) electrolyte for SIB and commercial 1 M LiPF₆ in EC/PC/DMC (1:1:1, Kishida Chemicals) for LIB. The electrochemical testing was performed (at 25 °C) using the Neware BTS-4000 battery tester in the potential window of 3-4.3 V at C/20 rate (1 C = 54 mAh/g considering $1e^{-}$ transfer from Co^{2+} to Co^{3+}).

2.7. Ex-situ analyses

Cycled swageloks were dissembled inside the glove box and the recovered electrodes were washed with dimethyl carbonate (DMC, anhydrous, \geq 99%) for performing ex-situ analyses. After drying, X-ray diffraction (XRD) patterns were acquired as discussed in section 2.2. X-ray photoelectron spectra (XPS) of the cycled electrodes were taken with a Thermo-Scientific K α XPS instrument operating at 12 kV/6 mA.

2.8. Computational methods

The ionic diffusion pathways in NCMo were calculated using the computationally economic bond valence site energy (BVSE) method [24,25] implemented in the softBV program. The BVSE method calculates the energy of the possible positions of the mobile ions in the 3D framework as a function of their mismatch ($|\Delta V|$) in bond valence estimated using the empirical bond valence sum model. Connecting the low-valence-site-energy E_{BVSE} positions of the mobile ion (Na⁺) forms the diffusion pathways. E_{BVSE}(Na) was calculated using grids spanning the structure model with a resolution of (0.1 Å)³.

Vienna Ab initio Simulation Package (VASP) was employed for first principles calculations using the projected augmented wave (PAW) potentials and spin polarization formalism [26–28]. The plane-wave basis set was expanded up to a kinetic energy cut-off of 520 eV and a dense, Γ -centered Monkhorst–Pack mesh with a density of 32 k-points grid per Å along each reciprocal lattice vector was used to sample the irreducible Brillouin zone [29]. The structure relaxation was performed using the conjugate gradient scheme with an atomic force convergence criterion of |0.05| eV/Å and a total energy convergence criterion of 10^{-5} eV [29,30]. The cell volume, shape, and positions of all ions were relaxed for all structures without preserving any symmetry. The magnetic moments of Co were initialized assuming a ferromagnetic ordering. while Mo does not exhibit a magnetic moment given its +6 oxidation state. The Hubbard U corrected strongly constrained and appropriately normed (SCAN + U) exchange-correlation functional was deployed as it estimates better relative stability and electronic properties of materials compared to the conventional generalized gradient approximation (GGA) or its Hubbard U variant (GGA + U) approaches [31]. We used an effective U of 3.0 eV for the *d* orbitals of Co to minimize the electronic selfinteractions, as derived in previous work [31,32]. Given that several Na-Co-vacancy configurations are possible in the alluau*dite* structure, we used the pymatgen package [33] to enumerate all symmetrically distinct orderings. Since the total number of enumerated structures were several hundred for each content of Na considered, we chose the 20 structures with the lowest electrostatic energies (as computed via the Ewald summation technique) for DFT calculations to reduce computational costs. Further, the lowest energy Na-Co-vacancy ordered structure among the 20 chosen structures at each Na composition, as determined by DFT, was considered for further calculations and analyses. For calculating the density of states (DOS), we used the SCAN + Urelaxed ground state structures and performed a "fake" selfconsistent field (SCF) calculation at a k-point density of 64 per Å. Note that during the fake SCF calculations, the *k*-points used in the initial structure relaxation were retained with their corresponding weights, while the new k-points were added with zero weights.

Na intercalation into the *alluaudite* host structure can be represented by the following chemical reaction:

$$xNa^{+} + xe^{-} + Na_{3.5-x}Co_{1.25}(MoO_4)_3 \rightarrow Na_{3.5}Co_{1.25}(MoO_4)_3$$

The average cell voltage of the intercalation process is directly related to the difference in the Gibbs energy of the sodiated and the desodiated phases. Neglecting volume and entropic contributions, the Gibbs energy (at 298 K) can be approximated as the DFT calculated energy at 0 K [34]. Finally, we compute the average intercalation cell voltage (vs. Na⁺/Na) from the ground state DFT energies as:

$$V = -\frac{\left(E_{Na_{3.5}Co_{1.25}(MoO_{4})_{3}} - E_{Na_{3.5-x}Co_{1.25}(MoO_{4})_{3}} - xE_{Na}\right)}{xF}$$

where, $E_{Na_{3.5}Co_{1.25}(MoO_4)_3} = Gibbs$ energy of the pristine material

 $E_{Na_{3.5-x}Co_{1.25}(MoO_4)_3}$ = Gibbs energy of the desodiated materials

 $E_{Na} = Gibbs \ energy \ of \ sodium \ metal$

x = Amount of Na (de)intercalating from the system

3. Results and discussion

3.1. Structural characterization

Over the last few decades, there has been a gamut of studies on the crystallography and phase transformation of different double molvbdates: Na_2MoO_4 -MMoO₄ (where, M = Mg, Mn, Co, Ni, Cu, Zn, Cd). These double molybdates can be broadly classified into three structures: (a) monoclinic alluaudite [35], (b) orthorhombic lyonsite [36], and (c) triclinic hawardevansite [37]. Tuning the synthesis conditions can trigger phase transformation among these phases. In our case, Na-Co-Mo-O system can exist in both alluaudite and lyonsite polymorphs with minor stoichiometric differences. Hence, a simple furnace cooling of the annealed pellet to room temperature inevitably led to the formation of a mixture of alluaudite and *lyonsite* phases with an overall composition of $NaCo_{2,31}(MoO_4)_3$. On the other hand, quenching the annealed material to room temperature from 600 °C yielded pure monoclinic type alluaudite product. Despite several variations of the synthesis protocols, it was not possible to synthesize the orthorhombic lyonsite phase.

Simultaneous thermal analysis (TG-DSC) was conducted on the precursor mixture from ambient to 700 °C (Fig. S1, ESI). After the initial endothermic peaks up to 300 °C corresponding to dehydration, the peak at ~500 °C hints at the formation of the target compound that is stable up to at least 650 °C. With insights from the TG-DSC data, the intermediate powder was annealed at 600 °C to yield the desired product phase with bright blue color. Comparative XRD patterns with different annealing duration are given in Fig. S2. Surprisingly, the product was formed even with a restricted annealing duration of just 1 min. Rietveld analysis of the final compound (Fig. 1a) confirmed the formation of pure alluaudite phase crystallizing in a monoclinic structure with C2/c space group. Detailed structural parameters are provided in Table S1 (ESI). This alluaudite framework is built from two CoO₆ octahedra forming Co_2O_{10} dimers, which are abridged by $Mo(1)O_4$ tetrahedra to form 2D sheets along the *ac* plane (Fig. 1b–f), which in turn are connected by Mo(2)O₄ tetrahedra to form a 3D tunnel-like structure (Fig. 1d). The NCMo structure consists of two wide tunnels along the *c* axis, similar to other *alluaudite* phases [8], and an additional narrow tunnel along the *a* axis (Fig. 1f), which is absent in case of other SO₄ and PO₄ based alluaudites. There are four different crystallographic sites for Na, namely Na2 and Na4 that reside inside the wide tunnels, Na3 that is located in the narrow cavity, and Na1 that shares the similar crystallographic position with Co. The Na present inside the tunnels (Na2 and Na4) can take part in the (de)insertion mechanism.

3.2. Physical characterization

The as-synthesized NCMo was found to have large micrometric particles in the size range of 10–20 μ m (Fig. 2a). High resolution transmission electron microscopy (HRTEM) revealed clear lattice fringes attesting the crystallinity of the compound (Fig. 2b). Selected area electron diffraction pattern (SAED) confirmed the existence of monoclinic structure (Fig. 2c). An overall Na-rich and Co-deficient composition, similar to synthetic *alluaudites* having general formula Na_{2+2x}M_{2-x}(XO4)₃ (M = 3d metals, X = P, S, Mo, W), with uniform distribution of all constituent elements (Na, Co, Mo, and O) was seen by energy dispersive (EDS) elemental analysis (Fig. 2d–g). Core electrons, emitted by the excitation of X-ray radiation, serve in analysing the chemical state of the as-synthesized sample. The X-ray photoelectron (XPS) spectrum of *alluaudite* product revealed signals of Na 1s, Co 2s, Co 2p, O 1s, Mo 3s, Mo 3p,



Fig. 2. a) Morphology of NCMo *alluaudite* as shown by SEM images composed of micrometric particles ranging from 10 to 20 μ m, **b**) High resolution transmission electron microscopy (HRTEM) and **c**) Selected area electron diffraction (SAED) patterns affirming crystallinity of the material, **d**-**g**) Elemental mapping with a homogeneous distribution of Na, Co, Mo and O, **h**) XPS survey spectrum revealing the Co²⁺ and Mo⁶⁺ states in the *alluaudite* product, **i**) FT-IR spectrum showing different vibrational modes of the MoO₄²⁻ moiety, j) Raman spectrum showing no trace of carbon coating in the material.

Mo 3*d* and C 1*s* located at 1072 eV, 927 eV, 780 eV, 532 eV, 498 eV, 398 eV, 232 eV and 285 eV respectively (Fig. 2h) attesting the presence of Co^{2+} and Mo^{6+} species in the as-prepared NCMo sample.

Earlier, sulfate-based *alluaudites* have been shown to be highly prone to moisture attack, triggering an irreversible alluaudite to bloedite phase transformation [12]. To check the stability of the NCMo alluaudite, infrared spectra of the as-synthesized compound was examined after keeping it in air for 2-3 days (Fig. 2i). The absence of a broad peak at ~3,500 cm⁻¹ proved the absence of any adsorbed/structural water content. In the wavenumber window of 300–1,000 cm⁻¹, three distinct kinds of vibrational modes were captured. Two of them have stretching modes [$v_1 \sim$ 915 cm⁻¹ = symmetric stretching mode and $v_2 \sim 847$ cm⁻¹, 766 cm⁻¹ and 731 cm⁻¹ = triply degenerate asymmetric stretching mode] and the third one $[\nu_3 \sim \text{below } 600 \text{ cm}^{-1}]$ represents all (a) symmetric bending modes [38]. During the synthesis, glycine was added as a carbon source to incorporate an in-situ carbon coating on product particles. But there was no signature D band $(\sim 1,400 \text{ cm}^{-1})$ and G band $(\sim 1,600 \text{ cm}^{-1})$ in the acquired Raman spectrum corresponding to the presence of carbon (Fig. 2j) which hints at the escape of carbon in the form of CO₂ during high temperature annealing. In the window of 300–1,000 cm⁻¹, three different peaks can be observed arising from the vibrations of MoO_4^{2-} tetrahedra. The bands above 750 cm⁻¹ stem from the stretching modes, while the bands below 400 cm⁻¹ correspond to the bending mode of MoO₄ tetrahedra in accordance with the FT-IR spectra.

3.3. Magnetic characterization

Fig. S3 shows the variation of magnetic moment as a function of temperature at field-cooled (FC) and zero field cooled (ZFC) states.

The FC and ZFC data are comparable with no anisotropic behavior. Further, no discontinuity was seen, indicating the absence of any long range magnetic ordering [39]. Even at low temperature (5 K), the magnetic moment (M) vs field (H) curve showed no significant hysterisis (Fig. S3, inset) which confirms the absence of ferromagnetic ordering. While plotting the inverse susceptibility $(1/\chi)$ vs. temperature (T) (Fig. S3, inset), following a Curie-Weiss behavior, a small deviation was seen at ~10 K from the linear fitted line that can be the ordering temperature (T_N) . From the linear curve, the Curie constant was calculated as C = 4.537 emu K/mol. The effective magnetic moment ($\mu_{eff} = \sqrt{8 \times C}$) was found to be 6.023 μ_{R} that is higher than the theoretical value of 3.87 μ_B for high spin Co²⁺ (d^7 , $t_{2g}^5 e_g^2$, S = 3/2). Similar deviation in μ_B is typical for divalent cobalt (Co^{2+}) ions [40] mostly due to the spin-orbit coupling present in the system. Overall, the low Weiss temperature value with the lack of apparent magnetic ordering indicates minor interactions between the neighboring metal centers, consistent with the structure having isolated transition metal octahedra.

3.4. Optical band gap

The band gap of NCMo *alluaudite* was calculated from the ultraviolet (UV)-visible-near infrared (NIR) spectroscopy. The peaks in the electronic spectra (Fig. S4, inset) were assigned to respective *d*-*d* electronic transitions using the Tanabe-Sugano diagram [41]. In particular, two distinct peaks are within the visible region (1.55–3.0 eV), which are responsible for the blue color of the sample. As per Kubelka-Munk plot (Fig. S4), the optical band gap was found to be ~3.26 eV, in accordance with the previously reported data [42]. Similar optical band gap values were observed for different molybdate-based compounds like NaBi(MoO₄)₂ (3.10 eV), Ag₂MoO₄ (3.37 eV), Pb(MoO₄) (3.30 eV), and K_{0.4}Na_{3.6}Co(MoO₄)₃ (3.37 eV) [43].

3.5. Thermodynamic calculations

The thermodynamic cycle relating the measured enthalpies of drop solution and the enthalpy of formation from binary oxides is shown in Table 1 and the measured enthalpies are summarized in Table 2.

The enthalpy of drop solution (ΔH_{ds}) for *alluaudite* Na_{3.36}Co_{1.32}(MoO₄)₃ was found to be highly endothermic, 537.42 ± 0.78 kJ/mol, and the enthalpy of formation $(\Delta H^{\circ}_{f,ox})$ for Na_{3.36}Co_{1.32}(MoO₄)₃ from binary oxides is -575.49 ± 7.75 kJ/mol, confirming that the sample is energetically very stable compared to its binary oxides. However, the enthalpy of formation for single cation molybdates such as α -Ni₃(MoO₄)₃ (-122.64 ± 3.60 kJ/mol), A₂Mo₃O₁₄ (A = Sc, Fe, In) (-47.22 ± 2.1 kJ/mol; 51.5 ± 4.5 kJ/mol; 7.4 \pm 2.9 kJ/mol), are less stable and are entropy stabilized compared to double cation molybdates as seen above [46,47].

3.6. Na-ion migration behavior

High ionic diffusion with low migration barrier is essential for efficient battery insertion material. Using bond valence site energy (BVSE) calculations, the migration barrier of NCMo *alluaudite* was estimated. From the iso-energy map (Fig. 3a), the presence of 1D pathways connecting Na2 and Na3 sites along the *b*-direction was observed with a high energy barrier of ~1.028 eV (Fig. 3b). The Co/Na1 (same crystallographic site) remain inactive in ionic migration. The binding energy of Na at the Na4 site is comparatively higher than those of Na3 and Na2 sites which possibly makes Na4 partially mobile within the structure (Fig. 3b). The energy barrier for Na4–Na4 pathway is lower (0.858 eV) as compared to Na3 and Na2. Moreover, a partial 2D migration pathway connecting Na3 and Na4 sites were found with an energy barrier of ~0.511 eV in accordance with the previously reported data [13,48].

Next, the ionic conductivity was examined by AC impedance spectroscopy. The AC impedance spectra of NCMo sample was acquired from ambient to 400 °C at an interval of 25 °C. The Nyquist plot at 200 °C is shown in Fig. 3c that consists of two entangled semi-circles. The impedance spectra were fitted with two semicircles (convoluted) using two circuits in series composed by R1|| Q1 and R2||Q2. R1 and Q1 refer to the resistance and capacitance of constant phase elements associated with the grains (semicircle at higher frequencies), respectively. Similarly, R2 and Q2 are associated with the grain boundary (semicircle at lower frequencies) [49,50]. The total resistance of the system is given by R = R1+R2. Bulk conductivity was calculated using $\sigma = 1/\rho = l/(R \times A)$ where l is the thickness of the pellet and A is the disk area. The ionic conductivity was calculated to be 1.477 \times 10⁻⁶ S/cm at 200 °C and 6.065×10^{-8} S/cm at 50 °C, similar to the ionic conductivity values of other alluaudite type materials [38,51]. Using Arrhenius equation of temperature dependance of ac conductivity, the activation energy for the ion migration was calculated as $\sigma = A_0 \exp(-\frac{E_a}{kT})$, where A_0 is the pre-exponential factor, E_a is the activation energy in eV, k is the Boltzman's constant in eV/K and T is the absolute

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Table 2

Enthalpies of drop solution of $Na_{3,36}Co_{1,32}(MoO_4)_3$, and corresponding binary oxides in $3Na_2O \cdot 4MoO_3$ at 800 °C.

Sample	$\Delta H_{ds} \left(kJ/mol \right)$	$\Delta H^{\circ}_{f,ox} (kJ/mol)$
Na _{3.36} Co _{1.32} (MoO ₄) ₃ Na ₂ O CoO MoO ₃	$\begin{array}{l} 537.42 \pm 0.78 \ (5) \\ -195.90 \pm 4.23^{b} \\ 21.92 \pm 0.36(8)^{b} \\ 87.38 \pm 0.99 \ (5)^{a} \end{array}$	-575.49 ± 7.75

Error is indicated by two standard deviations of the mean; numbers in parentheses are the number of experiments performed.

^a This work.

^b Reference [44,45].

temperature. Fig. 3d shows the variation of bulk conductivity (S/ cm) calculated from impedance spectroscopy with 1,000/T (K⁻¹). From the linear portion, the activation energy was found to be 0.63 eV.

3.7. Ab-initio computational studies

The exact composition of experimentally observed NCMo stoichiometry (Table S1) requires the construction of a bigger supercell that is computationally expensive. For simplicity, we chose the Na_{3.5}Co_{1.25}(MoO₄)₃ composition for all DFT calculations.

We observe that the lattice parameters calculated using the SCAN + *U* are underestimated compared to the experimental data, likely since the material was synthesized by quenching it directly from high temperature (600 °C or 873 K) to 298 K (thus not allowing for significant thermal contraction) and the fact that the experimental stoichiometry is not exactly reproduced in our structural model. The relaxed structures at sodiated and partially desodiated states (top panel) and corresponding CoO₆ octahedra (down panel) are presented in Fig. 4b (Fig. S5, Tables S2 and S3). Upon removing Na (to generate Na_{2.25}Co_{1.25}(MoO₄)₃ and Na_{1.0}Co_{1.25}(MoO₄)₃), we observe a shrinkage in the Co–O bond lengths and lattice parameters, as seen in the decrease of the unit cell volume (Table 3), which is in accordance with our ex-situ XRD data (see Sec. 3.8) and previous literature on *alluaudites* [10].

Fig. 4a presents the SCAN + U calculated average topotactic voltages (in units of V vs. Na⁺/Na), for the *alluaudite*-Na_yCo_{1.25}(-MoO₄)₃ hosts ($1 \le y \le 3.5$). The voltage steps at 3.98 V and 5.31 V represent the first redox (Co²⁺/Co³⁺) and second redox (Co³⁺/Co⁴⁺) processes, respectively. Importantly, we observed the calculated voltage for the first oxidation of Co is in good agreement with the experimental value ~4 V (vs. Na/Na⁺) (see Sec. 3.8) and earlier theoretical study [48]. The predicted high voltages for the second Na removal (Co³⁺/Co⁴⁺) indicates that it would be challenging to accomplish second desodiation in NCMo within the stable operating window of conventional Na-electrolytes.

The SCAN + *U* calculated projected densities of states (pDOS) are plotted in Fig. 4c-e for the monoclinic NCMo structures with different Na content. Specifically, panels c, d, and e correspond to the pristine (fully sodiated, Na_{3.5}Co_{1.25}(MoO₄)₃ or Na_{3.5} in short), partially desodiated (Na_{2.25}) and fully desodiated (Na₁) NCMo

Table 1

Thermodynamic cycle used to calculate the formation enthalpy ($\Delta H^{\circ}_{f,ox}$) of Na_{3.36}Co_{1.32}(MoO₄)₃ from binary oxides.

Reaction	ΔH (kJ/mol)
$ \begin{array}{l} Na_{3.36}Co_{1.32}(MoO_4)_3 \left(_{s,\ 25\ ^\circ C}\right) \rightarrow \ 1.68Na_2O \left(_{sln,\ 800^\circ C}\right) + \ 1.32CoO \left(_{sln,\ 800^\circ C}\right) + \ 3MoO_3 \left(_{sln,\ 800^\circ C}\right) \\ Na_2O \left(_{s,\ 25\ ^\circ C}\right) \rightarrow \ Na_2O \left(_{sln,\ 800^\circ C}\right) \\ CoO \left(_{s,\ 25\ ^\circ C}\right) \rightarrow \ CoO \left(_{sln,\ 800^\circ C}\right) \\ MoO_3 \left(_{s,\ 25\ ^\circ C}\right) \rightarrow \ MoO_3 \left(_{sln,\ 800^\circ C}\right) \\ 1.68Na_2O \left(_{s,\ 25\ ^\circ C}\right) + \ 1.32CoO \left(_{s,\ 25\ ^\circ C}\right) + \ 3MoO_3 \left(_{s,\ 25\ ^\circ C}\right) \rightarrow \ Na_{3.36}Co_{1.32}(MoO_4)_3 \left(_{s,\ 25\ ^\circ C}\right) \\ \Delta H_5 = \ \Delta H^\circ_{f,ox} = -\Delta H_1 + \ 1.68\Delta H_2 + \ 1.32\Delta H_3 + \ 3\Delta H_4 \end{array} $	$\begin{array}{l} \Delta H_1 = \Delta H_{ds} \; Na_{3.36} Co_{1.32} (MoO_4)_3 \\ \Delta H_2 = \Delta H_{ds} \; Na_2 O \\ \Delta H_3 = \Delta H_{ds} \; CoO \\ \Delta H_4 = \Delta H_{ds} \; MoO_3 \\ \Delta H_5 = \Delta H^\circ_{f,ox} \; Na_{3.36} Co_{1.32} (MoO_4)_3 \end{array}$



Fig. 3. a) Bond valence site energy (BVSE) map showing Na⁺ migration pathways for Na_{3.36}Co_{1.32}(MoO₄)₃, **b**) Corresponding energy plot depicts the activation energy barrier for Na⁺ migration exhibiting a high energy barrier for 1-D diffusion, **c**) AC impedance spectrum at 200 °C. The equivalent circuit is given in inset having two series connected parallel R-Q (resistor-constant phase element) circuits, **d**) Temperature dependence variation of ionic conductivity with an activation energy of 0.63 eV.



Fig. 4. a) Average voltage of $Na_xCo_{1,25}(MoO_4)_3$ as calculated by SCAN + *U* functionals. b) DFT (SCAN + *U*) relaxed crystal structure and Na ordering at different states of (de)sodiation $[Na_{3,5}Co_{1,25}(MoO_4)_3]$ and $Na_{2,25}Co_{1,25}(MoO_4)_3]$. **c-e**) Computed pDOS for of $Na_xCo_{1,25}(MoO_4)_3$ at different state of (de)sodiation. Blue, orange, red and purple curves correspond to Mo *d*, O *p*, Co *d* and Na *s* states, respectively. Positive (negative) values of pDOS correspond to up (down) spin electrons. Dotted blue lines represent the valence and conduction band edges, with the numbers indicating band gap values. The zero on the energy scale in each panel is referenced either to the valence band maximum or to the Fermi level.

Table 3

DFT (SCAN + U) calculated structural parameters of pristine and different desodiated states.

Alluaudites	a (Å)	b (Å)	c (Å)	α(°)	β (°)	γ (°)	Vol (Å ³)
Na _{3.5} Co _{1.25} (MoO ₄) ₃ (experimental)	11.74639 (12.63174)	13.34319 (13.49553)	7.11152 (7.12597)	91.1647 90	103.0679 112.1460°	89.2548 90	1085.35199 1125.160
$Na_{2.25}Co_{1.25}(MoO_4)_3$ $Na_{1.0}Co_{1.25}(MoO_4)_3$	11.89930 11.50039	12.90148 12.46605	7.08768 7.30223	92.3488 86.2457	102.6497 107.4426	91.1119 91.4990	1060.72661 995.444572

structures, respectively. The purple, blue, orange, red, and dotted blue lines in Fig. 4c–e represent Na s states, Mo d states, O p states, Co d states, and band edges respectively. Our calculated pDOS indicates a semiconducting electronic structure of the pristine NCMo (Na_{3.5}), with a predicted band gap of 2.89 eV, qualitatively consistent with the experimentally observed optical band gap (3.26 eV) using UV-visible-NIR spectroscopy (SCAN + U typically underestimates experimental optical gaps). The Co d state dominates near the valence band edge (VBE) in the sodiated state, with minor contributions from O p states, while the Mo d states are significantly below the VBE. Thus, our pDOS calculation of pristine NCMo suggests pure cationic redox process on partial Na removal from the host (i.e., $Na_{3,5} \rightarrow Na_{2,25}$), resulting in Co^{2+} oxidation to Co^{3+} . Furthermore, the on-site magnetic moments on Mo d states in $Na_{35}Co_{125}(MoO_4)_3$ and $Na_{225}Co_{125}Co(MoO_4)_3$ also indicate no contribution from Mo towards the redox activity, as also observed in our ex situ XPS measurement (Fig. S6).

With desodiation, we notice a considerable reduction in band gap. For example, upon partial desodiation ($Na_{3.5} \rightarrow Na_{2.25}$), the band gap decreases from 2.89 to 1.11 eV, while full desodiation ($Na_{2.25} \rightarrow Na_1$) causes a further drop in band gap to 0.86 eV. Note that the decrease in band gap with desodiation also coincides with a shift of the Co *d* states from the VBE to the conduction band, which corresponds to removal of electrons from Co *d* states (or effectively, an oxidation of Co from its +2 oxidation state to +4).

3.8. Electrochemical activity

The electrochemical activity of NCMo *alluaudite* was evaluated as a cathode material in both Li-ion and Na-ion battery configurations within 3.0 V–4.3 V voltage range (at C/20) without any particle size optimization or formation of carbonnanocomposites. The as-prepared micrometric NCMo product material was found to act as 4.1 V cathode in LIB (Fig. 5a) and 4.0 V cathode in SIB (Fig. 5b). While a 0.3 V potential difference is expected between LIB and SIB configurations, such deviation has been earlier reported for sulfate *alluaudite* cathodes [52]. The discharge capacity in the first cycle was ~34 mAh/g (in case of LIB) and ~27 mAh/g (in case of SIB). Although the theoretical capacity is expected to be ~54 mAh/g considering 1 electron $Co^{2+/3+}$ redox couple, only ~50% of the theoretical capacity was achieved due to large micrometric size. The dQ/dV plot (Fig. 5c) shows one broad reversible peak within the required voltage range suggesting a redox activity of Co^{2+} to Co^{3+} at around ~4.1 V (vs. Li), which is further validated by ex-situ analysis (see below).

To identify the underlying (de)intercalation mechanism, ex-situ XRD patterns of pristine, charged and discharged cathodes were acquired (Fig. 5d). The peaks ~13° and ~15° of the pristine compound shifted towards higher angles upon charging and reverted back to lower angles with discharging the cathode at 3.0 V. This reversible peak shift without appearance of any new peak indicates at solid-solution redox mechanism. To confirm the change in the oxidation state, ex-situ XPS spectra were collected for the pristine, charged (4.3 V) and discharged (3.0 V) cathodes (Fig. 5e). XPS spectrum of Co 2*p* orbital consists of two distinct peaks, Co 2*p*_{3/2} (~781.0 eV) and Co 2*p*_{1/2} (~797.0 eV), affirming that Co is in its +2 oxidation state [53]. Upon charging upto 4.3 V, these peaks shifted towards higher binding energy [Co 2*p*_{3/2} (~781.45 eV) and Co 2*p*_{1/2} (~797.5 eV)] owing to the oxidation of Co from Co²⁺ to Co³⁺. Upon subsequent discharging to 3.0 V, the Co-peaks shifted back to their



Fig. 5. Galvanostatic (dis)charge voltage profiles of NCMo **a**) vs Li and **b**) vs Na (at a rate of C/20, voltage range = 3.0 V–4.3 V), **c**) Corresponding dq/dV plots (against Li and Na) showing a single Co³⁺/Co²⁺ redox peaks at $\geq 4 \text{ V}$, **d**) Ex-situ XRD patterns for pristine phase, charged (C- 3.8 V and C- 4.3 V) state and fully discharged (D- 3.0 V) state showing gradual shifting of the peaks confirming a solid-solution redox mechanism, **e**) High-resolution XPS spectra for pristine phase, charged state and discharged state. The shifting of the Co peaks towards higher binding energy at the charged state confirms the change in the redox state of cobalt from 2+ to 3+.

initial positions. In NCMo *alluaudite*, apart from Co, Mo can also act as additional redox centre. However, absolutely no change in the Mo 3*d* peaks (Mo $3d_{5/2}$ and Mo $3d_{3/2}$) was noticed in XPS analyses, as shown in Fig. S6, thus confirming the entire high-voltage redox activity can be solely assigned to the Co redox centre.

4. Conclusions

In the quest to unveil new polyanionic battery insertion material, alluaudite Na3.36Co1.32(MoO4)3 was successfully synthesized by a rapid solution-combustion synthesis benchmarking the lowest reported annealing duration of 1 min (at 600 °C). Rietveld analysis confirmed phase-pure product assuming signature monoclinic alluaudite framework (s.g. C2/c). Unlike the sulfate analogues, this molybdate alluaudite was found to be moisture stable having a high positive dissolution enthalpy (537 kJ/mol). With an optical band gap of ~3.26 eV and ionic conductivity of ~6.065 \times 10⁻⁸ S/cm, it offered a partial 2D diffusional channels for Na⁺ transport. It was found to be electrochemically active, exhibiting high-voltage Co^{3+} Co²⁺ redox potential for both Li-ion (4.1 V) and Na-ion (4.0 V) halfcells, in sync with DFT calculations. Ex-situ analyses revealed the occurrence of a solid-solution redox mechanism. As per DFT calculations, this molybdate alluaudite can offer multiple electron reactions involving Co⁴⁺/Co³⁺ redox activity at ~5.31 V (vs. Na), which cannot be experimentally validated due to lack of stable electrolytes. Na_{3.36}Co_{1.32}(MoO₄)₃ forms a rare polyanionic cathode system with active Co^{3+}/Co^{2+} redox couple. It benchmarks the first Co-based molvbdate *alluaudite* offering a high-voltage (ca. > 4 V) electrochemical activity. This high-voltage activity is similar to other Co-based polyanionic cathodes (e.g. LiCoBO₃ [54], Na₂Co₂(-SeO₃)₃ [55]). Although its commercial prospect is hindered by poor capacity, Na_{3.36}Co_{1.32}(MoO₄)₃ forms a novel alluaudite-type versatile battery alkali-ion insertion materials, attesting the alluaudite frameworks as a fertile ground for potential discovery of high voltage cathode materials for secondary batteries.

Credit author statement

Pubali Barman: Conceptualization, data curation, formal analysis, investigation, methodology, writing — original draft; **Pawan Kumar Jha:** DFT calculations, formal analysis, writing — original draft; **Anshuman Chaupatnaik:** Conceptualization, data curation; **K. Jayanthi:** Thermochemistry data curation, writing — original draft, **Rayavarapu Prasada Rao:** BVSE calculations, data curation, formal analysis; **Gopalakrishnan Sai Gautam:** Supervision of DFT calculations, writing — review & editing; **Sylvain Franger:** Supervision, writing— review & editing; **Alexandra Navrotsky:** Supervision of thermochemistry, writing — review & editing; **Prabeer Barpanda:** Conceptualization, funding acquisition, formal analysis, project administration, supervision, writing — review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mtchem.2022.101316.

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