



Coupling Network Reconstruction-Driven Charge Transport Transition: Capacity Breakthrough and Wide-Temperature Sodium Storage in $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ Cathodes

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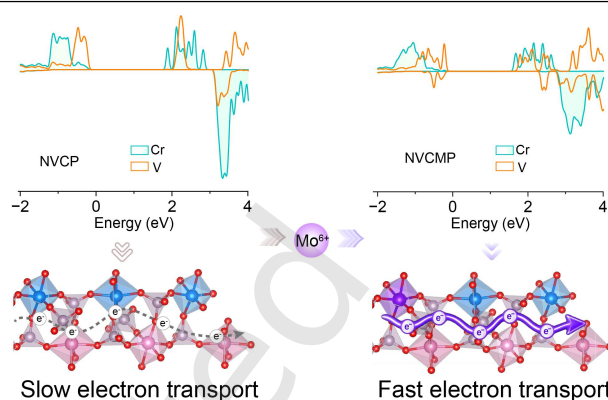
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Insufficient V-Cr orbital coupling in NVCP restricts electron transport within the framework. To address this issue, we propose a “coupling network modulation” strategy, in which trace Mo^{6+} with a $4d^0$ electronic configuration is introduced at the Cr site to enhance the effective V-Cr orbital coupling, while strong Mo-O bonding improves structural stability, thereby enabling a breakthrough in specific capacity and wide-temperature adaptability in NVCMP.

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Coupling Network Reconstruction-Driven Charge Transport Transition: Capacity Breakthrough and Wide-Temperature Sodium Storage in $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ Cathodes

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ABSTRACT

NASICON-type sodium-ion batteries (SIBs) cathode material $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ (NVCP) theoretically offers the advantage of high energy density. However, its practical capacity is severely restricted, rendering the theoretical potential unrealized. The root cause underlying this capacity limitation remains unclear to date, posing a fundamental obstacle to the material's practical application. Through the deep synergy of theoretical calculations and experiments, this study reveals that the electron state localization induced by insufficient V-Cr d-d orbital hybridization in NVCP is the core bottleneck constraining the intrinsic kinetics of charge transfer. To address this, we propose a "coupling network modulation" strategy, employing Mo^{6+} with a $4d^0$ empty orbital as a probe to implement precise intervention in the local bonding environment. The preferential occupation of Mo^{6+} at the Cr site efficiently reconstructs the Cr-O-V bonding topology and enhances V-Cr orbital overlap, boosting the bulk electronic conductivity by two orders of magnitude. Simultaneously, the strong covalent Mo-O bonds pin the lattice framework, significantly improving strain resistance and effectively suppressing structural degradation during long-term cycling. Consequently, the optimized $\text{Na}_{2.91}\text{VCr}_{0.97}\text{Mo}_{0.03}(\text{PO}_4)_3$ delivers an initial specific capacity of 105.2 mAh g^{-1} , achieving a 21.1% gain in specific energy, and exhibits excellent performance across a wide temperature range of -60 to 50°C . This work clarifies the root cause of NVCP performance failure at the electronic structure level. It thereby establishes a novel strategy for performance modulation based on local bonding reconstruction, offering theoretical guidance for designing high-energy and wide-temperature SIBs cathode.

KEYWORDS

Sodium-ion batteries, $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ cathode, high-voltage, coupling network modulation, Mo^{6+}

1 Introduction

Sodium-ion batteries (SIBs), characterized by the abundance of sodium resources, controllable costs, and electrochemical mechanisms highly compatible with lithium-ion systems, have emerged as one of the most competitive next-generation battery technologies for large-scale energy storage [1-5]. However, their practical energy density remains far below theoretical expectations,

with the core bottleneck lying in the insufficient capacity and voltage output of cathode materials [6,7]. As the decisive component for battery energy density, the working voltage and reversible capacity of the cathode directly define the upper limit of battery performance [8-10]. Therefore, developing cathode materials that combine high working voltage with high reversible capacity is the critical pivot for breaking through the energy density bottleneck of SIBs [11-13].

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Among diverse cathode systems, NASICON-type polyanionic materials $\text{Na}_x\text{MM}'(\text{PO}_4)_3$ ($\text{M}/\text{M}' = \text{Ti}, \text{V}, \text{Cr}, \text{Mn}, \text{Fe}, \text{Co}, \text{Ni}$) exhibit unique structural advantages, owing to their robust three-dimensional frameworks and open Na^+ migration channels [14-16]. In particular, $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ (NVCP) is highly compelling, where the introduction of Cr^{3+} significantly elevates the redox potential of V from 3.4 V to 4.1 V (vs. Na^+/Na), enabling continuous multi-electron reactions involving $\text{V}^{3+}/\text{V}^{4+}/\text{V}^{5+}$ [17]. With a theoretical specific capacity of approximately 117 mAh g^{-1} and an average working voltage of about 3.8 V, NVCP boasts a theoretical energy density as high as $\sim 439 \text{ Wh kg}^{-1}$ [18], intrinsically possessing a significant energy density advantage over conventional NASICON cathodes (e.g., $\text{Na}_3\text{V}_2(\text{PO}_4)_3$, with a theoretical energy density of $\sim 396 \text{ Wh kg}^{-1}$) [19]. However, this theoretical advantage is far from realized in experiments: the practical reversible capacity is significantly lower than theoretical expectations, and capacity continuously decays during cycling. The severity of the issue lies in the fact that the underlying mechanism causing this massive gap between "theoretical expectations and practical performance" still lacks systematic understanding, representing a core cognitive blind spot hindering the further development of this material.

To resolve this performance paradox, one must return to the electronic structure essence of NVCP. The framework of this material is assembled into a three-dimensional lantern-like structure via corner-sharing between $(\text{V}/\text{Cr})\text{O}_6$ octahedra and $(\text{PO}_4)_3$ tetrahedra [20]. While this topological configuration provides continuous migration channels for Na^+ , it effectively isolates adjacent $(\text{V}/\text{Cr})\text{O}_6$ octahedra via $(\text{PO}_4)_3$ polyanions. Consequently, electron transfer between V and Cr is forced to proceed through the long-range V-O-P-O-Cr path, rather than the more direct V-O-Cr bridging channel [21]. This structural feature inevitably weakens the effective overlap between V 3d and Cr 3d orbitals, inducing electron state localization and severely restricting charge transfer efficiency within the framework [22]. In other words, the electrochemical performance of NVCP is not only limited by the ion migration kinetics of Na^+ , but is more critically constrained by the charge transport capability determined by its intrinsic electronic structure, with the latter serving as the deep-seated intrinsic factor governing rate capability and capacity release.

In recent years, orbital engineering, which modulates d-p orbital hybridization strength through heterovalent ion substitution, has demonstrated potential in breaking the intrinsic conductivity limitations of various cathode materials. For instance, Mg^{2+} doping significantly enhances the electronic conductivity of sodium iron sulfate cathodes by strengthening Fe 3d-O 2p hybridization [23]; the synergistic effects among 3d orbitals of multiple transition metals such as V, Fe, and Mn have also been proven to effectively enhance the charge

transfer capability of phosphate-based cathodes [24]. These advances collectively point to a core insight: precise modulation of local orbital configurations and bonding topology can fundamentally reshape the electron state distribution of materials, thereby unlocking their sealed intrinsic electrochemical performance. For NVCP, the 3d orbitals of V and Cr possess distinct occupation states and energy level distributions. The coupling between them, as well as their respective hybridization with O 2p, offers abundant degrees of freedom for regulation, which presents both a challenge and an opportunity for performance breakthroughs. However, systematic research on the V-Cr orbital coupling state in NVCP and its influence mechanism on electronic transport remains scarce.

Addressing this knowledge gap, in this work, Projected Density of States (PDOS) analysis reveals that the effective coupling between V 3d and Cr 3d electronic states in NVCP is weak, hindering electronic transport within the framework. Based on this, we propose a "coupling network modulation" strategy, employing Mo^{6+} with a $4d^0$ empty orbital as an orbital probe to perform trace substitution at the V and Cr sites, respectively, to achieve differential intervention in the local bonding environment. Theoretical calculations indicate that doping Mo^{6+} at the Cr site modulates orbital interactions more effectively than at the V site, thereby enhancing the effective coupling between V and Cr. The optimized $\text{Na}_{2.91}\text{VCr}_{0.97}\text{Mo}_{0.03}(\text{PO}_4)_3$ (NVCMP) exhibits an increase in electronic conductivity by two orders of magnitude, significantly enhancing electron transport within the framework. Meanwhile, analyses of Crystal Orbital Hamilton Population (COHP), Electron Localization Function (ELF), and X-ray Absorption Fine Structure (XAFS) demonstrate that the robust Mo-O bonds possess stronger bonding strength, contributing to improved structural stability during cycling. Consequently, at a high voltage of 4.6 V, the initial specific capacity of NVCMP increased from 87.3 to 105.2 mAh g^{-1} , and the discharge specific energy rises from 312 to 377.8 Wh kg^{-1} . Furthermore, the material exhibits excellent electrochemical adaptability over a wide temperature range from -60 to 50°C . This work modulates electronic transport within the NASICON framework through orbital coupling among multi-transition metal electronic states, offering a novel electronic structure design strategy for high-voltage cathode materials.

2 Results and Discussion

We synthesized the NVCP cathode using a sol-gel method, yet its first-cycle discharge specific capacity is only 87.3 mAh g^{-1} at 0.1 C. As with NVCP materials previously reported in the literature, the first-cycle discharge specific capacity did not exceed 90 mAh g^{-1} , which is far below the theoretical value. (Fig. 1(a)) [25-28]. To gain deeper insight into the capacity limitation, first-principles density functional theory (DFT) calculations were carried out to elucidate the electronic structure of NVCP. The optimized local crystal structure is shown in Fig. 1(b), consists of

(V/Cr) O_6 octahedra and PO_4 tetrahedra forming a typical NASICON framework. The PDOS of the V 3d and Cr 3d orbitals reveal that the two orbitals exhibit weak coupling, particularly with no electronic state occupation in the spin-down channel near the Fermi level (**Fig. 1(c)**, **Figs. S1(a)-1(b)** in the Electronic Supplementary Material (ESM)). This weak V/Cr 3d orbital coupling and V/Cr 3d-O 2p hybridization hinder electron transport within the framework, ultimately resulting in a low practical specific capacity. To address this issue, we selected Mo^{6+} (**Fig. 1(d)**), which has a high oxidation state, a $4d^0$ electronic configuration, and strong Mo-O bonding ability, as a trace doping element for orbital regulation, and compared the modulation effects at different sites. The optimized local crystal structures of $\text{Na}_{2.91}\text{V}_{0.97}\text{Mo}_{0.03}\text{Cr}(\text{PO}_4)_3$ (NVMCP, with Mo doping at the V site) and NVCMP (with Mo doping at the Cr site) are shown in **Figs.**

1(e)-1(f). PDOS results show that Mo doping has a significant impact on the electronic state distribution at both the V and Cr transition metal sites. Compared to NVCP, the 3d electronic states of V and Cr in NVMCP and NVCMP exhibit stronger hybridization and a smoother electronic state, indicating an effective enhancement of the V-Cr coupling (**Figs. 1(g)-1(h)**). Furthermore, both V3d and O 2p exhibit distinct electron density distributions for the down-spin states near the Fermi level, indicating enhanced orbital hybridization between V 3d or Cr 3d and O 2p (**Fig. S1(c))-1(f)** in the ESM). Notably, NVCMP exhibits a more continuous electron density distribution than NVMCP, which is conducive to the formation of a continuous charge transport channel.

Further analysis of the Mo 4d PDOS reveals that in the lower spin part near the Fermi level, NVMCP exhibits two

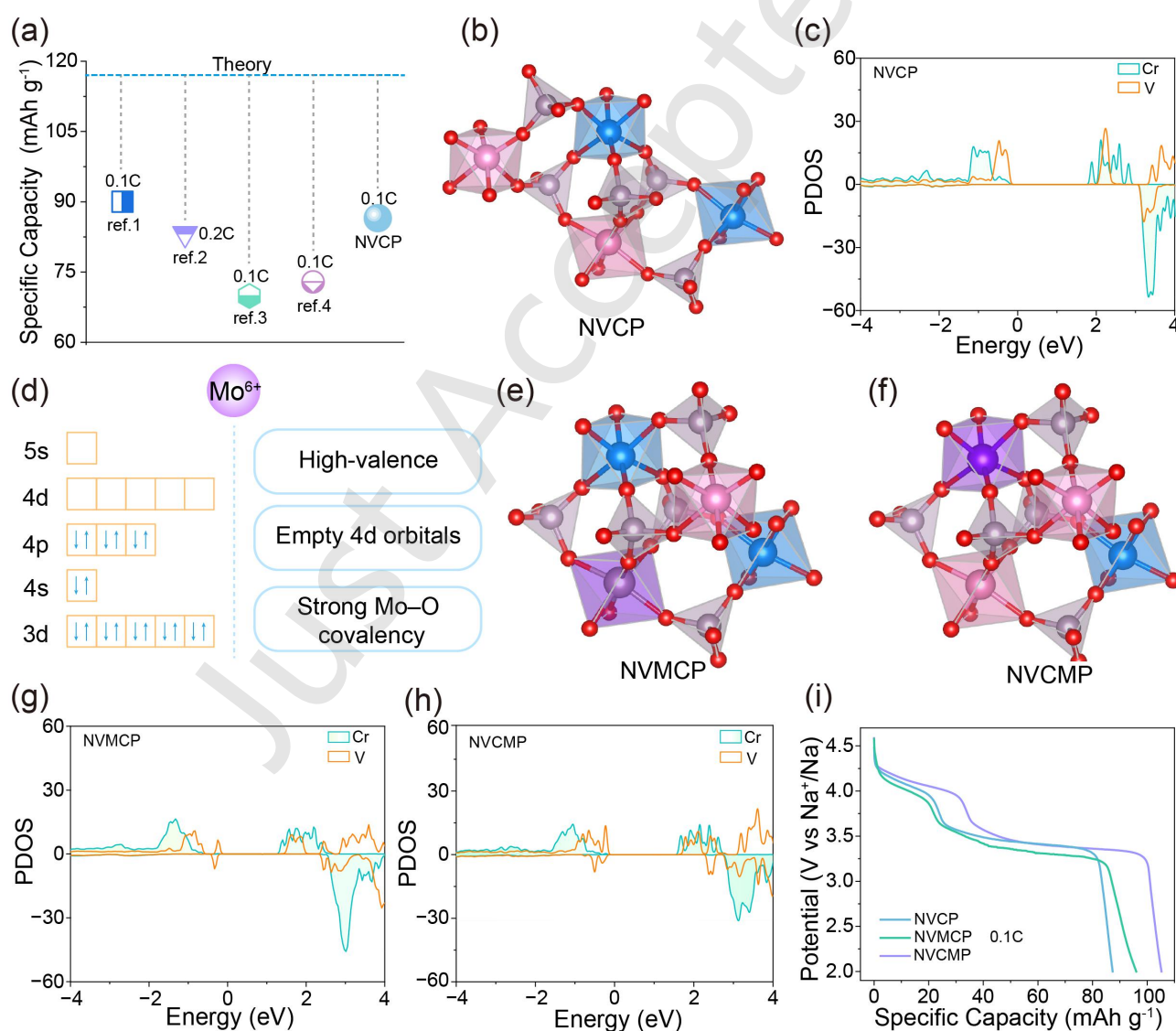


Figure 1 (a) The first discharge specific capacity of NVCP reported in the literature. (b) Local structure diagram of NVCP crystal. (c) The 3d orbital PDOS of V and Cr in NVCP. (d) Properties of Mo^{6+} . (e-f) Local structure diagram of NVMCP and NVCMP. (g-h) The 3d orbital PDOS of V and Cr in NVMCP and NVCMP. (i) Specific discharge capacity in the first cycle at 0.1C.

discontinuous peaks, while NVCMP shows continuous peaks (Fig. S2 in the ESM). These results indicate that doping Mo at the Cr sites can more effectively modulate the coupling between V and Cr as well as the hybridization strength between V/Cr 3d and O 2p, thereby facilitating electronic transport within the framework. Benefiting from this favorable electronic structure modulation, the initial discharge specific capacity of NVMCP at 0.1 C increases to 96 mAh g^{-1} , while that of NVCMP reaches 105.2 mAh g^{-1} , both significantly higher than that of NVCP (Fig. 1(i)).

XRD was employed to examine the crystal structures of

the samples. As shown in Fig. S3 in the ESM, the diffraction peaks of all samples agree well with the standard pattern of $\text{Na}_3\text{V}_2(\text{PO}_4)_3$ (PDF No. 00-062-0345), with no detectable impurity peaks, indicating that the introduction of a small amount of Mo does not alter the basic crystal structure. Further Rietveld refinement reveals that NVCMP crystallizes in the rhombohedral $R\bar{3}c$ space group, and the low weighted-profile factor ($R_{\text{wp}}=3.24\%$) indicates good agreement between the experimental and calculated patterns (Fig. 2(a)). The corresponding crystal structure model is shown in Fig. S4 in the ESM, while the detailed lattice parameters and

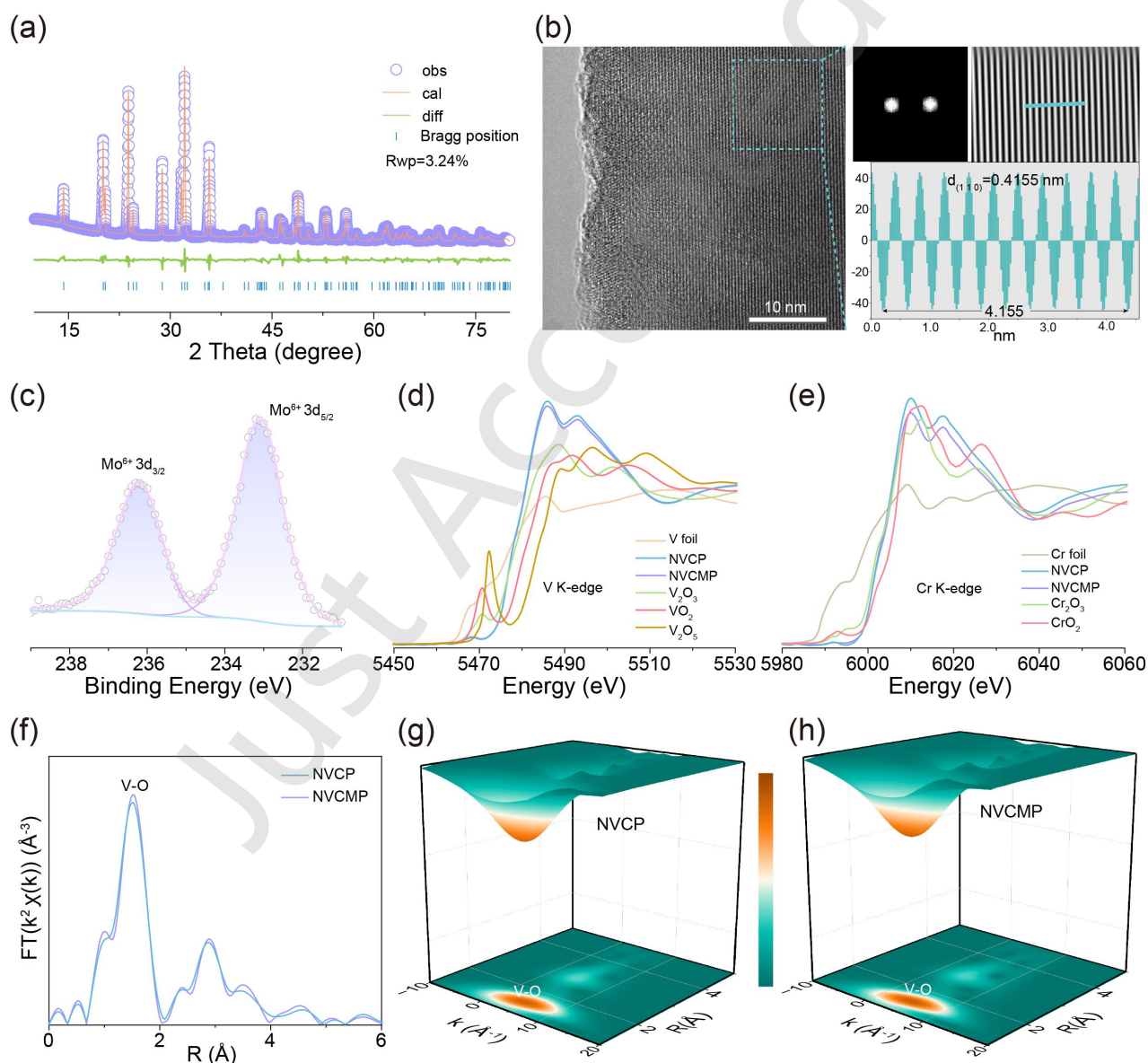


Figure 2 (a) Rietveld refinement results of the XRD pattern for NVCMP. (b) HR-TEM micrograph of NVCMP, accompanied by its FFT pattern (upper right) and the corresponding intensity profile (lower right). (c) XPS of Mo^{6+} . Normalized XANES spectra of the (d) V K-edge and (e) Cr K-edge. (f) Fourier transform of the EXAFS in the R space from V K-edge. Wavelet transform plots derived from V K-edge of (g) NVCP and (h) NVCMP

atomic occupancies are summarized in Table S1. Scanning electron microscopy (SEM) was used to evaluate the particle morphology. NVCMP exhibits noticeably less particle agglomeration than NVCP, which is favorable for shortening Na^+ transport pathways (Fig. S5 in the ESM). Fourier-transform infrared (FT-IR) spectra show characteristic vibrational signals associated with $(\text{PO}_4)^{3-}$ groups and $(\text{V/Cr/Mo})_6$ bonds (Fig. S6 in the ESM). In addition, high-resolution transmission electron microscopy (HR-TEM) of NVCMP reveals clear lattice fringes, with an interplanar spacing of 0.4155 nm corresponding to the (110) plane, while the corresponding fast Fourier transform further confirms its good crystallinity (Fig. 2(b)). Furthermore, thermogravimetric (TG) curves reveal that the carbon contents of both NVCP and NVCMP are below 2%, with NVCMP exhibiting a slightly lower carbon content than

NVCP, thus excluding a significant influence of carbon content on the subsequent performance comparison (Fig. S7 in the ESM). Energy-dispersive X-ray spectroscopy (EDS) elemental maps show homogeneous distributions of Na, V, Cr, Mo, P, O, and C throughout NVCMP, providing preliminary evidence for the successful incorporation of Mo (Fig. S8 in the ESM). X-ray photoelectron spectroscopy (XPS) was subsequently employed to analyze the surface composition and oxidation states. The survey spectrum clearly displays the characteristic signals of the constituent elements in NVCMP (Fig. S9 in the ESM). Deconvolution of the high-resolution spectra shows that the C 1s spectrum can be resolved into C-C, C-O, C=O, and O-C=O components, while the O 1s spectrum contains contributions from C-O, C=O, and O-C=O species (Figs. S10(a)-10(b) in the ESM). The V 2p and Cr 2p spectra indicate that both V and Cr are predominantly present in

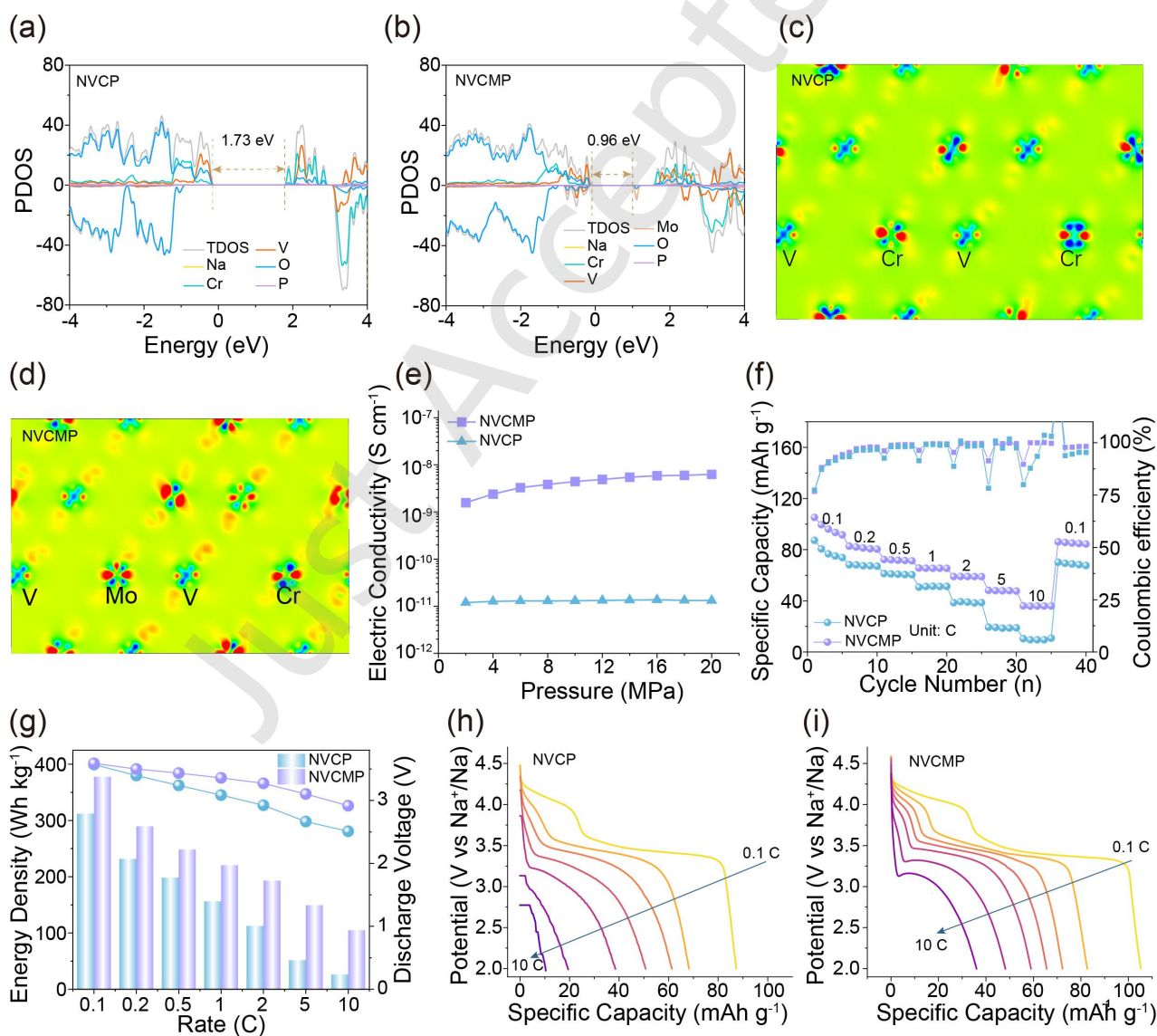


Figure 3 PDOS of (a) NVCP and (b) NVCMP. Differential charge of (c) NVCP and (d) NVCMP. (e) Comparison of electrical conductivity between NVCP and NVCMP. (f) Performance at different current densities of NVCP and NVCMP. (g) Discharge energy density and voltage at different rates.

Discharge curves at different rates of (h) NVCP and (i) NVCMP.

the +3 oxidation state (**Figs S10(c)-10(d)** in the ESM), whereas the Mo 3d spectrum confirms the presence of Mo^{6+} (**Fig. 2(c)**). XAFS was used to further investigate the effect of Mo substitution on the local coordination environment.[29] The V and Cr K-edge X-ray absorption near-edge structure (XANES) spectra are shown in **Figs. 2(d)-2(e)**. The V absorption edges of NVCP and NVCMP are close to that of V_2O_3 , while the Cr absorption edges closely match that of Cr_2O_3 , further indicating that the primary valence states of V and Cr are +3, consistent with the XPS results. Extended X-ray absorption fine structure (EXAFS) spectroscopy was then used to further analyze the local coordination environments. Wavelet-transform (WT) analysis of the k^2 -weighted EXAFS signals shows that the first-shell feature of the V K-edge at approximately 1.5 Å is assigned to V-O coordination, whereas the first coordination shell of the Cr K-edge is attributed to Cr-O scattering (**Figs. 2(f)-2(h)**, **Figs. S11-S12** in the ESM). The structural parameters obtained from least-squares EXAFS fitting are summarized in Tables S2-S3. Notably, Compared with NVCP, the Debye-Waller factors of both V-O and Cr-O in NVCMP markedly reduced, indicating that Mo substitution effectively suppresses the local structural disorder around V and Cr. In addition, the first-shell coordination numbers in NVCMP are increased and approach ideal octahedral coordination, further indicating that the first coordination shell around V/Cr is more complete and ordered. These results collectively demonstrate that Mo doping effectively modulates the local coordination environment of V and Cr, making the V-O and Cr-O coordination more regular and the $(\text{V/Cr})\text{O}_6$ octahedral framework more stable, which is consistent with the enhanced first-shell EXAFS amplitudes.

We further compared the overall electronic states, charge distribution, and electronic conductivity of NVCP and NVCMP, and evaluated the influence of orbital regulation on their rate capability. As shown in **Figs. 3(a)-3(b)**, the electronic states near the Fermi level are mainly contributed by transition-metal and O orbitals. The Mo-derived states shift the conduction-band minimum of NVCMP toward the Fermi level, reducing the band gap to 0.96 eV, substantially lower than that of NVCP (1.73 eV). The differential charge-density results show more pronounced electron accumulation and depletion around Mo and the neighboring transition-metal-O coordination environments in NVCMP, indicating enhanced local charge redistribution that is favorable for electron transport through the framework (**Figs. 3(c)-3(d)**). This electronic-structure modulation is directly reflected in the improved electronic conductivity. As shown in **Fig. 3(e)**, four-probe measurements reveal that the electronic of NVCMP is two orders of magnitude higher than that of NVCP over the tested pressure range. This significantly enhanced electron transport rate can effectively reduce electrochemical polarization during charging and

discharging, enabling more active material to participate in electrochemical reactions and significantly improving the initial specific capacity and rate performance. As shown in **Fig. 3(f)**, NVCMP consistently delivers a higher discharge specific capacity than NVCP at all current densities. Specifically, the specific discharge capacity of NVCMP is 105.2, 82.7, 72.3, 65.6, 59.0, 48.2, 36.0 mAh g^{-1} at 0.1, 0.2, 0.5, 1, 2, 5, and 10 C, respectively, while NVCP delivers only 87.3, 68.2, 61.3, 50.7, 38.5, 19.4, and 10.4 mAh g^{-1} under the same conditions. NVCMP delivers a discharge specific energy of 377.8 Wh kg^{-1} at 0.1 C, corresponding to an average discharge voltage of 3.59 V, significantly higher than the values of 312 Wh kg^{-1} and 3.57 V for NVCP (**Fig. 3(g)**). With increasing current density, both the energy density and average discharge voltage of NVCP decrease rapidly, whereas the corresponding decay in NVCMP is markedly suppressed. The discharge profiles at different current densities further reveal this difference (**Figs. 3(h)-3(i)**). As the rate increases, NVCP exhibits an increasingly pronounced voltage drop at the beginning of discharge, accompanied by a progressive downward shift and shortening of the discharge plateaus. In particular, the high-voltage plateau associated with the $\text{V}^{4+}/\text{V}^{5+}$ redox couple is significantly attenuated and nearly disappears at 2 C, indicating that the increasingly severe polarization under high-rate conditions limits the full utilization of the high-voltage redox reaction. This behavior may be associated with the relatively low electronic conductivity of NVCP, which hinders rapid electron transport at high current densities and consequently aggravates voltage polarization. In contrast, the substantially enhanced electronic conductivity of NVCMP effectively mitigates polarization, resulting in a smaller voltage drop and the retention of a distinct high-voltage plateau even at 5 C.

COHP and ELF analyses further reveal the influence of Mo substitution on local chemical bonding and structural stability. As shown in **Figs. 4(a)-4(b)**, the integrated COHP (ICOHP) values of the V-O and Cr-O bonds in NVCP are -2.53 and -2.57 eV, respectively, while the corresponding values in NVCMP are -2.51 and -2.58 eV, indicating that Mo substitution does not significantly alter the bonding strengths of V-O and Cr-O. Notably, the newly formed Mo-O bond in NVCMP exhibits a more negative ICOHP value of -3.62 eV, indicating a stronger bonding interaction than those of V-O and Cr-O and thus favoring enhanced local structural rigidity. Subsequent ELF analysis (**Fig. 4(c)**) shows more pronounced electron localization around Mo in NVCMP, consistent with the COHP results. This strengthened local bonding is beneficial for maintaining structural stability during repeated Na^+ insertion/extraction, thereby contributing to the superior cycling performance of NVCMP. As shown in **Fig. 4(d)**, NVCMP retains 86.7% of its initial capacity after 500 cycles at 5C, markedly higher than the 68.8% retention of

NVCP. Meanwhile, NVCMP exhibits lower energy loss during cycling and a higher average energy efficiency than NVCP (Fig. 4(e)). Figure 4(f) further compares the overall electrochemical performance of the two materials, where the discharge specific capacity, discharge specific energy, and average discharge voltage are derived from the first cycle at 0.1C, while the capacity retention and energy efficiency are taken after 100 cycles at 5C. NVCMP exhibits clear advantages across all these metrics. In addition, cyclic voltammetry (CV) tests conducted over a range of scan rates and galvanostatic intermittent titration technique (GITT) measurements were employed to evaluate the Na^+ transport kinetics of the two materials. As shown in Figs. S13(a)-13(b), both materials exhibit two

well-defined pairs of redox peaks at low scan rates, located at approximately 3.4 and 4.0 V, corresponding to the $\text{V}^{3+}/\text{V}^{4+}$ and $\text{V}^{4+}/\text{V}^{5+}$ redox couples, respectively. With increasing scan rate, both redox couples remain clearly distinguishable for NVCMP, whereas the high-voltage redox peak around 4.0 V becomes markedly weaker for NVCP. Compared with NVCP, NVCMP also exhibits sharper and more symmetric redox peaks with smaller peak-to-peak separations, indicating lower electrochemical polarization and faster reaction kinetics. The linear dependence of the peak current on the square root of the scan rate (Figs. S13(c)-13(d)) indicates pronounced diffusion-controlled characteristics of Na^+

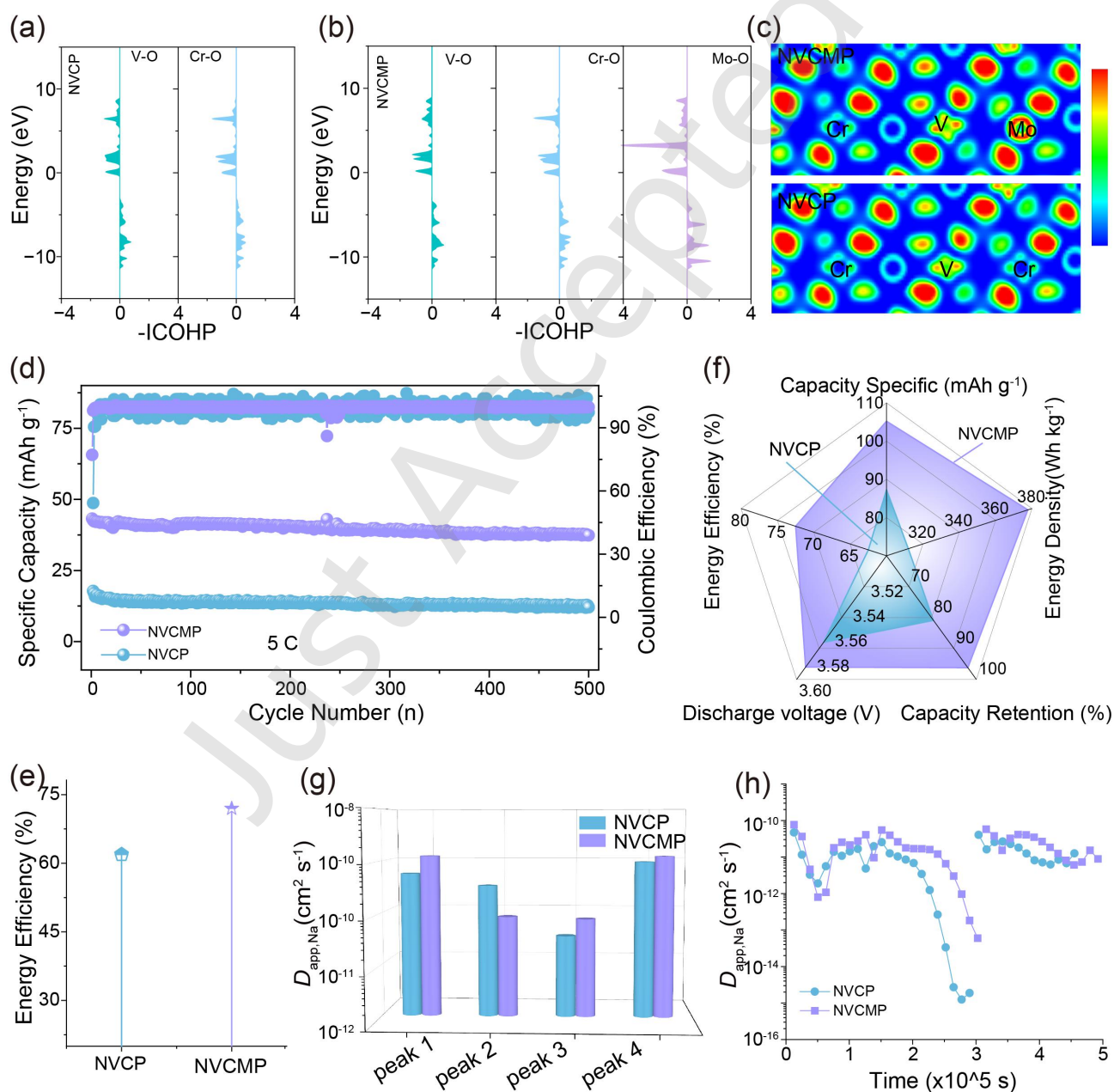


Figure 4 COHP analysis of (a) NVCP and (b) NVCMP. (c) ELF of NVCP and NVCMP. (d) Cycle performance at 5C. (e) The corresponding average energy efficiency during the cycle process. (f) Radar chart comparing the overall performance of NVCP and NVCMP. Diffusion coefficients

calculated from (g) multi-scan-rate CV and (h) GITT.

insertion/extraction. The apparent Na^+ diffusion coefficients ($D_{\text{app, Na}}$) calculated using the Randles-Sevcik equation further demonstrates faster Na^+ kinetics in NVCMP (Fig. 4(g)). GITT measurements further confirm this trend (Fig. 4(h), Figs. S14-S15 in the ESM). During the charge/discharge process, the average $D_{\text{app, Na}}$ of NVCMP reaches $2.15 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$, higher than $1.2 \times 10^{-11} \text{ cm}^2 \text{ s}^{-1}$ for NVCP.

In situ EIS was performed to gain deeper insight into Na^+ transport across the electrode interface and within the bulk during cycling. Figure S16 in the ESM shows the

Nyquist plots collected at different potentials. For both materials, the impedance spectra consist mainly of a semicircle and an inclined line, corresponding to the charge-transfer and diffusion processes, respectively. During charging, the impedance of both electrodes gradually decreases and then increases again upon discharge. However, NVCMP exhibits a markedly smaller variation in impedance than NVCP, indicating a more stable interfacial and bulk response throughout the electrochemical process. However, owing to the complex microstructure of the electrodes, the characteristic

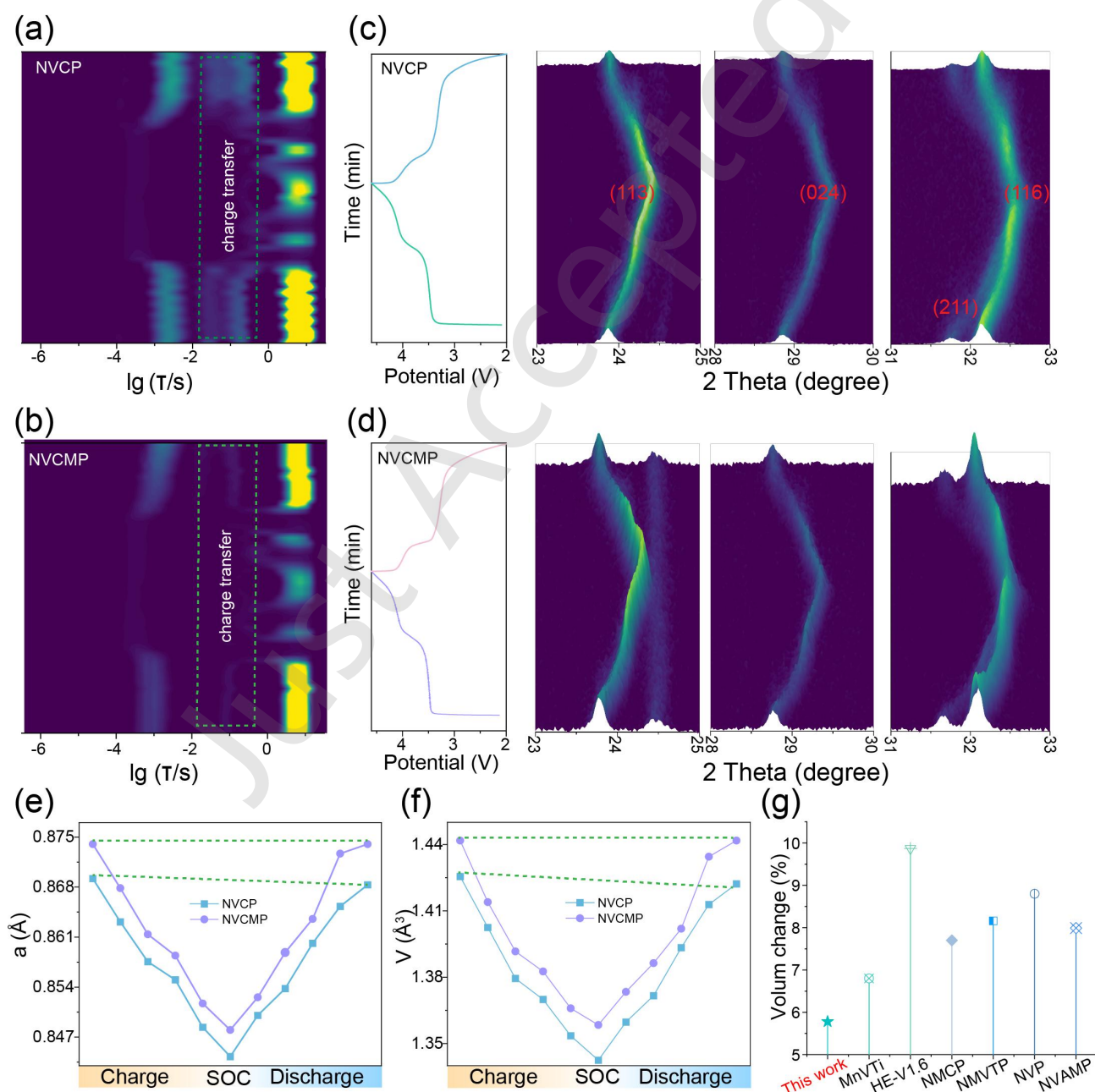


Figure 5 2D DRT contour maps derived from in situ EIS for (a) NVCP and (b) NVCMP. In-situ XRD contour plots and the corresponding GCD curves of (c) NVCP and (d) NVCMP. Evolution of (e) the lattice parameter a and (f) the unit-cell volume during the charge/discharge process. (g)

Comparison of volume changes in NVCMP with other reported cathodes.

frequencies of processes such as electronic conduction, ionic migration, physical contact, activation, and concentration polarization tend to overlap, making it difficult to deconvolute these processes solely through Nyquist plots. To address this limitation, the frequency-domain impedance spectra were transformed into the time domain using the distribution of relaxation times (DRT) technique, thereby enabling the identification of distinct electrochemical processes via characteristic peaks at different relaxation times. As shown in **Figs. 5(a)-5(b)** and **Fig. S17** in the ESM, three groups of characteristic peaks are clearly resolved in the DRT spectra. The peaks in the relaxation time range of 10^{-4} to 10^{-2} s are assigned to Na^+ transport at the electrode/electrolyte interface, those between 10^{-2} and 100 s correspond to charge transfer, and those in the range of 100 to 10^2 s are associated with Na^+ diffusion within the bulk material.[30] Throughout the entire charge/discharge process, the intensities of all three DRT peak groups are lower for NVCMP than for NVCP, with the most pronounced difference observed for the charge-transfer process, indicating reduced charge-transfer resistance and enhanced interfacial reaction kinetics in NVCMP.

In situ XRD analysis was conducted to investigate the sodium storage mechanism during the electrochemical process. **Figs. 5(c)-5(d)** present the charge/discharge voltage profiles of NVCP and NVCMP together with the corresponding three-dimensional contour plots of the (113), (024), (211), and (300) reflections during cycling, all of which can be indexed to the R-3c space group. For NVCP, the (113), (024), and (300) reflections gradually shift toward higher angles during charging and return toward lower angles during discharge. These peaks exhibit only continuous shifts, without the disappearance of existing peaks or the emergence of diffraction peaks, indicating a typical single-phase solid-solution reaction[31]. In contrast, the (211) reflection disappears and subsequently reappears, suggesting a phase-transition process associated with a two-phase reaction mechanism[32]. These results indicate that the sodium-storage process of NVCP involves the coexistence of solid-solution and two-phase reaction mechanisms. NVCMP exhibits a similar evolution of the diffraction peaks, indicating that Mo substitution does not alter the overall sodium-storage mechanism. Notably, the diffraction peaks of NVCP undergo more pronounced broadening during charge/discharge, whereas those of NVCMP remain more concentrated, indicating a more homogeneous structural evolution with lower lattice strain. This is further corroborated by the stacked XRD patterns in **Fig. S18** in the ESM. The evolution of lattice parameters as a function of the state of charge (SOC) is shown in **Figs. 5(e)-5(f)**. During charging, Na^+ ions are extracted from the cathode, accompanied by a gradual

decrease in the a -axis parameter, which reaches its minimum at the fully charged state. Upon discharge, Na^+ reinsertion leads to a gradual recovery of the a -axis parameter. The unit-cell volume follows a similar trend. Benefiting from the stable Mo-O bonding environment, NVCMP exhibits a volume change of 5.78% during cycling, slightly lower than that of NVCP (5.83%). Although the difference in volume strain between the two materials is not substantial, the volume change of NVCMP is fully reversible upon discharging, returning to its initial state, while NVCP shows a certain degree of irreversible deviation (dashed lines in Figures 5e-5f), indicating superior reversible structural stability for NVCMP. Furthermore, compared with other reported NASICON-type cathode materials, NVCMP demonstrates a favorable level of unit-cell volume strain (**Fig. 5(g)**)[33-38].

Finally, to evaluate the practical feasibility of NVCMP, we systematically assessed its wide-temperature adaptability. As shown in **Fig. 6(a)**, at high temperature of 50 °C, NVCMP retains 81.5% of its initial capacity after 200 cycles at 5C, significantly outperforming NVCP (55.6%), indicating that Mo incorporation effectively enhances structural stability at high temperatures. Moreover, NVCMP exhibits superior low-temperature performance. At -40 °C, it delivers a high initial discharge capacity of 82.1 mAh g^{-1} at 0.1C and maintains 62.1 mAh g^{-1} even at 1C (**Fig. S19** in the ESM). In contrast, NVCP achieves only 61.2 mAh g^{-1} at 0.1C, with a rapid decline to 37.2 mAh g^{-1} at 1C. After 100 cycles at 0.5C, NVCMP retains 52.1 mAh g^{-1} corresponding to a capacity retention of 82.7%, considerably higher than that of NVCP (65.4%, **Fig. S20** in the ESM). At -60 °C, NVCMP still delivers a discharge capacity of 62.4 mAh g^{-1} (**Fig. S21** in the ESM). **Figure 6(b)** summarizes the capacity retention of NVCMP at various temperatures relative to its room-temperature capacity, demonstrating outstanding wide-temperature adaptability. Compared with previously reported phosphate-based cathode materials, NVCMP exhibits a broader operating temperature range (**Fig. 6(c)**) [39-43]. To further assess its practical applicability, NVCMP was paired with pre-sodiated commercial hard carbon (HC) to construct a full cell (NVCMP//HC). We first evaluated the electrochemical performance of HC anode. As shown in **Fig. S22** in the ESM, the HC half-cell delivers a reversible charge capacity of 290.3 mAh g^{-1} at 0.1 C, providing sufficient sodium-storage capacity for matching the NVCMP cathode in the full-cell configuration. The working principle of the full cell is illustrated in **Fig. 6(d)**. During charging, Na^+ ions are extracted from the NVCMP cathode and inserted into the HC anode, with electrons flowing from the cathode to the anode through the external circuit; the reverse process occurs during discharging. **Figure 6(e)** shows the rate performance of the NVCMP//HC full cell, which delivers an initial discharge specific capacity of

103.7 mAh g⁻¹ at 0.1C and maintains stable operation over a range of rates. The corresponding discharge profiles retain well-defined voltage plateaus (Fig. 6(f)). Moreover, the NVCMP//HC full cell exhibits excellent cycling stability, retaining 80.9% of its initial capacity after 800 cycles at 1C (Fig. 6(g)). Clear discharge plateaus remain visible with prolonged cycling, further demonstrating its good cycling stability. The full cell was also able to power an LED, highlighting its practical application potential (inset of Fig. 6(g)). Based on the cathode mass, the NVCMP//HC full cell delivers a discharge specific energy of 370.2 Wh kg⁻¹ with an average operating voltage of 3.57 V, showing advantages in specific capacity, operating voltage, and specific energy over previously reported full cells employing HC anodes (Fig. 6(h)) [44-55].

3 Conclusion

In conclusion, regarding the issue that the capacity of NVCP is much lower than the theoretical value, this work investigated its intrinsic electronic-structure

characteristics and their influence on electron transport. PDOS results reveal that the effective coupling between the V 3d and Cr 3d electronic states in NVCP is weak, accompanied by weak V/Cr 3d-O 2p orbital hybridization, which impedes electron transport within the framework and limits the capacity release. To tackle this issue, we propose a "coupling network modulation" strategy. Specifically, Mo⁶⁺ with a 4d⁰ empty orbital was employed as an orbital probe to perform trace substitution at the V and Cr sites. A series of theoretical calculations and experimental characterizations demonstrate that Mo⁶⁺ doping at the Cr site can more effectively enhance the coupling between the V and Cr 3d orbitals and the V/Cr 3d-O 2p hybridization. The optimized NVCMP exhibits a two-orders-of-magnitude increase in electronic conductivity, significantly facilitating electron transport. COHP and ELF analyses indicate that Mo-O bonds exhibit stronger bonding capability than V-O and Cr-O bonds, while XAFS further confirms that NVCMP shows reduced

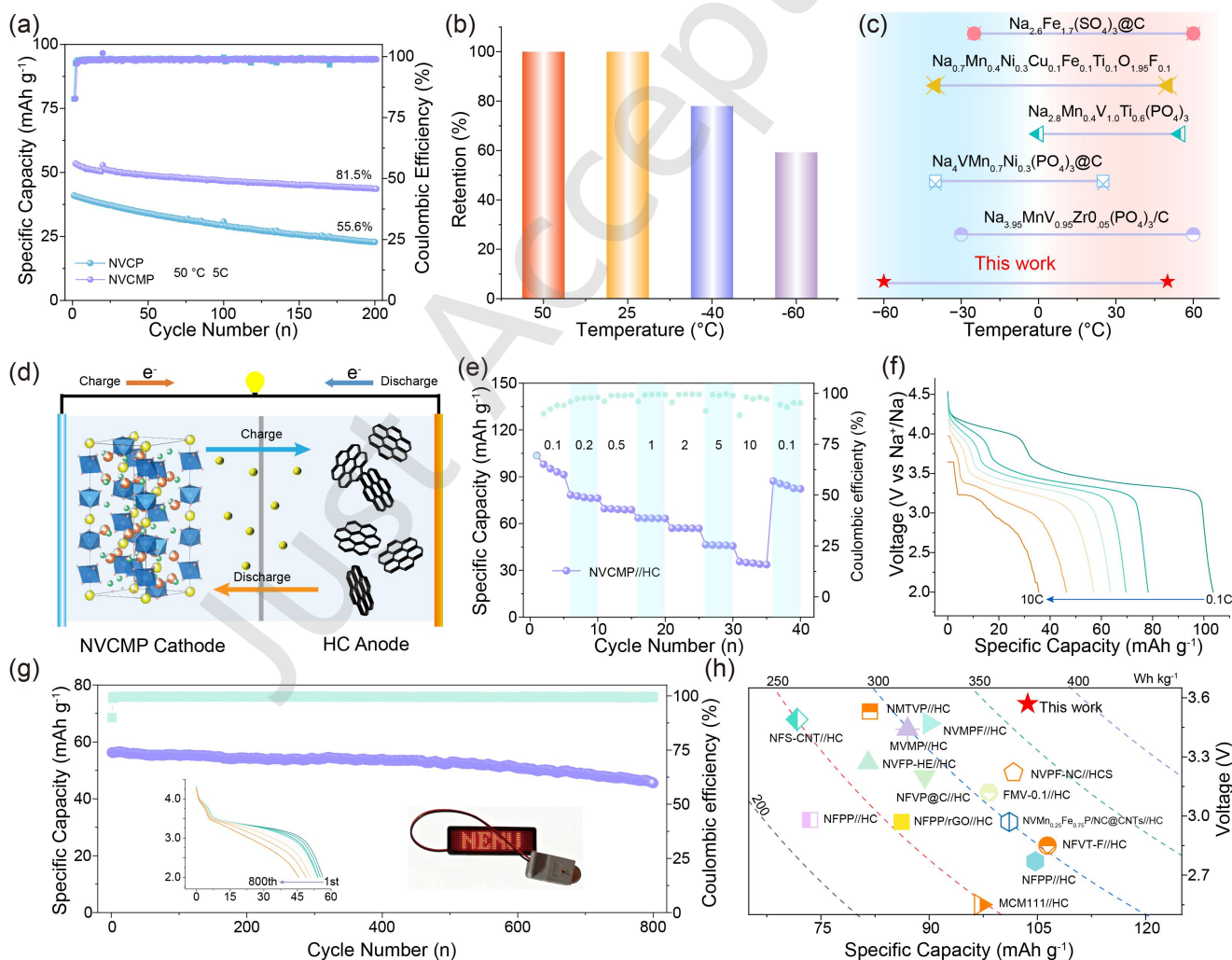


Figure 6 (a) High-temperature cycling performance. (b) Capacity retention rate at different temperatures compared to 25 °C. (c) Comparison with the temperature adaptability of the reported cathode materials. (d) Schematic diagram of the full battery working principle. (e) The rate performance of the NVCMP//HC full cell. (f) Corresponding discharge curves at different rates. (g) The cycling performance of the NVCMP//HC full cell (discharge curves at various cycle numbers, along with an LED powered by the full cell). (h) Comparisons of voltage, capacity, and energy

density with other reported SIBs full cells.

local structural disorder, contributing to improved structural stability during cycling. Consequently, the initial discharge specific capacity of NVCMP at 0.1C increases from 87.3 to 105.2 mAh g⁻¹, while retaining 86.7% of its capacity after 500 cycles at 5C under room-temperature, and well performances over a wide temperature range from -60 to 50 °C. The NVCMP//HC full cell delivers an energy density of 370 Wh kg⁻¹ (based on the cathode mass), together with excellent cycling stability. This work reveals that effective coupling between orbitals of different elements significantly influences electronic conductivity, thereby limiting capacity utilization, and demonstrates that electronic regulation can effectively enhance electron transport kinetics and electrochemical performance, offering a new design strategy for high-performance high-voltage cathodes.

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Electronic Supplementary Material

Coupling Network Reconstruction-Driven Charge Transport Transition: Capacity Breakthrough and Wide-Temperature Sodium Storage in $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ Cathodes

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1. Experimental Section

1.1 Materials synthesis

$\text{Na}_{2.91}\text{V}_{0.97}\text{Mo}_{0.03}\text{Cr}(\text{PO}_4)_3$ (NVMCP) and $\text{Na}_{2.91}\text{VCr}_{0.97}\text{Mo}_{0.03}(\text{PO}_4)_3$ (NVCMP) was synthesized via a sol-gel method and solid-phase ball milling process. CH_3COONa , NH_4VO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MoO_3 , $\text{NH}_4\text{H}_2\text{PO}_4$ and $\text{C}_6\text{H}_{10}\text{O}_8$ were used as sources for sodium, vanadium, chromium, molybdenum, phosphorus and carbon, and all chemical reagents were employed without further purification, respectively. The specific preparation process is as follows: First, NH_4VO_3 , $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, MoO_3 were dissolved into deionized water according to calculated stoichiometric ratio to form solution A. Next, $\text{C}_6\text{H}_{10}\text{O}_8$ was added to water to dilute, forming solution B. Solution B was then gradually added to solution A and continuously stirred in an 80 °C water bath. Following thorough stirring, $\text{NH}_4\text{H}_2\text{PO}_4$ and CH_3COONa solutions were added dropwise in turn. The mixture was stirred continuously at 80 °C until gelation occurred. The resulting gel was vacuum-dried at 100 °C for 12 hours, ground and then heated in an argon atmosphere at 400 °C for 4 hours. Finally, ground and then heated in an argon atmosphere at 800 °C for 8 hours with a temperature increase rate of 5 °C min⁻¹. For comparison, the $\text{Na}_3\text{VCr}(\text{PO}_4)_3$ (NVCP) composite was prepared using the same procedure without MoO_3 .

1.2 Materials characterization

X-ray diffraction (XRD) patterns were recorded with a Bruker D8 Advance Diffractometer, employing Cu K α radiation over a 2 θ range of 10-80°. The morphology and elemental distribution on the material surface were analyzed using a Scanning electron microscopy (SEM, Hitachi SU 8000) and a High-resolution transmission electron microscopy (HR-TEM, JEOL-2100F). The functional groups on material surfaces were determined by Fourier-transform infrared spectroscopy (FT-IR, Thermo Nicolet IS 5, USA). Thermogravimetric (TG) curves were measured using a simultaneous thermogravimetry-differential scanning calorimetry (TG-DSC) instrument (STA 409C) in air, and the carbon content was calculated from the weight loss due to carbon combustion. The valence states of transition metal elements were determined by X-ray photoelectron spectroscopy (XPS, VG Scientific ESCALab 220i-XL), with all XPS data calibrated based on the 284.8 eV peak of C 1s. The electrical conductivity of the materials was tested by High resistance weak current tester (ST2643). X-ray near-edge absorption spectra (XANES) were obtained using X-ray fine structure (XAFS) analysis (Anhui Absorption Spectroscopy Instrument Co., Ltd.) to analyze changes in the local coordination environment and electronic structure.

2. Electrochemical measurement

All CR2032 coin cells were assembled in an argon-filled glovebox with H_2O and O_2 levels below 0.1 ppm. The cathode material, conductive carbon black (C45), and carboxymethyl cellulose (CMC) were mixed in a mass ratio of 7:2:1. After thorough grinding, an appropriate amount of deionized water was added. The uniformly mixed slurry was coated onto carbon-impregnated aluminum foil and dried in a vacuum oven at 60 °C to produce the cathode electrode sheet. The electrode sheet was cut into circular discs with a diameter of 12 mm, each with an active material loading of approximately 2 mg cm⁻². The half-cells were assembled using metallic sodium as the counter electrode. Whatman glass fiber was used as the separator. The electrolyte was 1 M NaClO_4 dissolved in a mixed solvent of propylene carbonate (PC) and ethylene carbonate (EC) with a volume ratio of 1:1, containing 5 vol% fluoroethylene carbonate (FEC) as an additive. It should be noted that for tests below room temperature, the electrolyte was composed of 0.8 M NaPF_6 in a mixture of diethylene glycol dimethyl ether and 1,3-dioxolane with a volume ratio of 8:2.

The full cells were assembled using the NVCMP cathode and Hard carbon (HC) anode. The HC electrodes were composed of 80 wt% HC, 10 wt% CMC. And 10 wt% C45, with water used as the solvent. To achieve an appropriate capacity balance, the capacity of HC anode was slightly overmatched, with a capacity ratio of approximately 1.2:1 relative to the NVCMP cathode. Before cell assembly, the HC anode was pre-sodiated using a direct-contact method. Specifically, 60 μL of electrolyte was dropped onto the surface of a sodium-metal foil, after which the HC anode was placed flat on the sodium foil to ensure intimate and complete contact between the sodium metal and the HC electrode. The HC electrode was maintained in this configuration for 10 h to complete the pre-sodiation process.

Electrochemical performance was evaluated using a battery test system (LAND CT2001 and NEWARE CT-4000). The Cyclic voltammetry (CV) curves were recorded at scan rates of 0.1-1.0 mV s⁻¹ using an electrochemical workstation (CHI660). Electrochemical impedance spectroscopy (EIS) was

performed using the Princeton Applied Research P2000 workstation, with a frequency range of 0.1 to 106 Hz with a perturbation amplitude of 10 mV. The Galvanostatic intermittent titration technique (GITT) was performed following two activation cycles at 0.1 C, with a single drop charging time of 30 minutes and a relaxation time of 3 hours. The voltage range is 2-4.6 V.

3. Calculation Section

3.1 Calculation of Na⁺ diffusion coefficient

After conducting CV tests at various scan rates ranging from 0.1 to 1 mV s⁻¹, the apparent sodium ion diffusion coefficient ($D_{app,Na}$) was calculated using the Randles-Sevcik equation[1,2].

$$I_p = 2.69 \times 10^5 \cdot n^{3/2} \cdot A \cdot D_{app,Na}^{1/2} \cdot C_0 \cdot \nu^{1/2}$$

Where I_p is the peak current, n is the number of transferred electrons, A is the area of the electrode, C_0 is the concentration of Na⁺, and ν is the scan rate.

In addition, $D_{app,Na}$ can also be calculated using the GITT test based on the following formula[3,4]:

$$D_{app,Na} = \frac{4}{\pi\tau} \left(\frac{m_B V_M}{M_B S} \right)^2 \left(\frac{\Delta E_S}{\Delta E_\tau} \right)^2 \quad (\tau \ll \frac{L^2}{D})$$

Where τ corresponds to the constant current pulse time; m_B , V_M and M_B are the mass, molar volume and molar mass of the active material, respectively; S is the area of the electrode; ΔE_S is the voltage change between two consecutive steady-state potentials after relaxation, and ΔE_τ is the voltage change during a single titration step.

3.2 Theoretical calculation

The DFT calculations were performed using the Vienna ab-initio simulation package (VASP) software[5,6]. The projector augmented wave (PAW) methodology was utilized to describe the electron-core interactions[7]. The Perdew-Burke-Ernzerhof (PBE) formation of generalized gradient approximation(GGA) was employed to treat electron exchange and correlation[8]. A plane wave cutoff energy of 520 eV was used for total energy calculations, where the force convergence and the electronic self-consistent convergence were set to 0.01 eV/Å and 1×10^{-5} eV/atom, respectively. The van der Waals forces were corrected using DFT + D3. For computational procedures, Brillouin zone integration was implemented with $3 \times 3 \times 1$ Gamma-centre k-point sampling. Partial occupancy of V, Cr and Mo Coulombic interaction (DFT+U) was applied to the transition elements, employing a U-J value of 3.5 eV, 2.0 eV and 3.0 eV, respectively.

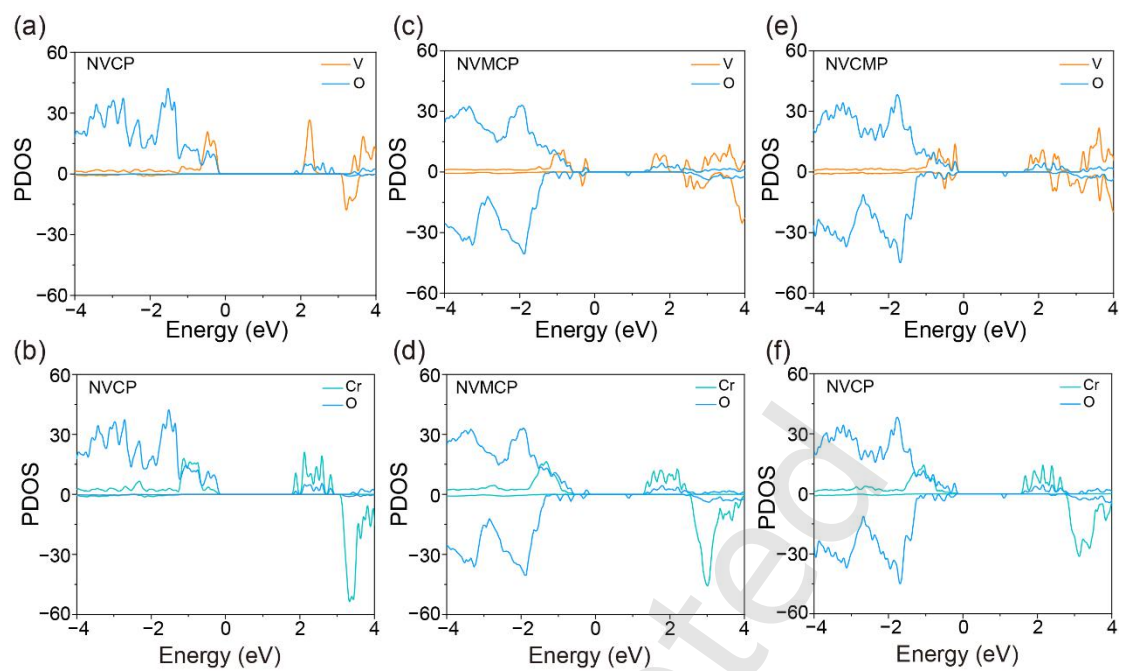


Figure S1. PDOS for the V3d-O2p and Cr3d-O2p orbitals: (a, b) NVCP, (c, d) NVMCP, and (e, f) NVCMP.

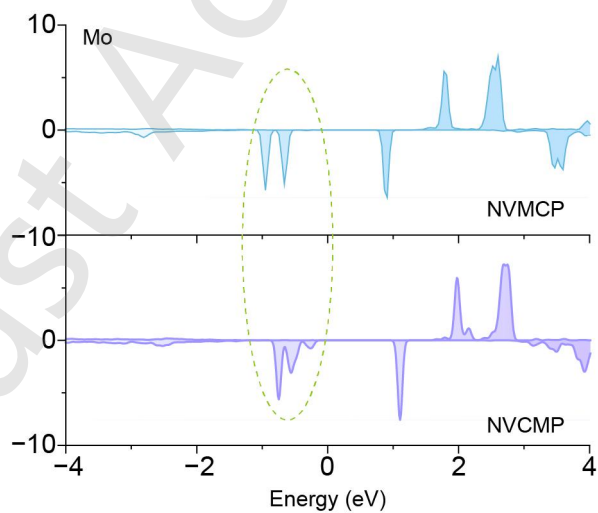


Figure S2. The 4d orbital PDOS of Mo in NVMCP and NVCMP.

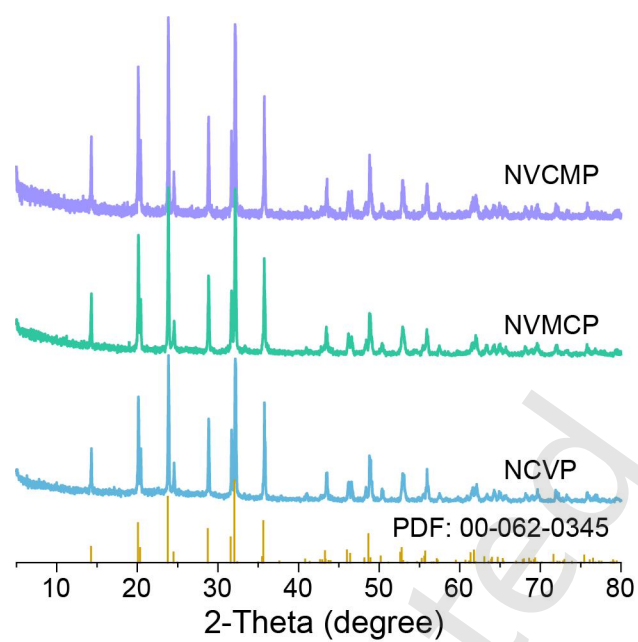


Figure S3. XRD patterns of NVCMP, NVMCP and NVCMP powder.

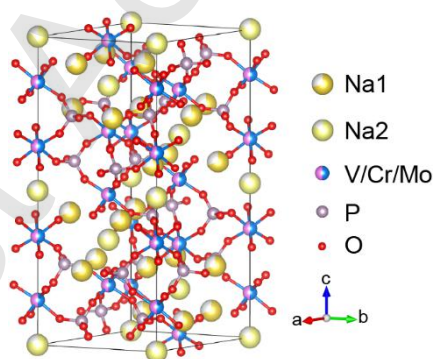


Figure S4. The crystal structure diagram of NVCMP.

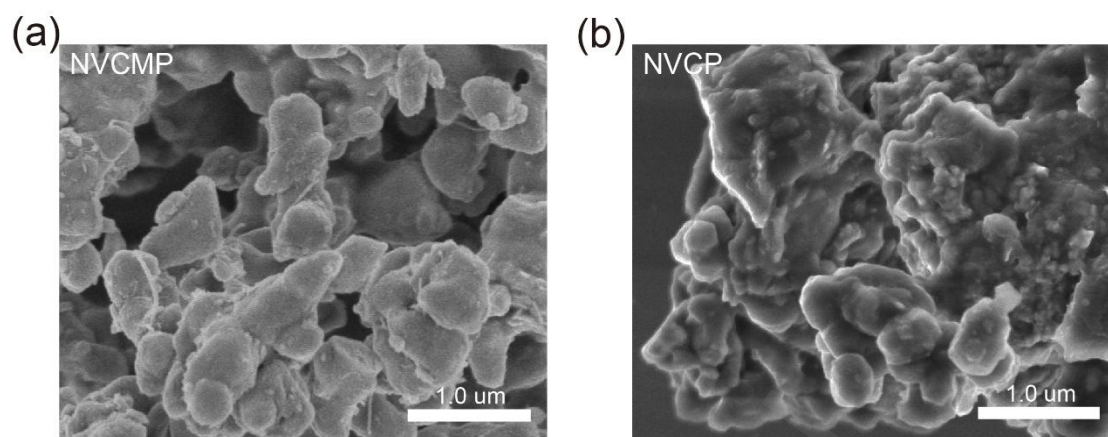


Figure S5. The SEM images of (a) NVCMP and (b) NVCP.

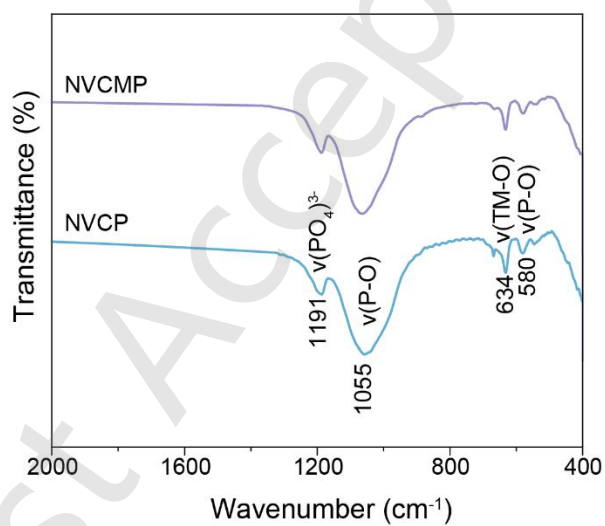


Figure S6. FT-IR spectra of NVCP and NVCMP.

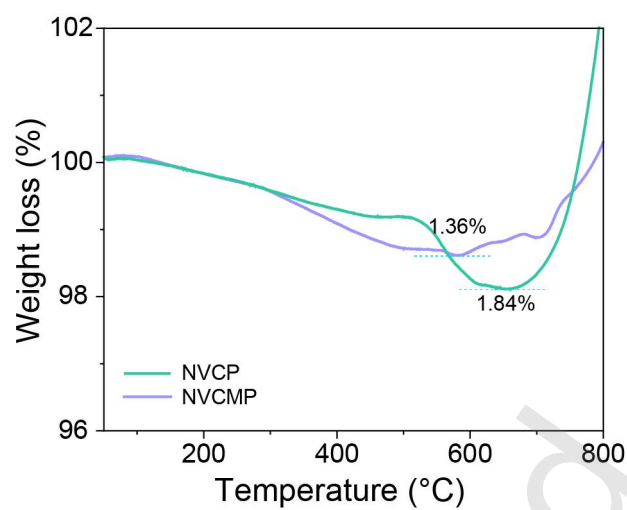


Figure S7. TG curve of NVCP and NVCMP.

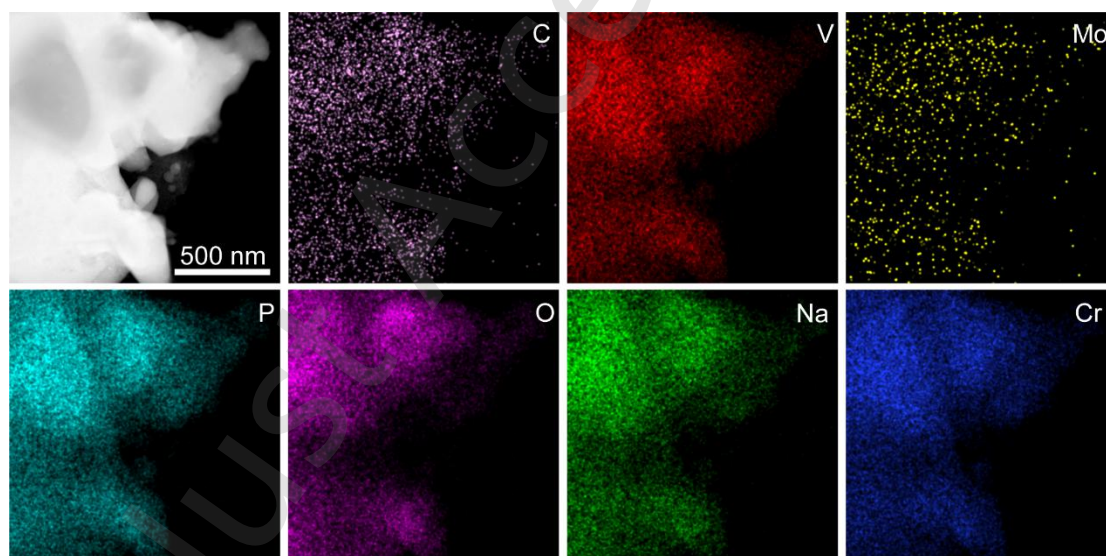


Figure S8. EDS mapping images of NVCMP.

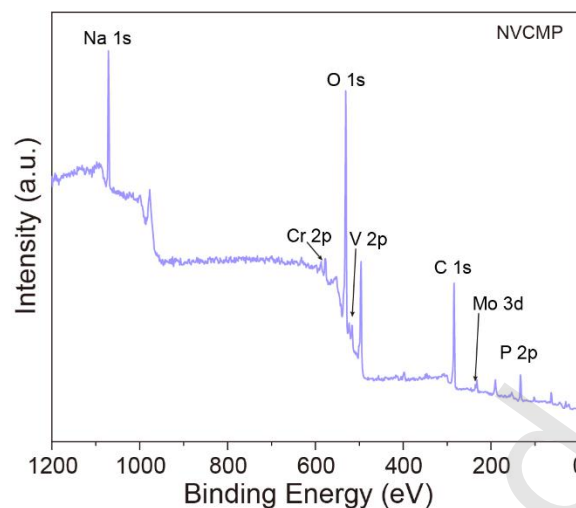


Figure S9. XPS survey spectrum of NVCMP material.

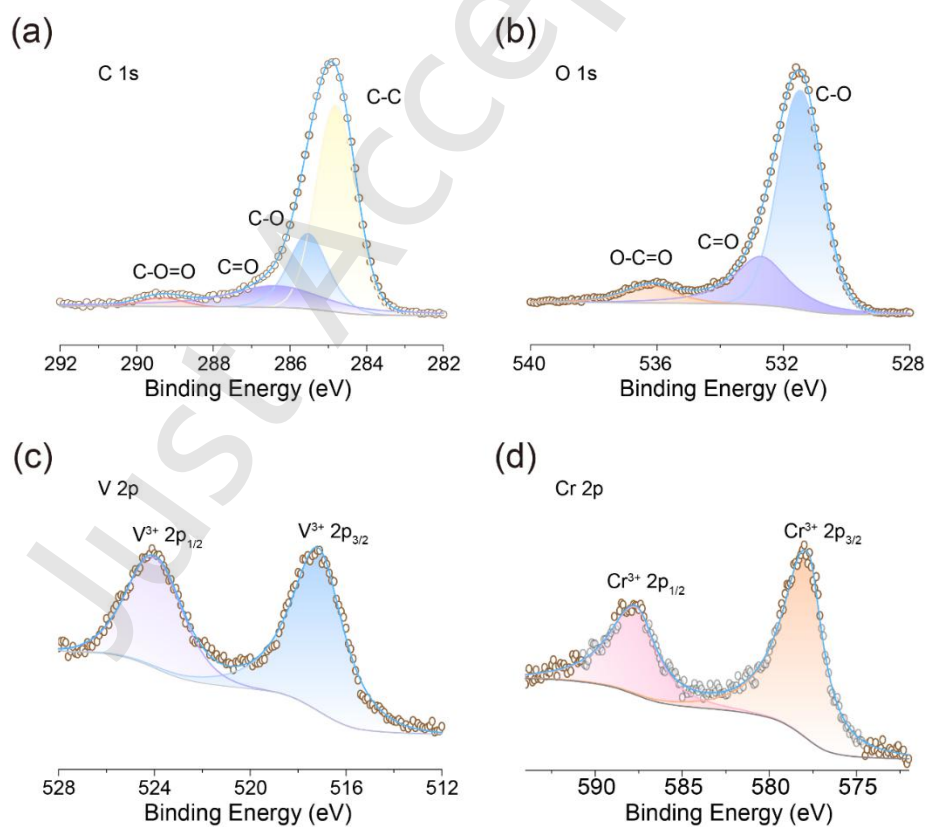
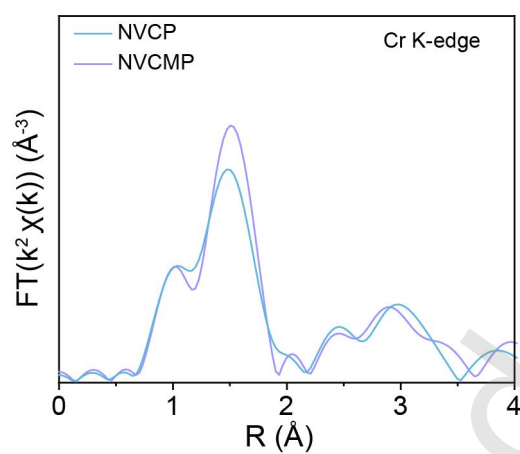


Figure S10. The high-resolution XPS spectra of NVCMP. (a) C 1s, (b) O 1s, (c) V 2p, (d) Cr 2p.

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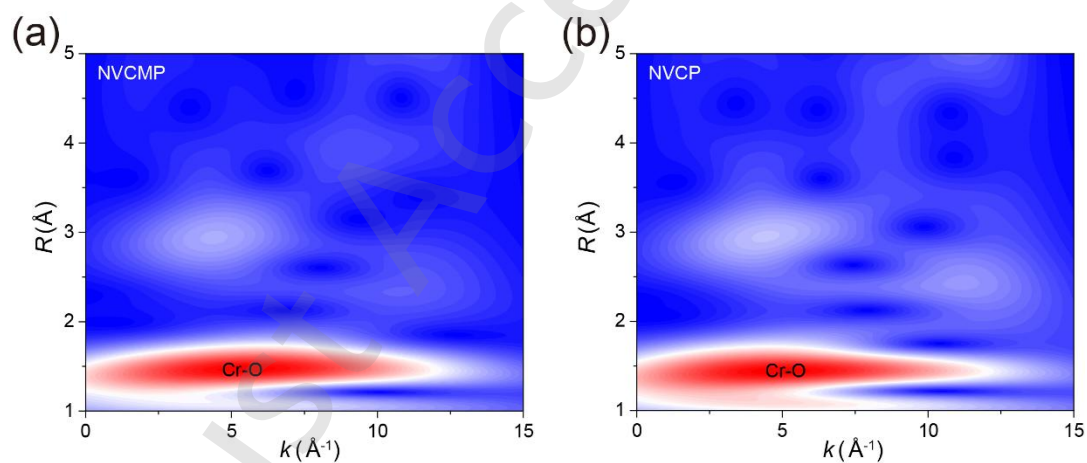


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3 **Figure S11.** Fourier transform of the EXAFS in the R space from Cr K-edge.

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7 **Figure S12.** Wavelet transform analysis at the V K-edge for (a) NVCMP and (b) NVCP.

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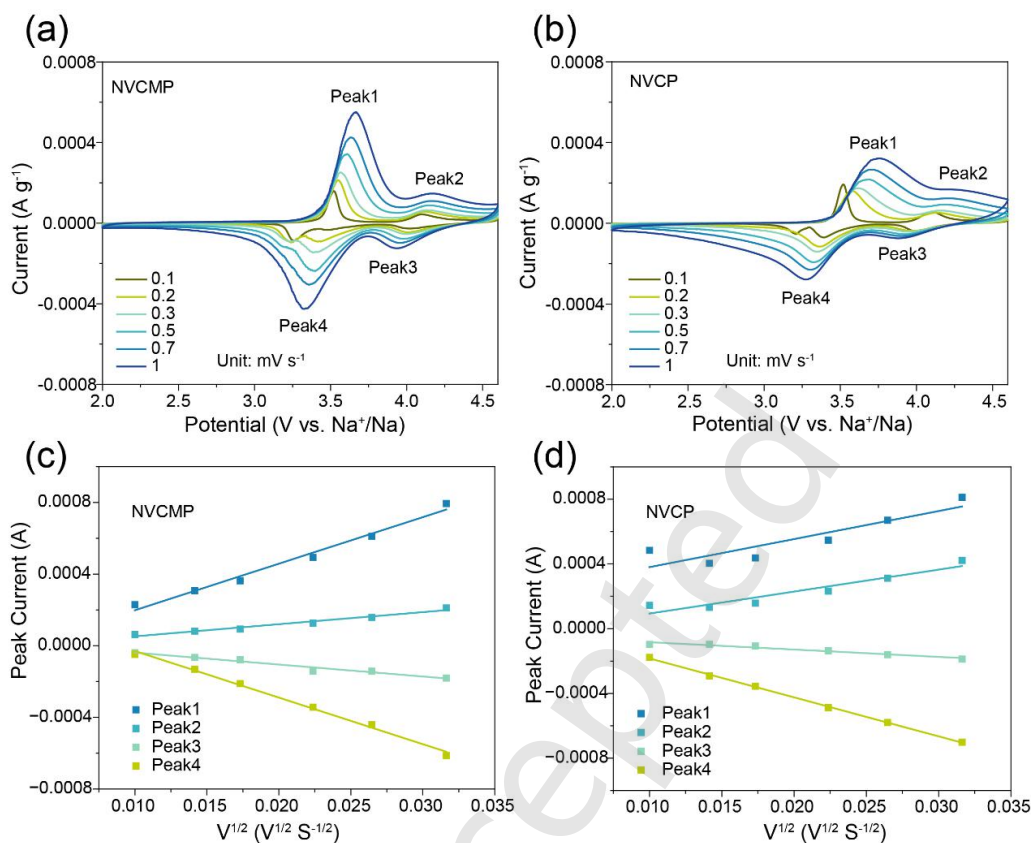


Figure S13. Multi-sweep rates CV curves of (a) NVCMP and (b) NVCP. The linear fit curves of I_p versus $v^{1/2}$ of (c) NVCMP and (d) NVCP.

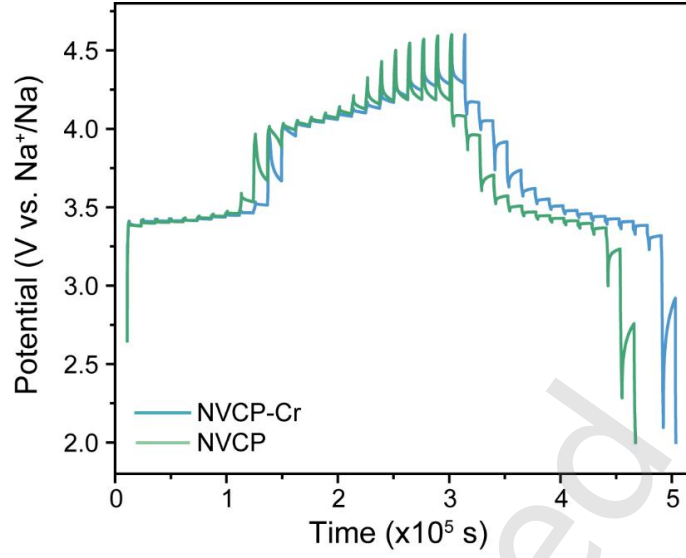


Figure S14. GITT curves of NVCMP and NVCP at 0.1 C.

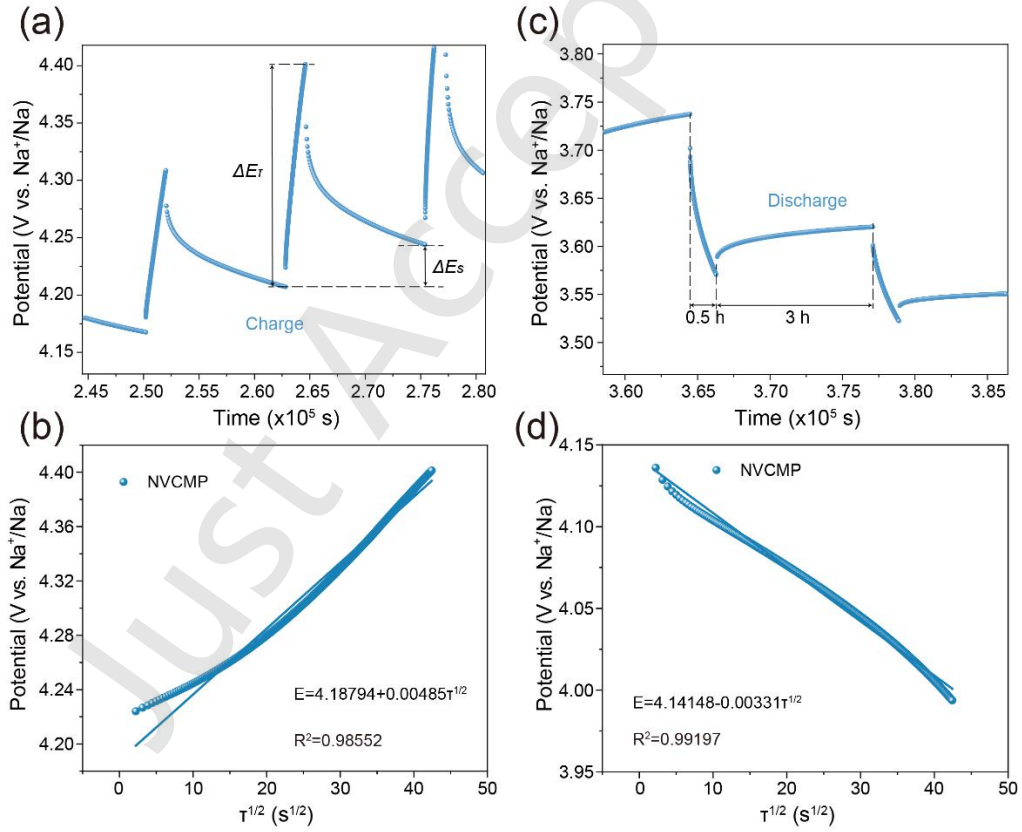


Figure S15. τ -E profiles during a single GITT process and linear fittings of E against $\tau^{1/2}$ for the NVCMP half-cell: (a, c) charging process; (b, d) discharging process.

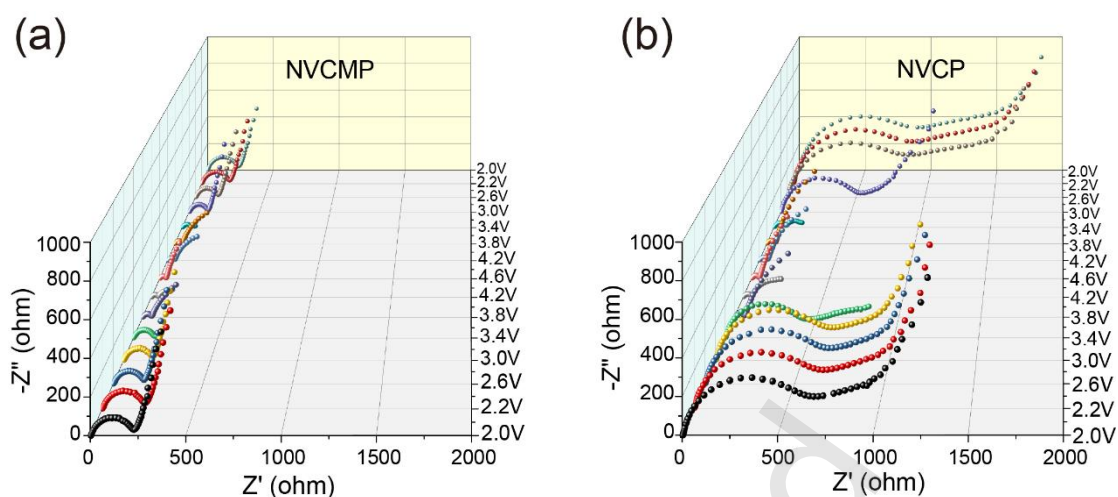


Figure S16. The Nyquist plots of (a) NVCMP and (b) NVCP at different voltages.

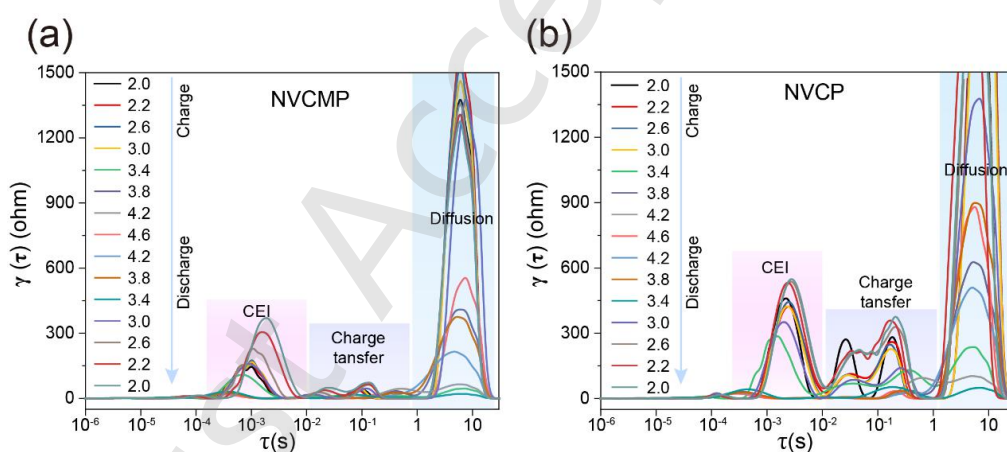


Figure S17. The DRT obtained by deconvolution EIS for (c) NVCMP and (d) NVCP.

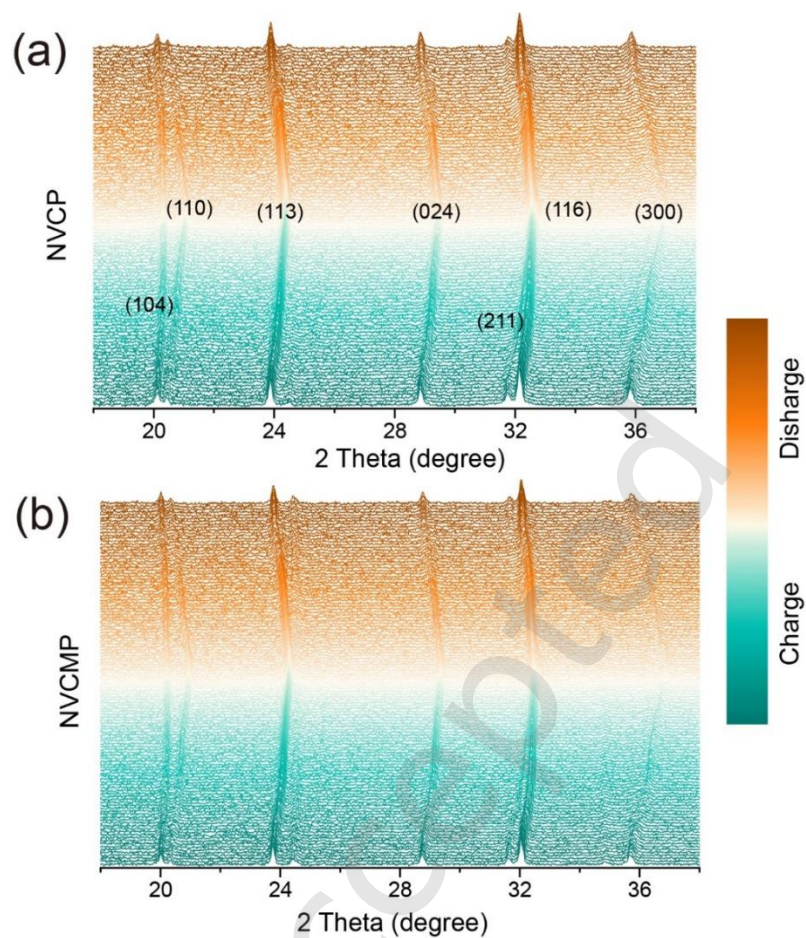


Figure S18. The images of in situ XRD testing results collected of (a) NVCMP and (b) NVCP

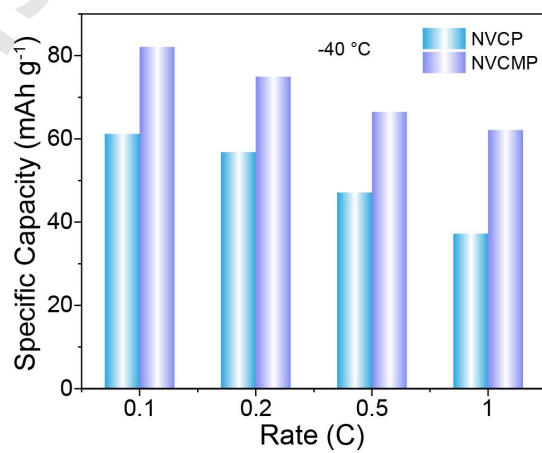
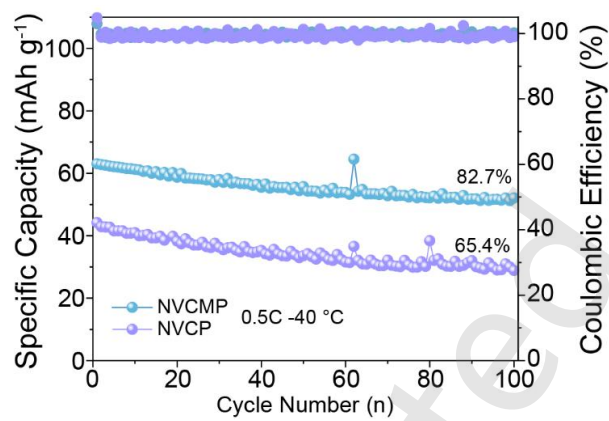


Figure S19. Rate performance at -40 °C.

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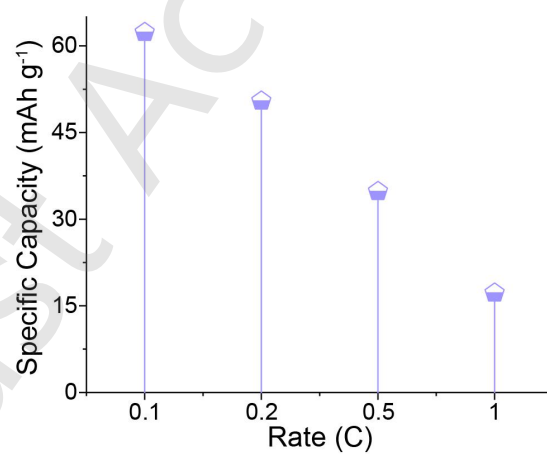


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4 **Figure S20.** Cycling performance at -40 °C.

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8 **Figure S21.** Rate performance at -60 °C.

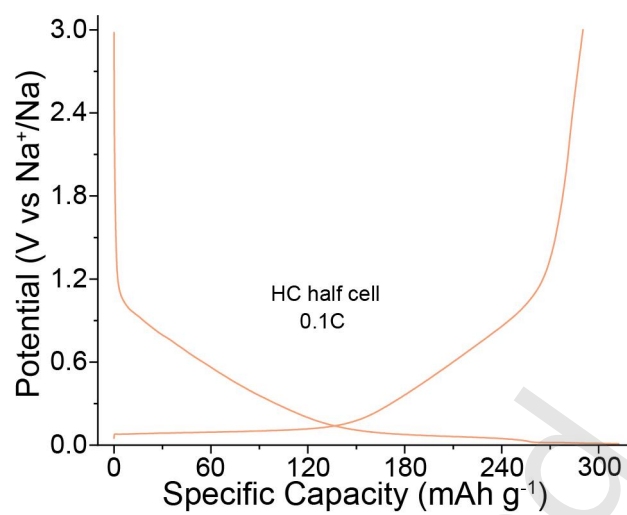


Figure S22. The charge-discharge curve of HC at 0.1C.

1 Table.S1 Refined structural parameters of the NVCMP from XRD Rietveld refinements.

Atom	Wyckoff	X	Y	Z	Occupancy
Na1	6b	0.33333	0.66667	0.16667	0.805
Na2	18e	0.66667	0.96178	0.08333	0.702
Cr1	12c	0.33333	0.66667	0.02040	0.485
Mo1	12c	0.33333	0.66667	0.02040	0.015
V1	12c	0.33333	0.66667	0.02040	0.500
P1	18e	-0.04633	0.33333	0.08333	1.000
O1	36f	0.14193	0.49765	0.07762	1.000
O2	36f	0.54047	0.84480	-0.02643	1.000
Space group: R-3c a=b=8.6888 Å c=21.7385 Å V=1421.279 Å ³					

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3 Table S2. EXAFS fitting parameters at the V K-edge for various samples.

Sample	Shell	CN	R(Å)	$\sigma^2 \times 10^{-3}$ (Å ²)	ΔE_0 (eV)	R factor
NVCMP	V-O	5.98	2.0027	2.66	0.59	0.0150
NVCP	V-O	5.73	2.0025	3.87	0.21	0.0109

4 CN, coordination number; R, distance between absorber and backscatter atoms; σ^2 , Debye-Waller
5 factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; R factor
6 indicates the goodness of the fit.

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9 Table S3. EXAFS fitting parameters at the Cr K-edge for various samples.

Sample	Shell	CN	R(Å)	$\sigma^2 \times 10^{-3}$ (Å ²)	ΔE_0 (eV)	R factor
NVCMP	Cr-O	5.92	1.9658	0.81	2.83	0.0159
NVCP	Cr -O	5.74	1.9707	6.15	2.43	0.0116

10 CN, coordination number; R, distance between absorber and backscatter atoms; σ^2 , Debye-Waller
11 factor to account for both thermal and structural disorders; ΔE_0 , inner potential correction; R factor
12 indicates the goodness of the fit.

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