Aliovalent-doped sodium chromium oxide (Na$_{0.9}$Cr$_{0.9}$Sn$_{0.1}$O$_2$ and Na$_{0.8}$Cr$_{0.9}$Sb$_{0.1}$O$_2$) for sodium-ion battery cathodes with high-voltage characteristics†

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NaCrO$_2$ with high-rate capability is an attractive cathode material for sodium-ion batteries (NIBs). However, the amount of reversibly extractable Na$^+$ ions is restricted by half, which results in relatively low energy density for practical NIB cathodes. Herein, we describe aliovalent-doped O$_3$–Na$_0.9$[Cr$_{0.9}$Sn$_{0.1}$]O$_2$ (NCSnO) and O$_3$–Na$_0.8$[Cr$_{0.9}$Sb$_{0.1}$]O$_2$ (NCSbO), both of which show high-voltage characteristics that translate to an increase in energy density. In contrast to NaCrO$_2$, NCSnO and NCSbO can be reversibly charged to 3.80 and 3.95 V, respectively, delivering 0.5 Na$^+$ along with Cr$^{3+/4+}$ redox alone. The reversible chargeability to Na$_0.9$[Cr$_{0.9}$Sn$_{0.1}$]O$_2$ and Na$_0.8$[Cr$_{0.9}$Sb$_{0.1}$]O$_2$ is not associated with the suppression of Cr$^{6+}$ formation. Both compounds show concentrations of Cr$^{6+}$ that are higher than that of Na$_0.9$CrO$_2$, with an absence of O$_3$ phases. This implies that aliovalent-doping contributes to a suppression of the Cr$^{6+}$ migration into tetrahedral sites in the interslab space, which reduces the possibility of irreversible comproportionation. NCSnO and NCSbO deliver capacities comparable to that of NaCrO$_2$, but show a higher average discharge voltage (2.94 V for NaCrO$_2$; 3.14 V for NCSnO; 3.21 V for NCSbO), which leads to a noticeable increase in energy densities. The high-voltage characteristics of NCSnO and NCSbO are also validated via density-functional-theory calculations.

The crystallographic structure and electrochemical properties of layered NIB cathodes are often compared to those of layered LIB cathodes because the fundamental chemistry of the former is similar to that of the latter. A slight difference in the ionic size of mobile ions [Li$^+$ = 0.76 Å vs. Na$^+$ = 1.02 Å], however, significantly affects the structural stability, which causes distinctively different phase-transition and voltage behaviors during charge/discharge (C/D). In general, large Na$^+$ ions tend to reside in a prismatic site rather than in an octahedral site, which induces multiple phase transitions with $x$ variations during C/D in Na$_x$MO$_2$ (M = first-series transition metals). For example, while O$_3$–LiCoO$_2$ is generally known to maintain its hexagonal structure up to Li$_{0.0}$3CoO$_2$ [18–20] the O$_3$ phase of NaCoO$_2$ is frequently changed to O$^3$ (Na$_{0.95}$CoO$_2$), P$^3$ (Na$_{0.90}$CoO$_2$), and P$3$ (Na$_{0.82}$CoO$_2$) during a charge process, which leads to inferior cyclic stability of O$_3$–NaCoO$_2$ compared with that of O$_3$–LiCoO$_2$.[13,21]

Another interesting example of the dramatic effect of ionic size is NaCrO$_2$. In contrast to O$_3$–LiCrO$_2$, which suffers from the hindrance of Li$^+$ diffusion due to Cr$^{3+/4+}$ ions generated during charging,[22] O$_3$–NaCrO$_2$ shows reversible Na$^+$ intercalation/de-intercalation within a reasonable voltage window.[22–23] Unless the high-voltage cutoff ($E^{\text{high}}$) exceeds ca. 3.6 V, the hexagonal O$_3$ phase of NaCrO$_2$ is reversibly transformed to a monoclinic
P'3 type via the monoclinic O'3 phase and delivers a capacity of ca. 120 mAh g$^{-1}$ (Na$_{0.9}$CrO$_2$). Further charging beyond 3.6 V results in the irreversible formation of another O3 phase (O'3) and a rock-salt structure with Cr$^{6+}$ in tetrahedral sites and Cr$^{4+}$ in octahedral sites between interlayers, respectively. The $\rho_{\text{high}}$ during C/D in NaCrO$_2$, therefore, is usually limited to 3.6 V to avoid a detrimental structure-transformation, which signifies that the voltage limitation must be solved to increase the energy density of NaCrO$_2$. To tackle this issue in NaCrO$_2$, Cr-based multi-metallic systems have been studied and possible increases in average operating voltage have been addressed. For example, Cao et al. claimed that the disproportionation reaction can be effectively suppressed in NaCr$_{13}$Fe$_{10}$Mn$_{15}$O$_{32}$ due to the presence of Fe$^{4+}$ and Mn$^{4+}$ when charged to 4.2 V. However, although Cr$^{3+/4+}$ redox is involved in these multi-metallic compounds, a significant fraction of electroactivity was the result of other metallic species, and the contribution from Cr$^{3+/4+}$ redox was not substantial. An effort aimed at structural stabilization by sodium-site doping with calcium has also been examined.

In this work, we describe aliovalent doping and its effect of on the electrochemical behaviors in NaCrO$_2$ (O3–Na$_{0.3}$[Cr$_{0.9}$Sn$_{0.1}$]O$_2$ and O3–Na$_{0.8}$[Cr$_{0.9}$Sb$_{0.1}$]O$_2$), in which Sn$^{4+}$ and Sb$^{5+}$ ions are electrochemically inert and their fraction is relatively small, in contrast to previous studies. First, we evaluate the structural stability via density functional theory (DFT) calculation and find that NaCrO$_2$ with higher contents of Sn$^{4+}$ and Sb$^{5+}$ does not retain the O3 structure. We also experimentally demonstrate that the title compounds can be reversibly charged to voltages exceeding 3.6 V until 0.5 Na$^+$ is extracted (3.80 V in Na$_{0.3}$[Cr$_{0.9}$Sn$_{0.1}$]O$_2$ and 3.95 V in Na$_{0.3}$[Cr$_{0.9}$Sb$_{0.1}$]O$_2$), which results in a higher energy density than pristine NaCrO$_2$. The origin of the reversibility and the high-voltage features are discussed based on structural analysis and theoretical computation.

**Experimental**

All chemicals were purchased from Sigma-Aldrich unless otherwise mentioned. The O3–NaCrO$_2$ was synthesized via a conventional solid-state method reported elsewhere. For the synthesis of O3–Na$_{0.3}$[Cr$_{0.9}$Sn$_{0.1}$]O$_2$ and O3–Na$_{0.8}$[Cr$_{0.9}$Sb$_{0.1}$]O$_2$, stoichiometric amounts of Na$_2$CO$_3$, Cr$_2$O$_3$, CrSb$_2$O$_6$, and SnO$_2$ were used as starting materials. CrSb$_2$O$_6$ was obtained by heating a mixture of Cr$_2$O$_3$ and Sb$_2$O$_3$ at 1100 °C for 12 h under an air atmosphere. The precursors were mixed in a mortar and the mixture was pressed into pellets (5 wt% excess of Na$_2$CO$_3$ was used in order to compensate for Na loss at high temperature). The pellets were sintered at 750 °C for 3 h, and then at 1200 °C for 8 h under a continuous flow of Ar. The samples were naturally cooled and stored in an Ar-filled glove box until further use.

*Ex situ* X-ray diffraction (XRD) was carried out to identify the crystalline phases of the as-prepared powders as well as C/D cycled electrodes. The measurements were performed using an X-ray diffractometer (Rigaku ULTIMA 4) with monochromatic Cu K$_\alpha$ radiation ($\lambda = 1.5406 \text{ Å}$). To prevent the exposure of samples to the atmosphere during XRD measurements, the samples were sealed in an air-sensitive holder covered with Kapton film. The XRD patterns of pristine powders and electrochemically charged films were characterized via Rietveld refinement using FullProf software. The surface morphologies and the compositions of the synthesized compounds were examined using a JEOL JSM-7100F field emission scanning electron microscope (FESEM) and energy dispersive X-ray (EDX). A Thermo Fisher X-ray photoelectron spectroscopy (XPS) with an Al K$_\alpha$ X-ray source was used to investigate the chemical state of chromium.

To prepare the electrodes, active material (80 wt%), acetylene black (10 wt%), and polyvinylidene fluoride (10 wt%) were mixed with N-methyl-2-pyrrolidone. The slurry was pasted onto Al foil using a doctor blade and was then vacuum-dried at 100 °C for 2 h. The electrodes were cut into a circular disk with a diameter of 16 mm. The typical mass loading of active material was ca. 2 mg cm$^{-2}$. For electrochemical tests, 2032 coin-type half-cells were fabricated in an Ar-filled glove box using Na metal as a counter/reference electrode, a separator (Whatman glass filter), and 1 M NaPF$_6$ dissolved in ethylene carbonate : diethyl carbonate (EC : DEC, 1 : 1) as electrolytes. Galvanostatic C/D tests were carried out using a WonATech (WBCS 3000) battery tester.

**Result and discussion**

In this study, we selected Sn$^{4+}$ and Sb$^{5+}$ ions for aliovalent doping of O3–NaCrO$_2$ because of the similarity in the ionic radii (r[Cr$^{4+}$] = 0.615, r[Sn$^{4+}$] = 0.69, and r[Sb$^{5+}$] = 0.60 Å) and the possession of the highest oxidation states, in which the latter ensures electrochemical inertness during a high-voltage charge. We first compared the structural stabilities of Na$_{1+}$(Cr$_{1-x}$Sn$_x$)$_2$O$_2$ and Na$_{1+}$(Cr$_{1-x}$Sb$_x$)$_2$O$_2$ in different phases (O3, P2, and P3) via ab initio DFT calculation. The total energies ($E_T$) for O3, P2, and P3 were calculated using R3m, P6$_3$/mmc, and R3m space groups, respectively. The 3 x 2 x 1 (O3 and P3) and 3 x 3 x 1 (P2) supercells, which contain the same number of formula units (18 units), were used to estimate the possible configurations for each composition (i.e., Na$_{14}$[Cr$_{14}$Sn$_3$]O$_{36}$ for x = 0.1; Na$_{14}$[Cr$_{14}$Sn$_3$]O$_{36}$ for x = 0.2; Na$_{15}$[Cr$_{15}$Sb$_3$]O$_{36}$ for x = 0.3; Na$_{15}$[Cr$_{15}$Sb$_3$]O$_{36}$ for x = 0.4; Na$_{15}$[Cr$_{15}$Sb$_3$]O$_{36}$ for x = 0.5; Na$_{16}$[Cr$_{16}$Sb$_4$]O$_{36}$ for x = 0.6). The total number of configurations for each composition was checked using a supercell program developed by Okhotnikov et al. Among them, we randomly selected 10 configurations for each composition, which appeared to be distinctive from each other and to be entropically plausible.

DFT calculations were executed using the Vienna ab initio simulation package (VASP5.3), in which a GGA-PBE (generalized gradient approximation parameterized by Perdew, Burke, and Ernzerhof) exchange correlation functional, a PAW (projector-augmented-wave) potential with an energy cutoff of 500 eV and a 3 x 3 x 2 k-mesh determined by the Monkhorst–Pack scheme were implemented. The atomic position and lattice size were allowed to relax until the total energy accuracy and ionic force components converged to 10$^{-6}$ eV and
and subjected to XRD measurements along with pristine O3 compositions, which were predicted to retain the O3 structures in DFT calculations, residuated in the octahedral sites (Sn4+ and Sb5+) of Na0.9Cr0.9Sn0.1O2 and Na0.8Cr0.9Sb0.1O2. The structure proved to be the most plausible phase in both Na0.9[Cr0.9Sn0.1]O2 and Na0.8[Cr0.9Sb0.1]O2, respectively. The on-site interaction (Hubbard U) value was set to 4.0 for a Cr d orbital.

The $E_T$ values for each composition with different structures, as compared in Fig. 1, clearly show that the most stable structure strongly depends on the composition. For example, the average $E_T$ value of $-24.94$ eV per FU for the O3 type of Na0.8[Cr0.9Sb0.1]O2 was appreciably lower than the $-24.83$ eV per FU for either P2 or P3 types. The O3 preference was also the case in Na0.9[Cr0.9Sn0.1]O2. The stability of Na0.8[Cr0.9Sb0.1]O2 and Na0.9[Cr0.9Sn0.1]O2, therefore, indicated that the O3 structure could be stable in a wide range of Na+ content after aliovalent substitution in contrast to the brief existence of an O3 phase in NaCrO2 during charge.

Further increases in the amounts of substituents (Sn4+ and Sb5+), and thereby a decrease in the content of Na+, changed the most stable phase to a P2 type, but the energetic preference over O3 was not so conspicuous as that for Na0.9[Cr0.9Sn0.1]O2 and Na0.8[Cr0.9Sb0.1]O2.

Na0.9[Cr0.9Sn0.1]O2 (NCSnO) and Na0.8[Cr0.9Sb0.1]O2 (NCSbO), which were predicted to retain the O3 structures in DFT calculations, were synthesized via a conventional solid-state method and subjected to XRD measurements along with pristine O3–NaCrO2 (NCO) (Fig. 2). We selected these two compounds because the goal of this research was to investigate the effect of aliovalent doping on the electrochemical behaviors of O3–NCO when Cr3+/4+ alone is involved in a redox process. Ex situ XRD revealed the formation of O3 layered structures in both NCSnO and NCSbO in accordance with the DFT results. The characteristic peaks of O3 phases (space group = R3m) were evident with small impurities (Na2CrO4 denoted by asterisks). The most intense (003) and (104) peaks showed well-defined symmetric shapes with neither peak-splitting nor shoulders, which indicated the absence of monoclinically distorted phases of O3, space group = C2/m in as-prepared compounds. The negligible peak intensities of (015) relative to (104) also suggested that Na+ ions resided in the octahedral sites (i.e., no P3 or P3′ phases) for all compounds. It was also obvious that the c-axis length increased with the incorporation of Sn4+ or Sb5+ because of a decrease in Na+ content with a concomitant increase in electrostatic repulsion between the MO6 layers. The (003) peak located at 16.62° in NCO was shifted to lower 2θ angles of 16.34° and 16.28° in NCSnO and NCSbO, respectively. This also implied that Sn4+ and Sb5+ ions were unlikely to occupy the octahedral sites in Na+ layers; otherwise, the c-axis lengths could be shortened in NCSnO and NCSbO. An increase in the relative intensities of (101)/(012) after substitution was another indication for the existence of Sn4+ and Sb5+ in the transition metal layers.

Prior to the extraction of detailed crystallographic information via Rietveld refinement, EDX studies were performed to confirm the chemical composition of as-synthesized compounds (Fig. S1†). FESEM images showed no morphological changes after substitutions with Sn4+ and Sb5+. The particles retained platelet shapes, which reflected the characteristic morphology of layered materials. The corresponding elemental maps also showed a homogeneous distribution of individual elements. The EDX spectra revealed the compositions of Na0.89±0.02Cr0.91±0.02Sb0.09±0.01O2 and Na0.80±0.02Cr0.91±0.02Sb0.09±0.00O2 for NCSnO and NCSbO, respectively, which indicated that the final compositions agreed well with the nominal compositions.

The change in the lattice parameters and atomic positions after aliovalent doping was estimated via Rietveld refinement (Fig. S2†). The positions of Na+ and Cr3+ (Sn4+, Sb5+) were fixed at special sites. Only the z coordinate of O2− was refined. The possibility for a site disorder between Na+ and Cr3+ (Sn4+, Sb5+) was excluded because the simulated profiles deviated substantially from the XRD patterns, particularly at relative intensities of (006)/(101). Excellent agreement between the experimental and calculated patterns was obtained using the space group of R3m for all compounds (Table 1). The refinement results indicated that the interlayer distance ($d_{\text{interlayer}}$) was slightly increased after substitution, which was due to the enhanced electrostatic repulsion between MO6 layers. In fact, the thickness of the Na+ layers was significantly increased from 3.069 Å (NCO) to 3.168 Å (NCSnO) and 3.186 Å (NCSbO), but the
simultaneous contraction in the thickness of MO$_6$ layers (2.258 Å for NCO → 2.208 Å for NCSnO and 2.214 Å for NCSbO) resulted in relatively small changes in $d_{\text{inter slab}}$ (Fig. 3). The volumes of MO$_6$ octahedra in both NCSnO and NCSbO (11.343 and 11.302 Å$^3$) were also slightly smaller than that in NCO (11.557 Å$^3$), despite the inclusion of larger cations in NCSnO.

The title compounds along with NCO were subjected to galvanostatic C/D at 20 mA g$^{-1}$ to examine how the substitution influenced the voltage behaviors (Fig. 4). As well known, NCO showed the good reversibility when the $E^{\text{high}}$ is limited to 3.60 V with a charge capacity of 122 mA h g$^{-1}$ (Na$_{0.5}$MO$_2$). An increase in the $E^{\text{high}}$ to 3.90 V resulted in serious decay in the corresponding discharge capacity due to the formation of O3' and/or rock-salt phases. The charge profiles of NCSnO and NCSbO also indicated that Na$_{0.5}$MO$_2$ can be attained by charging to ca. 3.6 V with capacities of 97 and 77 mA h g$^{-1}$, respectively. The sharp increase of the voltages in NCO, NCSnO, and NCSbO with those in NCO (Fig. 5). XPS spectra revealed that, while NCO charged to 3.60 V (Na$_{0.5}$CrO$_2$) contains negligible amounts of Cr$^{4+}$, the Cr$^{6+}$ content is substantial in NCO charged to 3.80 V (Na$_{0.5}$Cr$_2$O$_3$) due to the disproportionation of Cr$^{4+}$. The intense Cr$^{6+}$ peak in Na$_{0.5}$Cr$_2$O$_3$ was further observed in Na$_{0.5}$Cr$_{2}$Sn$_2$O$_7$ and Na$_{0.5}$Cr$_{2}$Sb$_2$O$_7$, because of the simultaneous contraction in the thickness of MO$_6$ layers (2.258 Å for NCO → 2.208 Å for NCSnO and 2.214 Å for NCSbO) resulted in relatively small changes in $d_{\text{inter slab}}$ (Fig. 3). The title compounds along with NCO were subjected to galvanostatic C/D at 20 mA g$^{-1}$ to examine how the substitution influenced the voltage behaviors (Fig. 4). As well known, NCO showed the good reversibility when the $E^{\text{high}}$ is limited to 3.60 V with a charge capacity of 122 mA h g$^{-1}$ (Na$_{0.5}$MO$_2$). An increase in the $E^{\text{high}}$ to 3.90 V resulted in serious decay in the corresponding discharge capacity due to the formation of O3' and/or rock-salt phases. The charge profiles of NCSnO and NCSbO also indicated that Na$_{0.5}$MO$_2$ can be attained by charging to ca. 3.6 V with capacities of 97 and 77 mA h g$^{-1}$, respectively. The sharp increase of the voltages in NCO, NCSnO, and NCSbO with those in NCO (Fig. 5). XPS spectra revealed that, while NCO charged to 3.60 V (Na$_{0.5}$CrO$_2$) contains negligible amounts of Cr$^{4+}$, the Cr$^{6+}$ content is substantial in NCO charged to 3.80 V (Na$_{0.5}$Cr$_2$O$_3$) due to the disproportionation of Cr$^{4+}$. The intense Cr$^{6+}$ peak in Na$_{0.5}$Cr$_2$O$_3$ was further observed in Na$_{0.5}$Cr$_{2}$Sn$_2$O$_7$ and Na$_{0.5}$Cr$_{2}$Sb$_2$O$_7$, because of the simultaneous contraction in the thickness of MO$_6$ layers (2.258 Å for NCO → 2.208 Å for NCSnO and 2.214 Å for NCSbO) resulted in relatively small changes in $d_{\text{inter slab}}$ (Fig. 3). The volumes of MO$_6$ octahedra in both NCSnO and NCSbO (11.343 and 11.302 Å$^3$) were also slightly smaller than that in NCO (11.557 Å$^3$), despite the inclusion of larger cations in NCSnO.

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prevention of Cr$^{6+}$ migration into the Na$^+$ layers, which is the route for the irreversible formation of O3$^-$ and/or rock-salt phases.

Since the electrochemical reversibility of NCSnO and NCSbO with high $E^{\text{high}}$ is not ascribed to the suppression of Cr$^{6+}$ formation, we investigated the difference in the structural evolution to understand the high-voltage features of the two compounds. *Ex situ* XRD patterns during charge were recorded at various states-of-charge with an interval of 0.1 in Na$^+$ content. For NCO, the change in the XRD patterns agreed well with the previously reported results (Fig. 6A). On charging, (003) and (006) peaks of an O3 phase were split with a new peak appearing at a lower $2\theta$. Two separated peaks were observed in 0.9 Na$^+$ that immediately merged into a single peak when further charged to 0.8 Na$^+$ and 0.7 Na$^+$. Note that the (104) peak in the O3 phase was also split into two peaks with substantial intensities ([111] and [20-2]), which is a signature for the formation of a mono-clinically distorted O3 phase. Therefore, the change in the XRD patterns indicated a phase transition from O3 to O'3 through a mixed O3/O'3 phase when NCO was charged to Na$_{0.7}$CrO$_2$. The O'3 phase was immediately transformed to a P'3 phase with a further charge, which was evident from the abrupt weakening of the (111) and (20-2) peaks of O'3 and the appearance of intense (201) and (11-2) peaks of P'3 in a $2\theta$ range of 44° and 45.5°. In appearance, the P'3 phase seemed to be maintained up to Na$_{0.3}$CrO$_2$ (charge to 3.80 V).

NCSnO and NCSbO showed phase transition behaviors that were noticeably different from those of NCO (Fig. 6B and C). During a charge, the O3 phases were maintained up to Na$_{0.7}$MO$_2$. Separation of the (003) and (006) peaks became evident at Na$_{0.6}$MO$_2$ in contrast to the incipient appearance in NCO (Na$_{0.9}$CrO$_2$). Furthermore, the structure of the two phases in Na$_{0.6}$MO$_2$ seemed to be different from that in Na$_{0.3}$CrO$_2$. The
composed of a single P\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} and Al; (C) P\textsubscript{3}–Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}). The peak broadening of (104). This two-phase region (O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}, and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}), closer examination calculated, and di

Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}, and (C) Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}

appreciable peak intensity at 2\theta of ca. 44.7° strongly signified the inclusion of a P\textsuperscript{3} phase. Despite no clear peak splitting, we also considered the presence of an O\textsubscript{3} phase in Na\textsubscript{0.6}MO\textsubscript{2} from the peak broadening of (104). This two-phase region (O\textsubscript{3}/P\textsuperscript{3}) was short-lived. It was immediately transformed to a P\textsuperscript{3} phase, which was maintained to the fully charged states (Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2}, and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}).

It is noteworthy that, although all three compounds appeared to have the P\textsuperscript{3} structures in a fully charged state (Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}, Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2}, and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}), closer examination revealed that, while Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2} and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2} are composed of a single P\textsuperscript{3} phase, Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} along with P\textsuperscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}. The generation of O\textsubscript{3} and rock-salt structures in Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} (x < 0.4), which led to irreversibility in Na\textsuperscript{+} migration, was addressed in a previous report. Our Rietveld refinement results also showed the presence of an O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} between the experimental data and the calculated pattern by using a relative P\textsuperscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}/O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} ratio of 84.4/15.6. Note that the addition of rock-salt Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} was avoided because of the strong diffraction peaks of an Al substrate, which closely overlapped those from rock-salt Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}. In contrast, the XRD patterns of Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2} and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2} films were fitted well with a single P\textsuperscript{3} phase and no O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} (Fig. 7B, C, Tables S3 and S4†). Aliovalent doping, therefore, is likely to suppress the formation of O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} in Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2} and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}, which enables a charge to higher voltages in NCSnO and NCSbO.

The high-voltage characteristics of NCSbO were further validated via DFT calculations. The formation energy (E\textsubscript{f}) was obtained for O\textsubscript{3}, O\textsubscript{3}, and P\textsuperscript{3} phases at various states-of-charge, using 3 × 2 × 1, 3 × 2 × 1, and 1 × 3 × 3 supercells, respectively (Fig. 8). The electrochemical potential was calculated using the configuration with the lowest E\textsubscript{f} for each x value. Eqn (1) was used, where E(Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}) and E(Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}) indicate the total energies of NCSbO with Na contents of x and 2, respectively. E\textsubscript{bulk}(Na) is the total energy of Na metal in a body-centered cubic (Im\textsubscript{3}m) structure, which corresponds to the chemical potential of Na in the anode. F is the Faraday constant.

\[
V = \frac{E(Na_{0.4}Cr_{0.9}Sb_{0.1}O_2) - E(Na_{0.3}[Cr_{0.9}Sb_{0.1}]O_2) + (x - x1)E_{\text{bulk}}(Na)}{(x - x1)F}
\] (1)

wherein one-third of Cr ions reside in the tetrahedral sites of Na\textsuperscript{+} layers (Fig. 7A, Tables S1 and S2†). We obtained good agreement between the experimental data and the calculated pattern by using a relative P\textsuperscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}/O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} ratio of 84.4/15.6. Note that the addition of rock-salt Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} was avoided because of the strong diffraction peaks of an Al substrate, which closely overlapped those from rock-salt Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}. In contrast, the XRD patterns of Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2} and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2} films were fitted well with a single P\textsuperscript{3} phase and no O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} (Fig. 7B, C, Tables S3 and S4†). Aliovalent doping, therefore, is likely to suppress the formation of O\textsubscript{3}–Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2} in Na\textsubscript{0.4}[Cr\textsubscript{0.9}Sn\textsubscript{0.1}]O\textsubscript{2} and Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}, which enables a charge to higher voltages in NCSnO and NCSbO.

The high-voltage characteristics of NCSbO were further validated via DFT calculations. The formation energy (E\textsubscript{f}) was obtained for O\textsubscript{3}, O\textsubscript{3}, and P\textsuperscript{3} phases at various states-of-charge, using 3 × 2 × 1, 3 × 2 × 1, and 1 × 3 × 3 supercells, respectively (Fig. 8). The electrochemical potential was calculated using the configuration with the lowest E\textsubscript{f} for each x value. Eqn (1) was used, where E(Na\textsubscript{0.4}Cr\textsubscript{0.9}Sn\textsubscript{0.1}O\textsubscript{2}) and E(Na\textsubscript{0.3}[Cr\textsubscript{0.9}Sb\textsubscript{0.1}]O\textsubscript{2}) indicate the total energies of NCSbO with Na contents of x and 2, respectively. E\textsubscript{bulk}(Na) is the total energy of Na metal in a body-centered cubic (Im\textsubscript{3}m) structure, which corresponds to the chemical potential of Na in the anode. F is the Faraday constant.

\[
V = \frac{E(Na_{0.4}Cr_{0.9}Sb_{0.1}O_2) - E(Na_{0.3}[Cr_{0.9}Sb_{0.1}]O_2) + (x - x1)E_{\text{bulk}}(Na)}{(x - x1)F}
\] (1)

wherein one-third of Cr ions reside in the tetrahedral sites of Na\textsuperscript{+} layers (Fig. 7A, Tables S1 and S2†). We obtained good agreement with the experimental C/D curves with the similar profile shapes and
电压的特性。新合成的 NCSnO 和 NCSbO 保持了 O3 结构，并且实现了在电压高于 3.60 V 时的可逆插层。这些实验结果与 DFT 计算相一致。

结论

NCSnO 和 NCSbO，两者都保持了 O3 结构，通过合成和测试其电化学性质，与 NCO 进行了比较。尽管 Na+ 含量较低，NCSnO 和 NCSbO 可以在电化学上可逆插层，且可以在高达 3.80 V 和 3.95 V，分别的电压下保持高电压特性。这些高电压的特性在 100 C/D 循环中保持不变，表明在能量密度方面的改善。

利益声明

没有利益冲突要声明。

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